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**EFFECT OF SOLUBLE ZINC ADDITIONS ON THE SCC PERFORMANCE
OF NICKEL ALLOYS IN DEAERATED HYDROGENATED WATER**

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EFFECT OF SOLUBLE ZINC ADDITIONS ON THE SCC PERFORMANCE OF NICKEL ALLOYS IN DEAERATED HYDROGENATED WATER

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ABSTRACT

Stress corrosion crack growth rates (SCCGR) of alloy 600, EN82H and X-750 were measured in deaerated hydrogenated water to determine if soluble zinc mitigates SCCGR. Constant load compact tension specimen tests were conducted at stress intensity factors from ~ 22 to $56 \text{ MPa}\sqrt{\text{m}}$ (20 to $51 \text{ ksi}\sqrt{\text{in}}$) at zinc levels from 15 to $110 \mu\text{g/kg}$ at 316 to 360°C (600 to 680°F). Two test strategies were used to discern a possible zinc effect. The first strategy employed separate SCCGR tests in zinc and non-zinc environments and compared the resulting crack growth rates. The second strategy varied zinc levels at the midterm of single specimen SCCGR tests and characterized the resulting crack growth rate effect through an electrical potential drop in-situ crack monitor.

Results from the direct comparison and midterm changing chemistry tests did not discern a zinc influence; any apparent zinc influence is within test to test variability ($\sim 1.5\times$ change in crack growth rate). AEM, AUGER and ESCA crack tip fracture surface studies identified that zinc was not incorporated within crack tip oxides. These studies identified nickel rich crack tip oxides and spinel, with incorporated zinc, (~ 5 atom percent) bulk surface oxides.

I. INTRODUCTION

The addition of soluble zinc to simulated boiling and pressurized water reactor coolants has been reported to mitigate the stress corrosion crack (SCC) initiation frequency and growth rate of iron and nickel

based alloys.¹⁻³ This study was conducted to quantify the effect of soluble zinc additions on the SCCGR of nickel alloys in pH buffered deaerated hydrogenated water at 316 to 360°C (600 to 680°F).

II. EXPERIMENTAL

The nickel alloys investigated in this study were mill annealed alloy 600, alloy 600 weld metal EN82H, X-750 condition HTH and X-750 condition AH. An additional heat treatment (982°C in air for 7 days and water quenched) was performed on the alloy 600 used to fabricate some of the alloy 600 specimens. The intent of this heat treatment was to create a microstructure with minimal carbide precipitation on the grain boundaries making it more susceptible to SCC. The alloy 600 and EN82H were fabricated into standard 25.4 mm CT specimens with 10% side grooves and the X-750 was fabricated into standard 10.2 mm CT specimens. Test specimens were air fatigue precracked to an a/W of approximately 0.5 prior to testing.

Constant load SCCGR tests were conducted in Instron 8562 servoelectric machines with Model 8500 digital control electronics monitored through a LabVIEW computerized data acquisition system. Crack lengths were monitored in-situ using DC electrical potential drop (EPD) according to ASTM E647, Annex 3, and were verified by post test destructive examinations (DE). In an effort to improve the EPD crack length estimate, a 10% daily unload was incorporated into numerous tests. In the majority of tests, specimens were prefilled at substantially reduced test loads in the

test environment at 260°C for roughly a week, prior to testing.

Figure 1 presents a schematic of a recirculating autoclave/load facility. The feed tank is maintained deaerated by a hydrogen sparge at an overpressure to maintain ~40 scc/kg H₂ in the liquid. The feed tank solution is buffered to maintain a near neutral autoclave pH at the test temperature. In zinc tests, soluble zinc is added to the coolant via a ballast vessel filled with sintered zinc oxide. Coolant flows through the ballast and the dissolution of the zinc oxide, at a controlled temperature, adds soluble zinc at a desired level to the water. Zinc concentrations are determined from samples, taken downstream of the loop cooler, using Inductively Coupled Plasma Spectroscopy (ICP).

