

## Oxide property of SG tube materials exposed to an alkaline environment as a secondary side of a PWR

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### 1. Introduction

Stress corrosion cracking (SCC) is an issue that should be overcome in nuclear power plants (NPP) [1,2]. Recognizing that cracks initiate and propagate through unavoidable breakdowns and alterations of the surface oxide on Alloy 600, the SCC behavior is closely related to the oxide property.

Corrosion resistance against SCC, in particular, was improved through a newly developed heat treatment process from LTMA (low temperature mill annealed) Alloy 600 to HTMA (high temperature mill annealed) Alloy 600, and then TT (thermally treated) Alloy 600. Intra-granular carbide widely spread in LTMA Alloy 600 dissolves, and inter-granular carbide is then formed during high-temperature mill annealing and cooling, which leads to a great SCC resistance enhancement. Inter-granular carbide is well developed, healing chromium depletion at a grain boundary, and residual stress is removed during additional thermal treatment following mill annealing, which improves the SCC resistance more [3]. In spite of this improvement of TT Alloy 600, Seabrook and Vogtle 1 in the US, using TT Alloy 600, also showed SCC due to a non-optimum microstructure, residual stress, Pb existence, and so on over a 20-year operation of an NPP even though SCC occurs less frequently than LTMA and (or) HTMA Alloy 600s [4,5]. SCC has also occurred for TT Alloy 600 tubes in Korea, whose main causes resemble US cases.

The pH at high temperature in the crevice of SG tubes distributes from acidic of 4 to alkaline above 10 at high temperature depending on the impurity concentration such as chloride and hydroxide ions including other corrosive impurities such as Pb known as very detrimental species even though the bulk pH of secondary water is a mild alkaline solution [6]. Regarding the aggressiveness of Pb, even Alloy 690 is also susceptible to SCC in a strong alkaline solution with lead [7].

Therefore, in the present work, the oxides were investigated in a leaded alkaline solution of pH(T) 9.9 at 315°C as a function of immersion time using TEM, SEM, EDS and EIS. Moreover, the oxide property formed in a laboratory for this experiment was compared with the oxide property made in the real operational condition of an NPP.

### 2. Experimental

A cross-sectional TEM sample for the cracked region of a pulled tube (TT Alloy 600) that had been exposed to the NPP operating conditions for over 20 years was prepared using an FIB to analyze the oxide composition at the crack tip. Oxide chemical composition was analyzed using a field emission (FE) TEM, equipped with an EDS (JEM-2100F).

The immersion test was performed for TT Alloy 600 and TT Alloy 690 in a 1 gallon Ni autoclave containing a deaerated 0.1M NaOH solution with 1,000ppm PbO at 315°C for 28 days. The test sample was fabricated for a plate specimen (10 mm x 10mm) from a 19.05 mm outer diameter (OD) Alloy 600 tube, which was thermally treated at 704 °C for 15 h after solution annealing at 975 °C for 20 min. The Alloy 690 plate specimen of the same dimension was prepared using a 19.05 mm OD Alloy 690 tube, which was thermally treated at 715°C for 10 h after solution annealing at 1105°C for 2 min. The 0.1M NaOH solution was made using high-purity water [room temperature resistivity of 18MΩ•cm]. The surface of the specimens was polished up to a 1 μm diamond suspension. Reagent grade PbO was added to the 0.1M NaOH solution as a source of lead. Deaeration was accomplished through high purity nitrogen gas purging for 20 h.

During the immersion test, an electrochemical impedance measurement was performed at the open-circuit potential with a perturbation level of 10mV in the frequency range of 10<sup>6</sup> to 10<sup>-3</sup> Hz using a Solartron 1260 frequency response analyser connected with a Solartron 1287 electrochemical interface for a 3 electrode system. A Nickel wire was spot welded to the specimen as the working electrode, and the wire was shielded with heat-shrinkable polytetrafluoroethylene (PTFE) tubing. The nickel and Pt wires were used as a reference electrode and counter electrode, respectively.

A potentiodynamic polarization experiment was performed for TT Alloy 600 in deaerated/non-deaerated 0.1M NaOH with/without PbO with a scan rate of 5mV/s at 315°C using a Solartron 1287. An external Ag/AgCl electrode was used as the reference electrode.

After the immersion test, the surface oxide morphology was observed using SEM (JEOL JSM-6300). The surface oxide layer and its composition for the TEM samples prepared by FIB were examined using a FE TEM-EDS.

### 3. Results and discussion

Fig. 1 shows a cross sectional TEM micrograph of the cracked region initiated on the OD surface of the pulled tube, exposed to the NPP operating conditions for over 20 years. A very tight crack can be seen in the TEM image. The SCC direction, area A, and area B are also indicated in the figure. For areas A and B, a line profile was carried out, as shown in Fig. 2. From Fig. 2(a), there is a relatively Cr rich layer on the crack wall, i.e., a matrix (Alloy 600) and Ni rich layer is formed in the center of crack, i.e., the farthest from the crack wall although another Cr rich layer is also seen the center region. According to previous work, it was found that outer Ni rich porous oxide and inner Cr rich relatively dense oxide are formed in an alkaline solution, which is fairly well consistent with the results obtained from the pulled tubes. It was also revealed that Pb was incorporated into the oxide leading to oxide passivity degradation and SCC by adding Pb at more than only 100ppm into an alkaline solution.

