IAEA-TECDOC-1316

Effects of radiation and environmental factors on the durability of materials in spent fuel storage and disposal



INTERNATIONAL ATOMIC ENERGY AGENCY

December 2002

The originating Section of this publication in the IAEA was:

Nuclear Fuel Cycle and Materials Section International Atomic Energy Agency Wagramer Strasse 5 P.O. Box 100 A-1400 Vienna, Austria

EFFECTS OF RADIATION AND ENVIRONMENTAL FACTORS ON THE DURABILITY OF MATERIALS IN SPENT FUEL STORAGE AND DISPOSAL IAEA, VIENNA, 2002 IAEA-TECDOC-1316 ISBN 92–0–113802–4 ISSN 1011–4289

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Printed by the IAEA in Austria December 2002

FOREWORD

Wet storage facilities continue to be the most common technology used for the management of irradiated fuel assemblies from power reactors, research and test reactors, and defence reactors. Some of the most important decisions that must be faced by the operators of these facilities involve the ageing of materials in ageing facilities. A broad variety of fuel types, involving numerous combinations of fuel and cladding materials, is currently stored in these facilities, which in many instances are at or near their design capacities and at or approaching their design lifetimes. Extending the licenses of such facilities as their regulatory periods expire is not a straightforward proposition, and answers to questions concerning the degradation and ageing of materials in spent fuel storage facilities, which may be posed by regulatory bodies, require a broadly based materials database. However, because examinations of radioactive materials are expensive, access is sparse to experience and materials data, especially quantitative data that provide an informed basis to analyse and extrapolate materials behaviour in wet storage environments. Moreover, to our knowledge, the available data, both quantitative and qualitative, for all the common types of fuel cladding, categories of fuel material, and the components used in spent fuel storage pools, have never been gathered together in a single review.

In 1993, a Co-ordinated Research Project (CRP) on Irradiation Enhanced Degradation of Materials in Spent Fuel Storage Facilities was initiated by the IAEA with the twin goals of filling in some of the gaps in the materials database, and providing input data to model and extrapolate materials behaviour. However, as the reality and immediacy of "extended storage" began to emerge, the supervisors of the CRP recognized the need for a broader treatment that included, but was not limited to, radiation effects. Therefore, one of the supervisors, A.B. Johnson, Jr., was charged with the job of collecting the required materials database and integrating into it the data and results developed by the CRP as it progressed. This review addressed materials behaviour in wet storage on the basis of important degradation mechanisms that apply to irradiated and unirradiated materials commonly found in wet storage facilities. It was issued under the title Durability of Spent Nuclear Fuels and Facility Components in Wet Storage, IAEA-TECDOC-1012 (1998).

Dry storage and waste disposal technologies also involve the need to investigate effects of the respective environments on materials. While these technologies were secondary to wet storage in the CRP, studies were also conducted addressing radiation effects on corrosion of canister materials and fuel cladding, radiation assisted stress corrosion cracking, and thermally induced hydrogen migration in Zircaloy cladding during dry storage. These studies complemented those addressing materials durability in wet storage and they are reported in this TECDOC, the second report to be published on work started during the CRP.

The IAEA wishes to express its thanks to A.B. Johnson, Jr., for his major work on compiling and technically editing the contributions to this report, and all of the participants in the CRP and their co-authors. The IAEA staff member responsible for this publication and scientific secretary of the CRP was I.G. Ritchie of the Division of Nuclear Fuel Cycle and Waste Technology.

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SUMMARY

1 Introduction

This is the second report that addresses results from the Coordinated Research Project (CRP) on Irradiation Enhanced Degradation of Materials in Spent Fuel Storage Facilities. The first report was entitled *Durability of Spent Nuclear Fuels and Storage Facility Components in Wet Storage*, IAEA-TECDOC-1012. Because of the enhanced importance of wet storage, the scope of the first report was expanded to include both irradiated and unirradiated effects on fuels and facility materials. This second report addresses results of topical studies that are relevant to issues important to materials behaviour in wet storage technology, but also involves topics on materials behaviour in dry storage and repository environments, including effects of radiation. The material is in seven separate papers contributed by the participants in the CRP and contains details of research studies started within the framework of the CRP and in several cases completed well after the CRP was finished.

The seven contributions fall into three broad subject areas.

1.1 Effects of temperature and radiation on aqueous and moist air corrosion of stainless steels

Stainless steels are prominent as cladding materials for nuclear fuels and as components in nuclear fuel storage facilities. They are susceptible to changes in grain boundary compositions that can promote intergranular corrosion phenomena, either from thermal treatments (sensitization), from radiation treatments (radiation-induced segregation), or from a combination for nuclear fuels irradiated at moderately high temperatures. Two studies reported here provide bases to understand thermal and radiation issues for stainless steels, including potential impacts during storage.

Several types of fuels with stainless steel (SS) cladding are or have been stored in water, including fuel from gas cooled reactors (GCRs), liquid metal reactors (LMRs), and light water reactors (LWRs). Some fuels have been susceptible to corrosion failures, while others have been durable (see summary of SS cladding behaviour in TECDOC-1012). The first two papers in this report summarize investigations of radiation induced segregation (RIS) in the United Kingdom and the United States, respectively.

1.2 Studies of materials behaviour in wet and dry storage

Three papers report studies on the behaviour of irradiated zirconium-niobium fuel cladding in wet and dry storage, hydrogen migration in Zircaloy during dry storage, and corrosion and electrochemical measurements in wet storage and behaviours of selected materials relevant to dry storage, respectively.

Zirconium-niobium alloys are materials of choice for fuel cladding and reactor components (e.g., RBMK channel tubes) in reactors designed in the former Soviet Union and operating in Russia and other East European countries. A study reported here addresses changes brought about by nuclear radiation and summarizes investigations of behaviours of the irradiated materials in wet and dry storage environments. Different Zircaloys are the leading materials for cladding and components in power reactors operating in the West. Behaviour of hydrogen introduced by aqueous corrosion during reactor service is reported here in the context of effects of temperature gradients in dry storage on the hydrogen distribution and its effects on

mechanical properties. A third contribution on fuel storage summarizes systematic studies of several corrosion-related issues in wet storage facilities.

1.3 Effects of gamma radiation on the durability of candidate canister materials for repository applications: carbon steel, titanium, and copper

Disposal of nuclear fuel and high-level waste is a pressing issue that has yet to be implemented. Among the important considerations is the demonstration of sufficient integrity of metal containers that must serve as barriers to isolate radioactive species over multi-century time frames that provide sufficient decay of activity. The two contributions in this subject area presented in this report deal with the effects of gamma radiation on corrosion of candidate materials for nuclear waste containers: in one case, titanium and copper for disposal in granitic formations and in the other carbon steel for disposal in salt formations.

Studies in Canada were directed toward radiation effects on candidate titanium and copper canister materials in aqueous and vapour phases. An element of the Canadian study was to predict effects of microbial activity on corrosion in repository environments. Studies were conducted in Germany to investigate radiation effects on candidate carbon steel canister materials exposed to salt brines.

2 Discussion of Contributed Papers

2.1 Radiation effects on corrosion of cladding in moist air and water in advanced gas reactors (AGRs)

Stainless steel fuel cladding in AGRs is irradiated in the temperature range 350°C to 520°C. The investigations reported in this study revealed evidence of radiation-induced sensitisation of the stainless steel linked to its accelerated corrosion in water and in moist air. Effects of storage temperature and humidity on the corrosion behaviour in moist air are discussed. It is hypothesized that aggressive conditions are due to the radiolytic formation of nitric acid in the moist air, which degrades the SS by intergranular attack.

2.2 Implications of effects of irradiation-assisted stress corrosion cracking during wet storage of irradiated stainless steels

Stainless steel fuel cladding and reactor components have failed in service in water reactors. Factors have been demonstrated to include oxygen in the reactor coolant and RIS that becomes significant beyond a threshold neutron fluence; this threshold appears to differ for boiling water reactors (BWRs) and pressurized water reactors (PWRs). As indicated for SS AGR fuel cladding, behaviour of irradiated SS cladding becomes important in projecting spent-fuel behaviour in wet storage. Investigators at the Pacific Northwest National Laboratory (PNNL) focused on corrosion behaviour of irradiated SS under reactor service conditions. More recently, they applied that knowledge to address expected behaviour of irradiated SS under wet storage conditions. Extrapolation of results from elevated temperatures suggests that time-dependent deformations, which influence in-core cracking of LWR SS are not expected to be significant at fuel storage temperatures.

2.3 Microstructure and composition of zirconium-niobium alloys after irradiation and storage

Studies conducted at the VNIINM laboratory in Moscow addressed changes in microstructures of Zr-1Nb fuel cladding and Zr-2.5Nb channel tubes resulting from service in

nuclear reactors. Radiation caused increases in dislocation densities and promoted precipitation of β -Nb particles. No significant evidence of amorphization of second-phase particles was observed. The baseline studies of radiation effects on the alloys were applied to investigate whether further changes occur during storage. No significant changes in dislocation structure, phase, and chemical composition of zirconium-niobium alloys were observed after 1 year of wet storage and 5 years of dry storage.

2.4 Hydrogen redistribution in Zircaloy cladding

In reactor service, Zircaloy fuel cladding absorbs hydrogen generated in reaction with the aqueous coolant. The hydrogen is generally not uniformly distributed because solubility and transport are affected by temperature gradients generally present in fuel cladding and reactor components. Charpy impact tests were conducted on Zircaloy specimens with 400 ppm of hydrogen. Two cases were investigated: (1) with the hydrogen uniformly distributed in some specimens and (2) with the hydrogen non-uniformly distributed in others. The impact strength was observed to be higher for specimens with non-uniform hydrogen distribution. Some tests were conducted at room temperature and may therefore be relevant to assess Zircaloy impact behaviour during fuel handling in wet storage.

2.5 Conducting corrosion evaluations in aqueous systems

Procedures to evaluate corrosion in aqueous media at the Bhabha Atomic Research Centre (BARC) are presented. General corrosion is monitored with electrochemical potential measurements and with corrosion coupons that are evaluated periodically after residence in fuel storage pools. Coupon racks are placed near irradiated fuel to ensure that radiation effects are evaluated. Coupons are scheduled for evaluation after 1, 3, and 10 years. To investigate effects of wet storage environments on Zircaloy fuel cladding, post-irradiation examinations on more than 200 fuel elements (BWR, pressurized heavy water reactors [PHWRs], and experimental fuels) have been reviewed. The review led to the conclusion that all evidence of cladding degradation could be related to reactor service. Ring tension tests were conducted on Zircaloy-2 cladding at room temperature. Ductility had decreased by about 10% from initial values near 30%, as a result of reactor irradiation. The residual ductility is quite adequate for post-irradiation fuel-handling operations for the relatively low-burnup fuel involved. Aluminium-clad uranium metal fuel developed blisters, presumed to be a result of reaction of uranium metal with water, but it was not certain whether the nodules occurred during reactor service or during storage. Hydrogen migration under the cladding could lead to formation of hydrides that could be potentially pyrophoric when exposed to air.

Procedures are outlined for preparation and evaluation of coupons to quantify general corrosion, including references to standards of the National Association of Corrosion Engineers, International, and American Society for Testing and Materials. Results of corrosion evaluations conducted at the BARC are reported, including general corrosion, electrochemical measurements, pitting corrosion, and crevice corrosion using crevice bent beam (CBB) specimens.

Water was sampled at several locations in the Tarapur fuel storage pool. Values of pH did not vary significantly, but water conductivity varied from 3.4 to $13.2 \,\mu$ S/cm.

Bacterial counts were conducted in water from a fuel storage pool in India. However, direct correlations to corrosion were not reported. Other investigators have reported difficulty in directly correlating bacterial counts with corrosion.

A Type 304 stainless tray used for more than 10 years in fuel-handling operations at the Tarapur pool was subjected to visual and metallographic examinations. Pit depths were less than 150 μ m. Pit clusters were denser around welds, but there was no evidence of crevice corrosion in the weld regions and no evidence of intergranular attack in heat-affected zones, even though the metal was highly sensitized. The trays were judged to be suitable for continuing service for at least another decade.

Simulation of fission product attack on Zircaloy cladding was applied at BARC to investigate effects of extending fuel burnup in PHWRs, referred to as SIM fuel (simulated high burnup fuel).

Ultrasonic testing was investigated at BARC as a method to inspect SS welds in fuel storage pool liners.

Elastomeric materials have occasionally failed in wet storage facilities. Results of studies of elastomeric ageing as a result of time/temperature and radiation, conducted in India and Canada, are reported to provide guidance to operators who may have applications that require durability of elastomeric materials.

2.6 Effects of gamma radiation on corrosion of candidate materials for nuclear waste disposal containers: titanium and copper

The Canadian waste disposal concept involves placing corrosion-resistant containers in vaults 500 to 1,000 m underground in granitic rock. Candidate materials include titanium and copper alloys. The expected gamma dose rate in the Canadian repository is <52 Gy/h. Gamma effects of corrosion are found to be minimal, and some effects of radiation appear to be beneficial. For titanium, irradiation inhibits crevice corrosion, but at high absorbed dose rates (>10,000 Gy/h) the rate of hydrogen absorption increases. At repository conditions, there is not an expectation of early failures by hydrogen-induced cracking.

