Influence of irradiation on stainless steel corrosion in PWR primary conditions

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Some internal components of pressurized water reactor (PWR) are made on stainless steel. They are exposed to:

- a corrosive environment which is the primary medium that is to say water at high temperature (290°C-330°C) and high pressure (155 bars) with boric acid (H_3BO_3), lithium hydroxide (LiOH) and dissolved hydrogen,
- a mechanical stress,
- an irradiation process due to neutron flux which can cause up to 1 displacement per atom (dpa) by year.

In these conditions, these materials can be damaged by a process of IASCC (Irradiation Assisted Stress Corrosion Cracking). This degradation process has been observed since the eighties with the formation of cracks on baffle bolts under operating conditions. Oxide film rupture is the first step in this corrosion process and thereby the properties of the oxide formed on stainless steels are key parameters relative to SCC initiation. The morphology and the structure of the oxide formed on stainless steel in PWR primary medium have been detailed by several authors [1, 2, 3]. The oxide layer is divided in two parts: an internal and continuous layer rich in chromium and an external discontinuous layer composed of crystallites rich in iron. Moreover a nickel enrichment has been observed in the alloy under the oxide close to the alloy/oxide interface. In this alloy layer with a higher composition in nickel, a trapping of hydrogen has also been observed [4]. The aim of this work is to study the influence of defects created in the alloy by irradiation on the oxide properties (thickness, morphology, composition) and on oxygen transport in this oxide scale during exposition of stainless steel in PWR primary medium. In order to simulate the defects due to irradiation, ionic implantation have been performed. So samples of austenitic stainless steel (316L) have been implanted with Xenon ions at energy of 240 keV. Transmission Electron Microscopy (TEM) observations indicate an affected depth of about 80 nm with the formation of small cavities. The implanted samples have been oxidized at 325°C in hydrogenated primary water which simulates the primary medium in different devices, static autoclave and corrosion loop during different durations. The oxide film properties have been investigated by a set of techniques (SEM, TEM, SIMS). As shown on Fig. 1, which presents implanted sample before and after 600 hours of oxidation, it has been observed a correlation between the affected area created by implantation and the morphology of the oxide formed after corrosion test. The composition of the internal layer is also linked to the defects created by implantation.

Fig. 1: TEM images on implanted 316L samples before (a) and after (b) 600 h of oxidation

Moreover the study of oxidation kinetic evaluated by ion beam analysis (NRA and RBS) have shown that the growth rate of the internal oxide layer follows a logarithmic-type law: after a 24 h exposure, the internal oxide reaches a thickness equivalent to the implanted affected depth which does not change much for longer exposition duration confirming the influence of the defect on the oxidation process.

Oxygen transport in the oxide layer has also been studied by two-stages corrosion experiments, a first stage in natural primary water (during 600h) followed by a second stage with water enriched in ^{18}O (during 16h). Comparison between TEM observation after implantation, EDX analysis after corrosion and SIMS analysis after these two corrosion sequences (Fig. 2) enable to link the distribution of defect created by implantation with the oxygen transport through the internal oxide layer formed during exposition in primary medium at 325°C.

Fig 2: Superposition of TEM image showing the microstructure samples after implantation, concentration profiles of ^{18}O obtained by SIMS after two corrosion stages and O, Fe, Cr and Ni EDX concentration profiles obtained after 600 h of exposition to primary medium.

As a conclusion, this study revealed an effect of the defect distribution (generated by prior Xe-implantation) on the oxide formed on of 316L in primary medium, on the oxidation kinetic and also on the oxygen transport properties in the oxide layer.

References

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Severe irradiation conditions
in PWR core (RPV+internals)

Material ageing and
potential degradation

Limit of reactor
operational life

IASCC of the baffle/former bolts

->IG Crack at the head to shank transition region
(8.5 dpa - 300°C)

IASCC initiation for PWR's bolts

IASCC STUDY AT CEA

Strain and stress evaluations in the alloys in function of irradiation (DMN/SEMI)

Modelling of initiation and propagation of cracks by finite element method (DMN/SRMA)

IASCC Test (DMN/SEMI)

Oxidation modelling : Ekinox (DPC/SCCME)

Mechanical properties of oxides (MD) (DPC/SCCME)

Effect of radiolysis (DPC/SCCME)

Effect of irradiation defect on oxidation (DPC/SCCME)

Irradiation Assisted Stress Corrosion Cracking (IASCC)

- Materials and methods
- Oxide layer characterization on non implanted sample
- Oxide layer characterization on implanted sample
 - Oxide layer properties
 - Oxidation kinetic
 - Oxygen transport

Chemical composition

Austenitic stainless steel 316L (composition in wt. %)

Fe	Cr	Ni	Mo	Mn	Cu	Si	Co	N	P	C	S
68.18	16.6	10.2	2.21	1.82	0.43	0.3	0.11	0.056	0.033	0.03	0.028