From Fig. 2, significant Pb at up to 5wt% was detected in the oxide, whereas there was no Pb in the Alloy 600 matrix. For area B, Pb above 10 wt% was also found along the crack through the line profiles (not shown here). It was reported [6] that a possible Pb threshold level for Alloy 600 was low at only 0.1 ppm. From this, it is suspected that a Pb above 10wt% observed at the crack tip would considerably affect SCC occurrence in the pulled tube. When the position analyzing EDS is near the crack tip, i.e., area B, a single Cr rich oxide layer is only observed, unlike the duplex oxide layer in Fig. 2. This shows that more passive Cr rich oxide is formed quickly prior to Ni rich oxide formation. Outer oxide is formed and grown by dissolution and a precipitation mechanism, while inner oxide is formed and grown by direct reaction of the matrix with water.

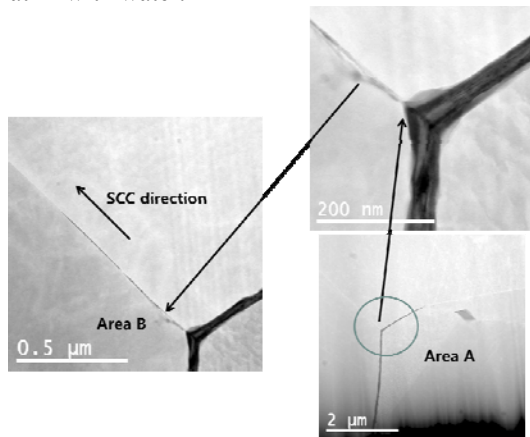


Fig. 1. TEM images of the cracked region initiated on the OD surface of the pulled TT Alloy 600 tube.

Fig. 3 shows SEM micrographs obtained from the surface of TT Alloy 600 specimens immersed in 0.1M NaOH + 1000ppm PbO at 315°C as a function of the immersion time. Polygonal shaped particles can be seen on the surface. The size and uniformity of the particles

were increased with time. The surface coverage of the particles was also increased with time. In spite of the surface coverage increase, the surface oxide seems to be porous rather than dense. The outer oxide reported in the literature is shown to be polygonal shaped Ni enriched oxide from the surface observation.

This polygonal shaped oxide was smaller in size for Alloy 690, which is caused by a relatively lower Ni content.

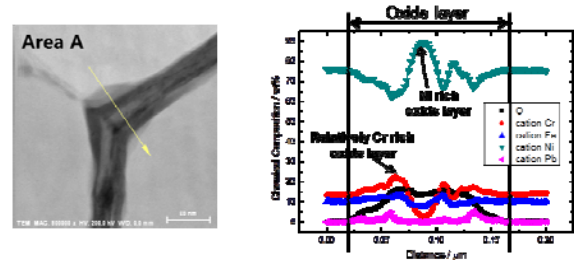


Fig. 2. TEM images and chemical compositions across area B for the pulled TT Alloy 600 tube.

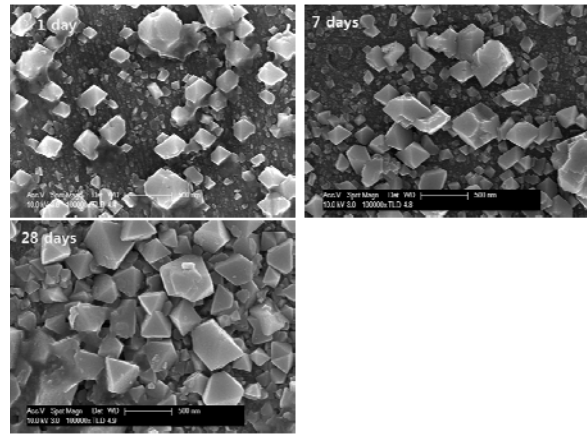


Fig. 3. SEM micrographs obtained from the surface of TT Alloy 600 immersed in 0.1M NaOH + 1000ppm PbO at 315°C as a function of the immersion time.

#### 4. Conclusion

The oxide at the crack tip of the pulled TT Alloy 600 tubes exposed to SG environment of NPP for over 20 years was composed of Ni rich outer oxide and relatively Cr rich inner oxide on the crack wall, which is similar to the oxide formed in an alkaline solution. At a deeper crack, only a single Cr rich oxide layer including Pb above 10wt% was observed, revealing that more passive Cr rich oxide is formed quickly prior to Ni rich oxide formation, and that Pb can affect the SCC considerably.

Electrochemical impedance for the oxide was increased to an almost steady value with increasing immersion time in a leaded 0.1M NaOH solution at 315°C, while the oxide thickness was increased to a steady state thickness. However, in un-leaded 0.1M NaOH solution at 315°C, electrochemical impedance for the oxide was decreased to an almost constant value with the immersion time. From this, it is suggested that

Pb mainly affects the oxide passivity in the early days. It is plausible that oxide formation competes with Pb electrodeposition and incorporation when bare metal is exposed to a leaded solution.

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