For copper, impacts of radiation on container lifetime are minimal. Production of oxidizing radicals at dose rates <27 Gy/h has not caused increases in uniform corrosion rates. However, detrimental effects may occur at 10,000 Gy/h. There is no evidence in the literature that copper containers will be more susceptible to pitting or stress corrosion cracking as a result of radiation effects. Radiation is expected to have a beneficial effect on microbially influenced corrosion because it will sterilize the container surface and surrounding environment, preventing biofilm formation. Further studies also indicate that heating mitigates microbial populations, possibly as a result of both temperature and associated desiccation of the buffer material. In fact, lack of available water may be equal to or more important than radiation in reducing the microbial population in the repository. Modelling has been developed to predict radiation and environmental effects on container lifetimes.

2.7 Effects of gamma radiation on carbon steel in salt brines

Carbon steels have been identified as promising for high-level waste containers in a rock-salt repository. Fine-grained steel TStE 355 resisted pitting corrosion in salt brines. Linear corrosion rates at 150°C suggest that corrosion allowances of 5 mm would be required for sodium chloride brines and 15 to 35 mm for magnesium chloride brines for a service life of 300 years. A gamma dose rate of 10 Gy/h did not increase corrosion rates in the sodium chloride brine. In the magnesium chloride brine, radiation increased corrosion rates by factors of 1.3 to1.5.

3 Conclusions

Spent fuel storage and disposal is the most problematic part of the fuel cycle in the eyes of the public. Generally the technologies involved are not very sophisticated and thus some of the problems that have arisen have not been studied in great depth. Wet storage facilities continue to be the most common technology used for the management of irradiated fuel assemblies from power reactors, research and test reactors, and defence reactors. Some of the most important decisions that must be faced by the operators of these facilities involve the ageing degradation of materials in ageing facilities. A broad variety of fuel types, involving numerous combinations of fuel and cladding materials, are currently stored in these facilities that in many instances are at or near their design capacities and at or approaching their design lifetimes. Extending the licenses of such facilities as their regulatory periods expire is not a straightforward proposition, and answers to questions concerning the degradation and ageing of materials in spent fuel storage facilities, which may be posed by regulatory bodies, require a broadly based materials database. However, because examinations of radioactive materials are expensive, access to materials data and experience that provides an informed basis to analyze and extrapolate materials behaviour in storage and disposal environments, especially quantitative data, is sparse.

The results IAEA-TECDOC-1012 published at the end of the CRP in April 1998 taken together with the results presented in this report attempt to fill a real gap in the liturature. They are relevant to issues important to materials behaviour in wet storage technology and also address topics on materials behaviour in dry storage and repository environments, including the effects of radiation.

A general conclusion that can be drawn from the CRP is that detailed scientific studies of the degradation of materials in spent fuel storage facilities are few and far between. However, these limited studies are augmented by a wealth of qualitative information on the behaviour of materials in spent fuel storage facilities gathered together from visual and photographic records over the last 40 years. The overall assessment of quantitative and qualitative information available shows that with the exception of few isolated cases, such as the corrosion of aluminium clad fuel in water of less that optimum quality and the sensitization of some stainless steels, the chosen materials for both fuel cladding and facility components have behaved remarkably well. Nevertheless, there can be no substitute for detailed scientific investigations of the ageing degradation of materials in interim storage and final disposal environments and increasingly such studies will be needed to satisfy the demands of regulatory authorities.

Corrosion of sensitized advanced gas reactor fuel cladding in moist air: Evidence for incubation periods before the onset of intergranular cracking

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Abstract. AGR fuel cladding in reactors operating at temperatures between 350°C and 520°C undergoes radiation-induced segregation, which produces compositional profiles at grain boundaries. As a result of this sensitization, the material becomes susceptible to intergranular attack when exposed to moist air environments. This paper presents evidence for incubation periods that precede corrosion of stressed sections cut from sensitized fuel pins. The interaction of the stochastic cracking process and the test sample area is also considered in relation to penetration rates.

1. Introduction

AGR fuel cladding irradiated at temperatures between 350°C and 520°C becomes vulnerable to stress-assisted intergranular corrosion when it is exposed to moist air. This susceptibility to corrosion is attributed to neutron-induced depletion of chromium at grain boundaries [1]. Such corrosion has been responsible for fuel pin failures during handling in air-filled post-irradiation examination (PIE) facilities [2] and has been identified as a threat to fuel integrity during storage in uncontrolled atmospheres.

Experiments to investigate the corrosion of sensitized AGR fuel cladding in moist air have used either small tensile samples cut from highly sensitized regions of pin cladding or intact sensitized fuel pins. In the case of small tensile samples, a technique has been developed to quantify corrosion kinetics; this goes some way towards providing a fundamental understanding of corrosion in terms of system variables such as tensile stress, air humidity, and temperature. The technique has used post-test fractography of samples to establish crack depths and by further assuming zero incubation times and linear corrosion kinetics. The approach has enabled some crack penetration rates to be estimated for different humidities. Work performed at 35°C and 50°C has established a threshold relative humidity of ~14%RH for the onset of cracking. For excursions in relative humidity above this threshold level, under constant conditions:

 $P_{35} = 0.12RH - 1.73$ and $P_{50} = 0.37RH - 5.26$

where P_{35} and P_{50} are the clad penetration rates in μ m/d at 35°C and 50°C, respectively, and relative humidity, RH, is expressed in percent [3].

Although most of the estimated corrosion rates from whole-pin experiments were bounded by the above equations, isolated pins from large populations have cracked at rates faster than those defined by small specimen tests. This may result from either the stochastic nature of the corrosion process, which in turn is influenced by the respective areas of test pieces, or from the presence of variable incubation periods before the onset of corrosion cracking. The latter argument notes that regions of whole pins may have been stressed at upper shoulder anti-stacking groove (ASG) positions following discharge from a reactor, whereas the tensile samples cut between ASGs were only stressed at the time of insertion into the test apparatus. Because initiation/incubation is expected to depend on stress and environmental conditions, it is probable that a whole pin may have used up part, if not all, of the required incubation time before testing. Conversely, a small specimen would only begin to incubate when stress was applied at the start of a test in air. As a result, the assessment technique to evaluate corrosion in small tensile samples may have produced underestimates of cracking rates when compared to those from isolated whole pins.

The objective of the work described in this paper is to identify the presence or absence of incubation periods before the corrosion of samples of sensitized AGR cladding stressed under the same environmental conditions. The relative areas of test samples are also considered and in this way it may be possible to account for the discrepancies in corrosion rates between isolated test pins and small test pieces.

2. Experimental design

2.1. Apparatus

The environmental conditioning and tensile test apparatus have been described in an earlier report [2]. On the outside of the shielding, air at ambient temperature and humidity is drawn into the conditioning loop. Steam injectors, heaters, and chillers then respond to the temperature and humidity probes within the loop. A fraction of the conditioned air is deflected from continuous circulation within the loop and enters pipe work to the test chamber. Six cobalt-60 sources are spaced evenly on a pitch-circle diameter of 75 mm to produce a gamma dose rate of 0.7MRad/h at the test sample. The specimen and load train are attached to a NENE M3000S tensile machine, which has computer-controlled displacement and logging facilities. Specimen temperature and air humidity are recorded continuously throughout the test. Control systems are capable of $\pm 2\%$ at 10%RH and $\pm 4\%$ at 80%RH. Specimen temperature varies by $\pm 0.50^{\circ}$ C.

2.2. Test material

Tensile samples with a gauge length of 25.4 mm and cross section of 1.84 mm² were sparkmachined from defuelled sections of element 1 pins. Pins 5 and 31 were used from element 1, stringer B4272, discharged from Hinkley R4 after a stringer mean irradiation of 11.5GWd/tU. Offcuts from these samples were given an accelerated Strauss corrosion test to confirm sensitization [4]. Although samples were cut from between ASGs and were therefore unstressed, adventitious cracking during handling was further avoided by minimizing exposure to cave air; both pins and samples were stored in dry argon before testing.

2.3. Test procedure

The test specimen was placed in the tensile machine and held free of stress until the environmental generator achieved the desired temperature and air relative humidity. This section of the test schedule took ~2 hours before the specimen was loaded to 2.5% strain at an initial strain rate of 2×10^{-7} s⁻¹. The cross head was then halted and the decay in load was monitored for a predetermined period. Load cycling attributable to cave-air temperature changes was not observed. The incubation period was investigated by fixing the test conditions to 80%RH at 35°C and varying the hold period from sample to sample at intervals up to 30 days. At the end of the exposure period the crosshead was restarted and the specimen strained to failure.

2.4. Metallography

Both the outer surface and the fracture surface of samples were examined using a scanning electron microscope (SEM). Most attention was given to the fracture surfaces to identify cracking and estimate crack depths. Cracks appeared to initiate from the outer surface of the clad. The intergranular nature of cracking was distinctive and provided detection limits better than $5\mu m$.

3. Results

3.1. Tensile test data

Table 1 lists the tensile results from tests S38, S34, S35, and S15. These tests considered incubation effects and employed a humidity of 80%RH at 35°C with hold periods of 11, 13, 21, and 30 days after straining to ~1.3 limit of proportionality (LOP). Ductility measurements gave no evidence of cracking after the 11- or 13-day hold periods but gave strong indications of corrosion after the 21- and 30-day hold periods, with reductions in strain to failure to 11.5% and 2.5%, respectively

Parameter	Test						
	S38	S34	S35	S15			
Specimen ID	272/1/5/3a	272/1/5/4a	272/1/5/4	272/1/31/7a			
Irradiation temperature (°C)	362	371	371	410			
$LOP(N/mm^2)$	382	335	346	335			
Strain (%)	19.0	20.1	11.8	2.5			
Stress at hold (N/mm ²)	508	379	416	487			
$\sigma_{\rm H}/\sigma_{ m LOP}$	1.33	1.13	1.20	1.45			
Hold period (days)	11	13	21	30			
Depth (µm)	ND	ND	219	240			
Section crack	No	No	No	Yes			

TABLE 1. TESTS TO INVESTIGATE THE INCUBATION PERIOD FOR CRACKING AT 35°C AND $80{\pm}1.5\%{\rm RH}$

ND – cracking not detected

3.2. Metallography

The four samples tested at 80%RH and 35°C, which aimed to investigate the influence of hold period on crack depths, were examined by SEM. Sample S38 (11 days hold) showed ductile tearing at rupture but provided no evidence of intergranular cracking on either the fracture surface or the outer surface. Cracking and spallation of the carbonaceous overlay was apparent. A similar set of results was obtained on sample S34, which had been given a 13-day hold. Intergranular cracking on the fracture surface to a depth of 219 μ m was clear on sample S35, which had been held for 21 days under the same test conditions (Figs. 1a and 1b). It should also be noted that samples S34 and S35 came from the same section of irradiated fuel pin and are expected to be equally sensitized. The results from sample S15 have been reported earlier [2]. In this case, the maximum single-sided depth of attack to 240 μ m assumed that any observations of full section cracking arose from overlapping lobes of attack initiated at both inner and outer clad surfaces. The results from these four tests provide evidence for an initiation/incubation period that precedes the cracking of sensitized fuel cladding at 80%RH and 35°C.

4. Discussion

If incubation periods exist before the onset of propagating corrosion, they can lead to an underestimation of crack penetration rates when experimental techniques are not capable of detecting the start of cracking. It is often assumed that incubation periods are of limited duration in an extended test [5] and as a result, crack kinetics are only marginally underestimated. However, larger errors in estimates of cracking rates can arise if the incubation period does represent a significant proportion of the total test duration; rates can then be underestimated by dividing the depth of attack by the total test duration.

In this work, it has not been possible to perform a single test to address incubation before corrosion cracking of sensitized AGR cladding in moist air. None of the accepted techniques, such as acoustic emission or electrochemical noise methods, capable of detecting the onset of cracking could be used in the severe environments employed in this work. As an alternative, a limited number of experiments have been performed using separate but equivalent specimens exposed to the same test conditions for different durations. Although variability in corrosion from specimen to specimen cannot be discounted, the results from these tests indicate an incubation period of ≤ 13 days at 80%RH and 35°C.

The development of intergranular cracks is a stochastic process. Given that all extraneous conditions (e.g., temperature, relative humidity, stress level) are the same, there will be a higher probability of obtaining cracking rates above a set value in large specimens than in small. Superficially this argument can explain the apparent discrepancies in penetration rate between small tensile samples and isolated whole pins, but it can be demonstrated that this explanation is unlikely to be correct [6].

First consider the maximum discrepancy between small specimens and whole pins based on their relative surface areas. For a small specimen, let the probability of finding a cracking rate greater than or equal to a set value P_u , be p. Thus the probability of not finding this rate is (1-p). Imagine that the larger specimen is made up of q small specimens where q is the ratio of surface areas of the large to small samples.



