Grain boundary selective oxidation and intergranular stress corrosion crack growth of high-purity nickel binary alloys in high-temperature hydrogenated water

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ARTICLE INFO

ABSTRACT

The effects of alloying elements in Ni-5at%X binary alloys on intergranular (IG) corrosion and stress corrosion cracking (SCC) have been assessed in 300–360 °C hydrogenated water at the Ni/NiO stability line. Alloys with Cr or Al additions exhibited grain boundary oxidation and IGSCC, while localized degradation was not observed for pure Ni, Ni-Cu or Ni-Fe alloys. Environment-enhanced crack growth was determined by comparing the response in water and N_2 gas. Results demonstrate that selective grain boundary oxidation of Cr and Al promoted IGSCC of these Ni alloys in hydrogenated water.

1. Introduction

Significant advances have been made in understanding basic mechanisms of intergranular stress corrosion cracking (IGSCC) of corrosion-resistant alloys in high-temperature water environments. Some of the most focused research has been performed to better understand processes controlling environment-assisted cracking in light-water-reactor components [1–5]. Of direct interest to the current research, grain boundary oxidation has been proposed [6–8] to control IGSCC of Ni-base alloys (such as alloy 600) in hydrogenated water based on corrosion and cracking behavior combined with high-resolution characterizations. However, fundamental understanding of interfacial oxidation and crack growth processes remains limited. The role of selective oxidation at grain boundaries is not well established, and proper single variable experiments have not been performed.

Most SCC mechanistic theories can be divided into two broad groups: those based on hydrogen processes and those based on oxidation at the crack tip. For high-strength alloys at low temperatures, hydrogen embrittlement [9–12] or enhanced plasticity [13–15] mechanisms describe observed phenomena quite well. However, these mechanisms are generally irreconcilable with the observed SCC dependencies on temperature, electrochemical potential or alloy microstructure in high-temperature water as argued by Scott [7] and others [16–18]. Slip-oxidation or film-rupture models [19–22] have been largely successful in predicting SCC behavior in Fe- and Ni-base alloys, particularly in *oxidizing* water conditions. In those models, a protective oxide film forms and prevents further IG corrosion. With stress, the oxide film breaks or thins, thus advancing the crack until the protective film can reform at the tip. However, slip oxidation has difficulty explaining the SCC response for Ni-base alloys in *hydrogenated* water and the increasing IGSCC susceptibility with temperature from 290 °C water to 400 °C steam [23]. Analytical transmission electron microscopy (ATEM) studies of crack tips in Ni-Cr alloys [24–30] have revealed a porous, non-protective grain boundary oxide microstructure often *without* a significant dislocation structure. The absence of both protective oxide films and extensive plastic deformation at crack tips are a significant divergence in mechanistic response from the expected slip-oxidation behavior.

An alternative model for IGSCC of Ni-base alloys in hydrogenated water has been proposed by Scott [6,7] based on grain boundary internal oxidation. This model involves the selective oxidation of the primary oxidizing species (e.g. Cr over Ni) *within* the metal grain boundary at the crack tip. The formation and breaking of a protective oxide layer is not required, but oxidation and crack advance is accelerated by high stress at the crack tip. The fundamental processes of internal oxidation are well studied in high-temperature (e.g. > 600 °C) gaseous environments for dilute solid-solution alloys [31–35] where the solute forms the most stable oxide and O has significant permeability in the alloy matrix. Traditionally, internal oxidation requires that a protective surface film is *not* created (consistent with ATEM observations) and the inward diffusion of O atoms exceeds the outward diffusion of the reactive element (neither proven nor disproven by current ATEM observations). As the exposure temperature decreases toward the 300–360 °C range of high temperature water, matrix diffusion becomes

negligible and grain boundaries become the preferred site for internal oxidation.

Early relevant support for internal oxidation at grain boundaries was provided by Panter and colleagues [36] who found evidence of deep O enrichment at triple points in alloy 600 oxidized in 315 °C hydrogenated water. Subsequent analyses of similar samples by others [30,37–41], with arguably more sensitive ATEM and atom probe tomography (APT) techniques have failed to confirm this finding, and the question of grain boundary internal oxidation in hydrogenated water persists. It is important to recognize that internal oxidation of a grain boundary is fundamentally linked with the solubility and mobility of the reactive species (both O and the solute element) along the metallic grain boundary. In particular, the diffusivity of reactive solute species must be slow enough to enable O ingress and subsurface (internal) oxide nucleation. This provides the opportunity for unique behaviors with different solute species, where the IG oxidation behavior may vary both by solute reactivity and diffusivity.

To isolate effects, this research evaluates key processes using high-purity Ni alloyed with ~5 at% of elements with differing oxidation response in high-temperature hydrogenated water. The 5 at% additions were selected to be comparable with previous studies of internal oxidation of Ni-Cr and Ni-Al alloys in high temperature gas [31–35] and to ensure that Al could be kept in solid solution after high temperature annealing. Pure Ni and Ni-5Cu are evaluated to establish corrosion and crack growth responses where no selective oxidation should occur at the test temperature and dissolved hydrogen (DH) conditions, while Ni-5Cr, Ni-4Al and Ni-5Fe alloys are expected to preferentially oxidize versus Ni.

