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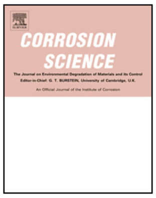

The influence of the high Fe and Cr contents of Alloy 800 on its inter- and intragranular oxidation tendency in 480 °C hydrogenated steam

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ABSTRACT

Alloy 800 was exposed to 480 °C hydrogenated steam with conditions maintained at an oxygen partial pressure well below the dissociation pressure of NiO. Oxidation phenomena in Alloy 800 were investigated using high resolution electron microscopy techniques. Limited oxygen penetration was detected at grain boundaries while extensive internal oxidation occurred intragranularly. Internal oxidation was possible in an alloy containing a reactive solvent element, Fe, with the solute element, Ni, displaced to the surface. Several stress relief mechanisms are observed to operate simultaneously. The relevance of the observed oxidation phenomena on the primary water SCC resistance of Alloy 800 is discussed.

1. Introduction

Alloy 800 (Fe-35Ni-21Cr) is a high alloy stainless steel currently used for steam generator tubing in Canada deuterium uranium (CANDU) nuclear reactors. The 800 alloy is also regarded as a possible replacement for ordinary austenitic stainless steel in water-cooled nuclear reactors internationally. Alloy 600 (Ni-16Cr-9Fe) was the material used previously for steam generator tubing but was found susceptible to stress corrosion cracking (SCC) in both primary and secondary side water and subsequently replaced; some plants use thermally treated (TT) Alloy 600 which is more resistant to SCC than annealed only Alloy 600 owing to the presence of intergranular Cr carbides. The elevated Cr and/or Fe content of Alloy 800 is thought to aid in the formation of more passivating external oxides which increase resistance to primary water stress corrosion cracking (PWSCC). Similarly, Alloy 690 (Ni-30Cr-10Fe) was used to replace Alloy 600 in pressurized water reactors (PWR) and is considered more resistant to PWSCC than the 600 alloy due to its significantly higher Cr content.

Alloys 690 and 800 have both exhibited reliable performance in-service and are resistant to PWSCC in the absence of severe cold work (CW). Several studies have reported that Alloy 690 is susceptible to PWSCC with severe CW [1–6]. Limited SCC testing has been done on Alloy 800 in representative primary water conditions. However, the 800 alloy is known to be susceptible to SCC in secondary side environments, such as acid sulfate [7–9] and caustic [9,10]. Recent work by Arioka et al. revealed that PWSCC can be induced locally in 20% CW Alloy 800 [11]; very shallow intergranular SCC was observed after exposure to 320 °C primary water for 6,903 h. Arioka et al. compared their data with SCC growth in 20% CW Alloy 600 and 20% CW Alloy 690 [11]. They reported excellent PWSCC resistance in 20% CW Alloy 800 compared with other steam generator alloys at 320 °C and 340 °C [11]. Further electrochemical work was performed by Wang et al. comparing Alloys 690 and 800 in primary water environments with varying dissolved oxygen contents [12]. They reported that the 690 alloy exhibited slightly better corrosion resistance in environments with a dissolved oxygen content less than 0.1 ppm. However, at dissolved oxygen contents greater than 0.1 ppm, where thermodynamics predicts the formation of $HCrO_4^-$ rather than stable Cr_2O_3, the 800 alloy was superior owing to its relatively balanced ratio of Fe to Ni [12].

Scott and Le Calvar proposed that the mechanism of PWSCC in Alloy 600 may be internal oxidation which results in

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intergranular embrittlement [13], similar to oxygen embrittlement observed in Ni superalloys at temperatures such as 800 °C [14–19]. Internal oxidation is a phenomenon which occurs in binary or ternary alloys with a noble solvent element and one or more reactive solute elements. In environments or at an external oxide-metal interface where the nominal oxygen partial pressure is within range of the equilibrium dissociation pressure of the noble solvent metal oxide, the solute element, if present in insufficient amount, can oxidize internally. The resulting internal oxides generate significant compressive stresses which, in some cases, are relieved through the expulsion of the noble solvent metal to the surface [14,20–26].

Internal oxidation has gained support as the mechanism of PWSCC in Alloy 600 from studies in both 300 °C to 360 °C primary water [27–37] and hydrogenated steam at temperatures of 400 °C and greater [20–23,38–45]. The use of hydrogenated steam to simulate accelerated primary water conditions stems from a study by Economy et al. where they found that PWSCC initiation times in Alloy 600 U-bend samples exhibited an Arrhenius relationship over temperatures ranging from 300 °C primary water to 400 °C hydrogenated steam [46]; therefore, the mechanism of SCC is likely similar in both environments. However, additional oxidation processes, unrelated to SCC, may be possible in high temperature hydrogenated steam due to the accelerated kinetics. Scenini et al. and Persaud et al. reported that internal oxidation, as classically defined, was possible in Alloy 600 when exposed to 480 °C hydrogenated steam [20,21,40]. They observed that Ni was expelled to the surface to relieve stress from internal Cr and/or Fe oxidation. Given that lattice diffusion is essentially negligible at 480 °C over short laboratory test durations, significant short circuit diffusion paths must be available. While metallic Ni expulsion has been proven to be possible in accelerated hydrogenated steam environments, it has never been observed in 300 °C to 360 °C primary water. However, similar intergranular internal oxidation and embrittlement has been reported in primary water and hydrogenated steam, which likely leads to PWSCC in Alloy 600 [27–37].

