C.E. Coleman





The Metallurgy of Zirconium

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The Metallurgy of Zirconium

C.E. Coleman

Volume 2

INTERNATIONAL ATOMIC ENERGY AGENCY VIENNA, 2022

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FOREWORD

The future of the nuclear industry worldwide depends primarily on the ability of the nuclear community to further improve our understanding of the materials used in the industry. Material science and metallurgy play an important role in reactor performance and safety.

This is the first time in nearly five decades that the International Atomic Energy Agency has gathered and updated information on the scientific and technological application of zirconium in the nuclear industry. The IAEA initiated a comprehensive project on The Metallurgy of Zirconium in 2005, at the request of Member States through the Technical Working Group on Fuel Performance and Technology.

For the greatest convenience of the users of this publication, it has been divided into three volumes. Chapters on fabrication are contained in Volume 1, chapters on the important properties of zirconium relating to its use in nuclear reactors in Volume 2, and information on ductility and fracture is presented in Volume 3.

The contributors to drafting and review were drawn from several countries — Canada, France, Germany, India, the Russian Federation, the United Kingdom and the United States of America. Each chapter was assigned to a leading expert in the field. The publication aims to provide the nuclear industry with a picture of the overall state of development and understanding of zirconium over the years. The first drafts were reviewed by five to seven reviewers, and contributions and appendices from additional authors were added to round out the perspective.

The IAEA wishes to express its gratitude to all the experts who contributed to this publication. Particularly, the IAEA appreciates the support of the main authors of the chapters and C.E. Coleman (Canada), who guided this project to its completion.

The IAEA officer responsible for this publication was M. Veshchunov of the Division of Nuclear Fuel Cycle and Waste Technology.

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Chapter 6

IRRADIATION DAMAGE

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6.1. INTRODUCTION

The aim of this chapter is to give a detailed overview of the effects of irradiation on zirconium alloys in reactors. The major use of zirconium alloys is linked to the core design for power generation in water reactors. Therefore, the evolution of the microstructure, and subsequent change in properties, in these alloys under various irradiation fluxes obtained in power reactors is of high interest. Irradiation conditions and history influence phase equilibria, mechanical behaviour, dimensional stability and corrosion resistance and these effects will be described in detail in the relevant chapters of this publication. In this chapter, the basic mechanisms involved in irradiation damage buildup will be described from a metallurgical point of view.

The structure of this chapter will follow a simple scheme for the analysis of irradiation damage in metals and alloys, starting from the atomic scale and ending with macroscopic behaviour.

- At the atomic scale, the first item to understand is the formation mechanism and the structure of point defects (PDs). Displacement energies, the morphologies of the PDs (vacancy, interstitial) and their clustering with themselves or with foreign atoms, such as alloying elements or impurities, will be analysed. Specific aspects of displacement cascades in hexagonal close packed (HCP) metals will also be described.
- The migration of these primary PDs will allow us to introduce the diffusion anisotropy of the PDs, a phenomenon that has to be considered for a description of the kinetic evolution of the PD. The formation of clusters of PDs will then be described; *a* type dislocation loops, either of vacancy or interstitial types, are formed by such mechanisms. Their morphologies will be detailed, including the effects of dose, flux, fluence and temperature. The consequences of their occurrence will be introduced. Under certain circumstances, dislocation loops with a $\langle c \rangle$ component Burgers vector are formed on the basal plane.
- As industrial alloys are not pure zirconium, but alloys with elements either dissolved in the α-zirconium HCP as solid solution or present as second phases (e.g. intermetallics, β-Nb), the effect of irradiation on these phases has been studied in detail. Irradiation enhanced precipitation or phase changes induced by irradiation will be described. The effect of irradiation on corrosion, growth and mechanical behaviour will be outlined.
- Irradiation of zirconium oxides will be discussed in a separate section. In a hot water reactor environment, the zirconium alloys develop a zirconia layer. This layer is affected by irradiation after its formation. Owing to the ionic character of the atomic bonds, this oxide is affected by the various kinds of irradiation fluxes present in the reactors, γ , β and neutrons. The various irradiation effects observed, by mechanisms that will be introduced, cause part of the enhancement of corrosion under irradiation.

— As the concern for zirconium alloy components does not end with their removal from the reactors, the evolution of irradiation damage after irradiation has to be accurately determined. This information could be critical for the end of cycle behaviour (e.g. dry cask transport, intermediate storage). Annealing and recovery of irradiation damage can be obtained either by plastic strain or by heat treatments; the mechanisms responsible will be described in detail.

In all these sections, the effects of the various parameters studied are described. These parameters will include temperature, flux, neutron energy spectra, specific environments, initial microstructure and textures. Many types of irradiation have been used for zirconium alloys, similar to analytical studies of irradiation mechanisms in other materials; these irradiations include high energy electrons, heavy or light ions, γ photons and different neutron sources. They are not analysed for their own sake but will be described in the appropriate sections as required to explain specific mechanisms, which are better illustrated by such irradiations.

6.2. DISPLACEMENT OF ATOMS AND POINT DEFECTS

6.2.1. Irradiation damage in solids

In metallic alloys placed in the core of a nuclear reactor, the major irradiation damage is caused by elastic interaction between fast neutrons¹ and the atoms constituting the alloy. These interactions displace the atoms from their crystallographic sites, creating PDs. These PDs migrate, recombine or aggregate, inducing important changes in the microstructure. The basic mechanisms operating under a fast neutron flux can be simplified as described below.

When a neutron approaches the nucleus of an atom, close enough that nuclear interactions can occur, several types of reactions are possible. The probability of the occurrence of a nuclear interaction is expressed by the following equation:

$$N_{\rm i} = N_{\rm v} \sigma_{\rm (E)} \,\varphi_{\rm n_{\rm (E)}} \tag{6.1}$$

where

Ni	is the number of interactions occurring per unit volume and unit time;
N _v	is the number of atoms that could interact in the unit volume;
$\sigma_{(E)}$	is the interaction cross section, that characterizes the probability of the interaction
	between the neutron and the target atom at a given neutron energy;

and $\varphi_{n(E)}$ is the neutron flux at the energy considered.

In this equation, the probability of interaction (i.e. the cross-section) depends on the energy of the incoming neutron (E_n) . The aim of the neutron physics computations is to

¹ Fast neutrons are those with energies greater than 0.1 or 1 MeV; the latter are 'fast' because they travel at 14 000 km/s for 1 MeV neutrons. Thermal neutrons have energies less than 0.025 eV; they are 'slow' because they travel at 2.2 km/s. Throughout this chapter, eV will be mainly used to express energy; eV is too entrenched in the literature on this subject to meaningfully convert the values using the correct SI unit of joule. The conversion is 1 eV = 1.602×10^{-19} J.

describe accurately the neutron energy spectra, to allow a precise description of the total interactions over the complete spectrum.

A cross-section can be defined for the various interactions that could occur as follows:

- A capture reaction, written ⁿA $(n, \gamma)^{n+1}$ A, leading to a heavier atom, with rearrangement of the nucleon orbitals and the release of a photon. This new nucleus is often unstable; therefore, a series of decay reactions may have to be considered further, with e, α and γ photon emissions. The recoil from the ejection of the prompt photon (γ ray) itself produces displacements. For zirconium, the capture cross-section of thermal neutrons is very low compared with most other metals — the reason for its use in nuclear reactors — and this mechanism for creating displacements is orders of magnitude smaller than those caused by the energetic neutrons that cause direct displacements of the zirconium atoms.
- An inelastic interaction, ⁿA (n,n') ⁿA*, where the nucleus of the target atom is excited during the interaction. In this case, a part of the kinetic energy of the incoming neutron is used for the change in nucleus configuration, and the balance is transferred as momentum. The cross-sections for this inelastic process are generally very small and insignificant. This reaction is only relevant for zirconium alloys when Nb is an alloying element as the (n,n') reaction for ⁹³Nb has a large cross-section that is used when calculating dose rates from neutron activation analysis. The excited target atom is in a metastable state and decays with the emission of a photon of characteristic energy. In the case of ⁹³Nb, the emitted γ ray is of lower energy than the prompt γ ray, insufficient to cause recoil displacements. All these inelastic reactions are described comprehensively in Appendix I to this volume.

An elastic interaction is shown in Fig. 6.1.



FIG. 6.1. Schematic diagram of an elastic interaction between a neutron and a target atom (using laboratory coordinates).

The structure of the nucleus is not modified, but part of the kinetic energy of the neutron is transferred to the nucleus of the target atom according to Eq. (6.2):

$$E_{\rm T} = 4E_{\rm n} \cos^2 \theta \,\frac{m_{\rm n} \cdot m_{\rm T}}{(m_{\rm n} + m_{\rm T})^2} \tag{6.2}$$

where

E _n	is the kinetic energy of the neutron before impact;
E_{T}	is the energy transferred to the target;

$m_{ m n}$	is the mass of the neutron;
$m_{ m T}$	is the mass of the target atom;

and θ is the scattering angle, expressed in laboratory coordinates.

After impact, the energy of the neutron is $(E_n - E_T)$. The maximum energy is transferred when $\theta = 0$; for zirconium struck by a 1 MeV neutron, T_{Max} is about 44 keV.

For an analysis of irradiation damage in zirconium alloys, the description can be restricted to the specific case of elastic interactions, with no modification of the target atom except for an increase in its kinetic energy.

The transfer of energy will have different consequences depending on its value. It has to be compared with a critical value required for atomic displacement out of the lattice site.

- For low values of the energy transferred, the target atom cannot leave its position in the crystal. The increase in kinetic energy only increases its vibration amplitude within the lattice site. This energy will be a source of local vibrations, a phonon that is nothing but a local source of heat that will diffuse in the alloy, by propagation of the phonons.
- If the energy transferred is larger than a critical value, called the displacement energy, E_d , the target atom can escape from its lattice site. E_d has a minimum value close to 20–40 eV for common metals:
 - For a low transferred energy (a few E_d), the displaced atom will not disturb the other atoms from their sites and only loses energy along its path, to stop as an interstitial when its energy is too low for further motion. (This interstitial atom is a self-interstitial atom (SIA), a zirconium atom as opposed to a solute interstitial atom, such as oxygen.) At the end of the process, the final damage is the combination of a vacancy, the former location of the atom and an interstitial, which is not necessarily the initial atom hit. This pair of PDs is called a Frenkel pair. Typically, this damage is what will occur during high energy electron irradiation, where the average transferred energy is a few tens of eV; for example, with irradiation by 10 MeV electrons, from Eq. (6.2), the value of T_{Max} is about 240 eV or about 10 E_d .
 - For high values of the energy transferred, as obtained with heavier particles (neutrons, ions, etc.), the target atom, now called the primary knock-on atom (PKA), interacts with the other atoms of the alloy along its track. For each interaction, the target atom transfers, on average, half its current energy to the secondary targets, as they have equal masses. These also interact with other atoms leading to a cascade of interactions. The result is a large number of atoms displaced (up to a few hundred), in a displacement cascade. After a few picoseconds, the highly damaged area restructures itself back to the original lattice, leaving a few isolated, surviving PDs and clusters of PDs.

Overall, the irradiation by neutrons results in a continuous creation of PDs, and heat, in the bulk of the alloys. These PDs cannot increase in concentration without limits. The PDs can recombine, migrate, agglomerate as large clusters of PDs or disappear on various sinks such as free surfaces, grain boundaries and dislocations.

A good knowledge of irradiation damage requires an accurate description of the various quantities involved in these processes. In the following sections, the probability of interaction (cross-sections), the displacement energies E_d , the PD energies and mobilities, the cascade

IRRADIATION DAMAGE

configurations and the strengths of the sinks will be described in detail for zirconium alloys. These data will be used to describe the formation of the resultant microstructures (dislocation loop formation, precipitation, phase instability) by combining all the processes involved in irradiation damage. It will then be possible to illustrate the consequences for the properties of alloys and their modified behaviour during and after irradiation.

6.2.2. Interactions of zirconium with neutrons

In addition to their good engineering properties, zirconium alloys are used in water reactors because of their low absorption cross-section for thermal neutrons. For natural zirconium, the average value of the thermal neutron absorption cross-section is equal to $\sigma_{abs-th} = 0.185$ b. The main contribution is due to the ⁹¹Zr isotope, which accounts for 11.2% of all the isotopes. Removing this isotope would reduce the thermal neutron absorption by one order of magnitude, resulting in an improvement of the neutron efficiency of the reactors. However, the other isotopes are equally distributed, either as heavier or lighter isotopes, and the depletion of ⁹¹Zr by isotope separation techniques, which are very difficult, would be of doubtful economic interest.

The chemical effects of neutron capture in zirconium are limited. For most of the natural isotopes of zirconium, the capture of a neutron leads to a heavier stable isotope and thus maintains zirconium in its initial chemical state (no transmutation). In ⁹⁴Zr, which accounts for 17.4% of the natural zirconium isotopes, a transmutation mechanism occurs via the decay chain: ⁹⁴Zr (n, γ) ⁹⁵Zr $\beta^- \rightarrow {}^{95}Nb \beta^- \rightarrow {}^{95}Mo$.

The corresponding capture cross-section ($\sigma_{abs-94Zr} = 0.08$ b) is very low and this process has only to be considered for the very long exposures obtained in some structural components of water reactors, such as pressure tubes. The decay chain of ⁹⁵Zr ends with the stable ⁹⁵Mo, within a few months. Typical values of the final Mo doping in pressure tubes may reach 0.9% after 25 years of operation in Canada deuterium uranium (CANDU) reactors, which have high thermal neutron fluxes compared with other reactor types. (Appendix I summarizes the chemical conversion in zirconium after 25 years in a CANDU reactor.) Neutron spectra with a high preponderance of fast neutrons are said to have a 'hard' spectrum. For cladding tubes in water reactors, the low exposure times and hard neutron spectra reduce the concern regarding any significant chemical evolution. The energy of thermal neutrons is too low to cause displacement damage.

For elastic interactions, the corresponding cross-section is almost independent of the energy of the incident neutron, as shown in Fig. 6.2. An average value of 6.4 b is used to compute the elastic interaction rates. Owing to their low dependency on the neutron energies, the frequencies of interactions are almost neutron spectra independent. However, the energies transferred to the PKA will vary with the spectra, a harder spectrum leading to a higher average transferred energy and hence more displacements.



FIG. 6.2. Natural zirconium interaction cross-sections with neutrons [6.1].

For a typical fast neutron of 1 MeV kinetic energy, the average transferred energy is obtained by solving for the energy and momentum conservation during the elastic impact (Eq. (6.2)):

$$T_{\text{Max}} = 4 \frac{m_{\text{n}} \cdot m_{\text{Zr}}}{(m_{\text{n}} + m_{\text{Zr}})^2} E_{\text{n}} \text{ and } \overline{T} = \frac{T_{\text{Max}}}{2}$$
(6.3)

where T_{Max} and \overline{T} are the maximum and mean transferred energies, respectively, for a neutron of incident energy E_{n} .

The ratio between T_{Max} and E_n is often called the energy transfer parameter, Λ . Due to the respective masses of the neutron and of the zirconium atom (ratio of about 1–100), the mean transferred energy for a neutron energy of 1 MeV is $\overline{T} \approx 22$ keV. This value is clearly large enough for the production of extended cascades, as described in Section 6.2.6.1.

For a typical fast neutron flux of $\varphi_n = 5 \times 10^{17} \text{ n} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ in a light water reactor (LWR), these physical parameters give a rate of PKA generated by elastic interactions of:

$$G_{\rm p} = N_{\rm v} \cdot \sigma_{\rm el} \cdot \varphi_{\rm n} \tag{6.4}$$

giving a value of the PKA production rate of $G_{PKA} \approx 1.3 \times 10^{19} \text{ m}^{-3} \cdot \text{s}^{-1}$. As will be described below, the development of displacement cascades induced by the PKAs will generate a total number of displaced atoms about two orders of magnitude larger than the PKAs.

6.2.3. Displacement energies

6.2.3.1. Experimental

In the HCP metals, the displacement energies have been measured by various physical methods and the values obtained compare favourably with the results calculated by molecular dynamics (MD) and ab initio methods.

Displacement energies in metals and alloys are usually in the range of 20-40 eV and depend weakly upon the recoil direction of the target atom. The major experimental method for measuring the displacement energies is based on high energy electron irradiation followed by observation of changes in various physical properties or microstructure evolution, above a given incident electron energy, induced by irradiation damage PDs. The computation of the minimum energy to be transferred to the atoms for the appearance of such effects corresponds to the displacement energy. Electron irradiations have been performed at low temperatures $(T_{\rm irr} < 10 \text{ K} (-263^{\circ}\text{C}))$ on zirconium of high purity and low oxygen concentration, and the irradiation damage was monitored by in situ electrical resistivity changes [6.2, 6.3]. In these two independent studies, the same behaviour was observed, with a minimum energy transferred to the zirconium atoms to induce variation of the electrical resistivity of $E_{d/h-min} = 21-24$ eV. The variations of the efficiency of the displacement with increasing transferred energy led to an effective displacement threshold energy of $E_{d,eff} = 28$ eV. These experiments gave the intrinsic resistivity increase due to a Frenkel pair of $\rho_{\rm FP} = 4 \times 10^{-7} \,\Omega \cdot {\rm m}^{\circ} ({\rm at.}\%)^{-1}$, which has been used to calibrate neutron irradiation damage. It was also possible to show that subtreshold displacements (for $T \le E_d$) appear to be rare in zirconium due to the low focusing efficiency in the compact HCP cell of α -zirconium [6.4].

In the case of single crystals, it is possible, by fine control of the orientation of the sample, to determine the anisotropic character of the displacement energies. Care should be taken with anisotropic crystals because an experimental artefact may lead to a small reduction in E_d anisotropy. Displacements can be obtained by the motion of the hit atoms in directions not parallel to the electron beam, but in a slightly different direction with a lower value of E_d . The irradiation damage is visible for an energy transferred from the incident electrons but not corresponding to the displacement energy in the direction of the electron beam [6.5].

Measurements of E_d for zirconium have been performed using a high voltage transmission electron microscope (HVTEM) to irradiate a thin foil of zirconium. The values obtained for close packed directions were found to be weakly orientation dependent and to correspond to the expected value of $E_d \approx 25$ eV, with only a 2 eV difference between different crystallographic orientations [6.6].

The effect of temperature on the displacement energy has been studied in different metals, usually with HVTEM observations [6.7]. For instance, variations in displacement energies with temperature have been observed for Cu, with a reduction of E_d from 17 eV at 10 K (-263°C), down to 10.5 eV at 550 K (\approx 280°C) [6.8]. Although not measured on zirconium, similar effects could be expected on zirconium. Several reasons are proposed for such a decrease in E_d with temperature as follows:

— The first is linked to the anisotropy of E_d . As the temperature is increased, averaging the different values corresponding to different recoil directions leads to a reduction of the effective displacement energy. This contribution would probably be small in zirconium, since E_d is almost isotropic [6.6].

- The second mechanism is linked to the average value of the transferred energy, when taking into account the thermal vibration energy of the target atom. For zirconium at 580 K (\approx 300°C), the decrease in effective displacement due to the contribution of the vibration energy would be about $\Delta E_d \approx 2.3$ eV compared with the value of E_d at 0 K. This reduction of the displacement energy could explain the small discrepancies between the low and high temperature measurements.
- A third contribution would be an increase in recombination volume, which would lead to a reduced number of surviving PDs and therefore to less observed irradiation damage at higher temperatures. This latter mechanism cannot be considered a reduction of displacement energy per se, but is a reduction of observed damage at high temperatures for the same irradiation dose. This contribution to the reduction in E_d should therefore not be considered when computing irradiation damage.

6.2.3.2. Direct computations

The development of computation capabilities has opened the path to an impressive amount of work related to the simulation of irradiation damage in materials. Among them, two techniques are used to compute displacement energies. One is based on MD, for which interatomic potentials are required. Then the values of E_d are obtained by searching the impact energy required for instantaneous atomic displacements. The second method is based on ab initio (i.e. first principle quantum physics) energy computation of a series of configurations of a crystal in which an atom is forced to escape from its lattice position. E_d is deduced from the energy barrier for stable atom displacement [6.9].

Up to 2009 only the first technique has been used for zirconium. Computations were performed using pair potentials in the early 1980s. The results are clearly limited to metals and alloys where the anisotropy is limited. In HCP systems, this corresponds to the case of crystals with a c/a ratio close to the ideal one (i.e. the ratio that applies for the close packing of spheres, $c/a_i = (8/3)^{1/2}$). Using a many-body potential developed according to the Finnis and Sinclair [6.10] form proposed for Ti, Ackland et al. have used the MD code MOLDY to compute at 0 K (-273°C) various crystallographic properties of the zirconium HCP structure (stacking fault energies, PD formation and migration energies, and displacement energies) [6.11]. They found that zirconium exhibits a higher anisotropy than Ti for displacement energies (Fig. 6.3). The displacement energy was found to be minimal for knocking out in the basal plane (i.e. in the $11\overline{2}0$ directions), corresponding to the most favourable direction for replacement collision sequences, and to the direction of development of a basal crowdion (i.e. an extended lattice distortion) [6.12]. The corresponding displacement energy obtained ($E_d = 27.5$ eV) is slightly above the one measured experimentally. The reason for the difference could be that the computations at 0 K led to higher values than at room temperature. The value averaged over all the directions computed was found to be 55 eV (Fig. 6.3).

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FIG. 6.3. Computed displacement threshold energies for zirconium and Ti (reproduced from Ref. [6.11] with permission courtesy of Taylor & Francis).

For other phases present in zirconium alloys, the displacement energies may be different. While substitutional solute atoms such as Sn or Nb with effective core radii close to that of zirconium could be expected to have similar displacement energies to zirconium, the situation for other phases or intermetallic compounds may be different.

The displacement energy of Nb in pure body centred cubic Nb has been measured accurately and the value obtained is similar to that of other cubic metals: $E_{d-Nb} = 28 \text{ eV} [6.13]$. For the β -Nb phase present in Zr-Nb alloys, which is rich in Nb, this value of the displacement energy should be valid for both the Nb and zirconium atoms.

For the intermetallics, the situation is more complex. Several displacement energies have to be considered, one for each chemical species, which should also depend on the crystallography of the phase considered. Analysing the amorphous transformation (detailed in Section 6.3.2) of various zirconium transition metal intermetallics present in Zircaloy, Howe et al. give an estimate of the different displacement energies for zirconium and the transition metal (TM) [6.14]. The values are reported in Table 6.1. The displacement energy of zirconium is almost independent of the phase considered, while the values for the transition metals (TMs) vary by more than 50%.

$\frac{\text{IABLE 6.1. DISPLAC}}{[\text{eV}] \setminus \text{Phase}}$	Zr ₃ Fe	$\frac{2r-1M}{Zr_2Fe}$	ZrCr ₂	
E _{d-Zr}	26	25	22	
E_{d-TM}	18	27	23	

TABLE 6.1. DISPLACEMENT ENERGIES IN Zr-TM INTERMETALLICS (after [6.14])

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The displacement energies measured or computed by the techniques described above remain close, in the range of $E_d \approx 20-25$ eV. The value of the displacement energy to be considered for irradiation damage is not the minimum obtained to move an atom in a specific crystallographic direction but the value averaged over all the possible recoil directions. A given energy transferred to a target atom slightly above the minimum displacement energy can either induce its migration or leave it excited in its lattice site, depending on the direction of its impact. Therefore, the averaging cannot be simply done over the different orientations, but requires a statistical approach based on the energy distributions of the hit atoms around the displacement threshold. For HCP crystal structures, the ratio between the mean average value of E_{d-av} and the minimum value to induce a displacement E_{d-min} (which is the one measured during the observation of the onset of irradiation damage) is about 1.5 [6.15]. This factor leads to a value $E_{d-av} \approx 40$ eV (i.e. equivalent to the value recommended in the standard procedure for the computation of irradiation damage [6.16]).

For a given displacement energy E_d , a knocked atom of energy T can produce v(T) displacements, according to the following equation:

$$\nu(T) = \begin{bmatrix} 0.8T/2E_d & \text{for} & 2E_d < T \\ 1 & \text{for} & E_d < T < 2E_d \\ 0 & \text{for} & T < E_d \end{bmatrix}$$
(6.5)

This computation is based on the Norgett et al. [6.17] cascade description approach, with equal partition of the kinetic energy to the zirconium atoms as the cascade develops. The factor 0.8 is a displacement efficiency that is introduced to take into account the departure from the hard sphere behaviour of the actual interatomic potential. This approximation gives a good description of the number of displaced atoms for low energy cascades but does not consider intracascade recombination and fails to describe correctly the higher energy cascades. This point will be discussed later in more detail in Section 6.2.6.

This simple approach leads to the number of atoms displaced in a cascade, n_p , following the formation of a typical zirconium PKA. For example, from Eq. (6.3), the average energy of a primary knock-on for the zirconium atom due to collision with a 1 MeV neutron is about 22 keV. Using $E_d = 40$ eV, the resulting collision cascade may contain about 220 displaced atoms:

$$n_{\rm p} = \frac{0.8\overline{E}_{\rm T}}{2E_{\rm d}} \approx 220 \tag{6.6}$$

The displacement probability should also take into consideration the inelastic losses [6.16] and the mechanisms of low energy displacements such as focusing and channelling along close packed directions. The result is a continuous description of the probability of migration of an atom, versus its transferred energy T, v(T). For practical purposes, the approximation given in Eq. (6.5) is sufficient [6.18].

6.2.4. Computation of irradiation damage in nuclear reactors

The dose for a given component is often expressed in the form of fast neutron fluence (n/m^2) and an indication of the 'fast' neutron energy limit, for example, E > 1 MeV, or with the effective damage in displacements per atom (dpa). The conversion factor will vary with the neutron physics of each reactor (i.e. according to the exact neutron energy spectrum). In water reactors, a rough conversion factor between fast neutron dose and displacement damage is that 1 dpa corresponds to a fluence of 5×10^{24} n/m² (E > 1 MeV).

A detailed conversion procedure is required to compare irradiations performed in different reactors. Conversely, the effect of irradiation parameters on various properties can be determined by testing materials in different reactors (e.g. LWR power plants, material testing reactors or fast breeders for high fluence irradiations). In addition, basic irradiation studies are often performed using electron or heavy ion irradiations and the results have to be compared with the reactor irradiations.

The irradiation damage is mainly obtained by elastic interaction between fast neutrons and the atoms of the alloy. Low energy neutrons (below a few hundred eV) do not transfer enough energy to induce atomic displacement. Nuclear interaction can occur with (n,γ) , (n,n')or (n,2n) reactions, the latter being measurable only at high energies. The contribution of these reactions, and their decay progeny, has to be computed with a consideration of the detailed neutron energy spectrum of each reactor, as well as each location inside the reactor. The irradiation damage is thus computed considering all the possible processes for transfer of energy to the target atoms. For zirconium, the direct displacements per neutron caused by the elastic collisions with energetic neutrons are by far the most significant. The rate of formation of displaced atoms is simply equal to the expansion of the previous equations to the full energy range of the neutrons:

$$R_d = N \int_{E_{d/A}}^{\infty} \varphi(E_n) dE_n \int_{E_d}^{AE_n} \sigma_n(E_n, T) \nu(T) dT$$
(6.7)

where N is the number of atoms per unit volume and Λ is the energy transfer parameter defined in Eq. (6.3) and the other terms described above.

The second integral defines the displacement cross-section, σ_d :

$$\sigma_d(E_n) = \int_{E_d}^{AE_n} \sigma_n(E_n, T) v(T) dT$$
(6.8)

This displacement cross-section has been determined for several chemical species using the nuclear data tables ENDF/BV. It is available for zirconium (Fig. 6.4) [6.19]. The data clearly confirm that irradiation damage induced by thermal neutrons is very limited in zirconium ($\sigma < 0.1$ b).



FIG. 6.4. Displacement cross-section $\sigma_d(E_n)$ for zirconium, with $E_d = 40 \text{ eV} [6.19]$.

The rate of irradiation damage is the integral of the product of this displacement crosssection by the neutron flux for each energy interval of the neutrons. Since different reactors have different neutron spectra, the ratio between damage formation rate and neutron flux varies accordingly [6.20, 6.21]. Care should be taken because $\sigma_d(E_n)$ includes an assumed, hidden parameter, the displacement energy E_d . The recommended value is 40 eV, but basic studies have sometimes used other values, such as the minimum E_d for detection of irradiation damage (25 eV) [6.22, 6.23]. The most important consideration is that using dpa rates to normalize for different neutron spectra in different reactors requires that the dpa calculations are all performed using the same cross-sections and displacement energies.

As dose is often expressed in terms of a neutron fluence for neutron energies greater than a defined threshold value, care must be taken when comparing doses for irradiations in different reactors. Comparing the effect of irradiation by scaling using fast neutron fluence is only valid when the neutron spectra are identical, as only then would equivalent fluence values have the same corresponding dpa. Estimates of the dpa can be made using the fast neutron spectrum only because the higher energy neutrons produce the more energetic cascades and therefore account for a large fraction of the displacement damage. Formerly a cut-off value of E > 0.1 MeV was used, while currently E > 1 MeV is commonly preferred. Other limits may also be used (0.85 MeV). Giving the flux of neutrons with an energy larger than a given value during irradiation is just a matter of scaling the flux. Decreasing the energy limit for the value of fast neutrons increases the flux considered but does not change the damage. Therefore, although the same fluences may be quoted but expressed as E > 1 MeV and E > 0.1 MeV; the number of displacements will be different and depend on the relative neutron spectra.

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As zirconium alloys are widely used as cladding and structural materials for fuel in water reactors, the irradiation is also often expressed using a quantity related to the fuel irradiation: the fuel burnup. This is expressed in terms of energy produced by unit mass of fuel $MW \cdot day \cdot t^{-1}$ U. The correspondence between burnup and dpa is complex because the neutron spectrum at any time during the fuel operation is itself a function of burnup or the state of the fuel at that stage in its operation. To a reasonable approximation, 1 dpa in zirconium is obtained in the cladding for a burnup of about 4000–5000 MWd/kgU in a pressurized water reactor (PWR).

To compare the behaviour of zirconium alloys irradiated in different reactors, a compilation of different data (mostly unpublished) has been performed. The total displacements for all possible interactions with all neutrons have been calculated and the corresponding flux for a given energy range corresponding with 1 dpa has been computed. In this way it is possible to compare the damage production rates in various reactors for a given quoted neutron flux or fluence for a defined energy range.

Results from different reactors are presented in Table 6.2. It should be noted that these calculations might have different sources for the calculation of the damage cross-sections using differing sets of nuclear data (e.g. ENDF/B-IV, ENDF/BV or ENDF/B-VI) and different codes for calculating the resultant damage cross-sections. Ideally, each group estimating irradiation damage should use one source as an industry standard. The spectra will vary spatially within a given reactor and accurate calculations require spectra specific to the location of interest. The spectra for some reactors may be coarsely defined and have few energy groups. Taking note of these cautions, the calculations are expected to be within 10% of the actual values. The important point is that the dose–damage relationship is similar in all the water reactors. The inclusion in the table of fast breeder reactors is justified by the use of this type of reactor for high fluence irradiation studies. Note that using zirconium alloys as cladding or structural materials would not improve the performance of fast neutron reactors.

Type of reactor	$E > 0.1 { m MeV}$	E > 1 MeV	Full spectrum
PWR	1.3×10^{25}	6.4×10^{24}	2.8×10^{25}
Boiling water reactor (steam 40%)	1.3×10^{25}	6.4×10^{24}	$2.6 imes 10^{25}$
Water cooled, water moderated power reactor in IAEAterm. (WWER)1000	$1.3 imes 10^{25}$	$pprox 7 imes 10^{24}$	
CANDU	$pprox 1.2 imes 10^{25}$	$5.8 imes 10^{24}$	
Graphite-moderated nuclear power reactor	2×10^{25}	$\approx 4 \times 10^{24}$	
Na fast reactor (Phénix)	1.8×10^{25}	$3.6 imes 10^{24}$	$3.2 imes 10^{25}$
Na fast reactor (BOR 60)	1.9×10^{25}	$\approx 4 \times 10^{24}$	$3.2 imes 10^{25}$
Material testing reactor (NRU, Osiris)	1.4×10^{25}	6.6×10^{24}	$3.4 imes 10^{25}$

|--|

6.2.5. Energies and configuration of the PDs

Following an impact inducing atomic displacements, two types of PD are created. The vacancy is the former site of an atom that has been removed from the crystal lattice, while the complement, the interstitial, is the location where an additional atom has been inserted between atoms in the crystal lattice some way from the vacancy. The detailed knowledge of the physical characteristics of these PDs is important for a good description of their evolution with time (formation rate, configuration, migration, interaction with other defects such as dislocations and clustering).

The formation energy of a given PD is equal to the difference in energy between a perfect crystal and the same crystal when an atom has been moved from the bulk to the surface, for the vacancy, and the reverse for the interstitial. Typical formation energies of PD are close to 1 eV for vacancies and a few eV for interstitials.

The migration energy of a PD is the energy gap required to pass the saddle point between two adjacent sites when it changes position. For the vacancy, the migration should be more strictly described as the migration of a surrounding atom. Due to the high lattice distortions in the surroundings of the interstitials, their migration energies are low $(E_{\rm mi} \approx 0.1-0.3 \text{ eV})$, while vacancies are more difficult to displace $(E_{\rm mv} \approx 1-2 \text{ eV})$.

The change in local lattice geometry induced by the presence of a PD corresponds to expansion or contraction. Using various X ray diffraction techniques (lattice, diffuse or Huang scattering) it is possible to measure these distortions and to express them in terms of equivalent volume of an inserted atom that would lead to the same distortions after elastic relaxation. This quantity is called the relaxation volume. It is close to the atomic volume for interstitials, and small (positive or negative) for vacancies.

The following sections will describe in detail these quantities for zirconium.

6.2.5.1. Vacancies

(a) Experimental values

In the HCP cell of the zirconium alloy matrix, all the positions of the atoms on the lattice are identical. Therefore, there is only one vacancy description, corresponding to the removal of one atom, and the value of the formation energy of a vacancy is unique. The measurement of vacancy formation energy by thermal equilibrium concentration cannot be performed at a temperature high enough in the HCP α phase of zirconium to obtain an accurately measured concentration of vacancies. Direct measurement of this energy is extremely difficult because the α - β phase transformation occurs at a low temperature; in zirconium the HCP structure is stable only below 1136 K (863°C).

Qualitative estimates have been performed. Using a correlation analysis of various diffusion coefficients of solute atoms in zirconium, Hood [6.24] obtained a minimum value of the formation energy of a zirconium vacancy of $E_{\text{fv} Zr} \approx 1.8 \text{ eV}$.

When analysing the diffusion activation energies, both the formation and migration energies of the vacancies are involved, and a hypothesis has to be made for the contribution of each process. Diffusion experiments performed by Hood lead to a self-diffusion activation energy of 3.17 eV [6.25]. This value is the reference experimental quantity to be used for the determination of the vacancy formation energy. A significant anisotropy in the diffusion coefficient with respect to the crystallography of the zirconium has been observed with faster diffusion along the $\langle a \rangle$ direction than in the $\langle c \rangle$ direction $D_{[0001](Zr)} \approx 0.6D_{<11\overline{2}0>(Zr)}$. Such a difference, only due to differences in migration energies, restricts the freedom in the contribution of the two components of the diffusion activation energy. Frank has discussed in great detail the diffusion behaviour of various solutes in zirconium, which increases the diffusion coefficients by the formation of complexes with PDs or shows a normal diffusion rate controlled by vacancy diffusion [6.26]. Frank proposed a range of vacancy formation energies of 1.4 eV $< E_{\text{fv} Zr} < 2.1$ eV.

This value was consistent with the lack of observation of vacancies in zirconium, as measured by positron annihilation spectroscopy at temperatures up to T = 1240 K ($\approx 970^{\circ}$ C) [6.27]. In these experiments, the attempt to observe the temperature dependence of the positron annihilation mechanism, induced by the expected increase in vacancy concentration with temperature, was not observed in α -zirconium. A sensitivity study of the minimum detectable signal leads to a minimum value of the vacancy formation energy of $E_{\text{fv}^{\circ}\text{Zr}} > 1.5$ eV.

Fortunately, Hf, a companion of zirconium in Group 4 of the periodic table with similar properties, remains HCP up to 2020 K (\approx 1750°C). This high temperature allows the experimental measurement of the vacancy formation energy in Hf in the HCP structure [6.28]. The value obtained, $E_{\rm fv Hf} = 2.45 \pm 0.2$ eV, is expected to be close to that for zirconium. While it may not be the value for zirconium, this value of $E_{\rm fv Hf}$ can be used to benchmark the computations performed using various other approaches, for which metals of similar structure, such as those of Group 4 (Ti, Zr, Hf), have been studied. This approach allows a high confidence in the values obtained for zirconium in such computations, as described below.

(b) Computation of the vacancy formation energy

Pair potential computations have been undertaken in many laboratories and the publications reporting vacancy formation energies in zirconium are numerous. In the early computations, only empirical pair or many-body potentials were used, with a set of suitable fitting parameters tuned to the bulk properties such as lattice parameter, c/a ratio and elastic constants. These potentials are used to compute the energy of a system of atoms incorporating one or several PDs. The values obtained were considered to be low (1.6–1.85 eV), as Bacon noted in his 1988 review [6.29].

Using an embedded atom model (EAM), Pasianot and Monti [6.30] proposed a formation energy for the vacancy of $E_{\rm fv Zr} \approx 1.74$ eV. In their discussion, they stressed the low value obtained, and expected the actual value to be slightly higher, to be consistent with diffusion experiments. However, using the formalism of Finnis and Sinclair [6.10] for the development of a many-body potential, Ackland et al. have obtained a similar value of $E_{\rm fv^2Zr} \approx 1.79$ eV [6.11].

Computations that give a slightly larger value of the formation energy of the vacancy are based on ab initio techniques. These techniques are much more accurate than the empirical methods because they do not require fitting parameters. However, they consume much time and require high numerical computational power.

With the help of the Vienna Ab-initio Software Package (VASP), Domain and Legris [6.12] have computed the formation energies of various PDs in zirconium, using the generalized gradient approximation (GGA), with the exchange correlation functional approach. The value of the vacancy formation energy varied between $E_{\text{fv} Zr} \approx 1.86-1.90 \text{ eV}$ for the relaxed configurations, depending on the number of atoms considered for the computation (96 or 36, respectively). These values of $E_{\text{fv} Zr}$ were higher than those obtained using empirical potentials.

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In the HCP structure, Le Bacq et al. [6.31] have performed computations using a full-potential linear muffin-tin orbital method on the three elements of the Group 4 metals (Ti, Zr, Hf), allowing a comparison of these similar metals, which all exhibit an α - β phase transition. The value obtained for the vacancy formation energy in zirconium by this method is higher than for interatomic potentials: $E_{\rm fv} = 2.07$ eV. Taking into account the contribution of the migration energy of the vacancy, this value is consistent with the activation energy for self-diffusion in zirconium, with a $E_{\rm fv}/Q = 0.65$. The same computations were performed on Ti and Hf and gave a value of the vacancy formation energy for Hf very close to the experimental measurements ($E_{\rm fv Hf exp.}/E_{\rm fv Hf cal.} = 1.034$ [6.31]). Although this value is the only experimental quantity available for comparison, it gives confidence in the computations.

6.2.5.2. Interstitials

The formation energy of an interstitial cannot be measured directly and the only values to be considered are deduced from computations which are similar to those used for vacancy formation energy; various techniques have been used.

A major difference between the two types of PDs is linked to the geometry of the interstitial. When adding an additional atom somewhere in the crystal, the location of this atom has to be considered. If the interstitial stays in the location where it was inserted, then only a limited number of configurations exist, namely one octahedral and one tetrahedral site. However, these sites are too small to accept the interstitial without a relaxation of the subsequently stressed crystal. The relaxation mechanisms by which two or more atoms rearrange themselves to share the volume around a given crystallographic site therefore have to be considered.

(a) Configuration of the interstitial sites

A description of all the interstitial configuration sites was proposed for titanium by Johnson and Beeler [6.32] and has been adopted for the HCP structure. These sites are described in Fig. 6.5:

- T is the tetrahedral site, while O is the octahedral site, with coordination numbers of 4° and 6, respectively.
- Basal tetrahedral and basal octahedral sites are similar sites on the basal plane. Both have three nearest neighbours, but with different numbers of second neighbours.
- For the extended defects, the crowdion in the middle of a segment linking two basal atoms is named the basal crowdion. C is the interstitial atom located between two adjacent atoms of different $\langle c \rangle$ planes ($\frac{1}{6} < 20\overline{2}3 >$). The split dumbbell position in the $\langle c \rangle$ direction is named S.





FIG. 6.5. Configuration of interstitial sites. (a) Static localizations [6.33]; (b) relaxed configurations (this image was published in Ref. [6.34], copyright Elsevier, 1993).

(b) Computation of the interstitial formation energies

Johnson and Beeler [6.32] found that the most stable interstitial configuration in Ti was the basal octahedral, with a formation energy of $E_{\rm fi BO} \approx 4.32$ eV. Several other sites were also found to be metastable, such as asymmetric variants of the T and C sites with $E_{\rm fi^{o}T/C} \approx 4.6$ eV. These analyses have been compared with similar computations for other HCP metals and lead to similar conclusions for the most stable site.

Numerous computations of interstitial configurations have been performed using various pair potentials. These potentials were fitted to the bulk properties and, in several cases, to the assumed vacancy formation energy. Usually the tetrahedral site is found to be unstable and to transform elastically into the basal crowdion or S configurations. As reviewed by Willaime [6.34], the relative stabilities of the various interstitial configurations were observed to be strongly potential dependent. In the majority of the computations, the formation energies of all the configurations varied only slightly and can be gathered under the generic expression $E_{\rm fi} \approx 4.0 \pm 0.6$ eV. Therefore, these types of computations do not distinguish the most stable configuration; their value is clearer for the computation of defect mobility, as will be described below.

The ab initio approach is of great help. In the framework of the density functional theory, with two different approximations for the exchange and correlation energy (the local density approximation and the GGA), Willaime has proposed that the basal octahedral should be the most stable configuration, immediately followed by basal split dumbbell; O and S cannot be completely excluded, owing to the small energy differences among these four configurations. Since these computations are performed at 0 K, no definitive conclusions could be drawn about values at reactor temperatures, owing to differences in vibration and electronic formation entropies.

Domain and Legris [6.12] have used the VASP with GGA to compute the formation energies of various PDs in zirconium. The octahedral position of an interstitial was found to be the most stable configuration, with a formation energy of $E_{\rm fi}$ o = 2.48 eV. The basal octahedral and basal crowdion configurations had less than 0.1 eV higher formation energy. For all the configurations studied, the difference in formation energy was less than 10%, leading Domain and Legris to the same conclusions as Willaime.

A comparison of the results of the computations performed by ab initio techniques for the vacancy and various self-interstitial configurations is given in Table 6.3. The lower formation energy of the interstitials obtained by ab initio methods compared with that computed using empirical potentials is probably due to the repulsive parts of these potentials being too stiff. These parts of the empirical potentials are difficult to adjust based on physical properties, while they contribute strongly to the SIA configuration, and therefore to their formation energy, owing to the high distortion the SIA introduces in its surroundings [6.34].

The small differences calculated for the formation energies of the different configurations of interstitials do not allow conclusions to be drawn about their actual configuration. The octahedral configuration appears to be the most stable in all the computations, but other site energies differ by a small amount, except for the crowdion C, which appears to be less stable, and the tetrahedral site, which is unstable. The effect of temperature on the frequency of occupation of each configuration of the defects will be analysed later. This analysis will introduce the mobility of the PDs, a critical point for the evolution of the irradiation damage. It will be shown that the exact initial configuration of the SIA is unimportant.

Method	Vacancy	0	Basal octahedral	Basal crowdion	С	S	Т	Ref.
Ab initio full-potential linear muffin-tin orbital method	2.07							[6.31]
Ab initio GGA	1.86	2.84	2.88	2.95	3.08	3.01	Unstable	[6.12]
Ab initio local density approximation		2.79	2.78	2.90	3.07	2.80	Unstable	[6.34]
Ab initio GGA		3.04	3.14	3.39	3.52	3.28	Unstable	[6.34]

TABLE 6.3. AB INITIO COMPUTATION OF SIA AND VACANCY FORMATION ENERGIES IN ZIRCONIUM

Note: The stable configurations for each computation are highlighted in bold. GGA — generalized gradient approximation.

6.2.6. Mobility of the PDs

During the formation of the irradiated microstructure, the PDs, whatever the mechanisms by which they have been formed, have to migrate to recombine, annihilate and agglomerate in larger defects. Before analysing the other mode of creation of these PDs in cascades obtained during neutron irradiation, knowledge of their migration modes is required, which is the topic of this section.

6.2.6.1. Elastic instability

In proximity, a vacancy and a self-interstitial will form an unstable cluster of PDs. The elastic recombination of these two antagonist PDs will occur when they are present within the recombination volume at the same time. Then an elastic recombination occurs in less than a lattice vibration period ($\approx 10^{-13}$ sec). This recombination volume is evaluated by analysing in situ a physical parameter sensitive to irradiation induced PD concentration, usually electrical resistivity, which can be measured remotely with great accuracy. The saturation with fluence of the physical property measured corresponds to the concentration of PDs leading to their continuous elastic recombination. In irradiations performed with electrons only Frenkel pairs are created and the recombination volume is simply the inverse of the PD concentration, PD recombination occurs within the cascades and the computation of the PD concentration should account for this in situ recovery.

At very low temperature (<50 K (-220°C)), the interstitials are not mobile and the computed concentration of PDs at the dose for saturation of the increase in resistivity gives the recombination volume. This measurement was not performed during the electron irradiations described earlier, but such measurements were performed at low temperature (24 K (-249.2°C)) with fast neutrons by Vialaret et al. [6.4] on high purity zirconium samples of various oxygen concentrations ([O] = 20 (molten zone refined zirconium) to 600 at. ppm). At this temperature, the mobility of the PD may still be considered very low, as deduced from the recovery kinetics after electron irradiation in liquid He [6.2, 6.3]. The recombination volume obtained was found to be oxygen concentration independent and the value obtained was $v_{\rm f} = 195 \pm 17 \Omega$, where Ω is the atomic volume ($\Omega_{\rm Zr} = 23.3 \text{ Å}^3 = 2.33 \times 10^{-29} \text{ m}^3$). This result means that a vacancy and an interstitial have to be separated by more than 4 atomic distances to remain stable and avoid recombination.

6.2.6.2. Vacancy mobility

(a) Experimental data

In most metals and alloys, the diffusion processes are understood as being induced by the migration of PDs. Since the formation energies of interstitials are usually too high for their thermal formation, only vacancies are responsible for self-diffusion mechanisms. It should be remembered that the 'migration of a vacancy' is a misnomer, since a vacancy is nothing but a lack of matter. Its 'migration' refers to the jump of a surrounding atom leading to a change in configuration of the system (a new location for the vacancy) and interpreted as the migration of the vacancy.

The analysis of the recovery of irradiation damage after low temperature electron irradiation (at ≈ 4.2 K (-269°C)) allows quantification of the migration energies of the PDs induced by the impact of electrons. During the thermal recovery of electrical resistivity following the irradiation of pure zirconium samples, stage III can be associated with the migration of vacancies. The detailed isochronal behaviour during these post-irradiation thermal recoveries allowed Neely to determine the migration energy of vacancies to be in the range of $E_{\rm mv} = 0.54$ –0.56 eV [6.2].

Analysing self and solute atom diffusion behaviour in the zirconium HCP structure, Hood [6.24] observed a strong correlation between the diffusion coefficients and the sizes of the diffusing species that can be extended to the activation energies for bulk diffusion. The α -Zr self-diffusion fits with other species of atoms and confirms the activation energy given earlier of 3.17 eV. This value is the sum of the formation and the migration energies of vacancies leading to a high migration energy of $E_{mv} = 1.4-1.6$ eV. Frank [6.26] has proposed similar values based on an analysis of the diffusion of various foreign atoms and their interactions with PDs: 1.1 eV < E_{mv} < 1.5 eV.

To estimate the effect of temperature on the mobility of the PD in zirconium alloys, Griffiths et al. [6.35] analysed the size evolution of dislocation loops, previously obtained by neutron irradiation, during HVTEM electron irradiation. In high purity zirconium, the growth of vacancy *c* dislocation loops was observed at temperatures as low as 230 K and 320 K (\approx -40°C and 50°C), indicating some mobility of the vacancies at these temperatures. The corresponding migration energy was not computed but was expected to be low. The aim of the experiment was to show that the vacancies were mobile at low temperatures.

Hood et al. [6.36] analysed the kinetics of recovery of irradiation damage by positron annihilation spectroscopy and observed a strong increase in the height of the annihilation photopeak in the temperature range of 260–300 K (\approx -10–30°C). Since this quantity is affected by cavity type defects (i.e. vacancy clusters and not interstitials) and by their concentration and size distribution, this technique is an indirect measure of the activation energy of their clustering (i.e. of the long range mobility of the vacancies). The activation energy corresponding to these temperatures is about $E_{\rm mv} = 0.6-0.7$ eV.

Hellio et al. [6.37] performed experiments on a thin foil of Van Arkel zirconium during irradiation in a 1 MeV HVTEM. They observed that the relative concentrations of interstitial and vacancy loops depended on the orientation of the zirconium grains with respect to the foil plane. Christien and Barbu [6.38] have analysed these differences in dislocation loop behaviour, according to their orientations. Using a modified cluster dynamics model, to take into account the anisotropy, they have explained the different behaviour of the loops according to the crystallography of each grain with respect to the orientation of the thin foil. The conclusion of the work is that the size evolution of the interstitial loops is mainly

controlled by the vacancy behaviour. The latter is also strongly affected by the anisotropy of the interstitial mobility. Such an analysis stresses the difficulty in measuring intrinsic behaviour of one type of PD, since the irradiation effects observed are due to the complex evolution of all the PDs.

A fast vacancy diffusion mechanism appears to control the evolution of irradiation damage and has to be taken into consideration. In low temperature irradiations analysed by positron annealing spectroscopy or by observing dislocation loop evolution during electron irradiation in a transmission electron microscope, the migration energies measured are smaller by a factor of about two, compared with measurements performed without irradiation [6.39]. The reason for such a large difference in measured value of E_{mv} is not well understood, but could be due to some contribution induced by the experimental conditions (very high damage rates, typically 10^{-4} – 10^{-3} dpa·s⁻¹ induced by the electron beam) that enhances the diffusion mechanisms; for example, irradiation enhanced diffusion by ballistic mechanisms. A possible effect of Fe enhancing vacancy diffusion will be discussed in Section 6.2.6.4.

An important phenomenon for the dynamic evolution of the PD is the anisotropy in E_{mv} . Any diffusion anisotropy of the PDs will affect their migration, and as a consequence, the spatial PD recombination and clustering mechanisms. At high temperatures (above 1070–1170 K (\approx 800–900°C)), a clear anisotropy in the diffusion coefficient of atoms in dilute substitutional solid solution and vacancies is observed [6.25]. Since the formation energy of the vacancy is independent of its future migration mechanism, but depends only on the lattice site, which is unique, the difference in diffusion coefficients in the $\langle a \rangle$ and $\langle c \rangle$ directions can be attributed to differences in migration energies according to the directions of migration (detailed in Section 6.2.5.1)

(b) Computation and modelling

The migration mechanisms of vacancies can be computed either by MD methods, in which the mean displacement distance versus time leads to the diffusion coefficient, or by static computation of the energy barrier corresponding to the transition between two positions of the vacancy. Migration energies of vacancies in zirconium are expected to depend on the migration direction since the jump sites surrounding a vacancy are not identical because the atom packing is not ideal; $c/a < (8/3)^{1/2}$. The migration of a vacancy could occur either within the basal plane with a $1/3 < 11\overline{20} > jump$ or with a component in the <c> direction, with a shorter $1/6 < 20\overline{23} > jump$. The jump probability is equally shared between these two types, since a vacancy has six surrounding sites of each type, but the jump frequency, and therefore the mobility, may differ according to the energy barrier for each type of jump (i.e. the migration energies in the <a> and <c> directions E_{mv-a} and E_{mv-c}). A summary of the results of these computations, as well as the computations of the SIA migrations, is given in Table 6.4.

The first computations were carried out using pair potentials, being limited by computation capabilities. As reviewed by Bacon [6.29], the results showed a low anisotropy of migration energy, with a less than 10% difference between E_{mv-a} and E_{mv-c} , and typical values in the range of 1.25 eV. As the power of the computers increased, more accurate computations were undertaken using many-body potentials, resulting in a decrease of the migration energies (about 0.9 eV), while the low anisotropy was confirmed [6.33]. With an EAM potential, Pasianot and Monti [6.30] have computed the energies of vacancies in

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various static configurations to determine the saddle points for migration. The migration energies were lower and also of very low anisotropy ($E_{mv-a} = 0.57$ eV and $E_{mv-c} = 0.59$ eV).

In a study aiming at the analysis of PDs in a series of ten different species of HCP crystal structures, Hu et al. [6.40] have used a modified embedded atom potential for running MD computations. For zirconium, they obtained intermediate values of the migration energies ($E_{mv-a} = 0.67$ eV and $E_{mv-c} = 0.72$ eV), with similar anisotropy.

Computations have also been performed by Osetsky et al. [6.41] using a Finnis–Sinclair [6.10] many-body interatomic potential for MD and molecular static computations of the migration of PDs. The values obtained by the two techniques were quite close, but higher than those previously computed, ($E_{mv-a} = 0.91$ eV and $E_{mv-c} = 0.96$ eV) and ($E_{mv-a} = 0.84$ eV and $E_{mv-c} = 0.89$ eV), respectively.

Using a density functional theory technique, Vérité et al. [6.42] have computed the migration energies of a vacancy in zirconium. By allowing relaxation at the saddle point, they similarly found a higher migration energy of the vacancies in the $\langle c \rangle$ direction than in the $\langle a \rangle$ direction, by about 0.15 eV, with the mean value being about 0.6 eV.

(c) Clustering of vacancies

During irradiation, the PDs can migrate and interact with other defects, either of similar types or with foreign atoms. The formation of a cluster of vacancies starts when two vacancies meet, and the total energy is reduced compared with the sum of the two isolated defects. The stability of this configuration is important to assess, as it will affect the mobility of the PDs and the nucleation processes of large PD clusters such as dislocation loops. Therefore, the binding energies of di-vacancies were studied as soon as PD computations were available.

Large clusters of vacancies have been obtained in a first attempt to model the defect behaviour in zirconium cascades. Using an oscillating pair potential and analysing by MD the natural evolution of a vacancy-rich, high temperature volume, simulating the displacement spike (a region in which atoms have been moved from their original locations as the result of a cascade), Kapinos et al. have observed the formation of complex, 3-D morphologies of the vacancy clusters [6.43].

Using pair potentials, Bacon observed that the di-vacancies are stable with binding energies $E_{2v-b} \approx 0.2$ eV, almost independent of the di-vacancy configuration [6.29]. Two configurations have to be considered, similar to the vacancy jumps. As the size of the cluster of vacancy increases, by acquisition of other vacancies, the possible number of configurations of the cluster increases. Three dimensional configurations were found to be marginally more stable than planar ones, with a continuous decrease of the system energy as the number of vacancies increased. The values of the binding energies of the vacancy clusters were found to remain in the range of 0.18–0.25 eV per vacancy, whatever the technique used to compute them [6.30, 6.40].

With respect to the mobility of di-vacancies, the jump of an adjacent atom to the cluster induces the migration of the di-vacancy either in the $\langle a \rangle$ or in the $\langle c \rangle$ direction and can transform the orientation of the di-vacancy. Using a modified EAM potential, Hu et al. [6.40] have analysed exhaustively the different modes of di-vacancy migration. They concluded that the migration energies of di-vacancies are almost isotropic in zirconium. They found a balance between the anisotropy of the formation energies of the di-vacancies of different configurations, and the anisotropy of the activation energies for the jumps of different adjacent atoms, leading to either in or out of $\langle c \rangle$ -plane migration. Computations of the

behaviour of planar vacancy clusters (7 in the basal configuration and 13 in the prism configuration) have shown a relaxation that could be described as 3-D-type defects. For instance, the prism cluster containing 13 vacancies relaxes as a triangular prism of $\{10\overline{1}0\}$ faults, with ends bounded by intrinsic basal faults [6.29].

These faults are consistent with the 3-D shape of the vacancy clusters observed during the MD simulation of cascades in zirconium [6.44]. Created by a 20 keV PKA, a 30 vacancy cluster was found to extend over 4 planes in a complex configuration that, similarly to the stacking fault tetrahedral in face centred cubic (FCC) crystals, is formed by interconnected faults on the prism and basal planes. Such vacancy clusters should remain immobile.

The clustering of vacancies is modelled to be three dimensional and the change to form a planar defect is a complex process. The role of this change in geometrical configuration, to act as nuclei for the formation of dislocation loops, will be discussed in Section 6.3.1.2.

6.2.6.3. Interstitial mobility

(a) Experimental data

The measurement of the mobility of the interstitials is not a direct one. The analysis of the recovery of zirconium samples after irradiation can give information on the mobility of the PDs induced by irradiation. The first measurements were performed after electron irradiation at very low temperature. After the formation of PDs by high energy electron irradiation, an increase in temperature permits the study of the recovery of the damage. The change in electrical resistivity can be used to follow this recovery. Since the mobility of the interstitials is known to be much easier than the mobility of the vacancies, the different temperatures observed for the various stages of recovery can be attributed to different mechanisms of interstitial mobility [6.2, 6.3, 6.45].

Such experiments require electron accelerators and high purity zirconium; small concentrations of impurities interact with the PDs created during irradiation and modify their migration energies.

After irradiation at 4.2 K (-269° C) of zone refined zirconium, with an oxygen concentration of 0.015 at.% (27 ppm(wt)), Neely [6.2] analysed the recovery of the samples by electrical resistivity measurements. Numerous recovery peaks were observed. The low temperature peaks (<75 K (-198° C)) were attributed to local recombination of PDs. The majority of the recovery occurred near 100–120 K (-173 to -153° C) (identified as peak *I*_F), and the analysis of the details of the kinetics led to a long range migration energy of $E_{\rm mi} \approx 0.26$ eV. Annihilation peaks were also observed at a lower temperature, providing evidence of mechanisms of interstitial migration with lower energies [6.2]. Diffusion mechanisms in 1-D, 2-D and 3-D should also be considered as described in Section 6.2.6.3(b).

Working with various amounts of oxygen in high purity zirconium, Vialaret et al. [6.4] observed the recovery of zirconium samples after being neutron irradiated at 24 K (-249° C). They obtained similar peaks in the same temperature ranges (Fig. 6.6).



FIG. 6.6. Temperature derivative of the fractional recovery of the electrical resistivity of Zr(O) samples neutron irradiated at 24 K (-250°C). The mobility of the interstitials corresponds to the peak at 110–125 K (-163°C to -148°C) (this image was published in Ref. [6.4], copyright Elsevier, 1975).

(b) Computations of interstitial migration energies

Following the position of interstitial defects versus time during MD computations, Pasianot et al. [6.46] have deduced the diffusion coefficients of the self-interstitials from the length of the random walk, in the different crystallographic directions. They have used EAM interatomic potentials for these MD computations. At low temperatures (i.e. below 150 K $(-123^{\circ}C)$), the mobility was found to occur only as a one dimensional mechanism with interstitial defect jumps along the $< 11\overline{2}0 >$ direction. The corresponding apparent migration energy is low, 0.05 eV. In the temperature range of 200–600 K (\approx -70–330°C), the diffusion is mainly of a two dimensional type, with motion in the basal plane, and apparent migration energy below the measured one, for the simulation time of the computation. The diffusion coefficient obtained in the basal plane is about $(3-4) \times 10^{-8} \text{ m}^2 \cdot \text{s}^{-1}$ for a temperature range of 300–700 K (\approx 20–430°C). A few jumps have been observed in the $\langle c \rangle$ direction starting at 300 K (room temperature), with increasing numbers as the temperature is increased, following a standard Arrhenius behaviour with an activation energy of $E_{\text{mi-c}} \approx 0.14 \text{ eV} (13.5 \text{ kJ} \cdot \text{mol}^{-1})$. At the maximum temperature studied of 700 K ($\approx 430^{\circ}$ C), the diffusion coefficient obtained for basal motion is twice as large as diffusion in the $\langle c \rangle$ direction.

Osetsky et al. [6.41] have performed similar computations using a Finnis–Sinclair [6.10] many-body interatomic potential for MD computation of the migration
of PDs in the temperature range for which the HCP structure remains stable with this potential (i.e. up to a computed melting temperature of 2120 K (\approx 2390°C)). The migration mechanisms of the interstitials were found to be temperature dependent, with a low migration activation energy for the basal plane mobility ($E_{mi-a} \approx 0.06 \text{ eV}$) and a higher one for the mobility in the <c> direction ($E_{mi-c} \approx 0.15 \text{ eV}$). A sequence of diffusion mechanisms has been found to change with increasing temperature: below 500 K (\approx 230°C) the main diffusion mechanism is the one dimensional $< 11\overline{20} > \text{crowdion}$. Above 600 K (\approx 330°C) rotation in the basal plane is possible, allowing basal and two dimensional diffusion and a low rate of <c> jumps. For the highest temperature. In the temperature range of interest for power reactors (T about 600 K, \approx 330°C), the diffusion coefficients obtained are the following: $D_{i-a} \approx 8 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ and $D_{i-c} \approx 1 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$.

Using a similar interatomic potential, Woo et al. [6.47] have analysed the interstitial diffusion behaviour in the temperature range of 500–1100 K (\approx 230–830°C). They also found the increase in dimensionality of the diffusion with temperature. An irregular behaviour of the migration in the basal plane has also been reported, with a very low activation energy ($E_{mi-a} \sim 0.01 \text{ eV}$, i.e. $\approx 1 \text{ kJ} \cdot \text{mol}^{-1}$), as well as a regular increase of the <c> component of the diffusion coefficient with temperature with a migration energy of $E_{mi-c} \approx 0.16 \text{ eV}$ (\approx 15 kJ·mol⁻¹), very close to the previous study. Computing the effective diffusion rate of the interstitials in all directions, with provision for the multiplicity of the jump configurations for each type of migration, they obtained the anisotropy factor for self-interstitial diffusion as a function of temperature. This anisotropy factor is slightly below 1, and the anisotropy decreases as the temperature increases (Fig. 6.6). The diffusion coefficients obtained for the temperature ranges studied ($D_{i-a} \approx 3 \times 10^{-8} \text{ m}^2 \cdot \text{s}^{-1}$ and $D_{i-c} \approx 1 \times 10^{-8} \text{ m}^2 \cdot \text{s}^{-1}$) are larger than in the previous study [6.41] and the higher off-basal migration rate induces a much lower anisotropy.

A comparison of the formation and migration energies for the different PDs computed in zirconium is given in Table 6.4. The temperature dependence of the interstitial diffusion anisotropy is given in Fig. 6.7.



Computed Anisotropy of interstitial diffusion

FIG. 6.7. Comparison of the computed anisotropy factors of the SIA diffusion coefficients (a) [6.47]; (b) [6.46]; (c) [6.41].

Relaxation volume (normalized to the atomic volume)		Formation energies (eV)		Migration energies (eV)			Year	Ref.	
Vac.	SIA	Vac.	SIA	Vac. < <i>a</i> >	Vac. < _C >	SIA < <i>a</i> >	SIA <c></c>		
		1.2–1.3	4–5	1.3	1.2	< 0.2	< 0.1	1988	[6.29]
-0.2	0.86	1.74	2.5-2.8	0.57	0.59			1999	[6.30]
-0.2	0.6	1.7	3.5	0.72	0.67			2001	[6.40]
				0.85	0.90	0.06	0.15	2002	[6.41]
		2		0.5	0.65			2007	[6.42]

TABLE 6.4. COMPARISON OF THE FORMATION AND MIGRATION ENERGIES OF THE PDs IN PURE ZIRCONIUM

Note: The data in the table are computed by ab initio, MD or molecular statics for the most stable configuration or easiest migration path.

(c) Clustering of interstitials

The binding energies of di-interstitials were found to be very high in computations performed with pair potentials. Typical values of $E_{2i-b} \approx 1.8-2.2$ eV were reported, with configurations of the di-interstitials as two adjacent basal octahedral defects in the same basal plane, allowing a migration along their own cylinder (one dimensional basal glide) [6.29].

De Diego et al. [6.48] have computed the mobility of a small cluster of interstitials by MD, using a Finnis–Sinclair main-body potential; they included the configuration and energies of up to 30 SIAs. In all cases, the most stable configuration is formed by stacking basal-split-dumbbell–type SIAs in the prismatic $< 11\overline{20} >$ planes. The binding energies increased with the number of SIAs in the clusters, from about 0.8 eV for the di-interstitial to more than 2 eV for clusters of 10 SIAs. The large clusters can be described as a perfect edge dislocation loop, with Burgers vector $1/3 < 11\overline{20} >$. These planar defects exhibit a fast mobility along their cylinder (i.e. one dimensional diffusion along the basal plane), with migration energies decreasing with cluster sizes (from 0.02 eV for a 4 SIA cluster to 0.01 eV for a 24 atom SIA cluster). The clustering of SIAs does not reduce their mobility. During MD analysis of defects created during irradiation cascades, the resultant dislocations were observed to readily migrate back and forth along their Burgers vector directions [6.44].

6.2.6.4. Interaction of PDs with solute atoms

When low temperature irradiation tests were performed on zirconium samples, generally with electrons, the recovery kinetics were analysed in terms of PD mobility, as described in the previous sections. Experiments on alloys, or with zirconium doped with controlled concentrations of various atomic species, allowed the observation of interactions between PDs and foreign atoms [6.4, 6.49, 6.50].

Oxygen, known to interact strongly with dislocations, was shown to affect the damage rate slightly, but does not affect the recovery kinetics very much. Interaction of this highly soluble interstitial species with PDs seems to be low [6.4]. The effect of O concentration on the kinetics of irradiation loop annealing could be explained by the effect of O segregation on dislocations, rather than on interactions of interstitial O with the PDs [6.51].

IRRADIATION DAMAGE

Irradiations performed on zirconium containing substitutional elements, such as Au, Ce or the more useful Sn, revealed that various types of interactions may be observed. Irradiation damage recovery can be observed during heat treatments, with various stages corresponding to different types of defects with different mobilities and annealing temperatures. Trapping of PDs by tin was observed to saturate with about 1 at.% (1.3 wt%) Sn concentration for stage I (interstitial mobility), and was not observed to saturate up to 2.3 at.% (2.97 wt%) Sn for stage III (vacancy mobility) [6.49].

Performing irradiations with neutrons of various incident energies, Zee et al. have analysed the effect of substitutional solute atoms (Au, Sn, Ti, Dy) on damage buildup and recovery at low temperatures. For these species, the presence of solute atoms drastically reduced the damage production rate measured by electrical resistivity and the recovery stages I and III [6.52, 6.53]. They concluded that such species interact with the interstitials and, for Sn, with the vacancies. By analysing the size of the atom of the doping element, it was possible to attribute the interaction to the absolute value of the atomic size difference between the doping elements and zirconium. The absence of interaction of the PDs with oxygen was also confirmed.

The PD behaviour in zirconium is manifested in the shape change that occurs in Zr-alloy components during irradiation. Irradiation growth is a strain induced by irradiation without applied stress and represents the intrinsic irradiation deformation behaviour of the material. There has to be a net difference in flow of PDs in a given direction that is due to sinks biased for one type of PD or anisotropic diffusion or both. As the PD diffusion is a function of the direction in the crystal, then the mass transport due to diffusion of PDs will be dependent on the crystallographic texture of the Zr-alloy components. Irradiation growth is described in detail in Chapter 7. In connection with the solute-PD interactions, the measurements of the irradiation growth of Zr-Sn (0.1 and 1.5 wt% (0.077 and 1.16 at.%)) alloys at 353 and 553 K (80 and 280°C) have been satisfactorily modelled for the 353 K (80°C) irradiation using the standard time dependant theory of defect concentration and an Sn atom vacancy binding energy of $E_{v-Sn} \approx 0.3$ eV [6.54]. Although this moderate binding energy suggests a significant reduction of growth rate with higher Sn concentration at low temperatures, the modelling failed to predict the behaviour at the higher temperature. The concentration of PDs was found to be independent of Sn concentration for standard power reactor temperatures, while the growth rates were reduced at higher Sn concentrations. This discrepancy could be due to the simple isotropic diffusion mechanism assumed; diffusion anisotropy may be strongly modified by Sn-vacancy interactions.

Similarly, a large transport of Sn has been observed from the bulk of 25 μ m Zircaloy-2 foils to the free surface during proton irradiation at 350 K (77°C) up to 3 dpa. The amount of Sn transferred to the surface induced precipitation of Sn crystals, corresponding roughly to 3 atomic layers. The results were analysed considering an interaction between PDs and Sn atoms, using a difference in energy of $E_{i/Sn} \approx 0.1$ eV for the substitution of an Sn atom instead of a Zr atom for the interstitial atom. This energy difference could be considered the binding energy between Zr and Sn when one of the atoms is in an interstitial configuration. While the transport distance was small (about 10 μ m) and cannot be considered for the behaviour of components in reactors, the result clearly confirmed the PD-Sn flux coupling and transport [6.55].

Of great industrial importance is the behaviour of Fe atoms. Fe exhibits a very low solubility in α -Zr. For pure zirconium, the solubility limit is below 120 ppm (0.02 at.%) at the temperature of maximum solubility (about 1073 K (800°C)) and is slightly increased with Sn additions [6.56]. As described in Section 6.3.2.1, the irradiation of the Fe-Cr rich

Zr(Fe,Cr)₂ precipitates induces their amorphization and the release of Fe into the Zr matrix. The interaction of the PDs with Fe atoms in solution strongly affects their mobilities and clustering behaviour. Working on high purity zirconium, with Fe concentration reduced below 1 appm (0.5 wt. ppm), Hood et al. have analysed the effect of Fe on the self-diffusion of zirconium and diffusion of various doping elements [6.25, 6.57]. They demonstrated the role of Fe in enhancing the diffusion of substitutional atoms, with diffusion controlled by vacancy mechanisms, and also the diffusion of interstitial atoms, diffusing by interstitial mechanisms. For the vacancy–Fe interaction, a binding energy of $E_{v-Fe} \approx 1.4$ eV has been proposed [6.58]. Such vacancy–Fe complexes would reduce the migration energy of the vacancies to $E_{m/v-Fe} \approx 0.7$ eV, a value consistent with the measurements of zirconium atoms (0.14 nm and 0.16 nm, respectively) support these interactions with PDs.



FIG. 6.8. Fast exchange mechanisms with fast interstitial (F_i) — vacancy (V) or solute (F_s) — vacancy mechanisms proposed by Frank (reproduced from Ref. [6.26] with permission courtesy of Taylor & Francis).

The detailed configurations of the complex formed by the Fe atom and the vacancy are not known in detail but are considered to allow a fast exchange rate between the SIA or vacancy and the Fe atom. Two qualitative models have been proposed, but remain speculative, though conceivable [6.59]. The binding of the vacancies with Fe atoms, developing a 'fast configuration', allows an increased mobility of both the vacancies and the Fe atoms (Fig. 6.8) [6.26]. Intrinsic mobility (i.e. vacancy diffusion) of the Fe atom is observed at high temperatures, while at low temperatures, the concentration of Fe atoms (or other fast diffusing solute atoms) exceeds the concentration of thermal vacancies and the formation of such complexes allows a significant increase of the Zr/Fe mobility.

Since any future direct experimental analysis of these complexes remains questionable, owing to the low solubility of Fe and therefore the low concentration of such complexes, standard microstructural experiments are not expected to be fruitful in this respect and fundamental progress in understanding is still required in this area. Quantum chemistry modelling techniques would open the possibility of describing the configurations and displacement mechanisms of such PD–Fe complexes. Valuable information has been obtained regarding the interactions of H atoms with planar defects in zirconium [6.60]. Expanding these computations to the cases of Fe and other low concentration solutes would be very useful.

6.2.6.5. Synthesis on PD mobility

The anisotropy in PD diffusion coefficients affects the evolution of the PD concentration and is postulated to be a major parameter of the physical phenomena responsible for the growth behaviour. The estimates of the migration kinetics described above do not agree in detail between themselves, but general tendencies can be observed:

- The migration energies of self-interstitials are much lower than the migration energies of the vacancies. Owing to the low formation energies of the Zr self-interstitials, compared with those of other metals, the contribution of interstitial diffusion to the self-diffusion transport mechanisms has to be taken into consideration [6.34].
- The migration energies of the interstitials are very low and appear to be weakly crystallography dependent, with a lower migration energy in the basal plane than in the $\langle c \rangle$ direction, therefore exhibit dominance at very low temperatures. The low values mean very fast diffusion above room temperature, in the range of a few $10^{-8} \text{ m}^2 \cdot \text{s}^{-1}$.
- The diffusion activation energies of vacancies appear to be weakly anisotropic; differences in the pre-exponential factor could affect the anisotropy of the diffusion coefficient.
- Due to a strong interaction of the PDs with various chemical species, their mobility is expected to be very different in the case of industrial alloys compared with mobilities measured in studies performed on high purity zirconium.

Despite significant differences in the history of the evaluation of the PD formation and migration energies, convergences can be observed between experimental data and computations. Likely values are given in Table 6.5.

	Formation energy (eV)	<a> migration (eV)	<c> migration (eV)</c>
Zr interstitial	3.0 ± 0.1	0.05 ± 0.03	0.15 ± 0.03
Vacancy	2.1 ± 0.1	0.5 ± 0.07	0.6 ± 0.07

TABLE 6.5. LIKELY VALUES FOR THE FORMATION AND MIGRATION ENERGIES OF PDs IN PURE ZIRCONIUM

6.2.7. High energy interactions: Cascade formation

6.2.7.1. Cascade computation

Using a Finnis–Sinclair–type potential that reproduces satisfactorily the properties of zirconium, Wooding and Bacon [6.61] and Gao et al. [6.62] have analysed the behaviour of the cascades in zirconium by MD computations. Starting with low PKA energies and low temperatures [6.61], they have increased the energies [6.44] and the temperatures to values typical of power reactors (T = 600 K, ($\approx 330^{\circ}$ C), and $E_{pka} = 20$ keV) [6.62]. Running several computations for each cascade condition, they have obtained enough data to draw statistically sound conclusions.

The temperature increase at the core of the cascade depends on the initial temperature of the zirconium crystal, due to the non-linear heat flow at the time and space scales of the event. For a 20 keV cascade, a zone of 'molten' zirconium is observed to have a radius of about 1 nm for 4 ps at 100 K (-173° C), while the increase of the temperature would enlarge the molten zone and duration (2 nm and 6 ps at 600 K (\approx 330°C)) [6.62]. These lifetimes and

sizes of 'molten zones', corresponding to thermal spikes, are consistent with the computations of cascades as molten and quenched zones described earlier [6.43].

For high energy cascades, the important observation was the formation of large clusters of PDs surviving at the end of the recovery phase. Large clusters of the two types, interstitials and vacancies, were observed. These clusters were stable and were more frequent as the energy of the PKA increased. A difference was noticeable between the two types of PD. In the case of vacancies, the number of surviving vacancies as individual or di-vacancies was high, and the number of larger vacancy clusters was low. The reverse was obtained for the interstitials. The fraction of surviving single interstitials was lower by a factor of 2 at 100 K (-173° C) and about 3 times lower at 600 K ($\approx 330^{\circ}$ C) than the number of free vacancies for the same conditions; large and stable clusters of interstitials were obtained in high numbers (Fig. 6.9). A major consequence, clearly seen in Fig. 6.10, is that the number of surviving isolated defects is not the same for the two types of PD. The cascades release a much higher number of isolated, free vacancies than interstitials. This effect is known as the production bias, which has to be considered when solving the rate equations in the mean-field approach of PD evolution [6.63].



FIG. 6.9. Size of the PD clusters in zirconium cascades as computed for cascades of different PKA energies in Zr (this image was published in Ref. [6.62], copyright Elsevier, 2001).

The analysis of the evolution of the cascades after the maximum damage shows that the clusters of SIAs are very mobile, due to their *a* type dislocation configuration. They can glide back and forth along their own cylinder (along the $< 11\overline{2}0 >$ directions of the basal plane) during the thermal spike (i.e. during the time for which the average kinetic energy of the atoms considered is well above thermal energy). It was observed that small clusters (up to 3 SIAs) can change their migration direction and switch to $< \overline{2}203 >$ in a non-basal migration. Such a change in glide direction could be explained by the very low energy differences between the $< 11\overline{2}0 >$ crowdion and the $< \overline{2}203 >$ crowdion-like clusters. As for the individual SIAs, their high mobilities allowed the observation of their recombination with vacancies during the short computation time of the cascade evolution. This observation is consistent with data obtained on recovery following low temperature irradiation and the different migration mechanisms assumed [6.2]. The restricted motion of these mobile interstitial clusters may help to explain the observed anisotropy of irradiation growth if they provide a significant contribution to the mass flow.

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Typical configurations of the remaining PD clusters after the development and early recovery phase of a cascade are presented in Fig. 6.10. As commonly observed in other metals, the final damage state consists mainly of a cloud of SIAs surrounding a highly disordered core. The configurations of the clusters obtained during the cascade computation were consistent with those described earlier on static computations.



FIG. 6.10. Computed final state of the damage for two typical cascades in zirconium at 600 K (\approx 330°C) (Interstitial: \circ , vacancy: \bullet) (this image was published in Ref. [6.62], copyright Elsevier, 2001).

As the clusters of PDs are expected to play an important role in the nucleation of dislocation loops, the geometry of loop-shaped clusters has to be examined. Interstitial clusters were found to be predominantly of the prism type, whatever the temperature, with a Burgers vector $1/3 < 11\overline{20} >$, while the vacancies clustered in more complex configurations, occasionally found to collapse during the end of the thermal spike, were found predominantly as a prismatic loop of Burgers vector $1/2 < 10\overline{10} >$. Although the effect of solute atoms is important for the behaviour of the PD clustering and migration, as described earlier, this type of PD clustering would serve as dislocation loop nuclei that characterize irradiation damage from irradiation-produced cascades.

6.2.7.2. PDs surviving from cascades

As with other metals, much recovery exists within the cascades, and the proportion of surviving PDs is lower than that obtained by the Norgett, Robinson and Torrens approach [6.17]. This quantity is critical for the computation of the irradiation damage, as the PD evolution will depend directly on the generation rate. The study provided the number of Frenkel pairs (N_F) at the end of the cascade process versus the energy of the PKA (E_p) (Fig. 6.11) [6.62].



FIG. 6.11. Final number of Frenkel pairs (NF) versus the energy of the PKA (Ep) in zirconium compared with the Norgett, Robinson and Torrens values (this image was published in Ref. [6.62], copyright Elsevier, 2001).

The number of remaining defects is observed to depart from the Norgett, Robinson and Torrens formula. Zirconium follows a general trend observed for most metals for the number of Frenkel defects:

$$N_{\rm F} = A \left(E_0 \right)^m \tag{6.9}$$

The numerical values at 600 K (\approx 330 °C) give a lower value of N_F than at 100 K (-173° C) owing to some intracascade recovery at this higher temperature: $A = 3.61 \text{ keV}^{-m}$ and m = 0.757. The corresponding data points and curves are shown in Fig. 6.11.

For a typical reactor temperature and fast neutron energy (1 MeV), the maximum energy of the PKA is $E_{pka} \approx 22$ keV, which induces 220 atoms displaced in the cascade. In-cascade recovery will lead to a reduced number of surviving defects; about 35 Frenkel pairs from Fig. 6.11. For lower energy impacts, the surviving rate is slightly increased, making low energy cascades more efficient in PD production.

6.2.8. Sinks for the PDs

Once formed, the isolated PDs can migrate and interact with any other crystal defects. Among them, the dislocations present in the alloy act as sinks for interstitials as well as for the vacancies. This absorption of PDs will result in the climb of these dislocations, inducing some irreversible strains. If the climb induced by the disappearance of the PDs on the dislocations is not isotropic, this anisotropy will result in a macroscopic strain. This strain will lead either to creep, when the anisotropy is induced by an applied stress, or to growth (strain in the absence of applied stress), when the anisotropy is caused by crystal anisotropy and crystallographic texture developed during thermomechanical processing of the HCP zirconium alloys. Clusters of PDs have also to be considered as nuclei for the formation of dislocation loops. Their geometrical evolution could also contribute to the macroscopic strain. These deformation mechanisms are described in detail in Chapter 7.

6.2.8.1. Line sinks: Dislocations and loops

In the theory of PD migration towards sinks, the sink strength of the dislocations is based on the elastic interactions between the dislocation strain field and the elastic distortion of the PDs. In the case of a cubic, isotropic system, this interaction increases with the relaxation volume of the PDs, which is higher for the self-interstitial than for the vacancy. Therefore, a higher interaction is obtained for self-interstitials, and since they also have a higher mobility, they disappear faster on dislocations than vacancies. This behaviour is the basis for the mechanism of a bias, always in favour of the interstitials, leading to their faster disappearance on dislocations and, therefore, to a higher concentration of vacancies under irradiation.

In the case of anisotropic crystals, such as zirconium alloys, the migration of the PDs, as described in Section 6.2.5, is not isotropic, especially for the interstitials. In that case, the net flux of PDs to the dislocations is not so simple to assess. It has been proposed that a diffusional anisotropy difference of self-interstitials relative to vacancies may induce different dislocation sink strengths, depending on the relative orientation of the dislocation is derived from the following equation:

$$\alpha = \alpha_0 \left[\frac{D_c}{D_a} \right]^{-\frac{1}{3}} \left(\cos^2(\lambda) + \left[\frac{D_c}{D_a} \right] \sin^2(\lambda) \right)^{\frac{1}{2}}$$
(6.10)

where

 α_0 is the strength of a dislocation in an isotropic medium;

 λ is the angle between the dislocation line and the $\langle c \rangle$ axis;

and D_i is the diffusion coefficient in the $\leq j >$ crystallographic direction.

For the differences in diffusion coefficient that can be expected, the bias can be as large as 100% and can be in favour of either type of PD, depending on local orientation, instead of being close to unity and slightly in favour of the interstitials, as for isotropic materials; see Fig. 6.12. An additional contribution due to the anisotropic elastic interaction exists. It has been found to be of second order, compared with the diffusional anisotropy difference induced effect [6.64].



FIG. 6.12. Computed dislocation bias for PDs disappearing mainly on dislocations in zirconium as a function of the diffusion anisotropy parameter $p = (D_{\sim}/D_{a})^{1/6}$ (this image was published in Ref. [6.64], copyright Elsevier, 1988).

6.2.8.2. Surface sinks: Grain boundaries, interfaces and free surfaces

For surfaces, either free surfaces or grain boundaries, the sink strengths are equivalent for both types of PD in isotropic materials. In anisotropic crystals, exhibiting diffusional anisotropy difference, a bias also exists that will enhance a flux of PDs to surfaces, according to their crystallographic orientation.

The efficient nature of grain boundaries as sinks for interstitials can be observed in Fig. 6.13, where a zone free of interstitial loops is observed in the vicinity of grain boundaries. The grain boundaries are strong sinks for interstitials and therefore reduce the local concentration of interstitials, inhibiting the nucleation of the interstitial loops in their vicinity, and allowing only vacancy loops to form.



FIG. 6.13. Band free of interstitial dislocation loops in the vicinity of a grain boundary (crystal bar zirconium irradiated at 700 K (\approx 425°C) to a fluence of 1.5 × 10²⁶ n·m⁻²) (this image was published in Ref. [6.65], copyright Elsevier, 1988).

6.2.8.3. Modelling the evolution kinetics of irradiation defects

An approach to model PD evolution under irradiation is to solve the kinetics equations for their interaction with the extended defects. A set of two coupled equations is obtained. For each species (vacancies or interstitials), the concentration evolution is equal to the balance between PD generation by irradiation, G, and their disappearance either mutually with the opposite type of defect, or on any kind of sink. Each sink can be assigned its own strength leading to a kinetic coefficient k. A set of equations is obtained [6.66]:

$$\frac{\partial c_{\rm v}}{\partial t} = G_{\rm v} - R_{\rm iv} D_{\rm i} c_{\rm i} c_{\rm v} - \sum_{\rm j} k_{\rm j,v} D_{\rm v} c_{\rm v} + \sum_{\rm j} k_{\rm j,v} D_{\rm v} c_{\rm v,j}^{\rm e}$$

$$\frac{\partial c_{\rm i}}{\partial t} = G_{\rm i} - R_{\rm iv} D_{\rm i} c_{\rm i} c_{\rm v} - \sum_{\rm j} k_{\rm j,i} D_{\rm i} c_{\rm i}$$
(6.11)

where for the vacancies, a thermal release from the dislocations and free surface, $\sum_{j} k_{j,v} D_v c_{v,j}^e$, is considered; $c_{v,j}^e$ denotes the thermally equilibrium values of the concentrations.

