



Analytical electron microscopy of a crack tip extracted from a stressed Alloy 800 sample exposed to an acid sulfate environment



S.Y. Persaud^{a,**}, A.G. Carcea^a, J. Huang^b, A. Korinek^b, G.A. Botton^b, R.C. Newman^{a,*}

^a Department of Chemical Engineering and Applied Chemistry, University of Toronto, 200 College Street, Toronto, ON M5S 3E5, Canada

^b Department of Materials Science and Engineering, and Canadian Centre for Electron Microscopy, McMaster University, 1280 Main Street West, Hamilton, ON L8S 4M1, Canada

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ABSTRACT

Alloy 800 (Fe–21Cr–33Ni) has been found susceptible to cracking in acid sulfate environments, but the mechanism is not well understood. Alloy 800 C-ring samples were exposed to an acid sulfate environment at 315 °C and cracks were found with depths in excess of 300 μm after 60 h. Preparation of a TEM sample containing crack tips is challenging, but the ability to perform high-resolution microscopy at the crack tip would lend insight to the mechanism of acid sulfate stress corrosion cracking (AcSCC). The lift-out technique combined with a focused ion beam sample preparation was used to extract a crack tip along the cross-section of an acid sulfate crack in an Alloy 800 C-ring. TEM elemental analysis was done using EDS and EELS which identified a duplex oxide within the crack; an inner oxide consisting of a thin 3–4 nm Cr-rich oxide and an outer oxide enriched in Fe and Cr. Preliminary conclusions and hypotheses resulted with respect to the mechanism of AcSCC in Alloy 800.

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1. Introduction

Alloy 800 is considered a replacement in nuclear power plants for Alloy 600 steam generator tubing and austenitic stainless steel in many locations, including reactor pressure vessel internals, due to a perceived increase in corrosion resistance. The nominal compositions of Alloys 600 and 800 are given in Table 1 (Staeble and Gorman, 2003; Baucio et al., 1993). Alloy 800 is certainly not immune to stress corrosion cracking in acid sulfate environments (Persaud et al., 2013; Gomez-Briceno et al., 2010), but has not been studied extensively. In the 1980s, research was done by J.F. Newman on the acid sulfate stress corrosion cracking (AcSCC) susceptibility of Alloys 600 and 690 (Newman, 1983). The author performed constant extension rate tests (CERT) and autoclave exposures in an acid sulfate mixture consisting of Na₂SO₄, NaHSO₄, and in some solutions FeSO₄ at temperatures ranging from 305 to 350 °C. Newman's work revealed the potential dependence, alloy composition dependence, and pH and sulfate concentration dependence of AcSCC. Sulfate reduction was suggested to occur in experiments at temperatures greater than 330 °C, but no direct

evidence was obtained. Reduced sulfur species are known to impair the passivating effect of surface oxides and/or activate metal dissolution (Marcus and Oudar, 1980; Marcus and Protopopoff, 1993; Marcus, 2002; Daret et al., 1999; Marcus and Talah, 1989). From a mechanistic point of view, AcSCC is not well understood in Ni–Fe–Cr alloys, especially in the 800 alloy.

Studying the oxide chemistry at the crack tip would allow for increased understanding of the mechanism of AcSCC. Transmission electron microscopy (TEM) provides the opportunity to do high-resolution chemical analysis, and possibly chemical state analysis, to provide microstructural and chemical composition information. The ability to prepare TEM samples containing SCC crack tips is challenging (Bruemmer and Thomas, 2001) but would lend great insight to the mechanism of cracking; in recent years, focused-ion beam (FIB) has been used to extract crack tips from SCC specimens for studies in intergranular and transgranular SCC of stainless steels (Huang and Titchmarsh, 2006; Huang et al., 2002; Wang et al., 1999) and SCC of Alloy 600 and stainless steels in high temperature hydrogenated water (Lozano-Perez et al., 2011; Lozano-Perez, 2008; Olszta et al., 2011; Schreiber et al., 2013). Similar approaches have also been applied in fatigue and hydrogen assisted cracking studies (Ro et al., 2012; Martin et al., 2011a, 2011b). The challenge with preparing an electron transparent region of a crack tip using a FIB is partly associated with the residual stress, which can cause the film to fall apart. Also, the depth of cracks is unknown without seeing the cross-section of the material. Methods have been

* Corresponding author.

** Corresponding author. Tel.: +1 4169460604; fax: +1 4169788605.

E-mail addresses: suraj.persaud@mail.utoronto.ca (S.Y. Persaud), roger.newman@utoronto.ca (R.C. Newman).

Table 1
Nominal compositions of Alloys 600 and 800 in wt.% (Staeble and Gorman, 2003; Baucchio et al., 1993).

Element	Alloy 600	Alloy 800
Ni	72.0 min	30.0–35.0
Fe	6.0–10.0	39.5 min
Cr	15.0–17.0	19.0–23.0
Mn	1.00 max.	1.50 max.
Cu	0.50 max.	0.75 max.
S	0.01 max.	0.015 max.
Ti	–	0.85–1.20
Si	0.50 max.	1.00 max.
C	0.025–0.05 max.	0.05–0.10

outlined for extraction of SCC crack tips using FIB (Huang et al., 2002; Lozano-Perez, 2008; Olszta et al., 2011), which has led to an increase in frequency of such studies in the literature. The method used for FIB crack tip extraction in this study is a modified version of the “lift-out” technique (Overwijk et al., 1993; Giannuzzi et al., 1998), similar to the procedure used by Lozano-Perez (2008), but with the added flexibility of a rotating manipulator.

