Evidence of Internal Intergranular Oxidation as a Mechanism of Primary Water Stress Corrosion Cracking in Alloy 600

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A PhD Level Submission

Summary

Alloy 600 specimens were exposed to a steam-hydrogen environment considered to simulate exposure to primary water conditions in nuclear power plants. Ni nodules were expelled to the surface indicating the likelihood of internal oxidation. A cross-section of the exposed specimen was prepared using a focused ion beam and a composition profile across the cross-section was generated to confirm internal oxidation of Cr. It was revealed that internal intergranular oxidation occurred, and embrittlement was confirmed by the appearance of cracks in the thin section. From these results, it can be concluded that in primary water-type environments Alloy 600 can undergo internal intergranular oxidation of Cr causing embrittlement of grain boundaries.

1. Introduction

Several components in the primary circuit of nuclear plants have been found sensitive to primary water stress corrosion cracking (PWSCC) such as: steam generator tubes, pressurizer nozzles, and reactor vessel head penetrations. Historically, Alloy 600, a Ni-Fe-Cr alloy, is used to construct these components. The composition of Alloy 600 and other commonly used Ni-Fe-Cr alloys is given in Table 1. In the present work, a mechanistic study on the PWSCC susceptibility of Alloy 600 in a simulated primary water environment is performed.

Table 1 – Nominal composition of Alloys 600, 690, and 800 [1].

Element	Alloy 600	Alloy 800	Alloy 690
Ni	72.0% min	30.0% – 35.0%	58.0% min.
Cr	14.0% – 17.0%	19.0% – 23.0%	27.0% – 31.0%
Fe	6.0% – 10.0%	39.5% min.	7.0% – 11.0%
Other (Mn, Ti, Si, C, Cu, P, S)	Bal.	Bal.	Bal.

Primary water is carefully monitored and controlled water with a negligible amount of impurities. The temperature in the primary circuit ranges from 280 ^{0}C to 320 ^{0}C [2]. Lithium hydroxide and boric acid are added to primary water in pressurized water reactors to maintain pH between 6.8 and 7.4. Also, 20 to 50 cm^3 H_2/kg H_2O is added at standard temperature and pressure (STP) to avoid net decomposition of water by radiolysis in the reactor [2]. The addition of hydrogen reduces the potential of primary water into the range of the Ni/NiO equilibrium potential [3]. Primary water conditions suggest the possibility of internal intergranular oxidation in Alloy 600.

Internal oxidation (IO) is a phenomenon first studied at scanning electron microscope (SEM) level of resolution by Rapp et al. in Ag-In alloys at temperatures in excess of 500 ^{0}C [4]. IO occurs in alloys which consist of a noble solvent element, such as Ni, and a lower concentration of a reactive element, such as Cr. The reactive element must be present in low enough quantity such that it does not undergo the transition from internal to external oxide. Under these conditions, the reactive metal can undergo IO when the oxygen partial pressure is within range of the dissociation pressure of the noble metal oxide. Stress relief is achieved by expulsion of pure nodules of the noble metal to the surface [5].

IO is becoming an increasingly well-supported mechanism for PWSCC of nickel alloys. IO can occur in nickel alloys at low nominal partial pressures of oxygen because minor alloying elements, such as Cr in Alloy 600, can oxidize internally if they are present in insufficient amount. The model was first proposed as a mechanism of PWSCC by Scott and Le Calvar [6] and received support from surface embrittlement studies done in steam and hydrogen at 400 ^{0}C [7]. Scenini et al. extended the studies by exposing Alloys 600 and 690 to a steam and hydrogen environment at 480 ^{0}C and atmospheric pressure; in all cases they found that Cr was internally oxidized and this caused the expulsion of metallic Ni nodules to the surface [8, 9]. This kind of environment is believed to reproduce selective oxidation phenomena that occur during PWSCC at much lower temperatures [10].

2. Experimental Procedure

Alloy 600 samples were exposed to hydrogenated steam using the atmospheric pressure reactor at Surface Science Western. Exposures were done in a tube reactor placed in a furnace at 480 °C and atmospheric pressure. Only hydrogen and steam were present in the tube during exposure. The hydrogen partial pressure and steam flow rate were manipulated to maintain an equilibrium oxygen partial pressure three times lower than the Ni/NiO transition within the tube.

2.1 Sample preparation

Flat Alloy 600 samples were prepared as coupons with dimensions of 2 cm by 1 cm. Samples were annealed in air at 1050 ^{0}C for one hour then immediately quenched. Following this, the coupons were abraded down to a 1200 grit finish, and then fine polished using diamond paste to 0.05 µm. The sample was ultrasonically cleaned in ethanol and de-ionized water for 10 minutes each between polishing stages. A desiccator was used to store samples until time of exposure.

2.2 Procedure for Atmospheric-Pressure Reactor Exposures

1. A quartz tube was cleaned using acetone and deionized water. Samples were placed in the centre of the tube and all connections were tightened.
2. The tube reactor was heated to a controlled temperature of 480 ^{0}C. An attached stainless steel block was heated to approximately 300 °C. While heating, the air in the tube was purged using argon for 1 hour followed by hydrogen gas for 1 hour.