This contribution to the vacancy concentration is important for PD recovery, either during high temperature irradiation or for post-irradiation heat treatments, since then the thermal vacancies are the only PDs responsible for atom mobility. The solution of this system of coupled differential equations allows a description of the evolution of the PDs with time, but it assumes that the sink concentration (e.g. the dislocations and loops) remains constant. For zirconium cladding in a water reactor, the steady state solution of this system of equations gives a concentration of vacancies in the range of $c_v \approx 10^{-5}$ and a much lower value for the interstitials: $c_i \approx 10^{-10}$ [6.67].

The size evolution of a single loop, considered isolated in an infinite medium surrounded by a given concentration of interstitials and vacancies, can be computed by methods based upon the balance of fluxes at the sink formed by the dislocation. The bias parameters of the loops acting as PD sinks are found to increase with loop size. The loop sink strength (i.e. the efficiency of PD trapping, a function of loop size, density and orientation), which controls the size evolution rate through the $k_{j,i}$ and $k_{j,v}$ factors, increases strongly as the loops become large, due to the increased density of dislocation lines. In addition, the sink strength depends on the type of PD considered. The loop growth is therefore expected to depend on the size and type of the loops. For interstitial loops, the net flux of PDs leads to a limited growth for small loops and early saturation, while for vacancy loops, growth to larger sizes is expected [6.68]. The calculated growth rate of the loops is predicted to be proportional to φ^x , where φ is the irradiation flux and $x \approx 0.5$, corresponding well to the observations in HVTEM on Ni [6.69] or Zr [6.37].

For extended defects such as dislocation loops, interacting with each other via the PD fluxes, their concentrations and size distributions have to be computed using another method, the cluster dynamics approach, in which the rate of growth and shrinkage of each loop is analysed by condensation and emission of individual PDs. The modelling is based on an extension of Eq. (6.11), with the reactions of the PD analysed on all the loops of different sizes. This approach leads to a much larger system of equations, since all the dislocation loop types and sizes have to be considered individually. For instance, the change in concentration of interstitial loops of size n is due to the balance in the growth of loops of size n - 1 by absorption of one interstitial, the shrinkage of loops of size n + 1 by absorption of one vacancy, and the change of loops of size n to $n \pm 1$ by the same two processes. The symmetric mechanisms hold for the vacancy loops are expressed as:

$$\frac{dc_{n,i}}{dt} = \beta_{n-1,i}^{i} D_{i} c_{i} c_{n-1,i} + \beta_{n+1,i}^{v} D_{v} c_{v} c_{n+1,i} - (\beta_{n,i}^{v} D_{v} c_{v} + \beta_{n,i}^{i} D_{i} c_{i}) c_{n,i}
\frac{dc_{n,v}}{dt} = \beta_{n-1,v}^{i} D_{v} c_{v} c_{n-1,v} + \beta_{n+1,v}^{i} D_{i} c_{i} c_{n+1,v} - (\beta_{n,v}^{v} D_{v} c_{v} + \beta_{n,i}^{i} D_{i} c_{i}) c_{n,v}$$
(6.12)

This large system of equations (more than a few hundred classes of loop size) representing discrete sizes can be transformed into a continuous distribution [6.70]. One of the critical aspects of this approach is to obtain a good description of the kinetic coefficients $\beta_{n,PD}^{PD}$. In the case of zirconium, a choice of suitable parameters for the evaluation of the betas permitted an explanation of the simultaneous stability of the two types of loop [6.71]. The method has been extended to the anisotropic case of zirconium, and it is able to explain the grain-to-grain variations in loop concentrations observed on HVTEM irradiation, relating the variation to the orientation of the grains with respect to the foil [6.38].

In summary, neutron irradiation causes damage in zirconium alloys by displacing atoms out of their normal lattice positions, forming vacancies and self-interstitials. These PDs interact, either with each other to mutually annihilate or with themselves to form dislocation loops. PDs also interact with intrinsic dislocations, which can then move by climb. Asymmetry in the production of single vacancies and interstitials and anisotropy of their migration produces changes in the shape of zirconium crystals.

6.3. IRRADIATION DAMAGE AND CHANGES IN MICROSTRUCTURE

6.3.1. Irradiation defects in the zirconium HCP matrix

6.3.1.1. Absence of voids

Early in the history of observation of irradiation damage induced by a high dose on metals and alloys, the formation of voids and the development of swelling was considered a general and unfortunate behaviour [6.72]. The first studies failed to show any cavities in zirconium alloys after irradiation [6.73]. With the performances of transmission electron microscopy (TEM) available at that time, it was not easy to determine the nature of the 'black dots' observed after moderate irradiation. Usually, light heat treatments were used, with the aim of coarsening the irradiation defects, to make their identification easier.

Improvements in the quality of the observations allowed the confirmation of the absence of cavities even for the case of high purity zirconium [6.74]. Minor elements were thought to impede the formation of voids and to avoid swelling. The very low production of He by (n,α) reaction during zirconium irradiation was suggested as a possible reason for this absence of voids. As a confirmation of this explanation, 1 MeV electron irradiation on zirconium samples pre-implanted with He at various concentrations showed the nucleation and growth of voids only for the samples doped with at least 100 ppm (0.23 at.%) of He [6.75]. The high solubility of the gases, oxygen and nitrogen, frequently found as impurities in metals, is an indication of the low tendency of these atoms to cluster within the alloys and then to precipitate and form nuclei for voids. Therefore, the absence of He creation, as well as the absence of a driving force for precipitation of the gases present as solute species, inhibits the usual mechanism of void nucleation by complex clusters of precipitating gases and vacancy sinks. A few observations have been made with the specific conditions required for very limited void formation.

After neutron irradiation in the temperature range of 680-760 K ($\approx 410-490^{\circ}$ C), cavities can be observed close to grain or interphase boundaries, as shown in Fig. 6.14 [6.65]. Cavities have been obtained with HVTEM irradiation on thin foils of various zirconium alloys, with a tendency for increased void formation for the samples of higher oxygen concentration [6.76]. The formation of voids appears to require specific irradiation conditions. As has been shown in Section 6.2.7.2, grain boundaries can be sinks either for vacancies or interstitials. For the conditions corresponding to grain boundaries acting as sinks for the interstitials, in the two cases considered (thin foils or grain boundary vicinity), the location of void formation is close to an efficient sink for interstitials. As a consequence, their local concentration is reduced, increasing the vacancy concentration and the driving force for their clustering.

For electron irradiations at 573 K (\approx 300°C), voids are observed in zone refined zirconium and various industrial alloys above 20 dpa and are frequent above 60 dpa. The presence of voids was not systematic and, for the industrial alloys, depended on the thermomechanical history before irradiation [6.76]. The voids obtained are facetted, having the form of a hexagonal cylinder, oriented along the HCP main crystallographic directions linked by (0001) and {1011} or {1010} planes, with typical dimensions of the order of 50 × 10 nm. In situ observation of their size evolution during irradiation indicated that once nucleated, the cavities grow slowly by enlargement in the $\langle c \rangle$ direction and shrinkage in the $\langle a \rangle$ direction, giving a direct observation of the effect of PD diffusion anisotropy on microstructure evolution.



FIG. 6.14. Small voids observed on pure zirconium irradiated at 700 K (\approx 425°C) to 1.5 × 10²⁶ n·m⁻² (this image was published in Ref. [6.65], copyright Elsevier, 1988).

For the neutron irradiation experiments, voids are observed with low frequency and only in crystal bar or sponge materials irradiated to high fluences at high temperatures, and not in industrial alloys [6.77]. The doses for which voids are observed are well above the lifetime limits obtained in cladding and channels but could be relevant to structural components such as pressure tubes. When observed, the volume fraction of cavities remains low and cannot contribute significantly to any geometrical change of the structural components. Any changes in geometry are mainly due to the mechanism of growth, induced by the net anisotropic annihilation of self-interstitials at sinks oriented to give an $\langle a \rangle$ type strain when absorbing PDs. The observation that basal c-component loops are invariably vacancy type in nature is consistent with this premise [6.77]. Measurements of the density variations in Zr-2.5Nb induced by irradiation showed the absence of any significant long term volume change after neutron irradiation up to doses of 1.7×10^{26} n·m⁻² at 533 K (260°C), while growth strain was observed to be in excess of 1% [6.78].

6.3.1.2. Dislocation loops

An unusual behaviour of zirconium alloys, compared with other metals and alloys, is the simultaneous presence of both vacancy and interstitial type of dislocation loops after irradiation. In addition, the dislocation loops have various orientations and Burgers vectors. The anisotropic behaviour of the zirconium HCP structure induces specific behaviour of the PD migration and clustering that controls both the nucleation and growth of the loops. Therefore, their generation and evolution mechanisms have to be detailed for any analysis of the dislocation microstructure obtained after irradiation.

The formation of loops in HCP metals has been studied on many systems with different c/a ratios. This parameter controls the energies of the defects and is therefore an important parameter for the nucleation and growth of dislocation loops.

For the vacancy loops, the clustering of PDs in a planar manner has to be followed by some slip in the loop plane to allow the atoms to recover a coordination number of 12, instead of 10 in an unfaulted loop. For planar clustering of the interstitials, a stacking fault is created

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as the loop forms, which could be removed by a similar process to that in a vacancy loop. In both types of loops, the process requires the formation of a stacking fault, extrinsic for interstitial loops and intrinsic for vacancy loops. The Burgers vectors and the stacking fault energies control the energy balance of the process, both possibly affected by the segregation of various types of solute atoms.

(a) Loop nucleation criteria — stacking fault energies

The first criterion for selecting the loop habit plane was based on the packing density of different planes on the HCP crystals. The critical c/a ratio is $\sqrt{3}$, above which the basal plane should be the loop habit plane. Another criterion compares the c/a ratio to the ideal HCP packing of hard spheres $(8/3)^{\frac{1}{2}}$. A survey of the loop planes for various HCP metals confirmed that these simple criteria were not sufficient for a valid description of the irradiation behaviour of the HCP metals [6.79].

The self-energy of a dislocation loop can be obtained from standard dislocation theory [6.80] and, for loops of large radii, is expressed by:

$$E_{loop} = 2\pi R \frac{\mu b^2}{4\pi (1-\nu)} \left(\ln \frac{4R}{\rho} - 1 \right)$$
(6.13)

where

R	is the radius of the loop;
μ	is the shear modulus;
ν	is the Poisson's ratio;
b	is the Burgers vector length;

and ρ is the cut-off radius for dislocation energy computation, usually considered similar to *b*.

The energy balance for the nucleation of a given dislocation loop is obtained as the sum of the dislocation line self-energy, of the stacking fault surface energy and of the energy recovered by annealing of the PDs. For a loop of radius R, formed by the clustering of n vacancies or interstitials, the energy balance for the loop formation is the difference in PD formation energies and final configuration energy. In a continuum mechanics description of the loop, this energy balance can be expressed as:

$$\Delta E_n = 2\alpha\mu b^2 \sqrt{\pi n\frac{a}{b}} + \gamma_{\rm SF} n\frac{a}{b} - nE_{\rm f-PD}$$
(6.14)

where

 $\alpha = \frac{1}{4\pi (1-\nu)} \ln \frac{4R}{\rho}$ is deduced from Eq. (6.13); Ω is the atomic volume; γ_{SF} is the stacking fault energy (SFE);

and E_{f-PD} is the PD formation energy.

For the formation of a cluster, the differences in stacking fault energies are expected to be the critical parameter controlling the plane on which the PDs will cluster. Consideration of the relative contributions of all the terms of Eq. (6.14) shows that the slight differences in stacking fault energy (SFE) between basal and prismatic loops are small compared with the other terms. The SFE parameter is not the only relevant parameter used to select the loop types; kinetic aspects of clustering of individual PDs and direct formation of loop nuclei in the cascades have to be included.

The energy barrier to be overcome for the nucleation of a loop corresponds to the maximum of Eq. (6.14) for the different values of *n*. Nucleation barriers do not exist for the interstitial loops for the likely values of PD formation energies given in Table 6.5. ($E_{fv} \approx 2.1 \text{ eV}$ and $E_{f-I} \approx 3.0 \text{ eV}$), and typical values of the crystallographic and elastic constants, in agreement with the positive binding energy reported in Section 6.2.6. For vacancies, the energy barrier corresponds to a cluster of $n_v = 5-8$ vacancies for the extreme values of the SFEs: $\gamma_{SF} = 0.1 \text{ J} \cdot \text{m}^{-2}$ and 0.5 $\text{J} \cdot \text{m}^{-2}$ (values consistent with the much lower binding energy for the vacancies as they cluster).

The low values of the PD numbers for the formation of the critical cluster for vacancy loop formation, n_v , compared with the size of the clusters obtained during the cascade computations described earlier, raises the question of non-thermodynamical nucleation processes for the loop formation. During neutron irradiation, a large number of loops nucleate directly in the cascade, a more efficient process than the clustering of individual vacancies. In contrast, for electron irradiation, the energy transfer induced by the electrons is too low to induce cascades and the PD clustering has to occur by migration of individual PDs for such nuclei to form. In themselves, these two types of irradiation are not expected to lead to similar mechanisms of loop formation, and therefore have no reason to exhibit the same types of loop. The electron irradiation would be more realistically analysed using thermodynamics (i.e. SFE considerations [6.79]), while damage induced by neutron irradiation should consider the PD clustering and evolution in the cascades.

The values of the SFE for the different types of stacking faults are not accurately known in zirconium. The reported absence of dislocation dissociation and the computations performed with many-body potentials, or ab initio, give SFE in the range of $0.125-0.250 \text{ J} \cdot \text{m}^{-2}$ for the various types of basal stacking faults. The most stable faults are intrinsic I₁ faults, while for the prismatic faults, values in the range of $0.150 \text{ J} \cdot \text{m}^{-2}$ are obtained [6.60]. Such low differences in SFE for the prismatic and basal stacking faults indicate the importance of the differences in the line energies of the dislocations induced by crystallographic and elastic anisotropy according to the Burgers vectors [6.81].

(b) $\langle a \rangle$ type loops — interstitial and vacancy loops

Owing to the low resolution of the electron microscopes available in the early days of the analysis of irradiation damage in zirconium alloys, the determination of the type of dislocation observed after irradiation was often obtained after a short heat treatment at 720–770 K (450–500°C) to allow the dislocation loops to grow [6.82, 6.83]. Kelly and Blake [6.82] analysed the loops produced, after neutron irradiation of pure zirconium at room temperature followed by heat treatments, and after irradiation at 573 K (300°C) without heat treatment. The Burgers vectors were observed to be all $\langle a \rangle$ types with b = $1/3 < 11\overline{20} >$ and the loops were a mixture of vacancy and interstitial loops, in a proportion of 2/3-1/3. The habit planes of the loops were slightly away from the prismatic planes (Fig. 6.15). The loops were not perfectly circular but exhibited a slight elongation in the $\langle c \rangle$ direction, and

with a large scatter in the results. No significant differences were observed on the spatial distribution of the two types of loop. At the irradiation dose evaluated $(10^{24} \text{ n} \cdot \text{m}^{-2})$, there were no loops lying in the basal planes, and no loops with any <c> component to their Burgers vectors.

The simultaneous observation of interstitial and vacancy loops was unexpected, since the growth of one type of dislocation loop requires a positive bias for the annealing of the corresponding type of PD on the dislocation line. This bias would be similar for the two types of dislocation and would lead to the shrinkage of the opposite type of dislocation loop. Therefore, the disappearance of one type of dislocation loop is expected. This point will be discussed later.

Irradiation of zirconium alloys at higher temperatures allowed the database of irradiation effects in zirconium to be extended. As the early theories of irradiation growth involved c component dislocation loops for the major mechanisms, a systematic search of these defects was performed. A large international 'round-robin' experiment was conducted in the late 1970s to determine accurately the characteristics of the dislocation loops induced by irradiation in zirconium and zirconium alloys [6.84]. It was an opportunity to stress the numerous artefacts that interfere with the determination of the loop character. The two major perturbations are the formation of hydrides during electropolishing and the formation of small oxide spots on the surface of the foil during storage and observation. The observation conditions and the precautions to be taken during TEM work were clearly standardized and are now agreed upon. The observations of pure zirconium samples irradiated at low fluences led to a description of the best examination conditions to be used, since the dislocation loop densities were low and the loops sufficiently far apart to avoid overlap and interference in their respective contrast during various diffraction conditions [6.83]. For the temperature range studied, interstitial and vacancy loops were observed, with a higher density of the latter. An important observation was the large variation of the ratio of interstitial to vacancy loop density on the same sample when analysing different grains on the same foil. The spatial distribution of the loops was not random, but the loops were aligned in rows parallel to the (0001) traces (Figs 6.16 and 6.17).



FIG. 6.15. Dislocation loop orientations observed in pure zirconium irradiated at low temperature to a dose of $1.4 \times 10^{24} \, n \cdot m^{-2}$ and annealed for 1 hour at 763 K (490°C) (reproduced from Ref. [6.82] with permission courtesy of Taylor & Francis).



FIG. 6.16. Alignment of a dislocation loops in pure zirconium irradiated at 668 K (395°C) after neutron irradiation to $6.4 \times 10^{23} \text{ n} \cdot \text{m}^{-2}$ (this image was published in Ref. [6.83], copyright Elsevier, 1977).



FIG. 6.17. Schematic distribution of the $\langle a \rangle$ dislocation loops observed in TEM in an irradiated zirconium thin foil (this image was published in Ref. [6.83], copyright Elsevier, 1977).

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The direct observation of the geometrical characteristics of these materials (sizes and loop planes) led to the same conclusions as those obtained after moderate annealing (comparing Figs 6.15 and 6.18), giving confidence in the early results obtained with intermediate annealing.



FIG. 6.18. Orientation distribution of the loops in pure zirconium irradiated to $6.4 \times 10^{23} \text{ n} \cdot \text{m}^{-2}$ at 668 K (395°C). Vacancy loops are represented by open circles and interstitial loops by full circles (this image was published in Ref. [6.83], copyright Elsevier, 1977).

The loop characteristics have been obtained on pure zirconium and Zircaloy-2, irradiated with neutrons between \approx 525 and 675 K (25 and 400°C). The general trends observed with respect to loop geometry are that at low irradiation temperatures, the loop sizes are smaller than at higher irradiation temperatures, while the loop density follows the reverse trend. The loops were identified as elliptical, always with a $1/3 < 11\overline{20} >$ and never with any <c> component for the Burgers vector (Fig. 6.19). Since the Burgers vectors of these loops are translation vectors of the HCP lattice, the loops are perfect and not faulted. They can therefore glide along their own cylinder, a very important property for the mechanical behaviour after irradiation (Section 6.4.3.3).



FIG. 6.19. Dislocation loop characteristics of the same sample. The a and b quantities are the major and minor axes of the elliptical loops (this image was published in Ref. [6.83], copyright Elsevier, 1977).

(c) Dose effects on the loop population

The evolution of the microstructure with a fast neutron dose has been studied on various materials, with samples taken from various parts of the same component, often located at different distances from the core axis. For Zircaloy-2 irradiated at about 573 K (300°C), no irradiation damage is visible on TEM before a total fast neutron dose of $\approx 2-3 \times 10^{23} \text{ n} \cdot \text{m}^{-2}$ (E > 1 MeV). Then only 'black spots' are observed, a contrast induced by dislocation loops whose diameter is below about 2 nm. Since damage is detected macroscopically for these conditions, 'invisible damage' should develop, responsible for irradiation growth or hardening [6.85]. The microscopic nature of this damage should consist of small clusters of various PDs. The existence of some measurable growth induced by this invisible damage confirms that even for such very small clusters, the clustering is anisotropic and occurs on selected crystallographic planes, a result consistent with the conclusions of Section 6.2.6.1. As the fluence is increased, the loop sizes increase, but seem to saturate quickly. Similarly, the loop density stabilizes near 3×10^{20} m⁻³ after a dose of 10^{25} n·m⁻² [6.85]. Figure 6.20 illustrates this behaviour at 573 K (300°C). A saturation of the $\langle a \rangle$ loops is apparent above a dose of $2-5 \times 10^{24}$ n·m⁻². This trend, obtained by various TEM observations, has been confirmed by bulk dislocation density measurements using X ray line broadening [6.86]. The existence of this saturation supported confidence in the stable behaviour of zirconium alloys under irradiation to high neutron doses.

The effect of irradiation temperature corresponds to what could be expected from simple considerations. At very low temperatures, the PDs are not mobile enough for their motion and clustering, and no damage is observed. At high temperatures, their diffusion rates allow long range migration and disappearance on remote sinks such as grain boundaries. Therefore, irradiation damage should be observed in a narrow temperature range. The temperature range at which this damage can be observed depends on the chemistry and microstructure of the material studied, owing to the possible interactions between PDs and solute atoms (Section 6.2.6.4).

For pure zirconium irradiated to a dose of $1.1 \times 10^{25} \text{ n} \cdot \text{m}^{-2}$, very small dislocation loops are observed at 573 K (300°C) and much larger ones at 673 K (400°C), and the damage disappears by in situ recovery at 773 K (500°C) [6.85]. Typical microstructures after irradiation of pure zirconium at various temperatures are shown in Fig. 6.21.



FIG. 6.20. Evolution with dose of the dislocation loop characteristics for Zircaloy-2 irradiated at 573 K (300°C) (N — density of visible defects; \tilde{d} — mean diameter of the defects; N_d — number of PDs involved in the damage, assuming all the defects clusters as perfect loops) [6.85] (this image was published in Ref. [6.87], copyright Elsevier, 1975).

IRRADIATION DAMAGE

Consistent with the previous observation, the chemical composition is expected to affect the microstructural evolution under irradiation. At 573 K (300°C), the higher the concentration of alloying elements in solid solution in the α -matrix, the lower the mobility of the PDs and the smaller the sizes of the dislocation loops. With irradiation at 673 K (400°C), the effect of alloying elements is less pronounced, especially in Zircaloy-2 [6.85].

The Zircaloys are usually used in either the stress-relieved or recrystallized state, depending on the temperature of the final heat treatment. In the former condition, the initial dislocation density is only slightly reduced, compared with the cold worked condition. The PDs from irradiation require only a short migration distance to disappear at the sinks provided by the high dislocation density. One should therefore expect differences in post-irradiation damage for these two initial microstructures. Owing to the high dislocation densities in stress-relieved materials, it is practically impossible to analyse the characteristics of the irradiated structure in these materials. In recrystallized samples tested in creep, it was found that only minor differences were observed in the dislocation loop characteristics between the strained areas and the unstressed zones [6.85].



FIG. 6.21. Effect of temperature on the microstructure of pure zirconium irradiated to a dose of $1.1 \times 10^{25} \text{ n-m}^{-2}$. (a) 573 K (300°C); (b) corresponding size distribution; (c) 673 K (400°C); (d) corresponding size distribution [6.85].

(d) Spatial distribution of the loops, alignment and corduroy contrast

One common observation reported by all the scientists analysing the $\langle a \rangle$ loop microstructure in zirconium alloys after irradiation was a particular band contrast oriented along the $[11\overline{2}0]$ direction of the basal plane. The bands form an alternating black and white contrast superimposed on the usual radiation damage normally visible on thin foils of irradiated materials. They are observed on any zirconium or recrystallized zirconium alloys after irradiation, whatever the irradiation temperature. The banding was connected to the alignment of the loops in the same direction, without a clear understanding of the origin of this contrast. Typical examples of this contrast, named 'corduroy' by Bell [6.88], are given in Fig. 6.22. These features are more easily revealed under low or moderate magnification TEM imaging, with conditions close to Bragg diffraction (near two-beam conditions with any diffraction vector), especially when the foil is seen in the prism orientation with a <0002>reflection; they are invisible with a $\{11\overline{2}0\}$ reflection, if the diffraction vector is oriented parallel to the corduroy traces. Their alignment direction does not change with diffraction conditions and remains $[11\overline{2}0]$. They appear as alternating bands of slightly different diffraction contrast, for which local orientation changes are lower than one degree. The cordurov spacing distance is of the order of a few tens of nm, typically a few loop diameters, decreasing at lower irradiation temperatures.

Based on clear observation of the corduroy contrast when the diffraction conditions corresponded to the reflection on the basal plane, the first explanation proposed some $\langle c \rangle$ contribution of the Burgers vectors of the dislocation-loop-induced strain in this direction [6.88]. The commonly accepted explanation of this phenomenon is based on the local elastic relaxation of the internal stresses in the TEM thin foils, in areas where pronounced alignment of 1/3 [11 $\overline{20}$] loops are present [6.89]. The model has been developed following two important observations: the bands of corduroy match closely the bands of dislocation loops, and the corduroy bands are observed only when there is an excess of either vacancy or interstitial loops. The aligned loops in a given band induce a long range strain field controlled by the nature of the dislocation type in excess. The thin foil geometry allows the relaxation of this strain field by elastic deformation. Following the band geometry, this relaxation induces a regular oscillation of the crystallographic orientation across the grain, with an amplitude of less than a degree. For the diffraction conditions reported (small s parameter), periodic variations in diffraction intensity will develop this corduroy contrast. The strains induced are not isotropic, but depend on the direction of the foil, explaining the absence of $\{11\overline{2}0\}$ diffraction contrast for a specific orientation, where no distortion in the $\langle a \rangle$ direction is possible. This model is also consistent with the absence of any $\langle c \rangle$ component of the Burgers vectors of the loops observed. When the densities of the two types of loops are similar, such long range strain fields do not exist and no corduroy contrast is observed [6.89].



FIG. 6.22. Typical corduroy contrast obtained during observation of irradiated zirconium (this image was published in Ref. [6.88], copyright Elsevier, 1975).

(e) $\langle c \rangle$ type loops

In pure zirconium irradiated with neutrons at 723 K (450°C), $\langle c \rangle$ component loops have been analysed as being faulted and of vacancy type [6.90]. They are large (up to 1 µm in diameter) and their formation condition was found to be strongly dependent on the impurity concentration, especially interstitial impurities. It was possible to obtain them by electron irradiation, showing that their formation mechanisms do not require the creation of vacancy clusters inside cascades, but do need some equilibrium growth involving the contribution of interstitial impurity atoms. Whatever the irradiation conditions, these $\langle c \rangle$ loops occur in conjunction with more numerous and finer $\langle a \rangle$ loops, making the former difficult to analyse in TEM, except when they are viewed in the 'edge-on' orientation (i.e. with the electron beam parallel to the plane of these loops).

Long, straight dislocations with a clear $\langle c \rangle$ component of their Burgers vector were observed in Zircaloy-2 and -4 samples irradiated in the Experimental Breeder Reactor-II at 690 K (417°C) to a neutron dose of $6.3 \times 10^{25} \text{ n} \cdot \text{m}^{-2}$ (E > 1 MeV) [6.91]. It was suggested that these lines may have been dislocation loops and it was later shown, in similar samples, that these lines corresponded with faulted dislocation loops with a vacancy character [6.92]. In Zircaloy-2 and -4, these loops have an average diameter of 80–200 nm and a density of $1-2 \times 10^{20} \text{ m}^{-3}$, depending on irradiation conditions (Fig. 6.23).

To observe these $\langle c \rangle$ component dislocation loops, it is necessary to avoid the imaging of the $\langle a \rangle$ type loops described earlier. This orientation corresponds to a condition for which the $\langle c \rangle$ loops are observed edge-on and appear as straight-line segments. These loops lie in the basal planes. Their density is much lower than that for the $\langle a \rangle$ loops, but they are much larger.



FIG. 6.23. $\langle c \rangle$ dislocation loops observed edge on in TEM in a Zircaloy-2 sample irradiated at 690 K (417°C) to $6.3 \times 10^{25} \text{ n} \cdot \text{m}^{-2}$ (this image was published in Ref. [6.91], copyright Elsevier, 1983).

It was also observed that at the beginning of their formation these dislocation loops appeared to be located close to the intermetallic precipitates present in the Zircaloy samples [6.93] (Fig. 6.24). The thickness of the foils was smaller than the sizes of the *c* dislocation loops and some clusters of loops appeared not to be linked to the presence of precipitates. The reason is that the corresponding precipitates dissolved during the foil preparation and were therefore not observed. When the c-loop concentration is higher, the distribution of *c*-loops is homogeneous. The difficult determination of their Burgers vector showed that the *c* type dislocations are always of vacancy type with a Burgers vector $b = 1/6[20\overline{23}]$. Because they form by the clustering of vacancies, they nucleate with a pure *c* character, b = 1/2[0001], forming an unstable stacking fault of type ABABBABAB... A shear has to occur at a given loop radius to return the 12-fold coordination, leading to a stacking fault of type ABABCBCB... or ABABCACAC. Their faulted nature has been confirmed [6.77].



FIG. 6.24. High density of < c-loops in the vicinity of the precipitates in a Zircaloy-4 sample irradiated at 585 K (312°C) to 6 × 10²⁵ n·m⁻² (arrow: diffracting vector [0002]) (reprinted with permission from Ref. [6.23], copyright ASTM International).

IRRADIATION DAMAGE

The formation of the $\langle c \rangle$ component loops, in conjunction with the $\langle a \rangle$ loops, is explained by the theories of PD evolution kinetics. The analysis of the consequences of the diffusion anisotropy difference of vacancies and of the sink strength of vacancy type $\langle c \rangle$ loops shows that such loops are more efficient at attracting vacancies than interstitials and would grow at a steady rate. As their growth is assured once nucleated, their nucleation mechanisms control their occurrence. The role of the interstitial elements on the nucleation of $\langle c \rangle$ loops has been demonstrated by quenching Mg of various purities [6.94]. In this metal, with a c/a ratio below the ideal, as zirconium has, it was possible to increase the fraction of $\langle c \rangle$ loops obtained by quenching from high temperature by increasing the concentration of metallic impurities (Mn, Fe, Zn, Cu...) in the range of a few hundred ppm. Similarly, the density of $\langle c \rangle$ loops of various zirconium and zirconium alloys after neutron irradiation was found to increase with an increase in impurity concentration [6.76].

Since at high irradiation doses, the precipitates exhibit an amorphous phase transformation induced by irradiation, with an associated release of Fe into the matrix (Section 6.3.2.1), iron was suspected to aid the nucleation of the $\langle c \rangle$ loops. However, its solubility in the unirradiated zirconium matrix is very low [6.56], limiting the expected efficiency of this effect. With irradiation, the role of Fe acting as an enhancer of the nucleation of $\langle c \rangle$ loops has been demonstrated in an electron irradiation experiment using a 1 MeV HVTEM on Zircaloy thin foils in which Fe had been implanted before electron irradiation. In the temperature range of 523–573 K (250–300°C) it was possible to induce $\langle c \rangle$ loop formation in the doped samples, with loop densities increasing with the increase in Fe concentration. Moreover, Fe was found to have segregated in the plane of the loops [6.23]. A nucleation model has been proposed based on the clustering of vacancy-Fe complexes on the basal planes of the zirconium matrix with a crystallographic arrangement similar to the stable Zr₂Fe compound. These clusters are predicted to act as nuclei for the $\langle c \rangle$ loops.

The <c> loops, appearing late in the irradiation history in power reactor components, are responsible for the accelerated growth observed above $5 \times 10^{25} \,\mathrm{n \cdot m^{-2}}$ [6.95]. This point will be described in more detail in Chapter 7.

6.3.2. Irradiation effects on secondary phases

Under irradiation, the classic thermodynamic approach is not valid to determine the phase equilibria. The basic reasons for this lack of validity are that atoms are displaced much more than they would be thermally and the concentrations of both vacancies and interstitials greatly exceed the thermal equilibrium values. Generally, radiation enhanced diffusion due to the higher vacancy concentration speeds up the transition to the stable state at a given temperature. Any precipitation that is stable during annealing after irradiation is irradiation enhanced. Non-equilibrium processes can also occur, inducing changes in the phases, or even new phases, that can be reversed on post-irradiation annealing. These phase changes are irradiation induced.

In classic thermodynamics, each atom is free to explore numerous modifications in local configuration, with energy changes in the range of a few kT at most, where k is the Boltzmann's constant. Typically, a process with an activation energy of 2 eV can be activated (i.e. observable at realistic time scales) at \approx 770 K (500°C). The most probable local configuration corresponds to the minimum local energy. Averaging over time and summing the system to minimize its free energy leads to the structure corresponding to the thermodynamical equilibrium. This configuration is not the case under irradiation, since, by ballistic impact, the change in energy of a given atom can be as high as a few keV. This extra

energy will allow configurations out of the range of what could be possible through statistical thermodynamics (i.e. extremely high energy barriers can be overcome). In addition, a system under irradiation is not isolated and receives energy and mass from its surroundings. Therefore, the system cannot be considered adiabatic, a mandatory condition for thermodynamics. Allowing the modification of the atomic configuration by overcoming very high energy barriers could lead, in specific cases, to metastable local minima or maxima in the concentration of alloying or trace elements and to the observation of dynamic structural equilibria, different from those observed without irradiation.

Ballistic mixing drives the system towards homogenization of the concentrations, while thermodynamics drives it towards a reduction of the gradients of chemical potentials. Also, the PDs created by irradiation have to be considered new species (at high concentration and fluxes to the sinks), for which interactions with alloying elements and flux coupling have to be taken into account. Therefore, a specific approach has to be used to forecast the phase evolution tendency under irradiation [6.96]. In alloys, this mixing can explain different behaviours, such as amorphous transformations, segregations at grain boundaries or free surfaces, and the increase or decrease of solubility limits. The applicability of such theories is still limited to a few systems for which the interaction between each species is known precisely.

Many equilibrium phase diagrams do not represent alloy systems under irradiation. Almost all the systems are affected, and a review by Russell lists many of them [6.97]. For zirconium alloys, a few specific behaviours were then known: Zr_3Al amorphous transformation in Zr-Al, β -Nb precipitation in Zr-Nb, segregation of Mo and precipitation of Mo₂Zr at grain boundaries in Zr-Mo alloys. Although a very large amount of experimental evidence was available, the complexity of the phenomena involved in phase stability under irradiation did not allow any direct forecast of the behaviour of a given system under irradiation. At the time the non-equilibrium caused by irradiation was realized, the Zircaloys had not reached neutron fluences high enough to activate the amorphous transformation of the intermetallic precipitates described in the next section, nor were they examined using high resolution TEM to characterize their behaviour under irradiation.

6.3.2.1. Zr-(Fe, Cr, Ni) intermetallics in Zircaloy

(a) Amorphous transformation

Simultaneously with the observation of $\langle c \rangle$ type loops, phase changes induced by irradiation were observed in Zircaloy-2 and -4 irradiated to high fast neutron fluences ((6–8) × 10²⁵ n·m⁻²), at temperatures typical of power reactors, 560–580 K (285–310°C) [6.98]. At these doses in the Zr(Fe,Cr)₂ precipitates present in Zircaloy-4, a crystalline core of precipitate was surrounded by an outer ring that was amorphized and much depleted in Fe.

This observation opened the door to a large body of scientific interest, as well as industrial concern. The correlation between the occurrence of $\langle c \rangle$ loops and the precipitate evolution could affect growth, since the accelerated growth was clearly linked to these $\langle c \rangle$ loops. The precipitates contain all the TMs Fe, Cr and Ni added as alloying elements; they are responsible for the control of corrosion resistance within the primary coolant. Therefore, a strong interest was raised in analysing the effect of irradiation on the corrosion properties, and on the evolution of the structure of the precipitates and their chemical composition.

The standard power reactor temperatures correspond to the conditions for which the amorphous transformation occurs efficiently. Not only were the precipitates transformed to an amorphous structure, losing their Fe, but dissolution of the precipitates was observed. For Zircaloy-4 irradiated at 561 K (288°C) to a dose of $5 \times 10^{25} \text{ n} \cdot \text{m}^{-2}$, the amorphous zone was about 100 nm in thickness, showing some tendency for faceting corresponding with the zirconium crystallographic orientations. Increasing the dose to $15 \times 10^{25} \text{ n} \cdot \text{m}^{-2}$ led to a large part of the precipitates being dissolved [6.99]. As a critical case, precipitates completely dissolved in samples with low values of ΣA , the intermediate annealing parameter, because these precipitates were initially small.

Various experimental programmes have analysed the effect of metallurgical and irradiation parameters on the evolution of these precipitates. The two types of intermetallic precipitate do not behave the same way. In Zircaloy-2, Ni is located in the $Zr_2(Ni,Fe)$ precipitates that were observed to be more resistant to amorphous transformation than the $Zr(Fe,Cr)_2$ precipitates in Zircaloy-4 under power reactor irradiation conditions [6.22, 6.100].

Many simulations of neutron irradiations have been performed with electrons, protons and heavy ions, to characterize the effect of composition, temperature and flux or dose on the amorphization process. The difficulties in comparing these different irradiation types include the facts that normalization of the damage is complex, knowledge of the displacement energies in intermetallic compounds is poor and there are intrinsic difficulties in transposing the irradiations induced by different means. General tendencies can be reported [6.101].

During the amorphous transformation of the $Zr(Fe,Cr)_2$ precipitates induced by neutron irradiation in the temperature range of power reactors, different mechanisms can be observed. At the lower temperatures (typically in the range of 520–590 K (250–320°C)), the amorphous transformation occurs by progressive thickening of an amorphous layer, starting at the precipitate–matrix interface. Typical morphologies of such precipitates being amorphized are given in Fig. 6.25. The thickening of the amorphous layer appears to depend on the integrated dose and corresponds roughly to a thickness of 10 nm per 10^{25} n·m⁻² (Fig. 6.26):

- At low temperature (below 100 K (-170°C)), Zr(Fe,Cr)₂ and Zr₂(Fe,Ni) can be rendered amorphous under irradiation, whatever the irradiation procedure used. Typical values of the dose required for amorphous transformation are in the range of 1 dpa. These transformations occur without any chemical changes.
- When increasing the irradiation temperature, a higher dose and dose rate are required for irradiation to induce the amorphous transformation. This increase is clear above 200 K (-70°C) for electron irradiation, and above 300 K (30°C) for ion irradiation. The transition for neutron irradiation is close to ≈600 K (320°C) for Zr(Fe, Cr)₂ and ≈500 K (420°C) for Zr₂(Fe, Ni). Above these temperatures the precipitates remain crystalline.
- For higher temperatures, the precipitates remain crystalline, but lose some Fe, and finally may dissolve completely without any microstructural change.

During the amorphous transformation of the $Zr(Fe,Cr)_2$ precipitates induced by neutron irradiation in the temperature range of power reactors, different mechanisms can be observed. At the lower temperatures (typically in the range of 520–590 K (250–320°C)), the amorphous transformation occurs by progressive thickening of an amorphous layer, starting at the precipitate–matrix interface. Typical morphologies of such precipitates being amorphized are given in Fig. 6.25. The thickening of the amorphous layer appears to depend on the integrated dose and corresponds roughly to a thickness of 10 nm per $10^{25} \text{ n} \cdot \text{m}^{-2}$ (Fig. 6.26).

With longer irradiations, the precipitates develop a higher fraction of amorphous phase, with a thicker layer. It is then common to observe that the precipitates are highly faceted [6.99]. The facets appear to be directly connected to the crystallographic orientation of the matrix and not to the initial precipitate crystallographic orientation. Eventually, the

precipitates may exhibit a rod-like shape (Fig. 6.27). The mechanism of such a morphological change is not clearly understood, as the dissolution process is assumed to be controlled by a ballistic process (i.e. without any thermodynamic equilibrium). Anisotropy of the surface tension of the α -Zr matrix cannot be invoked unless a significant contribution of the morphological evolution has to be attributed to the continuous recovery expected during the process. The diffusion anisotropy difference may be a major reason for such behaviour.



FIG. 6.25. Development of the amorphous layer surrounding the $Zr(Fe, Cr)_2$ precipitates in Zircaloy-4 samples irradiated at \approx 575 K (300°C) to $4 \times 10^{25} \text{ n} \cdot \text{m}^{-2}$ and $8 \times 10^{25} \text{ n} \cdot \text{m}^{-2}$ (reprinted, with permission, from Ref. [6.101], copyright ASTM International).



FIG. 6.26. Growth kinetics of the amorphous layer surrounding the $Zr(Fe,Cr)_2$ precipitates in Zircaloy-4 samples irradiated by neutrons at \approx 570 K (295°C) (this image was published in Ref. [6.102], copyright Elsevier, 1992).



FIG. 6.27. Irradiation induced amorphization and dissolution of $Zr(Fe,Cr)_2$ precipitates in Zircaloy-4 samples irradiated at \approx 560 K (285°C) to 5 × 10²⁵ n·m⁻² (A) and 1.5×10²⁶ n·m⁻² (B, C, D) (this image was published in Ref. [6.99], copyright Elsevier, 1988).

(b) Effect on precipitate chemistry

The behaviour under irradiation of the various types of precipitates was found to be strongly dependent on the structure of the precipitates. For the Zr-(TMs) series, the tendency for amorphous transformation decreased along the series: Zr(Fe,Cr)2; Zr2(Fe,Ni); Zr3Fe [6.103]. This behaviour, showing an easier amorphous transformation as the TM/Zr ratio increases, partly supports a mechanism based on much of the irradiation damage being chemical damage (one TM atom in the site of a Zr atom, i.e. anti-site formation). This simple explanation would forecast that, since the maximum chemical disorder achievable would be for a hypothetical ZrFe compound, the tendency for amorphization susceptibility would not increase continuously with the Zr/Fe ratio. An additional effect could be the dependence of the energy of an anti-site (chemical disorder) with the configuration of the site, which would change with the crystallography of the compound. Finally, the computation of the effective damage is not straightforward, owing to the poor knowledge of the displacement energies and PD mobilities controlling the recovery kinetics.

For Zircaloy-2 and Zircaloy-4, the chemical composition of the $Zr(Fe,Cr)_2$ precipitates, as expressed by the Fe/Cr ratio, was observed to affect the relative susceptibility to amorphous transformation. In these two alloys, the Fe/Cr ratio is different, owing to some Fe being located in the $Zr_2(Fe,Ni)$ precipitates in Zircaloy-2. In Zircaloy-4, the Fe concentration in the $Zr(Fe,Cr)_2$ precipitates is higher than in Zircaloy-2. With a higher Fe/Cr ratio, the

precipitates in Zircaloy-4 exhibit a less stable amorphous phase, such that the recrystallization temperature is lower than for similar precipitates in Zircaloy-2. This observation is consistent with the easier amorphous transformation of the Zr(Fe,Cr)₂ precipitates of Zircaloy-2, which develop an outer amorphous ring at a rate twice that of Zircaloy-4 [6.103].

The effect of major changes in the composition of the precipitates can be analysed by testing under similar conditions various types of alloys. In testing a variant of Zircaloy-4, substituting V for Cr, it was found that the $Zr(Fe,V)_2$ precipitates behaved the same way, with the formation of an amorphous ring and loss of Fe, but at a slightly lower rate than the $Zr(Fe,Cr)_2$ precipitates [6.104].

Another substitution has been obtained with Nb instead of Cr. In the Russian E635 alloy, $Zr(Nb,Fe)_2$ precipitates are formed during processing. They are of the same HCP crystallographic prototype as the $Zr(Fe,Cr)_2$ precipitates in Zircaloy-4. The observation by TEM of pressure tubes of this alloy, irradiated to $7 \times 10^{25} \text{ n} \cdot \text{m}^{-2}$ at $\approx 585 \text{ K}$ (310°C), revealed similar behaviour, with release of Fe from the precipitates. A thin amorphous layer was also reported that indicated a much slower development of the amorphous layer than in Zircaloy. In addition, the change in microstructure of the precipitates was associated with the formation of very small β -Nb precipitates [6.105].

After neutron irradiation in a PWR of a series of Zircaloy variants, Garzarolli et al. [6.106] have observed the effect of Si bearing precipitates. These $Zr(Fe,Si)_2$ precipitates, present in Si-rich alloys, disappeared after neutron irradiation. The reason for this disappearance was not fully clarified and may be due either to a release of Si being much faster than the release of Fe, without the precipitates disappearing, or to complete amorphous transformation and dissolution [6.106]. In this study, a large range of irradiation temperatures was used that allowed the confirmation of the range of stability of the $Zr(Fe,Cr)_2$ precipitates (Fig. 6.28).



FIG. 6.28. Temperature domains of amorphous transformation, dissolution and coarsening of the $Zr(Fe, Cr)_2$ precipitates irradiated in an LWR (reprinted, with permission, from Ref. [6.106], copyright ASTM International).

(c) Fe release

In addition to the amorphous transformation, a change in chemical composition has been observed. The amorphous layer has a much lower Fe concentration than the rest of the precipitate. The local composition drops from a value near 45 at.% to below 10 at.%. A profile of the chemical composition across a partly amorphous precipitate is shown in Fig. 6.29.



FIG. 6.29. Fe and Cr concentration profiles in the periphery of a precipitate with an amorphous layer induced by neutron irradiation (this image was published in Ref. [6.100], copyright Elsevier, 1986).

The mechanism of this release of Fe, and to a lesser extent of Cr, is still an open scientific question. Several mechanisms have been proposed, giving possible explanations. A simple thermodynamic model considers the free energy change of the intermetallic due to the PD density increase, and compares the free energy of the other possible phases, including the amorphous one, whose thermodynamic behaviour is extrapolated from the liquid solution [6.107]. A detailed examination of the thermodynamic properties of the Zr₂(Fe,Ni) and Zr(Fe,Cr)₂ led to an explanation of the higher stability of the latter phase under irradiation [6.108]. These models are not able to forecast the behaviour of Fe in the α -Zr matrix but predict a significant decrease of Fe in the amorphous ring of the precipitates. The increase of Fe concentration in the matrix may thus be driven by the release from the precipitates.

A model for the growth of the amorphous layer and the Fe release has been developed. It considers the flow of Fe being driven by ballistic jumps across the precipitate-matrix interface. The constant thickening rate of the amorphous ring requires an interfacial rate-controlling step, and not a diffusion controlled mechanism. The ballistic sputtering of Fe out of the intermetallic particle, reducing its local concentration, enhances the amorphous transformation in this external ring [6.102]. The rate of growth of the amorphous zone induced by this mechanism (about 10 nm per $10^{25} \text{ n} \cdot \text{m}^{-2}$) corresponds to the observed rates for standard LWR irradiation conditions of temperatures and neutron fluxes [6.109].

A detailed series of irradiations performed in the Advanced Test Reactor on Zircaloy-4 foils in a large range of irradiation temperatures and neutron fluxes allowed Bajaj et al. to evaluate the influence of these parameters on the conditions for amorphous layer development [6.110]. The results showed that neutron flux and irradiation temperature, not considered explicitly in the model of Motta and Lemaignan [6.102], strongly affect the amorphization process. As a result, this model is not able to describe the evolution of the amorphous layer for complex thermal histories during irradiation [6.110]. Taylor et al. have developed an empirical model that includes a continuous amorphization due to irradiation damage and simultaneous thermal recovery [6.111]. The formation of the amorphous layer is linked to the kinetics of Fe diffusion in the matrix, allowing a phase change from the interface by reduction of Fe concentration to below a value required for the chemically stabilized amorphous phase (Fe >10 at.%) [6.111].

Clearly, the understanding of the mechanism of amorphous transformation of the intermetallics in the Zircaloys has to be improved, to include the following physical phenomena:

- Low temperature irradiations (room temperature to 300–500 K (220°C)), with homogenous amorphous transformation without any release of Fe, mainly obtained by superposition of cascade induced damaged areas [6.112].
- Intermediate temperature irradiations (500–600 K (250–320°C)), corresponding to the most relevant case for power reactors, where the amorphous transformation occurs with the formation of an outer amorphous layer, associated with a major release of Fe. In this temperature range, some thermal recovery has to be considered, to explain the flux intensity effects [6.110].
- Higher temperature irradiations (600 K (≥320°C) and above), where much thermal recovery occurs and, at the limit, no amorphous structure forms under irradiation. In this temperature range (>650 K (>370°C)), Fe and Cr release can be observed without phase transformation.

The mechanisms of thermal recovery cannot be the same for the two modes of amorphization listed above, as the first is based on PD recombination and reduction of chemical disorder, while the second requires a return of Fe back into the precipitates.

The mechanisms by which the solubility of Fe is increased in the irradiated α -Zr matrix are not clearly understood. An increase in Fe solubility could be partly explained by a strong interaction between irradiation induced PDs and Fe atoms (see Section 6.2.6.4), but this interaction does not necessarily imply a large change in the solubility limit. Before irradiation, the solubility limit of Fe is in the range of 88–200 ppm (0.0144–0.033 at.%) at the maximum solubility (1048 K (775°C)) (see Chapter 2 in Volume 1 of this publication) falls below 50 ppm (0.0082 at.%) for the lowest temperature and tested (870 K (600°C)) [6.56]. After irradiation of a Zircaloy-2 plate in a PWR at 560 K (287°C), to very high neutron doses $(3 \times 10^{26} \,\mathrm{n \cdot m^{-2}})$, the solute concentration of Fe in the α -Zr matrix was found to have increased to 0.6 at.% (3600 ppm) [6.113]. Complex clusters of Fe, Sn and PDs may exist that contribute to the retention of Fe in the matrix. Another explanation could be linked to a dynamic equilibrium of Fe concentration in the matrix, induced by the ballistic transport of Fe from the precipitate to the matrix, with a diffusion controlled reprecipitation.

(d) Recovery and reprecipitation

The stability of the amorphous structure induced by irradiation has been studied either by measurements of the temperatures at which the amorphous transformation does not occur any longer or by the kinetics of recovery of the crystalline structure during heat treatments.

After the irradiation of Zircaloy-4 channel boxes to a dose of about $1.2 \times 10^{26} \,\mathrm{n \cdot m^{-2}}$ at a temperature of 560 K (287°C), almost complete amorphous transformation of the Laves phases has been obtained. Short heat treatments at 833 K (560°C) for one hour and 1023 K (750°C) for 600 s were performed to analyse the stability of these amorphous structures [6.99]. At 833 K (560°C), the amorphous phase remained amorphous, but a copious precipitation of Zr-Fe phase occurred at the grain boundaries. The diffraction patterns of this phase were attributed to the questionable Z phase Zr4(Fe,Cr), which was later corrected to the Zr₃Fe phase [6.114]. For the higher heat treatment temperature, the amorphous phase returned to a crystalline state, with significant increase of Fe concentration, showing Fe diffusion back to the precipitates during the heat treatment. The irregular shape of the cluster of recrystallized Zr(Fe,Cr)₂ precipitates confirms the large scale migration of Fe back to the precipitates (Fig. 6.30).



FIG. 6.30. Irregular shape of the precipitates recrystallized during a 1023 K (750°C) heat treatment after the amorphous transformation induced by neutron irradiation in a boiling water reactor (this image was published in Ref. [6.99], copyright Elsevier, 1988).

For high temperature irradiation (above 650 K (375°C)), the precipitates remain crystalline during irradiation, while losing their Fe. During irradiation of Zircaloy-4 in the fast neutron Phénix reactor at 650 K (375°C), the Fe/Cr ratio in the Zr(Fe,Cr)₂ precipitates decreased from 2 to 1 at a damage dose of 13 dpa, with a reduction of diameter from 310 to 200 nm [6.115]. Part of the Fe that was released had precipitated as fine Zr₅Sn₃ parallelepipedal precipitates containing a limited amount of Fe, growing in epitaxy with the basal plane of the α -Zr matrix. In addition, very fine needles of Zr(Fe,Cr)₂ were observed to form close to the initial precipitates.

After irradiation of the same alloys at lower temperatures (590–620 K (315–350°C)) and clear development of the amorphous layer, a thermal annealing was performed for one hour at 870 K (600°C). It induced several changes in the microstructure, including a weak recrystallization of the amorphous ring with a partial return of Fe from the matrix to this part of the precipitate (the Fe/Cr ratio returning to 1, instead of 0.5 after irradiation and 2 before irradiation). In addition, precipitation of large ((150 × 350) nm) Zr₃Fe crystals occurred at the grain boundaries [6.115].

For a typical cladding irradiation history, the temperature changes as the burnup increases. The increase of the outer zirconia layer adds a thermal barrier and increases the average local temperature. In addition, in the case of PWRs, the upper part of the fuel rod operates at a higher temperature than the lower part. This increase in temperature, in the range of the transition for amorphous transformation or recrystallization, results in a complex history of the microstructure. At the beginning of the irradiation, the precipitates tend to become amorphous. Later, as the cladding temperature increases, they return to a crystalline form, but with a very different morphology from the initial microstructure. The history of the microstructure, which is due to the temperature increasing with elevation and increased oxide thickness in the fuel rod, is expected to have noticeable effects on the corrosion and on the growth behaviour of Zircaloy-4 in PWRs.

6.3.3. Irradiation effects in Zr-Nb alloys

In binary Zr-Nb alloys, the evolution of the microstructure under irradiation is related to the initial microstructure. Depending on the initial chemistry and on the processing history, the microstructure is usually in a metastable state after the thermomechanical processing in the upper α range or in the ($\alpha + \beta$) domain. After cooling, the α -matrix is supersaturated in Nb and the second phases (which are Nb-rich, such as β -Nb or ω) are also at a composition corresponding to the equilibrium at the former temperature. During reactor operation, the α -phase progresses towards the equilibrium state. The β -phase reaches a steady state condition that is dependent on the fast neutron flux and temperature [6.86]. The kinetics of microstructure evolution of Zr-Nb alloys without irradiation have been measured by a series of annealing treatments in a temperature range of ≈670–825 K (400–550°C). It was observed that phase transformations still occurred after 10 000 h at 673 K (400°C) [6.86, 6.116]. A clear increase of the thermal precipitation of β-Nb in cold worked materials suggests a mechanism of pipe diffusion of Nb along the dislocations, since alignment of these fine precipitates suggests their nucleation on the dislocation network. Without any diffusion enhancing microstructural feature, the diffusion coefficient of Nb in the Zr α -phase is too low for equilibrium microstructures to be obtained within a useful experimental duration [6.117].

6.3.3.1. Change in chemistry in binary Zr-Nb alloys

During irradiation, for typical water reactor temperatures, the thermal migration of Nb cannot occur at any significant level. Under irradiation, the flux of PDs creates elastic interactions that promote the migration of Nb, allowing the thermodynamic equilibrium to be approached. The irradiation enhanced migration and precipitation of Nb in binary alloys leads to the formation of very fine Nb-rich precipitates in the α phase. The precipitates have been interpreted as β -Nb. Their size remains in the range of a few nanometres, and their density accounts for what would be expected from the phase diagram. The morphology of these precipitates can be seen in Fig. 6.31 [6.118]. A confirmation of the irradiation enhanced nature of this precipitation is provided by the fact that these precipitates do not dissolve during post-irradiation annealing [6.119].

This precipitation of β -Nb from the supersaturated matrix is observed in commercial binary alloys with 1% Nb, such as M5 or E110, as well as in Zr-2.5Nb [6.120–6.123].

The Nb-rich phases also undergo chemical changes under irradiation. The ω phase, obtained in Zr-2.5Nb by transformation of the β -Zr after extrusion, disappears and transforms into β -Zr [6.86]. For the β -Zr phase, whose composition is also out of equilibrium after thermomechanical processing, an evolution of the composition under irradiation has been observed. The changes in composition reported do not correspond to the evolution expected from thermodynamics. Instead of a lower zirconium concentration in the β -Zr that would be expected from the phase diagram for a lower temperature, a decrease in Nb concentration is observed. It is explained by a doping of the β -Zr precipitates by ballistic recoil of Zr atoms [6.122]. The Nb concentration seems to increase with the local temperature, but to decrease with the local neutron flux [6.86], supporting an efficient contribution of the ballistic mechanism for the doping of the β -Zr phase with Zr.

In a more detailed analysis of the stability of the phases of the Zr-Nb system under irradiation, one has to take into account the nature of the irradiation process. The presence of cascades, as in neutron or ion irradiation, affects the stability of the precipitates and may allow their dissolution at low temperatures. In addition, since the equilibrium under irradiation is a dynamic one, the size and nature of the β -Nb precipitates affects the behaviour. Ideally, pseudoequilibrium phase diagrams can be computed; however, they are strongly dependent on interaction parameters, which are poorly known [6.124].

6.3.3.2. Evolution of the Zr-Nb-Fe intermetallics

In ternary Zr-Nb-Fe alloys, various intermetallic precipitates can be observed after processing. Their exact crystallography and thermodynamics have been clarified with difficulty, owing to the very slow kinetics of the evolution of the phases, and to ambiguous crystallographic behaviour induced by variable substitution mechanisms between these three elements [6.116]. Two types of precipitates have to be considered. A hexagonal structure where Fe and Nb can substitute each other and of generic composition Zr(Nb,Fe)₂, and a cubic one with a larger unit cell, where the substitution occurs between Zr and Nb (Zr,Nb)₄Fe₂, the latter being favoured by a high Fe/Nb ratio [6.125]. The different possibilities in substitution led to poor agreement on the behaviour of these precipitates under irradiation. The studies based on chemical analysis did not allow separating the two crystallographic structures, causing some confusion. A correct understanding of their behaviour under irradiation seems to converge to a consensus among the different experimenters using three main types of ternary alloys: ZIRLO, E635 and experimental alloys.

The studies of the microstructures after irradiation agree on limited changes of the (Zr,Nb)₄Fe₂ precipitates. No changes in chemistry have been observed and only rare cases of unresolved contrast around the precipitates were reported [6.105, 6.122].

The $Zr(Nb,Fe)_2$ precipitates are susceptible to irradiation, with a marked Fe release into the matrix. Their evolution does not occur by the same process as the $Zr(Fe,Cr)_2$ precipitates described earlier. They remain crystalline and release Fe into the matrix in a homogeneous manner. There is no transformation layer, but a continuous decrease in Fe concentration, with a roughly constant Nb/Zr ratio [6.105, 6.122]. The reason for the stability of the crystalline phase that is depleted in Fe is not well understood.



FIG. 6.31. Irradiation enhanced precipitation of β -Nb in the Zr-Nb α -matrix [6.119].

In summary, the microstructure of zirconium alloys is changed by irradiation. Voids are not observed. Dislocation loops with an $\langle a \rangle$ type Burgers vector form from the clustering of both vacancies and interstitials. These loops increase in density and size with irradiation dose up to a saturation value; their density decreases and their size increases as the irradiation temperature is increased until a temperature is attained at which no microstructural changes are detected. At high irradiation doses, dislocation loops with a $\langle c \rangle$ type Burgers vector are observed. Foreign atoms in the zirconium may enhance the formation of these loops. One candidate is Fe, which is ejected from precipitates in Zircaloy simultaneously with their transformation from being crystalline to being amorphous. By increasing the migration of slow diffusing atoms of alloying elements, irradiation can enhance precipitation towards equilibrium, which would otherwise be unattainable; the formation of β -Nb in the α phase of Zr-Nb alloys is an example.

6.4. EFFECT OF IRRADIATION DAMAGE ON PHYSICAL AND MECHANICAL BEHAVIOUR

Any evolution of the microstructure and subsequent behaviour of zirconium alloys under irradiation are of high importance for the design and operation of power reactors. Many studies have been undertaken to analyse in detail the effects of irradiation on zirconium alloys
with various compositions, microstructural states and irradiation conditions (temperature, stress, flux and fluence, and irradiating particles: neutrons, ions, electrons). Owing to these wide variations in experimental conditions, the comparison of the results is not always straightforward, although general trends may be obtained. Special care should be taken to account for the complex behaviour during irradiation. In some instances, the behaviour after irradiation may not be directly due to the radiation damage itself, but to other phenomena occurring during the irradiation. This complication especially applies for the analysis of the behaviour of samples taken out of components removed from power reactors. For them, the environment will also induce modifications that could contribute to major changes.

For example, one has to consider corrosion effects. The creep rate after irradiation may be reduced by a strengthening effect of the oxide layer developed during corrosion [6.126]. Similarly, hydrogen picked up during water corrosion can reduce ductility at room temperature because of brittle hydride platelets [6.127], while at higher temperatures hydrogen enhances dislocation mobility, decreasing the creep strength [6.128].

Only well designed experiments, usually performed in material testing reactors using dedicated irradiation devices, can unambiguously describe the irradiation induced changes in behaviour. When analysing the irradiation effects, one has always to bear in mind the possibility of confounding factors.

6.4.1. Physical properties modified by irradiation

In general, the irradiation of zirconium alloys does not affect their physical properties, at least for engineering purposes. The only property affected by irradiation is electrical resistivity. As described in Section 6.2.6, irradiation damage obtained during low temperature irradiation can be measured by an increase in resistivity. The PDs act as scattering centres for the conduction of electrons and, as their concentration increases, the electrical resistivity increases. This phenomenon is restricted to low temperatures (below 100 K (-170° C)) and can be ignored for industrial applications.

In the rare cases of creation of voids during irradiation, a decrease in density would be expected. Since this behaviour is rare and limited in extent, it has never been quantified. No large changes in elastic or thermoelastic properties have been reported [6.129].

Irradiation affects several aspects of the mechanical properties, both under irradiation and after irradiation. Other chapters of this publication are devoted to in-reactor behaviour. In Chapter 7, in-reactor deformation is analysed, including irradiation creep, creep anisotropy and growth. In Chapter 8, dealing with corrosion, and in Chapter 9, dealing with fracture, aspects of the effects of irradiation are described. This section will be limited to the effects of irradiation damage on some post-irradiation properties.

6.4.2. Chemical properties: H solubility limit

As described in Section 6.3.2, chemical evolutions are observed under irradiation of zirconium alloys. For instance, Fe is released out of the intermetallic precipitates or Nb precipitates as β -Nb from the supersaturated solid solution. The irradiation induced or enhanced transformations are mainly controlled by PD migration, and the physical processes involved are at least qualitatively understood.

A specific effect, concerning hydrogen solubility, has been observed in irradiated Zircaloy. After neutron irradiation, the solubility limit of H was increased. Two independent studies have detailed the changes observed. McMinn et al. [6.130] studied various Zircaloy-2 and -4 samples, and measured the solubility limit of H by differential scanning calorimetry

for H concentrations of 4 ppm (0.036 at.%) to 75 ppm (0.68 at.%). Vizcaíno et al. [6.131] performed similar experiments on Zircaloy-4, with H concentrations in the range of 155–400 ppm (1.4–3.5 at.%). The conditions were slightly different in the two studies (materials, mode of H charging, heating rates, treatments of the differential scanning calorimetry scans), but similar conclusions were obtained. An increase in terminal solid solubility upon hydride dissolution is observed, leading to a shift of the solvus line of the Zr-H phase diagram: At 570 K (300°C) the H solubility limit increased from 75 ppm (0.68 at.%) before irradiation to 180–220 ppm (1.62–1.97 at.%) for irradiated material (Fig. 6.32). A lower increase is observed at lower H concentrations. A series of heat treatments at 773, 883 and 973 K (500, 610 and 700°C) returned the solvus to the values of unirradiated material [6.130, 6.131].



FIG. 6.32. Part of the zirconium-rich side of the Zr–H phase diagram showing the increase in H solubility for irradiated Zircaloy-4 (this image was published in Ref. [6.131], copyright Elsevier, 2002).

The suggestion of a trapping mechanism of H by the dislocation loops or other PDs is not consistent with the actual values of the density of these sites: the trapping of 1 H atom per atomic length of dislocation line corresponds, for the loop densities described in Section 6.3.1.2, to an additional solubility of 0.009 at.% (1 ppm) (i.e. a factor of 30 below the observations). A more propitious explanation would involve the change in chemistry of the precipitates. A decrease of the Fe/Cr concentration of the Zr(Fe,Cr)₂ phases is known to increase the solubility of H in these intermetallics [6.132]. The volume fraction of the precipitates (about 1.5%), and their increased H solubility, would be consistent with the results. Also, the recovery observed after annealing at high temperature is consistent with this explanation, since the Fe reprecipitates. Knowledge of the behaviour of intermetallic-free alloys, such as Zr-Nb alloys, would counter this lack of understanding.

6.4.3. Irradiation hardening

As for many other alloys, zirconium alloys exhibit an increase in yield strength after irradiation, usually combined with a reduction of ductility. The mechanisms involve the dislocation loops produced by irradiation that act as barriers for the mobility of the dislocations. In addition, above the yield stress, once plastic deformation has started, the mobile dislocations react with these loops, annihilating them in narrow bands. After a very low plastic strain, this localization of deformation leads to strain softening. This behaviour will be described in detail in this section.

6.4.3.1. Increase in yield strength

For irradiations at temperatures low enough to avoid continuous recovery, an increase in yield strength is observed, even for low doses. For pure zirconium irradiated at low temperature ($<370 \text{ K} (<100^{\circ}\text{C})$), the phenomenon is clearly observed; an increase in yield strength of about 110 MPa is induced by an irradiation damage dose as low as 0.1 dpa [6.133]. The increase in strength is combined with a reduction in strain hardening. However, at these doses, the loop densities are too low to induce channelling of the deformation (see Section 6.4.3.4) and strain softening behaviour is not observed. A major reduction in the strain to maximum load was observed only above 0.1 dpa (Fig. 6.33).

For industrial alloys, the low doses and temperatures are of limited interest. Annealed Zircaloy-4 has been tested in similar conditions as above and, although of higher yield strength before irradiation than pure zirconium, showed a 180 MPa increase in strength with irradiation of 0.1 dpa [6.134]. With Zircaloy-4, a drastic reduction in uniform strain has been observed for irradiation doses as low as 0.01 dpa (see below).



FIG. 6.33. Radiation hardening of pure zirconium irradiated near 355 K (80°C), tested at room temperature (numbers for each curve correspond to the damage in dpa) (this image was published in Ref. [6.133], copyright Elsevier, 2004).

For the conditions relevant to power reactor operation (i.e. temperatures in the range of $\approx 525-625$ K (250-350°C) and doses up to 20 dpa), a large number of studies have been undertaken. The materials tested have been irradiated either as coupons of sheets or tubes in material testing reactors, or are machined out of power reactor components, such as fuel assemblies or pressure tubes. In the latter case, the conditions are clearly identical to an industrial environment, but the control of the irradiation conditions is not as precise as in a test reactor. Therefore, samples of different origin and conditions have to be compared. As an example, Fig. 6.34 compares the behaviour after irradiation of flat samples that were machined out of rolled sheets or rings that were themselves machined out of irradiated cladding. Despite the differences in origin, reliable conclusions can be drawn on irradiation hardening and on the mechanisms involved [6.135].

Higgy and Hammad [6.136] have reviewed a large number of irradiation conditions, focusing on the increase in yield strength as a function of the irradiation dose for stress relieved and recrystallized Zircaloy-2 and Zircaloy-4. After a rapid rise in strength with low dose, the subsequent increase in strength is smaller, with higher neutron fluence leading to a saturation mechanism, both with low temperature irradiation and when the irradiation is performed in the range of \approx 525–570 K (250–300°C). For recrystallized alloys, the irradiation can induce a twofold increase of the yield strength.

For cold worked and stress relieved materials, which have a higher strength before irradiation, the relative increase in yield strength is smaller. The two conditions will exhibit similar yield strengths after an irradiation dose of about $10^{25} \,\mathrm{n \cdot m^{-2}}$, at which the irradiation hardening tends to saturate, as illustrated in Fig. 6.35 [6.136, 6.137].

For Zr-Nb alloys, similar radiation hardening is observed. During irradiation of Zr-2.5Nb pressure tube alloys, in their typical operating temperature range (523–538 K (250–265°C)), an initial transient hardening is reported for low doses (below $10^{25} \text{ n} \cdot \text{m}^{-2}$), which induces an increase of the ultimate tensile strength of about 180 MPa [6.138]. An additional continuous hardening is observed at a rate of 3.2 MPa for each $10^{25} \text{ n} \cdot \text{m}^{-2}$ (or 2.1 MPa·dpa⁻¹). The initial transient corresponds to an early increase in $\langle a \rangle$ type dislocation density that saturates at a low fluence. The additional hardening could be attributed to the continuous increase in $\langle c \rangle$ type loops, which do not seem to saturate [6.139, 6.140]. The Zr-2.5Nb alloys used in the designs from the Russian Federation exhibit similar behaviour and, whatever the initial metallurgical state, an increase in strength due to irradiation is observed to reach 200 MPa early in life [6.141]. For Zr-1Nb, the same evolution of radiation hardening was found as for other zirconium alloys [6.142].

The saturation in yield strength is often described using various empirical equations. Exponential or power laws are used, with similar efficacy with respect to design criteria.

The exponential approach defines a saturation dose $(\phi t)_{sat}$, typically at a fluence of about $5 \times 10^{24} \,\mathrm{n \cdot m^{-2}}$ and an increase in yield strength at saturation σ_{∞} near 400 MPa [6.143]:

$$\sigma_{\rm Y} = \sigma_{\rm Y0} + \sigma_{\infty} \sqrt{1 - \exp\left(\frac{-\phi t}{(\phi t)_{\rm sat}}\right)} \tag{6.15}$$

When saturation is less pronounced, a power law may be used with a low exponent (k) of the dose. Typical values of k are below 0.3, and may depend on irradiation temperatures [6.136, 6.137]:

$$\sigma_{\rm Y} = \sigma_{\rm Y0} + A\sigma_{\infty} \, [\phi t]^{\rm k} \tag{6.16}$$



FIG. 6.34. Strain-stress curve for Zircaloy-4 irradiated at different irradiation doses and deformed at 623 K (350°C) (reprinted, with permission, from Ref. [6.135], copyright ASTM International, 2002).



FIG. 6.35. Radiation hardening of Zircaloy-2 irradiated at water reactor temperatures (dose in $n \cdot cm^{-2}$) (this image was published in Ref. [6.136], copyright Elsevier, 1972).



FIG. 6.36. Saturation of the radiation hardening of Zircaloy-4 irradiated at 593–633 K (320–360°C) (dose in $n \cdot cm^{-2}$) (this image was published in Ref. [6.136], copyright Elsevier, 1972).

The increase in yield strength depends on the irradiation temperature, as the kinetics of defect development and recovery are temperature controlled. For irradiations performed above \approx 770 K (500°C), the radiation hardening is imperceptible, because the radiation damage starts to recover continuously at this temperature. When testing Zircaloy-2 at room temperature after irradiation between \approx 300 and 670 K (20 and 400°C), Yasuda et al. observed a reduction of the radiation hardening as the temperature increased [6.137]. The saturation yield strength reduced from 600 to 400 MPa, for an increase in irradiation temperature from \approx 570 to 670 K (300 to 400°C). Typical evolutions of the mechanical properties after irradiation for Zircaloy-4 are presented in Fig. 6.36.

In addition to the increase in yield strength, a reduction of the anisotropic behaviour is observed after irradiation. Tomalin has observed that the plane strain/tensile strength ratio is close to isotropic behaviour after irradiation, but returns to a strong anisotropy after recovery heat treatments [6.144]. The same effect has been measured using Knoop hardness on irradiated materials, and the results were analysed in terms of increased resolved shear stress on the prismatic planes [6.145].

Similarity, the creep strain shows a more isotropic behaviour after irradiation, which was explained by the activation of other glide systems, such as basal or pyramidal slip [6.146]. These indications of additional slip systems activated after irradiation will be detailed later. The similarity in the evolution in mechanical properties and in the changes in microstructures, especially the dislocation loop concentration, has driven the analysis of the increase in yield strength to a hardening effect caused by these loops; see Section 6.4.3.3.

(a) Radiation anneal hardening

In addition to the effect of temperature during irradiation, radiation anneal hardening (RAH) corresponds to some additional hardening occurring when an annealing heat treatment is performed after irradiation at a temperature higher than the irradiation temperature, but not

too high to allow full recovery [6.147]. During this heat treatment, a recovery process is normally expected.

However, an increase in strength is observed, at least if the temperature is below a critical temperature above which a general recovery occurs (\approx 720–750 K (450–480°C)). This phenomenon is more clearly observed for low dose irradiations and is not of concern for power reactor components or fuel cladding. Snowden [6.147] has tested Zircaloy-2 samples after irradiation at different temperatures. An increase in yield strength was observed, whose magnitude was not constant, but exhibited a maximum value \approx 625 K (350°C). As an example, Fig. 6.37 describes the RAH of Zircaloy-2 irradiated at \approx 350 and 600 K (75 and 325°C). A maximum increase in yield strength is found for an annealing temperature ($T_{\rm m}$) slightly above the irradiation temperature ($T_{\rm i}$). Similarly, in Fig. 6.38, a relative increase in strength, due to RAH, is found after recovery \approx 575 K (300°C) of Zircaloy-2 samples irradiated to low doses, about 3 × 10²³ n·m⁻² at 425 K (150°C) [6.148].

The mechanisms behind this phenomenon seem to be linked with an interaction between a hardening species in solid solution, mainly oxygen, and the dislocations. Oxygen diffuses to the dislocation cores, leading to a dynamic hardening in unirradiated zirconium alloys in this temperature range. When segregated on the dislocation loops, the pinning strength for the gliding dislocations provided by the oxygen is expected to increase and thus produce the increase in yield strength.



FIG. 6.37. RAH of Zircaloy-2 after irradiation at 350 K (75°C) (top) and 600 K (325°C) (bottom) (reproduced from Ref. [6.147] with permission courtesy of Taylor & Francis).



FIG. 6.38. Non-monotonic evolution of mechanical properties after irradiation due to RAH of Zircaloy-2 during tests at various temperatures (this image was published in Ref. [6.148], copyright Elsevier, 1980).

For higher doses, RAH is not observed and heat treatments induce only the expected recovery, with a reduction in yield strength with temperature. This recovery seems to start at a lower temperature than the temperature for final recovery when RAH can be observed [6.149]. These recovery kinetics are important for post-irradiation behaviour, for instance with respect to the behaviour of fuel in transport and intermediate storage. They will be described in detail in Section 6.4.5.

6.4.3.2. Localized deformation

In addition to the increase in yield strength, a large decrease in ductility, as measured by elongation, is induced by irradiation; typical examples of this effect are given in Figs 6.33 and 6.36. This reduction in elongation is linked to the localization of the deformation in narrow bands that produces a strong decrease in strain hardening. Elongation below 1% can be observed for zirconium alloy fuel cladding, after less than one cycle of irradiation in power reactors [6.135, 6.148, 6.150]. This low elongation is not an embrittlement (such as cleavage or intergranular fracture) but a change in the mechanism of deformation. The fracture surfaces remain characteristic of local ductile behaviour, with dimples and the absence of any traces of cleavage. The reduction in strain to failure is caused by a large reduction of the uniform strain from highly localized deformation (Fig. 6.39).



FIG. 6.39. Localized strain in a tensile sample of Zircaloy-4 strained 0.8% at 623 K (350°C) after irradiation to 6×10^{24} n·m⁻² at 553 K (280°C) (this image was published in Ref. [6.135], copyright ASTM International, 2004).

For very low doses (below 0.02 dpa), the reduction in ductility is not directly linked to a reduction in strain hardening. Even if localized deformation occurs above 0.05 dpa, when analysed in true stress / true strain the behaviour remains typical of strain hardening. A shift along the strain axis allows one to compare unirradiated and irradiated Zircaloy-4, assuming radiation hardening is equivalent to strain hardening. The low density of loops permits a behaviour equivalent to the effect of the forest of strain dislocations in unirradiated materials (Fig. 6.40) [6.134].

For doses relevant to the power reactor conditions (i.e. above $2 \times 10^{24} \text{ n} \cdot \text{m}^{-2}$), the ductility is very low and almost independent of the irradiation dose. Very early in the deformation process, localized deformation is observed, along shear bands in which all the strain is localized. Such a deformation behaviour raises the question of an adequate definition of the strain, as this quantity will depend strongly on the actual geometry of the sample [6.151]. In addition, the mode of loading (load or strain controlled) affects the ductility. This effect is of concern in the case of pellet–cladding interactions or reactivity insertion accidents, for which the strain of the cladding is induced by expansion of the fuel pellet in contact with the cladding [6.135].

The localization of the deformation is observed to be higher when tested at \approx 625 K (350°C) than at room temperature. Above \approx 675 K (400°C) some recovery occurs and restores the ductility, but around \approx 625 K (350°C), a maximum of localization is observed in narrow and sharp deformation bands [6.127, 6.135, 6.137].



FIG. 6.40. True stress–strain curves for Zircaloy-4 irradiated at low doses at 330-360 K ($60-90^{\circ}\text{C}$) and tested at room temperature. The tensile curves of the irradiated materials are shifted to exhibit their superposition (this image was published in Ref. [6.134], copyright Elsevier, 2004).

6.4.3.3. Dislocation loop hardening

The strong correlation between dislocation loop density and mechanical properties supports a hardening effect induced by these loops, whatever the exact mechanism. This phenomenon will be analysed below.

The presence of dislocation loops, described earlier as obstacles for the motion of the dislocations required for plastic strain, has been proposed to be the major mechanism of radiation hardening in metals and alloys [6.152]. Two main mechanisms of radiation hardening have been proposed, corresponding to the two steps of plastic strain. The loops reduce the mobility of the dislocations at their early multiplication step in the Frank–Read sources [6.153], a mechanism called source hardening, or they reduce the mobility of the dislocations within the grains on the slip planes, corresponding to the dispersed barrier hardening mechanism.

The model mostly used, dispersed barrier hardening, considers the loops as pinning centres for the gliding dislocations [6.153]. Similarly to the hardening induced by a dislocation forest, the concentration ρ_d of loops of diameter *d* formed during irradiation leads to a planar density of pinning centres with an average interaction distance *l* is given by:

$$l = (\rho_{\rm d}d)^{-1/2} \tag{6.17}$$

Depending on the strength of these obstacles, α , the critical shear stress for the mobility of a dislocation across this forest is given by:

$$\tau_{\rm c} = \alpha \mu b \sqrt{\rho_{\rm d} d} \tag{6.18}$$

where μ is the shear modulus and b is the length of the Burgers vector of the dislocation.

Considering more complex interactions, between the gliding dislocation and the loops randomly distributed, Foreman obtained a precise value of the shear strength for an FCC crystal with random prismatic loops [6.154]:

$$\tau_{\rm c} = 0.57 \,\mu b \sqrt{\rho_{\rm d}} d \tag{6.19}$$

In the source hardening mechanism, it is assumed that the increase in yield strength is due to the higher strength required for a dislocation segment, bound on two ends, to bow around them to activate a new source. The interactions of the bowing segment with all the loops will increase the shear stress required for its activation [6.155].

The development of discrete dislocation dynamic modelling has allowed consideration of the actual motion of such a dislocation segment embedded in a homogeneous distribution of interacting dislocation loops. The numerical results led to a radiation hardening related to the dislocation density ρ_d in a similar law for Frank sessile loops [6.156]:

$$\tau_{\rm c} \propto \rho_{\rm d}^{\chi} \tag{6.20}$$

where $x \approx 0.4$

(a) Dislocation loop interactions

The mechanisms of the interactions between dislocation loops and gliding dislocations can have two modes: remote and contact interactions.

If the gliding plane of the dislocation is not too far away from the dislocation loop (i.e. the minimum distance, d_{\min} , corresponds to a few loop diameters), the interaction between the loop and the dislocation depends on the orientations of the loop and of the respective Burgers vectors. It decreases as the square of the minimum distance [6.155]:

$$\tau_{\rm c} = \alpha \frac{\mu b}{(d_{\rm min})^2} \sqrt{\rho_{\rm d} d} \tag{6.21}$$

In the case of a small [111] loop in an FCC, interacting with a dislocation gliding on a $\{110\}$ plane, at a distance of half a diameter away from the loop, the interaction strength parameter α has been computed to be almost 0.5 (i.e. an interaction of high strength) [6.157].

If the gliding plane of the dislocation intersects the loop diameter, a junction of the two dislocations has to be considered. For this interaction to occur, the first point to consider is the energy balance of the reaction between the two Burgers vectors. For a junction to form, it has to be favourable (i.e. $b_{sum}^2 < b_1^2 + b_2^2$). In addition, the junction has to spread during the motion of the gliding dislocation and not disappear. In the case of $\langle a \rangle$ type loops on prismatic planes and an $\langle a \rangle$ dislocation gliding on a prismatic plane, this mechanism could occur only under specific conditions [6.158].

In zirconium crystals, three $\langle a \rangle$ Burgers vectors can be considered in the basal plane: a₁, a₂, and a₃. In the case of a given $\langle a \rangle$ prismatic dislocation intersecting an $\langle a \rangle$ loop of the other Burgers vector, the interaction is attractive, but leads to a new dislocation segment: $a_1 + a_2 = -a_3$.

This new junction dislocation can be assimilated in the gliding dislocation by further complex interactions along the intersection of the glide cylinders of the respective dislocation segments [6.158]. Any interactions that form an attractive junction, but do not annihilate the dislocation loop, will cause drag on the gliding slip dislocation. This drag cannot be overcome by the glide of the dislocation loop because such glide takes the loop segment out of the slip plane for the gliding dislocation. That this interaction has a high strength and radiation hardening is significant on those planes. In the case of an $\langle a \rangle$ dislocation gliding on the basal plane, the interaction leads to a mobile dislocation segment that can be dragged away by the gliding dislocation, because the glide cylinder for the loop lies within the same plane as the slip plane for the dislocation (Fig. 6.41). In addition, there are more possible variants for slip dislocations to interact with the dislocation loop on the basal plane (three) compared with the prism plane (one). The consequence is a clearing of the loops in their gliding plane by the numerous dislocations formed by the same source, leading to the strain softening behaviour detailed below.



FIG. 6.41. Sweeping of a prismatic loop by an $\langle a \rangle$ dislocation gliding on the basal plane. (a), (b) Loop and gliding dislocation with the same Burgers vector. (c), (d) With different $\langle a \rangle$ Burgers vector (this image was published in Ref. [6.158], copyright Elsevier, 1976).

6.4.3.4. Dislocation channelling and strain softening

The limited uniform elongation observed during a tensile test of irradiated zirconium alloys is the result of a specific mechanism of strain softening induced during deformation of the samples. Owing to the high density of dislocation loops, the yield strength of the irradiated material is increased and during a tensile test, the stress rises to a higher value. This behaviour has two consequences: the first is the ability for the dislocations that interacted with the loops to unpin themselves, allowing some plastic deformation. The second is the possibility for new gliding systems to be activated, since the resolved shear stress on these systems can reach the corresponding critical resolved shear stress.

Among the systems that can be activated, basal slip has to be considered in zirconium alloys. In all cases, an interaction between gliding dislocations and the loops can remove the loops in a band where the plastic strain is then confined [6.159].

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Observations by means of TEM have revealed the formation of channels free of dislocation loops, even at very low plastic deformations. Despite the fact that the average plastic strain in the sample is low, typically below 0.002, since the motion of the dislocations is restricted to these channels, the local strain may be as high as unity [6.73]. The nature of the channels has been a matter of discussion, as early observations reported mainly prismatic channels and later observations reported basal channels. A detailed statistical analysis has stressed the importance of the Schmid factor on gliding planes for the occurrence of a given type of channel [6.160]. Both prismatic and basal channels may be obtained, depending on the crystallographic orientation of each grain with respect to the major stress direction and, to a minor extent, on the concentration of alloying elements, such as oxygen [6.161].

Once a source of dislocations is activated, the clearing of the loops by each following dislocation allows easier glide for the following dislocations and can extend the width of the channel up to the grain boundaries. At the grain boundaries, the channel usually cannot propagate into the adjacent grain, due to crystallographic mismatch, and a dislocation pile-up develops, inducing some strain hardening [6.162]. These pile-ups result in the development of internal stresses responsible for the strain hardening observed before the maximum strength is obtained [6.142].

The width of the channels is limited and typically corresponds to a few loop diameters, with an average distance between them ten times as large, leading to a few channels in each grain on average. A model for the formation of the channels that considers the random climb of the dislocation (either up or down) when incorporating the loops, describes satisfactorily the channel width [6.135]. The distribution of the channels in the grains has been predicted to be proportional to the width of the channels, in agreement with the observations [6.163]. An example of such loop-free channels is given in Fig. 6.42, for Zircaloy-4 samples irradiated to 1.6 dpa at 570 K (\approx 300°C).



____200 nm

FIG. 6.42. Basal channels on Zircaloy-4 strained 0.8% after neutron irradiation at 570 K (\approx 300°C) (reprinted with permission from Ref. [6.135], copyright ASTM International, 2002).

The clearing of the loops in the channels results in strain softening, which is limited by strain hardening due to dislocation pile-up at the ends of the channels, for example, at the grain boundaries. Dislocation dynamic computations of the formation of these channels in a copper single crystal with a density of loops of 8×10^{21} m⁻³ allowed the confirmation of a local strain softening behaviour [6.164]. It was not possible to reproduce the macroscopic limited strain hardening due to the choice of periodic boundary conditions, which allowed the dislocations to escape from the grain, and therefore not to pile up. Similar computations for HCP crystals would be highly desirable.

6.4.4. Effect of irradiation on other mechanical properties

The changes in microstructure from irradiation affect other mechanical properties. The general hardening due to PD clustering in dislocation loops, described in the preceding section, is also observed for the creep behaviour of irradiated materials. The general behaviour of creep under irradiation is described in Chapter 7. The changes in microstructure affect the creep behaviour after irradiation. This behaviour is relevant to post-irradiation mechanical behaviour in conditions such as transport in dry casks or intermediate storage. After irradiation the creep rate may be much decreased due to the high density of loops acting as pinning centres for the dislocations. During this post-irradiation creep process, an in situ recovery process may also occur. The general behaviour may be complex, with a combination of thermal recovery (described below) and dynamic recovery from channelling. In specific conditions, a synergy between the two processes may be observed [6.165].

