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STRESS CORROSION CRACKING GROWTH**

C.D.Thompson, D.M. Carey, N.L.Perazzo

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KAPL ATOMIC POWER LABORATORY

SCHENECTADY, NEW YORK 10701

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EFFECTS OF HYDROGEN ON ELECTROPOTENTIAL MONITORING OF STRESS CORROSION CRACK GROWTH

Charles D. Thompson
Lockheed Martin Corporation
PO Box 1072
Schenectady, NY 12301
(518) 395-4107

David M. Carey
Lockheed Martin Corporation
PO Box 1072
Schenectady, NY 12301
(518) 395-4097

Norman L. Perazzo
Lockheed Martin Corporation
PO Box 1072
Schenectady, NY 12301
(518) 395-7318

ABSTRACT

Electropotential monitoring (EPM) has a crack growth measurement resolution that is an order of magnitude greater than methods that rely on crack mouth opening displacement. However, two phenomena have been identified that compromise the accuracy of the EPM technique. Coolant hydrogen concentrations above those needed to chemically reduce nickel oxide to metallic nickel cause EPM to underestimate the true crack length. The metallic nickel provides an electrical conduction path at contact points across the irregular crack surface thereby lowering the EPM potential. The coolant hydrogen concentration at which this reduction occurs is temperature dependent and correlates with an abrupt decrease in the rate of SCC crack growth.

It was also found that EPM can indicate large crack growth when none actually exists. At temperatures $>315^{\circ}\text{C}$ (600°F) the electrical resistivity of mill annealed Alloy 600 increased by as much as 5% in a period of weeks or months. Each 1% increase in resistivity results in a bias in the EPM indicated crack length of about 0.2 mm (0.008").

Smaller changes in the electrical resistivity of other alloys have been measured which rank as EN52 > X-750 > 304SS > nickel. It has been shown that these resistivity changes occur during exposure to high temperature water or inert gas. Strategies to minimize the effects of these two phenomena on EPM measurement are discussed.

I. INTRODUCTION

Electropotential monitoring (EPM) is an experimental technique used to monitor stress corrosion crack growth in compact tension or other

specimen geometries. A DC current is passed through the specimen and the electrical potential generated across the crack front is measured. As the crack grows, the remaining metal ligament gets shorter and the measured resistance of the specimen increases. The measurement technique is also referred to as DC Potential Drop. With proper equipment and technique this method can measure crack length changes as small as 0.002 mm (0.1 mils) in 1T compact tension specimen at test conditions. This paper discusses two phenomena that affect the reliability of EPM for nickel alloys in high temperature, hydrogenated water.

II. INFLUENCE OF HYDROGEN ON EPM MEASUREMENTS

The addition of hydrogen can cause the SCC crack length indicated by EPM to decrease. Figure 1 shows the results where the crack length of a 1T compact tension specimen of Alloy 600 was monitored by EPM while the cover gas of the recirculating autoclave chemistry loop was switched from nitrogen to hydrogen and back¹. The figure indicates an apparent decrease in crack length of about 0.3 mm (0.012") in 70 hours. This experiment has been repeated under a variety of load and temperature conditions and it was found that the EPM indicated crack shrinkage is usually 0.1 to 0.4 mm (0.005 to 0.015") and requires about one to two weeks to equilibrate.

We postulate that the cause of this phenomena is related to the thermodynamic stability of the oxide formed on Alloy 600. At 288°C (550°F) NiO is stable at hydrogen concentrations of less than about 15 scc/kg. However, at hydrogen concentrations greater than 15 scc/kg, the stable form is unoxidized nickel. These regions of thermodynamic stability are shown in Figure 2 for Ni/NiO and for NiCr_2O_4 . Although the

chromate and ferrite are thermodynamically more stable than nickel oxide, we have found that NiO is the predominant species at the tip of intergranular SCC cracks of Alloy 600 and Alloy X-750^{2,3}.

SCC cracks in Alloy 600 are generally intergranular. The two sides of the crack continue to touch even as the crack grows. This is analogous to a crack in the mortar joints of a brick wall where the two sides of the wall continue in contact even though the crack extends through the full thickness. Normally the Alloy 600 crack faces are protected by nickel oxide which maintains a partial or complete electrical isolation between the two crack faces. However, when sufficient hydrogen is added to the coolant to move into the domain where Ni is stable relative to NiO, the oxide is reduced, the electrical resistance between the two (touching) crack faces decreases and EPM indicates a shrinkage of the crack.

