Recent Development and Qualification of Materials for the European Contribution to ITER

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Abstract. The material development together with the important qualification of each individual material and joint are continuously providing new data valuable for the ITER design and construction. This paper provides results of material assessment for ITER components contributing to the First Wall/Blanket, the Divertor and the Vacuum Vessel. The work has been organized by EFDA and F4E together with EURATOM associations and industry. Assessment of data including the interfaces to the primary heat transfer systems under ITER operational conditions is highlighted. Due to the complex geometry and component assembly it is of great importance to understand the corrosion aspects. Taking into account highlighted corrosion issues along with results from previous and presently ongoing work it was possible to make an assessment of fundamental corrosion parameters. The assessment was done by analysis and simulation, which was followed up by experiments under ITER relevant operational conditions. The drying sequence of the vacuum vessel using hot nitrogen and hot dry steam was simulated using the computer code MELCOR. Radiolysis calculations were reviewed in a task to determine how the corrosion potential (ECP) changes during the plasma burning cycles. The paper also includes a new grade of carbon fibre composite (CFC), DMS 814 MEGGAGARD, which was recently developed by Meggitt UK. The CFC is used as a plasma facing material for the Divertor and it was concluded that this grade can be manufactured to meet ITER requirements.

1. Introduction

The ongoing material development together with the important qualification of each individual material and joint are continuously providing new data valuable for the ITER design and construction. Most efforts have been made on characterization of the materials and joints independently of each other, which of course is very important, but it is also necessary to investigate the interaction between materials and surroundings at interfaces during operational conditions. Corrosion is by far the most significant factor causing long downtimes and high costs for nuclear reactor systems. The selections of materials for the primary heat transfer system foreseen in ITER are based on these concerns. Possible weak points from a corrosion point of view were identified in previous studies such as crevices, joints and welds, within the primary heat transfer systems [1].

Corrosion has to be considered a dynamic process, which depends on various parameters, and it is necessary to carry out a comprehensive assessment of materials data under ITER relevant operational conditions for the Vacuum Vessel, the First Wall/Blankets and the Divertor. The purpose of collecting the materials corrosion data is to increase the preparedness for future situations with corrosion problems and to collect unique data that gives guidelines for the operation of the primary heat transfer systems. Even if the corrosion effects are found to emerge slowly it is important to follow up the margins against corrosion during the expected lifetime of ITER. The knowledge gathered from these studies also enables preventative actions to be available during operation.

A new grade of CFC (DMS 814 MEGGAGARD was developed by Meggitt and purchased within an EFDA contract [2]. This CFC fulfills the ITER requirements and is foreseen to be used for a Divertor inner vertical target prototype.

2. Radiolysis and ECP Estimates in the ITER Primary Heat Transfer Systems

In order to evaluate if metallic components will suffer from different types of corrosion in the ITER environment, it is of fundamental importance to know what electrochemical corrosion potential (ECP) the metal will acquire under the relevant exposure conditions. The major source of oxidants in the degassed cooling water is radiolysis, if no countermeasures are undertaken. This process splits the water molecule and as a result the oxidants H_2O_2 and O_2 are formed along with the reducing agent H_2 and a number of radicals such as OH. Depending on the nature of this process, and the boundary conditions set by the initial water chemistry and radiation, the resulting ECP can be either oxidizing or reducing. The situation in the ITER cooling system with respect to ECP has been discussed in a report prepared by Studsvik Nuclear AB [3]. In this report the production of oxidants through radiolysis is linked to the resulting ECP of the ITER cooling system.

Water containing radiolysis products such as H_2, H_2O_2 and O_2 is not in thermodynamic equilibrium and has no associated redox potential. The ECP of a metal in contact with water is a mixed potential that is kinetically determined by a balance between reduction of O_2 respectively H_2O_2 and oxidation of H_2, H_2O_2 and metal. The Studsvik ECP model [4] has been used to illustrate this process. Apparently, under ITER primary heat transfer system conditions e.g. 150 ^{o}C and a flow rate of several m/s, very low concentrations of H_2O_2 are sufficient to increase the ECP by several hundreds of mV.