A. Zinc and Non-Zinc Comparison Tests

Results from the zinc and non-zinc test comparison effort did not discern a zinc influence [e.g., the apparent zinc influence is within test to test variability (~1.5x change in crack growth rate)]. A synopsis of these results is provided in Figure 2. All symbols in Figure 2 represent a single specimen test except for the X-750 HTH non-zinc test which is the average of 13 specimens from three separate tests. Confidence intervals of 95% for the reported X-750 HTH non-zinc mean and zinc SCCGRs were estimated from the variance of these 13 specimens. In these tests, all efforts were made to control zinc and baseline test conditions as identical as possible. The crack growth rates presented in Figure 2 were determined by dividing the DE evaluated change in average crack length by the total test time since in all tests EPD indicated instantaneous crack growth. The agreement between EPD indicated cracking and actual cracking was excellent (< 20 percent difference) in the thermally treated alloy 600 tests. EPD, however, underpredicted the EN82H and X-750 cracking (approximately by a factor of 5 and 2, respectively) and overpredicted (roughly by a factor of 3) the mill annealed alloy 600 cracking.

One special test was devised to improve the likelihood of achieving a crack tip zinc concentration representative of the bulk autoclave level, assuming the crack tip solution zinc concentration was mass transport limited. The autoclave return flow (1.05 ml/sec through 1.4 mm ID stainless steel tubing) was forced directly through the notch of the specimen (e.g., perpendicular to the direction of crack growth) for approximately three-fourths of the test, see Figure 1b. The autoclave inlet flow was initially emptied into the top

of the autoclave (first ~350 test hours) and then subsequently directed through the notch of the specimen (final ~860 hours) in both the zinc and non-zinc tests. These tests are indicated as the "Directed Flow" tests in Figure 2. In both zinc and baseline tests, EPD did not indicate a change in crack growth rate upon changing the flow location. Of all the comparison tests, however, the "Directed Flow" test was one of only two tests in which the SCCGR in zinc was slower than the baseline (~8%). This small SCCGR reduction is well within the expected test variability (~50%).

B. Single Specimen Varying Zinc Level Tests

Single specimen tests where the chemistry changed from non-zinc to zinc and zinc to non-zinc were conducted to minimize the experimental systematic uncertainties associated with the comparison tests. These alloy 600 tests were conducted at 338°C with ~40 scc/kg H₂ at a K of 27 MPa√m with a 10% daily unload. Two midterm zinc addition tests were conducted with thermally treated alloy 600 and one midterm zinc suspension test was conducted with mill annealed alloy 600. In all three tests, the specimens were prefilled in the respective coolant environment for roughly a week at 260°C at a K of ~4.1 MPa√m. The EPD in-situ crack monitor was employed exclusively in these tests to infer changes in SCCGR as a function of time and as a result of chemistry changes. In the two thermally treated alloy 600 tests (midterm zinc addition tests), there was excellent agreement between the overall EPD indicated crack growth and the actual DE determined crack growth (~20% difference). The DE and EPD agreement in the zinc suspension test (mill annealed alloy 600) was, however, not as good (~48% EPD overprediction). The EPD indicated crack extension and SCCGR throughout one midterm zinc addition and the midterm zinc suspension test are provided in Figure 3. Analogous crack growth was observed in the two midterm zinc addition tests. In the zinc addition tests, the EPD indicated SCCGR was ~10⁻¹⁰ m/s prior to zinc addition and approximately 50% less during the portion of the test after zinc introduction.

The SCCGRs plotted in Figures 3c and 3d were obtained by linear regression through the respective EPD crack length verse time data (Figures 3a and 3b, respectively) for incremental ~250 hour periods. It is evident, from Figure 3, that the EPD indicated crack growth was independent of chemistry change sequence. In other words, the EPD indicated SCCGR

decreased with time regardless if zinc was or was not in the coolant. Thus no discernible zinc SCCGR effect was identifiable using this test method. And the apparent reduction in SCCGR in the midterm zinc addition tests was attributable to the materials natural or EPD response to the test environment.

