Growth Behavior of Surface Oxide Layer on SUS316L Stainless Steel at the Early Stage of Exposure to 288°C Water

Yasutaka Soma, Chiaki Kato and Masahiro Yamamoto

Research Group for Corrosion Resistant Materials, Japan Atomic Energy Agency (JAEA), Naka-gun, Ibaraki 319-1195, Japan

Surface oxide layer on SUS316L stainless steels exposed to 288°C pure water with 2 ppm dissolved oxygen (DO) for 1–100h were analyzed using Focused Ion Beam (FIB) and Scanning Transmission Electron Microscope (STEM) technique to understand the early stage of surface oxide layer formation. In order to analyze the multi layered surface oxide, the interfaces between the outer and the inner oxide layers and that between the inner oxide layer and SUS316L substrate were determined from Energy Dispersive X-ray Spectroscopy (EDX) line profiles. At 1 h exposure, double oxide layer which is composed of compact inner oxide layer and outer oxide layer with Fe-rich and Ni-rich oxide particles was formed. At the outermost region of the SUS316L substrate, Ni and Cr were enriched. At 100h exposure, growth of the inner oxide layer was suppressed and the Ni and Cr enriched region at the alloy substrate was preserved underneath the Ni-rich outer oxide particles. At 1 h exposure, most of the outer oxide particles were composed of Fe-rich ones, at 10 h exposure, another Ni-rich outer oxide particles were nucleated and grew faster than Fe-rich ones. Consequently, a part of pre-formed Fe-rich outer oxide particles were covered with Ni-rich ones.

1. Introduction

Boiling water reactor (BWR) environment is characterized by high temperature, high pressure and high purity neutral water containing O2, H2O2, and H2, which are produced by radiolysis of cooling water. Low carbon austenitic stainless steels, i.e. SUS316L, have been widely used for structural materials of BWRs because of their excellent resistance against corrosion. However, failures of stress corrosion cracking (SCC) have been detected at some parts of primary water loops of plants made of SUS316L stainless steels and SCC of stainless steels have been recognized as one of the important problems of ensuring safety of nuclear power plants. A number of studies based on fracture mechanics have been carried out and they were shown that the SCC phenomena were functions of environment, stress, and micro-structural properties of the material, as reviewed by Andresen.1) He also introduced the characteristics of BWR’s SCC as intergranular SCC (IGSCC).

In order to interpret IGSCC crack growth behavior, several mechanisms have been proposed. Andresen and Ford2) proposed the slip-film rupture-oxidation (S/FR/O) model. Where, crack propagates by the cycles of disruption of oxide film at the crack tip induced by dynamic strain and the subsequent dissolution and re-oxidation of the metal substrate. Tarnish rupture (TR) model, a similar mechanism with the S/FR/O model, has been proposed. In this model, crack propagates with brittle collapse of oxide film at the crack tip portion without active dissolution of the metal substrate.3) The relationship between the material’s electrochemical corrosion potential (ECP) and the IGSCC crack growth rates (CGR) have been investigated.4) It was reported that CGRs of stainless steels were suppressed if the ECP stayed below −0.23 V [vs. standard hydrogen electrode (SHE)]. The findings shown above suggest that the SCC of stainless steel propagates in electrochemical process on which corrosion and oxidation behavior of metal plays important role.

As for corrosion and oxidation of metal, researches of the surface oxide film have been done in both the actual and the simulated BWR environment. Oxide scales on SUS304 stainless steel5) and surface oxide of SCC crack wall in the BWR primary loop recirculation pipes6) and the oxidation behavior of SCC portion of the BWR core shroud7) have been investigated. The quite similar oxide films have been observed under the simulated conditions in the laboratories.8,9) These studies have shown that the oxide films had duplex structure which were composed of compact inner oxide layer (mainly Fe3O4 and FeCr2O4) grown into substrate, and the outer oxides particles (mainly α-Fe2O3, Fe3O4, and NiFe2O4) precipitated from the aqueous phase.8,9) However, most of these studies focused on the long term exposed oxide films where the surface was covered with outer particles. Little examination has been done from the viewpoint of initiation of oxide film within short exposure period. In addition, time dependence behavior of e.g., composition, morphology, nucleation, growth rate, and interaction between the different oxides layers and particles are unclear.