Another specific behaviour has been observed on pressure tubes at low neutron flux. When the dislocations act as PD sinks, their shapes change by climb and their ability to glide on the slip planes is reduced. This retardation is the mechanism by which a reduction in the thermal component of creep under irradiation can be observed. For low fluxes ($<10^{16} \text{ n} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$), irradiation damage cannot be observed, but the annihilation of PDs on dislocations, creating jogs and bowings, inhibits thermal creep in Zr-2.5Nb pressure tubes [6.166]. This observation introduced the concept of 'in-reactor creep suppression', which does not mean that creep stops under irradiation but that it is slower than would be expected; this concept should be used with caution.

The effects of environment on mechanical behaviour may be modified by irradiation. The specific case of corrosion by the primary heat transport water will be described in detail in Chapter 8. The fracture toughness of Zr-2.5Nb pressure tubes as well as Zircaloy fuel cladding is reduced by irradiation. A decrease of the toughness is observed early in life, at a fluence of $4 \times 10^{24} \text{ n} \cdot \text{m}^{-2}$, and it remains approximately constant with further irradiation. Similarly, an increase in delayed hydride cracking crack growth rate is observed that can be explained by the increase in strength due to higher dislocation density under irradiation [6.138, 6.139].

The fracture behaviour under an iodine environment, related to pellet-cladding interaction failures, is easier after irradiation. Experiments performed on irradiated cladding tubes showed a reduction of life during pressurization tests under iodine, after irradiation [6.167]. This result can be explained by localized deformation after irradiation [6.168]. These properties are described more fully in Chapter 9, in Volume 3 of this publication.

6.4.5. Recovery of the radiation damage

As with any heat treatment performed in alloys whose microstructures are not in equilibrium, a recovery process can be observed on irradiated zirconium alloys during a heat treatment at a temperature higher than the irradiation temperature.

Several experimental studies have analysed the kinetics of recovery of the irradiation damage on zirconium alloys after irradiation. Two types of measurements have been performed. The most frequent concern the mechanical properties after thermal treatments at various temperatures, usually tensile tests [6.73], but a few hardness test studies have also been reported [6.169]. For an improved understanding of the phenomena, TEM observations been made to correlate mechanical properties have and dislocation loop disappearance [6.170].

All the studies are in agreement and converge for a beginning of the recovery $\approx 655 \text{ K} (380^{\circ}\text{C})$ and total recovery above $\approx 825 \text{ K} (550^{\circ}\text{C})$, with only a few minutes being enough for total recovery at $\approx 800 \text{ K} (520^{\circ}\text{C})$. The thermal recovery of the mechanical properties of Zircaloy-2 after heat treatments at various temperatures is given in Fig. 6.43.



FIG. 6.43. Effect of one hour annealings on the recovery of the radiation hardening in cold worked and stress relieved Zircaloy-2 irradiated to $3 \times 10^{24} \, n \cdot m^{-2}$ (this image was published in Ref. [6.149], copyright Elsevier, 1960).

The kinetics of this recovery has been studied in detail at the temperatures where recovery is clearly active (i.e. between \approx 725 K and 800 K (450°C and 520°C)). The studies were focused on the mechanical properties [6.171] and also on the evolution of the microstructure [6.172]. A good correlation has been found between the kinetics of dislocation loop dissolution and the recovery of the mechanical behaviour.

The mechanism considered for such recovery is the thermal migration of vacancies leading to shrinkage of the interstitial loops and to coarsening of the vacancy loops [6.82]. Therefore, the kinetics of the process are assumed to be controlled by the migration of vacancies.

As detailed in Section 6.2.5 and summarized in Table 6.5, the migration energy of the vacancies should be about 0.5 eV, to which the formation energy of the vacancy has to be added. An activation energy between 2 and 2.5 eV at⁻¹ (200 and 250 kJ·mol⁻¹) is expected and corresponds to what has been measured for the recovery kinetics [6.173]. The recovery kinetics are described by the Johnson–Avrami equation [6.174], where the fraction of the normalized recoverable strength, *f*, is given by:

$$f = \exp\left(-\left(K_0 t e^{\left(-\frac{\Delta H}{RT}\right)}\right)^n\right)$$
(6.22)

where

is the activation energy of the process corresponding to about 2 eV at ^{-1}
$(200 \text{ kJ} \cdot \text{mol}^{-1});$
is the time;
is a constant;

and n is a kinetic exponent, whose value close to 1/2 confirms the diffusion controlled nature of the process.

The consequence of the thermal recovery is not only for the yield strength, but also for other mechanical properties. For instance, analysis of the creep behaviour of cold worked and stress relieved Zircaloy-4 cladding after 4 cycles of irradiation has shown that the creep strength at temperatures higher than the irradiation temperature can be explained only if a recovery process occurred early in the tests. A correlation between the reduction of dislocation loop density and the creep strength after irradiation has confirmed the mechanism of recovery [6.126]. This phenomenon is important for post-irradiation behaviour, such as creep during transport in dry casks or during the intermediate storage of spent fuel.

The modelling of the recovery of the dislocation loops has been done using two different approaches. The first is based on the diffusion of vacancies from one type of loop to the other (e.g. a vacancy migrates from a vacancy loop to an interstitial loop, resulting in the shrinkage of both). The equilibrium concentration of vacancies surrounding a vacancy loop depends on its diameter. In a similar way to chemical diffusion controlling coarsening of precipitates, the time evolution of the loop size distribution can be described by the following equation [6.175, 6.176]:

$$\frac{\partial r}{\partial t} = \frac{2D\mu b^2}{kT} \left(\frac{1}{r_{\text{mean}}} - \frac{1}{r} \right)$$
(6.23)

where

r is the loop radius;

D is the diffusion coefficient of the vacancies;

- μ is the shear modulus;
- *b* is the length of the Burgers vector of the loop;
- k is the Boltzmann constant;

and T is the absolute temperature.

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The equation leads to a time evolution of the loop diameters. An example of the evolution of the loop diameter distribution, normalized to the Burgers vector, as a function of the annealing normalized times, is shown in Fig. 6.44.



FIG. 6.44. Computed evolution of the loop size distribution during thermal annealing (reproduced from Ref. [6.176] with permission courtesy of Taylor & Francis).

Another approach is to describe the evolution of the loop size distribution using an extension of the kinetics evolution equations of the irradiation defects described in Section 6.2.8.3. In this 'cluster dynamics' approach, all the loops are considered individually and the kinetics of vacancy emission or trapping on each of them lead to an increase or decrease of their size by one atomic volume. Such a description of the dynamics of the loops has been used for the depiction of loop diameter evolution under electron irradiation and is extended to the case of recovery [6.165].

In summary, except for electrical resistivity, for most practical purposes irradiation has little effect on physical properties. Irradiation produces a large increase in short term strength and a reduction in tensile elongation. Parallel with dislocation loop formation, the strength increase approaches saturation with irradiation dose and declines with increase in irradiation temperature. Clearing out dislocation loops in narrow channels leads to strain softening and localized deformation, the latter reducing ductility. The pre-irradiation properties can be recovered by heat treatment above the irradiation temperature.

6.5. IRRADIATION EFFECTS ON ZIRCONIA

6.5.1. Oxide formation and irradiation enhanced corrosion

During in-reactor operation, all components made out of zirconium alloys that are in contact with water oxidize and exhibit a growing layer of zirconia (ZrO₂). As described in Chapter 8, on corrosion, the part of the layer closest to the metal acts as a barrier for further corrosion. Differences between the corrosion rates observed in reactors and those measured in autoclaves, even taking into account all thermal aspects, raise the question of irradiation effects on zirconia.

6.5.2. Zirconia phases and stability

Zirconia is a very stable oxide, with a formation free energy of 1090 kJ·mol⁻¹ at \approx 500 K (225°C). It exhibits several allotropic crystallographic structures (Fig. 6.44). At room temperature and up to \approx 1480 K (1200°C), the ground state of zirconia is monoclinic (space group P2₁/c or C⁵_{2h}). In this structure, the coordination of the zirconium atoms is 7 and there are two non-equivalent oxygen sites: half of the oxygens are tetrahedrally coordinated and the other half have a Z = 3 coordination. Above the transition temperature, a martensitic-like transformation leads to the tetragonal zirconia (P4₂/nmc or C¹⁵_{4h}). This transformation exhibits a large hysteresis and, on cooling this high temperature phase, the tetragonal phase may remain untransformed down to \approx 1200 K (900°C) or even lower, depending on the grain size. Tetragonal zirconia has three polymorphs, usually designated t, t' and t'', which differ mainly in minor variations of the *c/a* ratio. Above \approx 2650 K (2380°C), a fluorite-type cubic structure is observed (Fm3m or O⁵_h). The two latter phases are similar; the tetragonal phase could be considered to be the cubic phase expanded in one direction with the oxygen atoms being slightly displaced along the *<c>* axis. Thus, in these two phases, the oxygen atoms are in octahedral symmetry sites, and the zirconium atoms are tetrahedrally coordinated.

These phases have slightly different molecular volumes, being denser as the temperature increases. The volume variations are about -3.2% for the monoclinic \rightarrow tetragonal transition and about -1.2% for the tetragonal \rightarrow cubic transition. Therefore, an applied pressure tends to stabilize the tetragonal or cubic phases and a series of orthorhombic phases at very high pressures [6.177]. However, the differences between the three structures are limited, corresponding to a few percent local displacements of the atoms (Fig. 6.45).



FIG. 6.45. High similarity of the different allotropic structures of the Zirconia (Zr are the small atoms and O the large ones).

As the oxide forms at the metal–oxide interface, compressive stresses build up in the inner layer of the oxide, due to the Pilling–Bedworth ratio of 1.56, stabilizing the tetragonal phase (the Pilling–Bedworth ratio is the ratio of the volume of oxide to the volume of initial metal).

In addition to these volume changes, the highly anisotropic thermal expansion behaviour of each phase has to be considered (Table 6.6). The very different thermal expansion coefficients lead to significant internal stresses for any temperature changes. The stresses induced by this mechanism have to be taken into account when measuring the stress developing in the oxide during oxidation [6.178].

$\alpha (\times 10^{-6} \text{ K}^{-1})$	а	b	с		
Monoclinic	10.3	1.35	14.7		
Tetragonal	11.6	_	16.1		
Cubic	10.7				

TABLE 6.6. THERMAL EXPANSION COEFFICIENTS FOR MONOCLINIC AND TETRAGONAL ZIRCONIA [6.179]

The stability of the various phases is controlled not only by the stress state (isostatic pressure) but also by chemical aspects. Stabilizing the high temperature phases can be achieved with additions of various aliovalent ions that induce formation of vacancies for charge balance. A concentration of vacancies of 3% is required for tetragonal zirconia stabilization and 8% for the cubic form. This stabilization is obtained by specific additives. Among them, Ca^{2+} , Mg^{2+} and Y^{3+} are most frequently used; also possible, but of lower technical interest are the Yb³⁺ and Er³⁺ ions. A 2–3 mol% yttria addition is sufficient to obtain a fully tetragonal zirconia at room temperature, while increasing the addition to 6% stabilizes the cubic phase upon cooling after sintering. The increased stability of the tetragonal and cubic phases has been explained as due to the presence of oxygen anion vacancies formed in the doped zirconia achieving electrical neutrality [6.180].

A third parameter linked to the stability of the zirconia phases, and relevant to the behaviour of the layers grown on zirconium alloy components, is the grain size. The zirconia layers obtained during oxidation have a very fine structure (often the grain size ranges around 10–20 nm), due to its growth mechanism, and this small grain size may affect the relative stability of the phases to be considered. As Garvie [6.181] reported, small grain size, in the nanometre range, will stabilize the tetragonal phase, by changing the free energy of the system induced by the free surface contribution, a quantity that is dependent on the crystal structure of the phase.

Finally, the evolution of the stabilized phase in the presence of water has to be considered. Minor environmental changes induce crystallographic evolution of the zirconia phase equilibria. Zirconia has a very low solubility in water, however, chemically doped tetragonal or cubic phases in contact with water tend to transform to monoclinic zirconia. The process may include a selective dissolution of the dopant, if it has a higher solubility in water than zirconia, for example, MgO [6.182]. A process of continuous dissolution and reprecipitation may also be considered. The solubility of zirconia in water is not nil but is very low at room temperature, in the range of 10^{-10} mol·l⁻¹, with a limited increase with temperature, except for the passivation domain [6.183]. The solubility is a dynamic process with a dynamic equilibrium between dissolution and reprecipitation. Because the low temperature phase is monoclinic ZrO₂, the reprecipitation of the dissolved tetragonal phase leads only to new monoclinic crystals. This process is the reason for the first order kinetics observed for this type of evolution of oxide [6.184]. An alternative view is that the tetragonal or cubic transformation to the monoclinic does not require dissolution but is a martensitic transformation.

6.5.3. Gamma irradiation and photon-electron conduction

For ionic and covalent compounds, ionization is induced either by photon–electron or electron–electron interactions. The ejection of one electron results in local charge changes and degradation of the bonding. Two effects are then induced: electrons are released from the ions and are available in the conduction band, at least for a short period of time, and permanent damage may be induced by the local charge imbalance.

Under photon irradiation, oxides such as alumina, magnesia or zirconia show a loss of insulation properties known as radiation induced conductivity (RIC). This phenomenon is caused by the interaction of the photons with electrons, increasing their energies to allow them to be transferred to the conduction band. There they allow some electronic conductivity until they are trapped in any hole of the crystal. Under continuous irradiation, and in the presence of an applied potential, this irradiation produces a net electron motion (i.e. an electric current). Analysed in detail for alumina, magnesia and a few other ionic compounds, RIC has been found to be very similar for all the oxides, being almost linear with the energy deposition rate [6.185]. This phenomenon has been measured on oxide films grown on Zircaloy samples and an RIC has been observed during 1 MeV electron irradiation between room temperature and 670 K (400°C) [6.186]. The RIC observed for an energy deposition rate up to 7.5×10^4 Gy·s⁻¹ was shown to increase with temperature and was alloy dependent (Fig. 6.46). For the oxide thickness tested (3 μ m), the values obtained, in the range of 10⁻⁸ S/m at 670 K (400°C), are consistent with the measurements performed on other oxides [6.185]. Ultraviolet irradiation can cause increased corrosion at room temperature in zirconium alloys if a small anodic direct current (DC) potential is applied, so long as the radiation is energetic enough to exceed the band/gap of the zirconia. Discrepancies with other measurements reporting the absence of any RIC can be explained by the thick but porous oxide used or by the low dose rate obtained with X ray irradiation. Care should also be taken when measurements are made using alternating current (AC) rather than DC because electron/hole pairs generated by X ray or γ irradiation tend to recombine in AC fields. Whatever the discrepancies of the values reported, it is expected that the mobility of electrons required for charge balance in the oxide layer would not be a limiting step in the corrosion kinetics under irradiation.



FIG. 6.46. RIC of a zirconia layer grown on Zircaloy-2 (for the conditions used, $10^{18} \text{ e} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$) $\approx 5 \times 10^4 \text{ Gy} \cdot \text{s}^{-1}$) (this image was published in Ref. [6.186], copyright Elsevier, 1999).

6.5.4. Irradiation damage with atomic displacements

In addition to the RIC described above, irradiations with electrons of high energies, as well as neutron irradiations, can induce atomic displacement damage in the zirconium oxide. A detailed description of the PDs in zirconia is still lacking. Ab initio quantum chemistry computations have been used to describe the creation of vacancies and interstitials. As such PDs may induce a local charge imbalance, computations have to be performed for the various possible local charges [6.187].

It has been possible to predict the formation energies of the O vacancies, which have been found to be similar whatever the initial coordination of the O ion. In both cases (tri- and tetra-valent ion locations) the formation energy was found to be high for the removal of a neutral O atom (i.e. a vacancy of zero charge state), about 8.9 eV. In addition, it was computed that the vacancy is a source of electrons. The local removal of a first electron (V^+) corresponds to a gain in energy of 0.47 eV, and of 1.2 eV for two electrons (V^{2+}). These defects correspond to the F centres. This displacement results in a permanent change in electrical properties and the oxide becomes a semiconductor as in the case of Al₂O₃ or MgO [6.188]. Negatively charged O⁻ vacancies were not obtained and the corresponding extra electrons are only weakly localized near the vacancy. The neutral Zr vacancy is not expected to occur owing to its very high formation energy of 24.2 eV. For interstitials, computations are more complex owing to energy references of the isolated O atom, but the insertion of an O neutral atom can be expected to require 1.4 or 2.2 eV, depending on the insertion site. In both cases, the two O atoms close by are strongly linked by a covalent bond. The Frenkel pair energies (O vacancy + O interstitial) are also charge dependent: 7.3 eV for neutral defects to 5.4 eV for double charged defects. The general balance is that electrons tend to leave neutral O vacancies for neutral O interstitials, leading to V^+-O^- or $V^{2+}-O^{2-}$ complexes.

6.5.4.1. Displacement energies

In a similar way to that described in Section 6.2.3, computation of the damage induced by atomic displacements requires a knowledge of the displacement energies. In the case of zirconia, the displacement energies have not been measured, and can only be assessed by extension of the data obtained with other oxides. In these crystals, the displacement energies are not the same for the two ions. A twofold difference has been reported for various oxides, without any systematic tendency for the cation and the anion [6.185]. As a result, different authors use different displacement energies in different studies, varying from 40 eV for the two ions [6.189] to 60 eV for O and 20 eV for Zr by similarity to Al₂O₃ [6.190] or 20 eV for O and 40 eV for Zr based on relative atomic mass arguments [6.191]. Thus, care should be taken when comparing the irradiation behaviour of zirconia reported by different authors or comparing different types of irradiation (electrons, ions, neutrons).

6.5.4.2. Clustering of PDs

Whatever the intensity of the displacements induced by the elastic collisions, the PDs created during irradiation can migrate and coalesce with the constraint of maintaining local electrical neutrality. Therefore, no dislocation loops of any kind should exist by clustering O interstitials or vacancies. High voltage electron irradiation of single crystals of Y_2O_3 — stabilized zirconia single crystals — resulted in large interstitial dislocation loops consisting of slices of O-Zr-O interstitials, inducing a stacking fault in the loop [6.192], while the

dislocation line surrounding the loop may have some local line charge, depending on its local crystallographic orientation.

After O doping by 300 keV O^+ irradiation, O interstitial dislocation loops were observed during subsequent electron irradiation. They were found to consist of extra layers of O ions with a charge balance obtained by the trapping of electrons from the second (electron) irradiation [6.191]. A detailed analysis of the growth of these dislocation loops revealed increased mobility of the O ions at a level that indicated an important role of low energy recoils, or electronic excitation induced by the moderate energy electrons (200 keV) for the migration of O [6.193], or both. This result is an indication of a possible enhanced diffusion of O ions in zirconia under a high photon irradiation field.

In all cases, the sizes of the loops observed were in the micrometre range and therefore much larger than the grain sizes reported for zirconia growing during zirconium alloy corrosion in high temperature water. Thus, these dislocations cannot develop in the latter oxides and this explains why they are not observed in such oxide layers. This conclusion supports the general agreement that the high density of grain boundaries in fine grained zirconia layers, acting as sinks for the PDs, does not allow the formation of large clusters of PDs.

6.5.5. Phase changes under irradiation

The fluorite-type crystalline structure is known to be strongly resistant to irradiation, as is clearly the case for UO₂ [6.194], but is also the case in chemically stabilized cubic zirconia [6.189]. As zirconia is being considered as a possible long term storage matrix for nuclear waste or for an inert matrix for the transmutation of actinides, extensive irradiation programmes have been undertaken to study its behaviour under irradiation [6.194]. Contrary to the behaviour of mixed oxide zircon (ZrSiO₄), zirconia has never been observed to become amorphous under irradiation. Some irradiation effects have been observed, the nature of which depend on the crystallographic structure of the sample being irradiated.

The irradiations performed on the cubic phase, stabilized with various additions, lead to some observable damage that has been characterized by Rutherford backscattering spectroscopy. The damage parameter, recording the reduction in He ion channelling due to the increase in defects in the crystal, strongly increased in the range of a few dpa (Fig. 6.47). This phase remained crystalline, in its original form of cubic symmetry, as determined by X ray diffraction and TEM [6.189]. The irradiation damage has been determined to be a high density of dislocation loops interconnecting as a high density dislocation forest [6.193].

The behaviour is very different for the stable monoclinic phase. The low symmetry of this phase reduces its resistance to irradiation; some results suggested that it transformed to the more symmetric tetragonal (or cubic) phase but these results were questionable because of possible contamination, enhancing the tetragonal phase transformation [6.189]. Experiments with large, pure monoclinic crystals, using X ray and Raman spectrometry to analyse the phases, confirmed the tetragonal phase transformation occurring during ion irradiation, but no effect was detected with electron irradiation [6.190].

The tetragonal phase transformation under ion irradiation has been observed by several authors [6.195, 6.196], with similar results showing an almost, but not fully, complete tetragonal phase transformation above 2-5 dpa (Fig. 6.48). Various analyses have shown that the monoclinic to tetragonal transformation under pressure is caused by the development of a soft vibration mode [6.197]. This analysis has been applied to the case of ion irradiation, where the local pressure was induced during the development of the displacement

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cascades [6.198]. Annealing heat treatments after ion irradiations showed that the tetragonal phase started to return to the monoclinic phase at 520 K (\approx 250°C), for a total recovery above 600 K (\approx 330°C). Therefore, for water reactor conditions, the contribution of irradiation to tetragonal zirconia formation should not be significant [6.199].



FIG. 6.47. Damage accumulation parameter during ion irradiation of chemically stabilized cubic zirconia, remaining cubic after irradiation (this image was published in Ref. [6.189], copyright Elsevier, 1999).



FIG. 6.48. Fraction of tetragonal zirconia formed during ion irradiation of monoclinic zirconia with Bi ions (•) and Xe ions (O) (reproduced from Ref. [6.199] with permission courtesy of the American Physical Society).

In summary, the oxides of zirconium are stable. Irradiation, including photons, produces a loss in insulation by interactions with the electrons of the oxide. Although nuclear displacement energies have not been established for either ion, displacement is limited because the PDs tend to recombine to maintain electrical neutrality. Dislocation loops have been observed in model oxides. These loops are much larger than the grain size of the oxide produced during corrosion in water; they are not observed because of the high density of grain boundary sinks for PDs. The cubic phase is not affected by irradiation but the monoclinic phase transforms to the tetragonal phase with irradiation at low temperatures. This transformation is reversed at \approx 523 K (250°C), the lower limit for reactor operations.

6.6. CONCLUSIONS AND PROSPECTS

Owing to their specific uses in water reactor cores, zirconium alloys have been widely studied during and after irradiation. The mechanism of irradiation damage is understood clearly enough for safe design and operation. Several phenomena are not scientifically understood in detail, despite satisfactory phenomenological and quantitative descriptions. This lack of basic understanding reduces the capability to forecast behaviour beyond the conditions tested, and therefore hampers the development of new alloys or the broadening of the operating conditions of the current ones.

Among the phenomena for which a deeper scientific knowledge would be useful, the following are considered highly promising and recommended for further research:

- Zirconium alloys are subject not to swelling, but to growth, a phenomenon controlled by the diffusional anisotropy difference. It is recommended to develop predictive modelling of the jump mechanisms of the PDs in zirconium alloys, including a detailed description of the interactions between the PDs and any alloying elements (Sn, Nb, O or Fe), but also impurities. The description of the jumps of these complexes, by ab initio (i.e. quantum chemistry based) methods and MD to analyse the temperature evolution of the diffusional anisotropy difference would help the development of predictive creep and growth modelling of industrial alloys under power reactor irradiations.
- The interatomic potentials currently available do not allow a good description of cascades in complex alloys. In rare cases, only binary alloys have been studied. Even in the case of pure zirconium, the results on the configuration and energies of the PDs are highly dependent on the interatomic potential. The improved results will increase the accuracy of the source term, providing the bias for PD production. A coupling between ab initio and MD techniques would allow significant improvement in modelling, as soon as progress in computational power allows them as standard procedures.
- For the intermetallic phases, whose stability under irradiation affects the corrosion resistance, the exact mechanisms of their evolution under irradiation is not perfectly described. The differences between the bulk behaviour of these phases under irradiation or as dispersed precipitates in the Zr matrix highlights the importance of the ballistic contribution for the transformations observed. Modelling should include these different contributions.

— With respect to mechanical behaviour, the very important reduction of uniform plastic strain after irradiation, due to the channelling phenomenon, is exacerbated in zirconium alloys owing to the possibility of dislocation slip with the same Burgers vector on different systems (basal, prismatic or pyramidal), for which the critical resolved shear stresses are very different. It seems appropriate, due to the increase in concern regarding post-irradiation behaviour, to extend the observation of loop–dislocation interaction to the conditions of creep strain. Recovery can then occur by a mixture of dislocation interactions and thermal recovery.

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Chapter 7

DEFORMATION DURING IRRADIATION

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7.1. INTRODUCTION

Under normal reactor operating conditions, zirconium exists in the hexagonal close packed (HCP) phase, and many of its mechanical and physical properties are anisotropic (see Chapter 5, Volume 1 of this publication). Among these are irradiation growth and irradiation creep, which result in anisotropic dimensional changes relative to the crystallographic axis in each individual grain and in the orthogonal directions of reactor components. Here, irradiation growth refers to deformation caused by mechanisms that do not require an applied stress for their activation, whereas irradiation creep is deformation caused by mechanisms activated by an applied stress. Irradiation growth and creep are observed in both single crystals and in polycrystalline materials. This dimensional change in zirconium alloys, under an irradiation flux sufficiently energetic to produce atomic displacements, has important technological implications for the nuclear engineer. Irradiation deformation also provides interesting and complex problems for the research scientist attempting to measure and understand its fundamental behaviour.

Scientists and technologists use several different units when referring to irradiation damage caused by atomic displacements in the zirconium lattice. These differences are apparent from results referenced throughout this chapter. As the vast majority of the experimental data on irradiation growth and creep are derived from test and power reactors, it follows that 'fast' neutron units are often employed (i.e. those with energy E > 900 keV that are able to displace a host zirconium atom in the zirconium lattice). In practice, units of integrated neutron flux ($n \cdot cm^{-2}$ or $n \cdot m^{-2}$) with specified energies of either E > 0.1 MeV (less common but includes most of the energy spectrum that can produce irradiation damage) or E > 1 MeV (more common) are quoted. The latter is a convention used to compare fluxes in different reactors. An alternative, and more rigorous, approach is to quote displacements per atom (dpa) in which the whole neutron energy spectrum is employed in the dpa calculation. An approximate conversion is 1 dpa $\approx 5 \times 10^{24}$ n·m⁻² (E > 1MeV).

7.2. IRRADIATION GROWTH

7.2.1. Background and definition

Irradiation growth can be pictured as a cube transforming to the shape of a brick, at constant volume. The dimensional changes of single crystal zirconium under fission fragment irradiation were first reported by Buckley in 1962 [7.1], following a similar observation in textured α -uranium. Buckley attributed the growth in α -uranium to the formation of interstitial dislocation loops normal to the *b* axis of the orthorhombic unit cell and vacancy loops normal to the *a* axis. A similar explanation was applied to the HCP zirconium lattice. The observed expansion in single crystals along the *a* axis of the HCP unit cell, and the

contraction along the c axis, was attributed to the formation of interstitial loops on prism planes and to vacancy loops on basal planes. This simple hypothesis has not afforded a complete, or even accurate, explanation of all the subsequent growth observations, but it has provided the impetus for much follow-on work in this field. Similar growth phenomena occur in polycrystalline zirconium and zirconium alloys during displacement irradiation damage, provided the material has a non-random texture. This observation has had a significant technological impact on the design and operation of fuel assemblies in commercial reactors. Detailed differences in growth behaviour are observed between different alloys depending on composition, heat treatment, material microstructure and irradiation conditions. These aspects are covered separately in this chapter.

7.2.1.1. Anisotropy and texture in relation to growth

Irradiation growth in a single crystal of zirconium is a direct result of the anisotropic properties of the HCP unit cell. In polycrystalline zirconium, growth depends on the grain alignment, or texture, introduced during prior cold or warm work reduction — for example, by rolling for sheet material (Fig. 7.1) or pilgering for tubing — to produce the final product. Growth also depends on the state of intergranular stresses existing after cold working. The generation of texture in the material is due to the limited number of deformation systems available in the HCP zirconium lattice compared with cubic structured metals such as Cu, Ni or Fe. In zirconium, slip occurs primarily on the prism planes and any deformation in the basal planes requires twinning at high stress. Deformation perpendicular to the basal plane can also be accommodated by slip on pyramidal systems (e.g. $(10\overline{1}1)[11\overline{2}3]$), as shown by Tomé et al. [7.2]. In α -alloys the detailed texture depends strongly, but not entirely, on the final deformation step at room temperature [7.3]. For tubing, in particular, the direction of the peak concentration of the basal poles in the radial-circumferential plane depends on the reduction ratio of wall thickness to tube diameter. This ratio is generally referred to as the *Q* factor imposed during fabrication. For tubes made from $(\alpha + \beta)$ alloys, the texture is mostly controlled by hot working, usually extrusion, when the subsequent cold work is less than 30% [7.4]. The basal pole texture in tubing or flat sheet samples is commonly specified by the Kearns factors [7.5]; they are usually represented by f_n , where n denotes a direction, and are determined by X ray or neutron diffraction. The factors f_n describe the volume fraction of the (0002) diffraction poles of the individual grains in the three principal orthogonal directions: f_a in the axial (for tubes) or longitudinal (for sheet) direction, f_r in the radial (for tubes) or thickness (for sheet) direction, and f_t in the tangential (for tubes) or transverse (for sheet) direction. It follows that $f_a + f_r + f_t = 1$ [7.6].



FIG. 7.1. The basic HCP cell (top); usual texture in rolled sheet for the normal, longitudinal direction (LD) and transverse direction (TD) (bottom).

The Kearns factors for fuel cladding are typically $f_a \approx 0.05$, $f_r \approx 0.6-0.7$ and $t \approx 0.2-0.4$, with the basal pole maxima concentrated around $\pm 30-40^{\circ}$ to the radial direction of the tube, in the radial-tangential plane. The major component of stress-free irradiation growth strain depends only on f_a , as far as texture is concerned. For pressure tubes, which require high diametral creep strength, the Kearns factors are typically $f_a \approx 0.05$, $f_r \approx 0.30-0.36$ and $f_t \approx 0.60-0.64$, with the basal pole maxima concentrated in the direction around $\pm 30-40^{\circ}$ to the tangential direction of the tube, in the radial-tangential plane. In both light water reactor (LWR) fuel cladding and Canada deuterium uranium (CANDU) reactor pressure tubing, this texture causes an elongation of the tube due to irradiation growth. For further, detailed information on the development of textures see Chapter 5, Volume 1 of this publication.

7.2.2. Basis for the anisotropic growth process

Irradiation growth in Zr alloys is a phenomenon similar to void swelling in cubic metals, in the sense that a dimensional change occurs in the absence of an applied stress. Unlike swelling, growth is a shape change at constant volume, so it is therefore an anisotropic process. Growth depends strongly on the anisotropic characteristics of zirconium's HCP lattice structure and the consequent asymmetries in point defects (PDs) and defect cluster accumulation at various 'biased' sinks. The PDs are generated by irradiation damage originating in the displacement cascade (see Chapter 6 on Irradiation Damage for more detailed descriptions).

The shape change due to irradiation growth occurs as a result of an anisotropic distribution of sinks receiving a net flux of vacancies that is distinct and different from an anisotropic distribution of sinks receiving a net flux of interstitials. A complete mechanistic understanding of irradiation growth requires the identification of the possible sinks, a description of their evolution, the identification of the source of anisotropy and an explanation of the portioning of the PDs among the sinks.

7.2.2.1. Point defect sinks

The PD sinks present in zirconium alloys depend on the metallurgical condition. In the annealed state, single α -phase materials such as zirconium, Zircaloy-2 and Zircaloy-4 contain only grain boundaries and a very low density of network dislocations before irradiation. After a low fast fluence ($\approx 10^{24} \text{ n} \cdot \text{m}^{-2}$ (0.2 dpa)) they contain a high density of $\langle a \rangle$ direction

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prismatic dislocation loops of mixed vacancy and interstitial character. The Burgers vector and plane normal of these loops is parallel with the basal plane. With this combination of sinks, the growth rate is low. However, above a critical fluence, which decreases with increasing temperature, faulted $\langle c \rangle$ component vacancy loops appear on the basal planes. The latter are net vacancy sinks, which increase the net flow of interstitials to the $\langle a \rangle$ loops and the growth rate increases. This change is called 'breakaway growth' [7.7].

Unirradiated, cold worked (CW) α -zirconium alloys contain a and (c + a) network dislocation as well as grain boundaries. After irradiation the lattice contains an $\langle a \rangle$ loop structure that is similar to that of irradiated, annealed materials. This combination of sinks produces a high irradiation growth rate at all neutron fluences. The growth of the α phase materials corresponds in general terms to an expansion in the basal plane in the $\langle a \rangle$ direction and a contraction normal to the basal plane in the $\langle c \rangle$ direction. This directionality indicates that the $\langle a \rangle$ dislocations and loops are net interstitial sinks, while the $\langle c \rangle$ component dislocations are immobile sinks, being either faulted and sessile loops or having a high critical resolved shear stress characteristic of $\langle c + a \rangle$ slip. By contrast, the $\langle a \rangle$ network dislocations and loop segments are unfaulted and therefore glissile. The direct consequence of this intrinsic difference is that the $\langle a \rangle$ dislocations have a larger reaction range than the $\langle c \rangle$ type dislocations and can absorb more primary PD clusters, these being the main immobile products of the collision cascades [7.8, 7.9].

Apart from an experimental inference, theoretical studies indicate that there is an orientation bias resulting from differences in anisotropic diffusion of vacancy and interstitial PDs [7.10]. The high density of grain boundaries present in cold worked stress relieved (CWSR) materials has a strong influence on growth anisotropy.

Two phase alloys such as Zr-2.5Nb, in the CW condition, tend to have much finer and more anisotropic grain structures than the α phase alloys such as Zircaloy. The α - β interfaces comprise part of the grain boundaries in Zr-2.5Nb and these interfaces are important sinks for PDs. Although there is no evidence that the β phase has any influence on the deformation behaviour, the anisotropic growth is generally more complex in Zr-2.5Nb than in Zircaloy, involving transient contractions in the direction corresponding to a high concentration of $\langle a \rangle$ axis dislocations.

7.2.3. Experimental methods

By far the largest quantity of information on the deformation of polycrystalline zirconium alloys is derived from routine surveillance and post-irradiation measurement programmes on fuel assemblies, fuel rods, guide thimbles and pressure tubes. The components are measured in the spent fuel handling pool or in situ (for pressure tubes). Specially adapted, submerged equipment is employed to measure changes in length and diameter that are then transformed into growth strains from knowledge of the original dimensions. However, extracting information about growth can be difficult because of the superimposed effects of stress (generating creep strains), gradients of neutron flux and temperature as well as mechanical interactions with fuel or other core components.

Specially designed experiments to investigate irradiation growth include few continuous in-pile studies but many periodic, out-of-reactor measurements using a variety of methods. Techniques and instrumentation include a computer controlled underwater measuring bench equipped with linear variable differential transformer probes [7.11], photomicrodensitometer tracking [7.12] to measure length changes between specimens of
different texture, and comparator gauge length determinations on tubes and flat plate specimens [7.13–7.15]. The typical accuracy of the linear variable differential transformer measurements is $\pm 0.5 \,\mu$ m. Fast fluences can be determined by several methods, including the activation of copper wire monitors [7.16]. Irradiation growth at low temperatures has been measured in-pile in a liquid nitrogen cryostat at 77 K (–196°C) [7.12, 7.17] and during 4.4 MeV proton irradiation at 347 K (74°C) [7.18].

7.2.4. Characteristics of irradiation growth in zirconium and Zircaloy

7.2.4.1. Zr single crystals

Measurements of irradiation growth at 353 K (80°C) and 553 K (280°C) in single crystals of iodide zirconium in the annealed state show initially positive strains of $\approx 10^{-4}$ in the $\langle a \rangle$ direction and a contraction of around double that size in the $\langle c \rangle$ direction [7.14]. The growth rate is low up to a fast fluence of $4 \times 10^{25} \text{ n} \cdot \text{m}^{-2}$ (E > 1 MeV) or about 8 dpa. Beyond this fluence, the iodide zirconium crystal exhibits accelerated growth in the $\langle a \rangle$ direction at 533 K (260°C), with a rate equal to $\approx 40\%$ of the breakaway rate in annealed polycrystalline Zircaloy at the same temperature [7.19].

The introduction of cold work network dislocations with both $\langle a \rangle$ and $\langle c \rangle$ components significantly increases the steady state growth rate at 350 K (77°C) [7.20]. However, CW single crystals containing only a low density of *a* dislocations grow at a very low rate. Carpenter et al. [7.21] have reviewed the measurements and models for the irradiation growth of zirconium single crystals.

7.2.4.2. Recrystallized annealed Zircaloy

The growth of annealed Zircaloy is characterized by three stages as a function of increasing fluence, as shown in Fig. 7.2. In the first, transient stage, the growth strain is small, $\approx 0.1\%$. Growth is positive in directions containing a small fraction of basal poles (the 'cold working direction') and negative in directions containing a large fraction of basal poles. The growth transient is rapid at low temperatures of 350–380 K (77–107°C), has a maximum value at a temperature of \approx 570 K (297°C) and diminishes to zero at higher irradiation temperatures \approx 700 K (427°C) [7.22].

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FIG. 7.2. Typical irradiation growth of annealed Zircaloy in the LD ($f_d < 0.1$) as a function of fast fluence (E > 1 MeV) and temperature (this image was published in Ref. [7.22], copyright Elsevier, 1988).

In the second stage, growth saturates or achieves a low steady state rate $\propto (\phi_t)^n$, where $n \approx 0.4$ [7.12]. The duration of this stage decreases with increasing temperature. During the first two stages there is an increase in the density of *a* dislocation loops on prism planes due to irradiation damage. The loop character is mixed, with some being interstitial and some being vacancy, but the latter usually dominate. However, at low fluences the total area of loops present after irradiation at 570 K (297°C) is too small to account for the magnitude of the transient growth strain.

In the third stage, beyond a threshold fast neutron fluence, the growth rate tends to increase in an approximately linear manner with fluence breakaway growth [7.7]. The fluence at the onset of linear growth decreases with increasing temperature, and at high temperatures (>650 K (377° C)), the saturation 'plateau' region may disappear. The accelerated growth rate coincides (a) with the appearance in the microstructure of *c* component dislocations and (b) with the redistribution of Fe atoms into the zirconium matrix by radiation induced dissolution of the second phase particles (SPPs).

Once acceleration occurs, the growth rate correlates reasonably well with the quantity $(1-3f_n)$, where f_n is the resolved fraction of basal poles in the direction of measurement [7.17]. This ideal relationship corresponds to simple averaging of the shape change of all grains in a polycrystal when there is expansion along the $\langle a \rangle$ axis and contraction along the $\langle c \rangle$ axis. The *c* component dislocations are faulted vacancy loops with a total area that is sufficient to account for most of the observed growth strain [7.23]. This observation has been confirmed for both α and β annealed and quenched Zircaloy. At higher irradiation temperatures $\approx 600 \text{ K}$ (327°C), the initial *a* loops evolve into a network structure that resembles that produced by cold work but dominated by *a* type dislocations.

7.2.4.3. Cold worked stress relieved Zircaloy

The very early transient stage of irradiation growth in CWSR Zircaloy is similar to that of annealed material, but instead of a tendency to saturate, the growth continues at a steady rate, which is linear with fast neutron fluence up to high total exposures [7.24]. Typical behaviour is shown in Fig. 7.3. In the steady state region, the growth rate remains positive in the cold working direction, negative perpendicular to this direction and approximately obeys the $(1-3f_n)$ relationship with texture [7.17] for irradiation temperatures between 350 and 550 K (77 and 277°C). However, the long term growth rate increases by about 60% over this range. Above 570 K (297°C), the early transient strain is reduced, and the steady state rate decreases slightly before increasing at 670 K (397°C). At higher irradiation temperatures >570 K (297°C), the long term growth behaviour of annealed and CWSR materials can become indistinguishable because the post-breakaway rate in annealed Zircaloy is close to the steady state growth rate in CWSR material. This observation is a direct result of the ratio of <a > c > c > type sinks being similar in each material under these conditions [7.16, 7.25].

An increase in the growth rate at high fast fluences, similar to breakaway growth in annealed Zircaloy, also occurs in zirconium alloys in the CWSR state, as shown in Fig. 7.4. This acceleration changes the previous linear behaviour and makes the long term growth trend non-linear up to maximum measured fluences of around $10^{26} \text{ n} \cdot \text{m}^{-2}$ (E > 1 MeV), or $\approx 20 \text{ dpa}$ [7.16]. The acceleration coincides with an increase in the density of c component dislocations under the influence of the fast flux: an effect that is observed at all irradiation temperatures [7.18]. Accelerated growth was first deduced following the analysis of the elongation of Zircaloy-2 pressure tubes employed in both the CANDU and the steam generating heavy water reactor [7.25]. Accelerated growth was later confirmed, using supporting microstructural analyses, in specially prepared specimens of Zircaloy-2 pressure tubing irradiated in a material testing reactor [7.16]. These results showed that the increase in $\langle c \rangle$ component dislocation density is larger for crystals with their $\langle c \rangle$ axis in the radial direction of the specimen (i.e. fuel cladding) than for crystals with their $\langle c \rangle$ axis in the transverse or tangential direction (i.e. pressure tubes). It follows that CWSR fuel cladding should experience a larger increase in growth rate than pressure tubes.



FIG. 7.3. Irradiation growth of CWSR Zircaloy-4 at 555 K (282°C), as a function of prior cold work, texture and fluence (reprinted with permission from Ref. [7.24], copyright ASTM International).



FIG. 7.4. Non-linear growth of CWSR Zircaloy-2 irradiated in the OSIRIS (denoted GVR and GVU) and DIDO reactors at about 553 K (280°C) (reprinted with permission from Ref. [7.16], copyright ASTM International).

7.2.5. Growth and microstructure in recrystallized annealed Zircaloy and CWSR Zircaloy

A clear correlation exists between the observed macroscopic growth behaviour and the material microstructure [7.26]. In comparing recrystallized annealed (RXA) Zircaloy and CWSR Zircaloy at temperatures of commercial reactor interest, a distinction is made between (a) the pre-existing network dislocations and (b) the microstructure evolving under the influence of irradiation. For RXA material, only $\langle a \rangle$ component loops due to irradiation exist and at low fluences ($\leq 3 \times 10^{25} \text{ n} \cdot \text{m}^2$) the growth strains are small (<0.1%) and saturate. At higher fluences ($\geq (6-10) \times 10^{25} \text{ n} \cdot \text{m}^{-2}$), when $\langle c \rangle$ component loops begin to appear, the growth rate increases and becomes approximately linear with fast fluence. The growth strain in recrystallized reactor components irradiated at about 573 K (300°C) can reach 2.0% in the original rolling or working direction, at a fluence of $3 \times 10^{26} \text{ n} \cdot \text{m}^{-2}$ (E > 1MeV). By contrast, CW Zircaloy contains $\langle c \rangle$ component dislocations as part of the deformation induced structure, and more are formed during irradiation by atomic displacement processes. The growth rate is nearly linear with fluence, starting early in the irradiation, although the size depends on the degree of cold work. For example, in heavily CW material ($\geq 70\%$) a growth strain of 2.0% can be achieved by a fluence of $2 \times 10^{26} \text{ n} \cdot \text{m}^{-2}$ (E > 1MeV).

As discussed in Section 7.2.6.8, pre-breakaway growth strains in RXA Zircaloy can be recovered by annealing, but only a small fraction is recoverable in CWSR alloys, or after breakaway growth has occurred in either material. This variability in recovery indicates that different growth mechanisms are operative in the different growth regimes, dependent on the presence or absence of $\langle c \rangle$ component dislocations. A further connection with microstructure is suggested by the observation that $\langle c \rangle$ component dislocations are seen to nucleate near precipitates that have released Fe to the matrix through irradiation induced dissolution [7.23]. The Fe appears to promote the heterogeneous nucleation of loops from the diffusing PDs created by the irradiation damage.

The interrelationship between fast fluence, precipitates, precipitate dissolution, released Fe (or possibly Cr) and $\langle c \rangle$ component dislocations is not clear. No $\langle c \rangle$ dislocations are observed at low fluences, even though in some studies it has been observed that most of the Fe (but very little of the Cr) has already been released into the matrix during the precipitate amorphization process [7.27]. However, Fe dissolution is not necessarily a consequence of amorphous transformation [7.25]. It occurs in all irradiated zirconium alloys where Fe has segregated into second phases. Some observations of *c* loops support the view that Fe (and possibly other impurities) can enhance *c* loop formation near precipitates.

7.2.5.1. Accelerated or breakaway growth

Griffiths et al. [7.25] have used X ray diffraction and transmission electron microscopy to characterize the microstructural and microchemical changes produced by irradiation that accompany breakaway irradiation growth. The investigations included annealed Zircaloy-2 and Zircaloy-4, where the onset of accelerated growth rates is associated with the nucleation of new vacancy dislocation loops lying on basal planes. X ray diffraction and transmission electron microscopy results show that the change in microstructural behaviour is correlated with the dissolution of the intermetallic precipitates containing Cr and Fe and the subsequent stabilization of the <c> component loops by these alloying elements. Griffiths et al. proposed [7.25] that the slower diffusing Cr atoms and their interaction with anisotropically diffusing PDs from irradiation damage are more important than Fe in this process. Transmission electron microscopy of the specimens after high fluence shows that the loops are contained within layers of high Fe and Cr impurity concentrations parallel to the basal plane (Fig. 7.5).

In the case of CW materials that already contain <u>c</u> component network dislocations, it was shown that gradual, increasing rates of growth also occur due to dislocation multiplication by a process of helical climb on screw dislocations. Some additional growth may also arise from new loop nucleation by irradiation, but this contribution is not significant up to moderate fast fluences of around 10^{26} n·m⁻² (E > 1 MeV) or 20 dpa. The additional growth is caused by an increase in c dislocation density, according to an interpretation of X ray diffraction line broadening measurements. The difference between the microstructural evolution in CWSR and RXA Zircaloy is that in the CWSR state, evolution occurs primarily by the nucleation of helices on existing screw dislocation, thereby precluding the necessity for loop nucleation in the matrix that is required in the RXA state. The evolution in microstructure varies considerably from grain-to-grain, an observation that may be related to variations in impurity species and their concentrations or to stress in adjoining grains. Chemical composition is known to influence breakaway growth behaviour, as evidenced by the Zr-2.5Nb alloy, which is more resistant than Zircaloy to c component dislocation climb during neutron or electron irradiation [7.28, 7.29].



FIG. 7.5. Transmission electron micrograph showing alignment of c component dislocation loops and Fe/Cr-rich precipitates in bands parallel with the basal plane in sponge Zr after irradiation to $1.5 \times 10^{25} \text{ n} \cdot \text{m}^{-2}$ (E > 1 MeV) at 700 K (427°C): (a) diffraction vector = 0002 imaging c component loops; (b) many-beam diffraction, revealing impurity layers (this image was published in Ref. [7.25], copyright Elsevier, 1995).

Tomé et al. [7.2] have successfully predicted the accelerated irradiation growth behaviour of Zr-2.5Nb CANDU pressure tubes by means of a self-consistent model that takes into account the crystallographic texture and the intergranular stresses (see Section 7.2.6.3) that develop during fabrication. They have also derived basic single crystal growth and creep properties of Zr-2.5Nb that can potentially be used to accurately predict irradiation growth in components fabricated by complicated manufacturing routes.

7.2.6. Material properties and processing variables

7.2.6.1.Composition

Several alloying and impurity elements have been found to affect irradiation growth, namely niobium [7.30], carbon [7.31], tin [7.32, 7.33], sulphur [7.34] and oxygen [7.35]. The

evidence for the positive effect of niobium additions on the in-reactor dimensional stability of zirconium based materials is increasing [7.36, 7.37]. The influence on irradiation growth of niobium in Zr-Nb alloys is shown in Fig. 7.6, relative to CWSR Zircaloy-4, for irradiation in the temperature range 633–658 K (360–385°C). These data suggest that Nb is effective in the solute range up to about 0.5 wt% (\approx 0.5 at.%), after which any influence saturates. The detailed mechanism is not known, but soluble Nb may influence dislocation loop formation and the resultant mobility of irradiation produced defects that would otherwise drive the growth and creep processes. Sulphur also depresses the growth rate in the Zr-1Nb alloy M5 [7.34]. Controlled experiments have shown that changing the sulphur concentration from low (3 ppm (0.00085 at.%)) to high (30 ppm (0.0085 at.%)) reduces the growth strain by a factor of around 2.5 [7.34]. Based on a per atom effect, the influence of S is very strong and considerably greater than Nb. Tin and carbon additions to zirconium also affect irradiation growth. A change in the tin and carbon concentration in Zircaloy has a proportional and strong effect on growth for tin and a moderate effect for carbon (for concentrations >100 ppm (0.076 at.%)) [7.31]. An irradiation growth experiment using 4.4 MeV protons on nominally pure zirconium containing a range of iron concentrations (3-70 ppm (0.0005-0.011 at.%)) has demonstrated that iron has no influence on the radiation induced deformation rate at 347 K (70°C) [7.18]. However, the higher concentration of iron in the Russian Federation alloys E110 and E635 has a significant effect on the growth behaviour of these alloys, as discussed later. Regarding the growth behaviour of Zircaloy-2 and Zircaloy-4, there is no consensus among the measurement data on whether the compositional difference (mainly the presence of nickel in Zircaloy-2 and its absence in Zircaloy-4) influences growth behaviour. Growth data obtained from measurements on boiling water reactor (BWR) fuel channels in the same RXA state (see Section 7.5.2.1) show that under the reactor operational conditions of a BWR the growth rate of Zircaloy-4 exceeds that of Zircaloy-2.



FIG. 7.6. Effect of Nb on irradiation induced growth and creep at 658 K (385°C) (reprinted, with permission, from Ref. [7.36], copyright ASTM International, 2002).

7.2.6.2. Texture

Following the original, simple model of Buckley [7.1], the linear growth strain of polycrystalline material in a given direction, n, depends on the texture parameter, f_n , in that direction and is proportional to $(1-3f_n)$ [7.17]. This behaviour is a direct consequence of the texture introduced during fabrication. It is implicit in this formulation that each grain behaves as an independent single crystal and that there is no change in volume. Several growth experiments have been performed in which the growth strains in three orthogonal directions have been measured, e.g. [7.38, 7.39]. Adamson et al. [7.39] reported test results on RXA and CWSR Zircaloy-2 slab specimens, irradiated in a temperature range 660–700 K (327–427°C), and found that the growth strains in the longitudinal, transverse and normal (i.e. thickness) directions followed the $(1-3f_n)$ rule for low fluences. Other measurements at 330 K (57°C) on specimens of RXA Zircaloy-2 with a range of textures have demonstrated how the longitudinal growth strain varies with the texture parameter in this direction (Fig. 7.7).



FIG. 7.7. Irradiation growth of RXA Zircaloy-2 at 330 K (57°C) showing dependence of longitudinal strain on texture in the normal-transverse plane (this image was published in Ref. [7.40], copyright Elsevier, 1987).

Woo [7.41] has developed analytic expressions that relate irradiation deformation (growth and creep) of a polycrystalline, anisotropic material to that of a single crystal in terms of the specimen texture, for low and high neutron fluence regimes. An approximation is derived for intermediate fluences by a process of interpolation. It is shown that the steady state irradiation growth rate depends on the creep compliance and that growth and creep are additive (i.e. the external applied stress does not affect the growth). However, steady state

irradiation growth rates cannot be determined by simply averaging single crystal growth over grain orientations.

7.2.6.3. Internal stresses

Another component of growth strain in recrystallized zirconium alloys is due to the presence of intergranular stresses introduced in the material during cooling after thermomechanical processing. The stresses are relieved by internal irradiation creep that manifests as an apparent growth strain. The magnitude and direction of the internal stress effect depends on the heat treatment conditions and the distribution of the grains and can occur in directions that may be different from the simple texture driven growth described above. The influence and relief of internal stresses may be the dominant component of growth at very high fluences [7.42]. The effect has been modelled by Holt and Causey [7.40] and Tomé et al. [7.2]. Growth due to internal stresses tends to increase after low levels of CW. A small amount of CW does not change the texture, but CW of around 1.5% by either rolling or uniaxial tension can temporarily reverse the direction of the net macroscopic growth from positive to negative [7.42]. Negative growth eventually reverts to a 'normal' growth rate dictated by texture.

The long term, steady state behaviour is independent of the initial thermal stress conditions but remains influenced by the internal stresses generated by the incompatibility of grain-to-grain growth under the irradiating flux.

7.2.6.4. Cold work

Adamson [7.24] has measured the effect of CW level on irradiation growth over a temperature range of 550–620 K (277–347°C). Adamson found that the steady state growth strain (*G*) increases with increasing CW according to the empirical relationship:

$$G = G_0 + MC \tag{7.1}$$

where

 G_0 is the irradiation growth strain for RXA Zircaloy;

C is the CW level (%) before stress relief;

and *M* is a coefficient ($M = 2.0 \times 10^{-3}$ at 553 K (280°C) and 1.5×10^{-3} at 616 K (343°C)).

The results for Zircaloy-4 irradiated to about 555 K (282°C) are shown in Fig. 7.3. Holt [7.43] derived the dependence of growth on dislocation density from an analysis of the total deformation (growth and creep) of Zircaloy-2 pressure tubes manufactured by different routes (Fig. 7.8). Expressed in terms of the dislocation density $(\rho_d)^p$, the steady state growth rate at 330 K (57°C) increases approximately linearly $(p \approx 1)$, whereas at 550 K (270°C) $p \approx 0.8$.



FIG. 7.8. Comparison of calculated and measured growth rates as a function of dislocation density for Zircaloy-2 samples with different thermomechanical treatments, irradiated at 330 K (57°C) (this image was published in Ref. [7.42], copyright Elsevier, 1988).

During the early growth stage of Zircaloy at 320 K (47°C), low amounts of CW without subsequent stress relief produce a longer transient than after stress relief [7.44]. The direction of the second stage of growth is then reversed for both the working direction (from positive to negative) and perpendicular to the working direction (from negative to positive). This effect eventually dies out above a fluence of about (4–5) × 10²⁵ n·m⁻² (E > 1 MeV), or 8–10 dpa, and the growth anisotropy tends towards 'normal' (1–3 f_n) behaviour at high fluences. The size of this second stage effect increases with a CW level of up to 1.5% but then decreases for greater CW. Stress relieving restores the behaviour back to that of annealed material [7.22].

7.2.6.5. Grain size

The influence of grain size on the long term growth behaviour of zirconium alloys is generally found to be weak at low irradiation temperatures but becomes more important as diffusion rates increase at high temperatures, or for grain diameters less than about 2 μ m [7.22]. The initial transient growth strain in annealed polycrystalline zirconium is reported to be larger for a fine grained material between 353 and 553 K (80 and 280°C), but no systematic effect on the long term growth rate is found over the grain size range 5–75 μ m. Experiments on two different grain sizes (12 and 31 μ m) of annealed Zircaloy showed little difference in growth rate when irradiated at 320 K (47°C), but exhibited an inverse dependence on grain size in the temperature range 650–690 K (377–417°C) [7.35]. The finer grained material grows 15% faster at 650 K (377°C) and 100% faster at 690 K (417°C) than the coarser grained material.

These trends are in general agreement with the work of Murgatroyd and Rogerson [7.45], who also concluded that at 353 K (80°C) polycrystalline zirconium is only weakly sensitive to grain size in the range 5–40 μ m. However, at 553 K (280°C) they

observed significant grain size dependence: specimens of grain diameter of 5 μ m exhibit a higher strain than those with a grain diameter of 40 μ m. An exception to these grain-size-temperature trends are some growth measurements on annealed Zircaloy-2 at 330 K (57°C) that compare a small grain diameter (5 μ m) with a very large diameter (225 μ m) [7.35].

The results are shown in Fig. 7.9. The growth of the large grained material is very low and is similar to the growth behaviour of zirconium single crystals reported by Carpenter et al. [7.21]. This observation suggests a rapid buildup and then saturation of the irradiation damage microstructure, which becomes the dominant sink as the more distant grain boundaries are no longer able to provide a competitive sink for vacancies created by the irradiation.



FIG. 7.9. Effect of grain size on irradiation growth of recrystallized zirconium and Zircaloy-2 at 330 K (57°C) (reprinted, with permission, from Ref. [7.35], copyright ASTM International, 1987).

Statistical analysis of Zr-2.5Nb pressure tubes [7.46] has shown a strong inverse dependence of irradiation deformation (growth and creep) on grain size in the transverse direction (TD). Ex-reactor measurements and analysis support a model of increased growth (and creep) with smaller grain sizes.

7.2.6.6. Grain shape

The differences in the grain shape, grain size and microstructure of Zr-2.5Nb compared with Zr and Zircaloy result in a difference in growth behaviour, including some 'anomalous' growth of CWSR Zr-2.5Nb relative to 'normal' growth predicted from texture alone [7.22]. Zr-2.5Nb contains thin, platelet-like α -zirconium grains arising from the extrusion process. The main trends exhibited by growth measurements on longitudinal (axial) and transverse

specimens of Zr-2.5Nb irradiated at 553–583 K (280–310°C) are shown in Fig. 7.10. The ratio of transverse to longitudinal growth is typically about -0.5, independent of fluence above about $10^{25} \text{ n} \cdot \text{m}^{-2}$ (E > 1 MeV), or 2 dpa. Both growth rates tend to increase and exhibit an accelerating trend with increasing fluence [7.47].

The longitudinal growth strain decreases with increasing temperature and possibly with increasing Fe concentration in the matrix; the opposite trends are seen in the TD. The evidence for Fe in solution decreasing axial strain is not overwhelming as the statistics on potential Fe effects are confounded by variable grain sizes and textures. The $\langle a \rangle$ component dislocation structure evolves rapidly in the early stages of irradiation and achieves a saturation density. By contrast, the $\langle c \rangle$ type dislocations evolve slowly from the beginning and may explain the gradual increase in growth rate with fluence. 'Anomalous' negative growth, in which long term contraction occurs in both the working and the TDs, has also been observed in stress relieved Zr-2.5Nb irradiated at around 550 K (277°C) [7.22, 7.48]. The cause of this atypical behaviour seems likely to be related to the low dislocation density and a highly anisotropic grain structure with very fine (<1 µm) grain widths. This qualitative explanation by Woo [7.48] is a natural consequence of the predictions of his growth model based on diffusional anisotropy difference (DAD), as discussed in Section 7.2.11.2.



FIG. 7.10. Axial and transverse growth strains for unstressed tubular capsules Zr-2.5%Nb irradiated in OSIRIS at nominal temperatures of 553 K (280°C) (left) and 583 K (310°C) (right) (this image was published in Ref. [7.11], copyright Elsevier, 2003).

7.2.6.7. Density

Measurements of density change (or accurate and equivalent dimensional measurements in three orthogonal directions) are required to verify that irradiation growth is purely a shape change at constant volume. Such measurements, although infrequent, have generally confirmed that long term irradiation growth, in the absence of a stress, is a volume conserved process [7.44], including the growth of Zr-2.5Nb [7.38]. This conclusion is not always true at low fluences for transient irradiation growth strains [7.38]. Density measurements [7.49] have confirmed that some growth is accompanied by a small increase in volume due to a net aggregation of interstitials at distributed sinks. The interstitials will have originated either from very small voids or uncollapsed dislocation loops. The voids are speculated to be depleted zones from the primary irradiation damage event, as zirconium does not swell due to macrovoid formation as cubic metals do when irradiated with fast neutrons.

7.2.6.8. Thermal recovery of growth strain by annealing

Irradiation induced growth in recrystallized zirconium and Zircaloy in the prebreakaway growth region below about $4 \times 10^{25} \text{ n} \cdot \text{m}^{-2}$ (E > 1 MeV) or $\approx 10 \text{ dpa}$, can be completely recovered by a post-irradiation thermal anneal at a temperature in excess of 773 K (500°C) [7.24].

This recovery takes place because the defect structure producing the observed growth strains arises entirely from atomic displacement damage, which can be eliminated by recombination following a suitable thermal anneal. The measured activation energy for growth recovery of around 1.65 eV is similar to that of vacancy self-diffusion in Zircaloy, which suggests that this process is dominated by vacancy migration [7.24]. The situation is quite different for CWSR materials, where only a small fraction of the growth is recoverable [7.24, 7.50]. The contribution to growth from the network dislocations is not recoverable.

As the CW increases, the fraction of recoverable growth strain decreases (Fig. 7.11).



FIG. 7.11. Fractional recovery of irradiation growth as a function of prior (reprinted with permission from Ref. [7.24], copyright ASTM International, 1977).

7.2.7. Irradiation variables

7.2.7.1. Neutron flux and fluence

Murgatroyd and Rogerson [7.45] have compared the growth of 25% CWSR Zircaloy-2 irradiated at 300 K (27°C) in two different test reactors (the Advanced Test Reactor, Idaho Falls, United States of America, and DIDO, Harwell, United Kingdom) where the fast neutron flux differed by a factor of around 6. For the same total accumulated fluence, similar growth strains were measured in both experiments, indicating that there is little if any effect of flux on growth, at least at this low temperature. Beyond the initial transient, the irradiation induced growth strain of a given material is determined by the temperature of irradiation and the fluence but is independent of the time to achieve that fluence. The growth rate due to fast neutron damage, $\dot{\varepsilon}_g$, is linearly proportional to the displacement damage rate, *K*, so that n = 1 in the expression:

$$\dot{\varepsilon}_{g} \propto K^{n}$$
 (7.2)

Equation (7.2) is valid for temperatures above 300 K (27°C) [7.18] and for displacement rates $\geq 10^{-3}$ dpa·s⁻¹ [7.51].

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7.2.7.2. Accelerated particle irradiation

All energetic particles capable of causing atomic displacements in the zirconium lattice can, in principle, generate growth strain in a suitably arranged test. Chow et al. [7.18] used proton irradiation in an experiment to investigate the dependence of the growth rate of nominally pure zirconium on the atomic displacement rate.

The 4 MeV proton beam was sufficiently energetic to pass through the 50 µm thick specimen, which was maintained at a temperature of 347 ± 1 K ($74 \pm 1^{\circ}$ C). The dose in the specimen was estimated from the power generated by the beam and the displacement damage was calculated using the Norgett–Robinson–Torrens model [7.52], assuming an atomic displacement energy for Zr of 25 eV. The controlled displacement rates were in the range (1.4-6.9) × 10^{-7} dpa/s. Observations showed that the specimens ceased to grow if the proton beam was interrupted. The exponent in Eq. (7.2) was close to 1.0, showing that the deformation was independent of damage rate. Parsons and Hoelke [7.53] have employed ion irradiated cantilever beams to investigate the growth and creep of zirconium alloys and Zr⁺ ions have been used to study the influence of alloying elements on the creation of dislocation loops in α -zirconium [7.54].

7.2.7.3. Temperature

Growth rates in most zirconium alloys increase with the temperature of irradiation in an approximately linear manner, from low temperatures (\approx 350 K (77°C)) up to about 550–600 K (277–327°C). Expressing the growth rate, $\dot{\epsilon}_{g}$, as:

$$\dot{\varepsilon}_{g} = A \exp(-Q \cdot R^{-1} \cdot T^{-1}) \tag{7.3}$$

the temperature coefficient of growth, Q, is weak and $\approx 3 \text{ kJ} \cdot \text{mol}^{-1}$ up to 550 K (277°C). This result applies to both recrystallized and CWSR material states. Measurements on RXA Zircaloy (Fig. 7.12) at low fluences showed that growth initially increases with a temperature between 370 and 550 K (97 and 277°C) but then decreases rapidly at higher temperatures as vacancies start to become mobile [7.24]. However, Fidleris et al. [7.35] refer to measurements at high fluences showing that the growth rates of both RXA and with increasing irradiation temperature above CWSR Zircaloy increase rapidly 630 K (357°C), with an activation energy $Q \approx 150 \text{ kJ} \cdot \text{mol}^{-1}$. The change in the behaviour of RXA material coincides with the onset of accelerated or breakaway growth (see Section 7.2.5.1). This overall representation of temperature dependent growth is summarized in the form of an Arrhenius plot in Fig. 7.13. The data on polycrystalline zirconium are sparser but appear to exhibit a similar trend to those for Zircaloy, although the rapid rise in growth rate does not occur until around 680 K (407°C). Some of this rapid increase may be due to a form of swelling (i.e. an increase in volume due to microvoid formation that has been observed experimentally in zirconium and zirconium alloys) [7.55, 7.56].

There is no strong evidence that the temperature dependence of the growth rate remains positive with increasing temperature. For instance, Gilbon et al. [7.57] consistently measure larger growth at 553 K (280°C) than at 623 K (350°C) in all metallurgical states of Zircaloy. Measurements on Zr-2.5Nb also show a strong negative temperature dependence for growth, with an effective activation energy in the range $-22 \text{ kJ} \cdot \text{mol}^{-1}$ to $-25 \text{ kJ} \cdot \text{mol}^{-1}$ [7.58, 7.59].



FIG. 7.12. Irradiation growth of annealed Zircaloy as a function of temperature (reprinted, with permission, from Ref. [7.24], copyright ASTM International, 1977).



FIG. 7.13. Generalized representation of the temperature dependence of irradiation growth of Zircaloy material (reprinted with permission from Ref. [7.42], copyright Elsevier, 1988).

An irradiation growth process still operates at temperatures as low as about 78 K (-195°C) [7.12, 7.17]. This result has been verified following irradiation in a specially designed liquid nitrogen cryostat employed in the HERALD research reactor at Aldermaston, UK. Fully annealed and recrystallized Zircaloy-2 specimens were irradiated to a low fast fluence of $9.7 \times 10^{22} \text{ n} \cdot \text{m}^{-2}$ (E > 1 MeV, equivalent to about 0.02 dpa); the resulting growth strain, $\dot{\varepsilon}_{g}$, was 0.015%. The calculated growth rate, $\dot{\varepsilon}_{g}/\text{dpa} = 7 \times 10^{-3}$, is similar to that observed at 313 K (40°C), suggesting that an athermal growth process exists at these low temperatures. The fluences and the strains are small, so that it is likely that the observed growth in these experiments is transient and not steady state.

7.2.8. Other alloys of Zr

7.2.8.1. E110 and E635

E110 is a Russian Federation Zr-1Nb binary alloy and its microstructure is characterized by α phase grains containing a fine distribution of globular shaped precipitates of β -Nb with a diameter ≈ 50 nm. The majority of the α phase grains are recrystallized and their size is 4–5 µm. The initial dislocation density is low, representative of recrystallized material. At an irradiation temperature of around 623 K (350°C), the growth rate is low up to a fluence of 2 × 10²⁶ n·m⁻² (E > 0.1 MeV). At higher fluences, the growth accelerates rapidly (Fig. 7.14) due to the early formation in this alloy of $\langle c \rangle$ component (vacancy) dislocation loops [7.60].



FIG. 7.14. Comparison of E635 and E110 irradiation growth strain (%) as a function of fluence [7.61].

E635 is a Russian Federation quaternary Zr-1Nb-1.2Sn-0.4Fe alloy that also has a low irradiation growth rate but no tendency to break away. The unirradiated microstructure of E635 is characterized by incomplete recrystallization. The majority (\approx 90%) of the α phase grains are recrystallized with a mean size of 4–5 μ m with sharply defined, equiaxed grain

boundaries. These grains contain finely dispersed, rounded inclusions of mainly $Zr(Nb, Fe)_2$ Laves type SPPs in the size range 100–120 nm. During irradiation there is only a very slow formation of $\langle c \rangle$ component dislocation loops, which is an important difference from E110 [7.60]. Even at the highest neutron displacement dose of 39 dpa, the <u>c</u> loop concentration in E635 remains low compared with that of E110 and also with the general dislocation density of predominantly $\langle a \rangle$ component loops. This disparity in the nucleation of $\langle c \rangle$ component dislocations probably accounts for the significant difference in growth behaviour between the two Russian Federation alloys, as shown in Fig. 7.14.

The growth measurements in Fig. 7.14 are valid for the typical range of Fe concentrations in E635 of 0.35–0.40 wt% (\approx 0.57–0.65 at.%). However, Fe has a strong influence on the delayed incubation of $\langle c \rangle$ component loops. If the iron in E635 is reduced to a concentration of about 0.15 wt% (\approx 0.24 at.%) the alloy behaves in a very similar manner to E110, and the growth rate increases at low fluences. Conversely, if the iron concentration is higher than normal (\approx 0.6 wt% or 0.98 at.%) then no breakaway acceleration is observed. This behaviour is shown in Fig. 7.15 and is in sharp contrast to the effect of impurities on $\langle c \rangle$ component loop formation in Zircaloy described in Section 7.2.5.1.



FIG. 7.15. Influence of iron concentration on irradiation growth of E635. The Zr-1Nb curve represents E110 behaviour (reprinted with permission from Ref. [7.37], copyright ASTM International, 2002).

7.2.8.2. M5

M5 is a binary Zr-1Nb alloy developed in France primarily as a fuel cladding material for pressurized water reactors (PWRs) that require a high resistance to corrosion. It is also employed as a structural material in some PWR fuel assemblies, specifically spacer grids and guide tubes, due to its low overall irradiation growth behaviour. M5 is used in the fully annealed condition and therefore exhibits a saturating growth trend with increasing fast fluence shown in the fuel rod elongation data in Fig. 7.16. This behaviour contrasts with the linear growth with fast fluence for CWSR Zircaloy. The nominal irradiation temperature for the plotted data is that of commercial PWR cladding (i.e. about $623 \pm 20 \text{ K}$ ($350 \pm 20^{\circ}$ C)) [7.62].



FIG. 7.16. Growth of M5 alloy in the annealed state for different PWR fuel designs. The linear growth trend of CWSR Zircaloy-4 is also indicated [7.62].

The presence of Nb as an alloying addition to M5 suppresses growth in common with other Zr-Nb alloys [7.57]. The evolving microstructure of M5 during irradiation consists of a high density of small $\langle a \rangle$ direction dislocation loops and an almost complete absence of $\langle c \rangle$ component loops [7.63]. The reason has been conjectured to be because the Fe concentration ($\langle 500 \text{ ppm} \rangle$) in M5 is too low to stabilize a significant density of *c* type loops [7.57, 7.63]. As a result, no acceleration in the growth rate is observed up to current maximum fluences of around $1.3 \times 10^{26} \text{ n} \cdot \text{m}^{-2}$ (E > 1 MeV) or $\cong 26 \text{ dpa}$. It should be noted that the explanation for the absence of breakaway growth based on Fe concentration appears to be inconsistent with the observations on E635 alloy described in Section 7.2.8.1. The influence of S on breakaway growth behaviour is not known.

7.2.8.3. Zr-2.5Nb

Growth data on Zr-2.5Nb are derived almost entirely from CANDU pressure tube materials [7.11, 7.47]. A combination of metallurgy, manufacturing process and operational requirements produces a material that is significantly different from most other zirconium alloys used in the nuclear industry. The final condition of the tubing is about 27% CWSR containing thin, platelet-like α -zirconium grains resulting from the extrusion process. The latter also introduces a high density of mixed $\langle a \rangle$ and $\langle c \rangle$ component dislocations into the α -zirconium grains. These grains are mostly oriented with (0001) basal poles parallel with

the tube surface (i.e. in the tangential direction), although there is a spread of orientations within the radial-tangential plane. The basal pole texture of pressure tubing differs from fuel cladding mainly because of the need to maintain high creep strength in the TD in the former. Fleck et al. [7.64] have provided a detailed description of the effects of temperature and neutron fluence on the growth behaviour of Zr-2.5Nb pressure tube materials and Holt [7.65] has reviewed in-reactor deformation of CW Zr-2.5Nb pressure tubes, including irradiation growth.

7.2.8.4. ZIRLO

ZIRLO is a quaternary alloy of the type Zr-1Nb-1Sn-0.1Fe developed in the USA primarily as a fuel cladding material. It is used in the CWSR state. The specification for low-tin ZIRLO cladding has a tin concentration of 0.7 wt% (\cong 0.54 at.%) and it is used in the partially recrystallized condition. ZIRLO is also used in the RXA condition for some structural components of the fuel assembly (e.g. guide thimbles) because of its low irradiation growth rate. Measurements of fuel assembly elongation, driven mainly by the irradiation growth of the ZIRLO thimble tubes, are shown in Fig. 7.17 as a function of fast neutron fluence [7.66]. The total elongation is a combination of stress free growth, axial creep and hydrogen related effects. Comparison with the CWSR Zircaloy-4 data shows that the Nb in ZIRLO has the effect of reducing the assembly elongation by around 50%. Also, unlike for Zircaloy-4, there is no evidence of an increase in growth rate at high fluences.



FIG. 7.17. Elongation of ZIRLO clad fuel assemblies compared with CWSR Zircaloy-4 assemblies (reprinted with permission from Ref. [7.66], copyright ASTM International, 2002).

7.2.8.5. Excel

Excel is a potential pressure tube material for CANDU reactors. The alloy has the composition Zr-1Nb-3.5Sn-1Mo-0.1O-0.1Fe [7.67]. Excel is an ($\alpha + \beta$) alloy like Zr-2.5Nb, in which the grain structure is much finer (submicron grain dimensions) and much more anisotropic than Zr-2.5Nb [7.9]. Excel has nominally similar chemistry to ZIRLO but is

distinct in being very susceptible to accelerated growth. The high Sn concentration in Excel causes the Nb and Mo to segregate to the β phase. In ZIRLO the Sn and Nb coexist in solid solution, which may explain why ZIRLO is resistant to $\langle c \rangle$ loop formation whereas Excel is not [7.28].

7.2.9. Mechanisms for high temperature irradiation growth

Numerous qualitative and quantitative models have been proposed to explain irradiation growth in zirconium alloys. Holt provides a good historical summary of the various individual mechanisms elucidated up to 1988 [7.22] and Woo [7.9] provides a later update. Some mechanistic approaches that have led to the present generally agreed model of high temperature (T > 470 K (197°C)) growth are outlined below. The model is based on the anisotropic difference in diffusion of PDs to biased sinks. At and above this temperature, vacancies are considered to be mobile. Low temperature growth (80 < T < 470 K ($-93 < T < 197^{\circ}$ C)) is discussed in Section 7.2.11.2 and requires a different approach, according to Woo [7.9].

7.2.9.1. Texture and atomic size effects

The model proposed by Buckley [7.1] simply relates texture and growth strain:

$$\varepsilon_{\rm n} \propto 1 - 3f_{\rm n}$$
 (7.4)

where ε_n is the growth strain and f_n is the texture parameter in the direction n.

Equation (7.4) assumes a constant volume process and only strictly applies when single crystal growth can be described by the growth tensor [7.1], i.e. when sinks for PDs are dominated by a and c type dislocations. Although Eq. (7.4) provides a useful approximation for anisotropic, transient growth in annealed materials up to stage 2 (see Fig. 7.2), it cannot explain breakaway growth, steady state growth in CWSR Zircaloy or the growth in alloys such as Zr-2.5Nb [7.22].

To describe growth in all cases there is a need to include biased PD sinks such as dislocations and grain boundaries. Grain boundaries add another element of anisotropy and these sinks are not as closely linked to the crystal structure as dislocations are. Early models introduced the concept of biased sinks, in which PDs created by atomic displacement are segregated by a 'size effect' arising from the first order elastic interaction between the strain fields of the PD and a sink. This requirement originated from the rate theory modelling of irradiation induced void swelling in cubic metals. When applied to HCP zirconium, rate theory allows for the preferential attraction of a net flux of self-interstitials (i.e. zirconium atoms) to network dislocations with $<11\overline{2}0>$ Burgers vectors, leaving a net flux of vacancies to go to grain boundaries.

7.2.9.2. Dislocation and grain-grain interaction effects

Willard [7.68] introduced the idea that dislocation loops, nucleated from irradiation damage, can have a higher bias for self-interstitials than network dislocations. The resulting segregation in which loops attract a net interstitial flux and network dislocations a net vacancy flux leads to a growth strain caused by the glide of dislocations under the action of internal stresses produced by the growing loops.

Willard's model predicted reasonably well the observed temperature dependence of growth above 540 K (267°C) and the low sensitivity of long term growth rate to grain size.

The effect on the macroscopic growth strain of intergranular constraints due to differential growth strains between adjacent crystals of different orientation was recognized as a potentially important modification to growth anisotropy by several investigators [7.69]. Incorporation of this effect into a growth model required knowledge of the creep behaviour of zirconium single crystals [7.41] and formed the basis of the yielding creep model for polycrystalline zirconium alloys. Tomé et al. [7.2] have included intergranular stresses into a model of irradiation growth. These investigators, together with Woo [7.41, 7.70], also demonstrated that transient growth strains that are frequently observed in polycrystalline zirconium alloys [7.40] are mainly due to irradiation creep occurring in the individual grains (single crystals) as a result of the intergranular stresses that develop during the fabrication process.

Intergranular stresses are present even in recrystallized materials and are due to the large difference in the thermal expansion coefficients in the $\langle a \rangle$ and $\langle c \rangle$ directions of the single crystal [7.2]. The transient growth measured in polycrystalline samples is due to the creep of individual crystals under the action of internal stresses. During this transient period the stresses change from one state to a different one, but never disappear or relax to zero. Once they reach an equilibrium state in their evolution the apparent growth rate attains its steady state value, which is a function of the single crystal irradiation creep and growth processes [7.2, 7.41].

7.2.9.3. Anisotropic point defect migration and vacancy loop nucleation

The concept that led to an acceptable growth model is that the intrinsic diffusion properties of PDs are anisotropic [7.71]. Woo and Gösele [7.10] showed that differences in the anisotropy of migration between vacancies and interstitials can have a large effect on the biases of network dislocations and loops. This anisotropy promotes the partitioning of PDs among dislocations with different line directions. This concept is allied to the recognition, based on transmission electron microscopy observations, that high growth rates are associated with the presence of <c> component network dislocations and vacancy dislocation and vacancy dislocation anisotropy also has a strong effect on growth behaviour.

Holt [7.22, 7.40] has offered an explanation for the nucleation of vacancy loops, based on the generation of internal stresses in a polycrystalline material of varying grain size. In this model a compressive stress along the c axis is necessary, although continuous contraction in this direction should result in a tensile stress favouring interstitial loop formation. However, an isolated larger grain, by virtue of its remote grain boundaries, will grow at a lower rate than its surrounding matrix neighbours. The resulting growth differential produces a c axis compressive stress that encourages the nucleation of vacancy loops onto the basal planes. This loop nucleation results in a sudden acceleration of growth of the large grain such that the next largest grain then goes into compression. This sequential process proceeds through an incubation phase until the total grain assemblage experiences breakaway growth.

Whenever the anisotropy of self-interstitial diffusion differs from that of vacancy migration, then dislocation and loop segments with their line directions close to the $\langle c \rangle$ axis will exhibit a bias for one or the other type of PD, relative to segments parallel to the $\langle a \rangle$ axis. If there is a relationship between the line direction and the Burgers vector, growth will

occur [7.22]. Woo [7.9, 7.48] developed these ideas into a mathematical growth model using rate theory and introduced the term DAD as the source of bias for the various sinks.

7.2.9.4. Temperature dependent growth at high temperatures

The DAD theory alone does not predict the strong temperature dependence of growth at very high temperatures (T > 673 K (400°C)). Holt et al. [7.8] and Woo et al. [7.72, 7.73] recognized that some of the PDs formed in the displacement cascade remain in place as immobile 'primary clusters' but could still interact with sinks if these are themselves mobile. The model invokes a 'production bias' [7.8] to take into account irradiation damage within the immediate region of the cascade, as well as an asymmetry in the effective production of the PD clusters, which is different for interstitials than for vacancies. A key feature of the model — and the origin of the bias for growth — is the higher reaction cross-section of the primary clusters with the unfaulted *a* dislocations than with the <c> component dislocations. This larger cross-section is due to the higher mobility, by climb and glide, of the *a* dislocations (both loops and network dislocations), giving them an effective 'diffusivity'. Sessile primary defect clusters now become accessible to unfaulted *a* dislocations acting as mobile sinks.

The model explains the temperature dependence of growth by associating it with the evaporation of the vacancy clusters. At low temperatures, evaporation of clusters is insignificant, but above a critical temperature for zirconium (corresponding to the 'stage V' annealing of PDs, where vacancies are mobile) the vacancy clusters 'evaporate' and release free vacancies. Interstitial clusters remain sessile.

7.2.10. Mechanism for low temperature growth

A model has been proposed [7.74] that successfully predicts low temperature growth observations around 330–350 K (57–77°C) [7.7, 7.18]. The suggested mechanism is based on the direct deposition of vacancies in cascades close to sinks (dislocations and grain boundaries) and on the anisotropic diffusion to oriented sinks of self-interstitials created in the cascades. Interstitial diffusion at low temperatures, where vacancies are assumed to be immobile, is calculated to be about 20 times faster in the basal plane of zirconium than in the orthogonal $\langle c \rangle$ direction [7.9, 7.75]. An additional contribution to growth may arise from the anisotropic shape of the cascades in zirconium [7.74], which are longer in the directions normal to [0001] than when parallel to [0001]. A modification of these ideas involving just athermal, anisotropic cascades, with no diffusion, may apply at even lower temperatures down to 77 K (–196°C), where growth strains induced by irradiation have also been measured [7.17]. However, the model appears to be inconsistent with experimental observations showing that the $\langle c \rangle$ component dislocation structure evolves in a similar manner at 330 K (57°C) and at 570 K (297°C) [7.25].

7.2.11. Numerical models

Numerical models for the prediction of steady state irradiation growth fall into two broad groups: phenomenological or semimechanistic. In the phenomenological approach, constants are fitted to equations to be used by reactor designers; the in-reactor deformation is not correlated with variables such as microstructure, crystallographic texture, dislocation density, grain size or chemical composition. Alternatively, numerical models can have a mechanistic basis by drawing on physical processes suggested by a combination of theory and experimental observation. They will employ suitable constants for these processes to achieve as close an agreement as possible with measurement. Phenomenological models have been reviewed by Fidleris [7.13]. They typically deal with the effects of macroscopic variables such as stress, temperature, neutron flux and time on the accumulated growth strain.

7.2.11.1. Holt model

Holt [7.22] proposed a numerical model for long term irradiation growth that was intended as a framework for assessing various concepts and driving forces controlling growth. For instance, the size effect and DAD are considered viable driving forces and are incorporated into the physical model. The model is based on the earlier work of Wiedersich [7.76], who used chemical rate theory to demonstrate the sensitivity of the irradiation growth rate to the prevailing microstructure, assuming a first order size effect interaction between PDs and extended sinks (dislocations and grain boundaries). In this approach the strength of the interaction is linearly proportional to the misfit elastic strain of the PD in the crystal lattice. Holt assumed that anisotropic migration is only exhibited by the self-interstitial atoms and that they migrate more rapidly in the basal plane than normal to it. This assumption produces the correct growth anisotropy.

Taking account of different types and orientations of dislocation populations, the basic model yielded an approximation for instantaneous growth rates in three orthogonal directions for a given microstructure. By normalizing the calculated growth rates to measurement data on CWSR Zircaloy-2 pressure tubes [7.45, 7.77] it was possible to adjust the model parameters to fit experimentally observed values for network dislocations, grain size, texture, dislocation loop density and diameter. Precise details are given in Ref. [7.22]. It was recognized at the time that a fully mechanistic model could not be constructed because of uncertainties in the underlying physical parameters, particularly the diffusion properties of PDs in zirconium alloys. Within the framework of the model a number of deductions can be made:

- The linear fluence dependence of the growth rate of CWSR Zircaloy-2 at 330–350 K (57–77°C) implies that 'fast' vacancy migration is occurring.
- 'Normal' $(1-3f_n)$ growth can occur in CW microstructures containing (c + a) and a type network dislocations by partitioning vacancies to (c + a) dislocations and self-interstitial atoms to a dislocations.
- Accelerated ('breakaway') growth of annealed Zircaloy at high fluences is due to the appearance of basal plane dislocation loops that act as strong vacancy sinks.
- The negative growth observed in Zr-2.5Nb at 550 K (277°C) is due to the presence of thin elongated grains, which provide a strong sink for self-interstitial atoms. The model correctly predicts a regime in which the growth is negative in both the axial ($f_a = 0.03$) and transverse ($f_t = 0.56$) directions.

