

## **Evaluation of oxides formed on Alloy 600 in aqueous solutions containing additives**

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### **1. Introduction**

Alloy 600 material has been used for the last 30~40 years for steam generator tubing in pressurized water reactor(PWR) nuclear power plants(NPP) because it is known to have good mechanical and corrosion properties. However, even in the early 1960s, Coriou [1] showed that Alloy 600 can undergo a SCC in pure water in laboratory tests. The SCC of Alloy 600 began to appear in operating NPP in the 1970s, and a lot of other corrosion related problems have occurred in the SG tubes of the operating NPP since the time resulting in an increased maintenance and thus electric generation unit costs. Diercks [2] reported that the causes of SG tube plugging have evolved with time and, in recent years, outer-diameter stress corrosion cracking and intergranular attack (IGA) have become the predominant identifiable causes that lead to plugging of steam generator tubes.

It has been proposed that a SCC could be related to the oxide film that forms on an Alloy 600 surface because micro pores or cracks could be generated by a volume mismatch between the oxide film and the base metal during an immersion in an aqueous solution at high temperature, and a crack propagation could proceed through a breakdown of the oxide film [3]. Moreover it is presumed that a chemical state of an element consisting of an oxide and a chemical composition of an oxide influence the passivity and corrosion resistance of an oxide and hence a SCC resistance.

According to a previous work, the effect of a NiB as a SCC inhibitor on a SCC was investigated by using a slow strain rate test, a potentiodynamic experiment, a scanning electron microscopy and an Auger electron spectroscopy(AES) [4]. While NiB has been suggested to be an inhibitor, Pb is known as a SCC accelerator. It has been proposed that the possibility of releasing Pb to produce a PbSCC increases when the management of a water chemistry produces more pure systems. It has also been proposed that a PbSCC does not occur because Pb is immobilized by forming stable compounds with other species such as sulfur, carbon, phosphorous and silica, and forming stable adsorbed states with oxides such as magnetite and hematite [5].

The present work investigated the passive films formed on Alloy 600 in the presence of NiB and CeB<sub>6</sub> as SCC inhibitors and PbO as a SCC accelerator using an electrochemical impedance spectroscopy, and a transmission electron microscopy(TEM), equipped with an energy dispersive spectroscopy(EDS). Moreover in order to assess the effect of an applied stress on a surface layer formed on Alloy 600, oxide formed in the

gauge section of the fractured sample after slow strain rate tensile (SSRT) test was observed by using TEM and compared with the oxides formed on the plate specimens.

### **2. Experimental**

TT(thermally treated) Alloy 600 of a 1cm×1cm area as a working electrode was mechanically ground with silicon carbide paper up to #2400 followed by a polishing using a diamond suspension of 1μm particle and an ultra sonic treatment.

Specimen was immersed during 14 days in a 315°C NH<sub>4</sub>OH(pH 9.7) solution using a static autoclave made of Hastelloy C-276. The solution was prepared by a deaeration by an N<sub>2</sub> purging for 20hrs. In order to identify the composition, depth and morphology of the passive film, TEM(TECNAI, G<sup>2</sup> F30, JEOL TEM) analysis whose sample was prepared by use of a focused ion beam(FIB) was performed.

During an immersion of a sample, ac-impedance measurement was carried out in the frequency range of 10<sup>6</sup> to 10<sup>-3</sup> Hz at an open circuit potential (OCP) with a 10mV amplitude perturbation to investigate an electrochemical behavior of the passive films. An ac-impedance measurement was carried out with a Solartron 1255 frequency response analyzer connected to a Solartron 1287 electrochemical interface. A platinum wire and a Ni wire were used as a counter and a reference electrode, respectively during ac-impedance measurement.

TT Alloy 600 fabricated by KAERI was used for the SCC tests. SSRT tests were conducted in 315°C neutral high purity water using a static autoclave made of Ni-200. Before straining the samples, the solution was continuously purged with pure nitrogen gas for 24 hours. The samples in the aqueous solutions were strained at a strain rate of 2 x 10<sup>-7</sup> s<sup>-1</sup>. All the tests were performed at OCP.

After the tests the fracture surfaces and gauge sections of the samples were examined using an SEM. Also, using the values of the load and displacement, the UTS at the failure, the elongation to failure, etc. were determined.

### **3. Results and discussion**

Fig. 1 shows the TEM micrograph and composition profile for the surface film formed on Alloy 600 immersed in a deaerated NH<sub>4</sub>OH solution without an additive at 315°C during 14 days. It was found that the surface layer is composed of two kinds of oxide, i.e. a Ni-rich oxide of 300nm in thickness is formed on the outer surface and an inner layer with a relatively high Cr

content of about 50nm in thickness is formed on Alloy 600.