Surface oxide film growth at the initial stage seems to be important because new oxide formation occurs near the ongoing SCC crack tip. We investigate the growing process of surface oxide layer (hereafter, we use “oxide layer” rather than “oxide film”) on austenitic stainless steels under the 288°C pure water with relatively short exposure time (<100h). The objective of this study is to analyze nucleation and growing behavior of the outer oxide particles and the effect of outer oxides particles to the underlying inner oxide layer. The following experimental procedures were carried out. At first, austenitic stainless steels were immersed into the 288°C water containing high dissolved oxygen (DO) to accelerate corrosion and formation of surface oxide layer followed by SEM observation and Raman spectroscopy to confirm whether the typical corrosion products of the stainless steel in the actual BWR conditions were generated.
And then, their microstructure were analyzed in detail from cross sectional views obtained by focused ion beam (FIB) and scanning transmission electron microscope (STEM) technique together with Energy Dispersive X-ray (EDX) analysis.

2. Experimental

2.1 Specimen and preparation

SUS316L stainless steel (solution treatment 1015°C, 30 min, WQ) was used as specimen. The chemical composition of the sample is shown in Table 1. The specimen was cut into $10 \times 10 \times 2 \text{ mm}$ and polished by SiC paper and 1 µm diamond paste, and then, ultrasonically washed in ethanol.

2.2 Exposure test to 288°C water

Schematic illustration of the apparatus for immersion test in high temperature water is shown in Fig. 1. The apparatus is consisted of autoclave (material: SUS316L, capacity: 1.8 dm$^3$, flow rate: 5 dm$^3$·h$^{-1}$), high pressure pump, and analytical branch loop for monitoring pH, conductivity, and concentration of DO. The water in the loop was purified through couples of ion-exchange resin and micro filter, which maintain the conductivity of feed water below 0.060 µS·cm$^{-1}$ throughout the experiments. DO concentration was controlled at 2 ppm by injection of pure O$_2$ gas into the water conditioning tank. It was reported that the higher DO concentration increase growth rate of the inner oxide layer and generate dense outer oxide particles. In this work, the DO concentration was held at relatively high than that at the typical operating condition of BWR ($\approx 200$ ppb) in order to accelerate oxide formation. The feed water into the autoclave was preheated at 288°C. Temperature was measured at thermocouple put inside the autoclave. Figure 2 shows change in temperature with time during the operation. At point A, specimens were put into the autoclave and water circulation pump was started. At point B, water conditioning was completed and the heating up was started. At point C, temperature was heated to 288°C with 9 MPa. It took 2 h from B to C. Temperature was held at 288°C for 1, 10, and 100 h from C to D. At point D, heater was turned off and the specimens were ejected at point E. It took 3 h for cooling down from 288°C to RT. The exposure time means the time from point C to D.

2.3 Analysis of the surface oxide layer

Surface of the specimens after the exposure test were observed by FE-SEM (JEOL 6500). Corrosion products were identified by laser Raman spectrometer (JASCO NRS-3100). Cross sectional views of the surface oxide layers were obtained using focused ion beam (FIB, Hitachi NB-5000) and scanning transmission electron microscope (STEM, Hitachi HD-2700, accelerating voltage $= 200$ kV). EDX analysis was done together with the STEM observation. The small piece of surface oxide layer (ca. 10 µm in length and <100 nm in thickness) was fabricated by the FIB. Before the fabrication, carbon was deposited on the specimen surface using electron beam to protect the surface oxide layer.

3. Results

Figure 3 shows SEM micrographs of the specimens exposed for 1, 10, and 100 h. At 1 h, the entire surface was covered with small particles and the size of the particles enlarged with time of exposure. Figure 4 shows Raman spectrum of the specimen exposed for 100 h and reference peaks of $\alpha$-Fe$_2$O$_3$, Fe$_3$O$_4$, NiFe$_2$O$_4$, and FeCr$_2$O$_4$. The spectrum indicates oxide layer is composed of $\alpha$-Fe$_2$O$_3$, Fe$_3$O$_4$, and NiFe$_2$O$_4$. These oxides were reported to be observed in 200 ppb DO condition. These are the typical corrosion products on Fe–Cr–Ni alloys in the BWR condition.