Based on the calculated concentration of reducing and oxidizing species, the flow rate and the pipe dimensions, it is possible to estimate the resulting ECP of the ITER cooling system by application of the Studsvik ECP model [4]. Radiolysis will only take place in the plasma facing components of the ITER cooling system and only as long as the fusion process is ongoing. Outside this area of intense radiation and when the fusion process is not taking place the oxidants H_2O_2 and O_2 will be reduced and consumed by corrosion of metallic surfaces. The Studsvik ECP model showed that reducing conditions could appear rather soon after fusion had ceased in ITER. If 25 cm^3/kg H_2 STP (Standard Temperature Pressure) is added to the coolant as stated in the chemical specification, it was shown that reducing conditions will be achieved in the divertor primary heat transfer system in less than 30 min after the termination of the fusion process. Based on this estimation it is likely that during operation the ECP will shift from oxidating to reducing if ITER is run as planned, i.e. in pulses with duration of 400 s and with a dwell time of 1800 s in between [5]. This is illustrated in *FIG. 1*. For longer periods of no operation the system will be in a reducing condition.

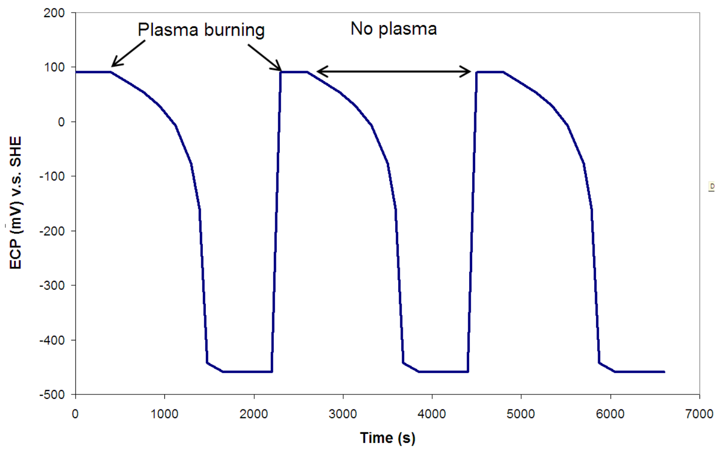

FIG. 1. The change in ECP of stainless steel piping as a function of the consecutive periods of plasma burning 400 s followed by dwell periods of 1800 s.

The shifting ECP, as shown in *FIG. 1.*, will have a few implications on corrosion related properties of the ITER cooling systems. During operation, the ECP will be close to 100 mv SHE (Standard Hydrogen Electrode). This potential should be compared to -230 mv SHE above which intergranular stress corrosion cracking of weld sensitized stainless steel appears in Light Water Reactors [6]. Further, the shifting ECP will most likely result in an increased release of corrosion products from system surfaces compared to stable conditions. The release of such loosely adherent corrosion products activated by neutron radiation will influence the activity build-up in the systems.

3. Effect of Soluble Copper on the Stress Corrosion Cracking Susceptibility of Stainless Steel

In the cooling system of the Divertor a copper alloy (CuCrZr) is used together with stainless steels (316L(N)-IG and XM-19) and a nickel alloy (Alloy 625). Corrosion of copper will lead to formation of Cu-impurities in the cooling water. The effect of Cu-impurities on the susceptibility of the stainless steels to stress corrosion cracking (SCC) was studied by slow strain rate testing. Sensitized stainless steel type 304 was included in the test matrix as a reference material, since this material is known to be susceptible for SCC. Round bar tensile tests specimens with a 25 mm gauge section were used. Also specimens that contained a joint produced by TIG narrow-gap welding of two massive sheets of 316L(N)-IG were tested. The joint was centered in the middle of the 25 mm gauge section of the specimens.

The exposure conditions were adopted to simulate the Divertor cooling system. The specimens were thus exposed to ultrapure water at 200 ^{o}C, to which 1000 ppb H_2O_2 had been added. In order to simulate different levels of corrosion rate of the CrCrZr piping in the plasma facing components 0, 10 or 100 ppb Cu^{2+} was added as $Cu(NO_3)_2$. The resulting corrosion potential was in the range 150 – 260 mV SHE depending on specimen material and the presence of Cu impurities. A strain rate of $3.7 \cdot 10^{-7}$ s^{-1} was used throughout the SSRT test.

