

## Surface Oxidation Phenomena of Ni-Based Alloy 600 in PWR Primary Water Conditions

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### 1. Introduction

Primary stress corrosion cracking (PWSCC) of Ni-based alloy 600 (Ni-16Cr-8Fe in wt%) has been a prevalent issue in the primary coolant circuits of pressurized water reactors (PWRs) [1,2]. Despite the fact that a number of laboratory studies have been performed and that several models have been proposed to explain the PWSCC phenomena, the exact failure mechanism involved are still not well understood. There is, nevertheless, growing evidence in support for the internal oxidation model by Scott [3], in which grain boundary oxidation is responsible for embrittlement and cracking.

Grain boundaries can act as an enhanced diffusion path for oxidation, and grain boundary oxidation can be regarded as a precursor for crack initiation. Oxidation of the grain boundary in almost all nickel-based alloys exposed to primary water is known to be detrimental for grain boundary cohesion [4,5]. Panter et al. [6] showed that the crack initiation time is strongly reduced when the specimens are pre-exposed in a simulated PWR environment in the absence of applied stress. The changes of the grain boundary structure and chemistry owing to oxygen penetration can increase the sensitivity to PWSCC under a load since grain boundary oxidation significantly weakens the grain boundary strength. Therefore, the oxidation process of the metal surface can be at the origin of crack initiation in this alloy.

The present study was aimed to analyze the surface grain boundary and oxide layers that form on Alloy 600 exposed in a PWR primary water at 325 °C with a hydrogen content of 30 cc/kg H<sub>2</sub>O. Nano-scale sized oxides present inside the oxidized grain boundary and on the oxide layer were precisely characterized using SEM and high-resolution TEM (HRTEM) imaging and a fine-probe chemical analysis method. Finally, the susceptibility of Alloy 600 to PWSCC was discussed in terms of the observed results.

### 2. Methods and Results

#### 2.1 Specimen Preparation

The test specimens were taken from a round mill-annealed Alloy 600 bar with an outer diameter of 120 mm. The material was finally heat-treated at 950 °C for 3 hours, and the chemical composition (wt%) was

measured to be 75.8 Ni, 15.45 Cr, 6.98 Fe, 0.055 C, 0.48 Si, 0.60 Mn, 0.18 Ti, 0.06 Co, 0.17 Al, 0.03 Cu, 0.005 P, and 0.001 S. The material used in the present study was the same as that manufactured for CRDM nozzles in some domestic nuclear power plants. From a preliminary examination of the bar, it was proved that the microstructure is homogeneous and isotropic, irrespective of its location and orientation.

80 mm wide x 40 mm deep x 1.5 mm thick specimens were taken from the round bar for an immersion test. Since the properties of the oxide layer and grain boundary oxidation are considerably sensitive to the surface state of a specimen under test, all specimens were finally polished down using 0.3 μm alumina powders in the same way before immersion in the autoclave. This was done both to minimize the surface damage layers formed by grinding, and to give all the specimens the same surface state.

#### 2.2 Immersion Test and Microscopic Examination

An immersion test was conducted for 5 months in a simulated PWR primary water environmental condition, that is, 1200 ppm B (weight) as H<sub>3</sub>BO<sub>3</sub> and 2 ppm Li (weight) as LiOH in pure water, at a temperature of 325 °C, dissolved oxygen content below 5 ppb, a hydrogen content of 30 cc/kg H<sub>2</sub>O, and an internal pressure of 2300 psi.

After the immersion test, the specimens were investigated using microscopic equipment, such as optical microscopy, SEM, and TEM. The specimens for the optical microscopy and SEM were prepared by chemical etching in a solution of 2 % bromine + 98 % methanol. The TEM foils containing surface oxide layers and grain boundaries were prepared through FIB milling using a dual beam Hitachi FIB-2100 system with a Ga<sup>+</sup> incident beam energy of 30 kV and a current of 1 – 5 nA. To eliminate the deformed surface layers generated from the sputtering of high energy Ga ions, subsequent ion milling was conducted with Ar ions with an incident beam energy of 300 V at an incidence angle of 10° for 10 minutes.