Figure 5 shows STEM images of cross sectional view of the surface oxide layer and EDX mapping data of O, Fe, Cr, and Ni. Mo and C were also measured, but they showed no distinct features. These data were omitted in the figure. EDX measurements were done at spots (a) through (h) and along lines (i) through (iv). The results of the EDX spot analyses are summarized in Fig. 6. Figures 7 and 8 show the results of EDX profiles along the lines (i), (ii) and (iii), (iv), respectively. Figure 9 summarizes the result of the line profiles.
Prior to analyzing the growth behavior of surface oxide layer, interfaces between the inner oxide layer, outer oxide layer, and SUS316L substrate were defined from the EDX line profiles. The each layer shown in Figs. 7 and 8 were determined by the following rule taking into account the consistency with the STEM images: The interface between SUS316L substrate and the inner oxide layer was at half between maximum O intensity and the alloy substrates’ O...
intensity. The interface between the inner oxide layer and the outer oxide layer was at half between local minimum Fe intensity and local maximum Fe intensity. The end of the oxide layer was at which intensity of O became 1/2 of maximum O intensity. The interfaces defined in this rule were schematically drawn in Fig. 9, in addition, thickness and composition of these layers are also shown in the figure. Compositions of the layers are obtained by eqs. (1) and (2).

\[ C_b^a = \frac{I_b^a}{\sum_b I_b^a} \]  
(a = O, Fe, Cr, Ni, and Mo. b = inner or outer oxide layer.)  
(1)

\[ I_b^a = \int_{x_1}^{x_2} i_b^a \, dx \]  
(2)

Where, \( C_b^a \) is concentration (at%) of element a in layer b. \( I_b^a \) was obtained by integration of the intensity \( i_b^a \) across the layer as given by eq. (2), where \( x_1 \) and \( x_2 \) are start and end of the layer shown in Figs. 7 and 8.

From Fig. 5, it is found at the all exposure times that the surface oxide layers are composed of outer oxides particles and compact inner oxide layers. The inner oxide layers have obviously lower Fe content and higher Cr content than the average of the outer oxide particles.

At 1 h exposure, two kinds of oxide particles were precipitated in the outer oxide layer. In Fig. 5 1 h, most of the oxide particles were composed mainly of Fe and O as represented by Fig. 7 line (i), while the only leftmost particle had higher Ni content than the others as shown in Fig. 7 line (ii). From now, we call the former as Fe-rich oxide particle and the latter as Ni-rich oxide particle, respectively. It was found from the STEM-EDX observation of whole area of a microsample that approx. 5% of the precipitated outer oxide particles were Ni-rich ones while the two kinds of particles cannot be distinguished from their shape. As for the inner oxide layer, thickness was 7–8 nm, Fe content was lower than the outer oxide layer. As shown in Fig. 7 lines (i) and (ii), Ni and Cr were concentrated at the outermost region of the alloy substrate. The concentration peak position of Ni appeared slightly inner region than that of Cr.

At 10 h exposure, the both inner and the outer oxide layers grew up and the new Ni-rich oxide particles which have triangle or tetragonal cross section have been observed (Fig. 5 10 h). As shown in Fig. 6, spots (a) and (b) are Ni-rich oxide and Fe-rich oxide particles, respectively. Spot (b) can be distinguished from the inner oxide layer [spot (c)] having relatively high Cr concentration. This behavior indicates that the Fe-rich oxide particles were covered with Ni-rich ones.

At 100 h exposure, there were round-shaped Fe-rich outer oxide particles (Fig. 5 100 h, left side) and a Ni-rich one (Fig. 5 100 h, right side). In Fig. 5 100 h, Fe-rich oxide particles were observed inside the Ni-rich ones as shown in the result of spots analyses (e)-(h) while no Ni-rich oxide particle was observed inside the Fe-rich ones.

