The Effect of Grain Boundary Chemistry on Intergranular Stress Corrosion Cracking of Ni-Cr-Fe Alloys in 50 Pct NaOH at 140 °C

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The role of chromium, carbon, chromium carbides, and phosphorus on the intergranular stress corrosion cracking (IGSCC) resistance of Ni-Cr-Fe alloys in 50 pct NaOH at 140 °C is studied using controlled-purity alloys. The effect of carbon is studied using heats in which the carbon level is varied between 0.002 and 0.063 wt pct while the Cr level is fixed at 16.8 wt pct. The effect of Cr is studied using alloys with Cr concentrations between 5 and 30 wt pct. The effect of grain boundary Cr and C together is studied by heat-treating the nominal alloy composition of Ni-16Cr-9Fe-0.035C, and the effect of P is studied using a high-purity, P-doped alloy and a carbon-containing, P-doped alloy. Constant extension rate tensile (CERT) results show that the crack depth increases with decreasing alloy Cr content and increasing alloy C content. Cracking severity also correlates inversely with thermal treatment time at 700 °C, during which the grain boundary Cr content rises and the grain boundary C content falls. Phosphorus is found to have a slightly beneficial effect on IG cracking susceptibility. Potentiodynamic polarization and potentiostatic current decay experiments confirm that Cr depletion or grain boundary C enhances the dissolution at the grain boundary. Results support a film rupture–anodic dissolution model in which Cr depletion or grain boundary C (independently or additively) enhances dissolution of nickel from the grain boundary region and leads to increased IG cracking.

I. INTRODUCTION

Nickel-base alloys are used extensively in the primary and secondary systems of nuclear power reactors. Single-phase, solid solution Ni-Cr-Fe alloys exhibit excellent corrosion resistance in high-temperature water and steam environments. However, alloy 600 has proven to be susceptible to intergranular stress corrosion cracking (IGSCC) in high-temperature caustic solutions. Although this susceptibility has been known since the early 1960s, the basic mechanisms are not very well understood.[1-3] Past and ongoing research has demonstrated that the susceptibility of alloy 600 to IG cracking in caustic solutions is a strong function of heat treatment.[4-8]

Recently, Lee et al.[6] performed systematic IGSCC tests with samples heat-treated at 700 °C for various times, with mill-annealed and mill-annealed plus solution-annealed samples in 50 pct NaOH at 140 °C. Mill-annealed samples experienced the maximum attack, with the IGSCC susceptibility significantly reduced by heat-treating at 700 °C for 10 hours or longer. However, for solution-annealed samples, heat treatment at 700 °C for 20 minutes increased the attack, while longer heat treatments decreased the attack. Among all the samples tested, the mill-annealed material was the most susceptible.

Although the standard thermal treatment (mill anneal + 700 °C/15 h) has generally yielded a beneficial effect,[6,9,10] in high-purity water, such an effect on caustic IGSCC resistance is not always apparent. McIlree et al.[11] demonstrated that thermally treated alloy 600 (1130 °C/1 h + 675 °C/2 h) exhibited high IGSCC susceptibility in 50 pct NaOH solution at 316 °C. He later noted that thermal treatment [solution anneal (SA) + 649 °C to 677 °C/2 h] was ineffective in 50 pct NaOH at various temperatures.[12] Pathania[13] observed that a mill anneal + 650 °C/4 h improved IGSCC resistance of C-rings exposed to 40 to 150 g NaOH/kg H2O at 290 °C, but had no effect on cracking of pressurized capsules following a mill anneal + 600 °C/5.5 h tested in the same environment. This discrepancy in the beneficial effect of the thermal treatment may stem from the poor definition of the thermal treatment (time and temperature) and the thermomechanical history of materials before heat treatments (mill annealed or solution annealed).

Heat-treatment temperature can also affect IGSCC in caustic solution. Pathania[13] showed that a mill-annealed sample heat-treated at 870 °C for 1 hour did not show improved IGSCC resistance in 40 to 200 g NaOH/kg H2O at 300 °C. Moreover, Airey[10] observed that mill-annealed samples heat-treated at 870 °C degraded IGSCC resistance in comparison with the mill-annealed sample. Also, as the heat-treatment time at 870 °C was increased from 1 to 5 hours, crack depth increased. When the mill-annealed samples were heat-treated at lower temperatures, such as 593 °C and 650 °C, for 100 hours, the crack depth was reduced by five times.

A detailed correlation between cracking behavior and microstructure (primarily grain boundary chemistry) due to heat treatment has not been adequately demonstrated. This lack of understanding of the IGSCC mechanism originates from a complex interaction of numerous variables, such as microstructure, thermomechanical processing, strain rate, environment, and electrochemical potential. Among those variables, the microstructure is the most difficult to control because most studies have
been conducted with commercial alloys for which there were not only heat-to-heat variations in composition but also different thermomechanical histories. It is now well established that a common thermal treatment applied to different starting microstructures can result in vastly different final microstructures and susceptibility to SCC. Hence, a complete definition of the microstructure is essential if the basic mechanisms are to be identified.