Figure 3 compares the results of EPM measurements made at the end of two SCC tests on Alloy 600 1T compact tension specimens. Following a test at 360C (680F) with 40 scc/kg H₂ the applied load was gradually removed. Under these conditions, where NiO, NiCr₂O₄ and FeCr₂O₄ are stable, the change in load had little effect on the EPM indication (Figure 3a). Similar measurements were made while decreasing the applied load at the end of a test at 288C (550F) with 50 scc/kg H₂ where Ni, rather than NiO, is stable. As the load decreased, the increased contact between the opposing surfaces significantly reduced the EPM indicated crack length (Figure 3b).

Rebak and Szklarska-Smialowska have proposed that the Ni/NiO transition corresponds to the rate maxima observed in SCC crack growth of Alloy 600 as a function of hydrogen⁴. We also find the rate of SCC is greatly reduced upon the addition of hydrogen. When the conditions of Figure 1 were repeated so that the crack advance is simultaneously monitored by measurement of the crack mouth opening, it was found that the crack growth rate was essentially stopped when the hydrogen concentration was increased above the Ni/NiO transition.

Irregular or branching crack fronts also cause EPM to underestimate the maximum crack length. Based on a comparison of EPM and destructive examination of 43 compact tension specimens, we find a factor of 2 to 3x underprediction attributable to the combined effects of hydrogen and irregular crack fronts.

III. INFLUENCE OF RESISTIVITY ON EPM MEASUREMENTS

A second issue with EPM is an indication of crack advance where little or none in fact exists. Figure 4 shows the indicated EPM crack growth for a 1T Alloy 600 compact tension specimen tested at 360C (680F) with a load of ≤ 16 MPa/m (15 ksi/in). After 4000 hours, the EPM indicated about 0.7 mm (0.027") growth. However, the destructive examination of the specimen indicated less than 0.05 mm (0.002") actual growth. Similar observations were found at temperatures as low as 315C (600F), and loads as low as 6 KSI/in. In fact, the phenomena has been observed in notched CT specimens where there is no cracking at all.

This false indication of crack growth by EPM is due to an electrical resistivity increase in the metal during the test. Figure 5 shows a test arrangement designed to measure the resistivity of six materials simultaneously in the autoclave. The rod or tubing sections were wired in series and a constant current applied. The voltage drop of each specimen was measured through platinum wires spot welded near the ends of the specimens. The test was performed at 338C (640F) for 720 hours in water containing 40 scc/kg hydrogen. The temperature was then raised to 360C (680F) for an additional 500 hours. The indicated resistivity for Alloy 600 showed the typical, roughly parabolic, increase also found with the compact tension specimens which the EPM falsely interprets as crack growth. The percentage increase in resistivity $[(R - R_0) \times 100 / R_0]$ for the five materials is shown in Table 1.

Hydrogen changes the resistivity of several metals, such as copper and palladium. It was hypothesized that the increases observed in this study resulted from hydrogen dissolved in the metal, and that the source of the hydrogen was from corrosion in the coolant.

Two experiments were conducted to investigate this hydrogen-resistance hypothesis. In the first experiment, a section of Alloy 600 tubing was charged with hydrogen while measuring the resistivity. A 10 cm (3.9") long section of 3.1 mm (0.12") OD, 1 mm (0.04") ID Alloy 600 tube was cathodically charged (110 MA current) while submerged in a 70C (158F) solution of 0.1 N H₂SO₄. Resistance was measured by passing a constant current through the tube and measuring the potentials at points 2 cm from

each end. After approximately 260 hours there was no appreciable increase in the potential. Sodium arsenate, a hydrogen recombination poison, was added to enhance hydrogen ingress. This caused the potential to increase, however, the change would correspond to a resistivity increase of less than 0.2%. Subsequent measurement of hydrogen in the Alloy 600 indicated that the specimen contained approximately 32 ppm hydrogen. Thus, the magnitude of the resistance change was smaller than expected for this relatively high hydrogen concentration.

In the second experiment, the resistance changes were monitored while load cycles were applied to a standard tensile specimen, compared to an unloaded specimen. The tests were conducted at 338C (640F) in deaerated pH 10.2 water containing 27 scc/kg hydrogen. It was suspected that the parabolic shape of the resistivity change was due to the reduction in corrosion rate as the passive oxide film thickened. When the resistivity change rate had begun to diminish, several load cycles were applied to the loaded specimen. It was thought that fracturing the oxide may increase the corrosion rate and in turn increase the resistivity change rate. However, load cycles made instantaneous changes in the resistance (apparently from plastic deformation), but no significant changes in the subsequent rate of resistance increase. Only 2 ppm hydrogen was measured in the specimens after the resistivity had changed by 1%.

Since these results contradicted the hydrogen ingress hypothesis, the resistivity was monitored during exposure to an inert gas. The resistivity of commercial Alloy 600 tubing was measured at 315C (600F) to 360C (680F) in an argon atmosphere with no applied load. As shown in Figure 6, the resistivity increased substantially in this inert gas environment.