Figure 1a. Cracking on fracture surface at S35 held for 21 days at 80%RH, 35 °C. Magnification X 70.



Figure 1b. Same area as Fig. 1a showing a lobe of intergranular facets surrounded by ductile tearing. Magnification X 210.

The probability of not finding the cracking rate P_u in this larger (composite) specimen requires that the rate is not obtained in any of its component specimens, i.e., this probability is $(1 - p)^q$. Thus the probability (P_u of finding or exceeding the cracking rate P_u in the large specimen) becomes

$$\phi = [1 - (1 - p)^q].$$

A simple comparison of surface areas of a small tensile specimen (~250 mm²) with a whole pin (~5 x 10⁴ mm²) gives q ~200. If, on the basis of small-specimen data, a penetration rate P_u was expected only once in twenty tests (i.e., p = 0.05), whole pin samples would be expected on the basis of the above equation, to experience this rate in every test (i.e., $\phi ~ 1$). The reason this argument becomes unsound is because the derivation of the equation assumes that each composite specimen experiences identical environmental conditions. Although it is conceivable that this could be so for clad temperature and relative humidity, it will certainly not be the case for the level of stress experienced by the clad in a whole pin.

For whole pins, the peak sensitization of the microstructure is confined to the irradiation temperature range of 380°C to 440°C, and the stresses are only expected at the upper shoulders of ASGs, where fuel is in contact with the cladding. Because both stress and sensitisation are required for attack, vulnerable sites correspond to only six samples. Furthermore, each of these stressed areas is only ~50 mm², which gives a composite sample with a total area of 300 mm². This space can be compared with the surface area of a small tensile specimen of ~250 mm². Thus, within the uncertainty of clad/fuel contact areas, it can be appreciated that q ~ 1 in this case, and it is expected that small specimens will be capable of modelling the behaviour of pins.

Clearly, further work is required to investigate the influence of system parameters such as temperature and humidity on incubation periods. This work may provide some mechanistic understanding of the early part of corrosion as well as allowing a full quantification of cracking rates in small-specimen tests. As an additional benefit, storage constraints may be reduced if it can be shown that incubation periods can be recovered by changes in environmental conditions. As a result, further work is planned to investigate the effect of relative humidity cycling on cracking of small samples cut from sensitized AGR fuel cladding.

5. CONCLUSIONS

Conclusions are as follows:

- Tests at 80%RH and 35°C in air have indicated an incubation period of ≥13 days, which precedes the onset of propagating corrosion in sensitized AGR fuel cladding.
- The observation of an incubation period can account for the discrepancies in penetration rates between small specimens and isolated test fuel pins.
- Interaction between the stochastic corrosion process and test sample area is not responsible for these variations in penetration rates.

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Addendum

GRAIN BOUNDARY — CHEMISTRY (MAJOR ELEMENT CHROMIUM) — THERMALLY INDUCED

Localized variations in major alloy elements can introduce susceptibility to intergranular stress corrosion cracking (IGSCC). These variations may result from thermal equilibrium effects and from non-equilibrium RIS.

Depletion of chromium at grain boundaries introduces a susceptibility to IGSCC, which may then be initiated during exposure to aggressive environments. The chromium depletion is found adjacent to chromium-rich carbide/nitride precipitates at grain boundaries; it is particularly evident at lower ageing temperatures where the bulk diffusion of chromium is slow. At higher temperatures, rapid diffusion of chromium from the grain matrix can infill the chromium-depleted region and remove sensitization. This form of sensitization to corrosion was first pointed out by Bain et al. in 1933 [A.1], and since that time much experimental and theoretical work has been performed on the topic (e.g., [A.2, A.3]). Most of this work is beyond the scope of the current document, and the reader is referred to one of the many extensive reviews on the subject (e.g., [A.4]). In this addendum, only some of the more important issues relevant to thermally induced sensitization of SS used as fuel cladding are considered.

At a particular service temperature, the final volume fraction of the chromium-rich precipitates and the initial level of chromium depletion will depend on the amount of carbon and nitrogen interstitial in solid solution that exceeds its solubility limit at that temperature. This in turn will depend on various parameters, such as the initial alloy composition, the solution/fabrication heat treatment and temperature, the cooling rate, and the final service temperature. Each of these parameters may ultimately determine the extent of chromium depletion and the susceptibility to IGSCC. For example, alloys with high carbon and nitrogen specifications (e.g., AISI 304), cooled rapidly from a high solution-treatment temperature, such as 1100°C, could have high levels of interstitial elements in solid solution and form chromium-rich precipitates and deplete chromium at grain boundaries at service temperatures in the range of 400°C to 700°C. Clearly, steel grades with low carbon and nitrogen (e.g., 304L, 304NG) are preferred to minimize this sensitization. Stabilized steel grades, with elements such as niobium or titanium deliberately added to combine with the interstitial during an intermediate anneal, may prevent the low-temperature formation of chromium-rich precipitates at grain boundaries. Stabilization treatments have been successful for many alloys, such as the 20Cr/25N1/Nb stainless steel used for AGR fuel cladding.

The microstructural changes and susceptibility to IGSCC are often summarized by time/temperature/sensitization (TTS) diagrams. An example is shown schematically in Fig. A1, where two separate areas are outlined for high (a) and low (b) interstitial levels. Diagrams of this form were traditionally obtained by combining metallography with the results of accelerated corrosion tests such the Strauss test (ASTIVI A 202-77a E) and the Huey tests (ASTIM A 262-77a C). The former test produces anodic dissolution of chromium-depleted grain boundary regions, and the latter test attacks both denuded zones and precipitates. More recently, high-resolution transmission electron microscopy, with compositional analysis perpendicular to grain interfaces, has also been used to confirm the extent of chromium depletion (e.g., [A.5]).

Considering the sensitization field for the high carbon and nitrogen steel, shown in Fig. A1, an isothermal exposure to time t, at temperature T, leads to chromium-rich precipitate formation and chromium depletion at grain boundaries. This metallurgical condition persists

Strauss test results taken from Samans et al. [A.7].at T, until time t, when matrix diffusion of chromium sufficiently infills the chromium depletion to 'heal' the microstructure.



Figure A1 Sensitisation fields in both high (a) and low (b) C+N stainless steel.



Figure A2 Influence of heat treatment on sensitisation of 18/8 stabilized stainless steel containing 0.059C and 0.32Ti.

For temperatures greater than T_1 , either the interstitial solubility is high enough to preclude precipitation, or, alternately, chromium-rich precipitation is accompanied by simultaneous healing. At the lower temperature, T_2 , many thousands of hours of exposure may be required for the nucleation and growth of chromium carbides/nitrides and the onset of sensitization. Unfortunately, for many grades of SS, data describing fields for low-temperature sensitization are sparse, and extrapolation from higher temperatures is often required. An example of this approach was given by Andresen [A.6] for the heat-affected zone of a pipe weld in AISI 304 steel. Here, it was concluded that low temperature sensitization could develop after many years of plant operation at low temperatures (e.g., 10 years at ~300°C in certain heats of Type 304 stainless steel). For irradiated components, such as fuel cladding, vacancy concentrations above thermal equilibrium levels may also facilitate lowtemperature sensitization.

Thermally induced sensitization may be present in SS fuel cladding after discharge from a reactor, and this may threaten fuel integrity by IGSCC during pond storage. Each cladding type should be

considered separately, but as a generalization, unstabilized high-carbon grade steels such as AISI 304, which have been exposed at temperatures greater then 600°C, will be healed after 1 year of service, whereas the same material would require about 10 years of service to heal sensitization at 550°C. As a result, it can be seen that for unstabilized SSs thermally induced sensitization may be expected in cladding discharged at temperatures below 550°C to 600°C. Stabilized SSs, such as the 20/26/Nb alloy used for AGR cladding, have not developed the chromium depletion associated with precipitation at temperatures above 550°C by the time of fuel discharge at ~6 years. Similar behaviour is expected for 18/8 titanium stabilized steels, provided that the appropriate intermediate anneal is carried out. This behaviour is shown by the TTS diagrams in Fig. A2, which is based on work published by Samans et al. [A.7]. It is also worth noting that unstabilized stainless steels that contain high carbon and nitrogen levels could also develop sensitization during slow cooling from a period of operation at high temperatures.

Phosphorus is an important segregant that may have a significant effect on corrosion of austenitic SSs in oxidizing media. IGSCC in high temperature and high-pressure water can often be inferred from this behaviour, and the appropriate TTS diagrams are available. An example is given by Marshall [A.8] for 18/10 steel, and this shows that, following exposures above 650°C, corrosion attributed to phosphorus segregation was not found.

5.1. Summary

Many of the changes in material condition described above can be found in the various types of austenitic SSs employed as fuel element cladding. As a result, all grades, including stabilized SSs, should be considered as susceptible to IGSCC during pond storage, and it would be prudent to adopt non-aggressive water chemistries. With the exception of steels bearing high carbon and nitrogen, which have been slowly cooled from high operating temperatures and developed sensitization by passing through the nose shown on the TTS diagram, it appears that those at greatest risk will have seen extended exposures at temperatures less than 550°C.

5.2. Implications and correlations to stress corrosion cracking

5.2.1. Grain boundary chemistry – thermally induced

Slow cooling of high carbon and nitrogen 304 SS from high temperature may have been responsible for sensitization of 304 clad fuel discharged from an Oak Ridge National Laboratory (ORNL) GCR. This particular fuel suffered intergranular corrosion during water storage and "hot cell" rot in moist air [A.9].

No examples of LWR clad corrosion have been reported during pond storage. Thermally induced sensitization may in this case have been delayed by the combination of low interstitial levels, low operating temperatures, and short exposure times when compared to the time for low-temperature precipitation of chromium carbides.

5.2.2. Grain-boundary chemistry – radiation-induced segregation

The 20Cr/25NI/Nb stabilized steel used as cladding for AGR fuel in used in a reactor operating at temperatures from 350°C to 760°C. Extensive microstructural work and accelerated corrosion testing have shown that sensitization to IGSCC develops in this steel over the temperature range of 350°C to 510°C, with the peak effect at a temperature of ~420°C. The principal mechanism is RIS and chromium depletion at grain boundaries. Fuel storage in the reactor pond uses water dosed with boric acid (for criticality control), with sodium hydroxide added to return the pH to 7. Chloride and sulphate levels are maintained below 1 ppm with a water temperature of 27°C. This phase of storage is short

term, covering about 100 days before the fuel is transported to Sellafield for reprocessing, and no significant corrosion has been observed. Interim storage at Sellafield was initially conducted in demineralized water and was found satisfactory, provided chloride and sulphate were maintained at low levels. Maintaining these levels proved difficult for open ponds at coastal locations, and occasional excursions in chloride up to 6 ppm produced IGSCC in a proportional sensitized AGR cladding. For this example, pond water chemistry has now been adjusted to a pH of 11.4, with chloride and sulphate at <0.5 ppm. This levl has provided excellent storage performance for up to 8 years [A.10].

Although LWR stainless steel cladding is expected to develop sensitization by RIS at irradiation temperatures below \sim 500°C, no examples of IGSCC have been reported after long storage times. Under these circumstances, it would be prudent to continue intermittent monitoring of clad integrity and water quality at a frequency that detects the onset of corrosion and thereby provides a sufficient lead time for the introduction of remedial action.

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Temperature implications for irradition-assisted stress corrosion cracking during spent fuel wet storage of stainless steel

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Abstract. IASCC of austenitic SS is known to occur in water environments at LWR temperatures near 288°C, but very little information exists to indicate susceptibility for irradiation and testing at non-LWR temperatures. In the present work, IASCC behaviour is assessed for spent-fuel storage based on the temperature dependencies of unirradiated intergranular (IG) SCC, the influence of RIS grain boundary chemistry, and the influence of irradiation on micromechanical deformation mechanisms. Implications for spent-fuel storage are reviewed with regard to storage conditions (temperatures less than 50°C) and irradiation conditions before storage. The relatively low temperatures for storage are distinct from the high temperatures for LWR operation. IGSCC of sensitized SS in the absence of irradiation exhibits maximum growth rates at temperatures near 200°C under conditions of anodic dissolution control, while analysis of hydrogen-induced cracking suggests a peak crack growth rate near 100°C. Although there is a potential for environmental cracking under anodic and hydrogen control, the necessary conditions for cracking can be avoided. Control of water impurity levels prevents anodic cracking, and low-stress intensities prevent hydrogen-induced cracking. The varied inventory of SSs requiring storage includes a wide range of irradiated conditions, grain boundary chemistry, and mechanical behaviour. Irradiation experiments and model predictions indicate that RIS dominates at high temperatures, low neutron fluxes, and high neutron fluences. Chromium depletion may be significant at temperatures below 100°C for irradiation doses greater than 10 displacements per atom (dpa). Irradiation effects on strength and ductility are not strongly dependent on temperature between 50°C and 288°C. However, temperature does significantly affect radiation effects on SS microstructural detail and micromechanical deformation mechanisms. Intergranular failure promoted by time-dependent deformation (i.e. creep) may influence LWR in-core cracking but is not expected during 50°C storage of spent fuel.