FIG. 2. shows the SSRT curves from the exposure of 316L(N)-IG and *FIG. 3.* the corresponding curves for the welded material. As a comparison, in air at around 200 ^{o}C an ultimate tensile strength of about 500 MPa and an elongation at rupture of 40 – 45 % is

expected [7]. Thus, from *FIG. 2.* it can be observed that the exposure to conditions representative for Divertor cooling system has not changed the stress strain behavior of the 316L(N)-IG material within the accuracy of the testing technique. In the case of the welded specimens the elongation at rupture is smaller and the yield strength higher compared to the homogenous specimens. The reason is that the weld itself constitutes a significant part of the gauge section, about 40 %. The weld material and the heat affected zone have a lower elongation at rupture and a higher yield strength. From the metallographic investigations of the 316L(N)-IG material with and without welds, only ductile fracture surfaces could be identified, see example in *FIG. 4*. From the SSRT testing it was thus apparent that 316L(N)-IG did not show any susceptibility towards SCC irrespective of the exposure conditions. This proved to be valid both when 316L(N)-IG was tested as a homogenous specimens [8] and when the specimens contained a welded joint produced through TIG narrow-gap welding [9].

Sensitized stainless steel 304 on the other hand showed susceptibility towards SCC, which was considerably aggravated through the increase of Cu impurities [8]. It should be pointed out that this material and material state is not intended for the ITER design. However, it is very illustrative to include this material in the study since it reveals the accelerating effect Cu impurities have on SCC of stainless steel, provided the material is susceptible.

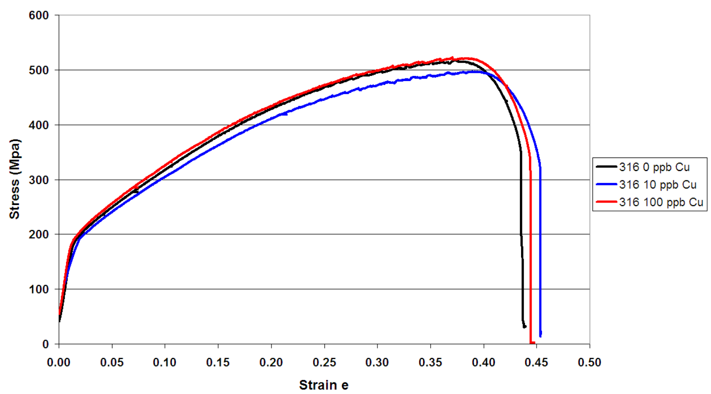

FIG. 2. Stress-strain curves for 316L(N)-IG specimens exposed to different levels of soluble Cu^{2+}.

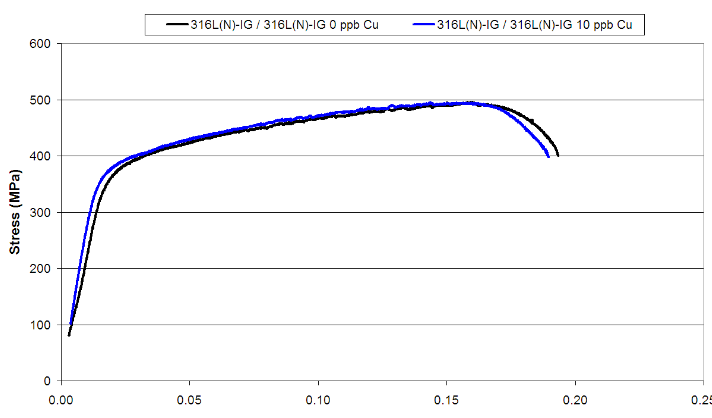

FIG. 3. Stress-strain curves for TIG narrow gap welded 316L(N)-IG specimens exposed to different levels of soluble Cu^{2+}.

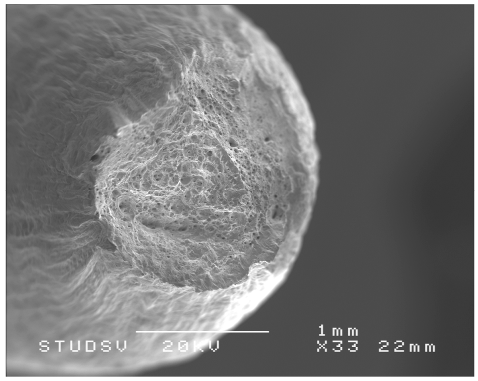

FIG. 4. SEM image of the fracture surface of a 316L(N)-IG exposed at 200 °C, in ultrapure water containing 1000 ppb H_2O_2 and 100 ppb Cu^{2+}.