III. DISCUSSION OF RESULTS

Auger Electron Spectroscopy (AES) and Analytical Transmission Electron Microscopy (AEM) test specimen examinations were conducted to provide insight into why zinc did not mitigate the SCCGR of the nickel alloys in this study. AEM bulk surface and crack tip oxide characterization results were similar to previous studies.⁴ These inspections have revealed that the bulk surface oxides are iron and chromium rich spinels. In some instances these spinels exist in a duplex layer with the chromium rich spinel beneath the iron rich layer. In other situations iron and chromium rich spinels appear scattered throughout the oxide film. AEM analysis indicates that zinc is primarily incorporated within the chromium rich spinel of these bulk surface oxides. However, a nickel rich oxide with a simple cubic structure was observed at the alloy 600 and X-750 HTH crack tips and a niobium/titanium rich oxide in addition to the nickel rich oxide was observed at the crack tip of the alloy X-750 AH specimens. It is noteworthy that zinc is not incorporated within this cubic crack tip oxide, even while it is present in bulk surface oxide films (~ 5 atom percent). AEM representative bulk surface and AES zinc surface concentration results, as a function of depth into the crack, are provided in Figure 4.

X-Ray Photoelectron Spectroscopy (ESCA) and X-Ray diffraction inspections of nickel, alloy 600 and X-750 HTH corrosion coupons exposed to deaerated primary water (DPW) containing 40-70 ppb zinc at 337°C for 5 to 15 weeks were performed. The alloy 600 and X-750 inspections confirm the above AEM CT specimen bulk surface oxide inspection results. Approximately 3 to 7 atom percent zinc was observed within the spinel oxides of the alloy 600 and X-750 corrosion coupons. Zinc was primarily incorporated in the chromium rich spinel. In contrast, significant zinc was not incorporated within the oxide of the nickel coupons (< 0.5 atom percent). This result indicates that zinc cannot significantly incorporate within the pre-dominant crack tip oxide, nickel oxide.

The beneficial effect of zinc [e.g., reduced cobalt

incorporation and corrosion product release,^{3,5} increased oxide rupture strain or oxide film repassivation kinetics⁶] has been attributed to zinc forming a thinner, more tenacious oxide layer. One reason a zinc SCCGR benefit was not realized in this effort is hypothesized to be due to the inability of zinc to incorporate within crack tip nickel oxides to form a more protective layer. This is consistent with SCCGR zinc benefits observed in stainless steel compact tension specimen experiments.⁶ AEM inspections of stainless steel specimens exposed to pH buffered deaerated hydrogenated water 338°C (640 °F) without zinc have revealed spinel crack tip oxides. Another possible explanation for the lack of discernible zinc effect in this study is zinc mass transport limitations as supported by the AES line scan analysis presented in Figure 4b. This figure identifies the surface zinc concentration from the notch of the Figure 2 described X-750 HTH zinc specimen through the precrack and SCC regions. A gradient in zinc surface concentration is observed with depth into the precrack with a lack of detectable zinc before the end of the precrack. It was not evident from this AES surface analysis if the zinc concentration gradient corresponded to or resulted from a transition from spinel rich oxides (notch) to nickel rich oxides through the precrack or if zinc was oxide incorporated or surface absorbed.

IV. CONCLUSIONS

In stress corrosion crack growth rates tests of nickel alloys in deaerated hydrogenated water at 316 to 360 °C (600 to 680 °F) at stress intensity factors from 22 to 56 MPa√m (20 to 51 ksi√in), soluble zinc additions (up to 110 µg/kg) did not mitigate growth rates. The inability of zinc to incorporate into crack tip nickel oxides is hypothesized as the reason a SCCGR benefit was not realized in this study. It is further expected that zinc additions will not mitigate SCC initiation and growth when the process controlling oxide is a nickel oxide. However, when the process controlling oxide is a spinel (e.g., SCC initiation of nickel alloys from a bulk surface) zinc mitigation is possible.

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FIGURE 1: Experimental Test Facility

a) Overview Schematic

b) Flow Configuration for A600 MA K=22 MPa√m
Zinc and Non-Zinc "Directed Flow" Comparison Tests

Figure 2: Zinc and Non-Zinc Comparison SCC Crack Growth Tests

* Average DE crack length divided by total test time

FIGURE 3: EPD Indicated Crack Growth in Changing Chemistry Tests

4a) Representative AEM bulk surface oxide results (A600 zinc "Directed Flow" test specimen)
Large dark crystals are iron rich spinels and smaller crystals are more chromium rich spinels

4b) AES line scan indicating surface zinc concentration as a function of depth into the crack
(Figure 2 X-750 HTH zinc specimen)