7.2.11.2. Woo model

Woo [7.9] concluded that the mechanisms involved in the irradiation growth of zirconium and its alloys are more complicated than those that can be described within conventional rate theory [7.10, 7.48]. For example, the temperature dependence is complex, and, in addition, there is a large variability in growth behaviour between differently conditioned materials. To understand and to model irradiation growth properly, Woo suggests that certain physical characteristics of the materials, as well as a correct description

of the nature of cascade damage, must be considered. The sensitivity of growth to the details of the pre-irradiation thermomechanical treatment (i.e. CW, CWSR or RXA) indicates that a large variety of sinks has to be included in a predictive, mechanistic model.

Woo's model, based on the reaction rate theory of anisotropically diffusing PDs created by irradiation, predicts that the DAD effect can produce a large bias for the migration of vacancies and interstitials to sinks. Because this bias is so strong, it completely dominates the conventional first order dislocation bias caused by the elastic interaction size effect. It follows that edge dislocations in zirconium have a bias that depends on their line direction, which can favour either interstitials or vacancies. (This view is contrary to conventional rate theory as applied to cubic metals, assuming isotropic diffusion.) Grain boundaries and surfaces also become biased sinks with a bias towards either interstitials or vacancies depending upon their orientations. As Woo remarks [7.9], this large variety of biases adds a new dimension to the complexity of modelling deformation behaviour occurring during the irradiation of HCP metals.

The model invokes the concept of a 'production bias' [7.8] to account for the creation and evolution of primary PD clusters, as well as the recombination that occurs, in and close to the cascades during irradiation damage. In the production bias theory, the individual vacancies and interstitials produced in the cascades are assumed to be mobile and to diffuse to sinks or to recombine, just as in standard rate theory descriptions of irradiation damage. By contrast, the clusters of PDs formed in the cascades are assumed to be immobile. Within this picture, the evolution of the microstructure can be affected by possible asymmetries in the effective production of PDs (hence the name 'production bias'), which biases their accumulation at the sinks. This bias permits a reaction between mobile dislocations and immobile vacancies to describe low temperature growth. The possibility of a fast diffusing iron-vacancy pair process [7.78, 7.79] is included in the model, which may account for the large increase in growth rate observed at temperatures above 673 K (400°C).

Woo [7.9] shows how the effective rate of production of individual mobile vacancies increases rapidly in the high temperature regime due to the dissolution of the vacancy clusters originally formed within the cascade. These free vacancies facilitate the nucleation of vacancy loops with a $\langle c \rangle$ Burgers vector and cause the high growth rate. Iron is initially present in Zircaloy mainly in the form of intermetallic precipitates that dissolve under irradiation, releasing soluble iron into the zirconium lattice. The effect of iron in solution is to lower the effective self-diffusion energy of zirconium, resulting in an increase in the solubility of the intracascade vacancy clusters. This effective increase in vacancy diffusivity enhances the production bias effect and thus the high temperature growth. Quantitative data on diffusional anisotropy required for the model were obtained from measurements of loop growth due to high energy electron bombardment in a high voltage transmission electron microscope [7.29]. Simulations, using molecular dynamics, of interstitial diffusion in zirconium [7.80], yield configurations and diffusivities with anisotropies in agreement with the high voltage transmission electron microscope loop growth results. Since the growth of each grain in a polycrystalline material is constrained by the collective deformation of neighbouring grains, their anisotropic deformation generates internal stresses. To maintain material integrity, the stress is relieved by intergranular creep. The requirement for grain-to-grain compatibility during macroscopic growth is satisfied using the self-consistent model, previously elaborated by Woo for this purpose [7.41, 7.70].

The predictions of Woo's growth model appear to agree well with experimental observation of CWSR Zircaloy-2. Figure 7.8 shows a comparison of calculated and measured values of growth rate for various initial dislocation densities created by different material

production methods. Temperature dependent growth is understood by considering three regimes: low temperature growth, controlled by recombination where vacancies are immobile; medium temperature growth, driven by DAD in which both interstitials and vacancies are mobile; and high temperature growth, driven by the production bias mechanism.

7.2.11.3. Summary

Irradiation growth measurements on zirconium and its alloys have been performed mainly in the following temperature ranges: (a) low, $323-353 \text{ K} (50-80^{\circ}\text{C})$; (b) intermediate, $553-673 \text{ K} (280-400^{\circ}\text{C})$; and (c) high, $673-723 \text{ K} (400-450^{\circ}\text{C})$. There have also been a small number of growth measurements at a very low temperature of around 77 K (-196^{\circ}\text{C}). In addition to temperature, irradiation growth is also sensitive to the initial metallurgical state of the material (grain size and shape, CW, thermomechanical treatment, texture and chemical composition) and to the microstructure developed during irradiation. In general, growth is characterized by an initial transient strain that, at higher neutron fluences, usually assumes a steady state with a constant growth rate.

Irradiation growth is the volume conserved shape change deformation that occurs under irradiation in the absence of an applied stress. The dimensional changes are caused by the segregation of vacancies and interstitials among two or more kinds of sinks, one of which must be biased to receive a net flux of one species of PD over the other. Each kind of sink produces a strain in a different crystallographic direction, such that the final deformation is anisotropic. In the case of a dislocation line or loop sink, the strain is a contraction for vacancies and dilation for self-interstitials (i.e. displaced Zr atoms) in the direction of the Burgers vector. For grain boundary sinks, the contraction or dilation strain is in the direction of the boundary normal. To produce a net growth strain in a polycrystalline sample the orientation distribution of the sinks must be different. In zirconium and its alloys, this arises from the texture and from the grain size and shape introduced during fabrication.

Since the discovery of irradiation growth in zirconium and its alloys, several mechanisms have been proposed to explain its operation. As more experimental results have accumulated it has been realised that the growth behaviour under irradiation is very complex, with many anomalous features. Among these observations are the production of large vacancy loops, the correlation of growth acceleration with the multiplication of *c* component dislocations, the anomalous anisotropy of the growth rate in very fine grain material and the large increase in growth rates in the high temperature region above 673 K (400°C).

The mechanisms involved with this behaviour are more complicated than those that can be understood within conventional rate theory models. The variability of irradiation growth measurements and their functional dependence on details of the pre-irradiation alloy condition also indicate that a large variety of sinks must be considered in a growth model. A comprehensive model, which provides an overall prediction of the experimental observations, includes:

- The effects of the anisotropic diffusion of PDs, where the DAD between vacancies and interstitials that occurs in the HCP Zr structure produces a large bias in their reaction rates with sinks. The result is to segregate PDs among sinks of different orientation, generating a macroscopic growth strain in a direction determined by texture and (in material with very small grain size) by grain shape.
- A mechanistic description of cascade damage, intracascade recombination and clustering.

Within these points there is a commonly accepted recognition that the complex temperature dependence of growth can be understood by assuming that low temperature growth rate is controlled by interstitial vacancy recombination, intermediate temperature growth is driven by DAD and high temperature growth is driven by the intracascade production of PD clusters.

7.3. THERMAL CREEP

7.3.1. Definition and background

Creep is the time dependent deformation of a material under the influence of a stress. The stress is most often externally applied, with tensile or compressive stresses both producing creep strain. Stresses may also be generated internally (e.g. from temperature gradients or growth) and these stresses are relieved or relaxed by the process of creep. Many metallurgical and environmental factors affect the rate of deformation, or creep rate, in zirconium alloys, including irradiation. The latter is discussed below. The term thermal creep denotes the creep behaviour in the absence of simultaneous irradiation. The thermal creep rate component in equations describing in-reactor deformation is not the same and is lower than the thermal creep rate of unirradiated material. As its name implies, thermal creep is strongly temperature dependent. Thermal creep is important for reactor components at the normal operating temperatures of zirconium alloys, but it is not the major cause of deformation. At the higher temperatures encountered in a loss-of-coolant accident, thermal creep is the main cause of significant deformation. Thermal creep of previously irradiated material is discussed in Section 7.3.7.) because of its importance for the dry storage of nuclear fuel.

7.3.2. Experimental techniques

Since the early days of the commercial nuclear industry and the use of zirconium alloys in fuel assemblies, there has been an interest in acquiring thermal creep data over a wide temperature range from normal operating conditions in the α phase (553–663 K (280–390°C)) up to high temperature accident conditions in the β phase (>1230 K (957°C)). There has also been considerable scientific interest in understanding thermal creep mechanisms covering a wide range of applied stress and temperature, and this interest has generated many experimental programmes since the 1960s. Usually the techniques employed have been either uniaxial tensile testing using standard creep machines with dead weight loading or internal pressurization of tubular specimens to measure diametral creep. Nam et al. [7.81] describe a typical example of the latter method for determining the creep strength of Zircaloy-4 fuel cladding as a function of applied stress and temperature over the stress and temperature ranges 90–195 MPa and 613–673 K (340–400°C), respectively. The hoop stress is applied via an argon gas line connected to the specimen using Swagelok-type fittings. The tensile hoop stress in the tube wall, σ_{θ} , is determined by the standard approximation for thin-walled tubes expressed as:

$$\sigma_{\theta} = 0.5 P_{\rm i} D_{\rm m} / W \tag{7.5}$$

where

P_{i}	is the internal pressure;
$D_{\rm m}$	is the mid-wall diameter;

and W is the wall thickness.

The creep specimen is located in a 3 zone furnace where the test temperature is controlled to 1-3 K. Variations in pressure are generally negligible. Diametral creep strain is measured periodically by standard digital micrometer or linear variable differential transformer methods at several axial locations. To preserve the dislocation microstructure for subsequent electron microscopy, the crept specimens are cooled rapidly in the pressurized state. To relate the creep behaviour to the specimen crystallography it is common practice to determine the basal pole texture by X ray diffraction in the circumferential-axial (θ -z) plane.

7.3.3. Creep characteristics

The general form of the thermal creep strain as a function of time at a given applied stress consists of three characteristic stages [7.82]: primary (I), secondary (II) and tertiary (III) creep (Fig. 7.18). The initial deformation rate in primary creep (I) is high, but this rate decreases to settle at a near constant value at the end of this stage as the dislocation microstructure evolves and the resistance to deformation increases as the material strain hardens.

Secondary, or steady state creep (II) is generally a long term deformation stage, for intermediate temperatures (453 < T < 773 K ($180-500^{\circ}$ C)) and stresses (20-100 MPa), where the creep rate is approximately constant, and the microstructure is in a state of dynamic equilibrium because concurrent thermal recovery and strain hardening processes are roughly balanced.

The state of balance is primarily a function of the applied stress and the temperature [7.83]. The third stage of tertiary creep (III) is where the deformation rate accelerates, due to an increasing stress as the material cross-section reduces, until the component fails by necking and rupture.



FIG. 7.18. Basic thermal creep curve above the elastic displacement limit (ε_e) (reprinted with permission from Ref. [7.82], copyright ASTM International, 1983).

The thermal creep process in Zircaloy involves slip on favoured crystallographic planes. However, unlike cubic metals, zirconium alloys have anisotropic yield properties. Some experimental evidence indicates that thermal creep is almost isotropic in zirconium alloys, especially in the preirradiated state [7.84], but there is not universal agreement on this conclusion. There are empirical data to show that tensile and compressive creep strengths are different in Zircaloy — creep rates being faster under tension than compression [7.85] — in line with, although not necessarily in proportion to, the yield strength differential [7.82] (see Section 7.3.5.4). However, this issue is also controversial. Foster and Abram [7.86] have argued that the steady state creep rate at equivalent values of stress (i.e. at the same values of applied stress normalized with the yield stress) should be insensitive to the direction of applied stress. These considerations present a more complex picture of thermal creep in zirconium alloys than in cubic metals.

7.3.4. Temperature and stress dependence

If the same material is tested under different load and temperature conditions, the sets of curves shown schematically in Fig. 7.19 are obtained [7.82]. The creep strain and the creep rate of zirconium alloys increase with increasing temperature and applied stress, as shown in Fig. 7.20, for both the RXA and CWSR states of the material [7.87, 7.88]. Experimentally, three temperature regimes are of interest [7.13]; these creep curves are shown schematically in Fig. 7.21. These curves are related to the melting temperature, *T*_M, of zirconium.



FIG. 7.19. Schematic diagram showing variation of thermal creep (a) with stress at constant temperature and (b) with temperature at constant stress (reprinted with permission from Ref. [7.82], copyright ASTM International, 1983).



FIG. 7.20. Thermal creep kinetics of RXA Zircaloy-4 (reprinted with permission from Ref. [7.88], copyright ASTM International, 2002).



FIG. 7.21. Thermal creep curve trends for Zr alloys in the low, intermediate and high temperature regimes (reprinted with permission from Ref. [7.82], copyright ASTM International, 1983).

7.3.4.1. Temperature

At T < 453 K (180°C), about 0.21 $T_{\rm M}$, logarithmic creep behaviour is observed where very little thermal recovery occurs to offset strain hardening and, as a consequence, the material does not achieve a steady state creep rate. Zirconium and Zircaloy creep specimens can exhibit strains up to 0.45% after 300–500 hours at a stress of 138 MPa but the creep rate declines throughout. By contrast, cubic metals only achieve a strain of about 0.1% in this temperature regime at stresses less than their yield stress [7.89].

At 453 < T < 773 K (180–500°C), between about 0.21 and 0.36 T_M , zirconium alloys have larger primary creep strains than at lower temperatures, but the thermal recovery of the microstructure is generally still not sufficient to overcome strain hardening. As a result, a true steady state creep regime is often not established, but after a minimum creep rate is reached (at a creep strain of about 1–2%) the material then enters a tertiary creep stage [7.13].

At 773 < T < 873 K (500–600°C), between (0.36–0.41). T_M , zirconium alloys undergo both recovery and recrystallization during creep and as a result the material achieves a constant secondary creep rate over quite a large strain range following a short period of primary creep. This temperature range is above the normal reactor operating range for zirconium materials but experimental creep data at short times and higher temperatures have been extrapolated to predict much longer design lifetimes of components at lower temperatures. High temperature creep data are required to investigate the behaviour of zirconium alloys under postulated accident conditions in power reactors. (A discussion of high temperature thermal creep is included in Chapter 9, Volume 3 of this publication.)

Generally, the temperature dependence of the creep rate can be expressed by:

$$\dot{\varepsilon} = D \exp\left(-\frac{Q}{RT}\right) \tag{7.6}$$

where

T is the absolute temperature;*D* is the material constant;

and Q is the activation energy, with measured values in the range 200–240 kJ·mol⁻¹ for Zircaloy-2 and Zircaloy-4 in either the RXA or CWSR states [7.83, 7.88].

Limbäck and Andersson [7.83] found that Q was insensitive to chemical composition, with a small standard deviation, for a range of Zircaloy materials and zirconium based alloys. A value of $Q = 201 \pm 7 \text{ kJ} \cdot \text{mol}^{-1}$ was proposed.

For Zr-2.5Nb alloys, the value of Q has been determined from analyses of CANDU pressure tube specimens stressed in both the axial and TDs [7.90]. The activation energy for thermal creep was found to be temperature dependent and consistent with the presence of dynamic strain ageing (see Section 7.3.6.4). For test temperatures in the range 373–475 K (100–200°C) Q was measured and determined to be about 42 kJ·mol⁻¹; for the temperature range 475–596 K (200–323°C) Q is about 88 kJ·mol⁻¹. These activation energies are lower than those measured by investigators on the same material at higher temperatures [7.91], but are similar to values found in other zirconium alloys at low temperatures [7.13].

7.3.4.2. Stress

Within the above temperature regimes, the creep rate at a given time is observed to increase with increasing applied stress in a systematic way that is characteristic of the prevailing and dominant creep mechanism. The most common formulation is:

$$\dot{\varepsilon} = B\sigma^{n} \tag{7.7}$$

where

 σ is the applied stress; n is the stress exponent;

and *B* is the material constant.

Many investigators have measured the stress dependence of creep in Zircaloy [7.92–7.94]. The stress sensitivity $n = (d \ln \varepsilon_s / d \ln \sigma)$ is not constant but increases with stress, as observed by Wood and Watkins [7.92] in CWSR Zircaloy-2 (Fig. 7.22).



FIG. 7.22. Uniaxial thermal creep of CWSR Zircaloy-2 as a function of applied stress and temperature (reprinted with permission from Ref. [7.92], copyright Elsevier, 1971).

Assuming viscoplastic creep behaviour (see Section 7.3.6.3), Rupa et al. [7.88] propose that the stress dependency should obey a hyperbolic sine law and the state equation for creep rate be of the form:

$$\dot{\varepsilon} = A_0 \left\{ \sin h \left[\left(\sigma_{\rm app} - X \right) / B_0 \right] \right\}^n \tag{7.8}$$

where X is the internal stress, or 'back stress'. This equation assumes that the flow stress (equivalent to the applied stress, σ_{app}) can be portioned into two components: the average internal stress \overline{X} and the effective stress, σ_{eff} .

The value of n in Eqs (7.6) and (7.7) varies depending on the temperature and stress ranges, and the material type, e.g. zirconium or Zircaloy.

Results from a number of experimental investigations are in general agreement and show that *n* increases from unity at low stresses ($\sigma < 20$ MPa) to n > 100 at higher stresses ($\sigma > 100$ MPa). This result appears to be valid for temperatures in the range 723–1023 K (450–800°C). At lower temperatures (573–673 K (300–400°C)) n \approx 6 for the stress range 100–150 MPa for Zircaloy-4 sheet [7.88]. For similar ranges of temperature and stress, Christodoulou et al. [7.90] have obtained values of $n \approx 4$ for Zr-2.5Nb pressure tube material. Bell [7.95, 7.96] measured the thermal creep of Zircaloy-2 pressure tubing in the LDs and TDs at 573 K (300°C) over the stress range 138–310 MPa. The stress exponent is similar in both testing directions and increases from n ≈ 2.4 in the stress range 138–241 MPa to $n \approx 6-8$ for stresses in the range 241–310 MPa.

At low stresses, $n \approx 1-2$ for both zirconium and Zircaloy, but at a given high stress the value of *n* may differ considerably for the two materials, with zirconium generally having the higher *n* value. The consequence of $n \approx 1$ at low stresses and at elevated temperatures is that zirconium alloys are 'superplastic' as a result of their high resistance to neck development. If n < 3, a local thin region of a specimen deforms uniformly at the same rate as the remainder of the specimen and is less sensitive to necking and early failure than is observed at higher stress exponents.

7.3.5. Metallurgical effects

7.3.5.1. Composition

The chemical concentration of certain creep strengthening elements strongly influences the thermal creep of zirconium alloys. Solid solution hardening elements that have the largest influence are tin, oxygen, sulphur, niobium, carbon and nitrogen. It should be noted that the latter two elements are controlled at a low level in zirconium alloys for nuclear applications. Sulphur [7.97] has a significant effect within its solubility range (up to about 15–20 ppm (0.0042–0.0052 at.%)), but only in the recrystallized annealed state of the material. This effect is now exploited commercially to increase the thermal and irradiation creep strength in the M5 alloy used to fabricate fuel cladding for PWR fuel rods. In Zircaloy, the majority of the creep strength is derived from the tin and oxygen additions. Oxygen is often considered an alloying element and has a specified range that must be met. Niobium is also a very effective creep strengthener (see Fig. 7.6) and all Zr-Nb alloys depend on this element, often with the help of one or more of the other elements mentioned, to provide the required mechanical creep strength. Above their solubility limits, precipitation hardening by the elements niobium, iron and chromium is also very effective at increasing the creep strength of zirconium alloys.

Based on thermal creep test results and post-irradiation diametral measurements on fuel rods, Seibold and Garzarolli [7.98] have defined an 'SNO parameter' (with SNO standing for Sn, Nb and O) for the diametral creep strength of PWR Zr based cladding materials. This parameter relates the creep strength dependence to the tin, niobium and oxygen concentrations expressed in percent by weight:

$$SNO = [wt\% Sn = 2 \times wt\% Nb + 6 \times wt\% O]$$
 (7.9)

Using SNO as an independent variable, both thermal and in-pile creep strains decrease monotonically with increasing SNO parameter (Fig. 7.23). Thermal creep rate is more sensitive than in-pile creep rate to changes in SNO due to the larger stress exponent ($n \approx 4$) of the former process. Using Eq. (7.9), Table 7.1 shows the SNO values (proportional to creep strength) derived for some of the common zirconium alloys used for fuel assembly cladding and structural applications.

Alloy	Condition	Sn (wt%)	Nb (wt%)	O (wt%)	SNO
E635	Partially recrystallized	1.25	1.0	0.06	3.61
ZIRLO	CWSR-partially recrystallized	1.0-0.7	1.0		3.0–2.7
M5	RXA		1.0	0.14	2.8
Zr-1Nb	PR	_	1.0	0.11	2.7
E110	RXA	_	1.0	0.06	2.31
Zr-4 (High tin)	CWSR	1.5		0.14	2.3
Alloy A	CWSR	0.6	0.3	0.16	2.2
Zr-2	RXA	1.3–1.5		0.12	2.0-2.2
Zr-4 (Optimized)	CWSR	1.3		0.12	2.0

TABLE 7.1. VALUES OF THE SNO PARAMETER FOR VARIOUS CLADDING MATERIALS



FIG. 7.23. Influence of Sn, Nb and O concentration on out-of-pile thermal creep and in-reactor creep (reprinted with permission from Ref. [7.98], copyright ASTM International, 2002).

McInteer et al. [7.99] have experimentally investigated the influence of tin concentration in the range 1.22 wt% (0.94 at.%) to 1.54 wt% (1.19 at.%) on the thermal creep of commercial CWSR Zircaloy-4 fuel tubing used in PWRs. Creep testing was performed at 672 K (399°C) over a series of stress ratios and for tensile stress values up to 207 MPa. The creep strength was found to be strongly influenced by the tin concentration, with the size of the effect depending on the stress state: the 0:1 and the 1:1 (hoop-to-axial) stress ratios show

larger effects than the biaxial 2:1 ratio. The steady state creep rates increased by factors of 2, 5 and 6 for the 2:1, 1:1 and 0:1 stress state, respectively, as the tin concentration decreased from 1.54 wt% to 1.22 wt%.

7.3.5.2. Heat treatment and cold work level

The heat treatment given to a specimen or component during fabrication determines the final dislocation density and grain size and can also influence the texture. Each of these factors has an effect on the thermal creep properties. CW during fabrication (e.g. pilgering, rolling or drawing) increases the dislocation density and the material hardness and thereby its resistance to plastic flow during creep. The presence of residual stresses, if sufficiently large, can also increase the dislocation density but these stresses can be recovered either by a stress relieving final anneal (at 673 < T < 773 K ($400 < T < 500^{\circ}$ C) for several hours), or during creep provided the test temperature exceeds 623 K (350° C) [7.100]. The effect of stress relief and recovery is to decrease the rate of thermal creep (Fig. 7.24).

Final annealing of a zirconium alloy specimen between 773–843 K (500–570°C) recrystalizes the grain structure and removes almost the entire CW dislocation network. This change in microstructure has a significant influence on thermal creep [7.101]; for example, in a biaxially stressed tube it reduces the longitudinal creep strength but increases the diametral strength. This behaviour implies a change to a more anisotropic crystallographic structure. The increase in diametral creep strength is due to a change in the active slip mode from $\langle c + a \rangle$ pyramidal slip in CWSR tubes to $\langle a \rangle$ prismatic slip in RXA tubes. It is a direct result of a 30° rotational shift in the prism plane texture that occurs during recrystallization (see Section 7.3.5.4). Recrystallization also tends to reduce primary creep strain compared with the CWSR condition, as shown in Fig. 7.24.

The relationship between creep at different temperatures and the amount of CW is complex. For example, below 623 K (350°C) the creep strength of CWSR Zircaloy exceeds that of RXA material, but at 673 K (400°C) they are similar [7.102]. Also, a prior annealing treatment at 793 K (520°C) results in a maximum creep strength after about 240 hours when tested at 673 K (400°C) [7.101, 7.103, 7.104]. Källström et al. [7.103] and Murty [7.104] speculated that the differences between the as-annealed mobile dislocation density and the dislocation density during steady state creep were responsible for the creep observations. A more probable explanation suggested by Frenkel and Weisz [7.101] is the change in prismatic $\langle a \rangle$ texture that occurs during recrystallization.

7.3.5.3. Grain size

The effect of grain size is complex and appears to depend on the testing conditions [7.13]. Based on the observations in many metals, the thermal creep strength of zirconium alloys might be expected to increase with decreasing grain size, but at low and intermediate temperatures such dependence is found to be weak or non-existent. At high temperatures (773 < T < 873 K (500–600°C)) and low stresses the creep strength generally decreases as grain size decreases. Diffusion controlled thermal creep and grain boundary sliding are both dependent on grain size and are discussed separately in Sections 7.3.6.1 and 7.3.6.5, respectively.



FIG. 7.24. Comparative creep curves for CWSR, CW and fully recrystallized unirradiated Zircaloy-4 under biaxial loading at 593 K (320°C) (reprinted with permission from Ref. [7.82], copyright ASTM International, 1983).

7.3.5.4. Texture

Texture hardening as a result of the preferred crystallographic orientations of the grains causes the creep strength to vary according to the testing mode and the direction of principal stresses, leading to creep anisotropy in polycrystalline zirconium alloys [7.82]. For zirconium alloy tubes, the mode of fabrication has a significant influence on creep behaviour such that when the basal poles approach the radial direction (as required for LWR fuel cladding) the diametral creep strength is reduced [7.103]. During final recrystallization from the CW to the fully annealed states, there is a rotation of the prism planes by 30° around the $\langle c \rangle$ direction. Although this crystal rotation does not affect the spatial distribution of basal planes, it changes the orientation, with respect to the applied stresses, of the principal slip planes (prism and pyramidal) and slip directions (normal to $\langle c \rangle$) involved in creep deformation. Stehle et al. [7.105] measured a correlation between creep strength and basal pole concentration in the test direction, at 150 MPa and 673 K (400°C). The general observation is that creep resistance in the <c> direction is high, and therefore less likely, compared with easier options of slip in the orthogonal $\langle a \rangle$ directions. When the basal poles are concentrated towards the TD (as they are for a reactor pressure tube), diametral creep strength is increased compared with fuel cladding. Bell [7.95, 7.96] has measured the thermal creep of Zircaloy-2 CANDU pressure tubes at 573 K (300°C) at stresses between 130 and 310 MPa and showed that creep is faster in the LD than in the TD by a factor of about 2.7 (Fig. 7.25). Holt [7.65] has reviewed inreactor deformation of CW Zr-2.5Nb pressure tubes, including the effect of texture and anisotropy on thermal creep.

A creep strength differential, which depends on the prevailing texture, has been observed in Zircaloy when comparing the creep strains in tension and compression in the same direction under the same load [7.105]. The effect has been seen in tubes and flat plate specimens, but generally only at applied stresses well in excess of 60 MPa. The phenomenon is not well understood because it is not predicted from considerations of prism slip alone, suggesting that an asymmetric $\langle c + a \rangle$ slip mechanism may be contributing to creep deformation [7.106]. Some support for this mechanism comes from the work of Jones and Hutchinson [7.107] on the stress state dependence of slip in Ti-6Al-4V alloy.



FIG. 7.25. Thermal creep of Zircaloy-2 pressure tube material measured in the LDs and TDs at 573 K (300°C) (reprinted with permission from Refs [7.95, 7.96], AECL, Canada).

7.3.6. Mechanisms

The widespread use of zirconium alloys in power reactors provides a strong incentive to understand creep mechanisms; therefore laboratory creep data, obtained at high temperatures and stresses (to permit short test times), may be extrapolated to service conditions. Because measured parametric dependencies and activation energies are observed to vary over a wide range of stresses and temperatures, it has been commonly assumed that different mechanisms control creep within defined ranges of stress and temperature.

7.3.6.1. Diffusion control

By analogy with cubic metals at low stresses ($\sigma < 20$ MPa) where the stress exponent $n \approx 1$, it has been assumed that thermal creep in α -zirconium or Zircaloy is controlled by a PD diffusion mechanism, such as Nabarro-Herring (N-H) or Coble creep. These mechanisms are shown schematically in Fig. 7.26. The basic mechanism assumes that there is a preferential migration of vacancies away from grain boundary segments perpendicular to an applied tensile stress and migration towards segments parallel to the stress axis. At the same time there is a mass transport of atoms in the opposite direction that causes the creep strain elongation in the direction of the applied stress. The difference between the N-H and Coble processes is that the vacancy migration is assumed to occur by volume diffusion through the grain itself in N-H creep, but by grain boundary diffusion along the boundary in Coble creep. If volume diffusion predominates, the N-H creep rate is given by Eq. (7.10) [7.108]:

$$\dot{\varepsilon}_{\rm NH} = \frac{14\Omega}{kT} \frac{D_{\rm v}}{d^2} \tag{7.10}$$

where Ω is the atomic volume and k is the Boltzmann's constant.
The N-H creep is linearly proportional to the applied stress, σ , and inversely proportional to the absolute temperature, *T*, and the square of the grain size, *d*. The activation energy in the volume diffusion term D_v is that for self-diffusion of zirconium atoms.

If grain boundary diffusion predominates, the Coble creep rate is given by Eq. (7.11) [7.108]:

$$\dot{\varepsilon}_{\text{Coble}} = \frac{14\Omega}{kT} \frac{\pi \delta D_{\text{GB}}}{d^3} \sigma \tag{7.11}$$

where δ is the thickness of the grain boundary.

Coble creep is also linearly proportional to stress but is inversely proportional to the cube of the grain size. The activation energy in the diffusion term D_{GB} is that for grain boundary diffusion.



FIG. 7.26. Diffusive transport mechanisms involved in Nabarro-Herring and Coble creep (reprinted with permission from Ref. [7.82], copyright ASTM International, 1983).

7.3.6.2. Dislocation control

At high applied stresses an exponent, n, in the range 4–6 (see Eq. (7.6)) has been measured by Bernstein [7.109] for thermal creep in zirconium and Zircaloy, in association with an activation energy approaching self-diffusion. This stress dependence suggests that the controlling mechanism may be dislocation climb or dislocation climb-glide, with the rate of creep deformation determined by the rate at which edge dislocations climb to surmount obstacles (e.g. precipitates) in their slip planes. The dislocation then glides on a new, parallel slip plane to generate creep strain. In thermal creep, the rate at which dislocations climb is determined by the rate of arrival of vacancies by a process of thermal diffusion. The creep rate is then given by Eq. (7.12) [7.108]:

$$\dot{\varepsilon}_{cl} = A\mu b \frac{D_{\rm v}}{kT} \left(\frac{\sigma}{\mu}\right)^{\rm n} \tag{7.12}$$

where μ is the shear modulus and b is the Burgers vector of the climbing edge dislocations.

In this mechanism, $n \approx 4$ and vacancies migrate by volume diffusion. Ardell and Sherby [7.110] proposed an alternative mechanism in which dislocations do not climb to surmount an obstacle but obtain sufficient energy, both thermally and from the applied stress, to cut through the obstacle in its glide path. This mechanism yields a creep rate given by:

$$\dot{\varepsilon}_{\text{glide}} = B \exp(C\sigma) \exp\{\left[-(Q + \eta/\sigma)\right]/RT\}$$
(7.13)

where

B and C	are constants;
$(Q + \eta/\sigma)$	is the stress-dependent activation energy;

and Q is approximately the energy for self-diffusion.

The climb-glide and glide mechanisms are both supported by thermal creep measurements in the temperature range 673–1123 K (400–750°C). To show how the mechanistic modelling may be combined, Knorr and Notis [7.111] proposed creep deformation 'maps' of stress as a function of homologous temperature ($T/T_{\alpha-\beta}$) for Zircaloy (Fig. 7.27). These maps are constructed on the assumption that dislocation glide (Eq (7.12)) and dislocation climb-controlled creep (Eq. (7.11)) operate sequentially and that these two mechanisms operate in parallel with Coble creep (Eq. (7.10)):

$$\dot{\varepsilon}_{\text{total}} = \dot{\varepsilon}_{\text{cl}} \dot{\varepsilon}_{\text{glide}} / (\dot{\varepsilon}_{\text{cl}} + \dot{\varepsilon}_{\text{glide}}) + \dot{\varepsilon}_{\text{Coble}}$$
(7.14)

From this analysis it is concluded that dislocation climb-glide creep is dominant at high stresses and dislocation glide creep dominates at intermediate stresses. At low stresses Coble creep predominates, from which it can be predicted that the stress-temperature region for which this mechanism is valid depends on grain size. The creep measurements for Zircaloy-2 in the temperature range 623–673 K (350–400°C) at high stresses fall below the predicted creep rates based on climb-controlled glide. This discrepancy may be a result of strain ageing effects during the tests that are not accounted for in the mapping analysis [7.82]. Strain ageing is discussed in Section 7.3.6.4.

7.3.6.3. Viscoelasticity, viscoplasticity

Like many materials, zirconium and its alloys exhibit viscoelastic properties under stress. Viscoelastic materials are those for which the relationship between stress and strain depends on time, for example, the materials creep under constant load and relax under constant strain. Anelastic solids that in time recover a fraction of the deformation strain (the anelastic part) following the removal of a transient load are a subset of viscoelastic materials. Zirconium and its alloys are anelastic as well as being anisotropic owing to their crystal properties [7.112, 7.113].

The theory of anisotropic viscoplasticity has been applied to RXA and CWSR Zircaloy-4-model thermal creep measurements over the range 283–673 K $(20-400^{\circ}C)$ [7.87]. The model incorporates anisotropy coefficients for the plastic flow (i.e. slip) in orthogonal directions that are found to be insensitive to temperature over this range. It also describes kinematic hardening and its dynamic and static recovery during the creep

process as well as a maximum in creep resistance around 573 K (300°C) caused by strain ageing.

Viscoplastic modelling has been applied to the long term thermal creep of irradiated and discharged fuel rods destined for dry storage conditions [7.114], as discussed in Section 7.3.7.



FIG. 7.27. Thermal creep deformation map for Zircaloy-2 with a grain size $d = 10\mu m$ (reprinted with permission from Ref. [7.111], copyright Elsevier, 1975).

7.3.6.4. Strain ageing

Strain ageing is an important feature of the thermal creep behaviour of zirconium alloys in the intermediate temperature regime 473–773 K (200–500°C). There are several observed mechanical property phenomena attributed to strain ageing [7.82], but in relation to the thermal creep of Zircaloy the most significant are:

- Occurrence of discontinuities and transitions in the creep strain-time curves, especially in annealed material;
- Significant reductions in the creep rate;
- Peaks in the temperature dependence of the activation energy for plastic flow.

Creep of α -zirconium is affected by dynamic strain ageing [7.115] during the deformation process as a result of temperature sensitive changes that occur in the dislocation microstructure. These changes are associated with the development of a distinct dislocation cell structure in which dislocations in the cell walls are pinned by interactions with interstitial solute atoms or precipitates. The cell structure develops up to a temperature of 623 K (350°C), beyond which it eventually transforms to a regular dislocation network. The most probable solute atom is oxygen [7.116], with a second element, possibly tin [7.117], also contributing. Precipitates form in zirconium alloys from a number of impurity or alloying elements that have low terminal solubility limits, such as iron, chromium, niobium and

silicon, when these solubility limits are exceeded. Dislocation pinning reduces dislocation mobility and lowers the rate of dynamic recovery during creep. As a result, strain hardening dominates and reduces the creep rate. Bursts of creep strain can occur when dislocations break free from pinning points (often called Cottrell 'atmospheres') or, if the atmospheres migrate, dissolve or are dragged by dislocations under the action of stress or temperature.

Christodoulou et al. [7.90] have shown that their results of measured activation energies for creep in Zr-2.5Nb are consistent with dynamic strain ageing. They were able to demonstrate the presence of dynamic strain ageing in creep tests by reducing the stress to a lower value. Following the stress reduction, the creep rate was practically zero; after the stress was then increased to the initial value the creep rate continued to be negligible.

7.3.6.5. Grain boundary sliding and creep rupture

At high temperatures and low applied stresses, a significant amount of creep deformation can arise from grain boundary sliding. This mechanism may result in creep rupture, although rupture is not a necessary consequence if superplasticity prevails. The process involves the movement of grains past one another under the action of a shear stress at the grain boundary. The rate of grain boundary sliding is governed by the rate at which thermal creep in the surrounding material relaxes internal stresses, which build up along the boundary or at triple points. Grain boundary sliding can promote the formation of cavitation or microvoids on the boundaries and lead to creep rupture by intergranular fracture. This type of cracking has been observed in Zircaloy-4 at 623 K (350°C) [7.118], leading to the proposal that grain boundary sliding operates at low temperatures [7.82]. Huang et al. [7.119] have also postulated that deformation by grain boundary sliding may contribute to the previously mentioned superplastic behaviour exhibited by zirconium. In this case the sliding would have to be accommodated by creep processes that maintain grain boundary integrity and avoid any separation that leads to rupture.

7.3.7. Thermal creep of previously irradiated material

Thermal creep of previously irradiated zirconium alloys is of particular interest under conditions of the long term dry storage of irradiated fuel elements. Highly irradiated fuel rods have their own internal thermal source term, producing gamma heating of the cladding, as well as possessing a source of stress arising from the pressure of the internal fission and helium gases. These conditions can produce cladding temperatures up to about 673 K (400°C) and tensile hoop stresses up to about 120 MPa during the early stage of dry cask storage [7.120]. Although gradual decay of the heat source produces a reduction in cladding temperature and internal gas pressure, the long storage duration allows a significant creep strain (\cong 1%) to develop. Compared with previous discussion on the thermal creep of unirradiated materials, the effect of pre-irradiation on the microstructure is to introduce (a) irradiation hardening and (b) hydrogen (from the waterside corrosion reaction) into the zirconium lattice, both of which can affect the creep process. A small influence on creep may also result from the mechanical strengthening effect of the external oxide layer. In addition, thermal creep measurements have shown that the degree of anisotropy is reduced by preirradiation [7.84].

Irradiation damage in zirconium alloys creates interstitial and vacancy loops. Depending on the creep test conditions, an increase in thermal creep rate would be expected due to the release of interstitials and vacancies during the annealing of irradiation damage. Irradiation also dissolves intermetallic SPPs and the elements released into the matrix will either re-condense as small precipitates or migrate to dislocation sinks. In either event it is possible that dislocation movement will be impeded, thereby increasing the creep strength. At test temperatures below about 673 K (400°C) little recovery of the irradiation produced microstructure occurs and the effect on thermal creep is small [7.121].

7.3.7.1. Influence of hydrogen and hydrides on the thermal creep process

The influence of hydrogen on thermal creep depends on its concentration (i.e. on whether it is completely dissolved in the α -zirconium matrix or partially precipitated in the form of hydrides) [7.88]. (The hydrogen concentration in 'as-received' Zircaloy fuel cladding is typically $\leq 20-25$ ppm (0.18–0.23 at.%).) In the former case, hydrogen in solid solution produces a softening of the mechanical properties and a decrease in creep strength (Fig. 7.28). In the latter case, hydride precipitation induces a hardening effect and a significant increase in creep strength (Fig. 7.29) for creep strains up to 0.25%, beyond which no further creep strengthening occurs. For hydrogen concentrations exceeding the solubility limit at a given creep test temperature, the hydride hardening dominates over the hydrogen softening effect. This behaviour has been observed in both the RXA and the CWSR states of Zircaloy-4 [7.122].

Hydrogen in solution at a concentration below the solubility limit does not change the dislocation microstructure, so an explanation for its softening effect on creep in the α -zirconium phase has had to be sought from ab initio lattice calculations. Softening is particularly observed when dynamic strain ageing is activated. Rupa et al. [7.88] showed that atomic hydrogen can be easily trapped by the core of the screw dislocations that are active in the creep process. The trapping decreases lattice friction and enhances glide on the prism planes. At elevated hydrogen concentrations, the creep hardening effect can be explained by hydride precipitates acting as obstacles to dislocation glide for small plastic strains $\approx 0.25\%$. This hardening is supported by observations of dislocation pileups close to hydrides. On a viscoplastic creep model, hydrides in Zircaloy generate a higher internal stress during deformation compared with non-hydrided material, up to the point where the internal stress attains a saturated value of about 9 MPa. For creep strains exceeding 0.25%, the hardening effect of the hydrides decreases as they are no longer obstacles to dislocation mobility because they can be surmounted.



FIG. 7.28. Effect of dissolved hydrogen on thermal creep of unirradiated RXA Zircaloy-4 (reprinted with permission from Ref. [7.88], copyright ASTM International, 2002).



FIG. 7.29. Biaxial thermal creep of as-received and hydrided CWSR Zircaloy-4 at 673 K (400°C) and a hoop stress of 140 MPa (reprinted with permission from Ref. [7.123], copyright the American Nuclear Society, La Grange Park, Illinois, 2000).

7.3.8. Summary

The thermal creep behaviour of zirconium alloys is sensitive to temperature and stress as well as to the metallurgical variables of chemical composition, retained CW and texture. The grain size dependence is generally weak except at high temperatures >773 K (500°C) where larger grain diameters tend to increase the creep strength.

The functional dependence of the thermal creep rate on the metallurgical variables changes with the applied stress and the test temperature, indicating that a variety of mechanisms contribute to the creep of zirconium and its alloys over the broad range of variables investigated experimentally. Several chemical elements exert an influence by decreasing the creep rate, notably tin, oxygen and niobium, as well as sulphur but only in its recrystallized state. Hydrogen in solution has a softening effect on creep strength but hydrides have the opposite effect up to a limiting creep strain ($\approx 0.25\%$), beyond which no further hardening occurs. The empirical relationship between creep at different temperatures and the amount of CW is particularly complex.

Strain ageing is an important feature of thermal creep behaviour of zirconium alloys in the intermediate temperature regime 473–773 K (200–500°C). Dynamic strain ageing causes significant reductions in thermal creep rates due to the pinning of dislocation by solute atoms of oxygen and possibly tin. The pinning inhibits the recovery process and allows strain hardening to dominate the creep process.

The thermal creep behaviour of previously irradiated Zircaloy and other zirconium alloys used for fuel cladding is technologically important because of long term dry storage considerations. The competing effects on thermal creep strength resulting from irradiation damage are not straightforward to evaluate and require careful experimental investigation over a range of stress, strain and temperature conditions.

7.4. IRRADIATION CREEP

7.4.1. Definition and background

The total deformation measured during, or following, irradiation of a specimen or a reactor component is the sum of all the dimensional changes that are caused by:

- Thermal and irradiation induced creep, generated by an applied or internal stress;
- Irradiation growth;
- The environment (e.g. temperature, corrosion and hydriding).

Each of these responses depends on the characteristics of the measured material (e.g. alloy composition, anisotropy and final heat treated condition).

The dynamic displacement of atoms during high energy irradiation sets up a number of interactions among lattice defects (interstitials, vacancies, dislocations and grain boundaries) that can modify normal thermal creep mechanisms. For example, at intermediate temperatures (573–773 K (300–500°C)) thermal creep strain is considered to result from the combined climb and glide of dislocations. In the presence of irradiation, dislocation climb over obstacles in the glide path can be significantly aided by the arrival of an excess of interstitials and vacancies. PDs also agglomerate to form dislocation loops, as well as inducing the migration of impurity species to matrix sinks. These processes can all impede dislocation glide and reduce creep rates. Irradiation can also accelerate the relaxation of internal residual stresses introduced during specimen or component fabrication. The resulting deformation can either reinforce or cancel out small creep strains caused by the applied stress. Therefore, a number of counteracting effects must be considered in the analysis of irradiation creep tests and post-irradiation measurements on components.

The complexity of the subject of in-reactor creep of zirconium alloys, together with the longevity of its study (initiated in the 1950s), has resulted in many theories and models to explain the sometimes contradictory experimental and operational data. The driving force has always been to safeguard the widespread use of Zircaloy and Zr-Nb alloys in fuel assemblies for light and heavy water moderated reactors and in pressure tubes mainly for CANDU and high-power channel-type reactors (RBMKs). These applications have generated a large amount of data and satisfied the need for predictive creep and total deformation equations for design and safety calculations. To improve the mechanistic understanding of irradiation creep, a large number of creep experiments have been performed in materials testing research reactors.

7.4.2. Experimental techniques

Pure irradiation creep (i.e. without any thermal creep or irradiation induced growth contributions) cannot be readily measured. In-reactor creep experiments based on shear tests using helical springs [7.124] or stress relaxation in bending [7.14] come closest to pure irradiation creep for conditions where the thermal creep is negligibly small. In most empirical investigations of irradiation creep there is a need to make allowances for the contributions from the other two components. These distinctions can be achieved by means of a zero stress sample irradiated under identical conditions of flux and temperature to measure irradiation growth. Thermal creep tests must be performed on preirradiated material; such tests are required because thermal creep tests at high stress, the specimens should be irradiated to a low dose without stress, otherwise premature rupture will occur.

The most common experimental approach has employed internally pressurized, tubular specimens that are either individually sealed [7.125] or, more often, connected to an on-line pressurization system. The latter can use hot water [7.126] or an inert gas (e.g. helium or argon), to produce a tensile hoop stress in the sample such as a fuel rod segment [7.85]. Early irradiation creep experiments employed air-gauging equipment to measure changes to the tube internal diameter to an accuracy of about 0.2% at a limiting creep strain of 1.6% [7.126].

Later determinations mostly use linear variable differential transformer measurement techniques such as a 3-point contact diameter gauge operated hydraulically to traverse the length of the specimen or fuel rod segment [7.85]. There have also been various attempts at continuous in-reactor measurements of irradiation creep involving uniaxial tests [7.123, 7.127, 7.128]. Diametral creepdown measurements on commercial or experimental fuel rods are also a common source of irradiation creep data [7.83, 7.129]. Additionally, there exist large databases of measurements of diameter changes and elongations of pressure tubes [7.58]. However, because of the variations in power and fluence there is an inherent uncertainty associated with these data that is generally larger than for dedicated experiments under well controlled test reactor conditions. The best results are obtained by measuring the same pressure tube at several time intervals. The conference proceedings edited by Cundy et al. [7.130] provide a good starting point for a reader who is new to the general subject of irradiation creep testing, while the contribution by Wood [7.131] describes measurement techniques specific to Zircaloy-2.

7.4.3. Characteristics of irradiation creep

7.4.3.1. General

The interaction between the effects of stress, irradiation and temperature on zirconium alloys has led to the development of analyses for the resulting deformation ε_{total} , which assume that it consists of separable and additive contributions from thermal creep, irradiation creep and irradiation growth:

$$\varepsilon_{\text{total}} = \varepsilon_{\text{th}}^{\text{creep}} + \varepsilon_{\text{irr}}^{\text{creep}} + \varepsilon_{\text{th}}^{\text{growth}}$$
 (7.15)

where

 $\begin{aligned} & \varepsilon_{\rm th}^{\rm creep} & \text{is the thermal creep;} \\ & \varepsilon_{\rm irr}^{\rm creep} & \text{is the irradiation creep;} \\ & \text{and } \varepsilon_{\rm th}^{\rm growth} & \text{is the irradiation growth.} \end{aligned}$

The component of thermal creep is understood to be that measured on preirradiated material and not from laboratory creep tests on unirradiated samples. As mentioned previously, pure irradiation creep, without any contributions from thermal creep and irradiation growth, cannot readily be determined, although for some reactor applications the temperature is sufficiently low that thermal creep can be neglected. It follows that in most examples of 'irradiation creep' there will be a need to make allowances for the contributions from the other two components. It should be noted that Eq. (7.15), and the underlying assumption that deformation during simultaneous irradiation can be separated into three components, owes more to analytical convenience than to a mechanistic modelling of the whole effect. The foregoing discussion is based on reactor data and creep induced by fast neutron irradiation. The effects of proton irradiation on creep deformation are described later (see Section 7.4.3.8).

The effect of neutron irradiation on creep has been succinctly summarized by Fidleris [7.42]. Figure 7.30 compares thermal creep and in-reactor creep of textured and annealed zirconium alloy material measured in (a) the LD (or working direction), and

(b) the TD, for an applied stress that is less than 50% of the yield stress of the irradiated material. Similar stages that are characteristic of thermal creep, i.e. primary, secondary and tertiary, can also occur in irradiation creep. Following Fidleris [7.42], it is useful to consider three notionally separate temperature regions:

- Region I: T < 453 K (180°C), where temperature has negligible influence on thermal creep rates due to rapid strain hardening.
- Region II: 453 < T < 773 K (180–500°C), the 'athermal' region where dynamic strain hardening dominates in the middle of the range but some thermal recovery occurs to offset some of the strain hardening, particularly during primary creep. Most reactor applications of zirconium alloys fall into this region.
- Region III: T > 773 K (500°C). In this region irradiation damage anneals rapidly and thermal recovery processes are sufficiently fast to balance strain hardening during creep to produce a steady state secondary thermal creep rate.

The trends of creep strain versus time, shown in Fig. 7.30(a), are converted into creep rates (log $\dot{\epsilon}$ vs. log t) in Fig. 7.30(b) for the three temperature regions. The main conclusion to be drawn is that the neutron flux has a marked effect on creep behaviour in temperature regions I and II and an insignificant effect in region III. Up to a temperature of about 800 K (527°C), irradiation accentuates the anisotropy of creep deformation in zirconium alloys and causes the long term irradiation creep rates to become constant and proportional to the fast flux, in contrast to the continuously decreasing thermal creep rates at these temperatures. At high neutron fluences in excess of about 4×10^{25} n·m⁻² (E < 1 MeV) or 8 dpa the in-reactor creep rate may increase due to irradiation induced microstructural changes, such as the formation of c component dislocations [7.132].



FIG. 7.30. Schematic representation of the effect of irradiation (solid lines) on the thermal creep (broken lines) of zirconium alloys at constant stress: (a) creep strain; (b) creep rate, in LDs and TDs (reprinted with permission from Ref. [7.42], copyright Elsevier, 1988).

7.4.3.2. Time dependent (primary) creep

Most zirconium alloys exhibit a time dependent strain rate during the early stages of irradiation creep, similar to that observed during thermal creep. This observation is indicative of a dislocation microstructure that is changing owing to contributions from irradiation damage (e.g. dislocation loop formation), strain hardening and recovery processes. During primary creep there is an uneven competition between these contributions, producing a generally decreasing creep strain rate with increasing time. Only when the dislocation population attains a steady state configuration does the material exhibit an approximately constant, secondary creep rate. The latter is then a function of the current operating conditions of flux, stress and temperature. Some alloys investigated under certain operating or test conditions never achieve a true steady state [7.42] and the irradiation creep process is considered to be only primary, with a continually decreasing rate as a function of time (or fluence).

There have been many different mathematical formulations to describe primary creep [7.83, 7.133]. A common and successful analytical approach is to express the total creep strain, ε_t , as a sum of the primary creep strain, $\dot{\varepsilon}_p t$ and the secondary creep strain, ($\dot{\varepsilon}_s t$):

$$\varepsilon_{\rm t} \propto [1 - \exp(-\dot{\varepsilon}_{\rm s} t)] + \dot{\varepsilon}_{\rm s} t \tag{7.16}$$

where the first term in square brackets represents primary creep, $\varepsilon_{p}(t)$, whose rate decays with time before transitioning to steady state secondary creep. It should be pointed out that Eq. (7.16) is a mathematical convenience and does not represent any mechanistic understanding of the primary creep processes, which are complex and therefore difficult to model.

All primary creep models have the general form:

$$\dot{\varepsilon} = \dot{\varepsilon}(\sigma, T, \varphi, t) \tag{7.17}$$

where

- $\dot{\varepsilon}$ is the instantaneous creep rate;
- σ is the applied stress;
- *T* is the temperature;
- φ is the irradiation flux;

and t is time.

If any of the three state variables σ , T and φ changes with time then the conditions that determine the primary creep rate are also predicted to change, introducing a new primary creep curve. This prediction has been confirmed experimentally [7.85, 7.97]. Two commonly used descriptions have been developed to address this situation: time hardening and strain hardening [7.82, 7.134], which have been applied to both thermal and irradiation creep.

Time hardening is shown schematically in Fig. 7.31 for a simple case where the stress increases at time t_1 from $\sigma_1 - \sigma_2$ and remains at σ_2 until t_0 [7.82]. Up until t_1 the material creeps along the creep curve corresponding to the initial conditions. For $t > t_1$ the material creeps according to $\sigma = \sigma_2$, and the total accumulated creep strain at t_0 is ε_t . A similar diagram to Fig. 7.31 can be constructed for a change in the value of φ . The physical

interpretation of time hardening is that the microstructure, and hence its hardness or creep strength, is simply a function of the length of time it is exposed to the operating conditions. For instance, if recrystallization, precipitation or radiation induced microstructure, or a combination of these processes, were taking place in a material, its hardness would be a function of time (or fluence). Hence, the name time hardening.



FIG. 7.31. The time hardening rule (reprinted with permission from Ref. [7.82], copyright ASTM International, 1983).

Strain hardening is shown schematically in Fig. 7.32, again for a case where the operating stress increases [7.82]. For $\sigma = \sigma_1$, the creep strain $\varepsilon = \varepsilon_1$ at $t = t_1$. After the increase in stress, the material creeps according to $\sigma = \sigma_2$ and the creep rate increases. At $t = t_0$ the accumulated creep strain $\varepsilon = \varepsilon_s$, which is considerably greater than the strain ε_t calculated by the time hardening rule (see Fig. 7.31). The opposite behaviour can occur if the stress decreases, instead of increases, after t_1 . The physical meaning of strain hardening is that the hardness or creep strength of a material is a function of the accumulated strain, not the time spent under a given set of conditions as with time hardening. The validity of one rule over the other depends on the range of stress and temperature concerned, as well as the application. Lucas and Pelloux [7.134] have investigated these considerations for thermal creep of unirradiated Zircaloy-2 and those by Mayuzumi and Onchi [7.135] for the post-irradiation thermal creep of Zircaloy-4 in the temperature range 626–693 K (353–420°C). Under both sets of experimental conditions the strain hardening rule was applicable.

7.4.3.3. Dependence on irradiation fluence

The initial effect of irradiation is to reduce the thermal creep component by hardening the zirconium lattice. The effect on primary creep is particularly evident in the annealed state, as depicted in region II of Fig. 7.30. It is not very noticeable in CWSR materials below 600 K (327°C); an exception is Zr-2.5Nb tested at high applied stresses (e.g. 580 MPa) at 573 K (300°C). The irradiation hardening increases with fluence before saturating at about 4×10^{24} n·m⁻² (E > 1 MeV), i.e. ≤ 1 dpa. The depressed primary creep stage is generally followed by enhanced steady state creep, which for a given flux, ϕ , is proportional to the fluence (i.e. $\varepsilon_{tot} \propto \phi t$). Note that ε_{tot} is the combined contributions of thermal and irradiation induced creep strains.



FIG. 7.32. The strain hardening rule (reprinted with permission from Ref. [7.82], copyright ASTM International, 1983).

7.4.3.4. Dependence on flux

Irradiation creep rates are generally assumed to be proportional to the fast (i.e. E > 1 MeV) flux (ϕ) raised to some power, p (i.e. $\dot{\epsilon}_{irr} \propto \phi^p$). Some uniaxial creep tests and data obtained from Zr-2.5Nb pressure tubes in the temperature range 530–570 K (257–297°C) can best be correlated by taking p = 1 for fluxes in the range (1–3) × 10¹⁷ n·m⁻²·s⁻¹ [7.42]. Over a wider range of fast neutron flux the dependence of the diametral irradiation creep of Zr-2.5Nb pressure tubes is found to be a complex function of flux [7.51]. Analyses of creep strain data measured over long periods of reactor operation have shown that the steady state creep rates are non-linear in ϕ . At fluxes up to about 0.3×10^{17} n·m⁻²·s⁻¹ the thermal creep component is suppressed by irradiation damage,

the latter consisting of small irresolvable vacancy and interstitial clusters [7.51], yet there is negligible dislocation climb to generate any irradiation induced creep strain. Under these conditions the in-reactor creep rate decreases with increasing flux. Above a critical flux ($\approx 1 \times 10^{15} \,\mathrm{n \cdot m^{-2} \cdot s^{-1}}$ for irradiation temperatures of 550–570 K (277–297°C)), the irradiation induced creep mechanisms dominate over thermal creep and the creep rate then becomes linearly proportional to fast flux.

Creep test measurements on Zircaloy-2 and Zircaloy-4 suggest that the best correlation with flux is for exponent values ranging between p = 0.25 and 1.0. Tinti [7.136] measured in-reactor creep of CWSR Zircaloy-2 relative to an adjacent unstressed specimen to eliminate the contribution from irradiation growth. The results are illustrated in Fig. 7.33 and show that the flux exponent increases from p = 0.6 at low fast fluxes ($\phi \approx (1-4) \times 10^{17} \text{ n} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$) to $p \approx 1.0$ at $\phi > 4.5 \times 10^{17} \text{ n} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$. However, the maximum duration of the tests of 2000 h suggests that steady state creep conditions had not been fully achieved and thermal creep may have contributed to the total strain. A correction for these effects was found to increase the value of p towards unity. An extensive programme of diametral measurements by Frenkel and Weisz [7.137] on internally pressurized CWSR Zircaloy-4 tubes irradiated at 623 K (350°C) yielded a value for p = 0.65 over a flux range of $\phi = (0.88-1.95) \times 10^{18} \text{ n} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$. Chapman et al. [7.138] irradiated Zircaloy-2 specimens with energetic protons over a wide damage rate range (equivalent to $\phi = (0.05-3.5) \times 10^{18} \text{ n} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$) at 553 K (280°C) and a stress of 181 MPa. Results showed that the creep rate was linear with displacement flux.

Nichols [7.139] determined the flux exponent in Zircaloy over a temperature range of 300–870 K (27–597°C). Results indicate that p decreases with increasing temperature, becoming negligible for T > 800 K (527°C). This result would be expected as thermal creep becomes increasingly dominant over the irradiation induced contribution at temperatures in excess of about 670 K (400°C).

7.4.3.5. Dependence on stress

Beyond the primary creep stage of most zirconium alloys, the dependence of in-reactor creep rate, $\dot{\varepsilon}_{total}$, on applied stress, σ , is commonly described by a power law, $\dot{\varepsilon}_{total} \propto \sigma^n$, for a given set of material and environmental conditions. A number of independent determinations of the value of *n* have been made for Zircaloy-2 and Zircaloy-4, as well as Zr-2.5Nb [7.42, 7.82]. Because of the relevance to reactor operations, investigations have concentrated in the temperature range 553–623 K (280–350°C). The database also includes corrosion resistant alloys outside the ASTM specification, such as M5 and E635 [7.61, 7.82]. The trends for standard zirconium alloys can be summarized schematically, as shown in Fig. 7.34. At applied stresses in the approximate range 0.15–0.3 of the yield stress of unirradiated material the stress exponent has the value of unity [7.42], but *n* is observed to increase with stress and temperature. Taking Zr-2.5Nb as an example, n = 1 for $\sigma < 200$ MPa, n = 2-3 for $\sigma = 200-400$ MPa, then *n* increases rapidly to values of around 100 at $\sigma > 600$ MPa as σ_{yield} is approached [7.140].

Investigations of in-reactor creep by Soniak et al. [7.129] on Zircaloy-4 fuel cladding yielded values for n in the range 0.8–2.0 at irradiation temperatures of 553–663 K (280–380°C) and stresses of 0–120 MPa. For modelling purposes Soniak et al. propose an average n = 1.6 for RXA and CWSR Zircaloy-4 that takes into account the combined effect of thermal and irradiation induced creep over the above ranges of temperature and stress. Limbäck and Andersson [7.83] took n = 1 for the irradiation induced creep contribution to the deformation of RXA and CWSR Zircaloy-2 and Zircaloy-4 fuel cladding, based on

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creepdown data given in Ref. [7.82]. This component was then added to the contribution from thermal creep, where n = 2 (CWSR), n = 2.3 (partially recrystallized) and n = 3.5 (RXA), representing three different final heat treatments [7.83].



FIG. 7.33. Flux dependence of in-reactor uniaxial creep of CWSR Zircaloy-2 (reprinted with permission from Ref. [7.136], American Nuclear Society, La Grange Park, Illinois, 1983).

At low stresses and for temperatures below 600 K (327°C) irradiation induced creep is dominant over thermal creep but the latter has a stronger sensitivity to stress (i.e. higher *n* values), as shown in Fig. 7.34. A variation in *n* with stress indicates that the deformation mechanism is also changing with stress. For irradiation creep, this variation takes the form of a change in anisotropy due to a modification of growth anisotropy by the stress. For thermal creep, the change in deformation rate is due to the activation of new slip systems and the breaking of forest dislocation barriers. An outcome of the low value of the stress exponent ($n \cong 1$) under typical in-reactor conditions is high creep ductility for zirconium alloys. 'Superplastic' behaviour has been previously noted for certain thermal creep conditions and a similar phenomenon is equally apparent for irradiation creep. It was first discussed theoretically by Nichols [7.141] and supported experimentally by Wood and Watkins [7.92]. (See further discussion of superplasticity in Chapter 9 on ductility and fracture, Volume 3 of this publication).



FIG. 7.34. Schematic comparison of the stress dependence of in-reactor and thermal creep rates at a temperature of about 570 K (300°C) (reprinted with permission from Ref. [7.42], copyright Elsevier, 1988).

7.4.3.6. Effect of temperature

Steady state in-reactor creep (i.e. strain that is linear with time at a constant flux) is often achieved at high fluences, with the rate depending only on the irradiation temperature and the fast neutron flux. The temperature dependence is commonly described by an Arrhenius equation, similar to that for thermal creep, of the form [7.82]:

$$\dot{\varepsilon}_{\rm irr} = B \exp(-Q_{\rm irr}/RT) \tag{7.18}$$

where

T is the absolute temperature;

B is the constant for a given set of conditions;

and Q_{irr} is the activation energy and a measure of the temperature sensitivity of the creep process due to irradiation.

If the material microstructure does not change with temperature or with the strain then the slope of log $\dot{\varepsilon}_{irr}$ vs 1/T plots can be used to calculate Q_{irr} , provided that the creep rates are constant.

The temperature dependence of the irradiation creep of zirconium alloys has been investigated by many researchers over a range of 320–800 K (47–527°C), although most of

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the testing has occurred in the region of technological interest (i.e. 470–670 K (197–397°C)). Fidleris [7.42] demonstrated that at temperatures below 623 K (350°C) irradiation creep is less sensitive to temperature than thermal creep, but at higher temperatures the irradiation and thermal creep rates have the same activation energies. An example of this dependence is shown in Fig. 7.35 for CWSR Zircaloy-2 measured at two different stresses of 128 MPa and 207 MPa [7.42]. Two observations should be made with regard to these results. Firstly, to make a valid comparison between thermal and in-reactor creep behaviour it is necessary to compare similar microstructures (i.e. the thermal creep tests should be on preirradiated material). Unfortunately, such a microstructure was not used for the data in Ref. [7.42]. Secondly, for moderate damage rates, thermal and irradiation creep rates are expected to be similar at high temperatures due to annealing of the irradiation produced defects. Thus, the steady state PD concentration is not enhanced, and the microstructures are similar.



FIG. 7.35. Temperature dependence of in-reactor and thermal (laboratory) creep rates of CWSR Zircaloy-2 (reprinted with permission from Ref. [7.42], copyright Elsevier, 1988).

The comparison and interpretation of the temperature dependence of in-reactor and out-of-reactor creep requires some care because results from short term tests may not represent long term behaviour. Gilbert and Harding's measurements [7.142] on CWSR Zircaloy-2 indicate that for T < 583 K (310°C) the temperature dependence of irradiation creep is weaker than for thermal creep, resulting in a low temperature region where the thermal creep rate is greater than the corresponding in-reactor rate (Fig. 7.36). The results were interpreted as the effect of irradiation hardening on in-reactor creep, although this effect does not appear to have been reported by other researchers. As testing took place over a short

duration, deformation may have been dominated by the primary creep process. Fidleris [7.42] observes that it can take up to 10 000 h of testing in a moderate fast neutron flux $(2 \times 10^{17} \text{ n} \cdot \text{m}^{-2} \cdot \text{s}^{-1})$ to establish a steady state creep rate, and during the interim period the thermal creep rate may exceed the in-reactor creep rate.

Fidleris [7.42] showed that the activation energies for the in-reactor creep of zirconium alloys are distinguished by two distinct temperature regions. Below about 570 K (300°C) the temperature dependence is weak and Q_{irr} has a value of 20–40 kJ·mol⁻¹. At higher temperatures Q_{irr} increases rapidly to values of 290–370 kJ·mol⁻¹ for T > 623 K (350°C), representing a large contribution from thermal creep. The temperature of transition from weak to strong dependence is a function of the chemical composition, metallurgical state (RXA to CWSR) and the stress. The transition temperature is observed to be lower for pure zirconium compared with zirconium alloys and to decrease with increasing stress and dislocation density [7.13]. The influence of other factors such as flux and texture on the transition temperature is believed to be small, but thorough experimental investigation of this area is lacking and further study is recommended.

Soniak et al. [7.129] have measured the influence of temperature on the in-reactor creep of RXA and CWSR Zircaloy-4 over the range 553–653 K (280–380°C) applicable to LWR fuel cladding. Using internally pressurized tubes, the hoop stress range was 60–120 MPa for both material conditions. The activation energies were found to depend on the neutron flux. In high fast fluxes ((1.68–1.98) × 10¹⁸ n·m⁻²·s⁻¹), Q_{irr} was in the range 35–60 kJ·mol⁻¹, with CWSR having lower values than RXA Zircaloy-4. At lower fluxes ((1.2–1.6) × 10¹⁸ n·m⁻²·s⁻¹) the order was reversed, with CWSR having higher values of Q_{irr} than RXA specimens in the range 35–77 kJ·mol⁻¹. The values measured for Q_{irr} were found to be well below the activation energy of thermal creep (about 125 kJ·mol⁻¹) for unirradiated Zircaloy-4.



FIG. 7.36. Temperature dependence of in-reactor creep of CWSR Zircaloy-2 in short term tests (reprinted with permission from Ref. [7.142], copyright ASTM International, 1969).

7.4.3.7. Irradiation creep in single crystals

MacEwen and Fidleris [7.143] have conducted experiments to measure irradiation creep in a single crystal of pure, crystal bar zirconium. The experiments were carried out in the Petten materials testing reactor in the Netherlands. They were designed to study the climb-glide creep mechanism (see Section 7.4.6.3) and in particular, by their elimination, the role of neutral (i.e. zero bias) grain boundary sinks. Such an experiment also shows whether

the absence of intergranular stresses generated by irradiation growth is important in the creep process. The tests were performed at 573 K (300°C) and a uniaxial stress of 25 MPa with neutron fluxes between $4.8 \times 10^{16} \,\mathrm{n \cdot m^{-2} \cdot s^{-1}}$ and $8.0 \times 10^{16} \,\mathrm{n \cdot m^{-2} \cdot s^{-1}}$ to a fluence exceeding $7 \times 10^{23} \,\mathrm{n \cdot m^{-2} \cdot s^{-1}}$ (E > 1MeV). The specimens exhibited periods of primary creep after which roughly constant secondary creep rates were achieved when the reactor was at power. The creep rate increased in an approximately linear manner with both stress and flux. During reactor shutdown the creep rates decreased rapidly with time, confirming conclusively that irradiation enhanced creep occurs in single crystals. The post-test microstructure consisted of prismatic dislocation loops created by irradiation and cleared channels formed by the passage of glide dislocations on the primary prism plane during the creep process. The clearance of damage was concluded to be the major source of the creep strain rather than the growth of prismatic loops, which are not thought likely to contribute significantly to the steady state creep rate.

7.4.3.8. Irradiation creep by proton bombardment

Energetic particles other than neutrons are also capable of inducing creep strain, provided that atomic displacements occur during irradiation. Parsons and Hoelke [7.53] measured the creep of zirconium alloys from the bending of ion irradiated cantilever beams. Faulkner and McElroy [7.144] used 4 MeV proton bombardment as an irradiation source to measure the stress dependence of primary irradiation creep in crystal bar zirconium, RXA and CWSR Zircaloy-2 and CWSR Zr-2.5Nb at 533 K (280°C). The range of stress was 5–100 MPa and the range of atomic displacement rate was 1.5–3.0 dpa/s. At low stresses < 60 MPa the creep strain rate was observed to increase linearly with the applied stress, while at higher stresses a thermal creep component contributes significantly to the total strain. For materials in the CW state a major fraction of the measured strain (\approx 80%) was due to irradiation growth, even at a stress of 100 MPa. In the early stages of irradiation, a significant portion of the total strain was due to the production of dislocation loops. It was postulated that at higher doses, in CW materials, strain contributions due to the climb (and possibly glide) of network dislocations dominate [7.144].

7.4.4. Metallurgical effects

7.4.4.1. Composition

Elemental zirconium has very low in-reactor creep strength but alloying it with combinations of tin, niobium, molybdenum and oxygen significantly increases creep strength. Chemical composition affects irradiation creep in two ways:

- Solid solution hardening by the main alloying elements oxygen, tin and niobium;
- Heat treatments that lead to the homogeneous nucleation of matrix precipitation [7.145].

The latter effect is most pronounced at higher temperatures. Niobium in solution up to ≈ 0.5 wt% (0.5 at.%) reduces irradiation creep rates by a factor of 2–3 [7.36]. Sulphur also has a marked strengthening effect on the transient creep of zirconium alloy materials, but only if they are in the fully annealed state [7.34]. The strong influence of sulphur appears to be due to the creation of Cottrell-type atmospheres at the core of the network dislocations [7.146].

7.4.4.2. Cold work

Most investigations have dealt only qualitatively with the influence of CW level, or dislocation density, on irradiation creep and are therefore applicable only to a particular material composition and microstructure. At creep test temperatures below that at which thermal recovery commences (about 770 K (500°C)) the general observation for Zircaloy-2 and Zr-2.5Nb is that long term in-reactor creep rates increase with increasing CW [7.42]. An attempt to correlate the in-reactor creep rate with dislocation density was based on the analysis of dimensional changes in CWSR Zircaloy-2 pressure tubes irradiated at 553–555 K (280–282°C) [7.43]. This study yielded a weak dependence of steady state creep rate, $\dot{\varepsilon}$, on dislocation density, ρ , i.e. $\dot{\varepsilon} \propto \rho^{0.16}$. Later analyses of stress relaxation data due to creep [7.147] confirmed this trend and showed the exponent to increase from about 0.2 at 570 K (297°C) to 0.4 at lower temperatures of about 320 K (47°C) (Fig. 7.37). The dislocation density dependence appears to be similar for both Zircaloy-2 and Zr-2.5Nb over the range of test parameters investigated. The creep rate of Zr-2.5Nb was found to increase with dislocation density (as estimated by X ray line broadening) to the power 0.23 [7.148].

7.4.4.3. Grain size

Investigations on the effect of grain size are sparse. Causey's [7.14] in-reactor stress relaxation results at 138 MPa on CWSR Zircaloy-2 and Zr-2.5Nb obtained at 568 K (295°C) in a flux of $2 \times 10^{17} \text{ n} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ showed a weak, positive dependence of creep rate on grain diameter over the range 1–70 µm. This result is similar to the variation of the thermal creep rate of Zircaloy-2 with grain size, under similar conditions of temperature (573 K (300°C)) and stress (138 MPa), in the grain size range 10–70 µm [7.13].

7.4.4.4. Texture and creep anisotropy

In a polycrystalline zirconium alloy specimen or component, the maximum irradiation creep rate is generally observed in the direction perpendicular to the majority of the basal plane normals. This direction is close to the working and major slip directions, which is consistent with the HCP zirconium lattice having minimum shear strength in directions containing the basal plane. The combined effect of a restricted number of HCP slip systems and the resulting texture causes the creep behaviour of almost all zirconium alloys to be anisotropic, unless special efforts have been made during fabrication to randomize the texture (see Section 7.5.2.1).

One manifestation of creep anisotropy is that tubular components such as fuel cladding, with the majority of the basal plane normals in the radial direction, and pressure tubes, with the majority of the basal plane normals in the TD, will have different creep strengths in their diametral and axial directions. These compliances have to be incorporated into design equations used to predict in-reactor deformation (including elongation due to growth) during a component's lifetime. Tests using internally pressurized tubes have been employed to measure irradiation creep anisotropy in Zircaoly-2 cladding [7.125] and in Zr-2.5Nb pressure tube specimens [7.11]. The results of the latter are described in the following subsection (7.4.5).

Creep anisotropy factors can be calculated from the measurements of crystallographic texture, represented by the basal pole figure, for any given creep model. Hill [7.149] proposed a formulation in which the anisotropy constants (F, G, H) are related to the principle stresses and the balance equations then allow the volume conserved creep deformation to be

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determined. The constants can be determined empirically without any assumption about the dominant deformation process. Ross-Ross et al. [7.150] used uniaxial, biaxial and stress relaxation measurements to determine creep anisotropy in CWSR Zircaloy-2 and Zr-2.5Nb alloys. For these materials the values of F, G and H are 0.5, 0.2 and 0.8, respectively. Other approaches [7.51] allow for a transition in dominant mechanisms during irradiation to account for the suppression of thermal creep (due to dislocation glide) caused by irradiation hardening. The degree of retained CW and the nature of the dislocation network can have a large effect on creep and may override the effects due to texture [7.42].



FIG. 7.37. Influence of dislocation density on irradiation creep rates: (a) Zr-2.5Nb at 570 K (297°C) (reprinted with permission from Ref. [7.148], copyright ASTM International, 1984); (b) Zircaloy-2 at 533–555 K (260–282°C) (reprinted with permission from Ref. [7.43], copyright Elsevier, 1979); and (c) Zircaloy-2 at 320 K (47°C) [7.147].

7.4.5. Irradiation creep of Zr-Nb alloys

7.4.5.1. M5

M5 is a nominal Zr-1Nb alloy used in the RXA condition. It also contains about 0.12 wt% (≈ 0.68 at.%) oxygen and about 20 ppm (0.0057 at.%) sulphur. Both of these alloying additions have the effect of increasing the creep strength of the material. The in-reactor diametral creep strength of M5 fuel cladding is about 20% greater than CWSR Zircaloy-4 for normal operating levels of hoop stress (between 60 and 90 MPa) in a PWR [7.57]. Figure 7.38 shows data comparing M5 with both stress relieved annealed (i.e. CWSR) Zircaloy-4 and recrystallized Zircaloy-4 at 623 K (350°C). Also included are measurements on the material M4, a Zr-0.5Sn-0.6Fe-0.4V-0.13 alloy in the RXA final state. Note that similar creep behaviour is observed for all the materials in the RXA condition, with no evidence to date that the creep rate of M5 increases at high fast neutron fluences. M5 has a high resistance to the formation of *c* component dislocations.



FIG. 7.38. Diametral irradiation creep of M5 cladding tubes at 623 K (350°C) and 90 MPa compared with Zircaloy-4 (reprinted with permission from Ref. [7.57], copyright ASTM International, 2000).

7.4.5.2. E110

E110 is a nominal Zr-1Nb alloy, containing between 0.06 and 0.08 wt% oxygen (≈ 0.34 and 0.46 at.%), and is used in the RXA condition as a fuel cladding material in reactors designed in the Russian Federation. The in-reactor creep strength of E110 is greater than CWSR Zircaloy-4 up to fast neutron fluences of about $5 \times 10^{25} \text{ n} \cdot \text{m}^{-2}$ (E > 0.1 MeV) or 10 dpa, after which the creep rate increases significantly (Fig. 7.39). The cause of the increase is related to the early formation of *c* component dislocations under fast neutron irradiation, which modify the creep process by increasing dislocation climb [7.151]. One of the differences between the performance of E110 and M5 appears to be linked to the ease of forming *c* component dislocations, although a convincing metallurgical explanation for the divergence in creep performance, based on composition or microstructure, is not yet available.



FIG. 7.39. Irradiation creep strain (%) of E110 compared with Zircaloy-4 as a function of fast fluence (reprinted with permission from Ref. [7.151], copyright ASTM International, 2000).

7.4.5.3. E635

E635 is a Russian Federation quaternary Zr-1Nb-1.2Sn-0.4Fe alloy used in the RXA final condition. As shown in Fig. 7.40, the in-reactor creep strength of E635 is significantly greater than E110 at fast fluences greater than about $5 \times 10^{25} \text{ n} \cdot \text{m}^{-2}$ (E > 0.1 MeV) [7.61]. This additional creep strength compared with E110 may be partly due to the strengthening effect of the tin but also to the intrinsic resistance of E635 — the nucleation of $\langle c \rangle$ component dislocations during irradiation damage.



FIG. 7.40. Irradiation creep of E635 compared with E110 as a function of fast neutron fluence (reprinted with permission from Ref. [7.61], Springer, 1996).

7.4.5.4. ZIRLO

ZIRLO is a quaternary Zr-1Nb1Sn0.1Fe alloy used in the CWSR condition. Based on steady state creepdown data on fuel rods irradiated for a single 18 month cycle [7.152], the irradiation creep strength of ZIRLO is around 20% greater than that of standard CWSR Zircaloy-4 (Fig. 7.41). The influence of niobium, working in conjunction with tin and oxygen, appears to be responsible for this extra creep strength. As with E635, ZIRLO appears to be resistant to the nucleation of c component dislocations.



FIG. 7.41. Irradiation creepdown of ZIRLO clad fuel rods compared with CWSR Zircaloy-4 (reprinted with permission from Ref. [7.152], copyright ASTM International, 1994).

7.4.5.5. Zr-2.5Nb

Zr-2.5Nb alloy is used as a pressure tube material in the CWSR condition in CANDU reactors. It is also used in the quenched and aged condition in KANUPP, Fugen, Ignalina (RBMK) and in the annealed condition in another RBMK in the Russian Federation.

The standard CANDU pressure tube has a texture in which the majority of the basal poles are in the transverse (circumferential) direction in the radial-transverse plane, and this together with the dislocation microstructure and grain structure causes the irradiation creep behaviour to be strongly anisotropic. Since both stress relaxation and uniaxial test results are available, the irradiation creep of Zr-2.5Nb tubes has been characterized in two ways:

- Measurement and then modelling of the in-reactor deformation of CANDU pressure tubes [7.58];
- Creep measurements on internally pressurized capsules, manufactured by the same process, irradiated in a materials testing reactor [7.59].

The axial and transverse (diametral) irradiation creep strains, after allowing for irradiation growth, are linear with fast fluence but the magnitude is strongly influenced by texture [7.11]. Figure 7.42 shows the irradiation induced component of creep for micropressure tubes and fuel sheathing. In the case of micropressure tube material, both transverse and axial creep rates are positive with an anisotropy ratio of axial-to-transverse of about 0.7. However, the diametral creep rate is approximately half that of the fuel sheathing textured material with basal poles predominantly in the radial direction. Compared with

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CWSR Zircaloy-4, the diametral creep strength of Zr-2.5Nb pressure tubing is greater by a factor of around three. Holt [7.65] has reviewed the in-reactor deformation of CW Zr-2.5Nb pressure tubes, including the influence of texture and anisotropy, on irradiation creep.

The irradiation creep of Zr-2.5Nb is linear in stress at power reactor conditions. Christodoulou et al. [7.58] have proposed a mechanism based on climb-assisted glide of a and (a + c) type dislocations operating on prismatic, basal and pyramidal planes. However, Griffiths et al. [7.46] point out that such a mechanism is not consistent with the observed weak but negative correlation between grain size and the diametral creep of Zr-2.5Nb pressure tubes. Also, (a + c) dislocations are primarily screw-type, and either cannot be assisted by climb or are bound in sessile junctions in the CW state of the alloy.



FIG. 7.42. Transverse and axial irradiation creep for two different textured Zr-2.5Nb tubes (fuel sheathing and micropressure tubes) for a hoop stress of 160 MPa irradiated at 553 K (280°C) and 583 K (310°C) (reprinted with permission from Ref. [7.11], copyright Elsevier, 2003).

7.4.6. Theories and models of irradiation creep

Many different mechanisms have been proposed since the late 1950s to attempt to explain the various experimental observations of irradiation creep behaviour and to provide a sound theoretical foundation. Many of these ideas were also discarded when they failed to provide adequate agreement between prediction and measurement, or when new data confounded earlier promise. An exact mechanism in which all modelling terms are physically defined is not available. Also, more than one process may operate concurrently as well as over the entire range of stress, temperature, flux and material variables of interest. However, several useful and valid theoretical approaches have gradually led to a position whereby irradiation creep can at least be understood in terms of the irradiation generated PDs and by modelling their anisotropic diffusional properties to biased sinks. Several useful and comprehensive reviews of the various irradiation creep mechanisms have been written; for an historical account of the theoretical developments see Refs [7.53, 7.82, 7.153–7.155].

Irradiation creep theories can be categorized [7.82] as either irradiation enhanced thermal creep mechanisms that promote an acceleration of normal thermal creep (of irradiated material), or irradiation induced mechanisms that operate in addition to thermal creep. In the latter case the total in-reactor creep is a superposition of both mechanisms. Although irradiation creep theories for HCP zirconium alloys and cubic stainless steels initially developed in parallel, some of the general conclusions related to irradiation damage analysis in the presence of a stress (for example, rate theory [7.156] and radiation enhanced climb-glide [7.157]) are applicable to both material systems. Four mechanisms are briefly

described that have been milestones in the development of an understanding of irradiation creep. Stress induced preferred nucleation (SIPN) of dislocation loops and stress induced preferred absorption (SIPA) of PDs are irradiation induced mechanisms that do not have a thermal creep counterpart. Climb-glide of dislocations is an irradiation enhanced process applied to a thermal creep mechanism. DAD has been linked with dislocation and grain boundary sink distributions to provide a powerful driving force for irradiation creep.

7.4.6.1. Stress induced preferred nucleation

The SIPN mechanism assumes that the existence of a tensile stress in the material will favour the nucleation of faulted interstitial dislocation loops onto planes that are normal (or close to normal) to the direction of the applied stress. The loops formed from the irradiation produced self-interstitials will bias the mass flow of atoms to planes perpendicular to the stress and generate a net elongation (i.e. creep strain) parallel to the stress direction, as shown schematically in Fig. 7.43. At the same time, vacancy loop nucleation may preferentially occur on planes parallel to the stress or vacancies may diffuse to grain boundary sinks. Voids as potential sinks do not generally form in zirconium under neutron irradiation. It was originally supposed [7.156] that SIPN would resemble irradiation growth in that after preferential nucleation by stress the aligned dislocation loops would continue to grow and generate strain in the absence of an applied stress. This conclusion was refuted by the observation that when the stress was removed the loops unfaulted [7.158], the anisotropic growth strain was transient, and that SIPN required a continuously applied stress to operate as a creep mechanism.

The SIPN irradiation creep rate, $\dot{\epsilon}_{irr}$ (SIPN) is given by [7.82, 7.158]:

$$\dot{\varepsilon}_{\rm irr}({\rm SIPN}) = N_1 b^2 \Omega \beta_{\rm i,v} \tag{7.19}$$

where

- N_1 is the number density of loops growing perpendicular to the direction of the applied stress at a given time;
- *b* is the Burgers vector;

 Ω is the atomic volume;

and $\beta_{i,v}$ is the difference in the net currents of interstitials and vacancies arriving at the loop perimeter.

 N_1 is a function of the fast neutron flux and the value of the stress normal to the loop plane. N_1 depends exponentially on the temperature via the total density of loops in the Zr grain. $\beta_{i,v}$ is also a function of flux and temperature. N_1 and $\beta_{i,v}$ are determined from coupled rate equations describing PD generation and diffusion to sinks.

The predictions of the SIPN theory [7.82] indicate that the mechanism could contribute significant irradiation creep strain only in the intermediate temperature regime (533 < T < 823 K (250 ≤ T ≤ 550°C)). At lower temperatures, <523 K (<250°C), the loop density is high but the PD currents are small because recombination dominates; at high temperatures (>823 K (>550°C)), the loop density is small owing to thermal recovery and $\beta_{i,v}$ is low because of the high rate of PD annealing. Creep due to SIPN is a linear function of stress at low stresses but depends strongly on the flux. The temperature dependence is weak.



FIG. 7.43. Schematic representation of irradiation induced creep by SIPN (reprinted with permission from Ref. [7.82], copyright ASTM International, 1983).

7.4.6.2. SIPA

SIPA creep is distinct from SIPN creep because the growth rather than the nucleation of dislocation loops is biased by the applied tensile stress. A process based on preferred absorption was first proposed by Heald and Speight [7.159] and independently shortly afterwards by Wolfer and Ashkin [7.160] to explain irradiation creep in austenitic stainless steels. MacEwen and Fidleris [7.161] subsequently applied this mechanism to zirconium alloys. Self-interstitial atoms are preferentially absorbed at dislocation loops that have their Burgers vectors aligned with the stress direction. A net deposition of interstitials causes the dislocation to climb and results in a positive creep strain parallel to an applied tensile stress. It follows that Burgers vectors aligned with a compressive stress experience a net flux of vacancies. The biased flux of PDs in SIPA was attributed to the different elastic interactions of interstitials and vacancies, treated as inclusions in the matrix, with the strain fields of the dislocations in a stress field. In CWSR materials the preferential absorption at irradiation generated loops is augmented by the preferential absorption of interstitials at edge dislocations with Burgers vectors parallel to the applied stress. The latter causes the dislocations to climb, again resulting in material elongation in a direction parallel to the stress.