While the FIB technique has been used to study cracks in several systems, the application in AcSCC or in Alloy 800 has not been demonstrated. A crack tip is extracted from an Alloy 800 C-ring after exposure to an aggressive acid sulfate environment using a FIB and thinned to electron transparency for TEM analysis. Analytical electron microscopy, in particular energy dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS), were used for chemical composition analysis to determine the composition and possibly the nature of oxides formed at the crack tip, giving insight to the mechanism of AcSCC in the 800 alloy.

2. Materials and methods

2.1. Materials

Alloy 800 C-ring samples were prepared using tubing purchased from Rolled Alloys Inc. The composition of the tubing is given in Table 2. The tubing was bright annealed and cold finished. Fig. 1 shows the dimensions of the C-rings. The samples were stressed using Alloy 600 bolts such that they were slightly yielded past the ASTM G38 standard (2007) to 2% plastic strain at the apex. The potential difference between Alloy 600 and Alloy 800 in the acid sulfate environments used in this study was found to be approximately 2 mV. Therefore, a galvanic effect would not be expected.

The samples were ultrasonically cleaned for 15 min in both deionized water and ethanol prior to exposure. C-rings were secured to a polytetrafluoroethylene (PTFE) base prior to being placed in the autoclave.

Table 2
Composition of Alloy 800 purchased from Rolled Alloys Inc. used to manufacture C-rings in wt.%.

Element	Alloy 800
Ni	30.9
Fe	45.8
Cr	20.4
Mn	1.15
Cu	0.03
S	0.001
Al	0.40
Ti	0.53
Si	0.54
C	0.07

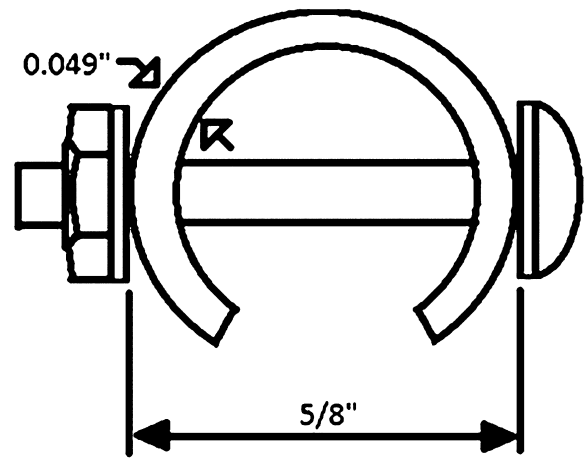


Fig. 1. Schematic of the cross-section of Alloy 800 C-rings used for AcSCC exposures (ASTM Standard G38, 2007).

2.2. Experimental methods

Stressed C-ring experiments were done in a 0.5 L Alloy 625-lined static autoclave vessel. The autoclave was deaerated using high purity nitrogen gas to remove oxygen from the system. Similarly, 230 mL 0.55 M NaHSO₄ acid sulfate solutions were prepared and deaerated for 12 h. After deaeration, acid sulfate solutions were pumped into the autoclave at STP. Finally, a 10 bar overpressure of high purity nitrogen gas was added to the autoclave at room temperature. The autoclave was heated to a controlled temperature of 315 °C, where it was maintained throughout the experiment.

Experiment duration was 60 h in an acid sulfate environment of 0.55 M NaHSO₄. All tests were performed at open circuit potential. The pH at 315 °C was only slightly acidic at 4.3 owing to the suppressed dissociation of the bisulfate anion at high temperatures. Alloy 800 was found to be highly susceptible to AcSCC with cracks in excess of 300 μm in depth. Additional experiments and electrochemical measurements were done on Alloy 800 in acid sulfate environments of different sulfate concentrations using a mixture of Na₂SO₄, NaHSO₄, with FeSO₄ added in some solutions (Persaud et al., 2013).

After exposure the maximum crack depth was determined through optical microscopy, using a Zeiss AX10 optical microscope. Alloy 800 C-ring samples were mounted in epoxy and cut into 0.5 cm slices along the length of the C-ring, revealing the depth of crack penetration at different planes. As expected, crack penetration depth was largest at the points of highest stress, in sections near the midpoint along the length at the apex of the C-ring. The section with the highest density of cracks was fine polished and optical microscopy was used to confirm that multiple cracks were present on the cross-section that would be suitable for FIB crack tip extraction. Fig. 2 illustrates the procedure for mounting, cutting, and polishing C-rings to produce suitable samples for use in the FIB-SEM.

2.3. Microscopy equipment

A FIB was used to extract a cross-section using a Ga⁺ ion beam at an accelerating voltage of 30 kV in the Zeiss NVision 40 FIB-SEM; this tool is equipped with a rotating micromanipulator (Kleindiek Nanotechnik, MM3A-EM) capable of full rotation, in addition to the conventional translational movements. The NVision system was capable of depositing tungsten in situ using the Ga⁺ ion beam. Final polishing was carried out at 10 kV with a current of 80 pA. TEM imaging and EDS work was performed using a FEI Titan 80-300

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