An SEM examination was performed using a JEOL 5200 (operating voltage 25 kV) and a JEOL 6300 (operating voltage 20 kV). A TEM analysis was carried out with a JEOL JEM-2100F (operating voltage 200 kV) equipped with an Oxford ISIS EDS system.

### 2.3 Microstructure of Alloy 600

The microstructure of the Alloy 600 base metal is considerably isotropic and equiaxial due to the final sufficient heat treatment at 950 °C for 3 hours. As shown in Fig.1, needle-like particles were precipitated inside the grain, and coarse precipitates were densely distributed on the grain boundaries. A TEM analysis of the diffraction patterns identified that the precipitates were Cr<sub>7</sub>C<sub>3</sub>, regardless of the locations where they were precipitated.

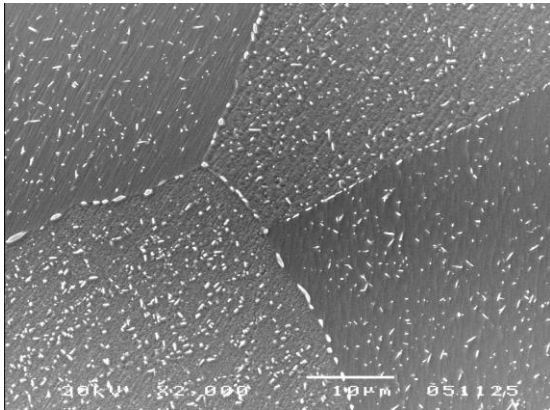


Fig. 1. SEM micrograph showing precipitation morphology in Alloy 600.

### 2.4 Identification of Surface Oxides

The GI-XRD result obtained from the test specimen after an immersion test is shown in Fig. 2. The peaks indicated by blue lines were originated from the surface oxides, and it was determined that the crystal structure was fcc with a lattice constant of 0.834 nm. This means that it is a spinel. On the other hand, the peaks indicated by the red lines were caused by the matrix. The crystal structure was also an fcc structure with a different lattice constant of 0.355 nm. Only a spinel structure was detected in the oxide layers. Therefore, it was confirmed that the major oxides formed on the surface of Alloy 600 in a primary water environment had a spinel structure.

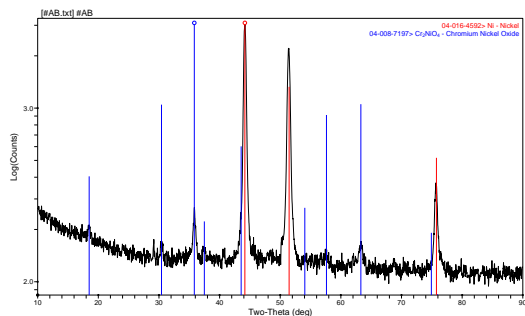


Fig. 2. GI-XRD result on Alloy 600 after an immersion test.

Fig. 3 shows a surface oxide morphology with a highly magnified view. As shown in the figure, several different types of oxide scales were found on the corroded surface of Alloy 600 after an immersion test in the primary water environment. Needle type oxides were formed in the inner layer of the oxide films. On the other hand, faceted (pyramid-shaped) spinel type oxides with sizes of 500 – 800 nm were found in the outer oxide layer. Very tiny unidentified particles with a size of below about 200 nm were also emerged all over the surfaces of the Alloy 600 under study. The complexity of the surface oxide film with different oxide structures was also confirmed by another study [7].

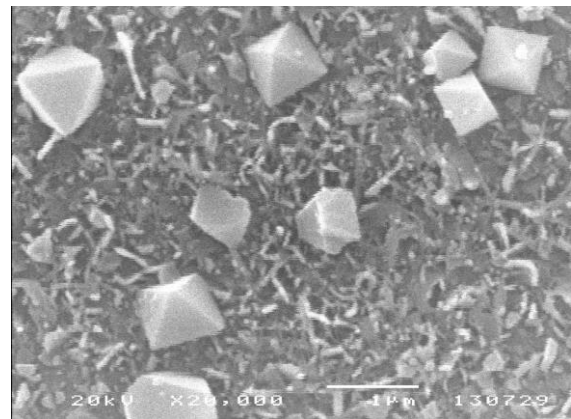


Fig. 3. SEM micrograph showing various oxides formed on the surface of Alloy 600 after an immersion test.