To a first approximation the SIPA irradiation creep rate, $\dot{\epsilon}_{irr}$ (SIPA), is given by [7.82]:

$$\dot{\varepsilon}_{\rm irr}({\rm SIPA}) = N_1 b_1^2 \Omega \beta_{\rm i,v}^l + N_d b_d^2 \Omega \beta_{\rm i,v}^d$$
(7.20)

where

 N_1 is the density of dislocation loops (respectively, perpendicular to the applied stress);

 $N_{\rm d}$ is the density of edge dislocation (respectively, perpendicular to the applied stress);

 b_1 is the Burgers vector of the dislocation loops;

- $b_{\rm d}$ is the Burgers vector of the edge dislocations;
- Ω is the atomic volume;
- $\beta_{i,v}^{l}$ is the difference in the currents of interstitials and vacancies arriving at the dislocation loops;

and $\beta_{i,v}^d$ is the difference in the currents of interstitials and vacancies arriving at the edge dislocations.

For a steady state microstructure the edge dislocation and dislocation loop densities are largely governed by the irradiation conditions of flux and temperature, not by stress as in the case of SIPN. The $\beta_{i,v}$ terms are exponential functions of the applied stress. At low stresses $\dot{\varepsilon}_{irr}$ (SIPA) is linear with stress and weakly dependent on temperature, in broad agreement with observation. The SIPA model does not explicitly include grain boundary sinks or texture.

7.4.6.3. Climb-glide

The climb-glide mechanism assumes that the climb of edge dislocations is enhanced during irradiation by the absorption of radiation produced PDs. It is an extension of Weertman's dislocation creep model for thermal creep [7.162]. Creep strain is produced by the subsequent glide of dislocations, in response to an applied stress, after they have surmounted an obstacle by climbing. Obstacles may include precipitates, depleted zones and PD clusters as well as dislocations themselves, all of which can pin dislocations. Nichols [7.139] first published such a mechanism for the irradiation creep of zirconium alloys and proposed a form of the creep rate, $\dot{\varepsilon}_{irr}$ (C–G), given by:

$$\dot{\varepsilon}_{\rm irr} = (C - G) = A\sigma^4 \varphi \cdot \exp(-Q_{\rm irr}/RT)$$
(7.21)

where

 σ is the applied tensile stress; φ is the fast flux; Q_{irr} is the activation energy of in-reactor creep;Tis the absolute temperature;

and A is the material constant.

Subsequent descriptions for the creep rate due to climb-glide became much more complicated than this relatively simple expression [7.163, 7.164], and in the case of Ref. [7.163], combined climb-glide and SIPA.

Nichols's original work [7.139] left open the question of whether irradiation truly enhanced thermal creep, because interstitials and vacancies are produced in equal numbers and their contributions to climb may cancel out. This question was subsequently resolved satisfactorily by Lewthwaite [7.165] and confirmed in a detailed analysis by Duffin and Nichols [7.166]. Lewthwaite [7.165] argued that thermal creep due to climb-controlled glide is expressed by:

$$\dot{\varepsilon}_{\rm th} = KV_{\rm a} + KV_{e^{\rm th}} \tag{7.22}$$

where

 V_a is the climb velocity due to thermal equilibrium vacancy absorption; V_e is the climb velocity due to thermal equilibrium vacancy emission;

and K is a constant.

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The first term is the creep strain contribution due to dislocations climbing over obstacles and the second term to dislocations climbing under obstacles. Under irradiation, the self-interstitials are more widely dispersed than the vacancies, and because of their larger strain fields they are preferentially attracted to dislocations and thereby produce a net flux, *J*, over vacancies. The climb velocity due to these interstitials is Jb^2 , where *b* is the Burgers vector. At low fluxes $Jb^2 < V_a$ and the dislocation climb velocity over obstacles $(V_a - Jb^2)$ is slowed. However, the dislocation climb velocity under obstacles $(V_e + Jb^2)$ is equally enhanced, so that:

$$\dot{\varepsilon}_{irr} = K(V_e + Jb^2) + K(V_a - Jb^2) = \dot{\varepsilon}_{th}$$
(7.23)

and there is no enhancement of creep. At high fluxes $Jb^2 > V_a$, the irradiation creep rate becomes:

$$\dot{\varepsilon}_{\rm irr} = K(V_{\rm e} + Jb^2) + K(Jb^2 - V_{\rm a}) = 2KJb^2 > \dot{\varepsilon}_{\rm th}$$
(7.24)

and there is an enhancement of the climb-controlled creep rate process. A bias in the arrival rates of interstitials over vacancies of about 0.5% is sufficient to match the magnitude of the irradiation creep rates that are observed in zirconium alloys.

Comparisons with experimental measurements [7.161, 7.167] provide support for a climb-glide model of irradiation creep. The model predicts a weaker dependence on stress than thermal creep, in agreement with observation, and a time dependence for the creep strain that is consistent with experimental measurements. Climb-glide does not preclude another mechanism such as SIPA or SIPN operating simultaneously to stimulate the climb of edge dislocations over obstacles. A modification of the climb-glide mechanism is Gittus's I-creep model [7.168], in which there is coordinated movement of arrays of dislocations by glide following climb.

7.4.6.4. Anisotropic PD diffusion

Woo [7.169] pointed out that one of the most important mechanisms contributing to the irradiation induced deformation of reactor materials is caused by the DAD of vacancies and interstitials generated by displacement irradiation damage. As previously discussed in connection with irradiation growth (see Section 7.2.9.3), intrinsic anisotropic diffusion due to the crystallographic anisotropy of zirconium produces a large difference in the annihilation rates of PDs at sinks, creating a strong sink bias. DAD can also be induced in all metals by stress, resulting in either SIPA or climb-glide creep mechanisms, as previously described. Hexagonal metals such as zirconium allow the simultaneous presence of intrinsic and stress induced DAD, with the latter producing irradiation creep strain. The geometric complexity of the HCP crystal structure makes the creep analysis considerably more complicated than for cubic metals, although Woo et al. [7.170, 7.171] have made some promising progress in this direction.

In papers on measurement and methods of analysis of irradiation creep in non-cubic metals, Woo et al. [7.41, 7.70, 7.170] show that the internal stresses generated by the anisotropic creep of individual grains must be taken into account to interpret correctly the creep of polycrystalline zirconium samples. A self-consistent analytical model was developed that relates the steady state irradiation creep of single crystals to that of polycrystals. The model also demonstrated that the creep rate is sensitive to the details of the dislocation structure, for either SIPA or climb-glide creep. This sensitivity arises as a direct

consequence of the partitioning of PDs among dislocations with different line directions resulting from the DAD effect [7.10]. It is shown that if irradiation creep strain is due to dislocation glide, a non-zero creep rate requires that the pyramidal or basal slip systems be operative in addition to the easier prismatic slip system. Experimental evidence does not seem to support this process because of the sessile nature of the (a + c) dislocations [7.29]. A further outcome of the analysis is that the generation of $\langle c \rangle$ component dislocation loops by irradiation is the cause of acceleration in irradiation creep and growth rates. Causey et al. [7.132] and Holt et al. [7.16] have confirmed this association experimentally. Because $\langle c \rangle$ component loops are faulted they are not able to glide, leading to the speculation that irradiation creep may be due to a dislocation climb process such as SIPA, rather than climb-glide.

Woo and So [7.171] have analysed the rate of irradiation creep due to dislocation climb produced by DAD for the case of an internally pressurized Zr-2.5Nb tube. The mechanism is essentially SIPA, assuming anisotropic PD diffusion and a dislocation microstructure consisting of *a* type dislocation loops on the prism planes, <c> component loops on the basal planes and <c> component network dislocations on the basal plane. The results demonstrated that diffusional anisotropy is very sensitive to the interatomic potential for interstitial and vacancy movement in the HCP lattice. Thus, to obtain a meaningful prediction of irradiation induced creep due to SIPA DAD, an accurate interatomic potential is required. Tomé and Christodoulou [7.172] have demonstrated that a satisfactory potential does exist and using it have succeeded in predicting accurately the in-reactor behaviour of Zr-2.5Nb pressure tubes. One qualitative conclusion reached by Woo and So [7.171] is that the hydrostatic component of the applied generalized stress can contribute to the creep strain, in addition to the usual, but dominant, prismatic shear stress components.

7.4.6.5. Anisotropic dislocation structures

As can be seen from the preceding descriptions, dislocations play a central role in governing the interactions that lead to macroscopic creep and its interrelationship with other effects of irradiation. Both the irradiation damage and the applied load drive dislocation multiplication. In hexagonal metals such as zirconium, anisotropy is present at the level of the individual grain and as Woo [7.41] has shown, creep in a polycrystalline material is not a simple orientational average of single crystal creep. Matthews and Finnis [7.155] have pointed out that even symmetric rate equations commonly have asymmetric solutions if the equations are non-linear — a phenomenon known as bifurcation theory — so it is therefore not surprising that the dislocation structure develops anisotropic characteristics. The contribution to irradiation deformation due to the development of an anisotropic dislocation structure induced by an applied stress was suggested by Woo [7.173, 7.174] and applied to irradiation creep of 316 stainless steel by Woo et al. [7.175]. Following the success of this application, this mechanism may also be an important creep component of irradiation deformation has yet to be confirmed.

The results from many experimental programmes have incontrovertibly verified the anisotropy of irradiation creep (see Section 7.4.4.4). With the exception of the highly irradiated state, most dislocations in zirconium have Burgers vectors in an a direction $\langle 11\overline{2}0 \rangle$, of which there are three classes at 60° to one another. The dislocation density distribution between the classes is a function of the angle between the applied stress and the Burgers vectors. The observations of irradiation creep in textured Zircaloy are consistent with slip by $\langle 11\overline{2}0 \rangle$ edge dislocations. The suggestion [7.176] that some degree of cross-slip from prism

to basal planes is also required cannot be applied to irradiation creep. This restriction is because cross-slip involves screw dislocations and any irradiation enhanced climb would be out of the glide plane, thus inhibiting any subsequent glide.

7.4.7. Summary

The popular view is that deformation during irradiation can be separated into three, additive components:

- Thermal creep;
- Irradiation growth;
- Irradiation creep.

This approach has been used historically to model the in-reactor deformation of zirconium alloy components. These models are restrictive because they are forced to apply at conditions well removed from the conditions of chief interest (i.e. in the reactor core where components are subject to high stress and high fluxes). Typically, models of deformation during irradiation are simple linear equations in flux and stress and do not adequately capture the complex transition from thermal creep to irradiation creep or irradiation growth to irradiation creep. Representing deformation as the sum of three additive components is a simplification that assists in model development. It may mislead readers into thinking that this mathematical expediency represents reality, so the following points are relevant:

- Thermal creep tests on irradiated materials out-of-reactor do not translate into the same behaviour in-reactor. Some of the same mechanisms may still operate, but at a reduced level, because of the radiation hardening effects. Radiation damage is effective in inhibiting glide.
- Irradiation growth and creep are not physically separable on a mechanistic basis. Creep deformation becomes growth in the limit of zero stress but individual PDs do not behave according to separate creep or growth laws (i.e. a PD does not know that it should provide a contribution to growth or creep). For zirconium alloys, one can suppose that the intrinsic deformation anisotropy that exists at zero stress (i.e. growth) is modified by an applied stress so that a stress induced anisotropy dominates at high stresses. This continuum approach is embodied in the theories based on DAD proposed by Woo et al. [7.173–7.175].
- A dominant climb and glide mechanism is only one possible explanation to account for the majority of irradiation creep in zirconium alloys. Although a small component of glide may contribute to creep it is likely that mass transport by diffusion dominates the creep strain process. Unlike irradiation growth, there is no consensus regarding the mechanism producing irradiation creep strain other than that it is related to net fluxes of PDs to sinks.

7.5. TECHNOLOGICAL CONSEQUENCES AND REMEDIES OF DIMENSIONAL CHANGES

Many of the components constituting the fuel assembly structures and containers used in the world's reactors moderated with light or heavy water or graphite are made from alloys of zirconium. As a consequence of the in-reactor environment of fast neutron irradiation, high temperature and stress, these components exhibit growth and creep deformation. Problems caused by irradiation induced deformation, and their solution, are described below.

7.5.1. Light water moderated reactors

7.5.1.1. Elongation

A common phenomenon, which is routinely detected by post-irradiation examination measurements, is fuel rod elongation (or axial growth) that is a result of up to four contributions:

- Stress-free irradiation growth;
- Anisotropic irradiation creep in the axial direction during creepdown of the cladding onto the fuel;
- Hydrogen pick-up from the corrosion reaction, leading to hydride precipitation with an associated volume increase (≈15%), a component of which produces elongation of zirconium alloy components [7.177, 7.178];
- Mechanical interaction between the fuel pellets and the cladding wall following gap closure.

The anisotropic creep strain, driven by the net external overpressure on the fuel rod, depends on the texture of the CW tube (i.e. on the relationship of f_t to f_t (see Section 7.2.1.1)). If $f_r > f_t$, creepdown of the cladding causes an increase in length that is additional to that due to stress-free growth. For a typical PWR fuel rod and cladding texture, the (positive) axial strain rate is about 20% of the (negative) diametral strain rate due to anisotropic creep [7.125].

Fuel rods with CWSR Zircaloy-4 cladding operating in PWRs generally elongate about 1% after a burnup of about 40 GW \cdot day \cdot t⁻¹U, whereas BWR fuel rods clad in RXA Zircaloy-2 material elongate by less than 0.5% at the same equivalent exposure. The breakaway growth observed in some RXA Zircaloy could reduce this difference between PWR and BWR rods as burnup is extended to higher values. Design and operating limits are met when the shoulder gaps between the fuel rod end-caps and the top and bottom fuel assembly end-fittings are exhausted, resulting eventually in rod bow if irradiation is continued. Alternative zirconium materials that contain niobium, which are used especially in PWR fuel assemblies, have greater resistance to irradiation growth and creep than Zircaloy and this improvement reduces rod elongation by up to 50%.

Elongation due to stress-free growth also occurs in PWR guide tubes, causing bowing of the fuel assemblies. The elongation can be mitigated to a large degree by replacing Zircaloy-4 with a low growth alloy material (e.g. M5 or ZIRLO).

7.5.2. BWRs

7.5.2.1. Fuel channels

BWR fuel channels operate at an internal pressure that causes outward loading of the walls. This loading induces an irradiation creep strain that manifests itself as a deformation termed bulge. Since the pressure differential, ΔP , across the channel wall is not affected by the deformation, the total bulge increases with irradiation fluence. The size of the bulge depends on channel wall thickness, material state, ΔP , operating conditions (neutron flux, temperature) and residence time. Bulge values are typically 1–2 mm for an exposure $> 2 \times 10^{26} \text{ n} \cdot \text{m}^{-2}$ (E > 1 MeV) (40 dpa), equivalent to a fuel burnup range of 40–60 GW day t⁻¹ U. Although ΔP is a maximum at the bottom of the assembly and zero at the top, a typical axial bulge profile shows the maximum deformation at approximately one third of the channel length from the bottom of the assembly. The location of the maximum is

due to the combined effects of both ΔP and neutron flux. The bulge is zero at the top of the channel.

Another important in-reactor deformation is bow caused by irradiation growth of the channel walls. As a result of radial neutron flux gradients across fuel assemblies in the core, the fluence accumulated by the channel walls has an asymmetrical planar distribution. Since irradiation growth depends on both material properties and fluence, channels tend to bow to accommodate the resulting uneven growth. Small variations in heat treatment, material composition or crystallographic texture accentuate differential growth and bow. In addition to bow, there is also an overall increase in channel length due to irradiation growth of the whole channel. The magnitude of growth and bow of channels is sensitive to core location and channel orientation. Typical values are: (a) growth strain of about 0.25% (\cong 10–16 mm increase in length for a BWR channel) at 60 GW·day·t⁻¹U fuel burnup; and (b) channel bow of 2–10 mm at 50 GW·day·t⁻¹U.

Both bulge and bow can, if excessive, lead to interference with the free vertical movement of the control blade that is external, but adjacent to, two walls of the channel. Although the control rod drive mechanism exerts a sufficiently high force to displace the channel walls laterally during an emergency reactor shutdown, it nevertheless contributes to an operational problem whereby the control blade cannot settle at a predetermined location. Since control blades are withdrawn under their own weight, slow withdrawal may occur in some fuel cells experiencing large bow and bulge. If a stuck blade cannot be withdrawn, normal reactor operations must be interrupted to remedy the problem. In an extreme case channel bow can also lead to fuel failure due to localized 'dryout' of the coolant. In this situation an excessive channel bow increases the water gap between adjacent fuel assemblies, resulting in higher neutron moderation and a rise in linear power. The localized heating causes a loss of coolability and potential dryout on the fuel cladding surface.

Channels manufactured with a randomized texture (by β quenching at their final dimension) significantly reduce the problems caused by irradiation growth and bow [7.179].

With this texture, the cumulative effect of irradiation growth in each zirconium grain is minimized in the bulk material. The main benefit of β quenching compared with standard Zircaloy-4 and Zircaloy-2 is much smaller channel elongation (Fig. 7.44). The majority of the elongation is due to irradiation growth but there may be a minor contribution from hydrogen uptake. As a result, differential growth across the β quenched channel, causing bow, is smaller than for standard channels (Fig. 7.45). A comparison of average maximum values of channel growth and bow for different materials (at an exposure equivalent to 45 GW·day·t⁻¹ U fuel burnup) is given in Table 7.2. Channel bulge due to creep is similar for all materials in the recrystallized condition.

	Zircaloy-4	Zircaloy-2	Late β quenched Zircaloy-2
Growth (mm)	12	7	3.5
Bow (mm)	6	4	2

TABLE 7.2. AVERAGE MAXIMUM VALUES OF GROWTH AND BOW FOR DIFFERENT BWR CHANNEL MATERIALS [7.179]

The heat treatment to produce a randomized texture requires heating the material into the stable body centred cubic (BCC) β phase above 1253 K (980°C) followed by quenching [7.179]. Quenching from the β phase back to the α phase produces a rapid phase transformation and the formation of α lamellae that nucleate either at impurities or at prior β grain boundaries. An α lamella has three orthogonal directions, all equally preferred, in which it can grow during the phase transformation. This lack of preference during phase nucleation produces the typical needle-like 'basket-weave' microstructure characteristic of β quenched zirconium alloy material. The important point is that, as a result of the phase transformation, the α grain orientations are random (i.e. there is no alignment or texture). As subsequent CW in the α phase would reintroduce a texture, it is clear that the practical elimination of irradiation growth by means of a β quenching stage can only be done after all CW has been completed (i.e. at the final dimensions of the sheet materials used to make channel boxes).

A perfectly randomized texture would result in all Kearns basal pole factors being equal to 0.33. Since the relationship between growth strain (ε_x) and texture (f_n) in the direction n is $\varepsilon_n \propto 1-1/3f_n$, a randomized texture (all $f_n = 0.33$) produces no preferential growth in any direction. In practice, channel wall material β quenched in its final dimensions is not perfectly randomized but has minor deviations (e.g. $f_r = 0.35$, $f_t = 0.38$, $f_a = 0.27$) [7.179]. With this texture, growth and bow are much reduced compared with conventionally produced BWR channel boxes.



FIG. 7.44. BWR channel growth as a function of fuel assembly average burnup: comparison of different channel materials (reprinted with permission from Ref. [7.179], copyright ASTM International, 2005).



FIG. 7.45. Channel bow as a function of fuel assembly average burnup: comparison of different channel materials (reprinted with permission from Ref. [7.179], copyright ASTM International, 2005).

7.5.3. PWRs

7.5.3.1. Interaction between spacer grids and fuel rods

Fretting wear of PWR fuel cladding can occur when a gap opens up between the retaining springs of a spacer grid and the fuel rod located at the centre of the grid cell. The fretting is induced by turbulence in the coolant flow setting up resonant vibrations in the fuel assembly [7.180]. Open gaps are often due to the enlargement of the cell dimensions caused by irradiation growth, combined with a decrease of the rod diameter by irradiation induced creepdown. A contributing factor is the stress relaxation due to irradiation creep of the grid spring force on the rod surface. Grid–rod fretting has posed a serious problem in some PWRs, causing many fuel rods to leak [7.181].

An innovative design for PWR fuel assembly exploits irradiation growth to counteract the tendency to open up gaps by using 'I-springs' developed by Garde et al. [7.182]. The concept was first demonstrated using a prototype material for the spring made from a specially selected zirconium alloy composition that enhanced early breakaway growth under irradiation. The spring material was in the CWSR condition to maximize the growth rate towards the centre of the cell and maintain a contact force on the fuel rod. The spacer strip material in the cell walls is a zirconium alloy in the RXA condition with a low irradiation growth rate. The prototype spring was made from the experimental alloy Zr-0.5Sn-0.4Fe-0.22O containing Fe-bearing SPPs that are more unstable under irradiation than the Laves-phase SPPs common to Zircaloy-4. Irradiation induced iron depletion occurs during early dissolution of the SPPs; it is proposed that the freely diffusing Fe atoms enhance growth by assisting in the nucleation of $\langle c \rangle$ oriented vacancy dislocation loops, as discussed in Section 7.2.5.1. Controlled dissolution of the Fe-rich SPPs can be achieved by regulating the initial amount of CW in the spring material [7.182]. The increase in spring stiffness due to radiation damage is also beneficial in restraining the rod.

Hot cell examinations of candidate grid cell alloys after irradiation verified that the SPPs in the mildly CW Zr-Sn-Fe-O alloy were the least stable, with most of the SPPs dissolved after one 24 month cycle. The growth of this alloy is also most sensitive to the amount of CW. This behaviour correlated well with the measured growth strains after two cycles, shown in Fig. 7.46, as a function of initial CW. The Zr-Sn-Fe-O alloy also had excellent corrosion resistance as well as low fractional hydrogen pick-up, both of which are necessary qualities for a PWR grid. The I-spring concept has been employed in several different fuel assembly designs, using Zircaloy-4 or ZIRLO for the spring material. It has proved successful in combating the problem of grid–rod fretting.



FIG. 7.46. I-spring growth strain after two cycle irradiations as a function of initial CW level, for different strip materials [7.182].

7.5.3.2. Fuel assembly bowing

PWR fuel assemblies are subject to a vertical loading imposed by a top spring to offset the upward thrust of the coolant. As a result, the guide tubes that provide much of the structural strength and rigidity to the assembly are susceptible to creep under a compressive stress. Elongation of the guide tubes due to irradiation growth tends to increase the loading. The first generation PWR fuel assembly designs were robust and deformation in the form of excessive bowing was successfully resisted by the overall high rigidity of the structure. The gradual reduction of the tin concentration in Zircaloy-4 tubing, commencing in the early 1990s to improve the corrosion resistance of fuel cladding and guide thimbles, also reduced their creep strength. This weakening was exacerbated in some instances by a reduction in

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structural rigidity due to changes to spacer grid designs to achieve improved thermal efficiency. The net result was that some PWR fuel assemblies bowed due to creep to an extent that interfered with the free insertion of the control rods into their respective guide tubes (thimbles) and subsequently into the dashpot located at the bottom of the control rod assembly. A condition termed 'incomplete rod insertion' affected some reactors and fuel and control assembly designs to the extent that many of the fuel assemblies in the core became bowed [7.183]. The deformed profiles of the assemblies were either a simple C-shape bow or a more complex S- or W-shape.

This deformation has serious consequences for reactor operations and capacity factors due to the increased frictional resistance encountered by the control assembly mechanism, causing increased control rod insertion times that threatened the technical specification limits for allowed reactor operation [7.184]. Safety regulations necessitated increased testing and early shutdown of the reactor in some instances. The remedies introduced to rectify the problem have followed two parallel routes: (a) mechanical design changes to strengthen the guide thimbles (including the dashpot); and (b) the use of other zirconium alloys, generally containing niobium (e.g. M5 and ZIRLO), that have increased the resistance of the guide tubes to creep in bending and compression. These remedies have been successful in correcting an existing bowed core and in preventing its reoccurrence. The use of Zr-Nb alloys, particularly in highly rated reactors, is at the focus of designs to increase discharge burnups in PWR fuel assemblies.

7.5.4. WWER-1000 fuel assembly

The first generation WWER-1000 (WWER stands for water cooled water moderated power reactor) fuel assembly design suffered from bowing problems caused by the combined effects of non-uniform fuel rod growth and an axial compressive force on the assemblies [7.185]. The bowing led to control rod drop times that were in excess of design values, therefore having safety implications.

New WWER-1000 fuel assembly designs with greater rigidity and resistance to bowing have been developed in the Russian Federation. The high stability TVSA design has a structural skeleton made from E635 zirconium alloy [7.186]. The main features of the TVSA design (also known as the alternative fuel assembly) are shown in Fig. 7.47. Emphasis is placed on enhanced dimensional stability provided by:

- A load bearing skeleton formed by six rigid angle pieces welded to the zirconium alloy E110 spacer grids.
- The use of E635 zirconium alloy for the angle pieces and the guide channels. E635 has a greater creep strength and resistance to irradiation induced hardening than E110.

The gradual replacement of original, bowed fuel assemblies in the Kalinin-1 nuclear power plant by TVSA assemblies resulted in the rectification of the deformed core [7.186]. Results from a test programme in which the TVSA assemblies were measured after each of four 12-month reload campaigns confirmed that after four years the maximum bow reduced from 21 mm to ≤ 5 mm (Fig. 7.48). Also, the maximum radial clearance between assemblies in the active core was reduced to < 5 mm.


FIG. 7.47. The advanced TVSA fuel assembly design for WWER-1000 reactors [7.186].



FIG. 7.48. Change in maximum fuel assembly bowing and interassembly clearance with annual fuel loading campaign in Kalinin-1 nuclear power plant [7.186].

7.5.5. CANDU pressure and calandria tubes

In the CANDU reactor the horizontal pressure tubes perform the function of a pressure vessel. A simplified illustration of a fuel channel is shown in Fig. 7.49. They are typically 6 m long with an inner diameter of 103 mm and a wall thickness of 4.2 mm [7.4]. The internal pressure is about 10 MPa, which creates a hoop tensile stress of about 120 MPa and an axial tensile stress of about 60 MPa. The inlet and outlet temperatures in high power channels are about 520 K (247°C) and up to 588 K (315°C), respectively. The pressure tubes are now made from CWSR Zr-2.5Nb, but they were originally made from Zircaloy-2. With the operating conditions of fast neutron irradiation, high temperature and pressure, the tubes undergo deformation due to irradiation growth and irradiation and thermal creep. The calandria tubes made from RXA Zircaloy-2 provide a thermal barrier between the pressure tubes and the heavy water moderator by forming an annular gas gap to minimize heat loss from the fuel and the primary heat transport system. The pressure and calandria tubes are separated by two or four garter springs that encircle the pressure tube. The operating conditions for calandria tubes are much less severe than those for pressure tubes because they operate at the temperature of the moderator (343 K (70°C)), rather than the primary heat transport system, and the hoop stress is low because the insulating CO₂ gas is at a pressure of 100 kPa. Compared with LWRs, deformation is less of a problem in CANDU fuel because:

- The collapse of the cladding onto the fuel is encouraged (due to a very thin clad wall and a fill gas pressure of 100 kpa, as opposed to 2 mpa in a PWR);
- The bundles are very short (500 mm in length compared with 3500–4000 mm);
- Burnups are almost 10 times lower than in an LWR.



FIG. 7.49. Simplified diagram of a CANDU fuel channel showing the pressure and calandria tubes [7.187].

The important changes in shape for pressure tubes are axial elongation (by irradiation growth and creep), increase in diameter (mainly due to irradiation creep) and sag (due to creep by bending). The sag of the whole fuel channel is controlled by the strength of the calandria tube. These effects are summarized in Table 7.3 [7.188] and are shown schematically in Figs 7.50 and 7.51.



TABLE 7.3. EFFECTS OF DEFORMATION ON CANDU PRESSURE AND CALANDRIA TUBES [7.188]

FIG. 7.50. Axial and differential elongation in CANDU fuel channels (reprinted with permission from Ref. [7.188], copyright Elsevier, 1988).



FIG. 7.51. Creep sag in CANDU fuel channel (reprinted with permission from Ref. [7.188], copyright Elsevier, 1988).

7.5.5.1. Elongation

The rate of elongation is proportional to the fast neutron flux (E > 1 MeV), integrated over the whole fuel channel, and is typically in the range $(11-13) \times 10^{-29}$ m²·n⁻¹ based on measurements averaged over a number of years at 80% capacity factor (7000 h) in several CANDU units [7.58]. This elongation translates into an increase in length in the range 2–5 mm per 7000 h. Pressure tube elongation due to growth can be accommodated by the design of the end-fittings.

However, excessive growth can still lead to problems for the support at the ends of the fuel channels and specifically to an increase in stress in the feeder connections. The end bearings in later CANDU units were modified to accept considerably more elongation and to provide for a 30 year lifetime at 80% capacity factor [7.188].

A change to the tube fabrication process, involving a heat treatment at 773 K (500°C) for 6 h that decreases the dislocation density, has been shown to modify the anisotropy and reverse the direction of irradiation growth in the axial direction [7.187, 7.189]. The annealing process has been qualified so that it does not change the fine elongated grain structure of the Zr-2.5Nb alloy. As the total axial deformation is taken as the sum of irradiation growth and irradiation creep, the reversal of growth implies a reduction in elongation. This reduction has been demonstrated by measuring modified tubes that are elongating about 30% slower than standard CWSR tubes in neighbouring fuel channels. However, diametral creep strain is considerably increased.

7.5.5.2. Diametral expansion

Excessive diametral expansion from creep causes coolant bypass around the fuel bundles, which reduces operating safety margins. A reduction in the diametral creep could be affected by a modification to the predominantly transverse basal pole texture. Holt et al. [7.11] have pointed out that this modification creates a trade-off between transverse creep strain and axial growth strain. As the basal pole maximum is shifted towards the radial direction, the diametral creep strain increases and the axial growth decreases.

The probable effects of changes to the tube microstructure to reduce diametral expansion, without increasing elongation, have been evaluated. This analysis has indicated the desirability of retaining a strong transverse texture. A proposed reduction in thickness of the grains to enhance grain boundary sink strength for PDs [7.190] leads to an undesirable increase in diametral creep strain [7.46]. To avoid this problem the manufacture of pressure tubes requires a change to the extrusion process to introduce higher hot work reduction of the wall thickness than in previous practice. Extrusion is then followed by a recovery anneal to reduce the dislocation density without causing grain recrystallization. One practical method employed to reduce diametral expansion is to match the variations in material properties along the tube length to the variations in temperature and fast neutron flux seen in service [7.187].

The back end of the tube exits the extrusion press last and has a smaller α grain size and a higher dislocation density than the front end; this microstructural difference results in a greater tensile strength and a higher creep rate at the back end. As there are two general types of axial flux profiles in a CANDU channel (normal cosine and flattened cosine), the diametral creep strain varies depending on the sense in which the tube is inserted into the channel (i.e. back end or front end at the channel inlet). A more uniform deformation behaviour and slightly lower maximum creep rate can be obtained by installing the tubes with their back ends at the inlet, particularly for flattened cosine-shaped flux profiles. Analytical codes have modelled this effect and attribute the end–end variations to the crystallographic texture, the size and shape of the α grains and the dislocation density [7.58]. The pressure tubes in Wolsong Units 3 and 4, for example, are now oriented with their back ends towards the inlet to minimize diametral expansion due to creep. In the reactors where this change has been implemented, it has proved successful.

7.5.5.3. Creep sag

CANDU pressure tubes are subject to bending stresses induced by the weight of the tube itself, the fuel bundles and the coolant (Fig. 7.51). The creep deflection or 'sag' of the tubes depends on the structural behaviour of the fuel channel assembly, which consists of a pressure tube supported through annular spacers and end-fittings by a concentric calandria tube [7.188]. The bending of the entire fuel channel is controlled by the strength of the calandria tube. The sag of the pressure tube with respect to the calandria tube may become a problem when the spacing between the spacers is too large and the tubes touch. Deflection due to sag is controlled by irradiation creep. The span between the spacer supports and between the supports and the end-fittings determines the clearance between the pressure tube and the calandria tube and thus the time to contact. Additional sag of the pressure tube between the calandria tube spacers results in a reduction in the gap between the pressure and calandria tubes. Originally, two spacers were a loose fit around the pressure tube, and they were prone to move out of position, thereby increasing the span between points of support and allowing contact early in the life of the pressure tubes. The current design is a tight fit for four spacers, which increases the time to contact to beyond the lifetime of the pressure tubes. The main concern is not the contact itself, but the migration of hydrogen within the pressure tube to the point of contact, leading to cracking (see Chapter 9 on ductility and fracture, Volume 3 of this publication).

Calandria tubes also experience sag due to creep but to a lesser degree than pressure tubes. The end-of-life duration for calandria tubes would be reached when they make contact with any core component below or when a pressure tube replacement is not possible without also replacing calandria tubes because of excessive curvature. Additional calandria tube life can be obtained by reducing its sag rate [7.188]. This longevity is achieved by a general increase in the wall thickness of the tube (typically by about 50% from 1.4 mm to 2.1 mm) or by limited wall thickening at each end of the tube over the length of about 1 m.

7.5.6. RBMK pressure tubes and graphite moderator

In the RBMK reactor core the vertical pressure tubes make thermal contact through a series of graphite rings that make alternate contact with the outside surface of the pressure tube or the bore of the graphite brick moderator (Fig. 7.52). An allowance of about 1.5 mm is made to accommodate changes in diameter. This allowance is called the gas gap. As a result of neutron irradiation, the pressure tubes expand by irradiation creep, the graphite shrinks and the gas gap is reduced, reaching zero after 15–20 years of operation, as shown in Fig. 7.53 [7.191]. The loss of gap may cause one or more of the following problems:

- Additional uncontrolled loads leading to damage of the fuel channel and its joints, and elongation;
- Impairment of the safety monitoring system;
- Increasing loads required to remove fuel channels;
- Cracking of the graphite bricks.

The temperature of the pressure tube is increased by 25–30°C when the gas gap is closed [7.192]; this extra temperature is more important for corrosion than for deformation because the pressure tube is now fully supported by the graphite.



Dimensions mm

FIG. 7.52. Details of graphite rings around pressure tubes within the bore of graphite brick moderator in RBMK reactors, showing gas gaps.



FIG. 7.53. Change in outside diameter of Zr-2.5Nb pressure tube and inside bore of graphite moderator with reactor operation; contact when lines cross (data from Ignalina Unit 1 [7.191]).

The solution to this problem is to replace all the pressure tubes and rebore the holes in the graphite bricks to a larger diameter. The gas gap is now unlikely to close in the projected lifetime of the reactors because of the renewed gap and the eventual reversal of the shrinkage of the graphite bricks, shown in Fig. 7.54 [7.193, 7.194]. The pressure tubes in Leningrad Units 1, 2 and 3 and Kirsk Unit 1 have been replaced [7.194–7.196]. These pressure tubes were annealed at 813 K (540°C) after final CW.

The diameter of the pressure tubes is readily measured, and the behaviour is analysed as linear with neutron fluence (burnup) and the anisotropy is described by Hill's method [7.149]. The bore of the graphite can only be determined once the pressure tube has been removed, so few measurements are available. A probabilistic approach has been used to predict the gas gap in Ignalina Unit 1 [7.191] based on data similar to those shown in Fig. 7.53. These pressure tubes were heat treated by water quenching from 1133 K (860°C) before final CW. The tubes in Unit 2 were quenched into an inert gas mixture before final CW. The subsequent microstructure of these latter tubes has improved resistance to irradiation induced deformation and the gas gap is predicted not to close, except for a few fuel channels [7.194, 7.197].



FIG. 7.54. Change in dimensions of graphite from irradiation by neutrons, E > 0.18 MeV [7.193, 7.194].

7.5.7. Summary

Deformation of zirconium alloy components used in nuclear power reactors is of general concern because of the potential effect of dimensional changes on the safe and efficient operation and performance of the plant. Since all reactor components are designed to function at stresses well below yield for normal conditions, the only significant deformation is time dependent. It follows that both stress-free irradiation growth and in-reactor creep must be correctly accounted for in the design and modelling of components made from zirconium alloys used in all reactor types.

Creep or growth induced deformation in LWRs has resulted in several phenomena that have required remedial actions to correct or mitigate their effects. These are fuel rod

elongation, BWR channel bow and bulge, PWR fuel assembly bow and grid spring relaxation leading to subsequent fuel rod fretting. The introduction of Zr-Nb alloys in PWRs has been beneficial in reducing irradiation growth rates as well as increasing the in-reactor creep strength. The problems that stem from both the overall and differential growth of BWR channels can be mitigated during manufacture by a β quenching heat treatment at the final dimensions of the component.

The first generation WWER-1000 fuel assembly design suffered from bowing caused by the combined effects of non-uniformly growing fuel rods and the axial compressive force on the assembly. This problem has now been remedied in redesigned assemblies that are more rigid and stable owing to the use of E635 zirconium alloy for the structural skeleton. This material has superior creep strength and growth performance compared with the original E110 material it replaced.

The zirconium alloy pressure and calandria tube components in a CANDU reactor undergo in-reactor deformation due to growth and creep processes. The important changes in shape are axial elongation (by irradiation growth and creep), increase in diameter of the pressure tubes (mainly due to irradiation creep) and sag (due to creep in a bending mode). Changes in both design and material manufacturing route can ameliorate most of these problems.

Deformation in CANDU fuel is less of a problem than in LWRs because of design differences and a much lower discharge burnup. Diametral creep of pressure tubes in RBMK reactors has led to unacceptable interference between the pressure tubes and the graphite moderator. Tube replacement and increasing the bore of the moderator solve the problem. A modified heat treatment of the Zr-2.5Nb decreases the irradiation creep sufficiently that the components will no longer interfere.

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Chapter 8

OXIDATION AND CORROSION OF ZIRCONIUM ALLOYS

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8.1. INTRODUCTION

Although zirconium alloys are widely used in the chemical industry, their use in the nuclear industry has driven the development of the many alloys currently in use.

Zirconium alloys are now the universal material for nuclear fuel cladding and other structural components in the cores of high temperature water cooled nuclear power reactors. They have almost completely displaced stainless steels and nickel alloys except for some remaining uses of these alloys as spacer grids and grid springs where Zr alloys do not have adequate creep strength. The development of Zr alloys for nuclear reactor use was formally revealed at the first United Nations Conference on the Peaceful Uses of Atomic Energy in Geneva in 1955 [8.1] by the United States of America. Their preferred alloying additions were tin, with minor additions of iron, chromium and nickel. These alloys were called Zircaloys; alloys Zircaloy-1, Zircaloy-2, Zircaloy-3 (which exists in three subtypes, a, b and c) and Zircaloy-4 were developed, as detailed in Table 8.1, and saw various extents of service [8.1–8.3]. Zircaloy-2 became the preferred cladding for boiling water reactors (BWRs) designed in the USA, while Zircaloy-4, with its lower hydrogen uptake rate, was the preferred cladding for pressurized water reactors (PWRs) designed in the USA with high concentrations of dissolved hydrogen in the light water used for heat transport or coolant.

At the second UN Conference on the Peaceful Uses of Atomic Energy in Geneva in 1958 and later, the then USSR revealed extensive corrosion data from their development of Zr-Nb alloys for fuel cladding and structural alloys in their water cooled reactors [8.4–8.6]. Of the alloys they reported, only Zr-1 wt% (0.98 at.%) Nb (E110) and Zr-2.5 wt% (2.46 at.%) Nb (E125) were in common use in water cooled, water moderated power reactors (WWERs) and high-power channel-type reactors (RBMKs); these are detailed in Table 8.2. Multicomponent alloys were under development at the same time. Later, variants on these alloys were developed outside the Russian Federation for use under severe thermohydraulic conditions; these are also described in Table 8.2.

The Zircaloys have provided sterling service in light water reactors for many years. The trend towards increasing temperatures, heat ratings, the duration of irradiation cycles and fuel burnups have resulted in unacceptably high oxidation and hydrogen uptake by Zircaloy-4 (and its low Sn and high Fe/Cr variants) in PWRs. This behaviour has led to the replacement of Zircaloy-4, mainly by derivatives of the Russian Federation alloys E110 (or M5 in France) and E635 (or ZIRLO in the USA), although some other alloys are under development, especially in France, Japan, the Republic of Korea and the USA (see Chapter 2, Volume 1 of this publication). This replacement has progressed to the point where Zircaloy-4 is becoming an 'endangered species' in high performance PWRs [8.7].

In BWRs, Zircaloy-2 has continued to be the preferred cladding alloy, but with careful control of heat treatment, a higher aim point for Fe concentration (still within the original Zircaloy-2 composition limits) and limiting second phase particle (SPP) size to minimize nodular corrosion.

Alloying (wt%)	g addition	Zircaloy-1			Zircaloy	-2	2	Zircaloy-3			Zircaloy-4				
							а	b	с						
Sn			2.5		1.50 (1.20–1.7	0)	0.25	0.5	0.5	1.50 (1.20–1.70)					
Fe					0.12 (0.07–0.2	.0)	0.25	0.4	0.2	0.20 (0.18–0.24)					
Cr			_		0.10 (0.05–0.1	5)		—	—	0.10 (0.70–0.13)					
Ni			_	0.05 (0.03-0.08)				—	0.2	<0.007					
Total Fe, Cr, Ni					(0.18–0.3	8)			—	>0.28					
O (ppm)			_		1000-140	00			—		1000-	1400			
				М	aximum i	impurity c	oncentrati	ons:							
Element:															
A1	В	Cd	С	Co	Cu	Hf	Н	Mn	Ν	Si	Ti	W	U		
						ppm:									
75	0.5	0.5	270	20	50	200	25	50	80	200	50	100	3.5		

TABLE 8.1. COMPOSITION OF THE ZIRCALOY ALLOY SERIES

TABLE 8.2. COMPOSITION OF ZR-NB ALLOYS DEVELOPED IN THE RUSSIAN FEDERATION AND THEIR LATER DERIVATIVES

Alloying addition (wt%)			Ozher	nnite		Zr-1Nb					Zr-2.5Nb			Zr-Nb-Sn-Fe alloys						
			0.5	5		E	110		M5			E125			E 635			ZIRLO		
Sn		0.20 (0.18–0.22)							_						0.8–1.2			0.7–1.0		
Nb		0.1 0 (0.09–0.11)				1.0 (0.9–1.1)			0.8–1.2			2.50			1.0			1.0		
Fe			0.1 (0.09–	0 0.11)		0.1			0.04-0.06			0.05			0.4			0.1		
Ni		0.10 (0.09–0.11)				< 0.007					< 0.007			_						
В*						(0.20) *			_		(0.10) *						—			
0			(0.09–	-0.12)		(0.07–0.1)			0.12		(0.09–0.12)		(0.09–0.12)			(0.09–0.12)				
Maximum impurity concentrations:																				
									Elen	nent:										
A1	В	Cd	С	Cr	Co	Cu	Hf	Н	Pb	Mg	Mn	Mo	N	Si	Na	Та	Ti	W	V	
									pp	m:										
75	0.5	0.5	270	200	20	50	150	24	130	20	50	50	60	120	10	200	50	200	50	

* Added when burnable poison is included in the fuel assembly.

One consequence of inhibiting nodular corrosion has been the development of increased uniform corrosion at high burnups due to the irradiation induced dissolution of the SPPs. Although 'shadow' corrosion adjacent to components of the fuel assembly made from a nickel alloy or stainless steel has always been present, examples of severe shadow corrosion [8.8] have led to reassessments of the optimum size of SPPs in as-fabricated Zircaloy-2 and of the corrosion mechanisms in BWRs. BWRs are susceptible to shadow corrosion because they lack the high dissolved hydrogen contents of the cooling water in PWRs; any reactor with low dissolved hydrogen in the heat transport water or coolant can be susceptible to shadow corrosion.

8.2. TYPES OF CORROSION

8.2.1. Uniform corrosion

From the very start of zirconium development, the aim has been to produce alloys that would form a uniform oxide film without blemishes. This aim can be achieved, at least initially, but the blemishes have been the source of most subsequent research. An oxide of uniform thickness can be achieved with careful fabrication and specimen preparation when the corrosion takes place in a laboratory.

8.2.2. White spots

White spots result from the presence of small metallic impurity particles in an alloy, and have been removed or reduced by improved specimen preparation and pickling techniques.

8.2.3. Breakaway corrosion

As the oxide thickens, the stress from the volume difference between metal and oxide (Pilling–Bedworth ratio) builds up until oxide breakdown occurs. These thick oxides appear initially as areas of white porous oxide in a matrix of thin black oxide. This effect also arises from oxide stress development and can be reduced (but not eliminated) by improved alloying procedures.

8.2.4. Nodular corrosion

Nodular corrosion is a severe form of white oxide spots that can be observed under irradiation and results from galvanic corrosion between intermetallic particles and the zirconium matrix when insufficient hydrogen to eliminate galvanic couples is dissolved in the coolant.

8.2.5. Shadow corrosion

Shadow corrosion is a severe form of nodular corrosion where other metallic components cast their 'shadows' by creating larger areas of galvanic corrosion — again caused by insufficient dissolved hydrogen.

8.2.6. Crevice corrosion

Crevice corrosion (or 'corrosion in crevices') is observed in cracks in Canada deuterium uranium (CANDU) reactor pressure tubes, especially those created by delayed

hydride cracking. High corrosion rates are caused by a concentration of LiOH and the much higher corrosion rate of Zr hydride on the crack surfaces than on Zr itself. The galvanic component of shadow corrosion may also contribute to the corrosion.

One consequence of these inadequacies in the behaviour of the traditional fuel cladding alloys has been a constant revision of our understanding of in-reactor corrosion mechanisms. As a result of this revision, some traditional views have failed to survive. Past reviews of zirconium alloy corrosion [8.1, 8.2, 8.9-8.15] contain sections that are not supported by improved experimental observations and some conclusions that can now be seen to be incorrect. In this review, an attempt will be made to correct these views, and to bring the understanding of corrosion mechanisms into the present century, while at the same time providing a comprehensive review of those mechanistic aspects that have not changed materially. The form of a later review of this topic [8.16] will be followed, but with more details of the evidence being presented. Much background information will also be presented. It is hoped that this review will stimulate researchers to design experiments whose results will fill in some of the remaining gaps in our understanding of corrosion mechanisms and also reveal further areas where the current understanding is erroneous. Although in-reactor behaviour in water cooled reactors is economically the most important use of Zr alloys, there are other uses in other environments that will be summarized so that a complete picture of zirconium alloy behaviour can be presented [8.17, 8.18].

8.3. BASIC FEATURES OF OXIDATION

At elevated temperatures the interactions of all zirconium alloys with oxidizing gaseous atmospheres and pure water or steam are oxidation reactions. These reactions result in the formation of oxide films by solid state diffusion processes and an increase in weight, provided the oxide does not spall. The oxide films so formed offer different degrees of protection. The new oxide on zirconium alloy forms underneath the old oxide depending upon the formation conditions, because, as the oxides thicken, they are liable to various types of breakdown. Corrosion processes determined by the electrochemical potentials between Zr and other metals in the system play a major role in aqueous solutions containing some specific chemical species in high concentrations, in certain corrosive chemical environments and in water cooled nuclear reactors. These potential differences will vanish if there is sufficient dissolved hydrogen in the environment to maintain all dissimilar metals at the reversible hydrogen potential. Also, processes involving the dissolution of Zr from the alloy as a chemical species can also be found [8.17, 8.18]. These situations will be discussed in detail.

The driving force for the zirconium oxidation process is the high free energy of the formation of zirconium oxide (about 1000 kJ/mol at 600 K (330°C) in oxygen), and the even higher thermodynamic stability of oxygen dissolved in the Zr metal matrix, as shown in Fig. 8.1 [8.19]. These thermodynamic quantities ensure that oxygen from the oxide film is always dissolving into the metal throughout the oxidation process [8.19, 8.20]. Because of the differences in the temperature coefficients of diffusion of oxygen in the oxide film, shown in Fig. 8.2 [8.21], and in the diffusion coefficients of oxygen in the metal, shown in Fig. 8.3 [8.11], the fraction of the oxygen that reacts with the metal and goes into solution is small at normal reactor temperatures (about 5% at 673 K (400°C) and t < 600 h), but can be a large fraction of the total oxygen at high temperatures (50–60% at 1100 K (830°C) and $t \ge 24$ h). No well established suboxide phases exist in the Zr-O system, as shown in Fig. 8.4 [8.22], therefore the oxygen

diffusion profiles in the Zr matrix are typically regular in appearance, as shown in Fig. 8.5 [8.15].



FIG. 8.1. Ellingham diagram of thermodynamics of Zr-O and other relevant systems [8.19].



FIG. 8.2. Diffusion of oxygen in ZrO_2 (reprinted with permission from Ref [8.21], copyright Elsevier, 1968). Figures adjacent to curve number are estimated defect concentrations, cm⁻³.



FIG. 8.3. Collected data for diffusion of oxygen in a-zirconium [8.11].



FIG. 8.4. The zirconium–oxygen phase diagram (reprinted with permission from Ref. [8.22], Springer).

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FIG. 8.5. Curve for the penetration of oxygen using the ${}^{16}(d,p){}^{17}O$ nuclear reaction with $E_4 = 900$ keV, compared with a calculated curve (error function complement) for a zirconium specimen oxidized at 1123 K (850°C) for 400 h [8.15].

X ray studies of oxide films on Zr alloys have shown that stresses develop in the oxide film because of the volume increase on converting α -Zr to ZrO₂ [8.20], and these stresses have been confirmed by the bending of thin foils oxidized in oxygen on one side only, as shown in Fig. 8.6 [8.23]. This volume increase (Pilling–Bedworth ratio 1.56) is normally accommodated by forcing the oxide to grow primarily in the specimen thickness direction, because the specimen is usually much thicker than the oxide film. In very thin specimens oxidized on both sides at 773 K (500°C), creep of the specimens was measurable [8.23]. Much more extensive creep and growth of specimens is observed in air at temperatures above that at which a continuous layer of ZrN forms at the oxide-metal interface (about 1070 K (800°C)). At these temperatures the metal is much weaker than at reactor temperatures, but specimen growth in air is about ten times faster than in oxygen, as shown in Fig. 8.7 [8.24]. The growth was roughly isotropic in the plane of the sheet specimens used, as shown in Fig. 8.8 [8.24]. Although the initial oxidation rates in oxygen and air are almost identical, a sharp breakaway increase in oxidation occurs in air but not in oxygen. Transferring specimens from oxygen to air at times longer than the time to transition in air results in an immediate breakaway increase in oxidation rate, shown in Fig. 8.9 [8.24]. Under the worst circumstances (transitions from N_2-O_2) specimens can ignite when the transition is made [8.11, 8.24].



FIG. 8.6. Average stress generated during oxidation at 773 K (500°C): (a) Zr, and (b) Zircaloy-2 (reprinted with permission from Ref. [8.23], Atomic Energy of Canada Limited, Canada).



FIG. 8.7. Comparison of the times to transition and the rates of specimen growth for arc-melted sponge zirconium scaled in air and oxygen (reprinted with permission from Ref. [8.24], Atomic Energy of Canada Limited, Canada).

сох



FIG. 8.8. Dimensional and colour changes of iodide zirconium scaled in air (reprinted with permission from Ref. [8.24], Atomic Energy of Canada Limited, Canada).

The only mobile ionic species in zirconia films on zirconium alloys is the oxygen ion. Studies using oxygen isotopes have shown that the migration of oxygen ions is much faster in the oxide crystallite boundaries than in the bulk of the grains; see Fig. 8.2 [8.21]. Zr cations are not mobile [8.25, 8.26] and charge balance is determined by electron transport through the oxide, which is a good insulator when pure. The highly ionic nature of the bonding implies that there are few free electrons and so electron hopping from Zr ion to ion appears to be the most probable electron migration process [8.27]. The probable source of the electrons is thermionic emission, leading to a Schottky emission mechanism. The question of whether 'electron-hole' injection is also contributing has not been examined.

8.3.1. General oxide film morphology

A planar Zr surface will always carry a thin air-formed oxide (about 2 μ m). This oxide can be dissolved by pickling in an HF-HNO₃ solution or dissolved in the metal by heating in a good vacuum at high temperature. The thin oxide cannot be removed by cathodic polarization in an aqueous electrolyte (although it may be cracked by the formation of a solid hydride layer between it and the metal). The air-formed film will immediately reform once the surface is exposed to an oxygen containing environment.



FIG. 8.9. Instantaneous scaling rate of iodide zirconium in air after prescaling in nitrogen at 1070 K (800°C) (reprinted with permission from Ref. [8.24], Atomic Energy of Canada Limited, Canada).

The air-formed oxide is nanocrystalline; some early investigators thought it was amorphous but Ploc [8.28] has established the epitaxial relationships between this initial oxide and the zirconium matrix. This oxide can be thickened anodically at room temperature (and above) in most neutral aqueous electrolytes [8.29, 8.30]. At elevated temperatures the oxide thickens thermally but, unlike the situation with anodic films in which the electric field ensures a uniform oxide thickness irrespective of the orientation of the metal grain on which it is forming [8.31], the thin, thermally formed oxides vary in thickness (and hence in their interference colours) with the orientation of the Zr substrate, as shown in Fig. 8.10 [8.28, 8.32]. As these thermal oxides thicken, the oxygen vacancy concentrations increase. The thicker oxide films appear black since they absorb light in the visible wavelength range [8.33]. During this period of oxide growth, the oxidation kinetics become regular; in the earlier stages there are various inflections in the kinetics, shown in Figs 8.11 and 8.12 [8.5, 8.15, 8.34, 8.35], that have not been firmly identified with any characteristic changes in the oxides. During this period, preferential growth of specific oxide crystallite orientations results in a highly textured oxide with the preferentially growing crystallites forming an array of columnar zirconia crystallites, shown in Fig. 8.13 [8.36]. These columnar crystallites are typically of the tetragonal zirconia type, while the small, almost equiaxed, crystallites are usually of the monoclinic zirconia phase. In high purity zirconium, these columnar crystallites can grow to a length greater than 10 µm, without cracking or renucleating (Fig. 8.14 [8.15, 8.37]), whereas in Zr alloys at 572–673 K (300–400°C) they seldom exceed 1–2 µm without renucleating, as shown in Fig. 8.15 [8.38]. This behaviour suggests that impurity accumulation at the crystallite boundaries may limit their ability to grow without cracking and renucleation occurring. This supposition seems to be supported by the observation that for oxidation in the β phase at 1575 K (1300°C) [8.39], for which all alloying elements and impurities will be in solution, these same alloys grow large columnar oxide crystallites, ≥20 µm in length, shown in Fig. 8.16 [8.39]. This observation suggests an important potential mechanism by which impurities and alloying elements may trigger breakdowns of the protective oxide film when it reaches a critical thickness.



FIG. 8.10. Summary of available zirconium oxidation anisotropy data (reprinted with permission from Ref. [8.28], copyright Elsevier, 1968).



FIG. 8.11. Oxidation of Zircaloy-2 (Ac) in water at 473–573 K (200–300°C) [8.34].



FIG. 8.12. Irradiation corrosion of Zircaloy-2 at 573 K (300°C). (a) Corrosion of Zr-1%Nb in water and solutions at 583 K (310°C). (b) — Curve 1: Deionized water, pH 5.8; Curve 2: NH4OH, pH 7; Curve 3: NH4OH, pH 9; Curve 4: NH4OH, pH 11; Curve 5: H₂SO₄, pH 5; Curve 6: NaOH, pH 7; Curve 7: LiOH, pH 9; Curve 8: NaOH, pH 9; Curve 9: KOH, pH 9 [8.5, 8.15].



FIG. 8.13. Transmission electron micrographs of a section of a post-transition oxide film on Zircaloy-2 ionthinned to obtain transparency. The enlarged shape of the small crystallites, the presence of fine pores at crystallite boundaries and the absence of gross cracks should be noted (reprinted with permission from Ref. [8.36], copyright ASTM International, 1974).

FIG. 8.14. Columnar oxide crystallites on Zr oxidized in air at 923 K (650°C) [8.15, 8.37].



FIG. 8.15. Overfocused image of oxide formed on Zr-2.5Nb in water at 573 K (300°C). Y — small precipitates; Z — cracks (reprinted with permission from Ref. [8.38], Atomic Energy of Canada Limited, Canada).



FIG. 8.16. SEM photomicrographs of scales formed on Zircaloy-4 at 1576 K (1303°C) in steam. Scale separation was affected by dissolving the metallic substrate (reprinted with permission from Ref. [8.39], Springer).



FIG. 8.17. Variation of values of $D_{(hki)}$ observed on the surfaces of zirconium monocrystal (reprinted with permission from Ref. [8.20], Atomic Energy of Canada Limited, Canada).



FIG. 8.18. Raman spectra at different depths of the oxide layer formed on the Zircaloy-4 alloy after 65 days in steam at 673 K (400°C) (reprinted with permission from Ref. [8.40], copyright ASTM International, 1994).

8.3.2. Oxide film crystallography

Although the initial air-formed oxide appears to be cubic (or tetragonal) ZrO₂, thicker oxides are primarily monoclinic zirconia [8.20, 8.41] when measured by X ray techniques in situ on the metal substrate. These techniques show a small component of tetragonal ZrO₂ in these films; see Fig. 8.17 [8.20]. This tetragonal ZrO₂ is primarily in the region of the oxide closest to the oxide–metal interface. Raman spectroscopy of oxide films in situ on the metal has suggested that it might be stabilized by the high compressive stresses in this region, as shown in Fig. 8.18 [8.40, 8.42, 8.43]. The small particle size, the high vacancy concentration and possible impurity segregation at the oxide–metal interface must also be considered. There have also been some questions about the location of some of the Raman spectral peaks [8.43]. There are at least three crystallographic

distinguishable forms of stabilized t-ZrO₂ with different arrangements of the oxygen atoms in the pseudofluorite unit cell [8.44] and these variants may have slightly different Raman peak frequencies. Some authors studying thermal oxide films on Zr alloys seem to be unaware of the different forms of t-ZrO₂, yet it is the creation of stabilized t-ZrO₂ films that is the key to good corrosion resistance. It should be noted that artificially stabilized zirconia can be obtained by adding yttria or other stabilizing materials.

When oxide films are stripped and studied by transmission electron microscopy there seems to be much less evidence for t-ZrO₂ in the films. This observation suggests that stress is the main stabilizing factor and relaxing this stress by stripping the oxide may cause a t-ZrO₂-m-ZrO₂ phase change. By gluing two specimens back to back, the t-ZrO₂ in oxide films has been preserved, and the layers of high and low t-ZrO₂ concentration alternate with low and high m-ZrO₂ layers, as shown in Fig. 8.19 [8.45]. These observations are important for an understanding of the cyclical nature of the oxidation kinetics in some alloys (see below). Although cyclical post-transition oxidation kinetics, based on weight gain, are only clearly seen in the Zircaloys, as shown in Fig. 8.20 [8.46, 8.47], the alternate layers of t-ZrO₂ and m-Zr-O₂ were also seen in ZIRLO, Zr-2.5Nb and Zr-2.5Nb-0.5Cu alloy specimens where cyclical kinetics are not usually evident.



FIG. 8.19. Layers visible (a) in oxide films in transmitted light, and (b) as cycles of monoclinic and tetragonal oxide, formed on ZIRLO at 633 K (360°C) for 784 days (reprinted with permission from Ref. [8.45], copyright Elsevier, 2004).



FIG. 8.20. Short time corrosion weight gain of Zircaloy-4 in water at 633 K (360°C) (reprinted with permission from Ref. [8.47], copyright ASTM International, 1984).

8.3.3. Rate determining steps

The possible rate determining steps in the oxidation of zirconium alloys are restricted by the fact that in the oxide film only oxygen ions and electrons are mobile.

Processes at the oxide–environment interface could be rate-limiting [8.46]. This suggestion is based on the fallacious premise that such dependence is the only way to explain the effects of irradiation on corrosion in BWRs, and that the layers of lateral cracks in the oxides are not artefacts of an inadequate metallographic technique. There are at least two established metallographic techniques [8.37, 8.48] that will produce oxide sections devoid of such lateral cracks under conditions where the technique of Bossis et al. [8.49] (and others) routinely generates lateral cracks. It is usual in scientific studies for only one negative result to be sufficient to demolish any particular hypothesis, and such is the situation here. The other evidence against any effect of surface reactions on corrosion kinetics is provided by the observations that pre-transition oxidation kinetics of Zr alloys in steam, water, uranyl sulphate, sulphuric acid solutions, oxygen, air, fused nitrate/nitrite melts and ammonia are all very similar in the temperature range 573–633 K (300–360°C) [8.35, 8.50–8.52]. Major effects of specific chemicals (e.g. LiOH) [8.52] therefore require a specific mechanism, as shown in Fig. 8.21 [8.52], by which they cause oxide film degradation to be adduced.



FIG. 8.21. Effect of water chemistry on Zircaloy-2 corrosion (reprinted with permission from Ref. [8.52], copyright Elsevier, 1962).
The conclusion to be drawn from the above is that the oxidation of zirconium alloys is controlled by the properties of the oxide film. The question is then whether it is oxygen ion diffusion that controls the oxidation rate or electron transport. Hauffe [8.53] discussed these questions in the 1960s. He showed that there were two experimental techniques that could identify the rate controlling process. The first is to deliberately short circuit the electronic current through the oxide by the use of a porous conducting contact on the outer surface of the oxide. Hauffe [8.54, 8.55] showed that for Zr specimens oxidized in oxygen at 1073 K (800°C), deliberately short circuiting the oxide resulted in an increase in the oxidation rate, thus showing that electron transport was the rate determining step, as can be seen in Figs 8.22 and 8.23 [8.54, 8.55]. Vermoyal et al. [8.56] have performed a similar experiment, the results of which are shown in Fig. 8.24, by short circuiting their oxides on a Zr-1Nb alloy in air at 773 K (500°C).



FIG. 8.22. History of the oxidation of zirconium at 1 atm oxygen at various temperatures with and without local cell action [8.54].



FIG. 8.23. History of the oxidation of zirconium with a Pt covered ZrO_2 layer at 1 atm oxygen at 1073 K (800°C) with and without short circuit [8.55].



COX

FIG. 8.24. Oxide thickness versus time at 773 K (500°C) determined by thermogravimetric analysis for preoxidized ZrNbO, preoxidized ZrNbO coated with Pt, preoxidized ZrNbO coated with Au and preoxidized ZrNbO coated with Ag (reprinted with permission from Ref. [8.56], copyright Elsevier, 2004).

The other approach to ascertaining the rate determining step is to measure the potential across the oxide film during oxidation. This potential is kinetically rather than thermodynamically determined and measures the field necessary to slow down the easier transport process and accelerate the slower process until both processes proceed at the same rate, when the potential will become constant [8.57]. All measurements of this type, even when performed in different environments (Figs 8.25–8.27 [8.56–8.58]), have shown a negative potential on the metal, indicating that electron transport is the rate determining step. These experiments also show the ease with which inadvertent short circuits can be achieved (seen in Figs 8.26 and 8.27 [8.56, 8,58]) at the start of such experiments when the protective oxide is very thin.



FIG. 8.25. Behaviour of potential developed during oxidization of zirconium at 973 K (700°C) [8.57].



FIG. 8.26. Potential in steam treated with hydrazine as a function of weight gain at 873 K (600°C) (reprinted with permission from Ref. [8.58], Atomic Energy Canada Limited, Canada).



FIG. 8.27. Variation of the potential difference versus time for preoxidized ZrNbO/Pt (reprinted with permission from Ref. [8.56], copyright Elsevier, 2004).

All these results have been obtained in dry gaseous environments at high temperatures (773–1073 K (500–800°C)) and show strong dependence of the oxidation rate on the electron transport process through the oxide film. Ideally, it is necessary to show that the same dependence is present in aqueous environments at 573–633 K (300–360°C). Such experiments are difficult to perform in aqueous electrolytes because of the poor reversibility of such systems for electron currents. Fused salts have much better reversibility for electron currents in this temperature range [8.51], and analogous experiments to those in gases at high temperatures have been carried out [8.59]. Results

showed that potentials across the oxide film were always negative on the metal, but that the negative potential decreased to much lower values as the oxide thickened in these low temperature tests; see Fig. 8.28 [8.59]. They also showed that a high temperature pre-oxidation apparently increased the oxide conductivity (probably by redistributing Fe in the oxide [8.60, 8.61]) so that on transferring to a low temperature, the potential on the metal could initially be positive, as shown in Fig. 8.29 [8.59], providing further evidence that the potentials are kinetic and not thermodynamic. Short circuiting the oxide in a fused salt produced only a small increase in the oxidation rate of zirconium, as shown in Fig. 8.30 [8.59]. This increase is much smaller than effects at high temperature, as shown in Fig. 8.31 [8.59], even though the potentials were clearly negative on the metal.



FIG. 8.28. Potential versus time curves for Zircaloy-2 in fused salt [8.59].



FIG. 8.29. Potential in Zr and Zircaloy-2 at 583 K (310°C) after a pretreatment at 708 K (435°C); similar results to Ref. [8.59].



FIG. 8.30. Weight gain for Zr specimens electrically biased during oxidation in fused salts at 548 and 573 K (275°C and 300°C) [8.59].



FIG. 8.31. Effect of biasing on the oxidation of Zircaloy-2 in fused salt [8.59].

Care should be taken in applying this evidence for the rate determining step. In isothermal tests the potential on the metal is always negative, and electron transport is rate determining. The difference in the rates of the two processes — diffusion of oxygen ions and electron transport — may be small at reactor temperatures, and the balance between the two processes can be reversed by phenomena that may redistribute

electronically conducting species in the oxide film. This point will be returned to below

8.3.4. Oxidation kinetics

when the effects of irradiation on corrosion are discussed.

Having examined the factors that are likely to affect oxidation kinetics, it is now possible to discuss how close the actual kinetics come to those predicted theoretically. The most widely used hypothesis for the kinetics of growth of oxidation scales on metals is that of Hauffe [8.53]. This hypothesis considers the diffusion of two ionic species (cationic and anionic) in the scale and the concentration gradients of each that develop. Using Fick's First Law, this mechanism results in a growth law for the scale that is inversely proportional to the scale thickness. The result is parabolic growth kinetics, with a parabolic rate constant, K.

There are severe limitations on the applicability of this hypothesis:

- Both metal and oxide should be homogenous in the plane parallel to the surface (i.e. ideally both should be monocrystalline, or, if not, there should be no preferential grain boundary diffusion).
- Only diffusional transport should be rate determining (i.e. both diffusing charged species should follow Fick's First Law).
- Ionic and electronic transport must be coupled to maintain local electroneutrality (i.e. an ion can only hop in one direction if an ion of opposite charge, or an electron, hops in the other direction at the same time).
- Cation and anion diffusion coefficients in the scale should be of similar sizes. None
 of these conditions is met for the oxidation of zirconium and its alloys.
- Even for Zr single crystals the oxide crystallite size is microscopic, and for even the smallest grain size $(0.1-0.2 \ \mu\text{m})$ of polycrystalline alloys the oxide crystallite size remains much smaller than the grain size $(10-20 \ \mu\text{m})$ initially). Wagner and Hauffe developed this model for metals that develop electrically conducting scales, which is not the situation for the zirconium oxide system.
- Although oxygen ion diffusion may follow Fick's Law, especially at high temperatures, as seen in Fig. 8.2 [8.21], at low temperatures crystallite boundary diffusion of oxygen ions is dominant, and electron transport does not follow Fick's Law.
- Electron transport is probably electron hopping from Zr ion to Zr ion (cations) and the high resistivity of ZrO₂ makes electron transport the rate limiting step. Oxygen ion diffusion is primarily along crystallite boundaries, so it is unlikely that local electroneutrality can be maintained and space charges will build up.
- Only oxygen ions (anions) diffuse. There is no evidence for cation diffusion until very high temperatures are reached (≥1770 K (1500°C)).

Thus, we need an oxide growth mechanism that can accommodate these critical differences from the requirements for the Wagner–Hauffe hypothesis. In particular, the paucity of studies of electron transport in oxide films in zirconium ions is regrettable. What little is available suggests that electron conduction follows Poole–Frenkel excitation [8.27].

The effects of Fe oxide deposits indicate that electron-hole conduction may be equally important. In this context the current tendency to use high frequency alternating current (AC) techniques rather than direct current (DC) techniques are disadvantageous,

since there are indications that such techniques may encourage electron-hole recombination and thus lead to erroneous results, especially under irradiation.

Hypotheses that handle both diffusion and electron transport processes are few. Those of Fromhold [8.62] may be useful in the thin film region, but do not seem to be able to accommodate the very high electronic resistance of ZrO₂. The breakdown of the protective film is of ultimate importance for long exposures, both in the laboratory and in-reactor, and arguments about the precise kinetics in the thin film region are not of long term consequence.

Polarization measurements in high temperature aqueous solutions have not been very helpful because of the poor reversibility of electrodes in such systems for the electronic current [8.63] when compared with polarization curves in an oxidizing fused salt; see Fig. 8.32 [8.11, 8.63, 8.64]. Continuous polarization in fused salt showed the expected increase in corrosion rate for zirconium on short circuiting, as shown in Fig. 8.30 [8.59], whereas Zircaloy-2 showed very little effect of anodic polarization on the corrosion rate, as shown in Fig. 8.32, suggesting that the anodic and cathodic processes were of roughly equal difficulty in the oxide [8.64]. The continuous cathodic polarization of Zircaloy-4 at 573 K (300°C) in an aqueous electrolyte resulted in thick cathodic hydride layers and an increase in oxide thickness from oxidation of the hydride [8.65]. More work is needed to understand these rate determining processes.



FIG. 8.32. Comparison of polarization curves for similar Zircaloy-2 specimens in aqueous solution and fused with salt at about 570 K (300°C) [8.11, 8.63, 8.64].

8.3.4.1. Unalloyed zirconium in gaseous atmospheres

The kinetics of oxidation of unalloyed zirconium in a variety of environments is compared here. Oxidation in oxygen at low temperatures is shown in Fig. 8.33, and at high temperatures in Fig. 8.34. The short term exposures at low temperatures were forced into a parabolic fit but testing for longer times tended to show that cubic kinetics were a better fit to long term data [8.11]. In these tests, high purity van Arkel zirconium generally did not undergo a transition to a higher linear rate, whereas Kroll sponge material did. When van Arkel material was oxidized in a 'discontinuous' sequence, it had a transition similar to the Kroll material, showing that both impurities and thermal cycling during oxidation play a part in triggering oxide breakdown. In general, the data from different sources do not compare well. This variability suggests that there are factors (possibly material processing variables) involved in the spread of the results other than just the impurity concentration in the alloy. These factors probably include the surface preparation of the specimens; the extent of residual stresses at the specimen surface prior to oxidation; the geometry of the specimens (proportion of edges to faces and presence of sharp edges), as shown in Fig. 8.35 [8.11, 8.24]; and the frequency of thermal cycling in the experiments and the technique adopted for starting high temperature oxidation experiments. It is recommended to study these factors before reaching conclusions from the early work in this area.



FIG. 8.33. Typical results for short term oxidation in oxygen at temperatures below 697 K (425°C) [8.11].



FIG. 8.34. Comparison of published oxidation curves from a number of laboratories for oxidation of zirconium at 870 K (600°C) in oxygen [8.11].



FIG. 8.35. Effect of specimen geometry on the propagation of the oxidation kinetic transition for Zircaloy-2 in steam [8.11, 8.24].1 atm = 0.1 MPa, 10 mm Hg = 1.333 kPa.

In air (at temperatures below which severe breakaway oxidation occurs because of the formation of nitride layers), shown in Figs 8.30 [8.59] and 8.36 [8.24], the pre-transition corrosion rates in oxygen and air are identical, as shown in Fig. 8.37 [8.11].



FIG. 8.36. (a) Transition to linear oxidation kinetics observed in air; (b) instantaneous scaling of iodide zirconium in oxygen and air after prescaling in either air or oxygen at 1170 K (900°C) (reprinted with permission from Ref. [8.24], Atomic Energy Canada Limited, Canada).



FIG. 8.37. Comparison of published oxidation curves from a number of laboratories for oxidation of Zircaloy-2 at 870-1070 K (600- 800° C) in oxygen and air [8.11].

Oxidation rates in carbon dioxide show the same variability as those observed in oxygen. Collected data at 970 K (700°C), shown in Fig. 8.38 [8.11], do not show any difference in oxidation rates at times greater than 6×10^4 s. Other data for oxidation at 970 K (700°C) in oxygen, shown in Fig. 8.39 [8.11], indicate similar behaviour. Variability seems to result from the method of starting the experiment. In general, no pressure dependence of the oxidation rate in oxygen is seen, as shown in Fig. 8.40 [8.11], until oxygen pressures are very low (<10 mm Hg (<1.3 kPa)), even though the Wagner–Hauffe hypothesis gives a $p^{1/6}$ power dependence (where *p* is pressure). At these low pressures the oxidation is dominated by oxygen dissolution in the metal and the development of local porosity and cracks in the oxide at the zirconium grain boundaries, as shown in Fig. 8.41 [8.66, 8.67]. Oxidation in molten NaK roughly follows what would be expected for the effective partial pressure of oxygen in solution in the liquid metal, as shown in Fig. 8.42 [8.11].

Oxidation of unalloyed zirconium in high temperature water is initially the same as for zirconium in oxygen at 633 K (360°C), as shown in Fig. 8.43 [8.11]. The difference arises with the severe breakdown of the oxide in water, whereas no such breakdown occurs in oxygen. The time at which this breakdown occurs depends upon the impurity concentration of the zirconium (other factors, such as surface preparation and thermal cycling, being constant). The breakdown is thought to be due to the reversion of the tetragonal protective ZrO₂ layers to monoclinic ZrO₂ in high temperature water.



FIG. 8.38. Collected data for the oxidation of zirconium in carbon dioxide at $970 \text{ K} (700^{\circ}\text{C})$ compared with oxidation in oxygen [8.11].



FIG. 8.39. Results of two long oxidation studies compared with short term data [8.11].



FIG. 8.40. Oxidation curves in low pressure oxygen compared with results in clean carbon dioxide at 971 K (700°C) [8.11]. 1 atm = 0.1 MPa, 50 mm Hg = 6.666 kPa.



FIG. 8.41. Ridges formed on the surface of the oxide film on zirconium and pore formation and film cracking at the grain boundaries [8.67].



FIG. 8.42. Collected data for the oxidation of zirconium in liquid sodium compared with oxidation in low pressure oxygen [8.11]. 1 mm Hg = 133.3 Pa.



FIG. 8.43. Long term oxidation of unalloyed zirconium in oxygen and water at 570–920 K (300–650°C). The three branches of the water curve correspond to the behaviour of different grades of zirconium [8.11]. 1 mm (Hg) = 133.3 Pa.

8.3.4.2. Effects of impurities and alloy additions

The severe oxide breakdown in van Arkel zirconium prevented its use in water cooled reactors and forced extensive studies of the effects of impurities on Zr oxidation [8.1], and ultimately the development of the Zircaloys [8.2, 8.3], which did not show such effects; see list in Table 8.1. It soon became clear that nitrogen, as shown in Fig. 8.44 [8.1], and carbon impurities in the zirconium, as shown in Fig. 8.45 [8.1], were among

the elements that causing the most rapid breakdown of the oxide film. Early explanations of the effects of nitrogen focused on its effect of increasing the vacancy concentration in the ZrO₂ lattice [8.1]. It is now known that the major oxygen ion diffusion route in the oxide film is along the crystallite boundaries and not through the bulk of the crystallites [8.16]. The kinetic effects of nitrogen, as seen in Fig. 8.44 [8.1], show that it has little or no effect on the diffusion controlled pre-transition corrosion rate, but accentuates the oxide breakdown without much effect on the time of onset of this breakdown. Nitrogen in ZrO₂ stabilizes the tetragonal form of the oxide by increasing the vacancy concentration [8.68]. The presence of t- ZrO_2 and its reversion to m- ZrO_2 in water [8.69] may be involved in the oxide breakdown process because of the volume change involved in the transformation [8.16]. No recent studies have helped to clarify the mechanism of nitrogen-induced degradation of corrosion resistance. The addition of tin to the alloy was found to counteract the effect of nitrogen [8.2, 8.3]. Although tin has some solubility in the Zr matrix, Sn segregates to the crystallite boundaries in the oxide film [8.70] and consequently might affect the oxygen ion migration. No investigation of this possibility has been reported.



FIG. 8.44. Effect of nitrogen on corrosion resistance of Zr at 588.7 K (315.6°C) [8.1].



FIG. 8.45. Effect of carbon on the corrosion resistance of zirconium in water at 600°F (589 K (316°C)) [8.1].

Carbon is almost insoluble in zirconium (solubility <100 ppm (0.076 at.%) at 670 K (400°C)) and occurs primarily as small zirconium carbide particles. Severe oxide breakdown around the boundaries of these carbide particles occurs in high temperature steam and water, as seen in Fig. 8.46 [8.71].

Degradation of the corrosion resistance of Zr in water at 561 K (288°C), as shown in Fig. 8.45 [8.1], exhibits two effects: at low concentrations an increase in diffusion controlled oxide growth that is proportional to the carbon concentration, and an added oxide breakdown effect at high concentrations. The latter may be due to local oxide breakdown around carbides, while the former may be related to the effects of carbon in solution on the crystallite morphology. Again, no recent studies of the phenomena have been reported.



FIG. 8.46. Electron micrographs showing carbide particles still visible in (a) zirconium (pickled) and in (b) Zircaloy-2 (attack polished micrograph) after eight days exposure to steam at 570 K (300°C) (reprinted with permission from Ref. [8.71] with permission courtesy of Atomic Energy of Canada Limited, Canada).

The beneficial effects of tin showed a minimal weight gain at about 0.5 wt% (0.38 at.%) Sn, as shown in Fig. 8.47 [8.2], although 2.5 wt% (1.93 at.%) Sn was selected for Zircaloy-1 to ensure good mechanical properties. The corrosion resistance of this alloy was poor [8.3], and so the effects of Fe, Cr and Ni additions to Zircaloy-1 were studied, as shown in Fig. 8.48 [8.2]. Whether serendipitous or not [8.3], the result of reducing the tin concentration to 1.5 wt% (1.16 at.%) and adding Fe, Cr and Ni was Zircaloy-2 (Table 8.1). Its behaviour in steam at 673 K (400°C) and higher temperatures remained poor, as shown in Fig. 8.49 [8.2]. Reducing the tin concentration to, at most, the position of the corrosion minimum (≤0.5 wt% (0.38 at.%) Sn) in the binary oxidation curve, shown in Fig. 8.47 [8.2], resulted in Zircaloy-3 (a, b, c). This alloy never achieved success because of problems arising in the inert gas melting techniques used at that time [8.72]. Elimination of the Ni from Zircaloy-2 resulted in Zircaloy-4, which had a lower hydrogen uptake rate — see below [8.2]. A low Sn version was adopted to improve corrosion resistance in high performance PWRs [8.73], ultimately with various adjustments to Fe and Cr concentrations. Zircaloy-3b achieved some use in high performance PWRs as a duplex cladding [8.74].





FIG. 8.47. Effect of tin concentration on corrosion resistance of sponge zirconium in water at 600°F and 800°F (589 and 700 K (315.6 and 427°C)) (reprinted with permission from Ref. [8.2], copyright ASTM International, 1964).

FIG. 8.48. Effect of Fe, Ni and Cr additions on the corrosion resistance of an arc-melted sponge zirconium 2.5 wt.% Sn (1.93 at.% Sn) alloy (reprinted with permission from Ref. [8.2], copyright ASTM International, 1964). $600^{\circ}F = 588.5 \text{ K} (315.6^{\circ}\text{C}), 680^{\circ}F = 633 \text{ K} (360^{\circ}\text{C}), 750^{\circ}F = 672 \text{ K} (399^{\circ}\text{C}).$



FIG. 8.49. Corrosion of Zircaloy-2 (line 2) and Zircaloy-3a (line 3A), Zircaloy-3b (line 3B) and Zircaloy-3c (line 3C) compared in steam at 750°F (672 K (399°C)) and 1500 psi (10.34 MPa). Specimens furnace-cooled from 1048 K (775°C) (reprinted with permission from Ref. [8.2], copyright ASTM International, 1964).

Table 8.1 gives the compositions of the Zircaloys. Studies of the allowable concentrations of a wide range of impurities in the Zircaloys led to their identification in the Unified Numbering System and to ASTM standards for these alloys, as shown in Table 8.3.

Unified Numbering System	R 60001	R 60802	R 60804	R 60904
Common name	Pure Zr	Zircaloy-2	Zircaloy-4	Zr–2.5Nb
ASTM standards	B352 (97) [8.75], B 811 (97) [8.76]			B 350 (96) [8.77]
Alloying elements mass (wt%)				
Sn	n.a.	1.2–1.7	1.2–1.7	
Fe	n.a.	0.07–0.20	0.18-0.24	
Cr	n.a.	0.05-0.15	0.07-0.1	
Ni	n.a.	0.03-0.08		
Nb	n.a.			2.4–2.8
0	n.a.	TBS ^(*)	TBS ^(*)	TBS ^(*)
Impurities (max. (ppm))				
Al	75	75	75	75
В	0.5	0.5	0.5	0.5
Cd	0.5	0.5	0.5	0.5
С	270	270	270	150
Cr	200			100
Co	20	20	20	20
Cu	50	50	50	50
Hf	100	100	100	50
Н	25	25	25	10
Fe	1500			650
Mg	20	20	20	20
Mn	50	50	50	50
Mo	50	50	50	50
Ni	70		70	35
Ν	80	80	80	65
Р	—			20
Pb				50
Si	120	120	120	100
Sn	50			50
Ta	—		—	100
Ti	50	50	50	50
U	3.5	3.5	3.5	3.5
V			—	50
W	100	100	100	100

TABLE 8.3. ASTM STANDARDS FOR Zr AND Zr ALLOYS USED IN THE NUCLEAR INDUSTRY

* TBS — to be specified on ordering, usually 900–1400 ppm.

For uses in CO₂ cooled reactors a similar development programme took place. Sensitivity to both alloying additions and impurities differed in CO₂ from that observed in water. The best alloys for in-reactor use in CO₂ cooled reactors were Cu containing alloys such as the alloys (0.5 wt% (0.7 at.%) Cu-0.5 wt% (0.48 at.%) Mo) and (1.0 wt%(1.4 at.%) Cu-1.5 wt% (1.43 at.%) Mo) used as fuel element supports in MAGNOX reactors [8.78]. The alloy Zr-1.8 wt% (2.56 at.%) Cu was used as fuel cladding and the Advanced Test Reactor (USA) (ATR) alloy was used for fuel assembly grids in the EL4 reactor, which was a CO₂ cooled, D₂O moderated reactor at Monts d'Arrée in France [8.79]. Significant pressure dependence was observed for Zr in CO₂, as shown in Fig. 8.50[8.11]. A more extensive discussion of the development of alloys for use in CO₂ is given in Ref. [8.11].



FIG. 8.50. Effect of temperature and pressure on the oxidation of zirconium in carbon dioxide (reprinted with permission from Ref. [8.11], Atomic Energy of Canada Limited, Canada).1 atm = 0.1 MPa.

Zirconium alloys behave similarly in CO_2 and in low pressure oxygen, as shown in Fig. 8.40 [8.11]; to some extent this behaviour may result from impurities in the CO_2 [8.11]. The same behaviour is observed for exposure of Zr in molten Na, shown in Fig. 8.42, or NaK [8.11]. A similar situation is found in fused eutectic mixtures of potassium and sodium nitrates, as shown in Fig. 8.51 [8.64]. This environment has been used for electrochemical measurements because it gives good reversibility with a smooth platinum electrode for the electronic component of the Zr oxidation reaction [8.11, 8.51].



FIG. 8.51. Effect of environmental conductivity on oxidation of Zr (reprinted with permission from Ref. [8.64], Atomic Energy of Canada Limited, Canada).

The majority of out-reactor experimentation on zirconium alloys has been carried out in high temperature water or steam, because Zr alloys in water cooled nuclear power reactors experience an environment close to these conditions.

8.4. CORROSION IN HIGH TEMPERATURE WATER, AQUEOUS SOLUTIONS AND STEAM

8.4.1. Water chemistry

BWRs operate with pure water at about 561 K (288°C). Most reactor operators add other species for various reasons:

- Hydrogen is added to reduce the electrochemical potential at the core inlet.
- Zn is added to reduce the release of radioactive corrosion products from the external circuit.
- Noble metal additions are made to reduce the electrochemical potentials where the hydrogen additions are ineffective.

PWRs operate with saturation temperatures at about 620 K (347°C), high H₂ (about 30 cm³·kg⁻¹), \leq 3.5 ppm Li (as LiOH) and 0–3000 ppm B (as boric acid) for reactivity control. Zinc injection has been initiated in PWRs to control the dose rates. Although the chemistry of the water in nuclear power reactors is often not high purity water, and is only approximately so in BWRs, out-reactor testing was generally carried out in high purity water at 570–630 K (300–360°C) or in pure steam at 670 K (400°C) or higher. Under these conditions the process being studied is still an oxidation process controlled

by processes within the oxide. The Zircaloys were developed to eliminate the sensitivity of zirconium to breakaway oxidation in water, as shown in Fig. 8.43 [8.11].