2. Materials and methods

2.1. Materials

Materials for this study were Ni and binary alloys with additions of Cu, Fe, Cr and Al, where an ultra-high purity Ni was used as the base material with high-purity additions of the alloying elements. The intent was to obtain a 5 at% addition of each element in each binary alloy, however slight differences were obtained as documented in Table 1. Compositional analyses are listed from glow discharge mass spectroscopy (GDMS) for all trace analysis, gas combustion analysis for C, N and O, and inductively coupled plasma mass spectroscopy (ICP-MS) for primary alloying elements. These measurements were performed after hot forging at 900 °C, solution anneal (SA) heat treatment at 950 °C for 1 h, and water quenching. As can be seen in Table 1, the starting Ni is extremely clean with only minor appm impurities of Fe, Cr and S plus low levels of C and O. The addition of the binary alloying elements introduced several additional impurities with the most significant being Fe and Cr in the Ni-Al binary, Si in the Ni-Cu binary and Ti in the Ni-Fe binary. Even with these impurities, the binary alloys remain very high purity and enable the assessment of the individual solute additions on corrosion and stress corrosion behavior.

All materials were tested in the SA condition with and without cold working to a 20% reduction by forging at room temperature. The SA produced equiaxed microstructures with no evidence of second phases. Average grain diameters were between 100 and 150 μm for the binary

Table 2
Yield strength (0.2% offset), ultimate tensile strength, and elongation at 330 °C for high-purity nickel alloys in the solution-annealed and 20% cold-forged (CF) conditions.

Alloy	Solution Annealed		Solution Annealed + 20% CF	
	Yield/Ultimate Strength (MPa)	Elongation (%)	Yield/Ultimate Strength (MPa)	Elongation (%)
Ni	136/201	39.0	254/262	20.3
Ni-5Cu	139/230	47.5	286/300	22.0
Ni-5Cr	165/276	44.0	329/341	19.0
Ni-4Al	203/280	38.5	348/356	21.5
Ni-5Fe	157/255	45.8	303/313	31.3

alloys, but was considerably larger for pure Ni at ~300 μm. Tensile tests were performed in air at 330 °C, and measured mechanical properties are summarized in Table 2. The low strength SA materials were cold forged (CF) by 20% using a single-step reduction to increase the yield strength. As expected, the 20%CF materials exhibited much higher yield strength, very limited work hardening, and a reduction in tensile elongation from ~40% to 20% (Table 2). This strength increase improved the creep resistance and enabled a more effective assessment of SCC response in high-temperature hydrogenated water.

2.2. Corrosion and crack-growth testing

Corrosion and crack-growth testing were performed in re-circulating pressurized water autoclave systems capable of operation up to 360 °C. Flow rate through the four-liter, stainless steel autoclave was maintained at 120 cc/min giving ~2 autoclave water exchanges per hour. Water chemistry was controlled through a combination of a boric acid and lithium hydroxide saturated mixed bed resin demineralizer, active stock solution injection, and a continuously circulating four-liter water column used to bubble gasses through the autoclave feedwater. Corrosion experiments were conducted on unstressed small coupons with one surface polished to a colloidal silica (0.05 μm) finish. Cross-section examinations by high-resolution scanning electron microscopy (SEM) and electron backscatter diffraction (EBSD) determined that this final fine polish effectively removed the near surface damage produced during earlier grinding and polishing steps to within 5 nm of the surface.

Crack-growth tests employed active load control through the use of software that interacts with a servoelectric load frame. Crack length was measured in-situ using a reversing direct current potential drop (DCPD) system. The intrinsic resistivity change of the test material at temperature is compensated for by a second DCPD voltage measurement at the back face of the 0.5T compact tension (CT) test specimen where the stresses are nearly zero. DCPD noise causes a data scatter of approximately ±1 μm enabling crack growth rates as low as 5×10^{-10} mm/s to be determined during long-term exposures. Testing was performed in 300–360 °C simulated pressurized water reactor (PWR) primary water (2000 ppm B and 2 ppm Li) with a dissolved hydrogen (DH) content corresponding to the Ni/NiO electrochemical potential (ECP) at each temperature. The outlet water conductivity was monitored continuously and used to actively control B/Li water chemistry throughout the test. A stress intensity (K) value of 20 MPa√m

Table 1
Bulk compositions of high-purity nickel alloys, atomic ppm or **atomic%**. All other elements are below 1.5 appm. (NM = not measured).

Alloy	Cr	Al	Fe	Si	Cu	S	Ti	V	Zr	C	N	O	B
Ni	3.0	0.2	5.8	0.9	0.3	1.4	0.5	< 0.01	< 0.01	54	4	66	< 0.01
Ni-5Cu	49	120	20	1500	**5.1 at%**	2.4	1.4	0.08	0.36	NM	NM	NM	0.6
Ni-5Cr	**5.5 at%**	11	45	27	0.8	3.3	4.4	15	0.06	84	8	74	0.3
Ni-4Al	660	**4.1 at%**	1800	22	0.3	1.6	2.0	1.7	13	88	4	59	< 0.01
Ni-5Fe	48	6.9	**5.0 at%**	4.0	0.6	2.6	99	0.03	0.1	88	4	59	< 0.01