Samples preparation

➤ Samples mechanically polished up to 0.04 μm colloidal silica suspension

⇒ Mirror finish and low surface roughness ($R_a = 13 \text{ nm}$)

➤ Implanted with Xenon at 240 keV ($2.10^{16} \text{ at.cm}^{-2}$),

Srim Calculation

Samples characterization after implantation

TEM observation after Xe-implantation

Comparison Xe profile between SRIM calculation and EDX analysis

⇒ Formation of an affected area of about 90 nm divided in two parts : an upper part with higher defect density and a lower part with lower defects density

Samples characterization after implantation

TEM underfocused observation

TEM overfocused observation

⇒ Defects created by irradiation → small cavities

Experimental conditions:

- Corrosion loop
- Temperature = 325°C
- Total pressure = 155 bar
- Exposure time = 24 to 600 h

Primary medium:

- Boron (H_3BO_3) = 1000 ppm
- Lithium (LiOH) = 2 ppm
- H_2 = 0,28 bar ($41 \text{ cm}^3.\text{kg}^{-1}$)
- O_2 < 5 ppb

Oxide characterization

- TEM and SEM : morphology, thickness, composition and structure of the oxide layer
- Ion beam analysis (NRA and RBS): oxide thickness in function of time (oxidation kinetics)
- SIMS analysis after two corrosion sequences using tracer : 600 h (H_2O) + 16 h (H_2^{18}O) : diffusion mechanism in the oxide layer

Oxide layer formed on stainless steel in PWR primary medium

SS 316L oxidized 600h in primary medium

Oxide layer formed on stainless steel in PWR primary medium

Corrosion in D₂O/ GD-OES analysis

(coll. M. Tabarant (LISL))

⇒ Enrichment of deuterium in the alloy underlying the oxide

Oxide layer formed on stainless steel in PWR primary medium

SS 316L oxidized 600h in primary medium

⇒ Well agree with other studies

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Diffusion in the internal oxide layer

Two oxidation sequences : 600 h H₂O + 16 h with H₂¹⁸O

SS 316L (TT) oxidized 600h in primary medium

⇒ Diffusion profile of ¹⁸O in the internal oxide layer (anionic growth)

⇒ Calculation of diffusion coefficient : $D_o = (9 \pm 1) \cdot 10^{-17} \text{ cm}^2 \cdot \text{s}^{-1}$

Diffusion in the internal oxide layer

Comparison with others values of O diffusion coefficient

⇒ Link between chromium content in the oxide layer and the diffusion coefficient of oxygen

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OXIDATION OF IMPLANTED SAMPLE

Oxide layer formed on implanted sample

600h in primary medium

Polycrystalline
spinel structure

Fe_3O_4 structure

- ⇒ Internal continuous layer and external layer with cristallites
- ⇒ Both spinel structure
- ⇒ Internal layer divided in two area with different chromium composition

OXIDATION OF IMPLANTED SAMPLE

Oxide layer formed on implanted sample

600h in primary medium

Xe-implanted sample before oxidation

Xe-implanted sample after oxidation

⇒ The implanted affected depth corresponds to the thickness of the oxide formed after 600h of oxidation (about 90 nm).

OXIDATION OF IMPLANTED SAMPLE

Oxidation kinetics

Evaluation of internal oxide thickness by NRA and RBS

logarithmic-type kinetics law

- ⇒ After 24 h of exposure, the thickness of the internal layer is estimated at about 90 nm.
- ⇒ The growth rate of the internal oxide layer is fast between 0 and 24 h and then strongly decreases after this first period → logarithmic-type kinetics law

Diffusion in the internal oxide layer

Two oxidation sequences : 600 h H_2O + 16 h with H_2^{18}O

- ⇒ ^{18}O diffusion regime does not correspond to a single diffusion profile
- ⇒ Different from profile obtained on non implanted sample
- ⇒ Two different profiles seem to be present

Diffusion in the internal oxide layer

Two oxidation sequences : 600 h H_2O + 16 h with H_2^{18}O

Comparison between O diffusion profil and oxide layer composition

⇒ Link between oxygen profile in the oxide layer and its composition

Diffusion in the internal oxide layer

Two oxidation sequences : 600 h H_2O + 16 h with H_2^{18}O

Comparison between O diffusion profil, oxide layer composition and defects created in the alloy

⇒ Link between the two diffusion regimes observed on ^{18}O profile to the initial microstructure of Xe-implanted samples

- Implantation of sample with Xe ions to create defects in the alloy
- Oxidation in simulated PWR primary medium
- Effect of the implanted microstructure on :
 - Oxide layer thickness and composition
 - Internal layer growth kinetic
 - Oxygen diffusion in the oxide internal layer