These alloys also eliminated sensitivity to variability due to short-circuiting the oxide, and to the presence of Fe₃O₄ deposits on the surface, as shown in Fig. 8.52 [8.64]. Thus, alloys are now available that are almost insensitive to effects of impurities, provided the ASTM limits, shown in Table 8.3, are achieved. Apart from in BWRs, reactor water is not high purity water; PWRs add LiOH to maintain a roughly neutral pH during operation in the presence of boric acid added to control reactivity. The amount of LiOH added [8.80] is much less than the concentration that leads to degradation of the corrosion resistance of the Zircaloys [8.52]. In high performance PWRs, where temperatures and heat fluxes are high, and the saturation temperature of the water may be exceeded, the concentration of LiOH in thick porous oxide films may exceed the levels where accelerated corrosion is possible. The high concentration of LiOH may particularly be a problem in the presence of heavy, low thermal conductivity deposits on the outside surface of the cladding — sometimes called crud [8.81]. Thus, there is a tendency to test all new alloys for susceptibility to LiOH attack using either 70 ppm Li as LiOH (0.01M) or 220 ppm Li (0.03M). The boric acid added for reactivity control protects against severe LiOH corrosion, as shown in Figs 8.53 and 8.54 [8.82, 8.83]. Since in PWRs there is always enough boric acid to counter any effect of concentration of LiOH, except right at the end of a reactor cycle, the question is whether there is any evidence of such effects during reactor operations. The answer to this will be determined by whether there is any evidence for LiOH and boric acid partitioning in thick oxides on Zr alloy cladding, because the borate ion (BO_3^{3-}) is much larger than the lithium ion (Li^+) . The Li^+ may be able to concentrate in fine porosity in oxide films that the BO_3^{3-} ion is unable to penetrate. Evidence on this question will be addressed during the discussion of in-reactor behaviour (see Section 8.6).



FIG. 8.52. Effect of environmental conductivity on Zircaloy-2 (reprinted with permission from Ref. [8.64], Atomic Energy of Canada Limited, Canada).





FIG. 8.53. Behaviour of Zircaloy-4 clad in simulated hideout environments with 220 ppm of lithium and boron additions in the range 0 to 8000 ppm (reprinted with permission from Ref. [8.83], copyright ASTM International, 1991).

FIG. 8.54. Corrosion of Zircaloy-4 in 220 ppm lithium environments in the presence and absence of 10 ppm of boron (reprinted with permission from Ref. [8.83], copyright ASTM International, 1991).

The effect of concentrated LiOH is a corrosion process since it involves the local dissolution of ZrO₂ (probably from the oxide crystallite boundaries) to generate porosity in the oxide film, and reprecipitate a LiZrO₃-type phase near the low temperature oxide–water interface in the presence of a heat flux [8.84–8.86].

Russian Federation WWERs use different water chemistry from PWRs. They employ a composition consisting of a combination of KOH and NH4OH, in neither of which does concentration by boiling result in severe degradation of corrosion resistance. They also use Zr-1 wt% (0.98 at.%) Nb alloy cladding [8.4–8.6]. Zr-Nb alloys are more sensitive to the degradation of corrosion resistance in concentrated LiOH than are Zircaloy-type alloys. The trend to replace Zircaloy-type alloys with Zr-Nb alloys in high performance PWRs highlights the importance of resolving the potential effects of concentrated LiOH if partitioning of boric acid occurs.

Pressurized heavy water reactors, including CANDU reactors, use heavy water coolant with low LiOH (about 0.4 ppm Li) additions and no boric acid (boric acid is added to the moderator if needed to control reactivity); the moderator is D_2O at low temperature (about 340 K (70°C)). These reactors have some boiling (and steam quality) in high power channels immediately after refuelling, but are usually free of deposits, and have small oxide thicknesses because the in-reactor lifetime of natural uranium fuel is short.

Although out-reactor testing of Zr alloys had previously been limited to the comparison of Zircaloys in various heat treatments in water and steam, as shown in Fig. 8.55 [8.87], and comparisons of minor variants of Zircaloy alloy compositions, as shown in Fig. 8.56 [8.88], derivatives of Russian Federation alloys (E110/M5 and E635/ZIRLO) are becoming standard fuel cladding alloys for high performance PWRs, and variants on Zircaloy-4 are vanishing. Results on these alloys are shown in Fig. 8.57 [8.4–8.6]. Out-reactor testing now includes comparisons of these alloys with Zircaloy-4, and routine testing in concentrated LiOH, as shown in Fig. 8.58 [8.89] and Fig. 8.59 [8.90]. These figures give good comparisons of the results of out-reactor testing for current cladding alloys but do not give enough details of the kinetics, which would be required if any mechanistic understanding is to be reached.



FIG. 8.55. Long term oxidation curves for (a) a annealed, and (b) β quenched Zircaloy-2 [8.87]. 1500 psi = 10.34 MPa, 500 $\mathcal{F} = 533 \text{ K} (260 \, \mathbb{C}), 550 \, \mathcal{F} = 560 \text{ K} (287.8 \, \mathbb{C}), 600 \, \mathcal{F} = 588.7 \text{ K} (315.6 \, \mathbb{C}), 680 \, \mathcal{F} = 633 \text{ K} (360 \, \mathbb{C}), 750 \, \mathcal{F} = 672 \text{ K} (399 \, \mathbb{C}), 850 \, \mathcal{F} = 727.6 \text{ K} (454.4 \, \mathbb{C}), 950 \, \mathcal{F} = 783 \text{ K} (510 \, \mathbb{C}), 1100 \, \mathcal{F} = 866.5 \text{ K} (593.3 \, \mathbb{C}) [8.87].$



FIG. 8.56. Autoclaved corrosion results from tests in water at 633 K (360° C) (top left), in steam at 672 K (400° C) (top right), in steam at 700 K (427° C) (bottom left) and in water with 70 ppm Li as LiOH at 633 K (360° C) (bottom right) (reprinted with permission from Ref. [8.88], copyright ASTM International, 1994).



FIG. 8.57. Corrosion of zirconium alloy with 1% niobium in water and superheated steam at various temperatures [8.4].

сох



FIG. 8.58. Autoclave corrosion of alloys in deionized water at 623 K (350°C), 16.8 MPa (left) and autoclave corrosion of alloys in water containing 70 ppm lithium at 633 K (360°C), 18.6 MPa (right) (reprinted with permission from Ref. [8.89], copyright ASTM International, 1996).



FIG. 8.59. Corrosion kinetics in water at 633 K (360° C) imitating (a) WWER-1000; (b) corrosion kinetics in water with 43 ppm O₂ at 633 K (360° C); (c) corrosion kinetics at 673 K (400° C) steam (reprinted with permission from Ref. [8.90], American Nuclear Society, La Grange Park, Illinois, 2000).

8.4.2. Detailed corrosion kinetics

The data shown in Fig. 8.55 [8.87] present a simplified view of corrosion kinetics — an approximately cubic pre-transition growth law followed by a sharp transition to an approximately linear post-transition corrosion rate. Similar plots can be seen in Fig. 8.49 [8.2]. The oxidation kinetics of Zircaloy-type alloys is much more complicated when studied in detail:

- The pre-transition kinetics in high temperature water are never parabolic and seldom fit a true cubic kinetic form, as shown in Fig. 8.60 [8.50]. The exponent in the rate law can range from 0.22 (close to quartic) to 0.43 (still short of parabolic).
- The breakdown of the oxide at transition takes a significant amount of time, as shown in Fig. 8.61 [8.91]. Although this transition appears to be smooth, at lower temperatures and higher pressures [8.46, 8.47, 8.92, 8.93] it can be a sharp discontinuity, as shown in Figs 8.20 and 8.62 [8.46]. This behaviour suggests a localized breakdown process, which can happen quickly over the whole surface, or can initiate rapidly locally, but spread slowly over the surface at low pressures.



FIG. 8.60. Histogram of oxidation rate exponents, n [8.50].



FIG. 8.61. Effect of pressure on the rate of propagation of the oxidation kinetic transition for Zircaloy-2 in steam at 723 K (450°C) (reprinted with permission from Ref. [8.91], copyright Elsevier, 1968). 1 torr = 133,322 Pa.



FIG. 8.62. Typical corrosion kinetics in high temperature water showing weight gains on Zircaloy-4 during corrosion tests in water at 633 K (360°C) (reprinted with permission from Ref. [8.46], copyright Elsevier, 1979).

During this transition, porosity is generated that penetrates completely through the oxide film to the metal-oxide interface at both low pressures, shown in Fig. 8.63 [8.94], and high pressures, shown in Fig. 8.64 [8.95]. The low residual electrical resistance confirms the deep penetration of the porosity once the pores are filled with mercury during porosity measurement; see Fig. 8.65 [8.16, 8.96].



FIG. 8.63. Oxidation curve obtained by changing steam or oxygen pressure [8.94].



FIG. 8.64. Weight gain vs. time for Zircaloy-2 (Z105 as rolled) 'cross-over' experiment (transferred between 1250 psi (8.62 MPa) and 1 atm (0.1 MPa) steam at 773 K (500°C)) [8.95].



FIG. 8.65. Development of porosity in oxide films formed on Zircaloy-2 in steam at 673 K (400°C). The appearance of porosity prior to normally accepted weight gain at transition (about 30 mg/dm²) should be noted. R_0 is initial resistance, R_p is resistance at any pressure (p) and R_f is final resistance at maximum pressure [8.96, 8.16]. 1 lb/in² = 0.0069 MPa.

— The post-transition oxidation process is not linear [8.46] but shows a steadily increasing rate, as shown in Fig. 8.66 [8.97]. Although the authors argue for a two-stage linear process, the first derivative of the data shows clearly that the rate continues to increase but at a decreasing rate. It should be possible to extrapolate the second derivative of the original data to zero and to predict the time at which the post-transition rate would become linear.



FIG. 8.66. Long term corrosion kinetics of Zircaloy-2 in water with a pH of 7 at 589 K (316° C) (reprinted with permission from Ref. [8.97], copyright Elsevier, 2000).

- The Zircaloy-type alloys are insensitive to the effects of heat treatment except in high temperature, high pressure steam where a form of nodular corrosion occurs. This phenomenon will be discussed in detail because it provides a good simulation of some effects of irradiation. In the presence of irradiation other factors come into play and introduce different behaviour.
- The oxidation kinetics of Zr-Nb alloys show differences from those of Zircaloytype alloys. The pre-transition kinetics of Zr-Nb alloys are close to cubic but show variation with the metallurgical condition. This behaviour is caused by the extensive presence of β-Zr and β-Nb phases, depending upon heat treatment. The β-Zr phase (about 19 wt% (18.7 at.%) Nb) has poor corrosion resistance, as shown in Fig. 8.67 [8.98], so that the presence of β-Zr 'stringers', or filaments, at α-Zr grain boundaries result in ridges of thicker oxide, as shown in Fig. 8.68 [8.99]. The microstructure of the tubes is determined during fabrication by extrusion in the ($\alpha + \beta$) phase field. With subsequent heat treatment, the filaments of the metastable β-Zr phase become discontinuous and through a series of transformations eventually become β-Nb (>85 wt% (84.8 at.%)Nb); these changes in microstructure suppress the formation of oxide protrusions and enhance corrosion resistance. Zr-1Nb alloy fuel cladding is generally used in the fully annealed condition, where the Nb will be present as small β-Nb particles, which have a small effect on the corrosion behaviour.



FIG. 8.67. Variation of weight gain with Nb composition at 570 K (300°C) after 5, 50 and 250 days [8.98].



FIG. 8.68. Ridges of thick oxide correlated with β -Zr filaments in Zr-2.5Nb after prefilming in steam at 673 K (400°C) followed by 56 d in lithiated water at 583 K (310°C); the figure shows the metal–oxide interface after the chemical removal of underlying metal (reprinted with permission from Ref. [8.99], copyright Elsevier, 1999).

A sharp acceleration in the corrosion rate at transition is seldom seen in Zr-Nb alloys where a paralinear kinetics that does not demonstrate any sudden acceleration is typical. There may be some acceleration and deceleration of the oxidation rate, as shown in Fig. 8.69 [8.100], but no clearly cyclical behaviour such as that seen with the Zircaloys.



FIG. 8.69. Corrosion of heat treated Zr-2.5%Nb in water at 473–573 K (200–300°C) [8.100].

- When the pressure of the oxidizing gas is suddenly changed, Zircaloy-2 exhibits a characteristic transition, shown in Fig. 8.70 [8.94], which is not observed in Zr-2.5% Nb because of the absence of porosity penetrating right up to the oxide-metal interface, demonstrated by the high resistivity in mercury porosimeter tests on the final oxides, as shown in Fig. 8.71 [8.101]. These observations suggest that there is a much more robust barrier film at the oxide-metal interface in Zr-Nb alloys than there is in the Zircaloys. It does not necessarily mean that there is a completely impervious barrier film, since a few pores penetrating the barrier would not lead to a completely linear pressure dependence of the oxidation rate as seen with the Zircaloys. If pores are present that are also much smaller in diameter than those in the barrier film on the Zircaloys, then the mercury could not penetrate as far in the Zr-Nb oxides without a higher maximum porosimeter pressure (which was not available when the experiments were done).
- The development of a technique using the ¹³C profile that develops in an oxide film from the ¹⁶O $(n,\alpha)^{13}$ C reaction and measuring the slope of this profile to estimate the oxidation rate throughout the lives of the individual Zr-2.5Nb pressure tubes [8.102, 8.103] has shown that some tubes show accelerations in their long term corrosion rates while other tubes do not, as shown in Fig. 8.72 [8.102].



FIG. 8.70. Pressure dependence of the oxidation of Zr-2.5%Nb alloy (reprinted with permission from Ref. [8.94], Atomic Energy of Canada Limited, Canada). 8 cm Hg = 10.666 kPa.



FIG. 8.71. Comparison of porosimeter results on oxide films on Zircaloy-2 and Zr-2.5Nb [8.101]. 1000 psia = 6.89 MPa.



FIG. 8.72. Selected data secondary ion mass spectrometry survey depth profiles through the waterside oxides on a low (top) and high (bottom) deuterium ingress Zr-2.5Nb pressure tube [8.102].

The oxidation kinetics, the permeability of the oxide film and hydrogen absorption (as described below) of Zr-Nb alloys are different from those of the Zircaloys and represent an increased tolerance to corrosion. This improved overall reactor performance is leading to the declining use of Zircaloys.

8.4.3. Detailed oxide morphologies

The general morphology and crystallography of oxides were summarized in Section 8.3.1 and 8.3.2. Detailed differences that might explain the differences in oxidation kinetics will now be explored. The general similarities between oxide films are that all films are largely arrays of columnar monoclinic zirconia crystallites. These crystals develop a texture as a function of preferential growth in some orientations, depending on the orientation of the underlying metal grains, as shown in Fig. 8.73 [8.20]. A noticeable fraction of t-ZrO₂ is formed at the oxide–metal interface and transforms to m-ZrO₂ further out in the oxide.

For Zircaloy-4 and ZIRLO, this transformation results in cyclic oxide layers, as shown in Fig. 8.19 [8.45], that match the cyclic oxidation kinetics of the Zircaloys, as shown in Fig. 8.20 [8.47]. An oxide section of a film about 13 μ m thick formed on Zr-2.5Nb pressure tube material also showed a sequence of layers in the oxide, although the oscillations of the t-ZrO₂ fraction are muted, as shown in Fig. 8.74 [8.45]. Zr-2.5Nb does not show any cyclical behaviour in the oxide growth; in this study none of the corrosion curves show any significant cyclical behaviour, as shown in Fig. 8.75 [8.45], although weighing intervals were long and variable making it improbable that any clear cyclical behaviour could be seen. The variations in t- and m-ZrO₂ layers may be out of phase in local areas of the surface in Zr-2.5Nb, as is thought to happen in the Zircaloys when only a few cycles are seen and the oxidation rate averages out to a quasi-linear rate. The micrographs show regular but discontinuous layers with thicknesses over 2 μ m, as shown in Fig. 8.76 [8.45], which is large enough that cycles should be visible in the oxidation kinetics of all the alloys reported if weighing is frequent enough.



FIG. 8.73. Inverse pole figure normal to the monocrystalline faces, after 130 h at 773 K (500°C) oxidation (inner circle) followed by 4 h at 923 K (650°C) oxidation (dotted line circle) (reprinted with permission from Ref. [8.20], copyright Elsevier, 1971).



FIG. 8.74. Tetragonal zirconia fraction measured in a range of zirconium alloys (reprinted with permission from Ref. [8.45], copyright Elsevier, 2004).



FIG. 8.75. Corrosion kinetics for the alloys measured in Fig. 8.74 (a) in water at 633 K ($360^{\circ}C$); (b) after an initial 200 days (reprinted with permission from Ref. [8.45], copyright Elsevier, 2004).



FIG. 8.76. Secondary (left) and backscattered (right) scanning electron images of cross-sections of oxide formed on Zr-2.5Nb exposed to water at 633 K (360°C) for 784 days (reprinted with permission from Ref. [8.45], copyright Elsevier, 2004).

These layers are postulated to be separated by long lateral cracks [8.49]. These cracks are regarded as artefacts of the cutting and polishing used to provide the metallographic sections [8.16, 8.37, 8.48]. In the investigations of Yilmazbayhan et al. [8.45], the sectioning technique avoided the production of long lateral cracks and produced a few features resulting from picking out clusters of small oxide crystallites along the boundaries of the layers, as shown in Fig. 8.76 [8.45]. The boundaries between the layers in oxide films may represent points at which the columnar oxide growth stops and small crystallites renucleate [8.37]; this transition should be an area where it would be easy to pick out clusters of small crystallites. The authors of Ref. [8.45] recognized that there were no long lateral cracks in their oxides but when these results were published for a second time [8.104] they retracted this conclusion, but did not claim to have seen lateral cracks, merely argued that such cracks might be real and not merely artefacts of poor metallographic techniques.

Initially, oxide films formed out-reactor on Zircaloys and Zr-Nb alloys are planar at both the metal–oxide interface and the oxide–corroding-medium interface, provided the corroding surfaces have been polished smooth. Once the thin, 'interference coloured' oxide region is passed, the metal–oxide interface becomes cusped, probably as a result of the development of the textured columnar oxide crystallite structure, as shown in Fig. 8.77 [8.31, 8.104]. To view the inner surface of the oxide the metal must be dissolved away. A solution of Br in dry ethylacetate is the preferred solvent, but a strong HF/HNO₃ pickling solution may also be used. The latter technique must be adjusted to protect the inner surface of the oxide, but must be strong enough not to leave some undissolved Zr-O solid solution. Trial and error, with comparative micrographs of the same oxide surface given different etching times and conditions, is necessary to avoid artefacts, in particular needle-like features, seen in Fig. 8.78, on the inner surface of the film due to incomplete dissolution of the Zr-O solid solution [8.66, 8.15].


FIG. 8.77. Cellular structure of the oxide–metal interface of unalloyed zirconium oxidized in 640 K ($400^{\circ}C$) steam (reprinted with permission from Ref. [8.31], Atomic Energy of Canada Limited, Canada).



FIG. 8.78. Incomplete dissolution of Zr-O solid solution at the oxide–metal interface after oxidation of van Arkel Zr in O₂ at 773 K (500°C) (reprinted with permission from Ref. [8.31], Atomic Energy of Canada Limited, Canada).

Oxide films on unalloyed Zr develop ridges of thick oxide at the metal grain boundaries. These ridges develop arrays of cracks parallel to the grain boundaries, as shown in Fig. 8.79 [8.15]. The ridges and associated cracking increase in severity as the purity of the metal decreases: Zr made by the Kroll process [8.105] is worse than Zr made by the van Arkel process [8.31] and graphite melted Zr is even worse [8.71]. These effects were attributed to the accumulation of impurities at the metal grain boundaries [8.35]. It was argued that, because all alloying additions to van Arkel Zr increase the pre-transition rate when compared with the pure Zr in oxygen at high temperature (970 K (700°C)), the effect of the intermetallic particles in the Zircaloys (if they were uniformly distributed) was to increase the corrosion of the metal grains to give an overall uniform oxide film that would not develop cracks early in the corrosion process, as shown in Fig. 8.79 [8.15]. The properties of the commonly observed intermetallic particles must be considered to see if such a hypothesis is plausible.



FIG. 8.79. Oxide film on electropolished reactor grade zirconium after 21 days in steam at 570 K (300° C) and 1 100 kPa. The ridges of thick oxide at grain boundaries and [1121] twins and occasional complete grains growing thick oxide should be noted. Cracks may form on top of ridges [8.15].

8.4.4. Properties of intermetallic phases

There are many stable intermetallic phases of zirconium; their metallurgical structure and general properties have been discussed [8.106]. From the viewpoint of their influence on oxidation and corrosion only a small subset of Zr intermetallic particles are important, and those are the intermetallic particles that occur as SPPs in the commercially

used Zr alloys. Their importance in the oxidation process depends primarily on the relative rates of three processes compared with those of the Zr matrix:

- The electrochemical potential of the SPP relative to the matrix [8.107];
- The oxidation rate of the SPP compared with the matrix;
- The ability of the SPP to absorb hydrogen and the diffusion rate of H in the SPP compared with the diffusion rate of H in the Zr matrix.

In general, electrochemical cells involving the SPP and the matrix have been largely ignored because it was thought that the possible potential difference between the SPP and the matrix would be small, and the resistivity of the oxides formed on the two components of the electrochemical cell at high temperature would be too high for any galvanic currents to pass. The electrochemical potentials of SPPs typical of the Zircaloys, both at room temperature [8.107] and in high temperature aqueous solutions [8.108] have been measured. Stability of SPPs under irradiation is an important factor for the alloy corrosion resistance under irradiation. That galvanic currents could not be ignored in-reactor was shown very early [8.109] by the hydriding failures of Zircaloy-2 flow tubes in the K-East Reactor (Hanford Site, USA) resulting from close proximity to Al alloy clad shield plugs. Attempts to simulate the phenomenon in the laboratory were complete failures [8.110]; the use of a gamma-cell or an electron accelerator to simulate the effects of reactor irradiation was not attempted to assess the galvanic currents that could be passed. In general, in laboratory tests, unless the SPPs are very coarse (when white oxide spots are seen) or if they form white oxide stringers because of severe segregation due to metallurgical problems (e.g. from inert gas melting), SPPs do not cause severe localized corrosion [8.72, 8.111].

In-reactor, where the radiation field increases the electronic conductivity of the zirconia film [8.112, 8.113], localized galvanic currents between SPPs and the Zr alloy matrix, or between other metals (e.g. stainless steels or nickel alloys) and the Zr alloy, can result in increased localized corrosion. These effects will be discussed in detail when the effects of irradiation are discussed below.

The effect of the intermetallic particles on the alloy oxidation in the absence of irradiation effects can be large. An early hypothesis [8.35] was that uniformly distributed small SPPs increased the local corrosion rate of Zr matrix around each individual SPP so that the oxide thickness on the metal grains matched the enhanced oxidation that was observed at the grain boundaries of unalloyed zirconium during oxidation in steam or oxygen. This matching of the oxide growth in the grains with that in the grain boundaries reduced the local stresses in the oxide and delayed any severe cracking of the oxide film. Because electron transport in the oxide film is very limited under these conditions (and remains the rate determining step) localized corrosion around intermetallic particles is limited to severe irregularities in SPP size and distribution, as shown in Fig. 8.80 [8.112]. This picture persists over the normal temperature range of testing (573-673 K (300-400°C) in water or steam). In steam at 773 K (500°C) with pressures above 6.9 MPa the situation changes. The oxide film apparently becomes sufficiently electron conducting that severe galvanic corrosion between SPPs and the surrounding matrix becomes possible. This extra corrosion leads to the production of nodules. The dependence of this nodular corrosion on SPP size is sufficiently similar to that observed in BWRs (in oxygenated water at 558 K (285°C) under irradiation) for the high temperature steam test to be used to evaluate batches of cladding for resistance to nodular corrosion in-reactor, Figs 8.81-8.85 [8.114].



FIG. 8.80. Zircaloy-4 batch susceptible to white oxide spotting, indicating localized corrosion around intermetallic particles. The batch was corroded in steam at 670 K (400°C) and 10 MPa for 14 days. The feature at the bottom right is the edge of a white oxide stringer [8.112].



FIG. 8.81. Nodular corrosion weight gain vs. temperature in steam at 10 MPa; samples A1 to A6 represent materials with a range of resistance to nodular corrosion (reprinted with permission from Ref. [8.114], copyright ASTM International, 1987).





FIG. 8.82. Nodular corrosion weight gain vs. time in steam at 770 K (500°C); samples A1 to A6 represent materials with a range of resistance to nodular corrosion (reprinted with permission from Ref. [8.114], copyright ASTM International, 1987).

FIG. 8.83. Nodular corrosion weight gain vs. pressure in steam at 780 K (510°C) after 16 h; samples A1 to A6 represent materials with a range of resistance to nodular corrosion (reprinted with permission from Ref. [8.114], copyright ASTM International, 1987). K psig = K psi + 14.7 psi = (K + 14.7) × 6895 Pa.



FIG. 8.84. Weight gains of Zircaloy-2 as a function of flow rate in steam at 780 K (510° C) and 1500 psig (103.4 bars = 10.34 MPa) in 16 h; samples A1 to A6 represent materials with a range of resistance to nodular corrosion (reprinted with permission from Ref. [8.114], copyright ASTM International, 1987).

FIG. 8.85. Weight gains of Zircaloy-2 samples as a function of test duration in 780 K (510°C), 1500 psig (104.4 bars = 10.44 MPa) in 16 h; samples A1 to A6 represent materials with a range of resistance to nodular corrosion (reprinted with permission from Ref. [8.114], copyright ASTM International, 1987).

It was initially thought that the chemical nature of SPPs was less important than their size and uniformity of distribution. This conclusion seemed to be borne out by the small differences observed in the oxidation kinetics of a range of Zircaloys, as shown in Fig. 8.86 [8.89, 8.72]. Most of this testing was done in steam at atmospheric pressure; conditions leading to severe nodular corrosion (\geq 770 K (500°C); \geq 6 MPa steam) were not tested. In early tests in high pressure steam at 770 K (500°C) [8.115], severe localized oxide breakdown was observed on some alloys but no nodular corrosion was seen; see Table 8.4.



FIG. 8.86. Variation in oxidation rate for various billets of Zircaloy-2 (reprinted with permission from Ref. [8.72], Atomic Energy of Canada Limited, Canada). 1atm = 0.1 MPa.

8.5. CORROSION OF ZIRCONIUM ALLOYS

This chapter has so far discussed oxidation producing oxide films that provided much protection and adherence to the underlying metal; these processes are often colloquially referred to as corrosion. Corrosion is also a process whereby Zr is oxidized to ZrO^{2+} ions, but here the material loses weight and zirconium goes into solution as the zirconyl salt of the environment, usually a strong acid. The corrosion resistance of zirconium in strong acids is excellent and so its alloys are widely used in chemical plant equipment, especially as liners. A brief summary of the conditions to which zirconium alloys are resistant is given in Ref. [8.17]; some of the data are summarized in Figs 8.87 and 8.88.



FIG. 8.87. Corrosion of zirconium in hydrochloric acid (reprinted with permission from Ref. [8.17], Atomic Energy of Canada Limited, Canada). 1 mpy (milli-inches per year) = 0.0254 mm/y (mm per year).

FIG. 8.88. Corrosion of zirconium in sulphuric acid (reprinted with permission from Ref. [8.17], Atomic Energy of Canada Limited, Canada). 1 mpy (milliinches per year) = 0.0254 mm/y (mm per year).

500

450

400

350

300

250

150

100

200 1

5

MPERATURE

Good alloys	Intermediate alloys	Bad alloys			
Nominalcomposition (wt%)	Nominal composition (wt%)	Nominal composition (wt%)	Remarks		
1.0 Cu (α)	1.0 Cu ($\alpha + \beta$)	Van Arkel 11B			
0.3 Cr-0.3 Ni	1.0 Ni	Unalloyed stock Zr			
0.5 Cu-0.5 W	0.1 Fe ($\alpha + \beta$)	0.1 Cu	Localized corrosion		
	0.3 Fe	0.3 Cu			
	0.3 Co	3.0 Cu			
	1.0 Co	0.1 Ni			
	0.3 Cr ($\alpha + \beta$)	0.3 Ni			
	1.0 Cr ($\alpha + \beta$)	0.1 Fe (α)			
	0.3 Mo	0.1 Co			
	1.0 Cr	0.1 Cr	Irregular behaviour		
		0.3 Cr (α)			
		1.0 Cr (α)	Irregular behaviour		
		0.3 Mn			
		1.0 Ag			
		0.3 V			
		0.3 W			
		1.0 Cu 1.5 Mo (α)			
		0.3 Cr 0.3 V (α)			
		1.0 Cu 1.0 W	High nitrogen (400 ppm)		
		1.0 Ni 1.0 W	High nitrogen (960 ppm)		

TABLE 8.4. EARLY CLASSIFICATION OF ALLOYS [8.115]

Note: Alloys were tested in steam at 773 K (500°C) and 10.3 MPa. Specimens were annealed at 1050 ± 25 K (775 ± 25°C) for 1 or 6 h — α — or water-quenched from 1170 K (900°C) — α + β . Both heat treatments gave similar results, unless otherwise indicated.

Zirconia is an amphoteric oxide, so it has both acidic and alkaline properties. Hence it is also soluble in strong bases. The relative severity of this dissolution was established from hydrothermal dissolution experiments [8.116], which showed a decreasing severity of ZrO_2 dissolution in the sequence LiOH>NaOH>KOH>NH4OH. This sequence is precisely in the same order of the corrosion rates observed in aqueous solutions at 633 K (360°C), as shown in Fig. 8.21 [8.52]. In these tests, Zircaloy specimens still showed weight gains and formation of oxide films, although in LiOH these oxides were very porous. Studies of the mechanism of these effects [8.84–8.86] have shown that the protectiveness of the normal oxide film formed in water at elevated temperature is reduced in LiOH solutions by a small amount of dissolution of zirconia at the oxide crystallite boundaries. This dissolution renders the oxide non-protective and increases the oxidation rate as attempts to regrow a protective oxide ensue. The solubility of ZrO₂ in LiOH at a pH of 12 and at 573 K (300°C) was measured to be about 1 ppb [8.86]. This solubility is sufficient to generate porosity in a protective oxide. The dissolved ZrO₂ reprecipitates on the specimen surface, the autoclave or elsewhere. In-reactor, where there may be a steep temperature gradient across the oxide film, the dissolved ZrO_2 probably precipitates as Li_2ZrO_3 in the outer layers of the oxide film, where it gives rise to the non-exchangeable Li incorporated into the outer layers of the oxide. This process has been argued to lead to accelerated corrosion when LiOH is concentrated by high temperatures (above saturation temperature) in thick oxides on high power rods. More likely, accelerated corrosion is caused by the oxide dissolution produced by locally concentrated LiOH near the oxide-metal interface as a result of the large elevation of the boiling point coefficient of LiOH [8.81].

The presence of boric acid has been found to inhibit the effects of concentrated LiOH [8.82, 8.83]; in PWR operating conditions there should be enough boric acid present to prevent accelerated corrosion by concentrated LiOH, except, perhaps, at the very end of a reactor cycle when the boric acid concentration has been depleted. In circumstances where LiOH has been concentrated in the pores of thick oxide films (where the temperature exceeds the saturation temperature of the water) it is uncertain whether the boric acid (which has a similar elevation of the boiling point coefficient to LiOH) is able to diffuse into the oxide porosity, because of the much larger ionic size of the borate ion compared with the lithium ion. In instances where Li profiles have been measured in severely degraded oxides [8.7], the boron distributions have been ignored. The fixed Li in the oxide in these tests was found in the outer layers of the oxide. This distribution is exactly what it ought to be if the Li arrived there by dissolution of ZrO₂ and reprecipitation in the colder part of the oxide. To have any direct effect on diffusion controlled oxidation kinetics, the Li should be present in the oxide at the oxide–metal interface, but it is completely absent.

Other corrosion-type processes that might influence the in-reactor oxidation rate are usually absent, since impurities such as chlorides and fluorides that might cause pitting are usually well controlled. This control has not always been the case in test reactor loops [8.117], where such pitting has occasionally been observed. The proposal that peroxide ions (transiently present in BWR chemistry, and elsewhere if insufficient hydrogen is added to the reactor water) can also cause the local dissolution of zirconia films [8.118], has been demonstrated by Nishino et al. [8.119] by corroding Zircaloy-2 during γ irradiation, as shown in Fig. 8.89.



FIG. 8.89. Weight gains of Zircaloy-2 in pure water at 561 K (288°C) with and without γ ray irradiation (reprinted with permission from Ref. [8.119], copyright Elsevier, 1997).

Most reactors operate either with high purity water or with low LiOH concentrations that require major concentrating effects due to boiling before they become concentrated enough to degrade the oxide films by the dissolution of ZrO₂. One early reactor (the Homogenous reactor at Oak Ridge National Laboratory, USA) operated with a solution of highly enriched (UO₂)SO₄, 0.12M H₂SO₄ and 0.05M CuSO₄ and an oxygen overpressure. Under irradiation, the bombardment by fission fragments and increased dissolution of the protective oxide led to severe corrosion and penetration of the Zircaloy inner reactor vessel [8.120, 8.121].

8.6. EFFECTS OF IRRADIATION

8.6.1. Effects on the metal

Fast neutron irradiation displaces atoms from their lattice sites, initially creating clusters of defects ('black spots' seen in transmission electron microscopy studies) that develop into dislocation loops that interact with the pre-existing forest dislocations and affect the mechanical properties of the alloy (see Chapter 6). In alloys containing Fe in the form of intermetallic particles, the fast neutrons displace Fe atoms from these particles into metastable solution in the Zr matrix. This displacement damage results in a progressive degradation of the oxidation resistance of the alloy, shown in Fig. 8.90 [8.122], in post-irradiation corrosion tests. Irradiation at low temperatures (573 K (\leq 300°C)) can also result in amorphization of the intermetallic particle; this loss in crystallinity can also be caused by electron or gamma irradiation, provided the bombardment is energetic enough to cause point defects (PDs) within the intermetallic particles [8.123], but it is not necessary for the irradiation to be energetic enough to displace completely the Fe atoms out of the intermetallic particles. Electron and proton radiation can contribute to the decomposition of β -Zr and induce precipitation of β -Nb from the supersaturated α phase in Zr-2.5Nb but cannot degrade the oxidation resistance of Zircaloys [8.124].



FIG. 8.90. Corrosion of Zircaloy-2 in steam at 673 K (400°C). BWR water rod materials irradiated at 561 K (288°C). Fluences are given in parentheses, $10^{25} n/m^2 (E > 1 \text{ MeV})$ (reprinted with permission from Ref. [8.122], copyright ASTM International, 1994).

8.6.2. Effects on the oxide

Fast neutron irradiation will displace atoms from their lattice sites in the oxide film. This increase in the PD concentration in oxide films during irradiation was expected to augment the diffusion controlled region of oxide film growth, and hence the oxidation rate [8.15]. No evidence for PD clusters, dislocation loops or other such features could be found for films grown under either proton [8.125] or Xe ion irradiation [8.126]. Features that were thought to be dislocations were probably twins resulting from the tetragonal to monoclinic phase transformation in the oxide, which takes place as the stresses decrease in the oxide as it grows away from the oxide-metal interface, shown in Fig. 8.91 [8.38]. This observation suggests that Frenkel pairs recombine rapidly in oxide films, aided by the very small crystallite size, since voids are commonly observed near grain boundaries in bulk ceramics. Nanopores have been observed in the outer layers of oxide films formed on CANDU Zr-2.5Nb pressure tubes, where the outer oxide has recrystallized, as shown in Fig. 8.92 [8.38]. These pores are thought to be small He bubbles resulting from the ${}^{16}O(n,\alpha){}^{13}C$ reaction, and correspond in frequency with the concentrations of ${}^{13}C$ measured in these oxides, as shown in Fig. 8.93 [8.103], which are used to calculate oxide growth rates during the lifetime of the pressure tube. That increased diffusion in the oxide under irradiation does not contribute to increased diffusion controlled corrosion rates is indicated by the absence of any rise in oxidation rate in the pre-transition stage, as shown in Fig. 8.94 [8.127], and confirms the conclusion that oxygen diffusion is not the rate determining step during Zr oxidation.



FIG. 8.91. High magnification underfocused electron image of twinned equiaxed grains near the surface region of an oxide on a Zr-2.5Nb pressure tube, showing cracks (indicated by an arrow) that are associated with twins intersecting the grain boundary (reprinted with permission from Ref. [8.38], Taylor & Francis).



(a)

(b)

FIG. 8.92. (a) Under focused and (b) overfocused images of equiaxed grains near the surface region of an oxide on a Zr-2.5Nb pressure tube, showing nanopores and cracks (indicated by arrows in Fig. (a)) at grain boundaries (reprinted with permission from Ref. [8.38], Taylor & Francis).



FIG. 8.93. Secondary ion mass spectrometry survey depth profile of ${}^{13}C$ through the waterside oxide near the outlet end of a Zr-2.5Nb pressure tube (reprinted with permission from Ref. [8.103], copyright ASTM International, 2005).



FIG. 8.94. Corrosion of Zircaloy-4 in a PWR in deionized water and in LiOH (reprinted with permission from Ref. [8.127], copyright ASTM International, 1996).

Electron and gamma irradiation, both in-reactor and in laboratory tests, cause enhanced electron conductivity in the oxide film, as shown in Fig. 8.95 [8.128]. If electron and gamma energies are high enough these radiations can also create Frenkel pairs. Displacement energies are lower in the metal than in the oxide so phenomena such as amorphization of intermetallic particles can occur, but no effect on diffusion in the oxide film would be expected because of rapid recombination of PDs [8.123].



FIG. 8.95. Change in oxide conductivities on Zircaloy with 1 MeV electron beam on/off: (a) Zircaloy-2; (b) improved Zircaloy-2; (c) Zircaloy-4 (reprinted with permission from Ref. [8.128], copyright Elsevier, 1999).

8.6.3. Effects on in-reactor water

Radiolysis of reactor water was thought to be the direct cause of nodular corrosion in BWRs by accelerating surface reaction rates, which were postulated to be the rate controlling process in zirconium oxidation [8.14, 8.48]. Such control by surface reactions is not feasible because the diffusion controlled pre-transition oxidation rates are not much different for O_2 , steam, water, 1.0M NH₄OH and 0.2M H₂SO₄ at the same temperature in the range 573–633 K (300–360°C). Thus, the details of the radiolytic processes in the water [8.15] can be safely ignored. Effects ascribable to radiolysis of the water are limited to electrochemical effects resulting from differences in redox potentials observed in BWR (shadow corrosion, nodular corrosion), effects on electron conduction in oxide films and possibly effects of peroxide, produced by radiolysis, on the degradation of zirconium oxide films [8.118, 8.119].

The high dissolved hydrogen concentration of PWR water not only inhibits radiolysis of the water, it also ensures that all metallic components operate at the reversible hydrogen potential, so that no galvanic couples are created [8.129].

8.6.4. Effects on in-reactor corrosion

Oxide films formed in the laboratory tend to be uniform and parallel sided at normal reactor temperatures (353–633 K (280–360°C)), and only in the early development of the alloys now in use were non-uniform features such as white oxide spots or stringers seen [8.72]. The exception to this behaviour was found on testing in steam at 773 K (500°C) at a pressure of 10 MPa where nodular corrosion was observed. In PWRs, provided dissolved hydrogen in the water is high enough, uniform oxide films are also formed, and only if no hydrogen (or less than about 5 cm³·kg⁻¹) is present is nodular corrosion observed.

In BWRs, nodular corrosion was almost universal initially, and was first reported under stainless steel grids in loop tests of steam generating heavy water reactor fuel assemblies. With more prolonged exposure, nodular corrosion becomes general over the tube surface in boiling conditions, as shown in Fig. 8.96 (see examples in Ref. [8.130]), but the oxide nodules were generally thicker (or more frequent) under stainless steel grids than in intergrid sections, shown in Fig. 8.97 [8.131]. That this severe corrosion was probably a galvanic effect of the proximity of the cladding to stainless steel was shown for steam generating heavy water reactor fuel by the 'mixed grid' experiment; alternate grids in the test assembly were made of Zircaloy and stainless steel. Nodular corrosion was only seen under the stainless steel grids [8.131].

In these experiments nodular corrosion was not very severe, and discrete nodules could be observed. More severe examples were seen in BWRs where shadows of stainless steel control blade handles were observed on the adjacent Zircaloy channel, as shown in Fig. 8.98 [8.132].

Serious concern about severe shadow corrosion was raised after very heavy corrosion of fuel cladding took place under the steel Inconel grids in the Liebstadt reactor, as shown in Fig. 8.99 [8.8].



(a)



(b)

FIG. 8.96. Severe nodular corrosion in a BWR: (a) uniform distribution of nodules; (b) nodules tending to align along scratches, possibly resulting from stainless steel or Ni smearing from grids during assembly of the fuel element (reprinted with permission from Ref. [8.130], copyright ASTM International, 1987).

It was suggested initially that these effects were a result of high β^- emissions from the stainless steel or nickel alloy, but experiments in the MIT Loop, USA, showed that this was not the case and that the effects were largely electrochemical galvanic corrosion, with a contribution from radiolytic species in the water, as shown in Figs 8.100 and 8.101 [8.133, 8.134]. That the stainless steel was the cathode and the Zr the anode was shown by the absence of extra H uptake [8.135]. This absence of additional H uptake for severe

corrosion under spacer grids was also seen in RBMKs (see Tables 8.5, 8.6). Caution should therefore be applied to all results from in-reactor loop tests where corrosion samples were tested in steel specimen holders (see Fig. 8.102 [8.136, 8.137]) and where H concentrations in the water did not exceed $5-10 \text{ cm}^3 \cdot \text{kg}^{-1}$.



FIG. 8.97. Summarized results of mixed grid experiment in a steam generating heavy water reactor (reprinted with permission from Ref. [8.131], copyright ASTM International, 1979).

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FIG. 8.98. The shadow of a stainless steel control blade handle on the adjacent Zircaloy channel (reprinted with permission from Ref. [8.132], copyright ASTM International, 1994).



FIG. 8.99. Maximum spacer shadow corrosion oxide layers measured at Leibstadt Nuclear Power Plant in 1999, compared with ABB Atom (Sweden) database from plants with iron surplus (reprinted with permission from Ref. [8.8], copyright American Nuclear Society, La Grange Park, Illinois, 2000).



FIG. 8.100. Shadow corrosion on Zircaloy-2 (Zry-2) caused by close proximity of other metals (reprinted with permission from Ref. [8.133], copyright American Nuclear Society, La Grange Park, Illinois, 2000).



FIG. 8.101. Oxide thickness as a function of the gap between the cladding and other metals (reprinted with permission from Ref. [8.133], copyright American Nuclear Society, La Grange Park, Illinois, 2000).



FIG. 8.102. Coupon holders made from stainless steel used for corrosion tests in the G-7 loop of the engineering test reactor at Hanford, Washington (reprinted with permission from Ref. [8.137], copyright ASTM International, 1964).

Fuel burnup (MW∙d∙kg ^{−1} U)	Time of operation	Uniform oxide film thickness (µm)	Maximum size of corrosion nodules (µm)		Mass fraction of hydrogen (%)	
	(h)		Outside spacer grid	Under spacer grid	Outside spacer grid	Under spacer grid
1.3	3 770	10–20	40	150	$(3-6) \times 10^{-3}$	
9.9	26 440	10–20	60	180	1×10^{-2}	
19.3	29 112	15–20	130	380	1×10^{-2}	$1.5 imes 10^{-2}$

TABLE 8.5. CORROSION CONDITION OF Zr-1N (E110) CLADDING OF FUEL RODS AFTER OPERATION IN RBMK-1000 (LENINGRAD NUCLEAR POWER PLANT)

TABLE 8.6. CORROSION CONDITION OF Zr-Nb-Sn-Fe CLADDING OF FUEL RODS AFTER OPERATION IN RBMK-1000 (LENINGRAD NPP)

Cladding material	Fuel burnup (MW·d·kg ⁻¹ U)	Time of operation (h)	Uniform oxide film thickness – (µm)	Maximum thickness of local corrosion nodules (μm)		Mass fraction of hydrogen (%)	
				Outside spacer grid	Under spacer grid	Outside spacer grid	Under spacer grid
Zr1Nb1.3Sn0.35Fe	11.4	25 488	10–20	0	0	7.5×10^{-3}	
(E635)	19.3	29 112	15–20	0	100	(1.5–2.0) × 10 ⁻²	(1.5–2.0) × 10 ⁻²

8.6.5. Zirconium alloy performance in power reactors

8.6.5.1. PWRs

PWRs operate with LiOH (2–3 ppm Li/l) additions to the water to control circuit corrosion and boric acid additions for reactivity control. Boron concentrations may be as high as 3000 ppm at the start of a cycle in a high performance plant. A high performance plant will have high power density fuel (i.e. high heat flux through the cladding), a high outlet water temperature (close to the saturation temperature of about 620 K (347°C) at the normal circuit pressure) and correspondingly high fast neutron fluxes. If the reactor operates with a high concentration of dirt particles in the water, leading to crud¹ deposits, then the potential for severe corrosion of the cladding is present. As the oxide thickness on the cladding increases with time the saturation temperature can be exceeded in the oxide film on the

¹ The term 'crud' comes from 'Chalk River unidentified deposit', used to describe the radioactive scaling that builds up on internal reactor components, first observed in the NRX research reactor at Chalk River Laboratories, Canada.

cladding, if in fact there is not already subchannel boiling in some of the most highly rated fuel assemblies. These conditions can lead to a concentration of LiOH in the oxide film and increased corrosion [8.81]. Severe deposition of crud from trace materials in the heat transport water can add to the problems by further raising the temperature at the oxide–metal interface if hard crud layers with poor conductivity are present [8.138]. These crud deposits are often composed of Fe and Ni oxides with contributions from other elements from the outreactor piping or from additions to the heat transport water such as Si and Zn [8.139].

As a result of the increasingly severe conditions faced by PWR cladding, the long established Zircaloy-4 has now reached its limit of usefulness. Initial changes to low Sn Zircaloy-4 did not produce major improvements (especially in hydrogen uptake), and adjustments to Fe and Cr concentrations resulted in only minor improvements in performance. Fuel cladding in high performance plants is now made from either ZIRLO (a modification of the Russian Federation E635 alloy: Zr-1%Nb-1.3%Sn-0.34%Fe) or M5 (a variant on the standard Russian Federation WWER E110 cladding: Zr-1%Nb). Comparative in-reactor data on these various alloys are limited, but some results are shown in Fig. 8.103 [8.140] and Fig. 8.104 [8.141, 8.142].



FIG. 8.103. Comparison of various zirconium alloys in a PWR (relative units, $1.0 \approx 100 \,\mu$ m) [8.140].



FIG. 8.104. Corrosion performance in PWRs of M5, various versions of ZIRLO and low tin Zircaloy-4 [8.141] (reprinted with permission from Ref. [8.141], copyright ASTM International, 2005).

ZIRLO being Even is now developed in а low tin version (Zr-0.75%Sn-1%Nb-0.1%Fe). In-reactor data for this version are limited, as shown in Fig. 8.105 [8.143], but the change is based on its improved resistance to concentrated LiOH in laboratory tests. Some of these results can be compared, as in Figs 8.58 [8.89] and 8.59 [8.90], although there seems to be no agreement on which LiOH concentration to use in such a test. In the absence of boiling in the oxide, accelerating corrosion with increasing burnup is largely the result of Fe displacement by fast neutrons, with some contributions from the increasing oxide-metal interface temperature as the oxide thickens.



FIG. 8.105. Eddy current measurements of oxide thickness along fuel rods clad in low Sn and standard ZIRLO (reprinted with permission from Ref. [8.143], copyright ASTM International, 2005).

8.6.5.2. BWRs

The severe nodular corrosion of some early BWR Zircaloy-2 cladding has been brought under control by careful control of the SPP size [8.144–8.147]. In essence, the SPPs must be not too big and not too small, as shown in Fig. 8.106 [8.145] and Fig. 8.107 [8.147]. The elimination of stainless steel grids has removed the shadow corrosion component of the cladding corrosion, but the remaining presence of Inconel X-750 grid springs still permits a small localized increase in oxide thickness at points of contact of the cladding with the grid spring, as shown in Fig. 8.108 [8.148], providing further evidence for the galvanic corrosion nature of the oxidation adjacent to dissimilar metals. The strong dependence of nodular corrosion away from stainless steel grids on SPP size strongly supports the argument that nodular corrosion itself is a galvanic corrosion phenomenon. The SPP is the dissimilar metal and is typically cathodic to the anodic Zr matrix.

The galvanic current that can be passed during irradiation, when the conductivity of intervening oxide films will be increased, will be controlled by the cathode (SPP) area in the exposed surface. Since the number of nodules formed on cladding is very much less than the number of SPPs in the surface layer, there must be other factors determining nodular corrosion. The observation [8.148] that nodules formed at sites where clusters of SPPs were present fits precisely with a galvanic corrosion model. The total cathodic area where a cluster of SPPs is present will ensure a much higher cathodic current than that due to a single small SPP, hence the restriction of the formation of thick oxide on the surrounding anodic matrix. For large SPPs, the necessity for SPP clusters may not be critical and larger numbers of nodules, perhaps one at each large SPP, will be formed.



FIG. 8.106. Effect of SPP size on the corrosion of Zircaloy (reprinted with permission from Ref. [8.145], copyright ASTM International, 1996).



FIG. 8.107. Influence of irradiation to very high fluences at 563 K (290°C) on corrosion and SPP dissolution of Zircaloy-4 with large SPPs (reprinted with permission from Ref. [8.147], copyright ASTM International, 2002).



FIG. 8.108. Enlarged views of eddy current scans of a fuel rod from a BWR, at the lowest three grid positions, showing peaks in oxide thickness in the 180° scan that are absent from the 0° scan. The lowest three grids are located at approximately 0.5, 1.0 and 1.5 m elevations [8.148].

The lower limit on useful SPP size results from the ease with which very small SPPs will dissolve in the matrix under fast neutron bombardment. Although nodular corrosion does not occur with such cladding, the metastable solution of Fe in the Zr matrix results in increased uniform corrosion, as shown in Fig. 8.90 [8.122] and higher hydrogen absorption, as shown in Fig. 8.109 [8.149].



FIG. 8.109. Hydrogen pick-up fraction in various versions of Zircaloy-2 vs. irradiation time in a BWR (reprinted with permission from Ref. [8.149], copyright ASTM International, 2005).

Hydrogen absorption by Zircaloy-2 in BWRs is low because of the high oxygen potential of the water in the core. The fact that corrosion hydrogen will be evolved at the cathodic SPPs probably contributes to the low H uptakes [8.135].

8.6.5.3. WWER

The Russian Federation WWERs use E110 (Zr-1Nb) alloy cladding. Heat fluxes and end of life burnups are not yet as high as in PWRs. The water includes a KOH/NH4OH mixture to control circuit corrosion. Boric acid is used for reactivity control but no LiOH is added. Li is continuously produced by the ¹⁰B (n,α)⁷Li reaction; the subsequent LiOH is removed by the water purification system, and is not allowed to exceed 0.2 ppm Li [8.150].

Oxide thicknesses reported in WWERs for the Zr-1%Nb cladding are small, and remain approximately constant with increasing burnup, as shown in Fig. 8.110 [8.15, 8.151]. This observation suggests some loss of oxide, perhaps by 'powdering off'. This phenomenon was observed with some early batches of Zr-2.5Nb alloy [8.16] where, as the oxide thickened in laboratory autoclave tests, some specimens would leave a fine powder on the balance pan after weighing. In contrast, the Zircaloys tend to spall in large flakes when oxides become very thick. Similarly, commercially pure Ti and Ta lose weight by powdering of the oxide film in 570 K (300°C) aqueous solutions [8.152].



FIG. 8.110. Corrosion of Zr-1Nb cladding in WWERs [8.151].

There have been some reported examples of nodular corrosion of E110 in early WWERs, as shown in Fig. 8.111 [8.153], but it is not known whether sufficient hydrogen was being added in these instances to suppress radiolysis. Hydrogen is generated by the decomposition of ammonia, so hydrogen concentrations may be low at the core inlet.



FIG. 8.111. Variations in the thickness of the oxide film along the perimeter of the E110 fuel cladding in a WWER [8.153].

8.6.5.4. RBMK

These reactors contain boiling water in vertical channels using Zr-2.5Nb (E125) pressure tubes and E110 (Zr-1Nb) fuel cladding. Grid spacers are stainless steel, although a change to Zr alloy grids is taking place. Both the pressure tubes and the fuel cladding suffer from nodular corrosion away from the grids and very severe shadow corrosion under the grids, as shown in Figs 8.111 and 8.112 and in Tables 8.5 and 8.6 [8.153–8.155]. Further evidence that shadow corrosion is galvanic is shown by the fact that the much thicker areas of shadow corrosion pick up no more hydrogen than the thinner nodular corrosion between the grids. Comparative tests of E635 cladding, the results of which are given in Tables 8.5 and 8.6, show that it is immune to nodular corrosion but does exhibit some shadow corrosion under the grids at high burnup. Alloy E635 has not been used for pressure tubes.



FIG. 8.112. Oxide film thickness on the inner surface of a Zr-2.5Nb pressure tube after 10 years' operation in an RBMK [8.154].

8.6.5.5. CANDU

As CANDU reactors operate at low temperatures (a 588 K (315°C) peak) and with short fuel lifetimes (as a result of the use of natural U fuel), corrosion is not a problem for the Zircaloy-4 cladding of this fuel.

8.7. HYDROGEN UPTAKE

Our understanding of the important mechanisms of hydrogen uptake are undergoing major revisions. The effect of hydrogen concentration on corrosion processes only becomes apparent at high hydrogen concentrations; reactor operators try to avoid such high hydrogen concentration because the implications for mechanical properties are more severe than those for corrosion. The discussion in this section will be divided into two main parts: firstly, studies aimed at understanding how hydrogen generated by the corrosion reaction enters the metal, and secondly, what effects the hydrogen concentration of the metal and its distribution have on the subsequent corrosion rate.

Nearly all studies of hydrogen uptake during corrosion are made by examining specimens after they have been cooled down to room temperature. Unless the specimens were

very rapidly quenched from the corrosion temperature, the hydrogen is no longer in the same place it was during the corrosion process, so great care must be exercised in reaching conclusions from observations of the final distribution of the hydrogen. What can be stated with some certainty is that:

- The hydrogen solubility limit in the metal differs measurably for different alloys and different metallurgical conditions of the same alloy, as shown in Fig. 8.113 [8.156–8.158].
- Hydrogen can be trapped at dislocations in the metal, as shown in Fig. 8.114 [8.158, 8.159], so that it is hardly surprising that irradiation induced dislocation loops in the metal will trap H causing an apparent increase in total soluble solids (TSS) of irradiated Zr, as shown in Fig. 8.115 [8.160] and recovery by annealing, as shown in Fig. 8.116 [8.161].
- There is no acceptable diffusion coefficient for H in the ZrO₂ crystal lattice [8.162].
- Evidence suggests that H measured in oxide films is actually OH⁻ absorbed on the walls of cracks or pores in the oxide.
- Hydrogen distributions measured in specimens after cooling to room temperatures bear little resemblance to the hydrogen distributions that were present at elevated temperature since hydrogen will redistribute during cooling. Only a fast quench from elevated temperature can preserve the initial H distribution. Subsequent mounting of specimens in cold setting resin may disturb this distribution, since setting temperatures of \geq 370 K (100°C) are sufficient to cause precipitation and some migration of H [8.163].



FIG. 8.113. Differences in hydrogen solubility limits in Zr alloys: (a) (\blacktriangle) Zry-2, (×) Zry-4, (+) Zr-2.5Nb; (b) TSS_d lines for hydrogen in Zr-Nb specimens with different Nb concentrations annealed at 1123 K (850°C) for 1 h. The lines for α -Zr and annealed Zr-20Nb (β -Zr) as well as the Kearns' line for unalloyed Zr are included for comparison (reprinted with permission from Refs [8.156, 8.157], Atomic Energy of Canada Limited, Canada).



FIG. 8.114. Effect of fabrication variables on H solubility; TSS_d for hydrogen in Zr-2.5Nb annealed at 1123 K (850°C) for 1 h, aged at 673 K (400°C) for 24 h and for 96 h and aged at 773 K (500°C) for 1000 h. The solid lines are best fits to the data (reprinted with permission from Ref. [8.158], Atomic Energy of Canada Limited, Canada).



FIG. 8.115. Effect of irradiation on hydrogen TSS of Zircaloy-4 (reprinted with permission from Ref. [8.160], copyright ASTM International, 2000).



FIG. 8.116. Change in TSS_{irrad} with isothermal annealing at 653 K (380°C) for 32 h, 884 K (611°C) for 83 h and 973 K (700°C) for 1 h showing the effect of recovery of irradiation damage (reprinted with permission from Ref. [8.161], copyright Elsevier, 2002).

8.7.1. Hydrogen uptake mechanism

The reaction of oxidized Zr alloys with H₂O leads to the release of hydrogen. When an oxygen ion vacancy diffuses out to the oxide–environment interface during the growth of the oxide film, a water molecule will react with the vacancy to form an oxygen ion within a lattice site, and release two protons:

$$V_0^{2+} + H_2 0 \to O_0(ox) + 2H^+(ox)$$
 (8.1)

When oxygen ion vacancies V_0^{2+} diffuse out to the oxide-metal interface, they will then be discharged by electrons e⁻ from the oxidation reaction at the oxide-metal interface:

$$ZrO_2(ox) + 2V_0^{2+} + V4e^- \rightarrow Zr(m) + 2O_0(ox)$$
 (8.2)

These electrons must then be conducted to the oxide-environment interface where:

$$4e^{-} + 4H^{+}(ox) \to 4H$$
 (8.3)

Some of these hydrogen atoms will then recombine to give H₂ molecules, which can diffuse into the environment. Some H atoms may migrate into the Zr matrix if they can do so faster than the recombination reaction can occur. It is these H atoms that represent the hydrogen uptake by the Zr alloy specimen; expressing this number as a percentage of the hydrogen liberated by the corrosion reaction (as calculated from Eqs (8.1)–(8.3)) gives the hydrogen uptake percentage. This percentage is not a physical property of a particular alloy because it results from a competition between two kinetic processes: H atom recombination and diffusion into the environment, and H atom migration into the Zr matrix.

The results of this competition vary as a result of a number of factors such as the temperature and pressure of the environment, the oxide thickness and morphology, the redox potential of the environment and the pre-existing hydrogen distribution in the specimen. The mechanism of the H ingress process will now be considered.

Since the proton discharge process (8.1) takes place at a site on the oxide–environment interface, and the electrons must be conducted through an oxide, which is a very good insulator (except in-reactor), the most probable sites for the electrons to discharge the protons will be those where the conduction path for the electrons is minimal. These sites will be where pores or cracks in the oxide approach most closely to the oxide–metal interface. These sites would seem to be the most probable locations for the H uptake process. During pre-transition oxidation the evidence for cracks penetrating through the oxide is uncertain. Cracks can be observed in most pre-transition oxide films, and polarization tests at room temperature (to deposit Cu at cathodic sites) showed that the cathodic sites were almost invariably at such cracks, rather than at the sites of surface intermetallic particles, shown in Fig. 8.117 [8.67, 8.164]. Cracks or pores that did not penetrate to the oxide–metal interface but did penetrate near to it could still be the shortest route for electron conduction, although there would still be an oxide barrier present through which the hydrogen could not diffuse. In such a circumstance what might be the H ingress mechanism?



FIG. 8.117. Scanning electron micrographs of Cu deposited cathodically on an oxidized Zircaloy-2 surface (1.2 μ m oxide): (a) distribution of large and small Cu balls on the surface; (b) close-up of group of large balls from (a); (c) crack pattern in oxide adjacent to right hand ball in (b); (d) nucleation site for this ball (indicated by an arrow) [8.67].

- If an intermetallic particle was present at such a site, it might be able to act as a window for hydrogen ingress. The only evidence for H associated with intermetallic particles at the oxide-metal interface was obtained at room temperature, and this hydrogen could have migrated into the intermetallic particle during cooling and would not have been there during the corrosion process [8.49, 8.165].
- If the hydrogen is being liberated at the bottoms of a few small pores or cracks, as is indicated by the small numbers of cathodic sites that are observed [8.164], then the hydrogen could build up at these sites until a 100% H₂ atmosphere was generated in the pore. Past experience has shown that this pressure would soon lead to the breakdown of any oxide barrier at the bottom of the pore, and direct uptake of hydrogen by the metal, Fig. 8.118 [8.166].



FIG. 8.118. Incubation times for absorption of hydrogen gas at 673 K (400°C) by zirconium with various initial oxidation treatments [8.166].

Until proponents of the 'intermetallic window' hypothesis obtain evidence of hydrogen in intermetallic particles at elevated temperature, doubts will remain. An examination of H uptake kinetics may resolve the question. The frequency of intermetallic particles at the oxide-metal interface should be roughly independent of the oxide thickness and corrosion rate; whereas the frequency of oxide porosity and cracking depends on oxide thickness and growth rate so the kinetics of H uptake should follow the kinetics of film growth.

8.7.2. Hydrogen uptake kinetics

The most extensive data on H uptake kinetics is for the Zircaloys. For these alloys it is observed that uptake is close to 100% for very thin films, and decreases as the pre-transition oxide thickens, as shown in Fig. 8.119 [8.92]. This result would be consistent with the observation that thin films have many flaws resulting from the initial surface preparation (whether this was by pickling or grinding) and that these flaws are repaired as the

pre-transition oxide grows. The onset of the kinetic rate transition (breakaway) is marked by an increased development of porosity in the oxides [8.92] and by a corresponding increase in the hydrogen uptake percentage, to a rate of 100% in many instances.

The repair of porosity in the pre-transition oxide films appears to be more efficient at high temperatures than at 573 K (300° C), since pre-transition uptakes are lowest at 873 K (600° C), and increase regularly at 773 K, 673 K and 573 K (500° C, 400° C and 300° C). Post-transition rates for Zircaloy-2 are about 60% at 673 K (400° C), and increase a little at higher temperatures, becoming close to 100% for post-transition corrosion at 873 K (600° C).



FIG. 8.119. Change in hydrogen uptake rate with oxide film thickness for Zircaloy-2 [8.92]. 500 psi = 3.45 MPa, 15 mm Hg = 2 kPa.

No hydrogen uptakes in excess of 100% were measured in this study, despite the accumulation of unabsorbed hydrogen in the steam. Thus, H absorption came only from corrosion hydrogen until high percentages of hydrogen (\geq 50%) were present in the steam, as shown in Fig. 8.120 [8.92]. Similar observations in water, shown in Fig. 8.121 [8.167], demonstrated that, while hydrogen uptake by Zircaloy-2 was proportional to the dissolved hydrogen content in the water, Zircaloy-4 was immune to this effect. A small increase in H uptake can be seen for β treated Zircaloy-4 at the highest hydrogen overpressure that was tested. These results are consistent with early observations [8.168] that, in T₂-H₂O mixtures at 573 K (300°C), no tritium was absorbed by the Zr until chemical exchange in the gas phase

had resulted in a significant fraction of HTO being present. Thus, the hydrogen absorbed by Zr alloys comes only from hydrogen released by the oxidation reaction, and not from any gaseous hydrogen overpressure in the environment. Hydrogen uptakes greater than 100% of that released by the oxidation reaction are only observed when a very high concentration of gaseous hydrogen is present, and then only for Zircaloy-2, not for Zircaloy-4. This observation suggests a direct involvement of the Ni content of this alloy.



FIG. 8.120. Hydrogen uptake by Zircaloy-2 in steam plus added gases at 773 K (500°C) [8.92].



FIG. 8.121. Hydrogen pick-up by Zircaloy-2 and Zircaloy-4 as a function of hydrogen overpressure after 14 days exposure to water at 616 K (343° C). 100% uptake is not exceeded for these specimens and conditions until 40 to 50 ppm hydrogen has been absorbed [8.167].

Hydrogen concentrations in water are thought to influence the rate of hydrogen uptake only by affecting the balance between H atoms that recombine and escape into the environment, and H atoms that diffuse into the metal at sites where protons are reduced by electrons arriving from the formation of fresh ZrO₂. The effect of the oxygen content of the water in reducing the hydrogen uptake percentage, shown in Fig. 8.120 [8.92], such as occurs in BWRs, is thought to be a converse effect of oxidizing species in the water, encouraging H atom recombination and thus reducing the fraction of the corrosion hydrogen entering the metal.

These observations are consistent with the hypothesis that the hydrogen uptake process is a much localized mechanism operating at a small number of sites where pores or cracks extend to, or very close to, the oxide-metal interface. Further support for such a hypothesis is given by observations that during hydrogen uptake in the post-transition region in steam, which is high and linear for Zircaloy-2, as shown in Fig. 8.119 [8.92], a decrease in uptake rate occurred at a point corresponding to the time when the H concentration of the alloy reached TSS. By varying the specimen thickness and the oxidation temperature it was found that this was a general observation and that the TSS could be matched at each temperature; see Fig. 8.122 [8.92, 8.169]. By using very thin Zircaloy-2 specimens it was possible to have the specimens reach TSS at the oxidation temperature during pre-transition oxidation. Again, there was a decrease in the H uptake rate when TSS was reached that was independent of the decreasing oxidation rate during pre-transition oxidation, as shown in Fig. 8.123 [8.67].



FIG. 8.122. Effect of specimen thickness on hydrogen uptake by Zircaloy-2 in steam at 773 K (500°C) and 100 kPa (reprinted with permission from Refs [8.92] with permission courtesy of Atomic Energy of Canada Limited, Canada).



FIG. 8.123. Oxygen weight gain and hydrogen concentration plots for 0.125 mm thick Zircaloy-2 sheet in steam at 573 K (300°C) and 100 kPa. The different symbols for hydrogen concentrations are for different groups of specimens prepared, oxidized and analysed at the same time (reprinted with permission from Ref. [8.67], Atomic Energy of Canada Limited, Canada).

The reduction in H uptake rates at TSS, whether during the pre- or post-transition kinetics phase, is best explained if H uptake is a much localized phenomenon. If so, then H uptake rates at any individual crack or pore site will be very high, possibly high enough for H precipitation to occur at or very near the H ingress site. This situation would be analogous to the formation of solid hydride layers at the metal–oxide interface during corrosion in concentrated LiOH solutions, when H ingress rates are very high over the whole specimen surface; see Fig. 8.124 [8.15, 8.170]. Estimates of the fraction of the specimen surface that is active in the H uptake process, using these data and the frequency of cathodic surface sites [8.67], gave a value of about 2×10^{-6} . The individual H uptake rate at each of these sites would be much higher than that needed to force hydrides to precipitate at the point of entry into the metal. That such local hydride precipitation is not usually seen in all oxidized Zr specimens is probably due to the transient nature of each individual ingress site. When a site becomes inactive, the hydride precipitated there will dissolve and be redistributed and the site itself will disappear as the oxide–metal interface advanced into the metal. Such sites do not appear to be associated with SPPs in the alloy.


FIG. 8.124. Temperature dependence for critical hydrogen fluxes for surface hydride layer formation [8.15, 8.170].

Further evidence for cracks or pores penetrating through pre-transition oxide films would seem to be provided by the evidence for tritium effusion from pre-tritided van Arkel Zr oxidized in oxygen at 573 K (300°C). In this instance there would have been no intermetallic particles to provide 'windows', and the tritium would be migrating in the opposite direction to the normal diffusion paths [8.168]. Thus, a hydrogen uptake mechanism via flaws in the oxide best fits the available evidence. The low hydrogen uptake by the Zr-2.5Nb alloy is matched by the low frequency of flaws in the oxide that show up as active cathodic sites [8.164]. While it is tempting to relate low hydrogen uptake to the absence of Zr intermetallics of the type present in the Zircaloys, there is no convincing evidence for these intermetallics acting as windows for H ingress. The hydrogen observed in some of these particles at the oxide-metal interface at room temperature [8.49] probably arises from H migrating into the particles during cooling because of the lower TSS for hydrogen in the intermetallic phases than the TSS for H in the Zr matrix. An influence of the intermetallics in the hydrogen uptake process due to their effects in locally disrupting the protective oxide, coupled with their typically cathodic electrochemical potentials compared with that of the Zr matrix [8.171], may be their contribution to the hydrogen uptake mechanism.

8.7.3. Effect of hydrides on corrosion

Bulk zirconium hydride oxidizes more rapidly in steam than initially hydrogen-free zirconium. An increase in oxide thickness due to this effect can be seen in fuel cladding that has operated in conditions that produce local solid hydride 'lenses' at the oxide-metal interface on the cooler, water side of the cladding as a result of a high heat flux, as shown in Fig. 8.125 [8.16, 8.172]. Without this heat flux, and at temperatures high enough to provide extensive oxygen diffusion profiles in the metal under the oxide film, hydrogen is largely excluded from the oxygen diffusion profile zone, and hydrides are not precipitated close to, or in contact with, the oxide-metal interface, as shown in Fig. 8.126 [8.173]. Thus, specimens prehydrided to high hydrogen concentrations (1000-3000 ppm (8.4-21.5 at.%)) when oxidized in high temperature steam give oxidation curves within the scatter band for asreceived specimens of the same batch of material (as shown in Fig. 8.127 [8.92]) if they have their surfaces repolished after hydriding. Specimens that were oxidized after hydriding, but without repreparation of their surfaces, show somewhat higher oxidation rates that are slightly outside the scatter band for non-hydrided specimens. Prehydrided specimens oxidized at low temperatures (633 K (360°C)), where a prominent oxygen diffusion profile does not develop, showed a steady increase in oxidation rate once the initial hydrogen concentration of the specimen exceeded about 300 ppm (2.66 at.%) and the oxidation curve was in the post-transition region, as shown in Fig. 8.128 [8.174]. Since the H concentration of the specimens will be increased by hydrogen uptake during corrosion, the TSS must be exceeded by at least a factor of two before any effect on oxidation rate will be seen. The precipitated hydrides seen in these specimens were still not heavily concentrated at the oxide-metal interface, except at the cut edges of the specimens, where the planar hydride layers extended right up to the initial sample surface (as shown in Fig. 8.129 [8.174]) and where obvious increases in oxidation rate had occurred. These regions of thicker oxide were much broader than the thickness of the hydride layers, suggesting that disruption of the protective oxide film during the transition in the oxidation kinetics had taken place in a much broader band than that of the actual hydrides. No effect of these hydrides on the pre-transition oxidation kinetics was evident.



FIG. 8.125. Increased oxide thickness adjacent to region of high hydride concentration [8.16, 8.72].



FIG. 8.126. Redistribution of tritium at the oxide-metal interface. The absence of tritium in the metal zone adjacent to the oxide due to the high oxygen concentration there and tritium enrichment in the metal zone with low oxygen concentration should be noted (reprinted with permission from Ref [8.173], Atomic Energy of Canada Limited, Canada).



FIG. 8.127. The effect of the initial hydrogen concentration on the oxidation of Zircaloy-2 [8.92]. 1 atm = 0.1 MPa.

Figure 8.127 gives data for specimens prehydrided in hydrogen gas at 673 K (400°C); half of them had their surfaces reprepared by abrading and attack polishing (to produce a smooth surface without the gross pitting that occurs if prehydrided specimens are pickled). All were oxidized in steam at 773 K (500°C) and at atmospheric pressure in the same furnace [8.92].



FIG. 8.128. Effect of initial hydrogen concentration on corrosion and oxidation of Zircaloy-4 at 633 K (360°C) in deionized water [8.174].



FIG. 8.129. Scanning electron micrograph of the metal–oxide interface at the edge of a specimen showing the preferential penetration of oxide at hydrides [8.174].

Another study of the effect of prehydriding, the results of which are given in Fig. 8.130 [8.175, 8.176], provides more confusing observations. The authors used two prehydriding techniques: cathodic charging (which initially leaves the hydrogen as a solid hydride layer at the specimen surface) and gaseous charging (after which a uniform H distribution can be achieved with a subsequent anneal). The gaseous charging technique resulted in only small increases in oxidation, which showed little effect on oxidation over the range of concentration from 400–1500 ppm (3.5–12.1 at.%) H. A major increase in oxidation rate, which was almost exponential with H concentration for the cathodically charged specimens, started at H concentrations below TSS at the oxidation temperature, 673 K (400°C). One possible explanation of this result could be non-uniformity in the initial H distribution, which could leave some local areas of the specimens with much greater than average H concentrations. Unfortunately, the authors [8.175, 8.176] present no micrographs of their prehydrided specimens. Specimens cathodically hydrided in the Advanced Test Reactor due to contact with Al specimen holders showed much variability in hydride layer thickness on the surface, as shown in Fig. 8.131 [8.16, 8.121].



FIG. 8.130. Influence of the initial hydrogen concentration on the weight gain of Zircaloy-4 after corrosion tests in steam at 673 K (400°C) (reprinted with permission from Ref. [8.175], copyright ASTM International, 1996).



FIG. 8.131. Cathodic hydriding of Zircaloy-4 specimens irradiated in the Advanced Test Reactor in Al specimen holders at about 323 K (50°C): (a) general hydriding on two sides of the specimen; (b) the most severe hydriding observed [8.16, 8.121].

8.8. MODELLING ZIRCONIUM ALLOY CORROSION IN-REACTOR

All current PWR models for in-reactor corrosion of Zr alloys are empirical in nature, with no physical models for the processes that are occurring under irradiation. Most models start with kinetic data for the pre- and post-transition oxidation kinetics obtained from laboratory testing. Most models then correct for increases in oxide-metal interface temperatures based on evidence available for changes in oxide thermal conductivity and the thermal conductivity of crud deposits. To this 'adjusted' out-reactor data, models may then either apply a reactor related factor to allow for the effects of irradiation, factors based on the LiOH concentration in the coolant and the hydrogen concentration in the metal, or both. None of the models attempt to apply factors based on the degradation of the alloy corrosion resistance resulting from Fe redistribution in the metal by fast neutron bombardment [8.123] or to calculate the possible LiOH concentration present in porosity near the oxide-metal interface based on the local temperature calculated at this site, the elevation of the boiling point coefficient for LiOH and the possible depletion of the boric acid in the fine porosity resulting from the large size of the borate ion (or the boric acid molecule if it is undissociated).

Current models are attempts to match observed in-reactor oxide thickness data with empirical factors applied to the out-reactor oxidation kinetics. These models were discussed extensively in IAEA-TECDOC-996 [8.15] and only those models to which major changes have been made since then will be discussed here. None of these changes introduce what could be described as a series of physical equations involving the actual processes that are occurring under irradiation.

Models of corrosion in BWRs also do not include a description of the physical processes, for example, the degradation of corrosion resistance resulting from SPP dissolution and the galvanic effects occurring under irradiation while the SPPs are still present as cathodes. A Russian Federation model includes factors for oxide dissolution by the peroxide produced by water radiolysis, but not the other components of in-reactor Zr alloy corrosion in BWRs [8.118].

Some components of these models are not controversial. The effect of increasing the oxide-metal interface temperature depends mainly on the oxide thermal conductivity in the

absence of any LiOH concentration effect, as shown in Fig. 8.132 [8.15]. This effect will only become measurable once the water saturation temperature (about 620 K (347°C)) at the oxide–metal interface is exceeded. The value used for the oxide thermal conductivity is still an uncertain quantity, especially for thick porous oxide, and to an even greater extent if delamination of the oxide is beginning [8.16]. Since the empirical models all use similar approaches the results are also similar, as shown in Fig. 8.133 [8.15]. The divergences mainly become apparent at long exposures and for thick oxides and, although the range of predicted oxide thicknesses at 1000 days is 60–100 μ m, this range is similar to the scatter band reported for Zircaloy-4 in reactors, as seen in Fig. 8.103 [8.140].



FIG. 8.132. Example of the effect of different oxide thermal conductivity values on predicted oxide thicknesses in Zircaloy-4 [8.15].



FIG. 8.133. Comparison between predicted oxide thicknesses for various models of corrosion of Zircaloy-4 [8.15].

The Westinghouse model presented in [8.15] continues to use a ((Li) \times time) component for which no LiOH concentration effects are contemplated. The COCHISE model has undergone a major overhaul [8.177]. It now contains modules that calculate the following data during normal reactor operation:

- Local water temperature;
- Cladding surface temperature;
- Excess concentration of water additives during boiling.

The thickness of the oxide is based on out-reactor autoclave tests and out-reactor and in-reactor loop tests. From this comparison a direct effect of heat flux on oxide vacancy concentration is postulated. This hypothesis seems improbable since most oxide thicknesses in these tests are beyond the point where oxygen vacancy diffusion is a controlling factor in the oxidation process. It seems more likely that this effect results from the degradation of the alloy corrosion resistance due to Fe redistribution under irradiation. A series of empirical constants resulting from the in- and out-reactor corrosion comparisons is included in the Westinghouse model.

The model deals with the effects of concentration of LiOH, both in the absence and presence of boric acid, by calculating the amount of steam production. No contribution from the elevation of the boiling point coefficient is incorporated. Thus, a situation where LiOH can concentrate without boiling by simple diffusion up the temperature gradient, so that the LiOH at the bottom of pores remains in equilibrium with that necessary to prevent boiling at any particular location, is not considered. No consideration of possible partitioning of Li⁺ and BO₃³⁻ ions in the porous oxide and the crud layers as a result of their different ionic sizes is given.

This version of the COCHISE model now uses thermal conductivities of $0.021-0.025 \text{ W} \cdot \text{cm}^{-1} \cdot \text{K}^{-1}$ for different Zircaloy-4 variants, compared with a value of $0.016 \text{ W} \cdot \text{cm}^{-1} \cdot \text{K}^{-1}$ used in earlier versions of the model. The effects of irradiation are based on the empirical constants derived from the tests noted above. The result is an irradiation amplification factor that increases with burnup (i.e. fast neutron fluence) and is higher at lower heat fluxes than at higher ones, as shown in Fig. 8.134 [8.177]. A further module allows for the enhancement of the corrosion due to hydride precipitation, as shown in Fig. 8.135 [8.177], at the oxide–cladding interface in pellet–pellet interface regions. This effect is modelled by adjusting the empirical irradiation factor as a function of clad surface temperature and the time duration following the onset of hydride precipitation. This allows the local oxide thickness at pellet–pellet interfaces to be calculated, as shown in Fig. 8.136 [8.177]. The constants are empirical, and their adjustments are based entirely on data fitting with no physical mechanistic input.



FIG. 8.134. Empirical irradiation amplification factors vs. burnup at 45 and 70 W/cm² [8.177].



FIG. 8.135. Empirical irradiation amplification factor vs. time at 590 to 620 K (317 to 347°C) [8.177].



FIG. 8.136. COCHISE modelling of oxide thickness at pellet–pellet interfaces [8.177].

8.9. OXIDATION UNDER DESIGN BASE ACCIDENT CONDITIONS

8.9.1. Loss of coolant accidents

The oxidation and hydriding of Zr alloys under postulated accident conditions are critical factors in determining the extent of cladding failures both before and during the reflooding stage of a loss of coolant accident (LOCA). Ballooned and burst cladding may change the cooling mechanism downstream of the flow blockage. This blockage may result in a reduction in coolant mass flow and in degraded fuel rod heat transfer. The mechanical aspects of the fuel are not relevant to this review, and only the oxidation and hydrogen embrittlement aspects will be discussed.

Typical heating and cooling cycles for design basis LOCAs in PWRs, see Fig. 8.137 [8.178], and BWRs with jet pumps, see Fig. 8.138 [8.179], are shown. Reflooding is much slower in externally pumped BWRs.



FIG. 8.137. History of Zircaloy-4 fuel rod cladding temperature and pressure during a double ended cold leg break LOCA (reprinted with permission from Ref. [8.178], copyright ASTM International, 1987).



FIG. 8.138. History of Zircaloy-2 fuel rod cladding temperature and pressure during a large break LOCA in a jet pump BWR [8.179] (reprinted with permission from Ref. [8.179], copyright ANT International, 2004).

Early oxidation studies were carried out at a range of temperatures up to 2273 K (2000°C). While an oxidation rate transition is seen at temperatures up to 1273 K (1000°C), as shown in Fig. 8.139 [8.180], above this temperature the kinetics are close to parabolic, as shown in Fig. 8.140 [8.181]. From these early results a correlation of the parabolic rate constants (the Baker-Just correlation [8.182]) was developed and adopted by the US Nuclear Regulatory Commission. More recent oxidation data almost invariably lie below the Baker-Just line, as shown in Fig. 8.141 [8.178]. This difference persists when transient

oxidation data are compared with transient data calculated from Baker-Just, as shown in Fig. 8.142 [8.178]. Much of the early work was done in atmospheric pressure steam. At high temperatures the oxidation rate in steam is pressure dependant, as shown in Fig. 8.143 [8.183], and so the pressure as well as the temperature profile of the LOCA must be used in correlations of predicted behaviour.



(a)

1000°C

30 min 60 min 180 min 360 min 1100°C

(b)

⊢100 µm

FIG. 8.139. Oxidation of Zircaloy-4 cladding tube in high temperature steam: (a) weight gain vs. time of exposure; (b) oxide morphology after isothermal oxidation of Zircaloy-4 in steam: typical breakaway (1273 K (1000°C)) and nonbreakaway (1373 K (1100°C)) (reprinted with permission from Ref. [8.180], copyright ASTM International, 1984).



FIG. 8.140. Oxidation kinetics of Zircaloy-2 at very high temperatures (reprinted with permission from Ref. [8.181]).



FIG. 8.141. Oxidation of Zircaloy-4 in high temperature steam: parabolic rate constant vs. reaction temperature (reprinted with permission from Ref. [8.178], copyright ASTM International, 1987).



FIG. 8.142. Oxidation of Zircaloy-4 in high temperature steam after a temperature transient: comparison of mass increase during a transient simulating a LOCA with those of isothermal exposure and as calculated by the Baker-Just equation (reprinted with permission from Ref. [8.178], copyright ASTM International, 1987).



FIG. 8.143. Zircaloy-4 oxide thickness at 1023 K (750°C) as a function of square root of time and steam pressure [8.183].

Other variables that must be taken into account in calculations of LOCA behaviour are differences between alloys (Fig. 8.144 [8.184]), which seem to be small at temperatures above 1273 K (1000°C), and hydrogen uptake during the transient, which shows a large increase in uptake rate after the kinetic transient at 1273 K (1000°C), as shown in Fig. 8.145 [8.184]. It is not clear how much of the transient in H uptake is due to the hydrogen partial pressure buildup in the experimental equipment. Hydrogen buildup in the reactor pressure vessel may be important during a LOCA.

Although the Zr-1Nb alloys E110 and M5 are nominally the same, their high temperature oxidation behaviours differ. This difference seems to be based on the impurity concentrations of the various base metals. Early E110 was made from a mixture Zr made by the van Arkel process and an electrolytic process, whereas M5 is made from Kroll sponge Zr. When large amounts of E110 were fabricated from sponge Zr the results for oxidation, shown in Fig. 8.146 [8.185], and hydrogen uptake, shown in Fig. 8.147 [8.185], were much closer to those reported for M5. The poor corrosion behaviour of the iodide-electrolytic-based E110 also showed up in extensive spalling of the oxide. These differences in behaviour may result from the high concentrations of Ca, Mg and Al impurities found in the E110 batches made by the iodide-electrolytic processes [8.185].

During oxidation at LOCA temperatures, a large fraction of the oxygen reacting with the Zr alloy goes into solution in the metal producing a stabilized α -Zr layer beneath the oxide, as shown in Fig. 8.144 [8.184]. Hydrogen and hydrides are largely excluded from the highest dissolved oxygen region immediately below the oxide–metal interface. This effect was shown by tritium autoradiography, as shown in Fig. 8.126 [8.173], and it may explain why there is little or no effect of hydrogen concentration on oxidation at 1473 K (1200°C), as shown in Fig. 8.145 [8.184]. It is generally assumed that there is no effect of irradiation during a LOCA because the irradiation damage anneals out very rapidly at high temperatures. This assumption seems less justifiable considering the simulation of nodular corrosion at 773 K (500°C) in 10 MPa steam [8.122]. If the high temperature oxidation arises by a similar mechanism to nodular corrosion in BWRs then one might expect to see nodular corrosion during a LOCA transient. Demonstrating this effect may require tests to be performed in steam at pressures \geq 10 MPa, which is not the usual practice. The fraction of the reacted oxygen going into solution in the metal varies with temperature because oxide formation and oxygen diffusion in Zr have different kinetics, as shown in Table 8.7 [8.11].



FIG. 8.144. High temperature oxidation kinetics of different Zirconium alloys [8.184].