1. Introduction

IASCC occurs above a critical neutron fluence in LWR water environments at 288°C [1-5]. The fluence threshold for cracking depends on complex environmental and material conditions, but is most clearly established for Type 304 SS in oxygen-containing water. Cracking has not been extensively evaluated at lower temperatures, but is of interest for spent-fuel storage, for startup and shutdown of LWRs, and for the design of fusion reactors. Many temperature-dependent processes are expected to affect IASCC susceptibility [6,7]. This paper examines temperature-dependent material and environmental parameters that may influence IASCC in austenitic SSs. Two temperature issues are evaluated: (1) temperature-dependent mechanisms for environmental effects during storage in water, and (2) temperature-dependent mechanisms for radiation effects on fuel condition during service of components before storage.

2. Low-temperature stress corrosion of unirradiated stainless steels

Unirradiated sensitized SSs typically exhibit a peak crack growth rate near 200°C, as shown by Andresen [8]. Maximum crack velocities were established by slow-strain-rate tests (SSRTs) and fracture mechanics tests under controlled environmental and material conditions. The IGSCC temperature dependence results from a complex interaction among corrosion potential, solution chemistry, and chemical equilibria (e.g., pH, ionization, and solubility). Above 200°C, crack growth velocity increases with increasing temperature for high-oxygen water, but decreases with temperature as O_2 is reduced to 0.2 ppm, as illustrated in Fig. 1. The temperature dependence for crack growth rate is parallel to the temperature dependence for iron solubility in the lower oxygen case [8]. At temperatures below 200°C, the crack growth velocity decreases with decreasing temperature for both environments. The temperature dependence at low temperatures does not reflect any single dominant kinetic process.

The evidence supporting a decreasing crack growth rate for temperatures below 200°C is extensive [8-12]. On the other hand, the evidence supporting a decreasing crack growth rate for temperatures above 200°C is sometimes contradictory. These contradictions can, in most cases, be resolved through consideration of high or uncontrolled concentrations of oxygen, impurities, or both. Attempts have been made to assign activation energies to crack growth rate and to relate the energies to transport in aqueous solutions (as compared to oxide films). However, the complexity of the temperature-dependent processes likely precludes assigning a single dominant activation mechanism [8].

Impurities, such as sulfates and chlorides, strongly increase crack growth rates [13] at low temperatures, as shown in Fig. 1. Crack growth rates in deionized water (DIW) have a maximum rate of about 4×10^{-6} mm/s, whereas in impure water, they can exceed 10^{-5} mm/s. For sensitized Type 304 SS, sulfate additions are more aggressive than chloride addition at temperatures less than 200°C [8]. Aggression of the two impurities is nearly equal above 250°C. Accelerating effects caused by impurities can result in crack growth rates at about 60°C that are comparable to and even greater than growth rates at high temperatures.

Material and test conditions can also strongly impact cracking susceptibility and growth rates. The extent of grain-boundary chromium depletion (degree of sensitization) controlled by bulk carbon contents and heat treatments significantly influences IG crack initiation and growth [14]. Material strength and surface condition can increase SCC susceptibility. For example, shot peening can promote cracking at low temperatures by reducing the initiation time for cracking. Finally, IGSCC also depends on test conditions such as strain rate. Critical grain-boundary chromium concentrations for IG cracking in high-temperature water have been shown to increase from ~14% to 17% when the test strain rate was reduced from 1×10^{-6} s⁻¹ to 2×10^{-7} s⁻¹ [15].

The examples reviewed above have emphasized dissolution-controlled cracking mechanisms expected for sensitized materials in oxidizing environments. However, hydrogen may play an important role in low-temperature IGSCC and has been proposed as contributing to IASCC [5]. Hydrogen can become enriched in SSs from several sources, including corrosion reactions and radiation-induced transmutations. A three-fold increase to 4,500 appm hydrogen was detected for a Type 304 SS irradiated to fluences from 1.9×10^{18} n/cm² (E>1 MeV) to 9×10^{21} n/cm² (E>1 MeV) in high-temperature water [16]. Internal hydrogen concentrations can reach much higher levels during irradiations with a fusion neutron spectrum and impact subcritical crack growth [17]. Hydrogen-induced crack growth rates were predicted to increase with temperature reaching a maximum rate near 100°C, then decrease sharply at higher temperatures as shown in Fig. 2. Although the predicted crack growth rates are fast, the assumed stress intensity for the calculations was 115 MPa-m^{0.5}, which is high for structures thinner than 1 cm. A stress intensity of 115 MPa-m^{0.5} requires a 1-cm flaw at a stress of about 800 MPa. These flaw sizes and stresses are unrealistic for spent-fuel conditions.



Figure 1. The temperature dependence of crack growth rate as compiled by Jones and Henager [13] for sensitized steel. The curves labelled for oxygen content are obtained in deionized water. The addition of sulfates and chlorides is seen to increase the rates.



Figure 2. Temperature dependence of predicted hydrogen-induced crack growth [17].

3. Stress Corrosion cracking of stainless steels irradiated at low temperatures

Only a few experiments have addressed SCC of alloys irradiated in water at temperatures less than 288°C. The limited studies indicate that SCC can occur in irradiated SSs at temperatures below 288°C, particularly at test temperatures down to 200°C. However, the observed IG crack growth rate is reduced as the temperature is reduced below 200°C.

3.1. Low-temperature dependence for low-dose neutron exposure

Irradiated Type 304 SSs from a Savannah River Reactor tank have been tested for SCC susceptibility [18]. Specimens were exposed to about 1 dpa of neutron irradiation at 150°C. One dpa corresponds to about 7×10^{20} n/cm² (E>1 MeV). Tests were conducted in water at 105°C with a pH of 5 and with an impure (compared to LWR) water chemistry plus 2 to 6 ppm O₂. IASCC was not observed during post-irradiation SSRTs (strain rates >10⁻⁷ s⁻¹).

Significant IG fracture was observed in high purity and commercial purity grades of Type 304 SS after irradiation at 50°C to a fluence of 3×10^{21} n/cm² (E> 1 MeV), i.e., 4 dpa [19]. The IG fracture was induced using SSRT at 2.5×10^{-7} s⁻¹ in 288°C water containing 32 ppm dissolved oxygen and having a conductivity of 0.1 µS/cm. Similar tests of nuclear-grade Type 316 SS showed no IG fracture.

3.1.1. Low-temperature dependence for high-dose neutron exposure

A Type 316 SS was irradiated to 8 dpa, and SCC evaluated using SSRTs, at a series of temperatures [20]. The higher temperature tests (irradiations at 330°C or 400°C, SSRTs at 300°C) showed more IG cracking compared to those at the lower temperature (irradiations and SSRTs at 60° C or 200°C). Specifically, the fracture morphology after SSRTs indicated no IGSCC at 60°C, mixed mode at 200°C with some IG features, and predominantly IG fracture for SSs irradiated at 330°C or 400°C.

Low-temperature SSRTs were also conducted on a Type 316 SS irradiated to 40 dpa in an experimental fast breeder reactor at 424°C [21]. Post-irradiation tests showed an increase in SCC with temperature. Fracture surface analysis indicated that the percent SCC (IG plus transgranular) was 0%, 5%, and 25% at 60°C, 200°C, and 300°C, respectively. Uniform elongation decreased from 6% at 60°C to 0.4% at 300°C. An SSRT in air did not exhibit the loss in ductility or IG fracture measured for the 300°C test in water.

3.1.2. Proton irradiation behaviour

Proton irradiation and post-irradiation testing of an ultra-high-purity Type 304L SS has suggested a decrease in IASCC susceptibility as the irradiation temperature was decreased from 400°C to 200°C [22]. IASCC susceptibility was indicated by the number of IG cracks on the irradiated surface of 288°C SSRT samples. IGSCC was documented after the 200°C irradiation, but much more extensive IG cracking was seen after a 400°C irradiation. Specimens were irradiated to 1 dpa and tested at a strain rate of 3.6×10^{-7} s⁻¹ in 2-ppm O₂ water at 288°C for both irradiated conditions.

4. Temperature dependence of irradiated material characteristics

For the purposes of this review, the influence of radiation on material characteristics will be divided into those that affect grain-boundary microchemistry and those that affect grainboundary mechanical behaviour. The evidence supports the conclusion that IASCC susceptibility is worse as the irradiation and test temperature is increased.

Grain-boundary RIS (e.g., chromium depletion) decreases with irradiation temperature below 288°C because of reduced survival of radiation-produced point defects (i.e., vacancies and interstitials). Significant changes in interfacial chemistries cannot be produced without the creation and relatively long-range diffusion of these point defects.

Irradiation affects mechanical behaviour on a macro- and micromechanical level. On a macromechanical level, irradiated yield strengths have a weak temperature dependence below 288°C, and uniform ductilities during SSRT in water exhibit a modest improvement with decreasing temperatures below 288°C. Less is known about irradiation effects on the deformation micromechanics, in particular, the stress-induced interactions between network dislocations, irradiation damage, and grain boundaries. Temperature-dependent processes will affect strain localization during deformation and dislocation interactions with irradiation-induced microstructural defects. Irradiations at 60°C versus 300°C will produce significantly different microstructural features and impact properties such as work hardening and irradiation creep.

4.1. Radiation-induced segregation model predictions and experimental results

Model predictions based on the inverse-Kirkendall mechanism and reference parameters recommended by Perks et al. [23] have been used to evaluate major alloying element segregation. The predicted temperature dependence at low temperatures [24] is controlled by mutual recombination of irradiation-produced self-interstitials and vacancies. In particular, RIS temperature dependence is a function of the assumed migration kinetics of the slowest defect, namely, vacancies. The present study uses measured temperature dependence of grain-boundary chromium depletion and nickel enrichment induced by ion or proton irradiation at low temperatures. The predicted grain-boundary concentrations were convoluted to take into account the field-emission-gun scanning-transmission electron microscopy (FEG-STEM) beam profile width. The inverse-Kirkendall predictions can then be compared directly to the FEG-STEM grain-boundary measurement.

4.1.1. Ion irradiation

The effect of irradiation on grain-boundary microchemistry in a microcrystalline SS was characterized as a function of temperature (180°C to 550°C) with Ni⁺⁺ ion irradiation and FEG-STEM analysis. Irradiations were conducted at a displacement rate of 5×10^{-3} dpa/s to a dose of 10 dpa. Irradiation procedures and material descriptions have been reported previously [25]. Specimens were analysed using a Vacuum Generator HB501 dedicated STEM and an energy dispersive X ray spectrometer. A through thickness resolution of 3 nm was obtained for microchemical analysis. The matrix iron, chromium, and nickel concentrations were assumed to be 59%, 21%, and 20%, respectively, to be in accord with matrix concentrations measured with FEG-STEM analysis.

Temperature dependencies of the measured grain boundary chromium and nickel concentrations are illustrated in Fig. 3. RIS is not effectively suppressed at 10 dpa until temperatures are lowered below 300°C. Model predictions of grain-boundary chromium and nickel concentrations are also shown in Fig. 3. The effect of the assumed vacancy migration energy is demonstrated. A value of 1.28 eV [26] is commonly assumed for austenitic alloys,

although annealing measurements on SSs indicate 1.17 eV [27]. In the present analysis, 1.15 eV is considered a reasonable estimate based on defect physics experiments [27]. A value of 1.0 eV is included to illustrate sensitivity to lower values of the vacancy migration energy and indicate the value for a better empirical fit to the RIS measurements. The damage efficiency for producing freely migrating defects by nickel ions is expected to be a few percent [28], and 3% is used in Fig. 3.



Figure 3. The temperature dependence of measured and predicted grain boundary concentrations of (a) chromium and (b) nickel, induced by ion irradiation at 10 dpa.

4.1.2. Proton irradiation

Similar to ion irradiation, proton irradiation [29] has been used to document the temperature dependence of RIS in an austenitic stainless alloy. Grain-boundary chromium and nickel concentrations measured by Auger electron spectroscopy (AES) are shown in Fig. 4. Dose level was considerably less for the proton study at 0.5 dpa, but a strong temperature dependence was observed as irradiation temperatures dropped below 400°C. Model predictions accurately track data using a vacancy migration energy of 1.15 eV and a damage efficiency of 10% for protons. Therefore, the model qualitatively predicts the temperature dependence for both ion irradiation and proton irradiation assuming the same material parameters. The apparent vacancy migration energy is in the range of 1.0 to 1.15 eV.

4.1.3. Neutron irradiation predictions

Comparable temperature-dependent RIS data are not available for neutron-irradiated SSs, but prior work [30] has shown that the inverse-Kirkendall model can reasonably predict chromium depletion as a function of dose at 288°C. Predicted low-temperature segregation behaviour is presented in Fig. 5 for temperatures from 50°C to 300°C and for doses up to 30 dpa. Significant chromium depletion is predicted during neutron irradiation at low temperatures; for example, chromium levels drop to less than 14% at 100°C as the dose exceeds 10 dpa.



