**ANALYTICAL ELECTRON MICROSCOPY INVESTIGATIONS OF
PRIMARY WATER STRESS CORROSION CRACKING IN NICKEL ALLOYS**

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August 1997

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Review in progress

AEM INVESTIGATIONS OF PRIMARY WATER SCC IN NICKEL ALLOYS

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ABSTRACT

The microstructure of nickel alloys, particularly the grain boundary composition and intergranular precipitates, plays an important role in high temperature primary water stress corrosion cracking (SCC) performance. Analytical electron microscopy (AEM) was used to examine SCC cracks in Alloys 600 and X-750 to investigate the role of grain boundary precipitates, dislocations and oxides in primary water SCC (PWSCC). Analysis of oxides by AEM and ESCA/Auger indicates that the crack tip oxides are different than the oxides formed on the outer surfaces. Comparison of heats with good and poor SCC resistance has identified metallurgical features that affect cracking. These AEM results show that the mechanism of PWSCC in nickel-base alloys does not involve void formation or blunting of the crack tip near intergranular carbides. The role of grain boundary composition, the interaction of cracks with carbides and other intergranular precipitates, and observations from AEM examinations ahead of the crack tip are discussed in relation to the mechanism of SCC.

I. INTRODUCTION

The observation that PWSCC of nickel base alloys under constant load is intergranular (IG)

emphasizes the importance of grain boundary composition and possibly micro-deformation near boundaries in the cracking process. It is not surprising that thermal treatments that alter the composition of grain boundaries have a significant impact on SCC resistance. Figure 1 shows a 2 to 3x increase in SCC crack growth rate of mill-annealed Alloy 600 due to a thermal treatment that decreased the amount of intergranular carbides and dislocation subcell structure. Numerous studies have shown that thermal treatments that produce a high density of intergranular carbides (and lack of intragranular carbides) improve the SCC performance of Alloy 600 in hydrogen deaerated primary water (DPW).¹ Alloy X-750, a precipitation hardenable alloy, exhibits a nearly 10x change in SCC growth rate as a result of thermal treatments that alter the grain boundary microstructure, as shown in Figure 2. This study used analytical electron microscopy to directly examine SCC cracks in Alloy 600 and X-750 to gain insight into the role of intergranular precipitates and chromium depleted regions, and to examine the composition of oxides present near the tip of SCC cracks.

II. EXPERIMENTAL PROCEDURE

SCC tests using constant load precracked compact tension samples and constant displacement

samples were conducted at 338°C and 360°C in hydrogen deaerated primary water (40-60 scc/kg H₂, pH at temp ≈ 6.7), or in 400°C steam with 11 psia H₂ overpressure. Samples of Alloy X-750 and Alloy 600 for AEM examination were selected to investigate heats exhibiting both good and poor SCC resistance. Specimens for cross-sectional AEM evaluation were sectioned near the crack tip. Thin foils were prepared through a series of grinding, dimpling, and ion milling steps to preserve the corrosion product and microstructure near the crack tip.²³ SCC cracks were examined using a Philips analytical electron microscope operated at 120 KeV and a JEOL 2010F field emission electron microscope operated at 200 KeV. The composition of the samples analyzed are shown in Table 1.

III. RESULTS AND DISCUSSION

A. Crack tip oxides

The oxides formed on the bulk surface and at the tip of SCC cracks in Alloys 600 and X-750 were analyzed using electron diffraction and energy dispersive X-ray spectroscopy (EDS). A schematic of the findings is shown in Figure 3. A duplex oxide film with an inner and outer layer developed on the outer surfaces exposed to the bulk coolant. The inner layer is chromium rich with varying amounts of iron and nickel. Based on electron diffraction, the inner layer contains both a hexagonal Cr₂O₃ type oxide and a chromium rich spinel which is believed to be (Fe,Ni)Cr₂O₄. The outer layer has a spinel structure with lower chromium and higher iron and nickel concentrations. It was also found that blocky precipitates of NiFe₂O₄ and/or NiO were often present on the outer surface of the oxide film. Depending on the hydrogen fugacity of the coolant metallic nickel was also present.

The oxide at the tip of SCC cracks in Alloy 600 and condition HTH X-750 is predominantly nickel oxide (NiO), as shown in Figures 3 and 7. X-ray spectroscopy indicated that the NiO contains chromium and iron, but the crystal structure is simple cubic rather than the spinel type oxide observed on the bulk surface of the sample. A smaller amount of chromium rich oxide was observed in SCC cracks, particularly near the chromium rich carbides (see Figure 5). In contrast to Alloy 600 and condition HTH X-750, the oxide formed at the tip of SCC

cracks in condition AH X-750 is predominantly a Nb-Ti rich oxide, but a smaller amount of nickel oxide (NiO) is also observed along the crack. The crystal structure of the Nb-Ti oxide has not been identified.