The rates and magnitude of the resistance change in argon with no applied load were comparable to those observed in Alloy 600 aqueous tests. The resistivity change rate of $3.64 \times 10^{-3}\%$ /hr seen after 100 hours at 338C (640F) would cause a false crack growth indication of about 7.9×10^{-4} mm/hr (0.031 mil/hr). Generally, each 1% change in resistivity results in about 0.2 mm (8.4 mils) of EPM indicated crack growth. These inert gas results clearly indicate that the observed resistivity increase is not due to hydrogen ingress into the metal. Near the end of the test in argon, the temperature was increased to 430C (806F) for several hours. At this temperature the

resistivity **decreased** sharply, indicating that the process causing the resistivity change approached some equilibrium that was temperature dependent.

Change in the EPM voltage wire leads has been ruled out as a possible cause of this phenomenon. The resistivity increases have been observed using both nickel and platinum wire. The nickel leads have been reused repeatedly so that any increase in lead resistivity should be saturated out.

We currently have no adequate explanation for the observed resistivity increases. One speculation is that diffusion of solute atoms to or from the grain boundary is the cause. This speculation is based on studies that have shown that diffusion of carbon⁵, boron⁶ and sulfur⁷ to free surfaces or dislocations occurs at the temperatures of the resistivity measurements. SCC crack initiation may be related to segregation of elements at grain boundaries and it is possible that the processes that cause the resistivity change also relate to the SCC performance.

EdF has not observed increasing resistance trends in uncracked WOL specimens in tests conducted at 290C (554F) for 11,000 hours nor at 315C (600F) for 3000 hours. Our experience indicates that at 290C (554F) the resistance increase is very slow. It is also possible that EdF uses a compensating pair of reference potential leads in their DC potential system which would mask any resistivity increase in the specimen.

IV. STRATEGIES FOR EPM USE

To mitigate the effects of these phenomena on EPM crack growth measurement, we have adopted several strategies. Where possible, tests are designed to have only a single combination of environmental and load/geometry variables. Where this is not possible, an independent and simultaneous method of assessing crack growth is used, usually crack mouth opening displacement measurements coupled with load variation to measure compliance. In all cases, specimens are destructively examined after completion of the test.

Since the resistivity increase accelerates at higher temperatures, it can be partially "saturated" by giving the specimens a thermal soak above the test temperature for about one week. An alternative is to place an identical unloaded specimen in the test environment which can be used to compensate for the

resistivity changes. However, we have not shown that the resistivity change is independent of load.

V. CONCLUSIONS

Electropotential monitoring of SCC growth has the highest resolution of all methods we have tried. However there are two problems associated with EPM that diminish its usefulness. Coolant hydrogen can reduce the electrically insulating oxide that protects the crack faces and this results in an underestimate of the true crack length. Irregular or branching crack fronts can also result in an EPM underestimate of the maximum crack length.

Overprediction of the true crack length is found in cases where the resistivity of the metal increases during the test period, which occurs at temperatures above 315C (600F). The cause of this increase is unknown, although we speculate that it is related to diffusion of species to or away from the grain boundaries. Corrosion related processes such as hydrogen ingress were eliminated as the cause.

Several strategies can be adopted to partially mitigate the effects of the two phenomena on EPM measurement of crack growth.

ACKNOWLEDGEMENTS

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Table 1 - Percent Change in Electrical Resistivity

	Alloy 600	EN52	X-750	304SS	Ni
720 hrs @ 338C (640F)	1.15	0.41	0.16	0.10	-0.03
500 additional hrs @ 360C (680F)	1.65	0.75	0.41	0.15	-0.03

Figure 1 EPM indicated crack length vs time

1.0T compact tension
A600
288C (550F)
pH 10.2
 $K = 27 \text{ MPa}\sqrt{\text{m}}$
(25 Ksi $\sqrt{\text{in}}$)
 $R = 0.2$
Freq = 0.01 Hz

Figure 2 Regions of Thermodynamic Stability For Nickel Oxide, Ferrous Chromite and Nickel Chromite

Figure 3. EPM indicated crack length as a function of applied load (lbs).

Figure 3a: 360C (680F) where $\text{Ni}(\text{OH})_2$ is the stable species

Figure 3b: 288C (550F) where Ni^0 is the stable species

Figure 4 EPM indicated crack growth vs time. Destructive examination indicated less than 0.002" growth

1.0T compact tension specimen of Alloy 600 tested at 360C (680F) at 16 MPa/m (15 ksi/in)

Figure 5 Schematic of test conditions for measurement of resistivity increase in six materials

Figure 6 ELECTRICAL resistance of 0.125" (3.2 mm) Alloy 600 tube measured in Argon