Figure 4. The temperature dependence of grain boundary concentrations of chromium and nickel induced by proton irradiation at 0.5 dpa.



Figure 5. Predicted grain boundary concentrations of chromium for neutron irradiation for a damage rate of 3×10^{-7} dpa/s.

The effect of radiation from different reactors is shown in Fig. 6 for the Fast Flux Test Facility (FFTF) reactor, advanced test reactor (ATR), BWR, and AGR. RIS induced during LMR exposure such as in FFTF is more than that for the BWR exposure because of a higher irradiation temperature. Similarly, the AGR exposure produces more RIS because of a higher temperature and a lower damage rate compared to the BWR condition. The ATR produces the least RIS because of the high damage rate and low irradiation temperature.



Figure 6. Effect of damage rate and temperature on predicted grain boundary concentrations of chromium at 1 dpa.

4.2. Low-temperature deformation

The effect of irradiation on deformation of austenitic SSs is evident in both macro- and micromechanical behaviour. Yield strength and ductility are strongly affected by irradiation and test temperature. In addition, dynamic irradiation and the evolving microstructural changes alter the micromechanics of deformation and may play a significant role in IASCC. These dynamic thermal processes will occur during service exposure but will not be significant during storage.

4.2.1. Strength

Yield strength of an austenitic SS increases with increasing irradiation fluence and has a maximum effect when irradiation exposure and mechanical testing is conducted at ~300°C. A typical strength dependence [31] on temperature for a highly irradiated steel is shown in Fig. 7. Radiation strength rapidly decreases with increasing temperature above 300°C, but decreases weakly with decreasing temperature below 300°C. The temperature dependence of the microstructural components that cause hardening [32] at 7 dpa is shown in Fig. 8. Yield strength in Fig. 8 is predicted to be nearly independent of temperature below 300°C. However, the relative importance of specific hardening microstructures does change. At temperatures less than 300°C, the Frank loop influence on strength decreases, while the black dot component increases. IGSCC processes that depend on the material strength level should not be strongly affected by temperature, but processes that depend on microstructural details may be strongly dependent on temperature.

4.2.2. Ductility

Tensile ductility decreases with increasing irradiation fluence and reaches a minimum near 300° C at high irradiation dose. Temperature effects on uniform elongation [31] are shown in Fig. 7 for an irradiated SS. The increase in elongation at temperatures above and below 300° C is consistent with the observed decrease in strength noted in Fig. 7. Results for a specific irradiation series on a Type 316 SS [33] are shown in Fig. 9. The data reflect the lack of temperature dependence for irradiated yield strength and an increase in ductility with temperatures below 300° C to 400° C. A comparison of uniform and total elongation indicates that work hardening is negligible near 60° C (i.e., the uniform elongation is nearly equal to the total elongation). Mechanical behaviour at low irradiation and test temperatures ($\leq 150^{\circ}$ C) is quite different from behaviour at high irradiation and test temperatures ($\geq 300^{\circ}$ C).

4.3. Deformation and fracture modes

Deformation modes affect both mechanical and environmental fracture. When stressed, irradiated SSs deform by competitive mechanisms of IG and transgranular processes. Matrix deformation can be either uniform or localized. Localized channels form at high temperature and localized twins form at low temperatures. Competition in deformation modes influences grain-boundary mechanical failure and is expected to influence environmental cracking. Interpretation of IASCC behaviour must include considerations of mechanical aspects for IG cracking that accompany IGSCC. During service exposure, the high temperature and active irradiation flux promote creep. During storage at low temperature, creep processes are suppressed but localized deformation may still occur.



Figure 7. The trend for yield strength and uniform elongation of irradiated stainless steels [31].



Figure 8. Predicted yield strength contributions from measured components of irradiated microstructure at 7 dpa [32].



Figure 9. Tensile properties of an irradiated austenitic stainless steel. Open and closed symbols represent solution annealed and cold-worked conditions, respectively. Circles indicate yield stress, and squares represent ultimate tensile strength [33].

4.3.1. Microscopic deformation

Irradiation defect microstructures are known to promote localized deformation in SSs. Dislocation channelling has been observed at high temperatures for post-irradiation and inreactor deformation. Dislocation channelling and channel fracture have been documented [34] at intermediate temperatures (about 300°C to 400°C), at high neutron fluence, and at high stress (strain rates appropriate for measuring tensile properties) as illustrated in Fig. 10. Stainless alloys irradiated by protons [35] or by heavy ions [36] also exhibit dislocation channels after SSRTs at 288°C. Ion-irradiated materials (to a dose of 5 dpa) show a transition to predominately twinning deformation as test temperatures are reduced to ambient. The above evidence documents the highly planar deformation that occurs in irradiated austenitic SSs. This localized deformation mode will create high stresses and strains at grain boundaries and may contribute to IASCC both during service exposure at high temperature and during storage at low temperature.

4.3.2. Macroscopic deformation

Irradiation creep can enhance deformation rates and stress relaxation during in-core IASCC. In-core creep rates of $\sim 2 \times 10^{-10}$ s⁻¹ have been measured [37] in stainless-alloy, helical springs stressed to 100 Mpa at 280°C. Similarly, creep strain greater than 10⁻³ was measured [38] for a 25% cold-worked, Type 316 SS at 60°C. Assuming a steady-state creep rate, the corresponding creep rate is about 2×10^{-10} s⁻¹. A low-temperature creep mechanism based on transient survival of point defects was proposed to account for the unexpected large creep strain at 60°C. Model predictions for an annealed SS indicated that the steady-state irradiation creep rate can vary from 10⁻⁹ s⁻¹ at 300°C to 10⁻¹² s⁻¹ at 60°C [39]. These measurements and model predictions suggest that in-core, irradiation creep will influence temperature-dependent stress relaxation and the micromechanics of localized deformation.

Post-irradiation SSRTs are typically run at LWR temperatures and strain rates faster than 10^{7} s⁻¹, whereas in-core strain rates controlling IASCC initiation and propagation are probably as low as 10^{-10} s⁻¹. Bulk deformation at such low rates may promote localized strain in channels and create stress concentration and affect grain-boundary sliding. The stress and temperature dependencies of the fracture behaviour in Type 304 SS irradiated to a high, fast-neutron fluence are shown in Fig. 10 [40]. A region of unstable grain-boundary crack propagation can be seen, reaching temperatures to 300°C. This propagation is promoted at lower stresses and lower strain rates. Boundaries for the individual fracture-mode regions are diffuse and depend on irradiation and test conditions. A transition from transgranular to IG fracture as strain rates were decreased to ~ 10^{-6} s⁻¹ was reported [41] for irradiated SS during SSRTs in 300°C argon. This "mechanical" failure along grain boundaries in irradiated SSs at this low temperature has not been reproduced. The few post-irradiation tests at strain rates down to ~ 10^{-7} s⁻¹ indicate that a water environment is required for IG fracture. However, SSRTs have not been performed at strain rates approaching in-core rates of 10^{-9} to 10^{-10} s⁻¹.

The fracture mode of irradiated SSs has been analysed using unirradiated fracture maps [42] and knowledge of radiation effects on strength and creep rupture time [7]. Fracture modes for unirradiated Type 316 SS are shown in Fig. 11. IG fracture is not expected for fracture times less than 10^8 s (3 years) and temperatures less than 450° C. However, when irradiation effects shift fracture-mode boundaries, mechanical IG fracture is predicted for the upper temperature range of LWRs for fracture times greater than 3 years. As shown in Fig. 12, IG fracture is not expected in LWRs, but IG mechanical damage may influence IG environmental cracking. These high-temperature creep processes will not directly affect cracking at low storage temperatures. However, the susceptibility of irradiated SS may be affected by early stages of IG damage that occurred during service.



Figure 10. Fracture map as proposed by Bloom [40]. At $300 \,^{\circ}$ C, the fracture mode is expected to change from channel fracture to grain boundary fracture as the stress and strain rate are decreased. The mechanism transitions are shown as a function of normalized shear stress and normalized temperature.



Figure 11. Unirradiated fracture behaviour of Type 316 stainless steel as a function of stress and temperature [42].

5. Conclusions

Temperature considerations affect IASCC during spent-fuel storage from two perspectives: (1) effects on cracking at storage temperatures and (2) effects on irradiation material susceptibility. The temperature dependence for IG cracking in water emerges because of the complex thermodynamic and kinetic processes that compete during concurrent corrosion and deformation. In the absence of irradiation, IG cracking in sensitized materials is most strongly promoted at temperatures near 200°C. An evaluation of possible influences of hydrogen embrittlement has suggested that the maximum hydrogen-induced crack growth rates may occur near 100°C. Cracking at low storage temperatures can be mitigated by controlling water purity and component stresses. Both of these conditions are reasonably controllable during spent-fuel storage.

The radiation-induced susceptibility of austenitic SSs to IASCC depends on the neutron damage rate, integrated damage, and temperature. An analysis of the temperature dependence for RIS indicated that segregation is reduced, but not eliminated, at temperatures below 288°C. Particularly at high-irradiation exposures, low-temperature RIS may produce a sufficient degree of chromium depletion and material susceptibility to cause IASCC. Radiation characteristics of several reactors were examined relative to RIS of chromium. The FFTF and AGR exhibit the greater-predicted RIS, whereas the ATR exhibits the lesser-predicted RIS compared to the BWR. The greater RIS for the FFTF is promoted by the higher irradiation temperature and the lower damage rate (more defect survival). The lesser-predicted RIS for the ATR is a result of the higher damage rate (less defect survival).

Temperature also affects deformation and fracture of irradiated SSs. With decreasing irradiation temperature, the macromechanics of irradiation strengthening and irradiation-induced ductility loss are only moderately reduced. However, the irradiated SS microstructure and micromechanical deformation characteristics do change with decreasing temperature. An important consideration is the influence of very slow strain rates (as for irradiation creep) on deformation mode and the propensity for IG fracture. Irradiation creep rates are significant at 288°C and have been measured at temperatures as low as 60°C. These in-core deformation rates are many orders of magnitude slower than commonly used during SSRTs. They may play a critical role in the mechanisms controlling IASCC during service and may affect the subsequent susceptibility to IASCC during storage.

ACKNOWLEDGEMENTS

This research was supported by the Materials Sciences Branch, Office of Basic Energy Sciences, and the Office of Fusion Energy, U.S. Department of Energy. Pacific Northwest National Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

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Examination of microstructure and composition of zirconium-niobium alloy cladding and channel tubes in unirradiated condition, after irradiation, and during storage

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Abstract. Studies conducted at the VNIINM laboratory in Moscow have addressed changes in microstructures of Zr-1Nb fuel cladding and Zr-2.5Nb pressure tubes resulting from service in nuclear reactors. Radiation caused increases in dislocation densities and promoted precipitation of β -Nb particles. No significant evidence of amorphization of second-phase particles was observed. The baseline studies of radiation effects on the alloys were applied to investigate whether further changes occur during storage. No significant changes in dislocation structure, phase, and chemical composition of zirconium-niobium alloys were observed after 1 year of wet storage and 5 years of dry storage.

1 Condition of Zr-1Nb claddings as operated in boiling water reactors and after wet storage

Some 46 power units of nuclear power plants (NPPs) in the former Soviet Union supply annually approximately 1300 t spent nuclear fuel (SNF) as burned-out fuel assemblies to various storage facilities. Therefore, the strategy of Russia is as also the strategy of most countries operating NPPs. It is based on long-term storage of discharged fuel before final reprocessing or disposal for dozens or perhaps hundreds of years. Today, Russia's main technology is wet storage in cooling ponds. However, dry storage is the main concept of longterm storage. In both, the options to provide for the integrity of fuel assemblies (FAs) and fuel rods are most important.

Today, RBMK spent nuclear fuel is stored in cooling ponds directly at the reactor site. Because the issues related to transporting and reprocessing fuel from this type of reactor have not yet been resolved, the quantity of spent fuel in RBMK storage facilities will increase in the near future [1].

The practice of SNF storage in refreshed water ponds demonstrates that this option is most reliable and indispensable during the initial period of FA storage, when the residual heat released after FAs discharged from a reactor must be removed. However, in the long-term storage of SNF, the influence of water on the corrosion of fuel rods and structural components of FAs must be taken into account. In view of this, the condition of fuel cladding and assemblies used in maximum power generation was examined after storage in cooling ponds.

After storage, the condition of fuel and cladding is characterized by investigating the influence of defects occurring during operation and possible subsequent damage under the action of the storage environment and the time of holding in cooling ponds. It is not always apparent what the direct influence of storage factors has been because investigations into the effect of the operational factor on the SNF condition assume the use of the respective FA components to prepare samples. Therefore, the operational and storage factors are differentiated by studying different FAs, namely, directly after their operation and after the

long-term storage in a cooling pond. Here, one must take into account the initial period of FA storage, when the residual heat released is high, after a FA is discharged from a reactor core.