For Alloy 600 immersed in a deaerated  $\text{NH}_4\text{OH}$  solution with an additive at  $315^\circ\text{C}$  during 14 days, a Ni-rich oxide is formed on the outer surface and an inner oxide with a relatively high Cr content is formed on an inner layer of Alloy 600 as seen in the TEM micrograph and composition profile for the surface film of Fig 2. It is worthwhile noting that a Cr depletion and a Ni enrichment on the outer oxide is relatively higher and the thickness of an inner layer is larger than that of a surface layer formed without an additive. It seems that an oxide layer composition and its thickness at the surface of Alloy 600 are modified due to an additive introduced to the electrolyte leading to an improvement in its SCC resistance.

#### 4. Conclusion

The surface layer on Alloy 600 was composed of two kinds of oxide, i.e. an outer Ni-rich oxide and an inner layer with a relatively high Cr content. From the combination of the results of TEM and ac-impedance, it was found that the outer oxide layer is less passive and the inner oxide layer is more protective. From the results of TEM and SCC in the presence/absence of an additive, it can be concluded that an improvement in a SCC resistance may be due to the modification of an oxide layer caused by an additive in the electrolyte.

#### REFERENCES

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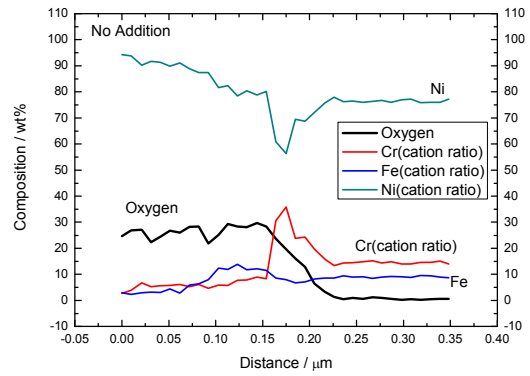
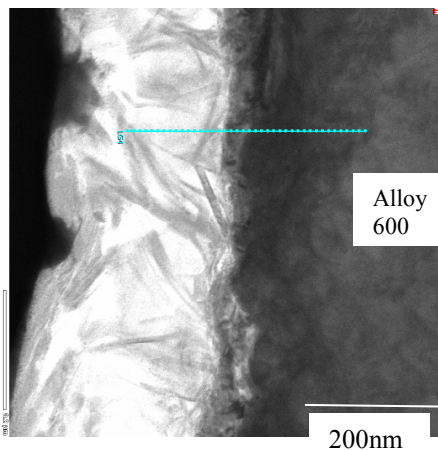


Fig. 1. TEM micrograph and composition depth profile for Alloy 600 immersed at OCP in deaerated  $\text{NH}_4\text{OH}$  solution without additive at  $315^\circ\text{C}$  during 14 days.

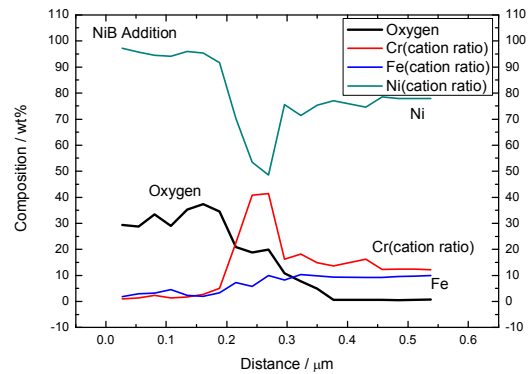
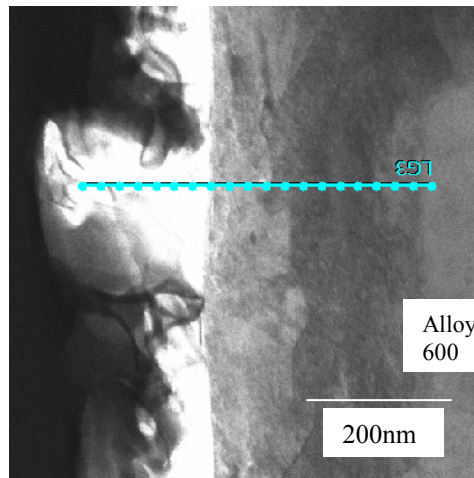


Fig. 2. TEM micrograph and composition depth profile for Alloy 600 immersed at OCP in deaerated  $\text{NH}_4\text{OH}$  solution with additive at  $315^\circ\text{C}$  during 14 days.