4. Endurance Testing and Drying Experiments with Vacuum Vessel Materials

During the cyclic operation of the ITER Vacuum Vessel (VV) including the baking/draining/drying processes, accumulation of ionic and other impurities in crevices can form a local corrosive environment. The objective of this ongoing work was to evaluate the corrosion resistance of stainless steels during drying of the ITER vacuum vessel and to monitor the drying process. The experimental work was carried out using tailor made methods in two identical autoclaves in a test laboratory (one with hot nitrogen gas and one with superheated steam). Hydrogen peroxide and chloride was dosed during the water exposure step. Repeated drying is presently being performed for about 1.5 years of exposure, 30 cycles of 7 days followed by 8 cycles of 30 days. Crevice corrosion data of shielding plate materials was provided using PTFE as washers to form crevices. The first assemblies of material specimens have been taken out for analysis of achieved results after 15 cycles, (*see FIG. 5.*). The ferritic stainless steel Type 430 showed the lowest corrosion resistance with pitting in open crevices.

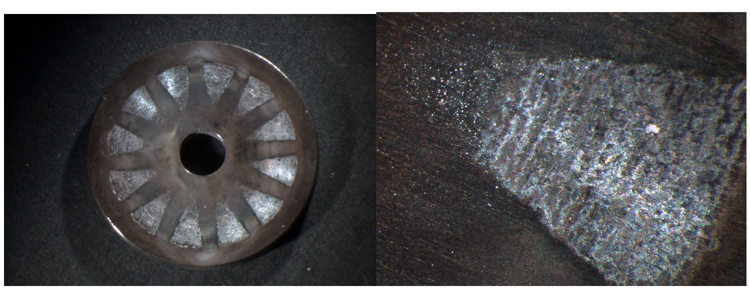

FIG. 5. Photographs of minor crevice corrosion attacks on a SS 430 specimen after 15 drying cycles using superheated steam.

Purpose-built conductivity cells, using ceramic powder to simulate capillary condensation in crevices, are used to register the progress of drying. The results show that using hot nitrogen gas, the conductivity decreases to almost zero after about 15 hours of drying. For superheated steam, the conductivity is still equal to its value during the water exposure operation, even after three days of drying.

5. Assessment of Parameters When Drying the Vacuum Vessel

The water filled structures of the VV have to be drained and dried before maintenance work and inspections can be performed. The drying of the VV was simulated using the computer code MELCOR 1.8.5 [10]. A complete model of the VV cooling system was used to investigate the dependence of the drying time on gas type, flow rate, gas temperature and initial temperature of the structure in order to support the decision of operational parameters. The initial condition of the simulations was the VV filled with water at a pressure of 2.4 MPa. Both the water and the VV structure had a temperature of either 200 or 110°C depending on the conditions simulated. The water was drained from the VV by the force of gravity. The pressure in the VV was gradually (-39 kPa/s) reduced down to 80 kPa above the pressure where boiling would occur. The drained water was replaced by nitrogen gas with a temperature of 150, 220 or 350°C. When the only remaining liquid water was a pool at the bottom of the VV (see *FIG. 6.*) the pressure was gradually (-10 kPa/s) lowered to 101.35 kPa (atmospheric pressure) where it was kept constant. Hot nitrogen was blown through the channels at a specified mass flow rate and the remaining water was allowed to boil off. Blowing hot dry steam with a temperature of 150°C was simulated for comparison. The simulation was stopped when all liquid water had evaporated and no steam was passing through the outlet (see *FIG. 7.* and *FIG. 8.*)

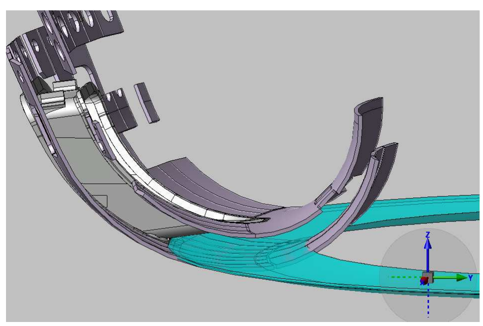

FIG. 6. 3D model of the water remaining at the bottom of the Vacuum Vessel after draining.

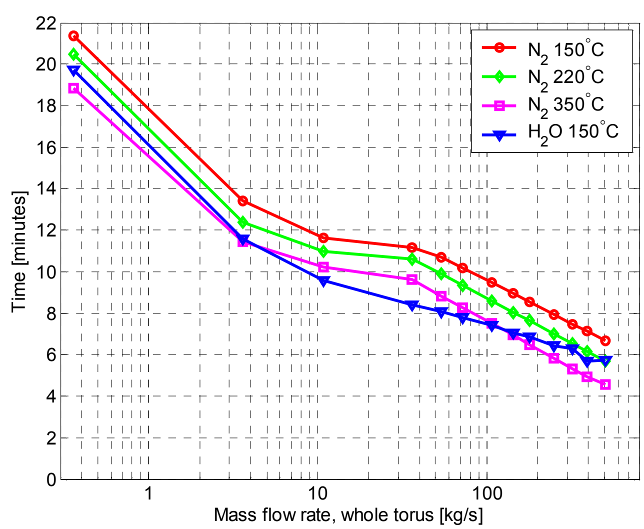

FIG. 7. Drying time when the initial water and structure temperature is 200 °C.