As studies of FAs show, the factor of operation makes a decisive contribution to fuel cladding damage, specifically, in reactors with a boiling type coolant, such as RBMKs.

Fuel rods and assemblies that have been in operation in BWRs (RBMK, VK-50) and PWRs (VVER) are subjected to long-term storage in cooling water ponds. This paper discusses the data on the condition of Zr-1Nb alloy claddings after they have been used in BWRs and stored long-term in water cooling ponds. The cladding was annealed at the final production stage at 580°C.

The objective of this work is to generate data on the corrosion of BWR fuel claddings and their strength characteristics with the aim of forecasting the feasibility of their further safe storage in cooling water ponds.

1.1 Characterization of spent-fuel cladding stored in cooling ponds

1.1.1 Operating conditions and cooling pond storage time

The cladding condition was analysed using fuel rods that had been in RBMK-1000 operation for up to 5 years at the fuel burnup < 20.3 MWd/kg uranium (average), followed by holding in a cooling pond for 0.7 to 17 years.

The condition of the VK-50 fuel rod claddings was studied after they had been in operation for up to 8 years at the fuel burnup < 34 MWd/kg uranium and holding in a cooling pond from 1.0 to 11 years.

The claddings of the vapour channel of BNPP (BAES) reactor were examined after a 10-year operation at the fuel burnup of 25.2 MWd/kg uranium and cooling pond storage for 4 years.

The cooling water chemistry conditions under which the fuel rods were operated are tabulated in Table 1.

1.1.2 VK-50 fuel rod claddings

The VK-50 assemblies [1] incorporate 6 absorbers and 162 fuel rods in the triangular pattern at the pitch of 13 mm. The fuel rod cladding is 9.15 mm in diameter with a 0.65-mm wall thickness. The tubes are stacked with pellets of UO₂, 10.2 g/cm³ dense and 3% U²³⁵ enriched. The pellet diameter is 7.58 mm; that of the central hole is 1.4 mm. The assembly has four SS spacer grids uniformly distributed over its length.

The mean operating conditions were:

- mean power density is 30 kW
- at the average reactor power of 141.5 MW, the mean linear heat generation rate of fuel rods is 57 W/cm
- at the maximum reactor power of 250 MW, maximum linear heat generation rate of a fuel rod is 180 W/cm
- inlet coolant rate is 0.85 m/s.

During the reactor core operation of the fuel rods, the water chemistry was neutral without control for radiolytic gases. The typical content of salts of hardness were 2.5 μ g/kg, that of oxygen160 μ g/kg, of chlorides less than 20 μ g/kg, of iron 22 μ g/kg, of copper 20 μ g/kg, and of zinc 2 μ g/kg.

The volume steam content of the coolant (in related units) varied from 0 at the core bottom to 0.65 two meters above the core bottom.

Reactor	Water	pН	Hardness		Con	centrati	on (µg/l	(g)	
	chemistry		(µg.eq/kg)	0	NH ₃	Fe	Cu	Cl	H ₃ BO ₃
VK-50	Neutral	6.2	2.5	200	-	20-50	20	-	-
	oxygen								
RBMK	Neutral	7.0	1-6	200	-	1-64	2-22	1-57	-
Vapour	Ammonia	9-10	1	10-15	2800-	5-60	1-6	20	-
channel					11200				
BAES									
MIR	Neutral	6-8	3-8	5-20	600	20-40	16-75	-	
VVER	Ammonia-	7-9.5	-	10	>5000	200	<20	<100	$0-10^{7}$
	potassium,								
	boric acid								

Table 1. Cooling water chemistry conditions of different reactors

1.1.3 RBMK-1000 fuel rod claddings

The RBMK-1000 fuel assembly incorporates 18 fuel rods with claddings 3645 mm long, 13.65 mm in diameter, and 0.95 mm in thickness. The tests were carried out under the conditions characteristic of the reactor operation at 1000 MW power. The coolant temperature was:

- at the inlet 270°C
- at the outlet 284°C
- coolant pressure 6.7 Mpa
- mass steam content 14.5 %.

For materials science studies, leak-tight fuel rods were selected at the design power density at the maximum storage time in the reactor cooling pond and in cans of a spent fuel storage facility [2]. The fuel rod operation and testing conditions are described in Table 2. Below, by way of illustration, the operation and storage conditions are given for the fuel rods. For fuel rod 4 at $2 \% U^{235}$ enrichment:

- power density 2283 MW d/assembly
- time of reactor operation 1623 calendar days
- time of storage in at a reactor pond 3776 days
- time of storage in a spent-fuel storage facility 2095 days.

For fuel rod 5 at 1.8 % U²³⁵ enrichment:

- power density 2090 MW d/assembly
- time of reactor operation 1865 calendar days
- time of storage in at a reactor pond 3776 days
- time of storage in a spent-fuel storage facility 2346 days.

To study the feasibility of spent-fuel assembly "dry" storage, fuel rod 6 was taken after 3 to 5 years of holding in a cooling pond; its characteristics are:

- U^{235} enrichment 1.8 %
- power density 2073 MW d/assembly
- time of reactor operation 1280 calendar days
- time of storage in a reactor cooling pond 1870 days
- time of "dry" storage 2.9 years.

The conditions of the pond storage are: $T = 50^{\circ}$ C, pH = 5.5 - 8.0; water transparency for observing objects 100 x 100 mm, visible at the depth of 7.5 m.

1.2 Procedures used to test and study

The studies of spent fuel rods as operated and stored used non-destructive and destructive methods. In a pond, the following investigations were carried out:

- inspection of the rod outer surface (for corrosion of claddings)
- measurement of geometrical sizes
- eddy-current flow detection
- neutron radiography
- γ scanning
- metallographic examinations of welds and regular cladding material to determine the oxide film thickness
- determination of the hydrogen content of claddings
- determination of short-term tensile properties of claddings.

The fuel rod outer surface was inspected visually and using a periscopic system that allows a 5.6 to 7 power magnification.

The measurements of the geometrical sizes and the eddy-current flow detection were carried out using a combined facility in a shielded chamber with two linear displacements and a differential transducer. The neutron radiography was implemented by transmission of fuel rod sections individually (400 mm) on the horizontal beam of the RBT-6 reactor.

The γ -spectrometry measurements (γ - scanning) were implemented in an automated measurement rig in a shielded chamber [3].

The metallographic examinations of the claddings were conducted using longitudinal and transverse sections of samples cut from different areas. Mechanically polished sections were photographed at 5 - fold magnification. The welds and fuel rod claddings were etched in 45 % $HNO_3 + 45$ % $H_2O + 10$ % HF and in 40 % $HNO_3 + 20$ % $H_2SO_4 + 20$ % HF + 20 % H_2O , respectively.

The microstructure was photographed in the metallographic microscope MIM-15 at magnifications of 100, 200, and 400 diameters. The hydrogen content of the cladding samples was found by spectral-isotopic balancing [4]. The short-term tensile tests in the transverse direction were conducted using annular samples 3 mm high in a MM-150D machine by the technique accepted. The rate of the tensile strain is 1 mm/min. The error of the yield point and ultimate strength measurements was 5 % and that of the total and uniform relative elongations was 10 %.

1.3 Results of studies of as-stored fuel rod claddings

The following sections provide the results of the visual inspection, metallographic examinations, and short-term tensile tests.

1.3.1 Condition of the oxidized surfaces of the cladding

The main experimental characteristics and conditions of testing BWR fuel rods as held in cooling ponds for various time periods are given in Table 2. The objective of studying the condition of fuel rods after long-term storage was to assess possible damage caused by the most aggressive phenomena capable of effecting loss of cladding integrity. Nodular corrosion is the most prominent water-side corrosion damage of Zr-1Nb items from in BWRs [5].

Intensive cladding oxidation takes place also under SS spacer grids (SGs). The corrosion of Zr-1Nb claddings of RBMK-1000 fuel rods is characterized by a uniform oxide film of 30 to 50 μ m maximum thickness at the surface contacting the coolant and by nodular damages up to 150 to 200 μ m deep. Under SGs, the depth of corrosion damage can reach 380 μ m. So, at a burnup of 18800 MWday/tU in RBMK-1000 fuel rod claddings, the thickness of the corrosion nodules under SGs was 380 μ m. In this case, the holding time in a pond was less than 1 year.

In fuel rods 2 and 3 at a lower burnup and with storage times from 1.5 to 6.2 years, the same corrosion damage of claddings was observed; namely, the nodule thickness did not exceed 180 μ m. In the areas outside SGs, the nodule thickness was 40 to 60 μ m. In both instances, the thickness of the uniform oxide film did not exceed 20 μ m.

Fuel rod 6, after reactor service, was held in a pond for 5 years and in a "dry" storage facility for 3 years. As in the case for fuel rods 1, 2, and 3, the storage conditions did not affect the cladding surface condition that had oxidized during the operation. The visual inspection of the cladding surface revealed white parallel annular corrosion at SG sites and round white spots under spalled oxide films in areas between SGs (Fig. 1).

On all fuel rods investigated, surface deposits were not essentially revealed. The cladding areas not subject to local oxidation are covered with black or dark-grey oxide films. On near end plugs, along with nodular corrosion (nodule thickness of 180 μ m), uniform oxide films are observed some 100 μ m thick (Fig. 2).

Reactor	In-pile	Burnup	Storage	Corrosion	Max oxide film	Hydrogen		20°C/350°C	
Assembly	time	(MWd/kg U)	time (y)		(µm)	(wt%)			•
	(years)						σ _{0.2}	δ_t	δ_u
							(Mpa)	(%)	(%)
	•		1		RBMK (LAES)	1			r
1	3	18.8	0.7	Uniform	10-20	0.013	600/410	9.2/12	3.0/
				Nodules	130 (380SG)	-			
2	3	13.0	1.5	Uniform	10-20	0.007	610/450	10/13	
				Nodules	40 (150SG)				
3	3	9.9	6.2	Uniform	10-20	0.016	480/390	12.5/13.5	2.8/2.5
				Nodules	60 (180SG)				
4	4.5	20.3	16	Uniform	NA	0.005	560/390	8.7/12	2.9/3.6
				Nodules	180 (250SG)				
5	5	18.6	17	Uniform	100	0.005-0.008	480/380	9.0/12.5	3.1/3.4
				Nodules	200 (180SG)				
6	3.5	18.4	5+3	Uniform	30	0.03	550/340	12.3/16.6	2.2/2.8
			dry	Nodules	NA				
					VK-50				
7	6	25	11	Nodules	200	0.01-0.07 tangen.	355/240	12/17	2.9/2.5
				Crud	100				
8	8	34	1	Nodules	250 (500SG)	0.02-0.07 tang-rad			
				Crud	100				
9	2	11.9	11	Nodules	100 (120SG)	0.02 chaotic	490/340	10/13	1.9/2.5
				Crud	80				
					BAES				
10	10	25.2	4	Uniform	50	0.06 tangen.	460/320	15/17	2.9/2.5
				Nodules	50				

Table 2. Characterization of Zr-1Nb fuel rod claddings performed after service in boiling water reactors and after wet storage

Fuel rods 4 and 5 had been in reactor operation for a longer period, up to 5 years, to reach the fuel burnup of 18.4 to 20.3 MWday/kg uranium; in other words, they were similar to fuel rods 1 and 6. Their holding time in cooling ponds was 16 to 17 years.

The metallographic examinations of the claddings of those fuel rods revealed a more intensive corrosion damage; the oxide film thickness at the surface outside SGs reached 180 to 200 μ m. The oxidized claddings in the areas between SGs show either singular nodules (Figs. 2, 3, and 4) or aggregates of nodules as bands that under SG transform to oxidized annular bands. The bands of nodule aggregates cover in areas at various heights from 1/3 to 5/6 of the fuel rod surface area. In fuel rod 4, aside from areas under SGs, the corrosion damage is revealed by the cladding near the plug and by the adjacent bottom of the cladding (Figs. 5, 6 and 7). This intensified oxidation of the cladding was observed in pilot fuel rods with the time of in-pile testing increased to 4 or 5 years. However, one cannot exclude the prospect of additional increased oxidation of claddings on their long-term storage in a pond. The investigations to clarify this issue are underway.

Holding fuel rods from reactor VK-50 in cooling pond holding for more than 11 years did not influence the condition of their oxidized surface (fuel rods 7 through 9). Compared to cladding in RBMKs, in this reactor the fuel rod cladding is subject to a more intensive oxidation characterized by thicker and looser films over the whole surface (Fig. 8).

Visual inspection of the surface of fuel rod claddings after holding in a cooling pond did not reveal any indications of fractures as cracks or ruptures. Along the whole fuel rod length, the sites of the SG locations are clearly visible, distinguished by a higher oxidation and spallation of oxide films as well as by a white oxide at spallation sites (Fig. 8).