3. Once the reactor reached 480 ^{0}C, steam was fed to the block and from there to the reactor using a peristaltic pump. The steam took approximately 15 minutes to reach the reactor.
4. After exposure for 5 days the heating and pump were turned off. The reactor was allowed to cool and the samples then removed.

3. Results and Discussion

Scanning electron microscope (SEM) imaging revealed the presence of nodules throughout the surface of exposed Alloy 600 samples. An SEM image of an exposed Alloy 600 surface is given in Figure 1. Compositional analysis using energy dispersive X-ray spectroscopy (EDS) verified that the nodules were 94%-97% metallic Ni. These results are typical of an internally oxidized material where a reactive element, such as Cr, oxidizes internally resulting in expulsion of the noble and abundant material, in this case Ni, to the surface. While these results are similar to previous studies [4,9], there are some notable differences:

- Ni nodules on exposed Alloy 600 samples have a maximum height of 1.5 µm and maximum length of 3 µm. They are approximately twice the size of the nodules on Alloy 600 samples exposed by Scenini et al., possibly indicating that more internal oxidation is occurring [9].
- Scenini et al. and Rapp et al. found that Ni nodules tended to segregate within grains and away from grain boundaries [4, 9]. However, in the current work Ni nodules had no preference and were present along grain boundaries in some cases. This is likely because the work of Scenini used a material heat-treated to produce a very large grain size.

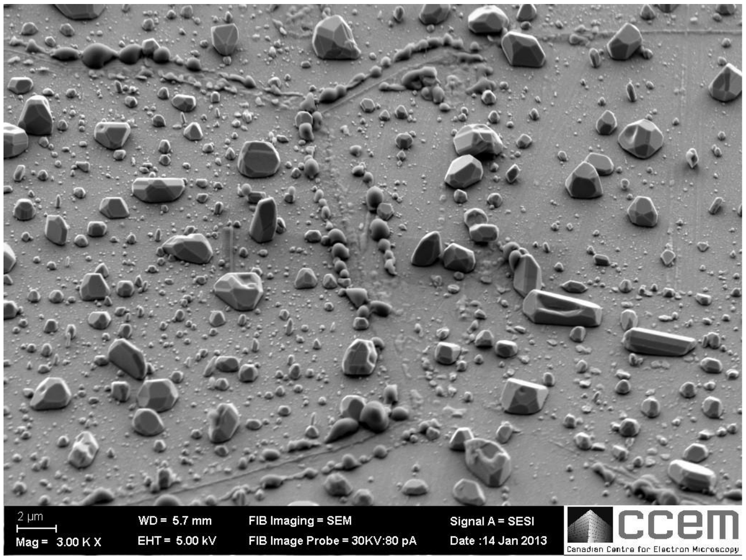

Figure 1 – SEM image of an Alloy 600 surface exposed to hydrogen and steam at a ratio maintaining conditions in the range of the Ni/NiO equilibrium P_{O2} at 480 ^{0}C and 1 bar.

To prove internal oxidation of Cr as the reason for metallic Ni expulsion, a focused ion beam (FIB) was used to remove a cross-section of the material beneath the surface for analysis. The FIB cross-sectioning process is illustrated in Figure 2 and can be summarized as follows:

1. A line of carbon is used to mark the area of interest and to prevent damage from sputtering on the top portion of the specimen.

2. Trenches are sputtered on either side of the area of interest using a Ga^+ ion beam.
3. A tungsten rod is attached to the top corner of the area of interest. The cross-section is cut on alternate sides using a Ga^+ ion beam.
4. The cross-section is removed and placed on a transmission electron microscope (TEM) grid where it undergoes nano-thinning in preparation for TEM analysis.

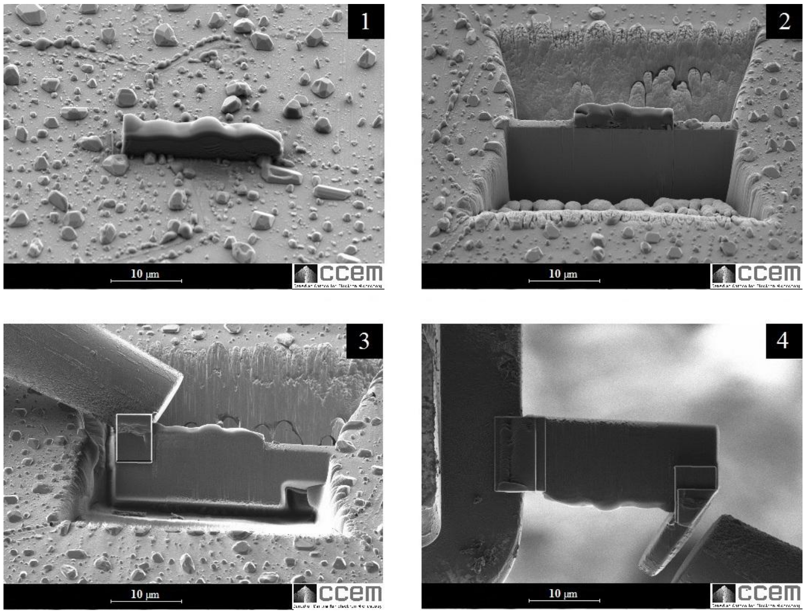

Figure 2 – FIB cross-sectioning process for the exposed Alloy 600 specimen shown in Figure 1

The area chosen on the exposed Alloy 600 surface contained a high angle grain boundary and an area with a residual scratch trace. The logic behind the chosen area was as follows: a high angle grain boundary would be more likely to experience internal oxidation and nodules tend to cluster in areas which have undergone plastic deformation. Figure 3 shows the FIB cross-section. A micro-crack was present along the grain boundary. In addition, Ni nodules were present on the surface.