FIG. 8.145. Effect of hydrogen concentration on high temperature oxidation of M5 and Zircaloy-4 at 1473 K (1200°C) (reprinted with permission from Ref. [8.184], copyright ASTM International, 2005).



FIG. 8.146. Oxidation kinetics of zirconium-niobium alloys manufactured from zirconium sponge at 1273 K (1000°C) showing unusual behaviour [8.185].



FIG. 8.147. Hydrogen pick-up of different E110 materials oxidized at 1373 K (1100°C) [8.185].

Temp. (°C)	Time (h)	Total O_2 (mg·dm ⁻²)	Fraction in solution in metal	Temp. (°C)	Time (h)	Total O_2 (mg·dm ⁻²)	Fraction in solution in metal
400	6	2.26	0.084	800	0.1	\approx 85*	0.247
	644	≈ 20	>0.05		1.0	$\approx 190*$	0.342
					6.41	235	0.306
450	6	5.91	0.085		10	≈430*	0.465
	6	5.12	0.082		20	\approx 850*	0.264
					22.9	415	0.39
500	6	11.2	0.071		50	\approx 4200*	0.054
	300	\approx 77	0.10 ± 0.02		78.75	700	0.407
	356	≈ 78	0.11				
	409	$\approx \! 80$	0.13 ± 0.02	840	7.0	460	0.35
	450	≈ 95	0.07		40.0	860	0.49
	500	≈ 97	0.12 ± 0.02		113.0	1300	0.555
	550	≈ 105	0.10		234.0	11710	0.635
					435.0	2190	0.635
550	6	25.4	0.087		601.5	2450	0.65
	316	≈ 146	0.19				
	341	≈ 152	0.14 ± 0.03	850	6	\approx 306	0.51
	371	≈ 154	0.13		6	371	0.394
	402	≈ 145	0.16 ± 0.05		16	\approx 543	0.42
	435	≈ 166	0.23		24	$\approx \! 800$	0.57
	457	≈ 165	0.19		24	671	0.556
	486	≈ 161	0.17 ± 0.03		48	≈ 1050	0.56 ± 0.05
600	6	44.9	0.085	900	0.1	$\approx 150*$	0.40
	100	≈ 160	0.22		1.0	≈410*	0.44
	125	≈ 172	0.17 ± 0.03		5.0	\approx 3300*	0.066
	150	≈ 194	0.22				
	186	≈ 196	0.18 ± 0.05	910	0.75	200	0.58
	209	\approx 226	0.21		4.0	550	0.45
	259	\approx 232	0.18		17.0	900	0.58
668	40.66	173	0.139		63.7	1470	0.58
	92.55	263	0.175		146.0	2080	0.675
700	0.2	$\approx 60*$	0.185	975	4.0	840	0.47
	2.0	≈130*	0.246		16.7	1350	0.67
	2.75	66	0.091		63.7	2350	0.72
	16.41	150	0.167		237.5	4240	0.765
	20	$\approx 280*$	0.358				
	100	\approx 500*	0.46	1000	0.1	\approx 630*	0.27
	447	676	0.494		1.0	$\approx \! 1800*$	0.28
					3.0	\approx 3000*	0.29
750	7.5	187	0.251		7.0	\approx 7000*	0.14
	23.1	315	0.315				
	96	\approx 590	0.37 ± 0.04	1100	0.1	$\approx 1500*$	0.20
					1.0	\approx 4600*	0.20
					4.0	\approx 9500*	0.18

 TABLE 8.7. FRACTION OF REACTED OXYGEN IN SOLUTION IN ZIRCONIUM [8.11]

* Specimens oxidized in air; all other specimens were oxidized in oxygen.

The onset of embrittlement (the zero ductility threshold) of the cladding is arbitrarily set at the point where the amount of oxygen reacted with the cladding is equivalent to 17% of the metal reacting; this is called the equivalent cladding reacted. This criterion does not recognize the differences in the ratio of O in oxide to O in solution in Zr, which can vary considerably with temperature and the kinetics of oxide growth. An increase in the rate of oxide thickening ('breakaway' oxidation) will result in a reduction in the fraction of oxygen in solution in the Zr metal, and vice versa for a reduction in oxide growth rate (e.g. the difference between Zircaloy-4 and M5).

8.9.2. Reactivity initiated accidents

A reactivity initiated accident may occur as a result of a control rod ejection from a PWR. Such an accident may arise if a mechanical failure of the control assembly housing allows the coolant pressure to eject the whole control rod assembly from the core. In a BWR the equivalent accident would be a control rod drop accident, which is due to a failure of the drive mechanism allowing a control rod to drop out of the core. The largest reactivity insertion in a BWR comes if a control rod drop accident occurs in cold, zero power conditions. This type of accident occurs very rapidly with a pulse width in the range of 30–80 ms. The pulse width is calculated to be longer in a BWR than in a PWR. As a result of the short pulses there is little oxidation or H uptake during the pulse, and failure by pellet–clad mechanical interaction will be determined by the prior distribution of oxygen and hydrogen in the cladding. Factors such as the presence of pre-existing radial hydrides in the cladding can play a part in determining the probability of cladding failure; consequently the conditions under which simulation tests are performed requires careful choice.

The unresolved possibility of liquid metal embrittlement in molten Na in the CABRI-REP-Na tests remains [8.188]. The potential for a significant fraction of the hydrogen in the cladding to be trapped at irradiation induced PD loops at operating temperature [8.160] means that hydrogen distributions observed after an accident may be very different from those observed under actual accident conditions. Major hydride blisters may be smaller at temperature but will probably not disappear completely.

A reactivity initiated accident transient is too short for any noteworthy oxidation. Failures of fuel cladding in such circumstances will be influenced by the pre-existing oxide film and by the amount and distribution of hydrogen as hydrides in the alloy. The actual cladding failure process will be a pellet–clad mechanical interaction mechanism with a small possibility that some redistribution of hydrides may occur during the transient. The fuel cladding may only be at high temperature (1000–1200 K (730–930°C)) for a short time (10 s) but this transient may be enough to put a significant quantity of hydrogen into solution and reprecipitate it radially under the high tensile stresses present in the cladding. Direct stress corrosion processes (e.g. pellet–clad interaction) will be too slow to cause any damage.

8.10. CONCLUSIONS

Since the last IAEA review of the metallurgy of zirconium [8.10], the view on what are the important factors in zirconium alloy corrosion, especially under irradiation, have changed considerably. The factors can be summarized as follows:

 Both ionic diffusion and electron transport are important in the overall corrosion process, and in many instances where the rate determining process has been identified it has proved to be electron transport. Such studies have usually been carried out in oxidation environments other than water.

- Beta and gamma irradiation results in large increases in the electron conductivity of oxide films, and an increase in the conductivity of the water.
- In the absence of sufficient dissolved hydrogen in the water to ensure that all metals operate at the reversible hydrogen potential (5–10 cm³·kg⁻¹) electrochemical potential differences between different metals (and between different Zr alloys) will be present.
- A combination of these potential differences together with the enhanced conductivities of oxides and water lead to a galvanic corrosion phenomenon called shadow corrosion in BWRs.
- Since SPPs in Zr alloys are effectively dissimilar metals, the nodular corrosion phenomenon in BWRs is thought to be a microscopic version of shadow corrosion with the SPPs acting as the cathodes. Since the cathode area (which is much smaller than the area of the anodic matrix) determines the rate of the galvanic corrosion process, the severity of nodular corrosion will be a function of SPP size. Noble metal deposits resulting from noble metal chemical additions may also act as dissimilar metal cathodes.
- The redistribution of Fe from the SPPs by a fast neutron recoil process degrades the corrosion resistance of Zr alloys with Fe-containing SPPs that are susceptible to this fast neutron process. Thus, when SPPs are completely dissolved in BWR cladding, nodular corrosion ceases but enhanced uniform corrosion ensues. A minor contribution from oxide dissolution by hydrogen peroxide (generated radiolytically) is also possible.
- Because of the high dissolved hydrogen concentrations in PWRs, these galvanic processes are inhibited, and only the degradation of the corrosion resistance by iron redistribution is operative, together with the irradiation effect on electron transport. No evidence has been found for the persistence of PD related structures in the oxide, and it is concluded that recombination of PDs in the oxide is rapid. The small extent of radiation effects in the early (pre-transition) stage of corrosion in PWRs suggests that the effects of irradiation on oxide electronic conductivity are small in this oxide thickness region.
- Other factors that contribute to enhanced corrosion later during in-reactor exposure are increases in the temperature of the oxide-metal interface as the oxide thickens, or as a result of tenacious crud deposits; precipitation of solid hydride layers at the oxidemetal interface; and concentration of LiOH in porous oxides when the saturation temperature of the coolant is exceeded (and diffusion of borate ions is inhibited).
- There is no evidence to support the suggestion that surface reaction rates (at the oxideenvironment interface) are ever rate controlling. Out of reactor pre-transition corrosion is nearly independent of pH and additives to the water (with the exception of fluorides or concentrated LiOH).

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Appendix I

THE EFFECT OF NEUTRON IRRADIATION ON THE COMPOSITION OF A SAMPLE OF PURE ZIRCONIUM

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I.1. THE EFFECT OF NEUTRON IRRADIATION ON THE COMPOSITION OF A SAMPLE OF PURE ZIRCONIUM

This appendix describes the change in the composition of zirconium after long irradiation by neutrons in a nuclear reactor. To limit the problem to a manageable size, some assumptions must be made concerning the magnitude of the neutron flux, the neutron spectrum and the duration of the irradiation. The chosen values are typical of those experienced by the pressure tube of a CANDU reactor:

- Thermal neutron flux $10^{18} \text{ n} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$;
- Neutron spectrum as shown in Fig. I.1;
- Length of irradiation 25 years.



FIG. I.1. Calculated neutron spectrum in the pressure tube of a natural uranium fuelled CANDU reactor.

In a thermal neutron flux of $10^{18} \text{ n} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$, a thermal neutron absorption cross-section of 1 b produces a transmutation rate that is equivalent to a radioactive decay rate with a half-life of $T_{\frac{1}{2}} = 0.692 \times (10^{18} \times 10^{-28})^{-1} = 6.9 \times 10^9 \text{ s}$, or 220 years. This estimate allows the relative importance of transmutation by neutron absorption and by radioactive decay to be assessed in various situations where they compete.

Some of the important nuclear properties that affect the transmutation of zirconium isotopes under neutron irradiation are given in Table I.1. The fourth and fifth rows of the table contain the thermal neutron capture cross-section and the capture resonance integral from Ref. [I.1]. The generally very low values of these parameters show why zirconium is such a valuable structural material for in-core applications. They also show why it may be necessary to consider other reactions with small cross sections that cause transmutation, such as the threshold reactions in which an energetic neutron causes more than one neutron or a charged particle to be emitted from the target nucleus. Some of these threshold reactions for which data are available in Ref. [I.2] are shown in the lower rows of the table. The reactions covered are (n,2n), (n,p), (n,d), (n,α) , (n,T) and (n,He^3) . For each of these reactions, two pieces of data are given for each stable zirconium isotope: the Q value of the reaction and the measured cross-section at a neutron energy of 14 MeV. The Q value is the difference between the summed masses of the reacting particles after and before the reaction, expressed in energy units [MeV]. A negative Q value means that unless the neutron has a kinetic energy at least equal to the magnitude of the O value the reaction cannot take place, hence the name threshold reaction. Because of the very tight binding of the alpha particle, most of the (n,α) reactions in the table have positive Q values. This observation does not mean that the (n,α) reaction competes effectively with neutron capture at low neutron energies; the cross-section for this reaction is negligible until high (10 MeV) neutron energies are reached. The crosssection data for the threshold reactions are quite limited, often only having been measured at around 14 MeV because of the ready availability of neutrons of that energy from accelerators employing the $D(T,\alpha)n$ reaction. Where it has been measured, the excitation function of the threshold reactions is typically a rapid rise from zero at or near the threshold energy over a range of a couple of MeV followed by a levelling off to a roughly constant value at about 10 MeV above the threshold. This behaviour makes estimating reaction rates in the neutron spectrum in the pressure tube very difficult because, as Fig. I.1 shows, the flux is decreasing with increasing energy just as the threshold reaction cross-sections are increasing.

Despite this difficulty it is possible to use the flux data in Fig. I.1 and the cross-section data in Table I.1 to estimate the fraction of the initial quantity of each isotope that undergoes each interaction during a 25 year irradiation at a constant thermal neutron flux of $10^{18} \text{ m}^{-2} \cdot \text{s}^{-1}$. In this estimate, resonance captures have been ignored and the threshold reaction cross-sections have been approximated by step function thresholds at one of the group boundaries in the figure, with constant value cross-sections thereafter. The results are shown in Table I.2.

The uncertainties to be associated with the numbers in Table I.2 are roughly a factor of two for the thermal capture reaction and about an order of magnitude for the threshold reactions. The thermal capture reactions are much larger than the threshold reactions, and of the latter, (n,d) and (n, α) reactions are much smaller than (n,2n) and (n,p) reactions. The effect on the zirconium composition is discussed under the heading of each reaction type.

The effect of thermal neutron capture is to move the isotope to the next highest mass number zirconium isotope. This capture does not change the chemical composition of the sample unless the resulting isotope is radioactive with a short half-life. Thus when 93 Zr (half-life 1.5×10^6 year) is produced, the competition between beta decay to 93 Nb (stable) and neutron capture to 94 Zr (cross-section ≈ 2.6 b) is won by capture, typically by an ratio of about 18 000:1. Only a very small quantity of 93 N and the products of its further irradiation will be produced.

Irradiation of ⁹⁴Zr produces ⁹⁵Zr (half-life 64 d). In this case beta decay is dominant leading to the production of ⁹⁵Nb (half-life 35 d) and finally ⁹⁵Mo (stable).

I UDDE I III	TAIAUAAAU	MARIE TITL VID				1 - 1 1			
		Zr-90	Zr-91	Zr-92	Zr-93	Zr-94	Zr-95	Zr-96	Zr-97
Half-life		Stable	Stable	Stable	$1.5 \times 10^6 \mathrm{a}$	Stable	64.02 d	Stable	16.8 h
Atom fracti	on (%)	51.45	11.22	17.15	0	17.38	0	2.80	0
Thermal $\sigma_{ m c}$	(q)	0.011	1.24	0.22	≈2.6	0.0499		0.0299	
RI (b)		0.14	5.20	0.63		0.23		5.3	
	Q [MeV]	-12	-7.20	-8.60		-8.2		-7.8	
(u,2n)	σ (14 MeV)	0.60	>0.80					1.5	
	Q [MeV]	-1.50	-0.80	-2.80		-4.2		-6.1	
(d,11)	σ (14 MeV)	0.045	0.03	0.02		0.01		0.013	
(r. 1)	Q [Me]	-6.2	-6.50	-7.10		-8.1		-9.1	
(n,u)	σ (14 MeV)	0.01							
()	Q [MeV]	+1.7	+5.60	+3.40		+2.1		+0.4	
(II,U)	σ (14 MeV)	0.015		0.01		0.005		0.003	
L T	${\cal Q}\left[{\sf MeV} ight]$	-11	-7.10	-8.80		-9.3		-10	
(11,11)	σ (14 MeV)	0.00004							
(± 11,2)	${\cal Q}\left[{\sf MeV} ight]$	-7.7	-8.30	-9.40		-11		-13	
(111,11)	σ (14 MeV)							0.000136	

TABLE I.1. NUCLEAR DATA FOR THE STABLE ZIRCONIUM ISOTOPES PLUS Zr-93 AND Zr-97

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Irradiation of 96 Zr leads to 97 Zr (half-life 16.8 h) which beta decays to 97 Nb (half-life 1.2 h) and thence to 97 Mo (stable).

The major effect of neutron capture is to change the isotopic distribution of the Zr by increasing the fractions of higher isotopes. In addition, most of the 2.1% of the initial 92 Zr that undergoes capture will remain as 93 Zr at the end of the irradiation. The 0.48% of 94 Zr and 0.29% of 96 Zr that undergo capture will end up as stable Mo isotopes; about 0.092% of the initial Zr atoms become Mo by neutron capture. The following neutron reactions take place:

- (n,2n): The effect of the (n,2n) reaction is opposite to that of neutron capture: a given Zr isotope is moved to the next lower mass number. Thus ⁹¹Zr becomes ⁹⁰Zr and ⁹⁶Zr becomes ⁹⁵Zr. Table I.2 shows that the numbers of reactions involved are much smaller than those in the capture reactions so that the consequence for the isotopic distribution of the Zr isotopes and the production of ⁹⁵Mo are negligible (an additional 0.00042% of the initial Zr is converted to Mo).
- (n,p): The (n,p) reaction converts a Zr isotope to an Y atom of the same mass number. In all cases the Y nuclei so produced are radioactive with short half-lives (the longest is 58.5 d, Y-91) and beta decay back to the original Zr isotope. This reaction therefore has no effect on the composition of the Zr.
- (n,d): Only ⁹⁰Zr has a measured cross-section for this reaction. The reaction product is ⁸⁹Y, the only stable Y isotope. This reaction has a very small neutron capture cross-section (0.001 b) and approximately 0.00005% of the Zr is converted to Y.
- (n,α): This reaction changes a Zr isotope into the strontium isotope three mass numbers lighter. In the case of ⁹⁰Zr, the product is ⁸⁷Sr, which is stable. For ⁹²Zr, the product is ⁸⁹Sr, which beta decays, with a half-life of 50.5 d, to stable ⁸⁹Y. For ⁹⁴Zr, the product is ⁹¹Sr (half-life 9.5 h), which beta decays to ⁹¹Y (half-life 58.5 d) and thence to ⁹¹Zr. For ⁹⁶Zr, ⁹³Sr (half-life 7.4 min) is produced, which decays through ⁹³Y (half-life 10.2 h) to ⁹³Zr. In summary, the conversion of about 0.00008% of the initial Zr to Sr is expected.

I.2. SUMMARY

The following changes to the composition of a pure zirconium sample irradiated in the neutron spectrum in a CANDU pressure tube (thermal neutron flux of $10^{18} \text{ n}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$) are expected:

- A modest increase in the average mass number due to neutron capture shifting zirconium isotopes to higher mass numbers;
- Conversion of about 0.2% of the initial Zr to 93 Zr (half-life 1.5 × 106 a);
- Conversion of about 0.9% of the initial Zr to stable Mo;
- Conversion of a very small amount (0.00005%) of the initial Zr to Y;
- Conversion of a very small amount (0.00008%) of the initial Zr to Sr.

In addition, short lived radioactive isotopes are generated during the irradiation, particularly Y isotopes resulting from (n,p) reactions. For instance, the equilibrium activity of 90 Y and 91 Y can be estimated as 1.3×10^9 and 1.8×10^7 Bq·g⁻¹ (1332 and 18.5 MBq), respectively. These levels decay rapidly (relative to the 25 year irradiation time), with half-lives of 2.7 d and 58.5 d respectively, when the neutron flux is removed.

The only threshold reactions that have been considered are those for which measured cross-sections are given in Ref. [I.2]. Where cross-sections have not been measured, one can suppose that they do exist and that they have similar magnitudes to those that have been

measured. If that were the case, the above discussion of the final fate of the transmutation chains indicates that the picture would not be much changed.

TABLE I.2.	PERCENTAGE	OF INITIAL	ISOTOPE	UNDERGOI	NG RE	ACTION	IN 25	YEARS	IN	THE
NEUTRON	SPECTRUM OF I	FIG. I.1 WITH	I A THERN	MAL FLUX O	F 10 ¹⁸ r	$m^{-2} \cdot s^{-1}$				

	Zr-90	Zr-91	Zr-92	Zr-94	Zr-96
Thermal cap.	0.11	11.2	2.11	0.48	0.29
(n,2n)		0.008			0.015
(n,p)	0.005	0.0003	0.004	0.001	0.0005
(n,d)	0.0001				
(n,α)	0.00015		0.0004	0.0002	0.0001

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Appendix II

THE EFFECT OF NEUTRON IRRADIATION ON THE COMPOSITION OF SAMPLES OF ALLOYING ELEMENTS

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II.1. INTRODUCTION

This appendix describes a first order estimate of the effect of neutron irradiation on various elements that are used in the formation of zirconium alloys for use in in-core applications in the nuclear industry. It is intended as an illustration and guide to potential damaging transmutations that may affect the metallurgical properties of the alloy during service in a particular reactor. The methods used previously in a similar review of the compositional changes during the irradiation on zirconium itself [II.1] are used here with some even greater simplification regarding the calculation of reaction rates of the various threshold reactions. Thus, a neutron spectrum typical of that in the pressure tube of a CANDU reactor fuelled with natural uranium is assumed to have a thermal neutron flux of 10^{18} m⁻²·s⁻¹. In the present study threshold reaction rates are estimated using 14 MeV cross-sections from the ENDF/B-VI neutron cross-section data base [II.2] combined with a flux value taken to be 0.035 of the thermal flux values. This factor of 0.035 was found by averaging over all the threshold reaction rates calculated in the previous study of the irradiation of zirconium isotopes [II.1]. Clearly, the spectrum considered strictly applied to only one position in one type of reactor. Also, since the method used in that study was itself approximate, this appendix constitutes an even simpler estimate that cannot be expected to have associated errors of less than one or two orders of magnitude for the threshold reactions. For the neutron capture reactions an uncertainty of about a factor of two is estimated.

The alloying elements considered are Nb, Mo, Sn, Fe, V, Cr, Cu and Ni. Two tables and one figure have been prepared for each of these elements. The first table shows the cross-sections for the various reactions considered for each of the stable isotopes of the alloying element; a dash indicates that no cross-section value was found for that reaction. The second table gives the calculated percentage of the total number of atoms of the element initially present that undergo the reaction indicated for that isotope. The figure is copied from the chart of the nuclides [II.3] and shows the region around the isotopes of interest that can be accessed by the various reactions and potential radioactive decays of the products. In the comments provided for each element, reference is made to the figure, in particular to half-lives and neutron capture cross-sections thereon, which are used to estimate the fractions of new elements that are produced.

II.2. NIOBIUM AND MOLYBDENUM

II.2.1. Niobium

Niobium consists of a single isotope, ⁹³Nb, with cross-section data presented in Table II.1. Table II.2 indicates that 8.7% of the ⁹³Nb undergoes thermal neutron capture to radioactive ⁹⁴Nb. Figure II.1 shows that this isotope has a half-life of about two years and beta decays to stable ⁹⁴Mo, or is converted by neutron capture to ⁹⁵Nb, which itself decays to stable ⁹⁵Mo. Thus, at the end of the 25 year irradiation about 8% of the Nb will have been converted to Mo. The following neutron reactions take place:

- The (n,2n) reaction leads to the production of 92 Zr via electron capture decay of 92 Nb.
- The (n,p) reaction produces 93 Zr.
- The (n,d) reaction also produces 92 Zr.
- The (n,α) reaction produces Y-90 which itself rapidly decays to 90 Zr.

In summary, about 8% of the initial Nb is converted to Mo and all the threshold reactions result in about 0.07% being converted into Zr. For Zr-2.5Nb the concentration of Mo at the end of life would be 0.2 at.% (2100 wppm).

	N. K. L.		N. C. 18					the second s		and the second second second second	the second se
10.8 s 1.0 m	Ru94 52 m	Ru95 5** 1,64 h 1,61 h	Ru96 5.54	Ru97 5*	Ru98 1.87	Ru99 5+ 12.76	Ru100	Ru101 5+ 17.06	Ru102 31.55	Ru103 3** 39.27 d # 221	Ru104 18.62
11 1305 8 Y 080.5. 11 134 4 10 1344 10 1348 10 13 48	y 367, 892,-	828.8,-	a _y . 25. 7	7 215 7, 326 5,	Ry+8	ny 6.1.862	4,58.11	2, 5, 1082 2, 4, 15,45	ay 13.47	$\theta_{g} < 20, 36.1$	ay .47, 6
235 6.3	E 1.59	6.2.57	95.90760	E 1.11	97.90529	86.905839	99.904220	100.805582	101.904350	6.793	103.905430
Tc92 (8)* 4.2 m (7:4.1 1 1 1508.0, 773.0.	U- Tc93 W* 43 m 2.73 h (7 391.8 x, # 35, 7 2544.6, y 1363.1,	(2)* Tc94 7* 52 m 4.88 h /* 2.44, e, p 32,- - e 7 8711, 7.8711, 7026,	10 TC95 W*	4+ Tc96 7+ 52 m 43 d 1342 + 718 2 713 - 545 8 545 8 718 2 718 2 718 2	91 d 4286 a	Tc98 (8)+ 4.255 a # 40 745 4, 852 4 3, (3+7)	M ⁻ Tc99 6.01 h 2.13E5 s 0.3427, 2.294, 2.2 (e ⁻¹) 7.3425 s 2.21 0.427 s 2.21	Tc100 ** 15.8 s # 3.4 2.9 > 539.5. 590.8 £ ce	Tc101 #* 14.22 m # 1.32 7 205.5	Tc102 ** 44m 53s #18- #42 14751 34.22 681 -051-	Tc103 %* 54 s 57 22, 2.0 - 7 346 4, 136 1, 210 4,
87.87	6.3.20	E 4 336 E 4 256	F.7104	1200.2	E 320	61.60	1 322 mr 4 1953	E 3 202	8.141	IT	E266
1.06 m 15.5 m	Mo92 14.84	211* Mo93 5* 53 h -3.583 a	Mo94 9.25	Mo95 5**	Mo96 16.68	Mo97 5+ 9.55	Mo98 24.13	Mo99 *** 2.7476 d	Mo100	Mo101 ***	Mo102
40 7 1507 0, 1507 0, 1507 0, 1508 0, E 4.43	n _p (2,xb + 6E1m0), .8 91.906810	1477.1. #"	ay 7. 8 83 905068	a, 54.0, 1.162 a, .00 mb 94.905841	ny 7.20 95.904679	0, 2.5, 15 0, Aµ0 96.000021	ay .53, 7.2 97.905408	140.5D E 1.357	ay . 10, 3.8 99.90748	1012 5, 506.0. E 2.82	E 101
4 Nb90 1+ 18.8 s 14.6 h 17.2.2. #1.500. 4' 122.30 = 128.2 2015.00 141.2	Nb91 ***	(2)* Nb92 (7)* 10.13 d 3.5E7 a 5 ast 1 7 834 5, 834 5	Nb93 ** 100 17 30 8, e 100 17 30 8, e	3* Nb94 #0* 6.363 m 2.064 * 7.655 # 411 9.12m # 100 7.855 # 411 9.12m # 100 9.855 # 100	Nb95 ************************************	Nb96 6* 23.4 h // 346 // 776.2.566.8. 1091.3	53 s 1.23 h (7 743.3 g 1.27, 7 657.9,	(5 *) Nb98 1* 51 m 2.3 s 7 180 7 46. 7 186 7 4. 7 197 4 7 1004.1	2.6 m 15.0 s 2.6 m 15.0 s 7.32 - 7.3.5 - 7.97.7 7.137.6 253.5 97.7 253.5 97.7 254.7 255.7 257.	5* Nb100 1* 3.0 * 1.5 * 7 5.8 - 7 6.2 7 535.6 5.3 600.2 7 535.6 159.5	Nb101 7.1 s # 4.3 7 276 1, 157.6
E 6.111	E 1,253	E 2,005	82.906378	E 2.045	E.8256	E 3.187	E 1.954	E 4 87 E 4 59	17.3651 E.3.64	E 8.74 E 8.25	E.4.57
V Zr89 W 4.16m 127 d 17.167.8 J.F W 4.17.801 J.F W 4.17.801 J.F W 4.17.801 J.F W 4.17.801 J.F W	5° Zr90 809 ms 51.45 17 2519 0 122.6 y 21.65.2 - ay .012	Zr91 5* 11.22 5/ 12.54	Zr92 17.15	Zr93 9* 1.566 * 7 30.60 4y -1.15	Zr94 17.38 ap-05028	Zr95 5* 64.02 d 2 368, 400 2 756 7, 724 2 -	Zr96 2619 a 2619 a 7 F	Zr97 14 16.8 h 7 192 7 743.30	Zr98 30.7 s	Zr99(1/*) 22 s (* 3.54, 3.50 -) 409 1, 546 1, 694.0, -	Zr100 7.5 s 7 504.3, 400.6
E 2.833	89.904704	90,905645	91,905040	E.091	93.908316	E 1.125	95.908276	E 2.658	E 2.25	E4.56	E2.34
Y88 106.65 d 7 1636.1, 698.0	11 + Y89 U- 15.7 = 100 17 00:1 4 _y (1.0 mb + 1.28). (006 + 1.0)	7* Y90 2* 3.19 h 2.67 d IT 476.5 F 2.281 7.2025 7.2016 2 7.2119.00 2 ¹⁰ 7.2119.00 2 ¹⁰ 7.2119.00 2 ¹⁰	49.7 m 58.5 d 17.555.8 p 1.545. p 1205 2, 1.4	Y92 2- 3.54 h 7.354 - 7.904 5, 1405 4 -	0.82 s 10.2 h 0.82 s	Y94 2- 18.7 m p ⁺ 4.92 - y 918.7, 1138.9, 500.9,	Y95 11- 10.3 m (* 4.45. * 854.0. 2175.6. 3576.0.	(8)* Y96 0* 9.6 s 53 s # 2.25 # 7.12 + 1790.6. 905.0. + 1790.4. 8(11) 1107.2	(%)* Y97 (1/-) 1.21 s 3.76 s # 5.1 # 6.7 6.0 - 7 3267.6, 7 1103.0, 3401.3, 161.4, 101.4	Y98 (0) 2.1 s 0.59 s (1227, 244 (1227, 244) 447.5, 1581.4 (1981, 1980, 1981, 1981, 1981, 1981, 1981, 1981, 1981, 1981, 1981, 1981, 19	Y99 (5(*) 1.47 s 7 6.64 7 121 8 724 3,- (1)
E 3.623	85 905648	16 2.280	E 1.545	E 3.64	E 2.89	E 4.92	E 4.45	67.10	E 6.60	E 55 E 8.82	E7.57

FIG. II.1. Chart of the nuclides in the region of the stable isotopes of niobium and molybdenum [II.3].

Nb-93		
Atom fraction ((%)	100
Thermal $\sigma_{c}(b)$		1.155
RI (b)		8.5
n,2n	σ (14 MeV)	1.29
n,p	σ (14 MeV)	2×10^{-2}
n,d	σ (14 MeV)	$7 imes 10^{-3}$
n,a	σ (14 MeV)	6×10^{-3}
n,T	σ (14 MeV)	2×10^{-4}
n, ³ He	σ (14 MeV)	_

TABLE II.1. NIOBIUM CROSS-SECTION DATA

TABLE II.2. PERCENTAGE OF INITIAL

NIOBIUM NUCLEI REACTED	
Nb-93	
n,y	8.7
n,2n	0.06
n,p	0.0009
n,d	0.0003
n,a	0.0003
n,T	—
n, ³ He	_

II.2.2. Molybdenum

Molybdenum has seven stable isotopes, but only three of them (⁹²Mo, ⁹⁸Mo and ¹⁰⁰Mo) produce other than stable Mo isotopes by neutron capture (Table II.3). Figure II.1 shows that ⁹³Mo decays by electron capture to ⁹³Nb, which has already been discussed. Molybdenum-99, a well-known medical isotope decays to very long lived ⁹⁹Tc and ¹⁰¹Mo decays quickly through ¹⁰¹Tc to stable ¹⁰¹Ru.

The situation is similar for the (n,2n) reaction: ⁹⁴Mo is converted to ⁹³Mo and ¹⁰⁰Mo is converted to ⁹⁹Mo, both of which are discussed above. This leaves the ⁹¹Mo produced from ⁹²Mo that decays quickly to ⁹¹Nb, which has a 700-year half-life for decay to stable ⁹¹Zr.

The (n,p) reaction converts 92 Mo and 94 Mo to long lived 92 Nb and 94 Nb (3.5 × 10⁷ and 2 × 10⁴ a, respectively). All the other Mo isotopes are converted to Nb isotopes that promptly decay back to the original Mo isotope.

The (n,d) reaction on ⁹²Mo, ⁹⁴Mo and ⁹⁵Mo produces long lived or stable Nb isotopes while ⁹⁶Mo, ⁹⁷Mo and ⁹⁸Mo produce Nb isotopes that quickly decay back to stable Mo isotopes. Molybdenum-99 is produced from ¹⁰⁰Mo.

The (n, α) reaction on ⁹⁴Mo through ⁹⁷Mo produces stable or very long lived Zr isotopes. Molybdenum-92 is converted to ⁸⁹Zr, which quickly decays to stable ⁸⁹Y. Molybdenum-98 is converted to ⁹⁵Zr that decays eventually to ⁹⁵Mo. Similarly, ¹⁰⁰Mo is converted to ⁹⁷Zr, which rapidly decays to ⁹⁷Mo.

Thus, based on the above and on the data in Table II.4, it is expected that roughly 0.27% of the initial Mo is converted to Nb, roughly 0.26% to Tc, about 0.15% to Ru and 0.0003% to Zr.
NEUTRON IRRADIATION AND ALLOYING ELEMENT COMPOSITION

		Mo-92	Mo-94	Mo-95	Mo-96	Mo-97	Mo-98	Mo-100
Atom fr	action (%)	14.84	9.25	15.92	16.68	9.55	24.13	9.63
Thermal	$1 \sigma_{\rm c}({ m b})$	$2.08 imes 10^{-2}$	$3.4 imes 10^{-1}$	13.6	$5.96 imes 10^{-1}$	2.20	$1.3 imes 10^{-1}$	1.99×10^{-1}
RI (b)		9.67×10^{-10}	1.46	110.9	17.5	17.5	6.55	3.87
n,2n	σ (14 MeV)	$1.51 imes 10^{-1}$	1.11	1.38	1.29	1.41	1.33	1.49
d'u	σ (14 MeV)	$1.28 imes 10^{-1}$	$5.3 imes 10^{-2}$	$3.6 imes 10^{-2}$	$2.1 imes 10^{-2}$	$1.5 imes 10^{-2}$	$4.8 imes10^{-3}$	$1.6 imes 10^{-3}$
n,d	σ (14 MeV)	$2.4 imes 10^{-3}$	$10 imes 10^{-3}$	I	$1.5 imes 10^{-4}$	$6.6 imes 10^{-4}$	$3.2 imes10^{-5}$	$1.2 imes 10^{-5}$
n,α	σ (14 MeV)	$2.14 imes 10^{-2}$	$1.75 imes 10^{-2}$	$1.4 imes 10^{-2}$	$9.7 imes 10^{-3}$	$6.9 imes10^{-3}$	$5.1 imes10^{-3}$	$2.2 imes10^{-3}$
n,T	σ (14 MeV)	$4.8 imes10^{-9}$	$1.5 imes 10^{-5}$	I	$4.7 imes 10^{-6}$	$1.5 imes 10^{-5}$	$2.8 imes 10^{-6}$	$1.1 imes 10^{-5}$
n, ³ He	σ (14 MeV)	$2.6 imes 10^{-7}$	$6.4 imes10^{-10}$	I	I	$1.5 imes 10^{-13}$	I	I

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TABLEI	I.4. PERCENTAG	E OF INITIAL MOI	LYBDENUM NU	CLEI REACTED			
	Mo-92	Mo-94	Mo-95	Mo-96	Mo-97	Mo-98	Mo-100
n,γ	0.024	0.24	10.0	0.77	1.5	0.25	0.15
n,2n	0.001	0.0046	0.0099	0.0097	0.0054	0.014	0.0065
n,p	0.00086	0.00022	0.00026	0.00016	0.000065	0.000052	0.0000069
n,d	0.000016	0.000042		0.0000011	0.000028	0.000004	0.0000005
n,a	0.00014	0.000073	0.0001	0.000073	0.00003	0.000055	0.0000096
n,T	0	0.000001		0	0	0	0
n, ³ He	0	0	I	I	0	I	

II.3. TIN

Tin has ten stable isotopes, but Fig. II.2 shows that only neutron capture by ¹¹²Sn, ¹²⁰Sn, ¹²²Sn and ¹²⁴Sn produce other than ultimately stable tin isotopes. Neutron capture by ¹¹²Sn produces ¹¹³Sn (half-life 115 d) that mostly decays by electron capture to stable ¹¹³In. Neutron capture by ¹²⁰Sn produces ¹²¹Sn (half-life 1.13 d), which decays to stable ¹²¹Sb. Similarly, capture by ¹²²Sn leads to the stable antimony isotope ¹²³Sb. Capture by ¹²⁴Sn leads ultimately to stable ¹²⁵Te although much of it remains as radioactive ¹²⁵Sb (half-life 2.76 a) for a significant time.

The situation is similar for the (n,2n) reaction where Fig. II.2 shows that ¹¹²Sn is converted to ¹¹¹Sn and thence by two beta+ or electron capture decays to stable ¹¹¹Cd, and that ¹¹⁴Sn is converted to ¹¹³Sn and thence to stable ¹¹³In, as described above. Tin-122 and ¹²⁴Sn are converted finally to stable ¹²¹Sb and ¹²³Sb respectively.

The (n,p) reaction on all of ¹¹⁶Sn through ¹²⁴Sn produces In isotopes of the same mass number, which decay rapidly by β^- emission to the original Sn isotope. Tin-112 is converted to ¹¹²In that decays 44% by β^- emission back to ¹¹²Sn and 56% by electron capture to stable ¹¹²Cd. Tin-114 is converted to ¹¹⁴In, which decays 99.5% by β^- emission back to ¹¹⁴Sn. Tin-115 is converted to stable ¹¹⁵In; since ¹¹⁵In has a large neutron capture cross-section of 203 b (equivalent to a half-life of about one year), it is partly converted to ¹¹⁶In and thence to ¹¹⁶Sn.

The (n,d) reaction on ¹¹²Sn ultimately produces ¹¹¹Cd, on ¹¹⁵Sn it produces ¹¹⁴Sn, on ¹¹⁶Sn it produces a mixture of ¹¹⁵In and ¹¹⁵Sn, and with all the other Sn isotopes it produces the Sn isotope of the next lowest mass number.

The (n,α) reaction first produces the Cd isotope of a mass number three less than the initial Sn isotope. For ¹¹⁴Sn through ¹¹⁷Sn and for ¹¹⁹Sn this reaction leads to stable Cd isotopes. Tin-112 produces ¹⁰⁹Cd, which decays with a 461 d half-life to stable ¹⁰⁹Ag. Tin-118 becomes ¹¹⁵Cd, which decays to ¹¹⁵In (see above). Cross-sections of tin nuclear reactions are presented in Table II.5.

In summary, based on the above and on the data in Table II.6, it is expected that roughly 0.42% of the initial tin atoms will be converted to antimony, 0.063% to indium, 0.061% to tellurium, 0.000044% to cadmium and 0.0000006% to silver. At the maximum concentration of Sn in the ASTM standard for Zircaloy [II.4], 1.7 wt.% (1.31 at.%), at the end of life the concentration of Sb would be about 0.0055 at.% (73 wppm).

Te112	Te113((*)	Te114 15m	11-Te115 :	Te116 2.48%	Tett7 X4	Tett8 saur	Tello	Te120 1.09	-164 188 188	Te122 2.88	*** Te123 ***	Te124 4.74	Tet25 14	Te126	Te127	Te128
Mamon.	7.874, 1014, 1101.	Jana.	TOTAL PROA	-87-	7 fpt. 17 41, 2008.	-	1014 (MIL) 1014	4.67+2	The wa	2,-24.801	175.401	R. 108 - 71.8		1,110 + 8. (?+8)	WA MAIN	/ J 7-1275-225 (274-135)
845	641	111	1.43	818	13.0	8.07	- (6236)	115.30402	6104	101.00047	COLUMN TO ANY T	121.002010	TRANSPORT.	125.00000	1.04	CTRONOT .
\$5111.0** 1.25 m	Sb112 1*	\$b113 **	\$b114 >* 148 m	\$b115 %*	* Sb116 3+ 1.005 18.m	Sb117 =-	Sb118 **	Sb119 SH	56120 1* 15.0 m	Sb121 9*	1 55122 1 4 191 m 172 d 7 21 1 172 d	Sb123 7* 4279	* Sb124 361m 00.204	\$b125 ** 178 *	Sb126	56127 1-
1561488	12011.002		- 108.5 MP.A.	2487.4.1		- 184 -	NUMET OF GRAT		1011 - 1014 10 X 10 X 10 X 10 X 10 X	4,05438,2002	The star	122104		1.70	14 000 000 14 000 000 000 000 000	110
Sn110	Sn111 2+	Sn112	1.4 Se 113	Sn114	Sn115 ***	Sn116 54.54	Set17 14	Sn118	Sn119 **	Sin120	11 Sa1211-	Sn122 4.63	411 1231	\$n124 179	3* Sn125 ***	Sn126 2.851 a
2 281.46	1.715- 1.11525 1018.1 NER 10105	1, (11 + A), (3 + 10)	1 114 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	9.28	n, 7. 181 n, 18 m	A, 1380-15 (8+15)	4.11-18	4,000+5.6	100	4,000-30.12	1215	4, (11 + 107) (11-7)	1903 -	n, 113 + 2005 (8+1)	Set a - Lima A Bill A Bill A Bill A	-
6.54	62.0	THE BOARDY	E128	113.002762	14,8054	198.801744	THENDROM	117 301404	TRANSPORT VIEW	*********	6.300	STATISTICS.	ELED TELED	10.000	COMP LINE	1.0
13 m 425	1- In110 1- 1-15 435 /722 /	220 1000 c	** in112 ** 258.0 1640 218.0 1.713	5 In113 0- 5557 439	40 81 4 1.756 m	CALLS MADE	- In116	1545 44 m	1118 ···	178m 23m	47 a 21 a	10121 V- 53m 21s 117 / 214	10.122 1- 10.3 4 1.54	6123	34x 394x	1123 ***
(m)	- 107 A - 107 A 107 A	1912	1874 882- 1 R	0.3+5+38. 0.82+805	雪湯	ALL	ALL ALL	and and		2001 7 214	1 mil	120.5	194. (B) 111	14.0	ally ar.	110
Cd108 6.89	Cd109 **	Cd110 12.49	din UN	Cd112 34.13	101 Cd113 U	Cd114 33.73	Cd115	Cd116 7.49 3619.4	Cd117	Cd118 SLIn	Cd119	Cd120	Cd121-	Cd122 53 s	Cd123	Cd124 138.8
5.18	1,32,30 5,110	3, (38 + 11) (2 + 481)	9, IK. 10	4, (211-3.2) 10	1,20403 1407 1,158 £ 298	(7 + 201) (7 + 201)	SAL 187	n, 28+52 min 13 100,000 min 13	TIN LIN		101 H	118	111	01.	m Aug	SALE-

FIG. II.2. Chart of the nuclides in the region of the stable isotopes of tin [II.3].

TABLEI	I.5. TIN CROSS	-SECTION D	ATA										
		Sn-112	2 Sn	1-114	Sn-115	Sn-116	Sn-1171	Sn	-118	Sn-119	Sn-120	Sn-122	Sn-124
Atom fract	ion (%)	9.7×10^{-10}) ⁻¹ 6.6	$\times 10^{-1}$	0.34	14.54	7.68	24	1.22	8.59	32.58	4.63	5.79
Thermal $\sigma_{\rm c}$	(p)	8.5×10) ⁻¹ 1.25	1×10^{-1}	58.0	1.28×10^{-1}	1.07	2.2	$\times 10^{-1}$	2.18	0.140	0.146	0.134
RI (b)		30	-	7.8	21	12.3	1.8		4	5.6	1.1	0.7	8
n,2n	σ (14 MeV)	1.14		1.22	1.46	1.39	1.56	1	.40	1.58	1.48	1.53	1.52
n,p	σ (14 MeV)	3.4×10^{-3}) ⁻² 3.6	$\times 10^{-2}$	$2.5 imes 10^{-2}$	$1.7 imes 10^{-2}$	$1.2 imes 10^{-2}$	2 5.5	× 10 ⁻³ 2	$4.4 imes 10^{-3}$	$3.3 imes 10^{-3}$	7.1×10^{-4}	$9.5 imes 10^{-4}$
n,d	σ (14 MeV)	1.2×10) ⁻³ 3.3	$\times 10^{-4}$	8.2×10^{-4}	$2.5 imes 10^{-5}$	$5.5 imes 10^{-4}$	4 1.6	× 10 ⁻⁶ 1	1.4×10^{-4}	$2.0 imes 10^{-8}$	$3.5 imes 10^{-10}$	$5.5 imes 10^{-14}$
n,a	σ (14 MeV)	1.3×10^{-1}) ⁻³ 6.6	$\times 10^{-3}$	4.7×10^{-3}	$3.2 imes 10^{-3}$	$2.3 imes 10^{-5}$	3 6.6	× 10 ⁻⁴ 1	1.1×10^{-3}	$2.5 imes 10^{-4}$	4.4×10^{-5}	$4.3 imes 10^{-6}$
n,T	σ (14 MeV)	5.7×10) ⁻⁸ 1.8	$\times 10^{-9}$	$2.7 imes 10^{-6}$	$3.5 imes 10^{-11}$	$7.6 imes 10^{-6}$	8 3.0 ;	$\times 10^{-13}$ 3	$3.4 imes10^{-8}$	$2.7 imes 10^{-14}$	$1.2 imes 10^{-16}$	$1.1 imes 10^{-18}$
n, ³ He	σ (14 MeV)	7.4×10) ⁻¹⁰ 1.4	$\times 10^{-13}$	$7.4 imes 10^{-16}$	Ι	I		I	I	I	Ι	I
	TABLE II.6. P	ERCENTAG	E OF INU	TIAL TIN	NUCLEI TI	HAT ARE RI	EACTED						
		Sn-112	Sn-114	Sn-115	: Sn-11	6 Sn-11	17 Sn-	-118	Sn-119	Sn-120	Sn-122	Sn-124	I
	μ,η	6.3×10^{-2}	$6.5 imes 10^{-3}$	3.4×10^{-3}	-1 1.5 × 1.	0^{-1} 6.2×1	10^{-1} 4.2 ×	× 10 ⁻¹	1.4	3.6×10^{-1}	$5.3 imes 10^{-2}$	6.1×10^{-2}	1
	n,2n	5×10^{-4}	3.6×10^{-4}	2.2×10	⁴ 9.1 × 1	0^{-3} 5.4 × 1	1.5 × 1.5 ×	$\times 10^{-2}$	$6.1 imes 10^{-3}$	$2.2 imes 10^{-2}$	$3.2 imes 10^{-3}$	4×10^{-3}	
	n,p	$1.5 imes 10^{-5}$	$1.1 imes 10^{-5}$	$4 \times 10^{\circ}$	-6 1.1 × 1	0^{-4} 4.2 × 1	10- ⁵ 6 ×	$\times 10^{-5}$	$1.7 imes 10^{-5}$	$4.8 imes 10^{-5}$	$1.5 imes 10^{-6}$	$2.5 imes 10^{-6}$	
	n,d	$5 imes 10^{-7}$	0	$1 \times 10^{\circ}$	$^{-7}$ 2 × 1	0^{-7} 2×1	10-7	0	$5 imes 10^{-7}$	0	0	0	
	n,a	6×10^{-7}	$2 imes 10^{-6}$	0	$2.1 \times 1_{0}$	0^{-5} 8×1	10 ⁻⁶ 7.2 >	$\times 10^{-6}$	4.3×10^{-6}	$3.7 imes 10^{-6}$	0	0	
	n,T	0	0	0	0	0	-	0	0	0	0	0	
	$n,^{3}He$	0	0	0	Ι	I	1	I	I	Ι	Ι	Ι	

NEUTRON IRRADIATION AND ALLOYING ELEMENT COMPOSITION

Ni54 (************************************												
Production Product				NI54 0.19 s	NI55 71- 202 ms	NI56 5.9 d	Ni57 3- 35.6 h	Ni58 68.0769	Ni59 3" 7.884 a	Ni60 26.2231	Ni61 3- 1.1399	Ni62 3.6345
Crist Cods = 1 + 1 + 1 + 1 + 1 + 1 + 1 + 1 + 1 + 1 +				7 837.5			F 3 204	ny 4.6.22 ng 4.03 mb	1,78,1282 2,14,20 0,2.2 1,072	ny 2.8.1.5	ay -2.51.8 ag ≤ .03 mb #0.491080	41 50 804
Product Product <t< td=""><td></td><td></td><td></td><td>0.25 × 0.34 ×</td><td>(7)* Co54 0* 1.46 m 193.2 ms</td><td>Co55 1- 17.53 h</td><td>Co56 4* 77.3 d</td><td>Co57 ***</td><td>1* Co58 2* 9.1h 79.88 d</td><td>Co59 77</td><td>2* Co60 1* 10.47 = \$.271 a</td><td>Co61 7</td></t<>				0.25 × 0.34 ×	(7)* Co54 0* 1.46 m 193.2 ms	Co55 1- 17.53 h	Co56 4* 77.3 d	Co57 ***	1* Co58 2* 9.1h 79.88 d	Co59 77	2* Co60 1* 10.47 = \$.271 a	Co61 7
Cr47 3* Cr48 Cr49 Cr43 Cr43 <thcr43< th=""> Cr43 Cr43 <</thcr43<>				P 1.55 F =====	p* 4.5 p* 7.220 = 5407, X == 1300, 411	F 150, 103, F 801.2, 477.2, 1408.4, F	7 846.8, 1238.3,-	7 122 L 138 L	A LARS - BURA	ny (21+16) (36+36)	· · · · · · · · · · · · · · · · · · ·	7 122- 7 12 A-
Cr47 Cr48 Cr49 Cr49 <th< td=""><td></td><td></td><td></td><td>E 8.30</td><td>E 8.441 E 8.2431</td><td>E 3.4513</td><td>E 4 566</td><td>E 836</td><td>8 2 307</td><td>58 833200</td><td>2 M2 E 2 8239</td><td>E 1.322</td></th<>				E 8.30	E 8.441 E 8.2431	E 3.4513	E 4 566	E 836	8 2 307	58 833200	2 M2 E 2 8239	E 1.322
Cr47 Sr Cr48 Cr49 Cr49 Cr49 Cr43 Cr44				(12+)Fe52 46 s 8.28 h	11 Fe53 7- 2.6 m 8.51 m 17 7012 - P24	Fe54 5.845	Fe55 3"	Fe56 91.754	Fe57 1-	Fe58 6.282	Fe59 3" 44.50 d # 486, 274	Fe60
E # 7 E # 7 <th< td=""><td></td><td></td><td></td><td>- 100 F.</td><td>7 138.1. 2.4 1011.5. 7 377.8</td><td>3, 23, 14 4, 01 mb, 1.1 mb</td><td>107 5, 13 7, -9 mb</td><td>ay 28.14</td><td>8, 25.18</td><td>ay 13.12</td><td>7 1088.2, 1291.8, 0₇ -13</td><td>7 56 60, 8-</td></th<>				- 100 F.	7 138.1. 2.4 1011.5. 7 377.8	3, 23, 14 4, 01 mb, 1.1 mb	107 5, 13 7, -9 mb	ay 28.14	8, 25.18	ay 13.12	7 1088.2, 1291.8, 0 ₇ -13	7 56 60, 8-
Mn 51 br P Mn 52 br Mn 52 br Mn 52 br Mn 55 br Mn				E 8.7 E 2.37	E 6.784 E 3.742	53,939615	E 2314	55,854942	56.855399	87 803280	E 1.565	E.237
Visci (sold) Visci (sold)<				Mn51 #- 46.2 m	2+ Mn52 (+ 21.1 m 5.591 d (* 263 - 1 . (* 575	Mn53 ***	Mn54 3+ 312.1 d	Mn55 5- 300	Mn56 2* 2.578 h # 2.54 1.54 - \$46.8, 1875.8	Mn57 %	(4)* Mn58 1* 65 * 10 *	Mn59/51- 4.6 s 3 4.4.47- 2 726.1.472.6
Cr47 S Cr48 Cr49 Cr49 Cr50 Cr51 Cr52 Cr52 Soft Cr53 Soft Cr56 Soft So				7 740 1 (c) 11480, 1164.4,-	1 3777 835.5 1 3777 835.5 1 44.2	0, 7EX. 3ET	1111	ny 13.3.14.0	2113.L-	692.0	1862 - 240 V 1771.78	575.5
Cr47 S* Cr48 Cr49 Cr50 Cr50 Cr50 Stats Cr50 Stats Cr50 Cr50 <th< td=""><td>0.47</td><td>0.40</td><td>0.40</td><td>0.50</td><td>C.E.L.</td><td>0.50</td><td>C.52 11</td><td>CrEA</td><td>C.55</td><td>0.50</td><td>0.57</td><td>0.50</td></th<>	0.47	0.40	0.40	0.50	C.E.L.	0.50	C.52 11	CrEA	C.55	0.50	0.57	0.50
F #7.5 P 308.1, 112.4. P 60, 112.8. # *55.8.**8.9 \$ 200.1 \$ 2, 8, 8 # *18.9 \$ 200.1 \$ 2, 8, 8 \$ 51.84052 \$ 53.84885 \$ 2.200 \$ 1.52 \$ 51.82.1 \$ 51.82.1 \$ 51.82.1 \$ 51.82.1 \$ 51.82.1 \$ 51.82.1 \$ 51.82.1 \$ 51.82.1 \$ 51.82.1 \$ 51.82.1 \$ 51.84.1 \$ 51.82.1 \$ 51	Cr47 3-	Cr48 21.6 h	42.3 m	4.345	27.702 H	63.789	8,501	2.365	3.497 m	5.9 m	Cr57 3"	Cr58 7.0 s
E7.45 E1.66 E 2.635 48.84665 E.7527 51.446512 12.84664 53.88885 E.200 E.162 E.162 <the.163< th=""> <the.163< th=""> <the.163< td="" th<=""><td>7.87.5</td><td>7 308.3, 112.4</td><td>7 90.6. 152.8. 62.3.</td><td>ay-15580</td><td>2300 1 2₁₀ < 10</td><td>Ry A. S</td><td>iy 18.0</td><td>oy 36.2</td><td>7 1928 Fac-</td><td>7 83.9.26.8</td><td>7 83.4, 860. 1752, 1538</td><td>7 683, 126,-</td></the.163<></the.163<></the.163<>	7.87.5	7 308.3, 112.4	7 90.6. 152.8. 62.3.	ay-15580	2300 1 2 ₁₀ < 10	Ry A. S	iy 18.0	oy 36.2	7 1928 Fac-	7 83.9.26.8	7 83.4, 860. 1752, 1538	7 683, 126,-
V46 0* V47 V48 449 77 V50 17 V51 77 V52 78 # 500 # 22.8 m # 22.8 m # 22.8 m # 22.8 m # 23.8 d # 24.8 d # 23.8 d # 24.8 d # 23.8 d # 24.8 d # 25.8 d	E 7.45	E 1.68	E 2.631	49.946050	E.7527	61.840512	52.940654	53.938885	6.2.000	E 1.62	6.5.1	E40
TI45 Tr TI46 TI47 S TI48 TI49 N° TI50 TI51 S TI52 TI53 S <th< td=""><td>V46 0+ 422.3 ms F 4.03 E 0 E 7.051</td><td>V47 3- 32.6 m # 1.89 # 1704.0,- E 2.508</td><td>V48 4* 15.98-d 7-895-7 7-953-5-1312+ E-4.012</td><td>V49 7/- 335 d</td><td>V50 6* 8,250 1,4517 * 1, 7 1502 8 5, 7 763 4, 21, 461 5, 0,71 46 6*2,200 45 947165</td><td>V51 7/- 99.750 ny.4.9, 2.7 50.943864</td><td>V52 3* 376 m F 242 T 1454.1 E 3475</td><td>V53 /- 1.54 m / 2.5 / 1006.2</td><td>V54 3* 49.8 s 7 854.8 988.8. 2259.2. E 7.04</td><td></td><td></td><td></td></th<>	V46 0+ 422.3 ms F 4.03 E 0 E 7.051	V47 3- 32.6 m # 1.89 # 1704.0,- E 2.508	V48 4* 15.98-d 7-895-7 7-953-5-1312+ E-4.012	V49 7/- 335 d	V50 6* 8,250 1,4517 * 1, 7 1502 8 5, 7 763 4, 21, 461 5, 0,71 46 6*2,200 45 947165	V51 7/- 99.750 ny.4.9, 2.7 50.943864	V52 3* 376 m F 242 T 1454.1 E 3475	V53 /- 1.54 m / 2.5 / 1006.2	V54 3* 49.8 s 7 854.8 988.8. 2259.2. E 7.04			
3.473 h 17 104 - z 7798 6 w, 1408 1 8.25 m, 8.4 7.44 72.72 5.47 5.78 m, 8.4 5.78 p. 21 A p. 20 A D. D. D. D. D. D. D. D. D. D. D. D. D.	Ti45 7/-	Ti46	TI47 5	Ti48	Ti49 7/-	Ti50	Ti51 2	Ti52	Ti53 00			
μ ² 1.04 2758.5 m, 1408.1 5758.5 m, 1408.1 15758.5 m, 1408.5	3.678 h	8.25	7.44	73.72	5.41	5.18	5.76 m	1.7 m	33 s			
E 2 002 45 85303 48 91784 47 347947 48 94792 E 2 471 E 1 37 E 6.5 4* Sc44 2 Sc45 3 50 1* Sc46 1* Sc46 54 9 Sc55 100 1* Sc46 1* Sc46 52 87 1* Sc46 52 87 1* Sc46 1* Sc47 Sc55 1* Sc46 1* Sc46 1* Sc47 1* Sc47 1* Sc46 1* Sc47 1* Sc46 1* Sc47 1* Sc46 1* Sc4	7719.6 m. 1408.1	9.8.4	ay 12, 18	ay 7.8.3.6	4, 22, 13	a _p . 177, 11	7 320.1,-	7 124.5. 17.0	# 3.1,- 7 127.6, 228.4, 1675.6, 100.8,-			
6* Sc44 2* Sc45 7* Sc46 * Sc47 7* Sc48 6* Sc49 7* Sc50 1* Sc51 (7) Sc52 3* 1272 7* 100 11525 7* 2482 427.5 77.3 7 Sc50 1* Sc51 (7) Sc52 3* 1272 7* 154.5 7* 7 Sc50 1* Sc51 (7) Sc52 3* 7 100 11542 7* 7 Sc50 1* Sc51 (7) Sc52 3* 7 100 11542 7* 7 Sc50 1* Sc51 7 Sc52 3* 7 100 11542 7 10 11542 7 Sc51 7 Sc52 3* 100 7 1048.00 11542 11521.4 7 11521.4 7 11521.4 7 11542.4 7 11642.7	E2.042	45.952529	48.951784	47 547547	48.847971	49.944792	6.2.471	E 1.97	E 5.0			
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E 2.000 E 2.00 E	7 1001 & # 1126 1. 7 1157.0. 1157.0	$\sigma_p (10+17), (5+7)$	889.3 2,8	7 198.4	1057.6	7 1762 (o),1623	7 1561.8, 1121.1, 523.8,-	1568	y 1048.7, 1267.8,			
	E 3.653	44.955910	£2.367	E.600	E 3.99	E 2.000	E 6.89	E 6.51	£9.1	10		

II.4. IRON, VANADIUM AND CHROMIUM

FIG. II.3. Chart of the nuclides in the region of the stable isotopes of iron, vanadium and chromium [II.3].

II.4.1. Iron

Iron has four stable isotopes, as shown in Table II.7. Neutron capture in ⁵⁶Fe and ⁵⁷Fe results only in the production of stable ⁵⁷Fe and ⁵⁸Fe, respectively. Neutron capture in ⁵⁴Fe produces ⁵⁵Fe (half-life 2.73 a), which decays by electron capture to stable ⁵⁵Mn. Figure II.3 shows that ⁵⁵Mn has a 13 b neutron capture cross-section, indicating that some of that produced will be converted back to ⁵⁶Fe by neutron capture and subsequent decay of ⁵⁶Mn. Neutron capture by ⁵⁸Fe produces ⁵⁹Fe (half-life 44.5 d), which decays to stable ⁵⁹Co, ensuring that a very small but certainly detectable amount of ⁶⁰Co will also be produced.

The (n,2n) reaction on ⁵⁴Fe produces ⁵³Fe, which rapidly decays to essentially stable ⁵³Mn. The same reaction on ⁵⁶Fe produces ⁵⁵Fe (half-life 2.73 a), which decays slowly to stable ⁵⁵Mn (see above comments on this isotope). The other iron isotopes do not produce elements due to this reaction.

Figure II.3 shows that ⁵⁴Fe undergoing the (n,p) reaction produces ⁵⁴Mn (half-life 312 d), which decays to stable ⁵⁴Cr. The other three iron isotopes are all converted to Mn isotopes of the same masses, which rapidly decay back to the original iron isotope. Only ⁵⁴Fe and ⁵⁶Fe have measured cross-sections for the (n,d) reaction. These reactions produce ⁵³Mn and ⁵⁵Mn, both of which are effectively stable and have been discussed above.

The (n, α) reaction on an iron isotope produces the chromium isotope of a mass number that is three lower. Thus ⁵⁴Fe produces ⁵¹Cr (half-life 27.7 d), which decays to stable ⁵¹V, ⁵⁶Fe produces stable ⁵³Cr, ⁵⁷Fe produces stable ⁵⁴Cr, and ⁵⁸Fe produces ⁵⁵Cr, which rapidly decays to stable ⁵⁵Mn (see above).

		Fe-54	Fe-56	Fe-57	Fe-58
Atom fraction (%)		5.845	91.754	2.119	0.282
Thermal $\sigma_{\rm c}({\rm b})$		2.25	2.59	2.43	1.15
RI (b)		1.21	1.35	1.45	1.49
n,2n	σ (14 MeV)	0.006	0.402	1.06	0.98
n,p	σ (14 MeV)	0.4	0.114	0.058	0.012
n,d	σ (14 MeV)	0.01	0.0063	_	_
n,α	σ (14 MeV)	0.086	0.044	0.033	0.021
n,T	σ (14 MeV)	_	3.0 E-6	_	_
n, ³ He	σ (14 MeV)	_	_	_	_

TABLE II.7. IRON CROSS-SECTION DATA

TABLE II.8. PERCENTAGES OF INITIAL IRON NUCLEI UNDERGOING THE VARIOUS REACTIONS

	Fe-54	Fe-56	Fe-57	Fe-58
n,y	$9.5 imes 10^{-1}$	17.0	3.7×10^{-1}	2.4×10^{-2}
n,2n	1.6×10^{-5}	1.7×10^{-2}	1×10^{-3}	$1.2 imes 10^{-4}$
n,p	1.1×10^{-3}	4.7×10^{-3}	5.5×10^{-5}	$1.5 imes 10^{-6}$
n,d	2.6×10^{-5}	2.6×10^{-4}	_	_
n,α	2.3×10^{-4}	1.8×10^{-3}	3.2×10^{-5}	$2.7 imes10^{-6}$
n,T	_	0	_	_
n, ³ He	_	_	_	_

In summary, using the above analysis and the data of Table II.8, about 0.97% of the initial iron nuclei are converted to manganese, 0.024% to cobalt, 0.0029% to chromium, and 0.00023% to vanadium. At the maximum concentration of Fe in the ASTM standard for Zircaloy-4 [II.4], 0.24 wt.% (0.39 at.%), the concentration of Mn at the end of life would be about 0.0038 at.% (23 wppm).

II.4.2. Vanadium

Table II.9 shows that there are two stable isotopes of vanadium: ⁵⁰V and ⁵¹V, the latter being by far the more abundant. The following neutron reactions take place:

- Neutron capture in 51 V leads to 52 V (half-life 3.76 m), which decays to stable 52 Cr.
- The (n,2n) reaction on ⁵⁰V leads to ⁴⁹V (half-life 331 d), which decays to stable ⁴⁹Ti.
- The (n,p) reaction on 50 V yields stable 50 Ti and on 51 V it yields 51 Ti, which quickly decays back to 51 V.
- The (n,d) reaction on both vanadium isotopes leads to stable titanium isotopes of a mass number one less than the initial vanadium isotope.
- The (n, α) reaction on ⁵⁰V and ⁵¹V produces ⁴⁷Sc and ⁴⁸Sc, which decay quite rapidly to stable ⁴⁷Ti and ⁴⁸Ti, respectively.
- The (n,T) reaction on 51 V produces stable 49 Ti.

In summary, using the above analysis and the data of Table II.10, about 33% of the initial vanadium nuclei are converted to chromium and 0.0088% to Ti. The large fraction converted to chromium means that, because of the simple calculation method used in this analysis, the fraction converted to Ti will be overestimated, but not by an amount that is large compared to the estimated error, which is at least one order of magnitude.

		V-50	V-51
Atom fraction (%)		2.5×10^{-1}	99.75
Thermal $\sigma_{c}(b)$		40.0	5.06
RI (b)		51.7	2.7
n,2n	σ (14 MeV)	2.5×10^{-1}	6.04×10^{-1}
n,p	σ (14 MeV)	6.4×10^{-2}	3.1×10^{-2}
n,d	σ (14 MeV)	3.3×10^{-3}	$4.5 imes 10^{-3}$
n,a	σ (14 MeV)	1.62×10^{-2}	1.56×10^{-2}
n,T	σ (14 MeV)	1.9×10^{-5}	1×10^{-3}
n, ³ He	σ (14 MeV)	_	_

TABLE II.9. CROSS-SECTIONS FOR VANADIUM REACTIONS

TABLE II.10. PER	CENTAGES OF THE INITIAL V	ANADIUM NUCLEI
	V-50	V-51
n,y	$2.4 imes 10^{-1}$	33.0
n,2n	2.8×10^{-5}	2.7×10^{-2}
n,p	$7.2 imes10^{-6}$	$1.4 imes10^{-3}$
n,d	$4 imes 10^{-7}$	2×10^{-4}
n,a	$1.8 imes 10^{-6}$	$7 imes 10^{-4}$
n,T	0	$4.5 imes 10^{-5}$
n, ³ He	-	_

II.4.3. Chromium

There are four stable isotopes of chromium. Figure II.3 shows that only neutron capture by ⁵⁰Cr and ⁵⁴Cr leads to production of elements other than chromium; in the case of ⁵⁰Cr it forms stable ⁵¹V (via ⁵¹Cr (half-life 27.7 d)) and in the case of ⁵⁴Cr it forms stable ⁵⁵Mn (via ⁵⁵Cr (half-life 3.5 m)). Note that neutron capture by ⁵⁵Mn will result in a small quantity of iron being produced. The following neutron reactions take place:

- The (n,2n) reaction on ⁵²Cr produces ⁵¹Cr and hence ⁵¹V, on ⁵⁰Cr it produces ⁴⁹Cr, which decays to ⁴⁹V (half-life 331 d) and thence to stable ⁴⁹Ti;
- The (n,p) reaction produces the vanadium isotopes of the same mass number as the initial chromium isotopes; of these ⁵⁰V is stable and ⁵²V, ⁵³V and ⁵⁴V all decay rapidly back to the corresponding Cr isotope;
- The (n,d) reaction on 50 Cr produces 49 V (half-life 331 d), which decays to stable 49 Ti;
- The (n, α) reaction on ⁵⁰Cr, ⁵²Cr and ⁵³Cr produces stable Ti isotopes. The reaction on ⁵⁴Cr produces ⁵¹Ti (5.76 m), which decays to ⁵¹V.

Cross-sections of chromium nuclear reactions are presented in Table II.11.

In summary, using the above analysis and the data shown in Table II.12, about 3.1% of all the initial chromium nuclei are converted to vanadium, 0.066% are converted to manganese and 0.0015% are converted to titanium. It should be noted that a small fraction of the manganese will be converted to iron by neutron capture. At the maximum concentration of Cr in the ASTM standard for Zircaloy-2 [II.4], 0.15 wt.% (0.263 at.%), at the end of life the concentration of V would be about 0.0082 at.% (46 wppm).

		Cr-50	Cr-52	Cr-53	Cr-54
Atomic fract	ion	4.345	83.789	9.501	2.365
Thermal $\sigma_{\rm c}$ (b))	15.93	$7.46 imes 10^{-1}$	18.07	3.60×10^{-1}
RI (b)		7.48	$4.53 imes 10^{-1}$	8.43	2.02×10^{-1}
n,2n	σ (14 MeV)	$8.3 imes 10^{-3}$	$2.60 imes 10^{-1}$	$9.34 imes 10^{-1}$	9.91×10^{-1}
n,p	σ (14 MeV)	3.03×10^{-1}	$8.9 imes 10^{-2}$	4.5×10^{-2}	1.4×10^{-2}
n,d	σ (14 MeV)	1.1×10^{-2}	_	_	_
n,α	σ (14 MeV)	9.1×10^{-2}	3.1×10^{-2}	$2.8 imes 10^{-2}$	1.16×10^{-2}
n,T	σ (14 MeV)	_	_	_	_
n, ³ He	σ (14 MeV)	_	-	-	_

TABLE II.11. CROSS-SECTIONS FOR CHROMIUM REACTIONS

TABLE II.12. PERCENTAGE OF ALL INITIAL CHROMIUM NUCLEI UNDERGOING THE VARIOUS REACTIONS

	Cr-50	Cr-52	Cr-53	Cr-54
n,y	3.1	4.8	7.2	6.6×10^{-2}
n,2n	1.6×10^{-5}	9.8×10^{-3}	4×10^{-3}	1.1×10^{-3}
n,p	$5.9 imes 10^{-4}$	3.4×10^{-3}	1.9×10^{-4}	1.5×10^{-5}
n,d	2.2×10^{-5}	_	_	_
n,a	$1.8 imes 10^{-4}$	1.2×10^{-3}	1.2×10^{-4}	1.2×10^{-5}
n,T	_	_	_	_
n, ³ He	-	_	_	_

II.5. COPPER

Ga63 (3/-) 32 s $\beta^* 4.5,$ $\xi \approx$ γ 636.9, 626.9, E 5.5	Ga64 0+ 2.63 m β ² 2.8, 6.14, ε γ 991.5, 807.9, 3365.9, Ε 7.165	Ga65 3/- 15.2 m β ² -2.11,,ε γ 115.1, E 3.255	Ga66 0+ 9.5 h β*4.153,ε γ 1039.3, 2752.2, 	Ga67 3/- 3.261 d 7 93.30, 184.6, 300.2, E 1.000	Ga68 1* 1.130 h β ⁻ 1.899, ε γ 1077.3, Ε 2.921	Ga69 3/- 60.108 3/- a _y 1.7, 14 68.925581
Zn62 9.22 h β ⁺ .68, γ 596.7. 40.8. 548.4. 507.6, Ε 1.63	Zn63 3/- 38.5 m β ⁺ 2.32 ² γ 669.7, 962.1 E 3.367	Zn64 48.63 1.1E19 a β ⁻ ε α ₇ .76, 1.5 63.929147	Zn65 5/- 243.8 d ^ε 1116.5,- β'-3.25 ω σ ₈ .7E1 σ _α 2.0 E 1.3519	Zn66 27.90 σ _γ .9. 1.8 σ _α < .02 mb 65.926037	Zn67 5/- 4.10 a _y 7, 25 d _a .4 mb 66.927131	Zn68 18.75 α _γ (.072 + .8). (.24 + 2.9) σ _{ct} < .02 mb 67.924848
Cu61 3/- 3.35 h β' 1.21,, ε γ 283.0, 656.0, Ε 2.237	Cu62 1+ 9.74 m β ⁺ 2.93, γ 1173.0 ω, 875.7, E 3.948	Cu63 3/- 69.17 a _y 4.5, 5.0 62.929601	Cu64 1+ 12.701 h ε.β ⁻ .578 φ-661 γ 1345.8 8, 352 Ε579 E+1.6751	Cu65 3/- 30.83 a _y 2.17, 2.2 64.927794	Cu66 1+ 5.10 m β 2.63 γ 1039.3 α _γ 1.4E2, 6E1 E 2.642	Cu67 3/- 2.580 d β ⁻ .39, 48, 58 γ 184.6, 93.30, E.58
Ni60 26.2231 a ₇ 2.9, 1.5 59.930791	Ni61 3/- 1.1399 α _y ~2.5, ~1.8 σ _{ct} ≤ .03 mb 60.931060	Ni62 3.6345 ay 14.5, 8.6 61.928349	Ni63 1/- 101. a β- 0.0669 no γ 8 _γ 24 E.08695	Ni64 0.9256 ay 1.6, 1.2 63.927970	$\begin{array}{c} {\sf Ni65} & 5^{\prime-} \\ {\sf 2.517 \ h} \\ \beta^{\circ} 2.14, 0.65, \cdots \\ \gamma^{\circ} 148, 9, 1115.5, \cdots \\ {\sf B}_{\gamma} & 23, 11 \\ {\sf E} 2.137 \end{array}$	Ni66 2.28 d β 20 no γ E .23
Co59 7/- 100 a _y (21+16), (39+35) 58.933200	2+ Co 60 5+ 10.47 m 5.271 a 17 586, 5- 1 13325 7 13325, 7 13325, 7 13325, 9 561, 6, 20, 4 2 3822 6, 20, 4 2 382 7, 20, 4 3 383 7, 20, 4 3 38, 4 3 38, 4 3 38	Co61 7/- 1,650 h β-1,22, γ 67.4, Ε 1.322	5+ Co62 2+ 13.9 m $\beta^{-}2.9$ $\gamma^{-}1173.0, 2.9$ 1163.6, $\gamma^{-}1173.0, \gamma^{-}$ E 5.34 E 5.31	Co63 7/- 27.5 s β ⁻ 3.6 γ 87.3D, Ε 3.67	Co64 1+ 0.30 s β ⁻ 7.0 γ 1345.8, 931.1 Ε 7.31	Co65 (7/)- 1.17 s β- 7 311 Ε 5.96

FIG. II.4. Chart of the nuclides in the region of the stable copper isotopes [II.3].

Table II.13 shows the properties of the two stable copper isotopes (Fig. II.4). Neutron capture by ⁶³Cu yields ⁶⁴Cu, which decays 61.5% to stable ⁶⁴Zn and 38.5% to stable ⁶⁴Ni. Capture by ⁶⁵Cu yields ⁶⁶Cu, which decays rapidly to stable ⁶⁶Zn. The following neutron reactions take place:

- The (n,2n) reaction on ⁶³Cu produces ⁶²Cu, which rapidly decays to stable ⁶²Ni. On ⁶⁵Cu the reaction produces ⁶⁴Cu, which decays as described above.
- The (n,p) reaction directly produces the stable nickel isotopes ⁶²Ni and ⁶⁵Ni.
- The (n,d) reaction on ⁶³Cu produces stable ⁶²Ni, on ⁶⁵Cu it produces ⁶³Ni (half-life 101 a), which decays to ⁶³Cu.
- The (n,α) reaction on ⁶³Cu produces ⁶⁰Co, which decays with a half-life of 5.27 a to stable ⁶⁰Ni. On ⁶⁵Cu it produces ⁶²Co, which decays rapidly to stable ⁶²Ni.
- The (n,T) reaction on ⁶⁵Cu produces ⁶³Co, which decays rapidly to ⁶³Ni.
- The $(n, {}^{3}\text{He})$ reaction on ${}^{63}\text{Cu}$ produces ${}^{61}\text{Co}$ (half-life 1.65 h), which decays to stable ${}^{61}\text{Ni}$.

In summary, using the above analysis and the data shown in Table II.14, about 13% of the initial copper nuclei are converted to zinc and 8.1% are converted to nickel. Additionally, about 0.0013% are converted to radioactive 60 Co.

		Cu-63	Cu-65
Atom fraction (%)		69.17	30.83
Thermal $\sigma_{\rm c}$	(b)	4.47	2.15
RI (b)		4.99	2.22
n,2n	σ (14 MeV)	4.35×10^{-1}	$8.95 imes 10^{-1}$
n,p	σ (14 MeV)	$4.8 imes 10^{-2}$	2.5×10^{-2}
n,d	σ (14 MeV)	9×10^{-3}	1×10^{-2}
n,α	σ (14 MeV)	0.043	1.1×10^{-2}
n,T	σ (14 MeV)	_	$3.9 imes 10^{-5}$
n, ³ He	σ (14 MeV)	$3.9 imes 10^{-6}$	$2.3 imes 10^{-6}$

TABLE II.13. COPPER	CROSS-SECTION DATA

TABLE II.14. PERCENTAGE OF ALL INITIAL COPPER NUCLEI THAT ARE REACTED

	Cu-63	Cu-65
n,y	21.0	4.8
n,2n	$1.4 imes 10^{-2}$	1.2×10^{-2}
n,p	$1.5 imes 10^{-3}$	3.5×10^{-4}
n,d	$2.8 imes 10^{-4}$	1.4×10^{-4}
n,a	$1.3 imes 10^{-3}$	1.5×10^{-4}
n,T	_	5×10^{-7}
n, ³ He	1×10^{-7}	0

II.6. NICKEL	II.6	. N	ICK	EL
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Zn58 0.08 s 7 203.848 E 9.4 Cu57 3'-	Zn59 3/- 183 ms /*8.1 ^c 481.4.914.2 (p) 1.76 e. 2.09, 1.82, 1.36,- E 9.09 Cu58 1*	Zn60 2.40 m # 2.5.31 # 7 670_61 E 4.16 Cu59 3/-	Zn61 3- 1.485 m §*4.4 [£] y 474.9, 1660.3 E 5.64 Cu60 2+	Zn62 9.22 h 6 ⁻ 60 566.7.40.8. 548.4.507.6 E 1.83 Cu61 3 ⁻	Zn63 3/- 38.5 m f ⁺ 2.32, f 7 669 7, 962 1, E 3.387 Cu62 1+	Zn64 46.63 1.1619 a 47 75, 1.5 63.929147 Cu63 3/-	Zn65 %- 243.8 d * 1115.5 #-325 % % 20 £ 1.3519 Cu64 1*	Zn66 27.90 e ₀ 9, 1.8 e ₀ < .02 mb 65.926037 Cu65 3 ²⁻	Zn67 5- 4.10 4, 7.25 4, 7.25 4, 4 mb 66.927131 Cu66 1*
196 ms \$-7.7 7 1113 E 8.77	3.21 s p 7.44, f 0 7 1454.5, 1448.3, E 8.563	1.36 m / ⁷ 3.8 7 1301 5, 878 0 E 4.800	23.7 m \$" 3.00,	3.35 h β ^{-1.21,ε} γ 283.0.656.0, Ε 2.237	9.74 m # 2.93 # 7 1173.0 m, 875.7 E 3.948	69.17 ay 4.5, 5.0 82.929601	12.701 h <i>t</i> , β' .578 <i>t</i> .601 7.1345.8 B ₇ .302 E .578 E+1.6751	30.83 a _y 2.17, 2.2 64.927794	5.10 m # 2.63 7 1039 3 8 _y 1.4E2.6E1 E 2.642
Ni56 5.9 d 5.1584.0118-	Ni57 35.6 h 35.6 h 4. <i>β</i> .85 7 1377.6 E 3.264	Ni58 68.0769 a _y 4.6, 2.2 a _g < .03 mb 57.935348	Ni59 3" 7.664 a 4" 0.00 ± 0.76.1262 0.76.1262 0.014.20 0.02.2 ± 1.072	Ni60 26.2231 ny 2.8. 1.5 59.930791	Ni61 3/- 1.1399 a ₁₇ -2.51.8 a ₁₇ <u>5</u> .03 mb 60.931000	Ni62 3.6345 87 14.5.0.6 61.928349	Ni63 U- 101.a # 0.0009 no 7 By 24 E.00095	Ni64 0.9256 a ₇ 1.8, 1.2 63.927970	Ni65 5- 2.517 h \$ 2.14, 0.65,- 7, 1481 9, 1115 5, 0, 23, 11 E 2.137
Co55 7/- 17.53 h β 1.50, 1.03 γ 931.2, 477.2, 1408.4 ε Ε 3.4513	Co56 4+ 77.3 d 7.3 1.459 7 846.8, 1238.3, E 4.566	Co57 7- 271.8 d 7 122.1, 136.5, 14.4, E.836	5* Co58 2* 9.1 h 70.88 d 17 24.9, 70.88 d 17 24.9, 70.86 d 1.0° 474 6, 7 474 6, 7 474 7, 1963 7, 1963 7, 1963 7, 1963 7, 1963 7, 1963 7, 1963	Co59 7/- 100 e _y (21+16), (39+35) 58.933200	2* Co 60 5* 19.47 m 5.271 a 119.46 318 11925 7 13925 7 13925 7 13925 9 2392 a 2.20,4 2.392	Co61 7/- 1.650 h β-1.22,- γ 67.4,- Ε 1.322	$\begin{array}{ccccc} 5* & \textbf{Co62} & 2* \\ \hline \textbf{13.9 m} & \textbf{1.50 m} \\ \beta & 2.9 - & \beta & 4.1 \\ \gamma & 1173.0 & \beta & 4.1 \\ 1163.6 & \gamma & 1173.0 \\ \hline \textbf{E} & \textbf{5.34} & \textbf{E} & \textbf{5.31} \end{array}$	Co63 7/- 27.5 s β 3.6 γ 87.30 Ε 3.67	Co64 1+ 0.30 s β 7.0 γ 1345.8, 931.1 Ε.7.31
Fe54 5.845 2, 2.3, 1.4 e _{cr} .01 mb, 1.1 mb 53.939815	Fe55 3/- 2.73 a # 107 # # 13 # # 9 mb E 2314	Fe56 91.754 a ₇ 2.6, 1.4 55.934942	Fe57 1/- 2.119 2, 2.5. 1.6 56.935399	Fe58 9.282 ay 1.3, 1.2 57 933280	Fe59 3- 44.50 d # 466, 274- 7 1099,2, 1291.6. 0 ₇ -13 E 1.565	Fe60 1.5E6 a / 147 7 53 50, 6- E .237	Fe61 6.0 m 9 2.8, 2.6 9 1205,1 1027.5. 297.9 E 3.98	Fe62 68 s § 2.57 7 506.1 E 2.53	Fe63 (5/)- 6 s 7 994.8. 5427.2 E 6.1

FIG. II.5. Chart of the nuclides in the region of the stable nickel isotopes [II.3].

Table II.15 shows the stable isotopes of nickel, their naturally occurring atomic percentages and the cross-sections of interest. Table II.16 shows the estimated percentages of all the initial nickel atoms that undergo the reactions for each isotope, and Fig. II.5 shows the chart of the nuclides in the region of the stable nickel isotopes.

Neutron capture by ⁵⁸Ni is significant because it leads to 21% of the initial Ni atoms being converted to ⁵⁹Ni, which has a half-life of 76 000 years and can therefore be considered to be stable for the 25 year irradiation under consideration. However, ⁵⁹Ni has unusually large thermal neutron interaction cross-sections — (n,γ) 78 b, (n,α) 14 b, and (n,p) 2 b — for a total neutron absorption cross-section of 94 b (see Fig. II.5). Using these cross-sections it is calculated that 15.3% of the initial Ni is converted through ⁵⁹Ni to ⁶⁰Ni, 2.7% is converted by (n,α) on ⁵⁹Ni to stable ⁵⁶Fe and 0.39% is converted by (n,p) on ⁵⁹Ni to stable ⁵⁹Co.

Neutron capture by ⁶⁰Ni and ⁶¹Ni leads to stable Ni isotopes. Capture by ⁶²Ni gives ⁶³Ni (half-life 101 a), a little of which will beta decay to stable ⁶³Cu, the rest remaining as nickel. Capture by ⁶⁴Ni gives ⁶⁵Ni, which rapidly decays to stable ⁶⁵Cu.

The (n,2n) reaction on ⁵⁸Ni gives ⁵⁷Ni, which decays with a 35.6 h half-life to ⁵⁷Co, which itself decays to stable ⁵⁷Fe with a 272 d half-life. The (n,2n) reaction on ⁶⁰Ni yields ⁵⁹Ni, which has already been discussed; the quantities produced are negligible compared with those made by neutron capture on ⁵⁸Ni, as Table II.16 shows. The reaction on ⁶¹Ni and ⁶²Ni produces stable Ni, while on ⁶⁴Ni it produces ⁶³Ni, which has already been discussed.

The (n,p) reaction leads to Co isotopes, which, in the cases of ⁶⁰Ni, ⁶¹Ni, ⁶²Ni and ⁶⁴Ni, all decay back to the initial Ni isotope with various half-lives, the longest of which is ⁶⁰Co, with a half-life of 5.27 a. On ⁵⁸Ni the reaction yields ⁵⁸Co, the fate of which is complicated: it can either decay to ⁵⁸Ni or ⁵⁸Fe or be converted to stable ⁵⁹Co by neutron capture. Most of it will apparently become ⁵⁹Co and most of the rest will transmute to ⁵⁹Fe.

The (n,D) reaction yields the Co isotope of mass one unit less than the target Ni isotope. Thus ⁵⁸Ni yields ⁵⁷Co, which decays with a 272 d half-life to stable ⁵⁷Fe. Niobium-60 yields stable ⁵⁹Co. Niobium-62 yields ⁶¹Co, which rapidly decays to ⁶¹Ni. Niobium-64 yields ⁶³Co and thence ⁶²Ni, which has previously been discussed (it mostly becomes ⁶⁴Ni by neutron capture but some decays to ⁶³Cu).