1.3.2 Hydrogen content of claddings

The important damaging factor that can affect the condition of fuel rods upon storage is the hydrogen content and the mode of hydride distribution (orientation in respect to walls) in cladding and the possible hydrogen accumulation in storage.

Fig. 9 shows the typical hydride distribution (tangential, random, and radial) in the cladding of the VK-50 fuel rods. In terms of the cladding integrity, radial hydride distribution is the one of most concern. In fuel rod cladding from BWRs, this distribution of hydrides is observed at corrosion centres. Table 2 contains data on the hydrogen content of the VK-50 claddings and RBMK-1000 fuel rods that reached various burnups and were in the cooling pond for different periods of time.

The hydrogen content of RBMK-1000 fuel claddings that were operated for 4 to 5 years and stored in water for 16 to 17 years is 0.005% to 0.008%. The 11-year storage of the VK-50 fuel rods did not affect their hydrogen content. In this instance, the claddings absorbed hydrogen for the main part during their operation.

Within the concentrations given in Table 2, the hydrogen content of the fuel rod claddings at different burnup and holding period did not deteriorate their mechanical properties. The ductile characteristics are retained at an adequately high level:

- at 20[°]C: $\delta_u = (2.0 3.6)$ %; $\delta_t = (9.1 12.5)$ %
- at 350° C: $\delta_u = (1.8 3.2)$ %; $\delta_t = (7.5 12.0)$ %.

1.4 Discussion of results

The complex studies of the condition of fuel rod claddings using non-destructive methods (profilometry, eddy-current flow detection) and metallographic analysis demonstrate the high efficiency of this combination. The non-destructive methods made it possible to establish the general mode of corrosion-induced damage of claddings and the regularity of a magnitude change of those damages along the fuel rod length. The results of the assessment of the oxide film extent generated from processing defectograms are in good correlation with the data of the metallographic analysis (Figs. 2 and 7). Signal spikes at the sites of SGs noted in the studies of BWR fuel rods reflect the regular higher oxidation of claddings at those sites and the central mode of oxidation in the areas between SGs, which is also corroborated metallographically.

Analysis of the data generated in this study and their comparison with the results of the lifetime operated assemblies subjected to long-term holding in ponds at a site and in spent-fuel storage facilities show that the extent of cladding corrosion damage does not essentially change and remains at the level of corrosion damage of rods that were not stored for a long period of time.

In fuel rods 4 and 5, as cooled in ponds and spent-fuel storage facilities for ≥ 16 years, as well as fuel rod 6 held under similar conditions for 8 years, the maximum oxidation is shown by the areas under SGs (150 to 200 µm) and plug locations, where the magnitude of the revealed nodules reaches 250 µm. However, it must be pointed out that increased oxidation of the claddings of those fuel rods was observed that is not typical of the RBMK fuel rod and also represents hardly explainable local oxidation of the cladding in the area of the end piece at the top of fuel rod 4, reaching 250 µm. In fuel rod 5, it does not exceed 100 µm. The same claddings show high hydrogen contents.

The tensile properties of the claddings are adequately high. The total elongation is 7.5% to 12 % and is weakly dependent on the fuel rod area. The ultimate tensile strength of fuel rod 4 cladding is 544 to 587 MPa at 20°C and 360 to 424 MPa at 350°C. This property of fuel rod 5 is 446 to 524 MPa at 20°C and 329 to 422 MPa at 350°C.

The investigations of the top of fuel rod 6 held for 3 years under "dry" conditions revealed its adequate corrosion condition and rather high tensile properties.

The results of the examinations of the VK-50 and RBMK-1000 fuel rods after their long-term (<17 years) storage in cooling ponds point to the absence of any extra oxidation damage of Zr-1Nb cladding that is capable of inducing leakage of fuel rods. The results do not contradict the general international experience gained in studying the problem of long-term storage. The long-term reactor operation results in hydrides of radial orientation near corrosion nodules. In terms of operation, this effect is undesirable, because under certain conditions, it can initiate a brittle fracture resulting from a sharp defect at the thinnest cladding site from cladding oxidation.

1.5 Conclusion for Section 1

The investigations did not reveal any essential changes in the condition of fuel rod claddings that were held in cooling ponds or a spent-fuel storage facility for up to 17 years. The fuel rod condition is essentially typical of fuel rods used throughout their life-time in BWRs but were not subjected to long-term storage.

A few individual observations suggest that some increase of oxidation and hydriding of Zr-1Nb claddings is possible upon their long-term storage in a cooling pond. However, the most significant changes in fuel rod cladding behaviour are determined by reactor operation conditions (burnup, heat flux, and cooling water chemistry). [See editor's note, p. 54.]

2 Electron microscope studies of structure and microchemical composition of zirconium-niobium alloys

Fuel cladding and pressure tube reliability is becoming more and more important. Development of modified composition and optimization of technology of cladding materials or their types cannot take place without a fundamental assessment of materials behaviour and transformation under irradiation in reactor and in spent-fuel storage facilities.

Related research and development activities are already in progress in storage facilities NIKIET, NIIAR, and VNIINM, Russia [6-10]. Main objectives are related to the better and more reliable understanding of as-received microstructure of cladding and pressure tube materials and their degradation after irradiation in reactors and in spent-fuel storage facilities.

Contract scope includes developing a methodological approach for structural examinations of zirconium-niobium alloys (Zr-1Nb, Zr-2.5Nb); studying grain and dislocation structure, and second-phase precipitations and their evolution under reactor irradiation and during wet and dry storage; and correlating between structural data and results of mechanical and corrosion testing. Results to date include the following:

- (1) A foil preparation technique has been developed for initial and irradiated electron microscopical specimens of zirconium-niobium alloy cladding and pressure tubes. The specimens were cut out of tubes before and after testing in experimental and commercial reactors MIR, BOR-60, and RBMK to the fluence of up to 1.10^{26} n/m² (E ≥ 0.1 MeV).
- (2) The grain and dislocation structure, phase, and microchemical composition of zirconium-niobium alloy tubes have been studied in as-received and irradiated conditions. Quantitative data of the structural characteristics of zirconium-niobium alloys have been obtained.

Our experimental results concerning the dislocation structure and phase composition transformation and comparison of irradiated, after-storage, and unirradiated materials structure are discussed below. Studies in this area have been directed toward improving understanding of zirconium-niobium alloy behaviour at VVER and RBMK conditions, including dependence on technological processing (cold-worked and heat treatment) and alloy composition of cladding and pressure tubes.

2.1 Materials studied and experimental procedure

2.1.1 Materials

Investigations were carried out using Zr-1Nb (E110) alloy samples cut out of fuel rod claddings before and after testing in the experimental and commercial reactors and Zr-2.5Nb (E125) alloy samples cut out of pressure tubes that had been operated for different periods of time (up to 15.5 years) within RBMK process channels. Table 3 (at end of chapter) notes the initial state of the items and reactor testing conditions. Before irradiation, all tubes were as cold-worked and annealed, fully or partially recrystallized. The structure of E125 pressure

tubes was also studied in quenched (870°C in water) and heat-treated condition (TMT-1). The cladding tubes were irradiated as stress-strained in the transverse direction to 4%. All samples have been studied after 1 year of wet storage and 5 years of dry storage.

2.2 Studies of structure

The microstructure, phase, and chemical compositions were investigated with a transmission electron microscope (TEM) using electron diffraction (EM-301G, JEM 2000FX), energy dispersive X ray microanalyses (LINK Systems 860, KEVEX-700), as well as X ray diffraction analysis with a diffractometer ADP-2 with monochromatized CuK_{α} radiation. Foils for TEM studies were prepared in a facility "Struers" by electropolishing discs 3 mm in diameter and 0.1 mm thick with a solution 90% CH₃COOH + 10% HClO₄ (T=13°C) and 80% C₂H₅OH + 20% HClO₄ (T=-30°C). The discs were cut out of cladding tubes in the plane of a tube surface and from pressure tubes in the cross section. The chemical composition of secondary-phase precipitates was determined using foils and carbon replicas with extracted particles. The mean grain size, the mean size and concentration of precipitates, and dislocation loops were evaluated from electron-microscopic patterns, taking account of the studied foil thickness. The dislocation density was calculated with the formula $\rho = 2L/N t$, where:

L is a secant circle length

N is a number of intersections with dislocations

and t is a foil thickness.

The Burgers vector of dislocations (b) was found from the condition of dislocation image extinction: $g \ x \ b = 0$, where g is a vector of a strongly acting reflection. The X ray diffraction data were used to assess the strains and domain sizes as well as (a) and (c) dislocation densities. Strains (ϵ) and effective domain size (D) were determined from the systems of planes of basal, prism, and pyramidal types. The results of the harmonic analysis were used to determine the density of dislocations containing (a) and (c) components with the formulae of [10]:

$$\rho_{a} = \frac{K_{a} \epsilon_{a}^{2}}{b_{a}^{2}}, \frac{1}{\ln(D_{a}/2r_{0})}, \rho_{c} = \frac{1}{b_{c}^{2}}, \frac{1}{\ln(Dc/2r_{0})}$$

where

K_a is 52.1

K_c is 26.1

b_a is 1/3 <1120>

 b_c is [0001], $r_0 = 1 \text{ nm}$

 ϵ_a , D_a are the strains and domain sizes calculated from the prism planes

and ε_c , D_c are the strains and domain sizes calculated from the basal planes.

2.3 Results

2.3.1 E110 alloy (Zr-1Nb)

The structure of unirradiated E110 alloy cladding contains a secondary phase as globular β -Nb precipitates about 0.05 μ m in size and a BCC lattice with the parameter a = 0.328 nm (content of niobium up to 90%) in the α -Zr matrix (0.6% niobium) (Fig. 11a). The dislocation density of (a) and (c) is not high in this alloy. The irradiation to a neutron fluence of 5 x1 0^{25} n/m^2 (E>0.1 MeV) at T=350°C results in an alteration of the dislocation structure, specifically, in irradiation induced clusters and dislocation loops. The analysis of the distribution of these defects revealed that they are ordered in the direction parallel to the basal plane (0001) (Fig. 11b). Using the condition of the invisibility of dislocations ($g \ge 0$), the Burgers vector of dislocation loops was found to be (b = 1/3 < 1120). The nature of the loops was not established because of their small size (~10 nm); however, in the same row both interstitial and vacancy loops are likely to be available lying on prism planes {1010} and $\{1120\}$ [6, 7]. Under the conditions of a strongly acting reflection, g = 0002, when (a) dislocations are invisible, (c) component dislocations are detected in the edge and screw orientations (Fig. 11c). The bends of the dislocation segments indicate how the dislocations climbed to the basal planes that were available before irradiation. In this instance the density of the (c) dislocations is even higher than that of the (a) dislocations in network. Under the same reflections, fine defects were identified as dark bands ~6 nm in the size (Fig. 11d). The preliminary analysis of their contrast shows that they are likely to be vacancy loops lying on basal planes. The irradiation did not induce any noticeable changes in the phase composition. The mean β -Nb precipitate size became slightly larger, the precipitate concentration was reduced and no amorphization of the precipitates was observed. Table 4 (at end of paper) provides the quantitative results on the microstructure and composition.

2.3.2 E125 alloy (Zr-2.5Nb)

Before irradiation, the studied tubes of both types (cladding and pressure ones) were partially recrystallized. The fraction of recrystallized grains varies with the fabrication process. For the state A (Table 3 - at end of paper) the fraction of recrystallized areas is ~75%; for the state B it is less than 15% (Figs. 12a, b, d). Non-recrystallized areas are described by an intensive grain fragmentation, low-angle boundaries and a high density of dislocations within walls. In both the states, the main fraction of dislocations is made up by (a) dislocations; the density of (c) dislocations does not exceed 1.0×10^{14} m⁻².

The phase composition of the unirradiated alloy structure consists of the α -Zr matrix with β -Nb precipitates and residual β -Zr phase (Table 5 – at end of paper). The β -Nb particles are mainly distributed along the grain boundaries, forming stringer pile-ups at the sites of the decomposed β -Zr phase and the former boundaries (Fig. 12c). In state A of the tube structure, the particle size range is rather wide, from 0.01 to 0.20 µm. In state B, the particles are finer and their mean size is ~0.03 µm. In the latter case, the higher concentration of precipitates is a result of the operations of quenching and low-temperature anneal. The chemical composition of the α -solid solution, grain boundaries, and alloy was analysed in an area of 0.2 x 0.1 mm using foils; to determine the composition of precipitates, β -Nb particles extracted onto a carbon replica were used (Fig. 13). The analysis of irradiated samples took account of not only the contribution made by the background, but also the activity induced by niobium isotopes. The investigations showed that the niobium content of the recrystallized α -Zr grains was lower compared to that of non-recrystallized areas in both states of the alloy. In the alloy of state B, the grains of both types contain more niobium than in the alloy of the state, which

is likely to be explained by a high supersaturation as a result of quenching. The composition of β -Nb precipitates is as much as 80% (at) niobium in unirradiated tubes in state A. The niobium content of coarse β -Zr precipitates is in excess of 9% (at). The results of the microdiffraction and X ray diffraction analyses agree well with the data of the microanalysis of the precipitate composition and corroborate the presence of the β -Nb and β -Zr phases having the BCC lattice as well as α -Zr with different niobium contents of solid solutions.