### 2.5 Grain Boundary Oxidation

The remarkable feature found in Alloy 600 after an immersion test under the PWR primary water condition was that the grain boundaries were attacked on the surface, as shown in the SEM image of Fig. 4. In the figure, it can be seen that the grain boundary just beneath the surface was corroded. To obtain a better understanding of the phenomena occurring on the surface grain boundary, a TEM/EDS study was conducted as follows.

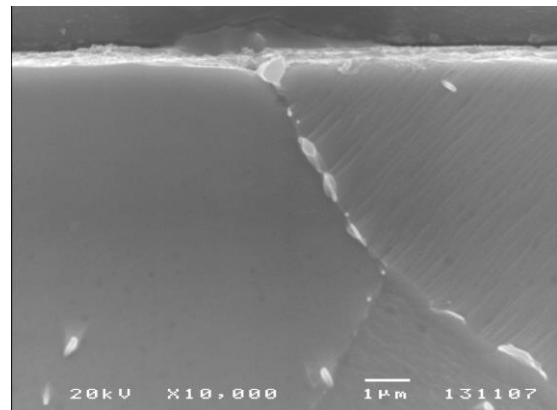


Fig. 4. SEM image showing grain boundary attack occurring in Alloy 600 exposed in a PWR primary water environment.

## REFERENCES

Fig. 5 shows a TEM image and composition maps of O, Cr, Ni and Fe around the surface grain boundary exposed in a PWR primary water environment. Fe enriched oxides with a faceted shape can be seen on the surface. Along the grain boundary, oxygen was detected. This means that oxygen diffused into the matrix through the grain boundary, since conventional Alloy 600 has a negligible oxygen content in a solid solution state. Cr was also enriched; however, Ni and Fe were depleted, which means that Cr oxides were precipitated on that grain boundary. The alterations of the grain boundary structure and chemistry owing to oxygen penetration can increase the sensitivity to PWSCC since grain boundary oxidization significantly weakens the grain boundary strength, as reported by Fujii et al. [4]. Therefore, it is believed that the high susceptibility of Alloy 600 to PWSCC can be caused by the oxygen penetration along the grain boundaries in a primary water environment of a PWR.

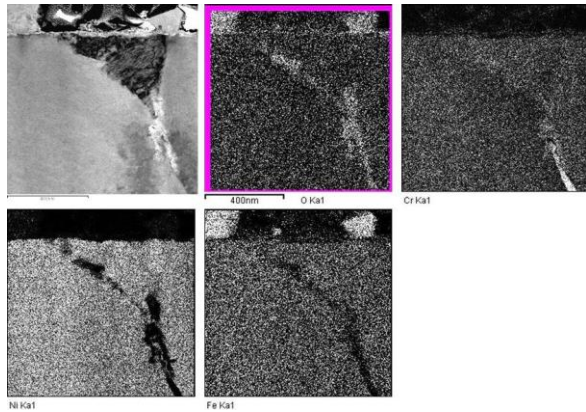


Fig. 5. A TEM image and compositional maps of O, Cr, Ni and Fe around a surface grain boundary of Alloy 600 exposed in a PWR primary water environment.

## 3. Conclusions

In the present study, the surface oxide layer and grain boundary of Alloy 600 tested at 325 °C in a simulated primary side environment of a PWR were analyzed through XRD, SEM and TEM/EDS. Most of the important experimental results obtained are believed to correlate with the oxidation penetration into the material. A spinel structure was detected by XRD in the oxide layers. Several different types of oxide scales were found by SEM examination on the corroded surface of Alloy 600 after an immersion test in the primary water environments. Surface grain boundaries were oxidized by oxygen penetration into the matrix through grain boundaries. Grain boundary oxidization is thought to be the main reason for intergranular cracking in this alloy in a primary water environment of a PWR.

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