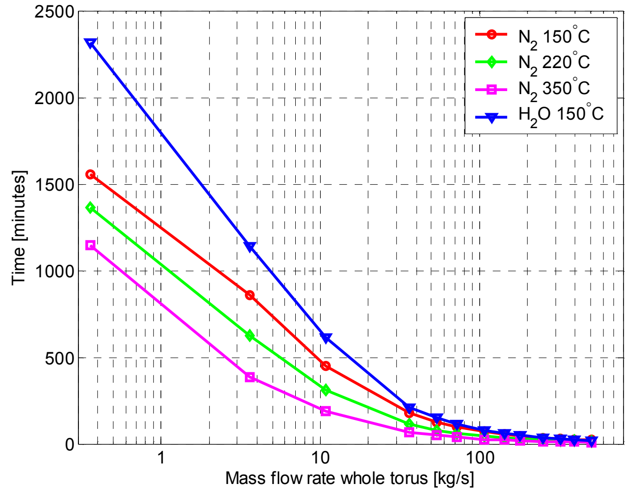

FIG. 8. Drying time when the initial water and structure temperature is 110°C.

Considering the large thermal mass of the VV structures it is not recommended to pre heat the water and the structures to 200 °C before starting the drying sequence if the only purpose of this is to shorten the drying time. Acceptable drying times can be achieved from a cooler initial state with a considerably smaller total input of energy. It was shown that if the gas temperature was increased to values above the temperatures of the structures, problems with recirculating zones due to natural convection could arise, hindering efficient flushing of the cooling system. Thus a higher gas temperature has a limited effect on the drying time.

6. Development and Small Scale Production of a 3D Carbon Fibre Composite

A new grade of CFC, Carbon Fibre Composites, was developed by Meggitt, UK, within an EFDA contract [2]. The CFC is used as a plasma facing material in the ITER Divertor. The purpose of the work was to study possible ways to manufacture 3D high thermal conductivity CFC material in a more reliable and effective way. After the development phase a 150 kg quantity of the optimized material (DMS 814 MEGGAGARD®) was supplied. The supply of this CFC is foreseen to be used for an Inner Vertical Target prototype. The development phase showed a route towards producing CFC with required Z direction strengths, while retaining all other mechanical, thermal and chemical properties to the desired limits. This was achieved by incorporating short PAN fibres into a continuous PAN fibre sheet at the preform stage. TABLE I and TABLE II shows the achieved strength and thermal conductivity.

TABLE I: AVERAGE TENSILE STRENGTH AT ROOM TEMPERATURE.

Tensile strength at room temperature	X-direction (Pitch fibre)[MPa]	Y-direction (PAN fibre) [MPa]	Z-direction (needling direction) [MPa]
Meggitt	205	26	8
IO Requirements	110	20	5

TABLE II: AVERAGE THERMAL CONDUCTIVITY AT ROOM TEMPERATURE.

Thermal conductivity at room temperature	X-direction (Pitch fibre) [W/mK]	Y-direction (PAN fibre) [W/mK]	Z-direction (needling direction) [W/mK]
Meggitt	282	126	62
IO Requirements	280	100	55

7. Conclusions

Radiolysis calculations in conjunction with ECP modelling show that the conditions in the Divertor cooling system most likely will be oxidising when fusion is ongoing in the reactor. Since fusion will be created in ITER under consecutive periods of 400 s followed by dwell periods of 1800 s, the ECP will shift from oxidizing to reducing in the cooling system.

The stainless steel 316L(N)-IG designated for ITER applications was shown to be resistant to SCC under conditions applicable to Divertor cooling systems through SSRT testing. This was also valid for a homogenous joint of the material.

The crevice corrosion attacks produced during testing of the drying sequence are small due to the short exposure time. Drying of capillaries is difficult using superheated steam, but feasible using hot nitrogen gas. Through simulation it was shown that drying of the ITER cooling system is most economically performed by using N_2 heated to 150^{o}C.

A new grade of CFC was made available to the market and the first supply of CFC material is being prepared for assembly on an Inner Vertical Target prototype.

8. References

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