The (n, α) reaction initially yields the iron isotope of mass three units less than the nickel target nucleus. Thus, for ⁶⁰Ni and ⁶¹Ni stable ⁵⁷Fe and ⁵⁸Fe are produced. Niobium-62 yields ⁵⁹Fe, which decays with a 44.5 d half-life to stable ⁵⁹Co. Niobium-64 yields ⁶¹Fe, which decays rapidly through ⁶¹Co to stable ⁶¹Ni, and ⁵⁸Ni yields ⁵⁵Fe (half-life 2.73 a), which decays to stable ⁵⁵Mn.

In summary, using the above analysis and the data of Table II.16, 2.7% of the initial Ni atoms are converted to iron, 0.40% are converted to cobalt, 0.34% are converted to copper, and 0.00037% to manganese.

		Ni-58	Ni-60	Ni-61	Ni-62	Ni-64
Atomic	fraction	68.08	26.22	1.14	3.63	0.93
Thermal $\sigma_{\rm c}$ (b)		4.62	2.76	2.50	14.41	1.52
RI (b)		2.21	1.40	1.56	6.00	0.77
n,2n	σ (14 MeV)	0.023	0.39	0.77	0.80	1.02
n,p	σ (14 MeV)	0.37	0.15	0.095	0.035	0.0037
n,d	σ (14 MeV)	0.016	0.0089	-	0.0029	0.0025
n,α	σ (14 MeV)	0.012	0.058	0.048	0.016	0.0080
n,T	σ (14 MeV)	_	_	_	—	—
n, ³ He	σ (14 MeV)	_	_	_	_	_

TABLE II.15. NICKEL CROSS-SECTION DATA

	Ni-58	Ni-60	Ni-61	Ni-62	Ni-64
n,y	21	5.1	2.0×10^{-1}	2.5	1.1×10^{-1}
n,2n	7.1×10^{-4}	4.6×10^{-3}	4.0×10^{-4}	1.3×10^{-3}	4.3×10^{-4}
n,p	1.1×10^{-3}	1.8×10^{-3}	$4.9 imes 10^{-4}$	$5.7 imes 10^{-5}$	1.6×10^{-6}
n,d	4.9×10^{-4}	1.1×10^{-4}	_	$4.7 imes10^{-6}$	1.0×10^{-6}
n,α	3.7×10^{-4}	$6.9 imes 10^{-4}$	2.5×10^{-5}	2.6×10^{-5}	3.4×10^{-6}
n,T	_	_	_	_	_
n, ³ He	_	_	_	_	_

TABLE II.16. PERCENTAGE OF ALL INITIAL NICKEL NUCLEI THAT ARE REACTED

II.7. FINAL COMMENTS

It should be remembered that this first order analysis is for a particular irradiation — 25 years in the neutron spectrum in a CANDU pressure tube with a thermal neutron flux of $10^{18} \text{ m}^{-2} \cdot \text{s}^{-1}$ — and can only be expected to provide approximate results. Therefore, if any of the predicted production of new elements raises any concerns it is strongly recommended that a much more rigorous calculation be undertaken for the reactions of interest. This calculation should use an appropriate reactor physics computer code with multi-group nuclear data prepared for all the reactions of interest. The code should be capable of accurately calculating the neutron spectrum at the irradiation location and preferably be able to follow accurately the transmutation of the materials of interest.

In all cases the greatest amount of transmutation of any isotope is caused by thermal neutron capture. Where this capture leads to a new element by subsequent decay this means of production dominates all others by at least one order of magnitude. The corollary is that production of new elements by the much less accurately calculated threshold reactions is only significant when that new element is not produced by neutron capture.

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- [II.4] ASTM INTERNATIONAL, Standard Specification for Hot-Rolled and Cold-Finished Zirconium and Zirconium Alloy Bars, Rod, and Wire for Nuclear Application, ASTM B351/B351M-13(2018), ASTM International, West Conshohocken, PA (2018).

Appendix III

CORROSION PERFORMANCE OF FUEL CLADDING IN POWER REACTORS (BWRs AND LWRs)

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III.1. INTRODUCTION

The thin-walled fuel rod cladding is the first barrier against activity release from the nuclear fuel to the heat transport fluid or coolant. The cladding must have sufficient resistance to corrosion by the coolant, have high strength and ductility that are maintained during and after irradiation, have a low thermal-neutron absorption cross-section, and be fabricated easily and economically. Zirconium alloys fulfil these demands for water-cooled reactors such as BWRs, including RBMKs; PWRs, including WWERs; and heavy water cooled reactors (i.e. CANDUs).

The corrosion behaviour of Zr alloys in-reactor depends on (a) alloy composition; (b) material condition; and (c) the environmental conditions (water chemistry, system pressure and operating temperature), which are different in each reactor system. Most studies report that irradiation increases the corrosion rate of zirconium alloys. This extra corrosion depends on the hydrogen and oxygen concentration in the water.

Figure III.1 shows the conclusion of a review performed in 1985 on the effect of hydrogen and oxygen in the water [III.1]. At H/O ratios above 100 (PWR, WWER and CANDU reactors) only uniform corrosion exists, which increases above a certain oxide thickness, and the hydrogen pick-up fraction (HPUF) is high. The HPUF value of 45% given in Fig. III.1 is representative of Zircaloy-2; Zircaloy-4 picks up less hydrogen in PWRs (10–20%). At H/O ratios below 10 (BWRs and RBMKs), where radiolytic oxygen and hydrogen peroxide are formed, an early increase of uniform oxidation occurs. In addition, nodular corrosion and shadow corrosion may occur in this H/O ratio regime. The HPUFs are low under irradiation, except for Zircaloy-2 at higher burnups. The total amount of hydrogen that could be picked up by the zirconium alloy is the product of the corrosion reaction and the HPUF.



FIG. III.1. Effect of water chemistry on in-reactor oxidation and hydrogen uptake rates [III.1].

III.2. IN-REACTOR CORROSION OF Zr ALLOYS UNDER OXYGENATED COOLANT CONDITIONS IN BWRs

Zircaloy-2 was originally selected for BWR fuel rod claddings, whereas E110, a Zr-1Nb alloy, was used for RBMK fuel rods. For structural components of BWRs, Zircaloy-4 and Zircaloy-2 have been applied, while E125, a Zr-2.5Nb alloy, was selected for the pressure tubes in RBMKs.

The system pressure is about 7 MPa in BWRs and RBMKs. The coolant inlet temperature is at about 545 K (270°C) and the maximum cladding surface temperature ranges from 563 to 598 K (290 to 325°C). The fast neutron flux (E > 1MeV) is (3–8) × 10¹⁷ n·m⁻²·s⁻¹ in the BWR core and about (1–3) × 10¹⁷ n·m⁻²·s⁻¹ in an RBMK. Under these conditions, a thin uniform oxide layer forms on fuel cladding and structural components during exposure, but three different types of excessive corrosion may occur:

- Nodular corrosion starting after 10–100 days of irradiation;
- Shadow corrosion starting after a few days of irradiation;
- In zircaloy-2, an increase in uniform corrosion (acceleration of both hydrogen pick-up and uniform corrosion) starting at high burnup.

The corrosion attack that may occur on BWR and RBMK fuel components made by Zr alloys during in-pile exposure is shown schematically in Fig. III.2.



FIG. III.2. Principal corrosion attack of Zr alloy components during in-pile exposure under oxygenated coolant conditions in boiling water reactors, using BWR as the example (courtesy of ANT International).

III.2.1. Uniform oxide

The uniform oxide that forms in BWRs and RBMKs is thin because of the low operating temperatures. The layer thickness is larger than that measured out-of-pile after exposure in pressurized water at the same temperature for the same time, as shown in Fig. III.3 [III.2–III.16]. That the in-pile oxide layer is thicker than the out-of-pile oxide layer can be seen for Zircaloy even after 10 days. A transition in corrosion rate is usually seen out-of-pile at an oxide thickness of about 2 μ m after about 800 days at 558 K (285°C). The time dependency (t^n) of oxide growth is similar in-pile to the dependency out-of-pile in the pre-transition range, with an n of about 0.33, but no rate transition is observed in-pile. Under oxygenated coolant conditions in-pile, the cubic corrosion behaviour proceeds to higher oxide thickness values and longer times than in non-oxygenated coolant, without any obvious corrosion rate transition.



FIG. III.3. In-reactor uniform corrosion behaviour of Zircaloy-2/4 and Zr1Nb/E110 under oxygenated coolant conditions; data from Refs [III.2–III.16] (courtesy of ANT International).

Sometimes an increase in the uniform corrosion rate can be seen at long exposure times to high fast fluences. This late acceleration is probably connected to the irradiation-induced dissolution of SPP and will be discussed later.

The effect of irradiation on uniform corrosion under oxygenated coolant conditions is different for the Zr-Sn-FeCrNi alloys and the binary Zr-Nb alloys. The corrosion of Zircaloy, which is not affected by oxygen in the corrosion environment out-of-pile, exhibits an increase in corrosion due to irradiation by a factor of 2–4. Binary Zr-Nb alloys that exhibit an increase in corrosion when oxygen is added to the environment out-of-pile tend to have a lower corrosion rate under irradiation.

The fast neutron flux is an important parameter affecting the uniform corrosion rate. With Zr-Nb materials, the in-pile corrosion rate increases at very low fluxes ($<10^{17} \text{ n} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$) and saturates at low fluxes ($>2 \times 10^{17} \text{ n} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$), as can be seen in Fig. III.4 [III.3, III.17]. This increase in the corrosion rate is probably related to the formation of oxidizing species by radiolysis in the coolant.



FIG. III.4. Effect of neutron flux on uniform corrosion in an oxygenated environment; data from Refs [III.3, III.17] (courtesy of ANT International).

III.2.2. Nodular corrosion

The nodular oxide — a localized thick oxide — that can form within the thin uniform oxide, appears on visual inspection as white spots in an otherwise dark oxide. Thick nodular oxide thicknesses (up to $380 \ \mu$ m) were observed on BWR and RBMK fuel rods. The tendency for nodular corrosion on Zircaloy-2 fuel rods can vary over a wide range between different BWRs, cycles and material lots, as shown in Fig. III.5 [III.18].



Oxide Thickness (average lift-off) at peak position

FIG. III.5. Corrosion of Zircaloy-2 fuel rods produced between 1965 and 1980 in BWRs [III.18].

Nodules usually nucleate within 10–20 days for Zircaloy-2, as shown in Fig. III.6, and after 30–100 days for Zircaloy-4 [III.19]. Nucleation can be accelerated by increased impurities in the coolant [III.18]. Not enough data are available for the Zr-1Nb alloy to estimate the incubation time for nodule nucleation. The nodular corrosion is characterized by the formation of irregularly shaped patches of thick oxide, which grow laterally on the surface but also in depth with increasing BU or neutron fluence (φt). At the peak flux position the nodular growth rate is related to (BU)^m or (φt)^m, with m = 0.5-0.7 for Zircaloy-2 and m = 0.9-1.5 for Zircaloy-4 [III.19].



FIG. III.6. Growth characteristic of nodular oxide on Zircaloy-2 with increasing exposure time [III.19].

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The thickness profile of nodular corrosion along the fuel rod axis mostly follows the rod burnup profile, although sometimes a pronounced nodular corrosion peak is observed in the bottom part of the rod or at some other axial position [III.20]. The usual axial profile of nodular corrosion indicates that burnup (fast fluence) has a larger effect on nodular corrosion than on uniform corrosion. In general, the nodule number density remains constant and no new nodules are formed with time after the first nodules have nucleated. In extreme cases, the nodules can grow together, coalesce on the material surface and form a thick uniform nodular oxide. Nodular oxide layer thickness values of >100 μ m can be reached after long exposure times.

The tendency for nodular corrosion depends largely on the particular reactor water chemistry and on the microstructure of the Zircaloy material, especially the size distribution of the SPPs, which depends on fabrication temperatures and times. The SPP size can be correlated to an annealing parameter, the *A* parameter [III.21]. The *A* parameter used in the following is calculated from the temperature (T_i in K) and time (t_i in hours) of the different annealing treatments after the last β quenching step during fabrication using the equation $A = \Sigma t_i \exp(-40000/T_i)$. A correlation between the nodular corrosion oxide thickness and this *A* parameter is shown in Fig. III.7 [III.20] from experimental irradiations of different fuel rods with varying cladding materials on equivalent positions in one fuel element. In BWRs nodular corrosion starts to increase at an *A* parameter of > (5–10) × 10⁻¹⁹ h. Nodular corrosion can be formed at ≥773 K (500°C) out-of-pile in high pressure steam. The out-of-pile nodular corrosion also increases above a similar *A* parameter as in a BWR.



Oxide thickness (µm)

FIG. III.7. Nodular corrosion of Zircaloy-2 cladding in a BWR plotted against the accumulated annealing parameter, A [III.20].

The Zircaloy-2 cladding used up to 1984 had an A parameter of 3×10^{-19} – 1×10^{-16} h depending on the supplier and historical time period. To increase the resistance against nodular corrosion, the A parameter of the BWR cladding was reduced by all suppliers. For instance, GE (now GNF) modified the cladding fabrication several times in the time period 1984–1990. The A parameter was reduced at first to 2×10^{-19} h and later to 8×10^{-20} h (tube-shell heat treated cladding) and in a third step to 2×10^{-20} h (in-process heat treated cladding) [III.22].

Siemens (now AREVA) developed a low temperature process (LTP) with an *A* parameter of 6×10^{-19} h. ABB Atom (now Westinghouse), originally used LK-0¹ cladding with an estimated *A* parameter of about 1×10^{-18} h. They then developed LK-2, with an improved resistance against nodular corrosion, using an additional inductive β quenching step before the second to last rocking step, and an estimated *A* parameter of about 5×10^{-21} h [III.23]. At high burnups, the LK-2 cladding showed an increased corrosion in a number of BWRs, and an accelerated corrosion in the spacer region in one BWR [III.24]. As a consequence, the LK-3 cladding was developed with an estimated *A* parameter similar to that of LTP [III.25].

Several studies have evaluated the effect of alloying elements and impurities on BWR nodular corrosion tendency of Zircaloy-2 and -4. The nodular corrosion tendency can be mitigated by keeping the Sn concentration within 1.2-1.7 wt% (0.92-1.3 at.%), the Si concentration within 60-120 ppm (0.019-0.039 at.%), the oxygen concentration at <1500 ppm (0.85 at.%) and the P concentration at <10 ppm (0.003 at.%) [III.26]. The reported effects of Fe and Cr concentrations on BWR nodular corrosion rate are contradictory. The Fe and Cr elements may affect the SPP size. For material with a moderate *A* parameter, a reduced nodular corrosion rate may be obtained for material with a high Cr concentration, whereas for material with a very low *A* parameter, a high Fe concentration may be beneficial.

Zircaloy-4 is more sensitive to nodular corrosion than Zircaloy-2, if fabricated with a similar *A* parameter, as shown in Fig. III.8 [III.27]. Usually Zircaloy-4 exhibits some nodular corrosion at medium burnups under isothermal conditions, as can be seen in structural components.



Fig. III.8. Corrosion behaviour of Zircaloy-4 and Zircaloy-2 fuel channels in a BWR [III.27].

Binary Zr-Nb alloys, such as E110, are much more sensitive to nodular corrosion than Zircaloy-type alloys, as discussed in Refs [III.2, III.28]. Little is known about the effect of coolant chemistry on nodular corrosion in binary Zr-Nb alloys. Water chemistry is most likely responsible for the tendency for reactor-to-reactor and cycle-to-cycle variation in nodular corrosion. The O_2 , Cr^{6+} , and H_2O_2 water chemistry species increase the corrosion potential and are likely the species with the largest influence on the nodular corrosion rate. An increase in O_2 and Cr^{6+} concentrations in water was observed to increase the nodular corrosion tendency

¹ LK is derived from the Swedish låg korrosion (low corrosion).

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in mini-autoclave tests in the Halden test reactor [III.29]. In addition, a strong correlation between the coolant Cr^{6+} concentration and the nodular corrosion tendency was found in the evaluation of water chemistry effects on BWR Zr corrosion performance [III.19].

The pick-up of corrosion hydrogen is low in BWR and RBMK fuel rod cladding, at least up to 50 MW·day·kg⁻¹U. The hydrogen pick-up (HPU) of BWR fuel rods is not affected by nodular corrosion, as can be seen from Fig. III.9 [III.30]. The reasons for the increase in uniform corrosion rate at >55 MW·day·kg⁻¹U will be discussed below. In another study [III.5], it was shown that the HPU was only 80 ppm (0.72 at.%) in 0.85 mm thick cladding, even when a thick uniform nodular corrosion layer, 70–250 μ m, was formed. Thus, one may conclude that HPU is only due to uniform corrosion in fuel rods. Assuming that the HPU values reported by Refs [III.7, III.30] are only related to uniform corrosion, the HPUF would be between 10 and 30%.



FIG. III.9. Corrosion behaviour of Hitachi and Toshiba Step II TSHT cladding (A parameter about 8×10^{-20} h) [III.30]: (a) oxide layer thickness; (b) hydrogen pick-up.

In isothermal samples, nodular corrosion contributes to the HPU, although somewhat less than uniform corrosion does, as can be seen from Fig. III.10 [III.26]. Uniform corrosion would cause an oxide weight gain of only 50–150 mg/dm² after 2–6 cycles. Higher weight gains are caused by nodular corrosion and also contribute to the overall HPU. The figure indicates furthermore that HPUF values are different in different BWRs under isothermal conditions. The reason for these differences is probably differences in coolant chemistries. The surprising conclusion, that nodular corrosion does not contribute to the HPU in fuel rod cladding, which operate under a heat flux, does not hold for structural components, which operate under isothermal conditions. This difference is probably related to the corrosion environment, which for nodular corrosion is the environment inside the pores contained in the outer oxide layer. In fuel rods, steam is formed in the oxide as a consequence of the heat flux causing wick boiling; water enters through fine pores and steam escapes through larger pores. This process refreshes the environment continuously. In isothermal samples, the environment in the pores is stagnant water, which becomes enriched with hydrogen from the corrosion reaction.



FIG. III.10. HPUF values as a function of isothermal oxide weight gains in BWR-A, BWR-B and Cooper [III.26].

III.2.3. Shadow corrosion

Shadow corrosion occurs when a component made from a Zr alloy is close to, or in contact with, components made from stainless steel or Inconel, such as control rods, spacers and spacer springs. The shape of the component is often reproduced by the corroded area, suggestive of a shadow. The shadow corrosion area has a thicker oxide that usually has a different appearance (lighter or darker) compared with the adjacent unaffected area. A typical example of shadow corrosion on a fuel channel induced by a control rod handle is shown in Fig. III.11 [III.4].



FIG. III.11. Photograph showing shadow corrosion on a fuel channel. The shadow seen in the photograph is associated with a control rod adjacent to the fuel outer channel during irradiation [III.4].

The shadow oxide can be uniform but often exhibits a nodular character. Shadow corrosion starts in BWRs after a few days (at a neutron fluence $>1 \times 10^{24} \text{ n} \cdot \text{m}^{-2}$, E > 1 MeV), grows very quickly, and saturates at high fluences (burnups). Peak shadow corrosion values can reach thicknesses above 100 µm [III.19, III.31–III.33]. In an unusual case, perhaps due to a special water chemistry, accelerated shadow corrosion appeared at high burnup [III.34].

A variety of dissimilar materials are observed to cause shadow corrosion on Zr alloys, such as stainless steel, Pt, Hf, Inconel and welded regions on Zircaloy [III.4, III.35–III.37]. Platinum was found to be almost as effective as Inconel in causing shadow corrosion and therefore it has been speculated that the enhanced Zircaloy corrosion that has occasionally been seen after noble metal chemical application (a water chemistry applied in BWRs, in which noble metals are injected into the coolant to protect structural components) could be related to some type of shadow corrosion phenomenon.

The shadow oxide thickness is largest at the point of contact between the dissimilar and Zircaloy materials and the shadow oxide thickness decreases with increasing distance between the dissimilar and Zircaloy materials. There is a maximum distance (a few mm) between the dissimilar and Zircaloy materials beyond which the dissimilar material cannot cause any shadow corrosion on the Zircaloy component [III.31, III.35].

Quite large variations in the shadow corrosion tendency have been found for Zircaloy-2 and Zircaloy-4 materials used in different reactors, as shown in Fig. III.12 [III.32, III.34, III.38]. These variations are primarily related to differences in water chemistry between the different reactors but are also, to some extent, dependent on material microstructural variations. No systematic study on the effect of water chemistry on shadow corrosion rate has been reported. Preoxidation of the Zr alloy component, to about 1 μ m, can reduce the tendency towards shadow corrosion, but is not always effective. Covering the dissimilar material with a layer of ZrO₂ was found to much reduce shadow corrosion on the Zircaloy component [III.31].

Shadow corrosion has never been reproduced without irradiation. Shadow corrosion appears only in oxygenated environments, at least in Zircaloy-type alloys. Zr-1Nb materials

seem to be more sensitive to shadow corrosion compared with Zircaloy and the Zr-1.3Sn-1Nb-0.4Fe (E635) alloy. Zr-1Nb (E110) fuel rods exposed in an RBMK to a burnup of 19.3 MW·day·kg⁻¹U showed extremely large fuel rod oxide thickness layers, up to 380 μ m, at the point of contact with the stainless-steel spacer. Fuel rods clad in Zr-1.3Sn-1Nb-0.4Fe were reported to have much smaller oxide thickness values, up to 100 μ m, at similar positions and burnups as the E110 clad fuel rods [III.2].

Hydrogen pick-up is normally lower in the shadow corrosion area in comparison with adjacent areas subjected to normal corrosion [III.39]. However, large HPU values in shadow corrosion areas at high burnups have been observed, which caused channel bowing [III.40].



FIG. III.12. Shadow corrosion data of various BWR fuel vendors' cladding; data from Refs [III.32, III.34, III.38] (courtesy of ANT International).

III.2.4. Experience at high burnups

At high burnups an accelerated uniform corrosion can arise in Zr alloy components in BWRs. Figure III.13 [III.41] shows the uniform oxide thickness of several Westinghouse BWR fuel claddings versus burnup. The figure depicts an increase in the oxidation rate at high burnups for all materials. The onset of the increased uniform corrosion rate occurs at a higher burnup for the LK-3 material compared with the LK-2 material. The reason for this difference



is most likely the initial SPP size, which is larger in the LK-3 material than in the LK-2 material, due to higher temperatures and longer fabrication times, providing a higher *A* parameter.

FIG. III.13. Mid-span oxide thickness observed for different Westinghouse cladding types [III.41].

Long term irradiation experiments have revealed a tendency towards the neutron induced dissolution of the SPPs in Zircaloy material, especially for materials with a low SPP size, as shown in Table III.1. After dissolution of the SPPs, an increase of the HPU followed by an increase in the uniform corrosion rate often, but not always, occurs. As Fig. III.14(a) [III.26, III.42–III.44] reveals, in Zircaloy-2 materials HPU increases at lower burnups than the oxide layer growth rate. For Zircaloy-2 structural materials, as used between 1980 and 2007, HPUF increases at a burnup in excess of about 30–50 MW day kg⁻¹ U; in Zircaloy-2 fuel cladding, as used between 1995 and 2007, HPUF increases at a burnup in excess of 45–55 MW day kg⁻¹ U. Zircaloy-4 does not show any increase of HPUF at high burnups when used for structural components, as can be seen from Fig. III.14(b) [III.3, III.13, III.29, III.45–III.48]. Zircaloy-4 in structural components has higher corrosion at medium burnups than Zircaloy-2, as shown in Fig. III.8, and as a consequence, higher hydrogen concentrations.

WESTINGHOUS	SE CLADDING	TYPES	S [III.4]									
Material	A parameter (h)	Mea	Mean SPP size (nm)			SPP density $(n \cdot \mu m^{-2})$			Oxide thickness (µm)		H-content (ppm)	
at burnup (MW·d·kg ⁻¹ U)		0	25	40	0	25	40	25	40	25	40	
LK2	≈5E–21	92	89		0.39	0.01		15	30	287	522	
LK2+	≈1E–19	95	87	80	0.33	0.10	0.03	17	20	155	329	
LK3	≈7E–19	154	123	93	0.47	0.26	0.09	10	15	95	129	

TABLE III.1. SPP CHARACTERISTICS AND CORROSION BEHAVIOUR OF DIFFERENT WESTINGHOUSE CLADDING TYPES [III.4]







(b)

FIG. III.14. BWR fuel rod cladding hydrogen concentration versus burnup: (a) hydrogen concentration in various fuel rod claddings [III.26, III.42, III.43, III.44]; (b) hydrogen pick-up fraction of structural components [III.3, III.13, III.29, III.45–III.48] (courtesy of ANT International).

The critical burnup values for the onset of increased HPU and increased uniform corrosion rate in Zircaloy-2 indicate a dependency on the SPP size and *A* parameter, as shown in Fig. III.15 [III.26, III.30, III.40, III.41, III.49, III.50]. Figure III.15 shows a large scatter of the critical burnup values, which is probably related to the different water chemistries in the different BWRs.



FIG. III.15. Critical burnup value for late increased uniform corrosion and late increased HPUF in BWRs; data from Refs [III.26, III.30, III.40, III.41] (courtesy of ANT International).

Figure III.16 [III.26] shows that the onset in corrosion acceleration for a material with very fine as-fabricated SPPs varies between reactors and cycles [III.26]. Similar variations in the threshold burnup at which HPU and corrosion acceleration starts between different BWRs were reported for the Westinghouse LK-2 cladding material. The ranking of the corrosion resistance of the various LK variants is different in the German BWR Brunsbüttel compared with that of Swedish BWRs (shown previously in Fig. III.13 [III.51]). The root cause of these differences is probably the water chemistry; the Cu concentration of the water possibly plays some role in this difference in behaviour.



FIG. III.16. Increased corrosion of late β quenched Zircaloy-2 claddings (with very fine SPP) in BWR-C and BWR-D [III.26].

From the available information up to 2009, it can be concluded that BWR corrosion behaviour will be good for cladding materials for burnups up to around 50 MW·day·kg⁻¹U. At higher burnups an increase in HPU and oxidation may be seen. The increased uniform corrosion rate probably depends on the initial SPP size and composition. Cladding materials

such as LTP produced by AREVA and LK3 produced by Westinghouse might be more resistant to late increased uniform corrosion compared with those of the Step II cladding produced by Hitachi and Toshiba and the GNF cladding, attributable to the lower *A* parameter for the Hitachi, Toshiba and GNF cladding. However, as a consequence of their higher *A* parameter, the LTP and LK3 claddings may be more prone to nodular corrosion than the Hitachi, Toshiba and GNF claddings. Below, the corrosion data, as reported by the different BWR fuel suppliers, are reviewed.

The Westinghouse experience with their LK-3 fuel cladding in BWRs is shown in Fig. III.13 versus burnup; it shows low oxide layer thickness up to about 60 MW day kg⁻¹ U. An increased HPU is observed for LK-3 in excess of about 50 MW day kg⁻¹ U.

Owing to a low A parameter (about 2×10^{-20} h), the resulting as-fabricated SPP size is small in the GNF fuel cladding. GNF point out that no increased corrosion was observed with their cladding up to high burnups, as shown in Fig. III.17 [III.52]. However, an increased HPU (up to 200 ppm (1.8 at.%) hydrogen) was seen in the upper part of GNF fuel rods at 52 MW·day·kg⁻¹ U [III.43]. These observations are in agreement with Japanese results [III.42, III.47] that did not indicate an increase in the oxidation rate of their Step-II Zircaloy-2 fuel rod cladding up to 60 MW·day·kg⁻¹ U, but revealed increasing HPU at >50 MW·day·kg⁻¹U, as shown in Fig. III.14.



FIG. III.17. Eddy-current lift-off measurements for fuel rods clad with Zircaloy-2, irradiated in a GNF commercial BWR: (a) relative trend, according to Ref. [III.52]; (b) TVO data in comparison to GNF's database [III.53].

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LTP Zircaloy-2 fuel cladding has also not shown an increased uniform corrosion rate up to 75 MW·day·kg⁻¹ U, as shown in Fig. III.18 [III.27] but some increase of the HPU can be deduced at burnups >55 MW·day·kg⁻¹ U, as shown in Fig. III.14a.



FIG. III.18. Corrosion behaviour of AREVA LTP Zircaloy-2 fuel cladding as a function of fuel rod burnup [III.27].



FIG. III.19. Influence of temperature on in-pile corrosion of Zircaloy in an oxygenated environment [III.54].

III.2.5. Limits to oxide thickness in BWRs

The maximum allowable oxide thickness for BWR fuel rods depends on the temperature dependence of the corrosion rate in oxygenated reactor coolant. The temperature variation in fuel cladding tubes in BWRs and RBMKs is small, which means that the available information is limited on the temperature dependence of uniform and nodular corrosion rates in oxygenated environment under irradiation. Data showing this temperature dependency, seen in Fig. III.19 [III.54], reveal that the nodular corrosion rate decreases with increasing temperature while the uniform corrosion rate increases with increasing temperature dependence of the uniform corrosion rate is much smaller in a BWR than out-of-pile (i.e. without irradiation).

If massive deposits (often called crud²) are formed on fuel rods, there will be an increase in the fuel rod surface temperature. Figure III.19 suggests that under such conditions the nodular corrosion rate is unaffected while the uniform corrosion rate is increased. In cases of crud induced localized corrosion, steam blankets are formed in the nodular oxide. Such steam blankets, with low thermal conductivity, act as a barrier for the heat flux and will thereby increase the temperature at the oxide–metal interface resulting in a local increased uniform corrosion rate that could eventually lead to fuel defects. Without any crud deposits, the nodular corrosion phenomenon does not appear to limit the burnup of the fuel rods. The nodular oxide layer growth rate decreases with increasing time. At oxide layer thicknesses of >200 μ m, where metal-oxide transition temperature should increase with increased oxide thickness, no accelerated corrosion has been observed. This situation probably reflects the high porosity of nodular oxide resulting in a good thermal conductivity, and a low, or even negative, temperature dependency of the nodular corrosion rate.

III.3. IN-REACTOR CORROSION OF Zr ALLOYS UNDER HYDROGENATED COOLANT CONDITIONS IN PWRs

Zircaloy-4 was originally selected for PWRs based on North American designs while for the Russian Federation WWERs, the Zr-1Nb alloy called E110 was used. Later, several other Zr alloys, with an enhanced corrosion resistance, were supplied by the different fuel vendors; these alloys include ZIRLO, DX ELS-and M5.

The system pressure is about 12.5 MPa in the 440 MW WWERs and 15.5 MPa for the PWRs and 1000 MW WWERs. The coolant inlet temperatures are between 543 and 568 K (270 and 295°C) and the average outlet temperatures between 563 and 603 K (290 and 330°C). The maximum cladding surface temperature is about 623 K (350°C) for the PWRs and the 1000 MW WWERs. The average fast neutron flux (E > 1MeV) is (3–9) × 10¹⁷ n·m⁻²·s⁻¹. In PWRs 25–50 cm³ hydrogen per kg water are added to suppress oxidative radicals, boric acid (<1700 ppm) is added for reactivity control and LiOH (<6 ppm) is added for pH control. In WWERs, besides boric acid, 6–30 ppm NH₃ are added to suppress oxidative radicals and 5–20 ppm KOH are added for pH control.

² Chalk River unidentified deposit — CRUD. The term was originally used to describe the incrustation of particles precipitated from loop water onto experimental fuel rods during their irradiation in a research reactor in the 1950s. Increasing the pH of the loop water from 7 to 10 eliminated the problem in these loops by diminishing the dissolution of out-reactor piping.

III.3.1. Corrosion behaviour

Under operating conditions, a thin uniform oxide layer forms on fuel claddings. The growth rate of the oxide layer for all Zr alloys increases exponentially with temperature. The temperature dependency is usually described by the following equation:

$$Corrosion rate = Constant \times exp(-Q/RT)$$
(III.1)

where

Constant	is the corrosion rate constant that depends on material composition and condition;
Q	is the activation energy;
R	is the universal gas constant;

and *T* is the temperature (in K) at the metal-oxide interface.

In PWRs, Q/R is about 14 000 K, as in out-of-pile conditions. Above a certain oxide layer thickness ($\geq 5 \mu m$), there is an additional increase in corrosion due to neutron irradiation. Figure III.20 [III.55] shows schematically the effect of irradiation and heat flux on the corrosion of Zircaloy-4. Corrosion initially follows normal out-of-pile behaviour. When an oxide layer thickness of about 5 µm has formed, light spots appear on the previously black surface and the corrosion rate increases in Zircalov-4 by a factor of 3–4, less in low-Sn Zr alloys, and very little in binary Zr-Nb alloys. This factor of increase is almost independent of temperature and exposure time, and therefore oxide thickness, at least up to a burnup of 55 MW·day·kg⁻¹ U (fast neutron fluence of 1×10^{26} n·m⁻², E > 1 MeV). The neutron flux dependency is usually described by φ^m , where φ is the fast neutron flux and m the flux dependency exponent; *m* is about 0.2 in PWRs [III.20]. Under the high heat flux of fuel rods, the increasing oxide thickness leads to an increase in the temperature at the metal-oxide interface (which controls the corrosion rate) and therefore the growth rate of the oxide layer increases owing to this feedback effect. Measurements of the thermal conductivity of 15–50 µm thick oxide layers on zirconium alloy gave consistent values of 1.8–2.2 W·m⁻¹·K⁻¹ for unirradiated and 1.5–1.9 $W \cdot m^{-1} \cdot K^{-1}$ for irradiated material [III.20]; these values are nearly ten times lower than those found in Zircaloy, about 13.4 W·m⁻¹·K⁻¹. A fraction of the hydrogen, from the corrosion process, is picked up by the zirconium alloy. This HPUF depends on the particular alloy and probably also on temperature, water chemistry and startup procedure. At high fast fluences and burnups, an acceleration of corrosion may occur, which will be discussed below.



FIG. III.20. Effect of irradiation and heat flux on the corrosion of Zircaloy-4 in PWRs [III.55].

The fuel rod oxide profile is governed by the surface temperature of the fuel rods. In PWRs and WWERs, the water enters the reactor core with a temperature of 543-568 K (270–295°C) and heats up over the length of the fuel rods. The fuel rod surface temperature in the active zone is higher than that of the water but is reduced locally in and immediately above the spacers, as shown in Fig. III.21 [III.20], owing to increased turbulence in this area. In the upper part of the hottest fuel rods, surface boiling may occur, which limits the surface temperature and creates steam bubbles at the fuel rod surface. This temperature profile explains the typical axial profile of the oxide layer, as show in Fig. III.22 [III.20]. The profile is characterized by an increase of oxide thickness with length of fuel rod up to about three quarters of the active length, where normally the maximum oxide thickness is observed. Oxidation is locally suppressed in and above the spacers and locations of intermediate flow. Large variations in the oxide layer may be observed around the circumference owing to non-uniform thermohydraulic conditions surrounding individual rods in the fuel rod bundle or assembly. In regimes of fuel rods where sub-cooled boiling occurs, the circumferential variations disappear because of the almost uniform surface temperature at such positions. Analysis of positions with boiling and without boiling has not indicated any major effect of the sub-cooled boiling in Siemens PWRs [III.55].



FIG. III.21. Typical thermohydraulic characteristics of fuel rods in plants with high fuel duty; the temperature drop at spacer sites should be noted [III.20].



FIG. III.22. Spiral oxide thickness traces of PWR fuel rods with and without nucleate boiling [III.20].

The peak oxide thickness of PWR fuel rods increases with burnup, peak temperature and time. Figure III.23 [III.20] shows the thickness of several peak oxide layers on fuel rods with Zircaloy-4 cladding versus fuel rod burnup. The figure indicates that oxide layer buildup varies between reactors, and is accelerated at high oxide layer thicknesses owing to the feedback effect of the oxide layer itself (the increasing temperature rise over the oxide layer, as mentioned before). The reasons for the large variations between data sets can be explained by differences in fuel duty; the different thermohydraulic boundary conditions, such as inlet temperature, fluid flow, active length and average heat flux; and the individual power history, which is influenced by the fuel loading strategy and enrichment of ²³⁵U.



FIG. III.23. Increase in peak oxide layer thickness with burnup [III.20].

Corrosion increases after the oxide layer thickness reaches about 5 µm in PWRs. The rate constant at >5 µm, deduced from oxide thickness measurements by a corrosion model considering the temperature and power history, provides a good characterization value of the corrosion resistance of a particular cladding material in PWRs. This value is often given as a multiplication factor of the out-of-pile corrosion resistance of Zircaloy-4 with an Sn concentration of 1.5 wt% (1.16 at.%). Usually only peak oxide layer thicknesses are reported as a function of burnup. Such data can only be compared if the data are obtained from fuel rods exposed under similar fuel duties. A much better comparison is possible if the oxide layer thickness data are reported versus the normalized time, $time \times \exp(-Q \cdot R^{-1} \cdot T^{-1})$, as proposed in Refs. [III.56–III.58], or versus the duty factor proposed by Westinghouse [III.59].

The existing worldwide database exhibits a good overview on the major factors affecting the corrosion rate in PWRs. Minor differences in water chemistry do not play an important role. However, LiOH, which is added for pH control, may concentrate in a thick oxide layer due to sub-cooled boiling (e.g. due to high heat fluxes). As the protectiveness of the oxide deteriorates, the corrosion process accelerates. Whether void fraction from incipient boiling affects corrosion in PWRs due to the formation of oxidative radicals is still not clear; high power experiments in the Swiss PWR Gösgen (KKGG) build by Siemens did not show any obvious effect for Zircaloy-type alloys for void fractions up to 0.2 [III.28]. For ZIRLO, an effect of the steam factor is assumed [III.59], and for M5, a potential effect of void fraction was discussed in combination with surface impurities [III.60]. A detailed analysis of the oxide layer data has shown that the material conditions and alloying chemistry have a marked effect on corrosion in PWRs.

III.3.2. New alloys and optimization

A continuous search is in progress to increase fuel burnup to improve the economics of nuclear power. This increasing fuel duty made it necessary to optimize Zircaloy-4 with respect to corrosion, and later to develop alternative Zr alloys with higher corrosion resistance for non-Russian PWRs. These alloys include DX ELS, ZIRLO and M5. Surveillance and further improvement of these alloys remain the most important issue for fuel cladding. Table III.2 gives the nominal alloying concentrations for Zircaloy-4 and the new materials. These new Zr alloys can be categorized into three groups:

- (1) The Zr-Sn-Fe,Cr,V alloys are all based on the Zircaloys (developed in the USA in the 1950s and 1960s). In a first phase, tests were performed on Zircaloy-4 cladding with varying alloying concentrations, impurity concentrations and material condition. The goal was to optimize the corrosion behaviour of Zircaloy-4. These tests showed that Sn, C and Si influence corrosion negatively in PWRs [III.20]. As result, a Zircaloy-4 cladding with a restricted chemistry, the low-Sn-Zry-4 cladding (PCA-1), has been specified and applied for reloads (fuel rods and structural components) since 1988. Further tests revealed that the transition metal alloying concentration and the microstructure also have a pronounced effect on corrosion. The effect of transition metal on corrosion in PWRs was summarized in Refs [III.56, III.61]. On the basis of these results the optimized Zircaloy-4 cladding (PCA-2), with Fe in the upper range of the ASTM specification and an optimized microstructure (used since 1989), and the modified Zircaloy-4 cladding (PCA-2b), with an Fe and Cr concentration above the range specified for Zircaloy-4 (applied since 1995), were developed by Siemens (today AREVA NP). The modified Zircaloy-4 is still used for structural components and called PCAm. Siemens (today AREVA NP) also developed DX ELS (applied since 1989), and HPA-4, which were tested extensively, and used in high duty Siemens-designed PWRs to very high burnups. DX ELS is also used by Westinghouse for their fuel reloads in high duty Siemens-designed PWRs. A large database of experience exists confirming that these cladding materials have a much higher corrosion resistance than the original Zircaloy-4. The NDA alloy, developed in Japan, has been applied for reloads with a burnup of up to 55 MW \cdot day \cdot kg⁻¹ U since 2004. A low-Sn version of NDA, called S2, has been developed [III.62].
- (2) The Zr-Sn-Nb Fe(Cr) alloys are all based on the alloy E635, the latter being developed in the Russian Federation. Zr-Sn-Nb Fe(Cr) alloys are currently being applied and explored by many organizations. The most important material in this group, apart from E635, is ZIRLO, applied by Westinghouse and its licensees for cladding and structural components since the late 1980s. Since the corrosion resistance of ZIRLO is only slightly better than that of Zircaloy-4, an optimized ZIRLO, with reduced Sn concentration, has been

developed by Westinghouse. In a first step (LT-ZIRLO) only the Sn concentration was reduced; in a second step (optimized ZIRLO) the material condition was also changed (stress relieved (SR) \rightarrow partially recrystallized (PR)) to compensate for the reduction of cladding creep strength due to the reduced Sn concentration [III.63]. MDA, with a similar corrosion resistance to ZIRLO, was developed for the Japanese market and has been applied for reloads since 2004. As with ZIRLO, a modified MDA (M-MDA) is being developed with reduced Sn and increased Fe + Cr concentrations [III.64]. In the Republic of Korea, HANA alloys are being developed by the Korea Atomic Energy Research Institute [III.65].

(3) The Russian Federation alloy E110, Zr-1Nb, has been used for the fuel rod cladding of WWERs and RBMKs for several decades. It is used in the RX condition. The binary Zr-1Nb-0.1O-S alloy M5 is derived from E110. The RX M5 was developed by Fragema (today AREVA NP). It has been supplied for most of their PWR fuel assembly reloads since 1996 [III.66]. The corrosion resistance of stress relieved duplex cladding with a Zr-2.5Nb outer layer was found to be even higher than that of Zr-1Nb alloys, if it has an optimized microstructure. J-alloy is being developed in Japan for very high burnups [III.67]. Zr-2.5Nb and E125 have been used for the pressure tubes of CANDU and RBMK reactors for many years. The binary Zr-Nb alloys are very corrosion resistant and have a very low HPUF, but their corrosion properties are probably more sensitive to impurities compared with those of the Sn containing alloys, such as ZIRLO. Abnormal corrosion has been seen occasionally and will be discussed below [III.66].

The largest in-PWR test programme to study the corrosion behaviour of different Zr alloys was performed in KKGG under very high fuel duty conditions. Experimental fuel rods with many different Zr-alloy claddings, as well as corrosion coupons, were exposed for up to 9 years. Figure III.24 [III.28, III.58, III.61, III.68] shows the continuous reduction of oxide thickness resulting from the different development steps of Siemens (today AREVA NP) for Zr-Sn-FeCr alloys and binary Zr-Nb alloys. In Fig. III.25 [III.56] the corrosion behaviour of other experimental Zr alloys that were tested as fuel rod cladding in KKGG are shown. Fuel rod corrosion in PWRs decreases with decreasing Sn concentration in Zr-Sn-(TM) and Zr-Sn-Nb-TM alloys, and in Zr-Sn-TM alloys with increased Fe concentration.

Alloy	Sn (%)	Nb (%)	Fe (%)	Cr (%)	V (%)	Others	Condition*
Zry-4	1.2-1.7		0.18-0.24	0.1		1000–1400 ppm O-2	SR/RX
Low-Sn Zry-4	1.3		0.2	0.1		1200 ppm O-2	SR/RX
Optimized Zry-4	1.3		0.22	0.1		1200 ppm O-2	SR
Modif. Zry-4	1.3		0.3	0.2		1200 ppm O-2	PR/RX
NDA	1	0.1	0.3	0.2		1200 ppm O-2	SR
S2	0.8	0.1	0.3	0.1			RX
DX ELS 0.8a	0.8		0.2	0.1		1200 ppm O-2	SR
DX ELS 0.8b	0.8		0.3	0.2		1200 ppm O-2	SR
DX 3b	0.8		0.5			1200 ppm O-2	SR
DX D4	0.5		0.5	0.2		1200 ppm O-2	SR
HPA-4	0.5		0.5		0.3	1200 ppm O-2	SR
E635	1.3	1	0.4			900 ppm O-2	RX
ZIRLO	1	1	0.1			1200 ppm O-2	SR
E635M	0.8	0.8	0.35			700 ppm O-2	RX
MDA	0.8	0.5	0.2	0.1		1200 ppm O-2	SR
LT-ZIRLO	0.75	1	0.1			1200 ppm O-2	SR
Optim. ZIRLO	0.67	1	0.1			1200 ppm O-2	PR
M-MDA	0.5	0.5	0.4	0.3			SR, RX
HANA-4	0.4	1.5	0.2	0.1			
HANA-5	0.8	0.4	0.3			Cu - 0.1%	
HANA-6		1.1				Cu-0.05%	
E110		1	0.01			600 ppm O-2, F-impurity	RX
M5		1	0.04			1200 ppm O-2, 20 ppm S	RX
J-Alloys		1.6-2.5		0.1			RX
DX Zr2.5Nb		2.5	0.04			1200 ppm O-2	SR
Zr-2.5Nb		2.5 - 2.7	>0.04			1100 ppm O-2	SR
E125		2.5	0.01			600 ppm O-2, F-impurity	RX

TABLE III.2.	CHEMICAL	COMPOSITION	OF	ALTERNAT	TIVE Z	Zr ALLOYS	5 FOR	PWR
APPLICATIO	N							

* of fuel rod cladding or structural parts. PR — partially recrystallized; SR — stress relieved; RX — fully recrystallized; Zry — Zircaloy.



FIG. III.24. Corrosion behaviour of low-Sn Zircaloy-4, optimized Zircaloy-4, PCA-2b, DX ELS 0.8b, DX D4, Zr1Nb and DX Zr-2.5Nb; data from Refs [III.28, III.58, III.61, III.68].



FIG. III.25. Corrosion behaviour of different experimental fuel rods in KKGG [III.56]: (a) fuel rods with Zr-Sn-(Fe, Cr, V) claddings; (b) fuel rods with Zr-Sn-Nb-(Fe, Cr, V) claddings.

A large database exists for ZIRLO. A good comparison of the corrosion behaviour of low-Sn Zircaloy-4, ZIRLO, MDA, LT-ZIRLO, M-MDA and S2 can be deduced from the results gained in Vandellos-2 under high duty conditions (Fig. III.26) [III.62–III.64, III.69]. Fuel rods with ZIRLO and MDA cladding develop a thinner oxide thickness than those with low-Sn Zircaloy-4 cladding at high burnups. At <40 MW day kg⁻¹ U low-Sn Zircaloy-4 exhibits similar peak oxide thickness values to ZIRLO and MDA but shows an acceleration of corrosion during the third cycle for several fuel rods caused by the formation of a hydride rim

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during the third cycle [III.70]. As will be discussed later, such hydride rims can only be formed above a critical heat flux and hydrogen concentration. Most low-Sn Zircaloy-4, MDA and ZIRLO rods were close or even above these critical conditions at the end of cycle 3. Five of the measured low-Sn Zircaloy-4 rods and two of the examined MDA rods had obviously formed hydride rims. During the 4th cycle, the power was so low that no new hydride rim could be formed; those rods in which a hydride rim had formed at the end of cycle 3 continued to corrode in an accelerated mode. The SR low-Sn variants LT-ZIRLO and M-MDA had a low oxide layer thickness at a burnup of about 55 MW · day · kg⁻¹ U. The recrystallized S2 cladding material behaved well, whereas the RX M-MDA did not exhibit reduced corrosion compared with standard MDA. The lack of benefit for corrosion behaviour from recrystallization compared with stress relieving will be discussed below.



FIG. III.26. Corrosion behaviour of low-Sn Zircaloy-4, ZIRLO, MDA, LT-ZIRLO, M-MDA and S2 in Vandellos-2; data from Refs [III.62–III.64, III.70] (courtesy of ANT International).

III.3.3. Hydrogen pick-up

Some of the hydrogen formed by corrosion in PWRs is picked up by the zirconium based metal. HPU is usually correlated with the thickness of the oxide layer (oxide weight gain). Figure III.27 [III.20] summarizes data on the HPU of Zircaloy-4 versus the oxide layer thickness for several PWRs. At low oxide layer thicknesses, the hydrogen uptake may include a certain fraction from the moisture of the fuel. From data on thick oxide layers up to 1991, it can be deduced that the HPUF was about 10% for Zircaloy-4. Most of the later HPUF values from Zircaloy-4-type alloys were higher.

In Fig. III.28 [III.71], HPUF data from the different alloys tested in KKGG by Siemens (today AREVA) under very high duty conditions are shown against the oxide layer thickness,
after correction for the hydrogen in the oxide layer. The average HPUF value for DX ELS claddings is 20–23%; for PCA-2b: 12%; for HPA-4: 10% and for Zr-Nb alloys: 9%. Seibold et al. [III.28] reported average HPUF data from different Zr alloys tested under very high fuel duty conditions on a relative basis, including from the materials reported by Goll and Ray [III.8] and from low-Sn Zircaloy-4. The average HPUF of low-Sn Zircaloy-4 under very high fuel duty conditions is between 20 and 23% in the PWRs built by Siemens.



FIG. III.27. Hydrogen uptake of Zircaloy-4 cladding in PWRs [III.20].



FIG. III.28. Hydrogen pick-up fraction of commercial cladding materials [III.71].

HPU values of low-Sn Zircaloy-4, ZIRLO, MDA and NDA in Vandellos-2 and Ohi-4 are shown in Fig. III.29 [III.69–III.72] against the oxide layer thickness. The HPUF of all materials is between 10 and 20%. Low-Sn Zircaloy-4 may have a slightly higher HPUF and ZIRLO may have a slightly lower HPUF than the other materials.



FIG. III.29. Hydrogen pick-up of low-Sn Zircaloy-4, ZIRLO, MDA and NDA in Vandellos-2 and Ohi-4; data from Refs [III.69–III.72] (courtesy of ANT International).

The data collected since 1991 provide higher HPUF values than the early data on Zircaloy-4. The highest values have been reported for Zircaloy-type materials from very high fuel duty irradiations in KKGG. The reasons for these differences are not known. Zr-Nb binary alloys (Zr-1Nb, Zr-2.5Nb, M5 and E110) generally show the lowest HPUF values ($\leq 10\%$).

III.3.4. Alloy chemistry and microstructure

An evaluation of the measured oxide thickness values using corrosion models has shown that the corrosion rate constant in PWRs depends on alloying chemistry and impurity concentration. Of the impurities, C was found to increase in-PWR corrosion at >100 ppm (0.076 at.%) and Si to reduce it in the concentration range 30–100 ppm (0.0097–0.032 at.%) [III.20]. Of the alloying elements, Sn increases in-PWR corrosion and Nb, as well as the transition elements Fe, Cr and V, decrease in-PWR corrosion, as can be seen from Fig. III.30 and Fig. III.31 [III.56].



FIG. III.30. Influence of Sn on corrosion of Zr-Sn alloys and Zr-Sn-Nb alloys with different transition metal concentrations (TM = Fe, Cr, V) [III.56].



FIG. III.31. Influence of transition metals (TM = Fe, Cr, V) on corrosion of Zr-Sn and Zr-Sn-Nb alloys [III.56].

Material condition also has an important effect on the corrosion of Zircaloy-type alloys in PWRs. The most important microstructural feature is the SPP size. Materials with very fine SPPs exhibit early acceleration of corrosion in PWRs and in out-of-pile tests. As with BWR fuel cladding, the SPP size can be correlated to the degree of annealing using the A parameter.

The burnup where corrosion accelerates decreases with decreasing A parameter, that is, as the size of the SPPs declines, as shown in Fig. III.32 [III.72]. Zircaloy-4 with a very low A parameter (below 3×10^{-18} h) exhibits not only an increased in-PWR corrosion rate, but also a different neutron flux and temperature dependency. Such material has an almost linear flux dependency (*rate* = $f(\Phi^m), m \approx 1$) and an activation temperature (Q/R) of about 2500 K, whereas

Zircaloy-4 with $A > 3 \times 10^{-18}$ h exhibits a flux dependency, *m*, of about 0.2 and a Q/R of about 14 000 K. These *A* parameter dependencies exist only for Zr-Sn-Fe,Cr,V alloys. Zr alloys that contain $\ge 0.5\%$ Nb, do not show such an *A* parameter dependency. The corrosion behaviour of the latter alloys may even exhibit a weak optimum behaviour at very low *A* parameters. For almost all Zr alloys the final cold work and the final annealing temperature has a large effect on in-PWR corrosion; the effect of these two fabrication variables is opposite in-PWR to what is seen in out-of-pile corrosion tests. In PWRs, when the Sn and Nb concentrations are high, to promote a high creep strength, these two fabrication variables have a large effect. The effect of the important alloying elements can be described by the SNO parameter, as defined in Ref. [III.56], representing the concentrations of Sn, Nb and O. The SNO parameter can be calculated by the following equation:

SNO = wt% Sn + 2 × wt% Nb (only soluble fraction,
$$\leq 0.5\%$$
) + 6 × wt% 0 (III.2)

The effect of final cold deformation and final annealing, controlling the degree of recrystallization, is only seen when the SNO parameter is >1.2; the effect increases with increasing SNO value, as shown in Fig. III.33(a) [III.28]. The SNO values for several alloys are as follows: ZIRLO: 2.8; optimized ZIRLO: 2.4; MDA: 2.5; M-MDA: 2.3; NDA: 2.0; S-2: 1.8; and Zr-1Nb: 1.7. The unexpected high corrosion of RX M-MDA (mentioned previously in Fig. III.26) is in line with the observations of Zircaloy-4 in Fig. III.33(b). S2 with a low SNO of about 1.8 retains some benefit from the reduction of Sn, even in the RX condition.



FIG. III.32. Correlation between corrosion in a PWR and the accumulated A parameter [III.72].



FIG. III.33. Effect of cold work and final annealing on in-PWR corrosion: (a) effect of final cold deformation; (b) effect of final annealing; data from Ref. [III.28] (courtesy of ANT International).

III.3.5. Increases in corrosion rate

At very high fluences and fuel burnups, a late acceleration of corrosion can occur, as can be seen from Figs III.34 and III.35 [III.28]. The critical fluence for late corrosion acceleration decreases and the extent of acceleration increases with increasing Sn concentration and decreasing temperature. The large increase in corrosion at low temperatures is probably due to an irradiation induced dissolution of the SPPs, Zr(FeCr)₂, but the reason for the effect of Sn is not known.



FIG. III.34. Influence of neutron fluence and irradiation temperature on corrosion of coupons of Zircaloy-4 (1.5% Sn, medium cold work) [III.28].



FIG. III.35. Influence of fast neutron fluence on in-PWR corrosion of Zr-Sn-TM alloys with different Sn concentrations [III.28].

Several examples of unexpected increased corrosion have been observed:

- Nodular corrosion in a WWER with an oxygen concentration in the coolant of 15 ppb [III.73]; in the WWER loop in the MIR reactor with 20 ppb oxygen in the coolant, especially at high void fractions [III.74]; and in the PWR BR-3 with coolant oxygen concentrations up to 40 ppb with binary Zr-Nb alloys [III.75]. The nodular corrosion at slightly elevated oxygen concentrations in the coolant is due to the high sensitivity of binary Zr-Nb alloys to oxygen; this sensitivity is much higher than that of Sn-containing alloys, such as Zircaloy-4, ZIRLO and E635.
- Increased corrosion and oxide flakings due to non-optimized SPP size were observed in PWRs in several reloads in the late 1980s. The principal mechanism was described above.
- Several incidences of increased corrosion of E110 cladding in WWERs occurred in the 1980s and 1990s owing to C impurity ingress in the coolant [III.76]. Zr-1Nb alloys appear to suffer under certain conditions from galvanic-type corrosion near the Inconel spacer springs and at positions with C deposits. Zr-1Nb seems to be more sensitive to this type of corrosion than Zircaloy-4 or ZIRLO. The oxide layer on Zr-1Nb probably has a lower electrical resistance than that formed on Zircaloy-4 or ZIRLO and is thus more sensitive to galvanic corrosion phenomena. In-pile tests are needed to confirm this explanation, because irradiation increases electrical resistance.
- Increased corrosion at medium burnups due to the formation of hydride rims, especially in low-Sn Zircaloy (e.g. PCA-1), were found in Siemens (now AREVIA) PWRs operating under very high fuel duty condition in the early 1990s; see Ref. [III.77]. Later, this phenomenon was observed in other PWRs. This type of corrosion is described below.
- Crud induced increased corrosion and even corrosion failures due to local overheating have been observed several times; see Refs [III.78, III.79].
- Cases of abnormal corrosion of M5 were reported in Ref. [III.66]. Three different types were observed:
 - Increased corrosion by galvanic coupling to the Inconel spacer springs;
 - Increased corrosion in the bottom of the fuel rods (oxide thickness about 40 μm) after three cycles in a Spanish PWR, probably caused by surface contamination;

- Increased corrosion (maximum oxide thickness about 70 μ m) on some one-cycle rods at the top of the fuel column in a PWR in Germany. Some comments on these abnormal corrosion observations are made below.
- Crevice corrosion, with a local oxide thickness up to 200 μm, was observed in very thin gaps of spacers made from Zircaloy-4 and exposed in PWRs up to a burnup of 52 MW·day·kg⁻¹ U [III.80]. Oxide thicknesses up to 90 μm were observed in spacers made from E110 and irradiated in WWERs up to 50 MW·day·kg⁻¹ U, also in larger gaps [III.81].

The experience with the low-Sn Zircaloy-4 was good for the first years of reactor operation. Since 1991, several lots of low-Sn Zircaloy-4 were found that exhibited unexpected increased corrosion. The oxide profile of such rods is characterized by a sudden transition from normal corrosion to increased corrosion at a certain axial position, as shown in Fig. III.36 [III.77]. The increased corrosion started mostly in the second cycle and accelerated during the third cycle. Metallographic cross-sections taken during post-irradiation examination from positions with increased corrosion have all shown the presence of a fully developed hydride rim at such positions. In addition, the pick-up fraction of corrosion hydrogen was high. Post-irradiation examination has shown that hydrides are formed once the solubility limit is exceeded (about 150 ppm (1.35 at.%) in PWR fuel cladding) above a certain oxide layer thickness, 15–20 µm. At low heat fluxes these hydrides precipitate as circumferentially oriented platelets uniformly distributed across the cladding wall and do not affect the fuel cladding behaviour. At high heat fluxes, these hydrides concentrate at the colder outer rim of the cladding, owing to the thermal diffusion of hydrogen, forming a dense ZrH₂ layer. The influence of an increasing hydrogen concentration and heat flux on hydrogen distribution was examined out-of-pile. These tests showed that a dense hydride rim only forms at heat fluxes >500-600 kW·m⁻² and at hydrogen concentrations above about 300 ppm (2.66 at.%). Post-irradiation examination of fuel rods showed a dense hydride rim formation at average hydrogen concentrations \geq 200 ppm (1.79 at.%) [III.70] to 300 ppm (2.66 at.%) [III.82]. Once a dense ZrH₂ rim is formed, corrosion will increase owing to the lower corrosion resistance of hydride compared with Zr alloy metal, especially at the low temperatures typical of the last cycle, resulting in the oxide profile shown in Fig. III.36.



FIG. III.36. Oxide thickness profile of fuel rod H₄ clad in low-Sn Zircaloy-4, after two and three exposure cycles [III.77].

Water chemistry has a much lower importance for corrosion in PWRs than for corrosion in BWRs. Corrosion in PWRs does not depend on variations in the normal impurities in the water. Also, Zn (5–40 ppb), which is added to the heat transport water in an increasing number

of PWRs to reduce the plant activation, to inhibit inter-granular SCC of steam generator Inconel 600 tubing and to decrease the metal release from structural parts by corrosion, does not affect corrosion of Zr alloy cladding. Boric acid and lithium hydroxide, which are added for reactivity and pH control, may affect HPU and corrosion. In isothermal corrosion tests, Li was found to increase corrosion when its concentration was above about 30 ppm [III.83]. Whereas the normal PWR bulk coolant Li concentration is too low to increase corrosion, an enrichment of the Li during boiling at the surface, or in crevices or in the oxide layer of the cladding could concentrate Li, as shown in Fig. III.37 [III.83], and affect fuel rod corrosion. The B concentration at beginning of cycle can be increased to accommodate the optimized core design, use of mixed oxide fuel and an increase in the cycle length. To minimize crud and plant radiation fields, the increased B concentration needs an increased Li concentration at beginning of cycle. In some cases, Li concentrations up to 7 ppm have been applied at beginning of cycle. Furthermore, core optimization has increased the heat fluxes. Depending on the plant strategy, Li in the oxide layer could increase to a critical concentration, which has to be avoided. Boric acid, which can counteract the negative effect of LiOH, does not concentrate in the outer porous part of the oxide [III.83]. Boric acid additions may reduce the HPUF [III.84].



FIG. III.37. Li pick-up into the oxide layer of PWR fuel rod cladding [III.83].

III.3.6. Limits to oxide thickness in PWRs

The maximum allowable oxide thickness depends on the heat flux and particular design aspects of the fuel. The following aspects of fuel rod corrosion have to be considered:

- Violations of loss of coolant accident or reactivity insertion accident criteria (e.g. the 17% equivalent cladding reacted (ECR) criterion). For loss of coolant accident analysis, a maximum ECR criterion is specified to avoid unacceptable embrittlement. In many countries, the allowable oxide thickness formed during normal operation is determined by the loss of coolant accident–equivalent cladding reacted criterion. For reactivity insertion accidents, local hydride blisters or dense hydride rims are often forbidden; they may reduce the allowable average radial fuel enthalpy, which determines the size of the temperature gradient through the wall of the cladding.
- Violation of criteria for final storage and transport.

- Excessive local wall thinning; wall thinning can degrade the behaviour of fuel during normal operation, transport and final storage. Often a 10% criterion is used to exclude excessive wall thinning. This criterion would limit the allowable oxide thickness to 90 μ m for a 0.6 mm wall cladding, based on a Pilling-Bedworth ratio of 1.5. A 10% criterion for cladding loss may be too conservative.
- Local heat flow blockage by circumferential cracks in the oxide.
- Local oxide spallation that may lead to a large hydride blister.
- Unacceptable embrittlement or dimensional changes due to HPU.

During normal operation, two different processes have been observed that can limit the oxide thickness on fuel rods at high burnups. The first process is due to the feedback by the oxide layer on its growth rate. The controlling temperature is the oxide-metal interface temperature, which depends on the oxide layer thickness, heat flux and thermal conductivity of the oxide layer. During high power experiments (1.4 MW·m⁻²) in a PWR, local perforations of the cladding wall occurred due to a loss in integrity of the oxide layer at a certain thickness (>50 µm) [III.54]. This type of failure is caused by circumferential crack formation in the oxide (local 'lift-off'), resulting in local blockage of heat flow in the oxide resulting in high temperatures and excessive local corrosion. For more realistic heat fluxes, there is a competition between local corrosion due to high temperatures and spalling of the oxide layer at such positions. In the second process, at the position of local oxide spallation, either a hydride blister or a hydride free zone can be observed (see Ref. [III.85]). A local enrichment of hydrides is seen where spalling of the oxide occurred before the end of irradiation; hydride blisters are formed owing to the thermal diffusion of hydrogen to the cold spot with reduced oxide thickness. A hydride-free zone is caused by a hot spot from a circumferential crack before the oxide spalled. At such positions, the temperature increase has driven the hydrogen out of the hot zone. Any oxide spallations occurred after irradiation. Defects in PWR at thick oxide layers (>140 μ m) and high heat fluxes (700 kW·m⁻²) are caused by massive hydride blisters that extend over almost the whole wall thickness at positions with severe local oxide spallations [III.18]. Figure III.38 [III.18] summarizes the experience with thick oxide layers in a diagram showing oxide thickness and heat flux for each data point. A locus curve of constant corrosion rate (approximately a hyperbola) was drawn as a threshold for 'go: no-go' with respect to the stability of the corrosion process.



FIG. III.38. Maximum allowable uniform oxide layer thickness; cladding wall thickness of 0.73 mm [III.18].

III.4. SUMMARY

This appendix summarizes the corrosion and HPU data gleaned from fuel cladding that has been in service in BWRs and PWRs. Despite the emergence of localized oxidation processes, the maximum burnup achievable by fuel cladding in the original Zircaloys of about $30 \text{ MW} \cdot \text{day} \cdot \text{kg}^{-1}$ U has been increased to around 60 MW $\cdot \text{day} \cdot \text{kg}^{-1}$ U. These improvements have been achieved through the manipulation of alloy composition and careful attention to the microstructure, especially the geometry of precipitates.

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Appendix IV

CORROSION PERFORMANCE OF FUEL CLADDING IN POWER REACTORS¹ (PHWRs)

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IV.1. INTRODUCTION

Pressure tube reactors operate with either light water or heavy water as their heat-transport fluid or coolant. The inside surface of a zirconium alloy pressure tube reacts with the water to form a protective zirconium oxide film and atoms of hydrogen isotope:

 $Zr + 2H_2O \rightarrow ZrO_2 + 4H \tag{IV.1}$

The pressure tube absorbs a fraction of the hydrogen generated by the corrosion process. The corrosion and the amount of hydrogen picked up can vary with alloy composition, temperature, irradiation and water chemistry. The design and operating conditions of pressure tube reactors are summarized in Table 1.3 in Chapter 1, Volume 1 of this publication. The wall thickness of pressure tubes varies between reactors from 4–6.8 mm. Consequently, oxidation does not present an integrity problem, but the danger represented by the resulting hydrogen has to be carefully monitored. The outside surface of the tubes is exposed to carbon dioxide, nitrogen or helium, which, with rare exceptions, present a benign environment with little oxidation.

A deuterium profile typical of that measured along a CANDU-PHWR reactor pressure tube is shown in Fig. IV.1 [IV.1]. Also shown are the temperature and flux profiles along the pressure tube. Increased deuterium ingress is seen at each end of the tubes due to galvanic contact with the stainless steel end-fitting used to make a rolled joint [IV.2]; along the body of the pressure tube, the deuterium concentration increases from the inlet end of the tube and peaks near the outlet end, in this example at about 5.1 m. Oxide thickness also increases along the body of the pressure tube and tends to peak near the outlet end, as shown in Fig. IV.2 [IV.3]. The peaks develop towards the outlet end of the tube from the synergistic effects of temperature and fast neutron flux on corrosion [IV.4]. The lack of extra oxidation at the ends of the tubes in the rolled joints confirms different sources of hydrogen at this location.

Pressure tube reactors operate in either pressurized water or boiling water modes. In the pressurized water mode, chemical control of the heat transport fluid is maintained through additions of lithium and dissolved hydrogen. Lithium (and in some cases ammonia) is added to the coolant to minimize corrosion of the carbon steel primary system (coolant) piping while an excess of dissolved hydrogen is maintained to make the coolant 'reducing' by suppressing the production of radiolytic oxidizing species in the core.

In the boiling water mode, the coolant is maintained neutral (no pH additives in the coolant) and the absence of deliberate hydrogen additions makes the coolant 'oxidizing' due to the radiolytic production of oxygen in the core. The trends in corrosion and hydrogen uptake behaviour as a function of water chemistry are shown in Fig. IV.3, where both the corrosion rate and the hydrogen uptake fraction for Zircaloy-2 are plotted as a function of the H/O ratio

¹ The information in this section was developed within the Zirconium Alloy Technology (ZIRAT) Programme and is provided herein through the courtesy of ANT International. Information on the ZIRAT/IZNA programs can be obtained at:

 $https://www.antinternational.com/index.php?id=zirat_full_information and https://www.antinternational.com/index.php?id=izna full information and https://www.antinternational.com/index.php?id=zirat_full_information antinternational.com/index.php?id=zirat_full_information antinternational.com/index.php?id=zirat_full_information antinternational.com/index.php?id=zirat_full_informational.com/index.php?id=zirat_full_informational.com/index$

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in the coolant [IV.3]. Zirconium alloy corrosion is generally low in 'reducing' coolants (H/O > 10) but tends to increase as the coolant becomes more 'oxidizing' (H/O < 10); however, the fraction of corrosion generated hydrogen picked up by the alloy is generally higher under 'reducing' conditions and much less when 'oxidizing'. This behaviour can result in only small amounts of hydrogen being picked up in 'oxidizing' coolants, except in instances where corrosion under extremely oxidizing conditions becomes excessive.



FIG. IV.1. Deuterium concentration profile along a CANDU pressure tube after about 17 operating years [IV.1].

The alloys for pressure tubes in power reactors have been limited to Zircaloy-2 and Zr-2.5Nb. Zr-2.5Nb was initially developed because of its high strength, which permitted a reduction in the pressure tube wall thickness, with a concomitant improvement in the neutron economy compared with Zircaloy-2. The beneficial effect of niobium additions to zirconium on hydrogen ingress also provided an incentive for its development. The Zr-2.5Nb alloy is a two phase material and can exhibit several different microstructures depending on how the pressure tube is made. Pressure tubes made from Zr-2.5Nb alloy have been used in various reactors in either the cold worked (CW), annealed or heat treated conditions. The different microstructures of these three metallurgical conditions respond differently in terms of their corrosion and hydrogen ingress in-reactor.

Corrosion and hydrogen ingress data from various pressure tube reactors around the world have been collected and are presented here. Criteria have been established to place the comparisons on the same footing; these include:

- Only data from pressure tubes irradiated in power reactors were used (with the exception
 of pressure tube material exposed as coupons in the Fugen reactor core).
- Corrosion is reported as the maximum uniform oxide thickness observed along the length of the tube based on metallography (thick patch-type or nodular oxides are only noted where prevalent).
- Hydrogen pick-up (HPU) values are corrected for initial hydrogen (when initial hydrogen values are not reported, values are assumed based on reports from similar references on the same pressure tube material).
- Deuterium pick-up was converted to its hydrogen equivalent for pressure tubes irradiated in heavy water.

- Hydrogen ingress was converted to units of mg·dm⁻² to account for variations in pressure tube wall thickness.
- Operating days, defined as hot days when the reactor is at power, were chosen for the time scale (data reported as effective full power days would tend to underestimate the time taken for corrosion and hydrogen uptake).



FIG. IV.2. Oxidation of cold worked Zircaloy-2 and Zr-2.5Nb pressure tubes in Pickering Nuclear Generating Station (NGS) [IV.3].



FIG. IV.3. Effect of changing water chemistry on corrosion and hydriding of Zircaloy-2 in a reactor [IV.3].

IV.2. PRESSURE TUBE DATA

IV.2.1. Zircaloy-2

Data have been reported for Zircaloy-2 pressure tubes from the Hanford N-Reactor [IV.5], steam generating heavy water reactor (SGHWR) [IV.6] and the CANDU type pressurized heavy water reactors (PHWRs). The sources of CANDU PHWR type reactor data include Pickering NGS [IV.4], the Nuclear Power Demonstration (NPD) reactor [IV.7] and the RAPPS 1&2, MAPPS 1&2, NAPPS 1&2 and KAPPS 1 reactors, located in India [IV.8, IV.9]. Zircaloy-2 pressure tubes are typically extruded between 1073 and 1123 K (800 and 850°C), cold drawn 20–30% and stress relieved by autoclaving at about 673 K (400°C).

All available corrosion data are consistent and bounded by the two curves shown in Fig. IV.4. The upper curve is initially defined largely by the Hanford N Reactor data up to about 4000 operating days but the Pickering inner zone (high flux) and SGHWR data for uniform oxidation are consistent with extrapolations of the Hanford data beyond that time. Acceleration in corrosion is seen after about 2000 operating days. The lower curve showing less acceleration is largely defined by the long term NPD data and is likely a consequence of the low operating temperature (550 K (277°C)) and low fast neutron flux — about $1 \times 10^{17} \text{ n} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$.



FIG. IV.4. Corrosion of cold worked Zircaloy-2 pressure tubes in operating reactors [IV.4–IV.9].

The corresponding HPU data are plotted in Fig. IV.5 and show trends similar to that seen for corrosion in Fig. IV.4. Both the Hanford N Reactor and Pickering inner zone data indicate a sharp acceleration in HPU that begins at about 2000 operating days. After about 4000 operating days, the HPU (about 100 mg·dm⁻²) is equivalent to 380 ppm (3.35 at.%)

H in a 4 mm thick pressure tube. The percentage theoretical uptake, using the corresponding oxidation from Fig. IV.4, is determined to be about 60%. Again, the lower curve is largely defined by the NPD data obtained at lower temperatures and fast neutron fluxes than by the rest of the data. The data from the reactors in India fall within the observed range and show acceleration intermediate to the Hanford and NPD data. Although the SGHWR corrosion data are in the upper part of the data range, the SGHWR HPU data lie near the bottom of the data range. This behaviour is likely a result of the oxidizing water chemistry in SGHWR and the low percentage hydrogen uptake characteristic of this environment (see Fig. IV.3).



FIG. IV.5. Hydrogen pick-up of cold worked Zircaloy-2 pressure tubes in operating reactors [IV.4–IV.9].

IV.2.2. Cold worked (CW) Zr-2.5Nb

Data for CW Zr-2.5Nb come primarily from tubes removed from CANDU PHW power reactors [IV.1, IV.3, IV.10, IV.11] although data exist for one tube from the NPD reactor [IV.12]. CW pressure tubes are typically extruded at 1088 K (815°C), cold drawn 20–30% and stress relieved by autoclaving at 673 K (400°C). The fabrication route for tubes in the reactors in India are CW in two steps of 20–25% with an intermediate anneal at 833 K (560°C). Two tubes removed from the KAPS-2 reactor have been examined [IV.13, IV.14]. Corrosion data for all removed irradiated CW Zr-2.5Nb tubes are shown in Fig. IV.6. Oxide thickness for only one of the two tubes from KAPS-2 was reported in the literature. The spread in all the data was quite large and the corrosion measured on the KAPS-2 and NPD pressure tubes were consistent with the large database from commercial CANDU power reactors.

Unlike Zircaloy-2, which shows acceleration in corrosion beyond about 2000 operating days in-reactor (reproduced from Fig. IV.4), the corrosion of CW Zr-2.5Nb is substantially less with no evidence for accelerating corrosion based on the curve defining the upper bound of all the data.



FIG. IV.6. Corrosion of cold worked Zr-2.5Nb pressure tubes in operating reactors [IV.1, IV.3, IV.10, IV.14].



FIG. IV.7. Hydrogen pick-up of cold worked Zr-2.5Nb pressure tubes in operating reactors [IV.1, IV.3, IV.10–IV.14].

The corresponding HPU data for removed tubes are plotted in Fig. IV.7. Most noticeable is the considerably lower HPU in Zr-2.5Nb compared with that for Zircaloy-2, as shown by the curve reproduced from Fig. IV.5. After about 4000 operating days, the HPU (about $4 \text{ mg} \cdot \text{dm}^{-2}$) is equivalent to 15 ppm (0.14 at.%) H in a 4 mm thick pressure tube. The percentage theoretical uptake, using the corresponding oxidation from Fig. IV.6, is determined to be about 10%. HPUs in the KAPS-2 and NPD tubes are equally low and consistent with the CANDU PHW data. Beyond about 4500 operating days, there is some increase in scatter and an indication that the hydrogen ingress rate may be increasing in some tubes, even when point 'A' in Fig. IV.7 is excluded. The point labelled 'A' is the tube from channel L09 in Pickering NGS Unit 3. The insulating gas annulus surrounding the pressure tubes in Unit 3 was nitrogen that was maintained at an extremely low dew point to ensure early detection of a leaking pressure tube. The non-oxidizing conditions in the gas annulus led to the degradation of the oxide on the outside of the tube permitting hydrogen, there as an impurity in the annulus gas system, to be absorbed by the pressure tube. Carbon dioxide is now used as the insulating gas.

IV.2.3. Heat-treated Zr-2.5Nb

Data for heat-treated Zr-2.5Nb come from a limited number of removed tubes: one from the NPD reactor [IV.12], one from KANUPP [IV.15] and two from Ignalina-1 [IV.16, IV.17]. The remaining data come from a series of pressure tube surveillance specimens irradiated in the Fugen reactor [IV.18]. The NPD, KANUPP and Fugen pressure tubes were solution treated in the (α + β) phase, water quenched, CW 15% and aged at 773 K (500°C) for 24 hours. The Ignalina-1 tubes (TMT-1) were solution treated in the (α + β) phase, water quenched, CW 23% and aged at 788 K (515°C) for 24 hours.



FIG. IV.8. Corrosion of heat treated Zr-2.5Nb pressure tubes in an operating reactor [IV.12, IV.15–IV.18].

Corrosion data are plotted in Fig. IV.8 and compared with those for Zircaloy-2. Oxidation of heat treated Zr-2.5Nb is significantly less than that for Zircaloy-2, especially for tubes in Fugen, KANUPP and NPD reactors. The corrosion data from tubes in Ignalina-1 show a wide variation in oxide thickness. This variability is largely a result of rapid oxidation in regions adjacent to the fuel spacer grids, which are made of stainless steel. Oxide patches up to 220 μ m have been reported at these grid locations. Reported values of 10 μ m or less in these regions are likely a result of oxide loss due to spalling. Away from the grid regions, uniform oxides are reported to have a maximum thickness of 30 μ m. This value is greater than the uniform oxides measured on the NPD tube after a similar exposure and is probably due to the higher operating temperature and more oxidizing water chemistry in Ignalina-1 compared with NPD.

The corresponding HPU data are shown in Fig. IV.9. The heat treated Zr-2.5Nb tubes in all reactors show exceptionally low HPU compared with Zircaloy-2. The data shown for the two tubes in Ignalina-1 are the maximum pick-ups measured, and they apply even within the spacer grid areas where the corrosion was quite severe. After about 4000 operating days, the HPU (about 2 mg·dm⁻²) is equivalent to 8 ppm (0.07 at.%) H in a 4 mm thick pressure tube. The percentage theoretical uptake, using the corresponding oxidation from Fig. IV.8, is determined to be about 10%. A considerably lower percentage uptake would be calculated at

longer times where the thick oxides associated with spacer grid locations are even greater. The low percentage hydrogen uptake, characteristic of oxidizing water chemistries, is likely contributing to this behaviour.



FIG. IV.9. Hydrogen pick-up of heat treated Zr-2.5Nb pressure tubes in operating reactors [IV.12, IV.15–IV.18].

Zr-2.5Nb alloys consistently pick up less hydrogen than Zircaloy-type alloys and Zr-2.5Nb in the heat treated condition has the optimum metallurgical structure for low hydrogen ingress. Following the initial water quench from the $(\alpha+\beta)$ region and the intermediate CW stage, the thermal ageing process produces a near-equilibrium microstructure with a distribution of fine β -Nb precipitates along twin boundaries within the martensitic α -Zr structure of the prior β -Zr grains. The precipitation also reduces the concentration of Nb in the α -Zr matrix, which was initially supersaturated with Nb following the water quench. Both factors contribute to the low pick-up behaviour for the heat treated condition.

IV.2.4. Annealed and TMT-2 Zr-2.5Nb

The corrosion and HPU data for Zr-2.5Nb pressure tubes in both the annealed and TMT-2 conditions are summarized in this section [IV.19, IV.20]. The annealed pressure tubes (CW 23% and then annealed at 813 K (540°C) for 5 hours) were used in all the RBMK 1000 reactors. The TMT-2 pressure tubes (solution treated in the (α + β) phase, quenched into a He/Ar gas mixture, CW 23% and aged at 813 K (540°C) for 24 hours) were used in the RBMK 1500 Ignalina 2 reactor.

Corrosion data are plotted in Fig. IV.10 and compared with data for CW Zr-2.5Nb. Uniform corrosion for annealed Zr-2.5Nb in the RBMK 1000 reactors is low and the data are contained within the upper bound of the CANDU PHW data for CW Zr-2.5Nb (dashed curve in Fig. IV.10); non-uniform oxides up to 425 µm thick are observed in the spacer grid regions. For the TMT-2 material in Ignalina-2, the reported observations are mixed. In one tube, the range of oxide thicknesses was small and contained within the upper bound of the CANDU PHW data for CW Zr-2.5Nb. In two other tubes the reported range of oxide thicknesses varied by several orders of magnitude with the maximum values likely to be associated with spacer grid locations.



FIG. IV.10. Corrosion of annealed and TMT-2 Zr-2.5Nb pressure tubes in operating reactors [IV.19, IV.20].

HPU data are plotted in Fig. IV.11 and compared with data for CW Zr-2.5Nb. HPU in annealed pressure tubes is low, with pick-up values close to those in the upper range of the CW Zr-2.5Nb data. After about 4000 operating days, the HPU (about 6 mg·dm⁻²) is equivalent to 24 ppm (0.22 at.%) H in a 4 mm thick pressure tube. The percentage theoretical uptake, using the corresponding oxidation from Fig. IV.10, is determined to be about 2%. The HPU in TMT-2 tubes is considerably less than that for CW Zr-2.5Nb tubes and similar to the pick-up in heat-treated (TMT-1) tubes from Ignalina-1 shown earlier in Fig. IV.9. After about 4000 operating days, the HPU (about 2 mg·dm⁻²) is equivalent to 8 ppm (0.07 at.%) H in a 4 mm thick pressure tube. The percentage theoretical uptake, using the corresponding oxidation from Fig. IV.10, is determined to 8 ppm (0.07 at.%) H in a 4 mm thick pressure tube. The percentage theoretical uptake, using the corresponding oxidation from Fig. IV.10, is determined to be about 2%. The three tubes are specified associated with the spacer grid locations are major contributors to the low percentage uptakes calculated for these tubes.



FIG. IV.11. Hydrogen pick-up of annealed and TMT-2 Zr-2.5Nb pressure tubes in operating reactors [IV.19, IV.20].

IV.3. SUMMARY

Oxide thickness and HPU have been evaluated on pressure tubes removed from power reactors after up to 25 years of operation. The oxide growth increases with operating temperatures along the length of the tube and with neutron flux. The two main alloys, Zircaloy-2 and Zr-2.5Nb, differ in their behaviour. After some time, the oxidation rate and rate of HPU increases in Zircaloy-2. In Zr-2.5Nb oxidation does not accelerate but the rate of hydrogen ingress increases slightly late in life. Oxidation of Zr-2.5Nb pressure tubes becomes severe when in close proximity to stainless steel fuel spacer grids, particularly in oxidizing water chemistries.

The percentage theoretical uptake for all reported materials is summarized in Table IV.1. The HPU in Zircaloy-2 pressure tubes can be very large and the low values in Zr-2.5Nb with all its heat treatments confirm it as the preferred alloy for pressure tubes.

Material	Theoretical HPU (%)	HPU (ppm (at.%))
Zircaloy-2	60	380 (3.35)
Zr-2.5Nb (CW)	10	15 (0.14)
Zr-2.5Nb (heat treated)	10	8 (0.07)
Zr-2.5Nb (annealed)	2	24 (0.22)
Zr-2.5Nb (TMT-2)	1	8 (0.07)

TABLE IV.1. HPU IN 4 mm THICK PRESSURE TUBES AFTER 4000 DAYS

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ABBREVIATIONS

ATR	Advanced Test Reactor
BCC	body centred cubic
BWR	boiling water reactor
CANDU	Canada deuterium uranium
CW	cold worked
CWSR	cold worked stress relieved
DAD	diffusional anisotropy difference
dpa	displacements per atom
EAM	embedded atom model
ECR	equivalent cladding reacted (also: effective cladding reduction)
FCC	face centred cubic
GGA	generalized gradient approximation
НСР	hexagonal closed packed
HPU	hydrogen pick-up
HPUF	hydrogen pick-up fraction
HVTEM	high voltage transmission electron microscope
LD	longitudinal direction
LOCA	loss of coolant accident
LTP	low temperature process
LWR	light water reactor
MD	molecular dynamic
MDA	Mitsubishi Developed Alloy
M-MDA	modified Mitsubishi Developed Alloy
PCI	pellet-clad interaction
PD	point defect
PHWR	pressurized heavy water reactor
РКА	primary knock-on atom
PR	partially recrystallized
PWR	pressurized water reactor
RAH	radiation anneal hardening
RBMK	high-power channel-type reactor
RIA	reactivity insertion accident
RIC	radiation induced conductivity
RX	recrystallized
RXA	recrystallized annealed
SFE	stacking fault energy
SGHWR	steam generating heavy water reactor
SIA	self-interstitial atom
SIPA	stress induced preferred absorption
SIPN	stress induced preferred nucleation
SPP	second phase particle
SR	stress relieved
TD	transverse direction

TEM	transmission electron microscope
ТМ	transition metal
TMT-1	thermomechanical treatment in water
TMT-2	thermomechanical treatment in inert gas
TSS	total soluble solids
WWER	water cooled water moderated power reactor
XRD	X ray diffraction

Since the last publication on zirconium by the IAEA in 1971 there has been a need to gather and update relevant information. In an effort to bridge the years-long gap on zirconium, its development and use in industry, and to provide comprehensive information on the material the IAEA initiated a comprehensive project on the metallurgy of zirconium, which resulted in this publication. These volumes cover a wide range of the applications, properties and irradiation behaviour of zirconium.