Three possible explanations for the differences between surface and crack tip oxides are: differences in the crack tip and bulk solution environments, differences in composition between grain boundaries and the bulk alloy, and reprecipitation of metal ions that exceed the solubility of the solution at the crack tip.

B. Role of Intergranular Precipitates

1. **Alloy 600.** Figure 4 shows SCC cracks following grain boundaries with and without chromium carbides. In general, the SCC cracks were found to follow grain boundaries that are free of carbides, even in thermally treated material that has well decorated grain boundaries. Examination of over 100 foils containing SCC cracks revealed that cracks were not blunted in the vicinity of IG carbides, and that an increased dislocation density is not observed as SCC cracks pass carbides. Thus, no evidence that the beneficial role of carbides results from mechanical blunting or a decrease in crack tip stress intensity via increased dislocation activity near carbides was found.

Shen and Shewmon⁴ proposed that SCC occurs due to microvoids produced ahead of the cracks. According to this mechanism, atomic hydrogen reacts with free carbon segregated along the grain boundaries and creates high pressures of methane gas which creates voids along the boundary. However, bright field examinations at magnifications up to a million times did not show any evidence of voids, cracks, hydrides, or oxides up to 100 μm in front of the crack tip. Furthermore, no increase in oxygen concentration was detected ahead of the crack by X-ray spectroscopy using a 5 nm probe. Future studies should investigate whether low concentrations of oxygen are present and embrittling the grain boundaries ahead of the SCC crack as suggested by the internal oxidation mechanism proposed by Scott.⁵

Another possible beneficial role of carbides concerns their electrochemical reactivity. This reactivity was evaluated by the extent of dissolution

or reaction of precipitates present along the flank of SCC cracks, and the findings are summarized in Table 2. Titanium and niobium rich carbides (MC) preferentially dissolved, but the Cr_7C_3 carbides remained intact. Figure 5 shows that a thin oxide (~5 nm thick) is present along the perimeter of chromium rich carbides (Cr_7C_3), but otherwise the carbides are intact. This is consistent with Rebak et al.⁶ who showed that a galvanic couple between Alloy 600 and the carbide in hydrogenated water (250-350 °C, pH of 9) does not produce accelerated corrosion of either material.

Depending on the thermal processing, a significant degree of chromium depletion may be present due to chromium carbide precipitation. Even so, AEM results show that SCC cracks are extremely tight suggesting that the walls of the SCC crack passivate and prevent extensive dissolution. Thus, in hydrogen deaerated primary water, neither the chromium depleted regions nor the carbides themselves are preferentially attacked. However, in a caustic environment (deaerated 10% NaOH at 307°C) it has previously been shown that Cr_7C_3 carbides are dissolved, and in an acidic environment the chromium depleted matrix is attacked.³

The effect of IG carbides on the SCC resistance of Alloy 600 is difficult to distinguish from the influence of carbon dissolved in the matrix or carbon segregated along grain boundaries. Was⁷ has recently shown that increased dissolved carbon improves the PWSCC resistance of high purity Ni-Cr-Fe alloys during constant extension rate tests due to a reduced creep rate. However, this must be reconciled with the fact that IG carbides which reduce the overall carbon content of the matrix also improve SCC resistance. A possible explanation is that IG carbide precipitation reduces the amount of carbon segregated along grain boundaries which may inhibit the passivity at the tip of SCC cracks. Angelu and Was⁸ showed that higher carbon levels and lower chromium concentrations promote the formation of nickel rich oxides over more protective chromium rich oxides. As noted above, it was found that NiO is the dominant oxide at the crack tips of both Alloy 600 and condition HTH X-750. According to this view, carbon dissolved in the matrix should improve SCC resistance, but carbon segregated along grain boundaries is detrimental.

2. Alloy X-750. The SCC susceptibility of X-750 is strongly dependent on thermal processing and grain boundary microstructure. Figure 2 shows that X-750 in the AH condition has a significantly faster crack growth rate than most heats of material in the HTH condition. These two heat treatments result in the greatest difference in SCC performance for Alloy X-750 and consequently present an opportunity to identify metallurgical features that affect PWSCC resistance.

Grove and Petzold⁹ showed that phosphorus segregated to grain boundaries in the AH material and proposed that high levels of grain boundary phosphorus were responsible for the poor SCC resistance of AH heats. Phosphorus may be deleterious to SCC resistance in several ways, including acting as a hydrogen recombination poison or affecting the passivity of grain boundary surfaces. However, phosphorus alone cannot explain the SCC performance of X-750 since some heats of HTH X-750 with high grain boundary phosphorus concentrations exhibited the best SCC performance. Similarly, Airey¹⁰ has shown that thermal treatments of Alloy 600 that promote IG carbide precipitation also produce the greatest degree of phosphorus segregation and improve primary water SCC resistance.