According to high temperature oxidation theory, internal oxidation in Alloy 690 and Alloy 800 should not be possible due to their elevated Fe and/or Cr contents, which are well above the critical solute element concentrations required for external oxide formation. The increased outward Fe and/or Cr flux should allow for external oxidation which consumes oxygen and impedes inward oxygen penetration. However, at lower temperatures, where lattice diffusion is essentially negligible over short laboratory timescales, intragranular penetration of oxygen has been demonstrated in 360 °C primary water and 480 °C hydrogenated steam [22,47,48]. In the latter environment Persaud et al. reported that classical internal oxidation, resulting in metallic Ni expulsion, was possible intragranularly in Alloy 690 due to the hindered lattice diffusion kinetics and the presence of short-circuit pathways, such as dislocations [22]. Enhanced grain boundary diffusion allowed for external oxidation on grain boundaries in Alloy 690 which prevented the intergranular embrittlement observed in Alloy 600 [22]; therefore, the likely PWSCC resistance of Alloy 690, in the absence of severe cold work, can be attributed to its high Cr content. The mechanism of PWSCC observed in CW Alloy 690 has been suggested to be a result of high grain boundary strains or grain boundary damage related to cluster of intergranular vacancies and cracked intergranular carbides [1,2]. The possibility of internal oxidation inter- or intragranularly in Alloy 800, with or without applied CW, has not been investigated in high temperature hydrogenated steam; in general, limited Alloy 800 studies have been done in primary water environments.

In the current work, Alloy 800 will be exposed to an accelerated primary water environment consisting of 480 °C hydrogenated steam with conditions maintained at an oxygen partial pressure well below the dissociation pressure of NiO. The possibility of internal and/or external oxidation in Alloy 800 will be investigated using high resolution analytical electron microscopy techniques. Observed oxidation phenomena will be compared with Alloy 600 and Alloy 690 previously exposed to a similar environment [20–22]. Final remarks will be made with respect to the relevance of the observed oxidation phenomena on the likely PWSCC resistance reported in Alloy 800 in the absence of CW.

Table 1
Composition of Alloy 800 purchased from Rolled Alloys Inc. (in wt. %).

Alloy	Ni	Fe	Cr	C	Mn	S	Si	Cu	Al	Ti
800	32.0	Bal.	20.9	0.08	0.8	0.001	0.35	0.27	0.47	0.56

2. Experimental methods

2.1. Materials and sample preparation

Alloy 800 was purchased from Rolled Alloys Inc. as a 1.3 mm thick plate; Table 1 reports the composition of the material. The material was cut into flat coupons measuring 1 cm by 1 cm. Coupons were solution annealed at 1050 °C in Ar-5% H_2 gas for one hour and immediately water quenched to ensure complete dissolution of carbides and homogeneous composition.

Samples were ground with 400, 800, and 1200 grit paper. Following this, coupons were fine polished using diamond paste (9 μm, 3 μm, and 1 μm) and then with alumina suspension to a 0.05 μm finish. Coupons were ultrasonically cleaned in ethanol and de-ionized water for 10 minutes each between polishing stages and dried with air. A desiccator was used to store samples until time of exposure.

2.2. Experimental conditions and procedures

Alloy 800 flat coupons were exposed to hydrogenated steam using an atmospheric pressure reactor at Surface Science Western (SSW). The experiments were similar to those performed previously by Scenini et al. on Alloy 600 [38–40] and Persaud et al. on Alloy 600, Alloy 690 and Alloy 82 dissimilar metal welds [20–23].

Conditions that would promote internal oxidation were achieved by maintaining an oxygen partial pressure in the reactor below the Ni/NiO equilibrium oxygen dissociation pressure. Determining the equilibrium dissociation pressure of oxygen was done using the thermodynamic relationship for the molar Gibbs free energy of formation for the NiO dissociation reaction and confirmed using an Ellingham diagram. The oxygen partial pressure used for exposures was set 30 times below the calculated equilibrium oxygen dissociation pressure for Ni/NiO. Using the thermodynamic relationship for the standard molar Gibbs free energy of formation for the steam dissociation reaction at 480 °C the necessary ratio of steam to hydrogen can be calculated; this ratio can be used to calculate the necessary water and hydrogen flow rates by performing a simple mass balance. A more detailed outline for calculation of environment conditions was presented in a previous study by the authors and can be found in literature [21].

Reactor design was based on work originally done by Scenini et al [40]. Exposures were carried out at 480 °C for 120 h in a tube reactor enclosed in a furnace. The furnace is unable to encase the ends of the tube and high temperature tapes are used to heat exposed areas. Argon gas is used to purge the system of air prior to experiments. Hydrogenated steam is continuously refreshed. Deionized water is pumped into the system using a peristaltic pump. Steam and hydrogen are fed into a stainless steel block at 300 °C where they are mixed prior to entering the reactor. Upon exit from the reactor, the hydrogenated steam is separated into hydrogen and water by way of a condenser. The hydrogen is combusted using a

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