The alloy irradiated in different structure states to fluences of (0.5-1.0) $x10^{26}$ n/m² (E>0.1 MeV) at 305°C to 350°C has different grain and dislocation structures as well as phase and chemical compositions (Figs. 14a, b, c). The alloy irradiated to a fluence of 5 x 10^{25} n/m² at 350°C experienced a full recrystallization and β -Zr decomposition to form β -Nb precipitates (Fig. 14c). The mean size of precipitates both newly formed and grown from initial ones and coagulated is 0.16 µm, while the grain size is increased from 2 to 4 µm to 5to 6 µm. No amorphization of β -Nb precipitates was detected (Fig. 14d). The lower temperature (305°C) irradiation caused little recrystallization of the alloy in either state. However, in the irradiation-thermal anneal process, stress relaxation takes place, the grain boundaries are more clearly defined, and new grains nucleate in non-recrystallized areas. The phase compositions of the alloy irradiated in the A and B states are close (α -Zr + β -Nb). The mean size of β -Nb precipitates and the matrix calculated from the TEM results adequately agree with the data of the X ray diffraction and microanalysis. The niobium content of β -Nb is slightly increased with the fluence (Table 4 – at end of paper).

The dislocation structure is subject to more substantial changes that are related to a reduction in the (a) dislocation density, nucleation, and growth of irradiation-induced defects as (a) dislocation loops at the concentration above $2 \times 10^{22} \text{ m}^{-3}$ (Fig. 15a). Loop alignments to form rows with a direction parallel to (0001) are more clearly revealed in the alloy irradiated under stress conditions. The Burgers vector of the loops found by the $g \ge 0$ method was established to be b = 1/3 < 1120. As in the Zr-1Nb alloy at the foil orientation [1010] defects in basal planes were detected with a size of ~ 10 nm; they are likely to be vacancy (c) loops (Fig. 15b). The mean size of the dislocation loops in the rows and their spacing depends on a number of factors that cover the alloy heat treatment conditions, irradiation temperature, and fluence. The common regularities consist of the fact that the mean loop size grows with the fluence and temperature and is reduced with an increase of the supersaturation of the α -solid solution. The (c) dislocation densities determined by the TEM method under conditions of the acting reflection (g =0002) and the X ray diffraction analysis are in a good agreement and do not exceed 1 x 10^{14} m⁻² (Figs. 15c, d). Under the above diffraction conditions, non-basal dislocations with the (c) component were also revealed climbing to the basal planes. The pileup of the (c) dislocations was detected near the grain boundaries and precipitate aggregates (Fig. 15c). This can be the result of stresses produced by an anisotropic growth of adjacent grains or growth of precipitates.

2.4 Discussion of results

The specific feature of zirconium-niobium alloys as irradiated under conditions of stresses is defects appearing in basal planes at the acting reflections of the type g =0002. They are aligned parallel to (0001) or at an angle of $<20^{\circ}$ C and have a dislocation loop contrast in "profile" when imaged edge-on with a 0002 diffraction vector. Similar features observed in the Zr-2.5Nb alloy structure [8] were identified to be niobium-enriched precipitates. As

distinct from [8] in this work, the solid solution is not supersaturated because niobium for the most part precipitated from the solution as β -Nb particles.

It is counted that precipitates in the E110 and E125 alloys contain about 80% of the total niobium content of the alloys. In the previous work [9] on the E110 alloy also irradiated under conditions of strain, it was shown that until the fluence of 1×10^{25} n/m² (E>0.1 MeV) is attained, only mixed dislocation loops of the (a) type were formed, while at higher fluences in the temperature range of 290°C to 400°C, (c) loop lattices with b =1/6<2023> were observed, 70% being vacancy loops of 10 to 15 nm in size.

In this work, the alloys were studied that did not experience an accelerated growth ($\Phi < 1 \text{ x} - 10^{26} \text{ n/m}^2$); therefore, it was only feasible to assess the tendency toward a dislocation structure evolution. The dislocation structure and phase composition that are substantially different in unirradiated E110 and E125 alloys were similar in many respects after irradiation. As a result of long-term irradiation and thermal effects the β -Zr phase decomposed to form a disperse β -Nb phase, the alloy transformed to more equilibrium state. The initial fine β -Nb precipitates became coarser and their volume fraction increased.

In all the alloys studied, (c) dislocations were observed on basal and non-basal planes. Their density increased with the fluence and depended on the initial density. Of all the recrystallized alloys investigated the highest density of (c) dislocations was observed in E125 and E110 alloys (0.5 to 2.0 x 10^{14} m⁻²). Many of the (c) dislocations are dislocations of the initial structure that climbed onto basal planes. The latter process depends on the (c) dislocation loop nucleation and is much facilitated if (c) dislocations are available in the unirradiated alloy.

The influence exerted by the alloying elements in solution on the defect structure evolution under irradiation is far from clear. It is believed that, as a result of an anisotropic diffusion in α -Zr, sinks for vacancies and interstitials are separated on basal and prism planes, respectively, to form dislocation loops under specific conditions. Results show that the recrystallization grade of the alloy is heavily depends on the irradiation temperature and composition of the alloy. The E125 alloy irradiated at 350°C was, for example, fully recrystallized, while no recrystallization is observed upon irradiation at 305°C to 315°C, even to higher fluences.

2.5 Conclusion for Section 2

The previously reported data on the neutron-irradiation-induced evolution of the alloy structure are corroborated [6, 10]. In the structures of the E110 and E125 alloys irradiated to a fluence of $\leq 10 \times 10^{25}$ n/m² (E ≥ 0.1 MeV) at 350°C, the density of (c) dislocations is substantially higher and reaches 2×10^{14} m⁻². After irradiation of E125 alloy, this dislocation is similar or less in comparison to those of the E110. The initial structure of E125 tubes and the time of reactor operation during up to 15.5 years little affect the density of (c) dislocations. None of the materials studied showed any significant evidence of amorphization of secondary-phase particles. No sufficient changes have been observed in dislocation structure, phase, and chemical composition of zirconium-niobium alloys after 1 year of wet and 5 years of dry storage.

Text cont. on page 145.



Figure 1. Oxidation of RBMK-1000 fuel rod 6 claddings after 5 years in cooling pond and 3 years in dry storage—a) between spacer grids and b) under spacer grids.

Figure 2. Microstructure of longitudinal section of RBMK-1000 fuel rod 4 cladding after 16 years in cooling pond—a) nodular corrosion under spacer grid and b) extended corrosion nodule at a plug.

Figure 3. Surface of RBMK-1000 fuel rod 4 cladding (under spacer grid) after 16 years in cooling pond.

Figure 4. Surface of RBMK-1000 fuel rod 5 cladding (between spacer grids) after cooling pond storage.

Figure 5. Surface of RBMK-1000 fuel 4 rod cladding (between spacer grids) after 16 years in cooling pond—a) plug area and b) middle of fuel rod.

Figure 6. Transition from nodular oxidation in the form of a bond between spacer grids to annual oxidation under spacer grid in RBMK-1000 fuel rod 4 after 16 years in cooling pond.

Figure 7. Microstructure of cross-section of RBMK-1000 fuel rod 4 cladding after 16 years in cooling pond—a) corrosion under spacer grid and b) corrosion between spacer grids.

Figure 8. Cladding surface of VK-50 fuel rod 9 after 11 years storage—a) bottom, b) middle, and c) under spacer grid.

Figure 9. Microstructure of cross-section of VK-50 fuel rod cladding (8 years operation) with differently oriented hydrides—a) tangential, b) chaotic, and c) radial.

Figure 10. Cross-section of RBMK-1000 fuel rod 5 cladding.

Figure 11. Microstructure of recrystallized Zr-1Nb alloy—a) initial and b) irradiated to fluence of 5×10^{25} nm⁻² at 350 °C: grain structure, β -Nb precipitates, (a) dislocation loop ordering; c) (c) dislocations, climbing onto basal planes; and d) fine defects, possibly (c) dislocations loops.

Figure 12. Microstructure of partially recrystallized unirradiation Zr-2.5Nb alloys—a) coldworked and annealed (state A), β -Nb, and β -Zr precipitates; b) distribution of fine dispersive β -Nb precipitates along non-recrystallized grains; c) distribution of β -Nb precipitates, dark field; and d) quenched and stress-relieved condition (state B).

Figure 13. X ray microanalysis spectra of β -Nb precipitates in unirradiated Zr-2.5Nb alloy. Particles extracted on a carbon replica: a) not processed spectrum, b) background spectrum, and c) processed spectrum.

Figure 14. Microstructure of irradiation Zr-2.5Nb alloy: a) at 305 °C (RBMK-1000), state A; b) at 315 °C (RBMK-1500), state B; c) at 350 °C (5 x 10^{25} nm⁻², MIR), state A, β -Zr decomposition into β -Nb chains; and d) β -Nb precipitation in alloys.

Figure 15. Dislocation structure of irradiated Zr-2.5Nb: a) (a) dislocation loops, g=1011; b) structure defects at 350 °C under stresses, likely to be basal dislocation loops; c) image of (c) dislocations on basal and non-basal planes, g=0002; and d) (c) dislocations revealed at g=0002, basal loops (irradiation at 305 °C).

Table 3. Materials Studied and Irradiation Conditions

Alloy	Item	Initial F State	Recryst. Grade, %	Reactor /	Tempe- rature, ⁰ C	Neutron fluence, (E≥0.1MeV) n/m ² ,10 ²⁵
E110	Cladding 9.15x0.7mm	C.W.+ 580°C,2h	100	MIR	350	5
E125,A	Cladding 9.15x0.7mm	C.W.+ 540°C,5h	75	MIR	350	5
E125,A	Pressure tube 88x4mm	C.W.+ 540°C,5h	75	RBMK- 1000	305	20
E125,B	Pressure tube 88x4mm	quenching+ 515°C,24h (TMT-1)	15	RBMK- 1500	315	16

TABLE 3.3. MATERIALS STUDIED AND IRRADIATION CONDITIONS

Alloy	Fluence	Mean	Precip	itates	Dislocat	ion	Dislo	cation lo	ion loops		
		grain	mean	conc,	density (TEM)	mean	conc.,	type		
		size,	size,		a	c	size,				
1	n/m ² ,10 ²	25 μm	µm i	m ⁻³ ,10 ²⁰	m ⁻² ,1	014	nm	m ⁻³ ,10 ²²	2		
E110	0	4	0.05	2.5	0.2	0.2					
	5	8	0.07	1.0	0.1	0.4	9	3	ā		
							6	4	ī		
Conditio	n Fluen	ce]	Precipita	ites	Dislo	cation	Disl	ocation	loops		
		mean	conc.	compo	- densi	ty	mean	conc.	type		
		size,		sition	, a	ī	size,				
	n/m ² ,10	²⁵ μm	m ⁻³ ,10 ²⁰	%Nb	m-2,	1014	nm i	n ⁻³ ,10 ²²			
E125,A	0	0.04	7.0	79 •••	4.0*	0.5*					
T _{ir.} =350 ⁰	с			83**	1.0**	0.9**					
	5	0.16	0.2	80***	0.1*	1.0*	11	5	ā		
							10	4	ī		
E125,A	7	0.05	1.0	75 •••	1.7•	0.5*	10	1.5	a		
rir.=305°C	C			85**		0.6**					
	20	0.05	1.0	81 ***	1.5*	0.5*	14	2.0	ā		
				90**		0.4**					
E125,B	0	0.03	3.0	79 •••	6.0*	0.4*					
ir.=315°C	;			90**	2.0**	0.9**					
	10	0.04	0.0						_		

Alloy	Phase	Lattice	Parametres, nm	Composition, at.%
E110	β-Νb	bcc	a=0.328	(85-90) Nb
E125	β-Nb	bcc	a=0.328	(75-90) Nb
	β-Zr	bcc	a=0.359	>9 Nb

ACKNOWLEDGEMENTS

The authors would like to thank V.L. Panchenko, V.E. Kalachikov, Yu.G. Kostyuk, and V.M. Zyablov for their technical assistance in obtaining TEM, electron diffraction, and X ray diffraction measurements used in this paper, and V.B. Kozlyaeva, E.G. Afonina, and O.A. Simonova for translation, typing, and layout.

[Editor's Note: The author raises the prospect that some degradation of Zr-1Nb cladding may be occurring during storage in water. It seems important to indicate that Zircaloy-clad fuel has been examined after periods of wet storage up to 27 years. Examinations were conducted in Canada, Germany, the U.K., and the U.S. There was no indication that the fuel cladding was degrading in these examinations, though the alloy composition differs from the composition addressed in this report. Results of the Zircaloy-clad fuel examinations are referenced in IAEA-TECDOC-1012.

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