Over 70% of the grain boundaries in condition AH material were covered with precipitates. Analytical electron microscopy indicated that the predominant grain boundary precipitates were gamma prime and primary carbides (MC) containing almost equal amounts of titanium and niobium. In contrast, the grain boundaries of the HTH material were predominantly decorated with chromium rich carbides (Cr_7C_3 or Cr_{23}C_6) and $\text{Ni}_{23}(\text{B,C})_6$ precipitates.

Figures 6 and 7 show SCC cracks in AH and HTH material tested in 338 and 360°C primary water. AEM examinations of precipitates along the flanks of the cracks indicate that chromium carbides, nickel borides and gamma prime are not preferentially attacked in primary water. However, MC carbides are not observed along SCC cracks (see Figure 6) but are present ahead of the crack tip. This is consistent with the Nb-Ti oxide observed at the crack tip of condition AH X-750. Thus, it is hypothesized that

the preferential dissolution/oxidation of MC carbides which are prevalent along the grain boundaries in condition AH X-750 may contribute to its poor SCC resistance compared to HTH material. Other studies have shown that preferential oxidation of niobium contributes to enhanced environmental degradation of nickel base alloys. Creep tests of nickel base alloys in high temperature air or water vapor at 650°C have shown that the intergranular crack growth rate is increased as the niobium (Nb) content of the alloy is increased.^{11,12} This effect is believed to be due to the formation and fracture of Nb oxide films formed along the grain boundaries during creep.

IV. Summary

AEM results show that the mechanism of PWSCC does not involve the formation of voids or oxides ahead of the crack tip or dissolution of chromium depleted regions. The beneficial role of IG carbides is not the result of crack blunting, but instead IG carbides may improve passivity at the crack tip by reducing the amount of carbon segregated along grain boundaries. The corrosion product formed at the tip of SCC cracks in condition AH X-750 is a Nb-Ti oxide that results from preferential dissolution/oxidation of titanium-niobium carbides which may also contribute to the poor SCC resistance of this alloy.

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Table 1. Bulk Composition of Alloys for AEM Studies (wt%)

Alloy/ Condition	C	Ni	Cr	Fe	Ti	Al	Mn	Si	Nb+ Ta	B	P	S
Alloy 600 MA and HTA ^a	0.07	75.4	15.54	7.76	0.35	0.17	0.25	0.29	---	0.003	0.007	<0.001
X-750 AH ^b	0.05	72.6	15.75	7.09	2.39	0.61	0.15	0.24	0.86	---	---	---
X-750 HTH ^c	0.04	71.4	15.35	7.97	2.56	0.73	0.08	0.3	1.02	0.0018	0.004	0.001

Notes to Table 1

- Mill-annealed (MA): final anneal at 1010°C and air cooled.
High temperature annealed (HTA): 982°C for 1 week followed by water quench to remove IG carbides
- AH: Hot worked→ aged at 885 °C for 24 hours, aged at 704 °C for 20 hours.
- HTH (solutionized and aged): Hot worked→ solution annealed at 1093 °C for 1 hour, aged at 704 °C for 20 hours.

Table 2. Reactivity of IG Precipitates in Primary Water

Microstructural Feature	Reactivity in DPW (40-60 scc/kg H ₂)
Chromium carbides (Cr ₂₃ C ₆ or Cr ₇ C ₃)	Low
MC Carbides (M= Nb, Ti)	High
Gamma Prime (Ni ₃ Al,Ti)	Low
Nickel Borides (Ni ₂₃ (B,C) ₆)	Low
Chromium depleted regions near gbys	Low

Figure 1 Constant load SCC growth rate of Alloy 600 with (MA) and without (HTA) intergranular carbides. (See Table 1 for composition and thermal treatments).

Figure 2 Constant load SCC growth rate of several heats of condition AH and condition HTH Alloy X-750.

Figure 3 Schematic of oxide films formed on the outer surface and at the tip of SCC cracks in Alloy 600 and X-750.

Figure 4 AEM photomicrographs of SCC cracks in Alloy 600 following grain boundaries with (a) and without (b) chromium carbides. SCC tests were conducted at 338°C, K= 25 ksi/in.

Figure 5 AEM photomicrographs showing Cr_7C_3 carbides located along SCC crack in Alloy 600 specimen tested in 400°C steam for 5 weeks. A thin band of corrosion product less than 5 nm thick formed around the carbides. EDS spectra show composition of oxide along carbide.

Figure 6 AEM photomicrograph of SCC crack tip in Alloy X-750 condition AH tested at 338°C , $K=25$ ksi/in. Chromium carbides and gamma prime (Ni_3AlTi) along the grain boundaries are not preferentially attacked.

Figure 7 AEM photomicrographs of SCC cracks in Alloy condition HTH X-750 tested at 360°C , $K=45$ ksi/in. Chromium carbides (Cr) and nickel borides (Ni) along the grain boundaries are not preferentially attacked.