As shown in Fig. 9, thickness of the inner oxide layer along line (iii) is 54.8 nm, and that of line (iv) is 12.3 nm, respectively. The large difference is estimated to arise from the composition of oxide particle of outer layer. The former
is Fe-rich and the latter is Ni-rich particle. The difference of them indicates that the growth of the inner oxide layer is suppressed underneath the Ni-rich oxide particles. In addition, Ni and Cr enriched region in the alloy substrate was preserved underneath the Ni-rich oxide particle as shown in EDX profile along line (iv). This result is typical one whose EDX-analyzed lines lie at the center part of the Ni-rich oxide particles.

4. Discussion

On the basis of the experimental results, change in the surface oxide layer with time was summarized schematically as shown in Fig. 10.

(i) Selective dissolution of Fe and Cr occurred at initial stage and Ni-enriched layer was formed in the outermost region of the alloy substrate.

(ii) The dissolved metal ions precipitated preferentially as Cr enriched inner oxide layer. Then, the dissolved Fe ions precipitated as Fe-rich oxide particles at the outer layer.

(iii) Ni-rich oxide particles precipitated at the outer layer.

(iv) Ni-rich oxide particles grew faster than Fe-rich ones. The difference of growth rate of the oxide particle caused incorporation of a part of Fe-rich oxide particles into Ni-rich ones. The inner oxide layer grew with time and Ni–Cr enriched region at the alloy substrate was disappeared underneath the Fe-rich oxide particles on the contrary the growth is suppressed and the Ni–Cr enriched region was preserved underneath the Ni-rich ones.

Figure 10 stages (i) and (ii) were estimated from the EDX line profiles in Fig. 7. In Fig. 7, the intensity peaks of Ni appeared at slightly inner region than that of Cr suggests that Ni and Cr were concentrated as metal and oxide, respectively. The Ni and Cr concentration considered to be caused by selective dissolution of Fe and Cr at stage (i) and precipitation of Cr enriched inner oxide layer at stage (ii), respectively.

Figure 10 stages (iii) and (iv) can be observed directly in Fig. 5 1 h and 10 h, respectively. The continuous growth of the Fe-rich oxide particle throughout the experiment suggests that Fe\(^{2+}\) or Fe\(^{3+}\) is saturated near the surface at the all stage. It can be presumed that Ni component was gradually dissolved and when the Ni\(^{2+}\) reached the critical concentration of precipitation, Ni-rich oxide particle nucleated and grew faster than Fe-rich ones. As for the Ni-rich oxide particle’s suppression effect against growth of the underlying inner oxide layer, following mechanism can be presumed: As shown in Fig. 5 10 h, Ni-rich oxide particles had larger apparent contact area with the inner oxide layer than that of Fe-rich ones prevented the invasion of reactant from the solution.

The suppression effect of inner oxide layer growth by the precipitated Ni-rich oxide particles is the first observation of the analysis for early stage of oxide layer in high temperature
pressurized water. It suggests that the outer oxide layer is not only a “corrosion product” but also act as barrier layer to underneath one. But it is uncertain that the difference between Fe-rich and Ni-rich oxides continues for long period. It should be investigated with more long term exposure. Long term test under stress induced condition is also needed to examine whether this local unevenness in the inner oxide thickness acts as initial site for the SCC.

5. Conclusions

Surface oxide layer on SUS316L stainless steels exposed to the 288°C pure water with 2 ppm DO for 1–100 h were analyzed by FIB and STEM technique and the following characteristic oxide growth behaviors were observed. The inner and the outer oxide layer were defined from EDX line profiles shown in Figs. 7 and 8.

(1) At 1 h exposure double oxide layer which is composed of the compact inner oxide layer and the outer with Fe-rich and Ni-rich oxide particles was formed. Ni and Cr were enriched at the outermost region of the SUS316L substrate.

(2) The growth of the inner oxide layer was suppressed and the Ni and Cr enriched region was preserved underneath the Ni-rich oxide particles.

(3) In the outer oxide layer, Fe-rich oxide particles were major precipitates at 1 h exposure and then other Ni-rich oxide particles nucleated and grew faster than Fe-rich ones result in incorporation of a part of pre-formed Fe-rich oxides particles into Ni-rich ones.

Acknowledgement

The authors wish to thank Dr. T. Sato for his help in construction of the experimental setup.

REFERENCES