In this study, controlled-purity Ni-Cr-Fe alloys were used to determine the effect of chromium, carbon, chromium carbides, and phosphorus on IGSCC behavior in 50 pct NaOH at 140 °C. The role of bulk chromium content was studied using alloys with varying bulk Cr levels. Effects due to variations in grain boundary Cr content were studied by heat-treating Ni-Cr-Fe-C alloys to induce chromium carbide precipitation and chromium depletion. Carbon was selected as a major compositional variable as it is a common impurity existing in alloy 600 and can strongly affect the microstructure through carbide precipitation and concomitant chromium depletion. Bulk carbon level is also varied, and the grain boundary carbon concentration is tracked through the carbide precipitation process. Phosphorus was chosen because it is the only impurity which is consistently detected at grain boundaries in commercial alloy 600. This study represents a systematic approach to identifying the grain boundary chemistries which are responsible for IG cracking and the mechanisms of IGSCC in caustic solution.

II. EXPERIMENT
A. Materials and Sample Design

Controlled-purity heats of Ni-Cr-Fe were prepared by the Materials Preparation Center, Ames Laboratory, University of Iowa. Some heats were doped with either carbon or phosphorus or both. Cast ingots (13-mm diameter) were swaged down to 3.175-mm rod. The chemical composition of the heats used in this study are listed in Table I. Carbon concentration was measured using a combustion chromatographic analysis. Mass spectroscopy of the undoped reference alloy, UHP1, yielded additional impurity contents. These included Cl = 3 appm, Co = 5 appm, Cu = 6 appm, Al = 7 appm, and O = 39 appm. Mass spectroscopy was not performed on the other alloys.

Samples for constant extension rate tensile (CERT) tests in caustic solution were made from a 3.175-mm-diameter rod. Pieces of the rod were machined into cylindrical tensile samples with gage lengths of 14.3 mm and gage section diameters of 1.59 mm. After final heat treatments, samples were ground with 1200 grit SiC paper and polished with 1-μm diamond paste. After polishing, the samples were ultrasonically cleaned with methanol.

B. Heat Treatments and Microstructural Analysis

Heat treatments were performed in a Lindberg Model 54232 tube furnace in an argon atmosphere. Samples were dusted with levitated alumina and wrapped with stainless steel foil to minimize oxidation of the specimens in the furnace during heating. The wrapped specimens were placed in the furnace for an SA at 1100 °C/20 min followed by a water quench. The SA resulted in an average grain size of 130 μm for all alloys except the HCD. The higher C content in the HCD alloy required an SA temperature of 1200 °C for 30 minutes to resolutionize the carbon and resulted in a grain size of 350 μm. Following the SA, samples were rewrapped for lower temperature heat treatment, if necessary. A heat treatment of 550 °C/1 h was conducted to segregate carbon to the grain boundaries but is not experimentally verified. All samples were water quenched following subsequent heat treatments, and all of the heat treatments just described were designed to avoid carbide precipitation in order to study bulk effects of C and Cr.

The effect of varying grain boundary composition on the IGSCC behavior was studied by applying thermal treatments and measuring or calculating the grain boundary Cr and C levels. Heat treatments generally consisted of an SA followed by a single thermal treatment at 700 °C from 0.1 to 100 hours. The two-step heat treatments shown in Table II were conducted to increase the carbon level at the grain boundary in the absence of significant chromium depletion. The grain boundary Cr content was measured for several heat treatments by energy-dispersive spectrometry in the scanning transmission electron microscope (STEM-EDS on a

| Table I. Alloy Compositions (Weight Percent/Atomic Percent) |
|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| Ni | balance | balance | balance | balance | balance | balance | balance |
| Cr | 16.8 | 16.4 | 15.5 | 16.6 | 16.4 | 16.6 | 16.4 | 5.22 | 29.7 |
| 18.4 | 18.04 | 17.2 | 18.26 | 18.11 | 18.25 | 18.03 | 5.9 | 32.2 |
| Fe | 9.0 | 9.3 | 9.0 | 9.1 | 9.1 | 9.3 | 9.1 | 9.11 | 9.10 |
| C | 0.002 | 0.002 | 0.035 | 0.032 | 0.063 | 0.004 | 0.025 | 0.0001 | 0.0019 |
| 0.01 | 0.01 | 0.16 | 0.15 | 0.29 | 0.02 | 0.12 | 0.0005 | 0.01 |
| Dopant | none | none | none | none | none | P: 0.039 | P: 0.035 | none | none |
| Alloy designation | UHP1 | UHP3 | CD1 | CD4 | HCD | PD | CPD | LCr | HCr |

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