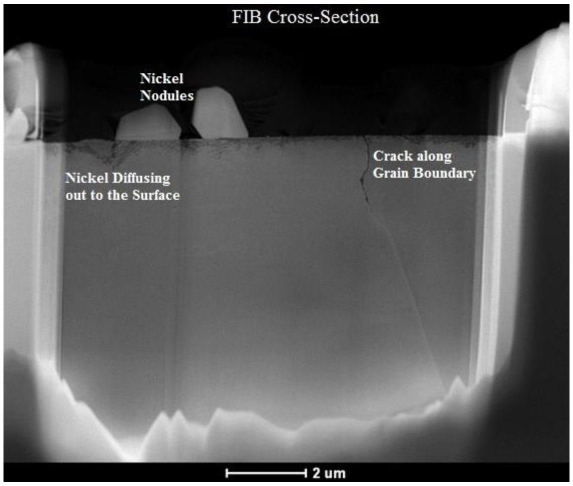

Figure 3 – Cross-section of exposed Alloy 600 sample created using a FIB.

The micro-crack present in the cross-section is a result of direct embrittlement of the grain boundary by internal oxidation of Cr. To confirm internal oxidation the EDS composition profile given in Figure 4 was generated. The area selected for a composition profile was the grain boundary crack near the surface of the material. The results indicate enrichment in Cr, Ti and oxygen and Fe and Ni depletion in and along the crack. Thus our hypothesis is confirmed: internal intergranular oxidation of Cr in Alloy 600 causes embrittlement of grain boundaries and expulsion of metallic Ni nodules to the surface.

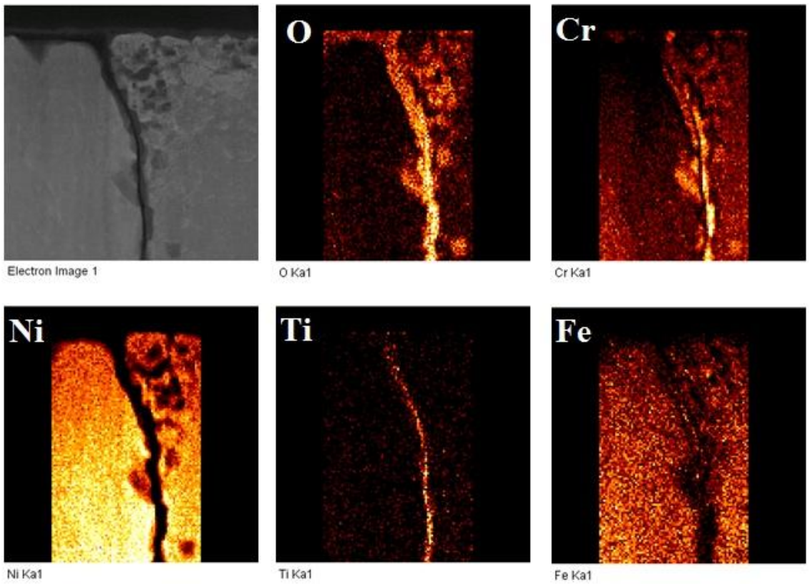

Figure 4 – EDS map of FIB cross-section on exposed Alloy 600 specimen. The region chosen is the top of an intergranular crack near the surface of the material. There is indication of Cr, Ti, and oxygen enrichment and Ni and Fe depletion.

4. Conclusions

In the present work, the internal oxidation model as a mechanism of PWSCC of Alloy 600 was evaluated. Initial surface analysis on Alloy 600 specimens exposed to a simulated primary water environment revealed the presence of Ni nodules on the surface which indicated the possibility of internal oxidation occurring. A FIB was used to prepare a cross-sectional slice below the surface of the material to confirm internal oxidation of Cr. The section chosen contained a crack along a grain boundary and metallic Ni nodules on the surface. EDS mapping was done on the FIB cross-section which indicated enrichment in Cr, Ti, and O and depletion of Ni and Fe along the intergranular crack. From these results it can be concluded that in primary water-type environments Alloy 600 can potentially undergo internal intergranular oxidation of Cr resulting in embrittlement of grain boundaries and expulsion of pure Ni to the surface.

5. Acknowledgements

The author would like to acknowledge Surface Science Western (SSW) for providing their facilities and equipment, and the University Network of Excellence in Nuclear Engineering (UNENE) and the Natural Sciences and Engineering Research Council of Canada (NSERC) for funding this research.

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