



Internal oxidation of alloy 690 in hydrogenated steam



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ABSTRACT

Alloy 690 was exposed to a hydrogenated steam environment at 480 °C and 1 bar, considered to simulate primary water in a pressurized water reactor. The possibility of internal oxidation in Alloy 690 was evaluated and the likely relevance to SCC in primary water is discussed. Initial surface imaging revealed intragranular metallic Ni nodules, indicating that internal oxidation had occurred. Grain boundaries provided a short circuit for outward Cr diffusion and an external surface oxide was observed at grain boundaries. FIB trenching was used to study oxidation phenomena occurring beneath the surface and EDX elemental maps were generated.

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1. Introduction

Primary water stress corrosion cracking (PWSCC) of Alloy 600 has been a prevalent issue in the primary circuit of pressurized water reactors (PWRs) for many years. In recent years, Alloy 690 (Ni–30Cr–10Fe) has been implemented as a replacement material for Alloy 600 (Ni–16Cr–9Fe) in the primary circuit of PWRs. The 690 alloy is thought to be more resistant to PWSCC due to increased Cr content, which promotes the formation of protective oxide films on the surface when exposed to primary water.

The addition of 25–50 cm³ H₂/kg H₂O to primary water results in reducing conditions, near the Ni/NiO transition potential. The PWSCC susceptibility of Alloy 600 and its weld metals are known to peak near the Ni/NiO transition [1–4]. Conditions within range of the Ni/NiO transition suggest the possibility of internal oxidation. Internal oxidation can occur in Ni–Fe–Cr alloys in conditions where the oxygen partial pressure is in the range of the dissociation pressure of the more-noble metal oxide, NiO; the reactive element, Cr, when below a critical concentration can oxidize internally rather than externally [5–7]. The phenomenon was first observed at a scanning electron microscopy (SEM) level of resolution by Rapp et al. in Ag–In alloys [7,8] and is known to occur in Ni–Cr alloys at temperatures such as 800 °C [9–11]. Internal oxidation was first proposed as a mechanism of PWSCC by Scott and Le Calvar [12] and has received support from surface embrittlement studies done on Alloy 600 in hydrogenated steam at 400 °C [13–15]. Economy et al. [16] found that using hydroge-

nated steam at 400 °C produced a tenfold decrease in PWSCC initiation time; also, the crack growth rate of Alloy 600 U-bend samples exposed to hydrogenated steam and 360 °C primary water lay on one Arrhenius line [16]. They concluded that while the kinetics were accelerated in hydrogenated steam, the cracking mechanism and the role of microstructural variables was similar to high pressure reducing water at 360 °C [16].

Internal oxidation as a mechanism of PWSCC in Alloy 600 has been reported in several studies [17–26]. Scenini et al. exposed Alloy 600 to a steam and hydrogen environment at 480 °C and atmospheric pressure; they found that in Alloy 600 chromium was internally oxidized and stress relief was achieved by the expulsion of metallic nickel to the surface [20–23]. Persaud et al. extended the studies and found that intergranular embrittlement occurred in solution annealed (SA) Alloy 600 resulting in fracture under stress [24,25]. Also, Persaud et al. reported that thermally treated (TT) Alloy 600, which is concentrated in Cr at grain boundaries due to Cr carbide precipitation, forms a Cr-rich oxide at or near the surface of grain boundaries, likely contributing to the observed SCC resistance of Alloy 600TT [24,25]. Alloy 690 contains significantly more Cr and has been found to oxidize externally when exposed to hydrogenated steam [20]; however, internal oxidation may be plausible in Alloy 690 in such environments because back diffusion of Cr to the surface intragranularly is limited at temperatures below 480 °C. If internal oxidation occurs it would likely be intragranularly where lattice diffusion rates are negligible. Conversely, grain boundaries provide a short circuit for diffusion at lower temperatures resulting in diffusion rates being enhanced.

Alloy 690 is regarded to be generally resistant to PWSCC. However, the alloy has been shown to undergo PWSCC with severe cold work [27–31]. Severe cold work causes grain boundary damage in

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Alloy 690TT by creating small voids and cracking Cr carbide precipitates. Bruemmer et al. showed that the intergranular SCC susceptibility of cold worked Alloy 690TT can be greatly reduced by annealing the alloy to remove localized strain, leaving grain boundary damage intact, suggesting that localized strain is the primary reason for high SCC rates [27]. Selective internal intergranular oxidation, which is regarded to cause embrittlement in Alloy 600 [24,25], is not thought to occur in Alloy 690 due to high Cr content, which should promote external surface oxidation and consumption of oxygen. Olszta et al. performed surface oxidation studies on Alloy 690 by exposing mechanically polished flat samples to primary water conditions at 360 °C with conditions at the Ni/NiO stability line [32]. They found that a thin, protective chromium oxide formed on grain boundaries, possibly preventing intergranular SCC; however, penetration of oxygen occurred intragranularly, to a depth of approximately 100 nm, through the non-protective mixed oxide surface layer. Oxygen penetration was likely due to slow Cr lattice diffusion kinetics and followed a dislocation substructure [32]. The work by Olszta et al. suggest the possibility of intragranular internal oxidation in Alloy 690, but their exposure conditions, at the Ni/NiO equilibrium line, are too oxidizing to determine conclusively whether internal oxidation, as classically defined, is actually occurring.

In the present work, the possibility of internal oxidation in Alloy 690 exposed to a hydrogenated steam environment at 480 °C and 1 bar is explored. Conditions are maintained well below the Ni/NiO dissociation pressure to give clear results regarding the role of Ni and Cr. From a theoretical point of view, internal oxidation would not be expected to occur in Alloy 690 at a Cr content so far above the classically determined critical Cr concentration; however, while this may be true in Ni–Cr alloys at temperatures such as 800 °C, at the 'low' temperatures used in this work lattice diffusion of Cr is essentially negligible, leading to transgranular penetration of oxygen being a possibility. Final conclusions will be drawn with respect to the occurrence or not of internal oxidation in Alloy 690 and the likely effect on PWSCC susceptibility.

2. Materials and methods

2.1. Materials

Alloy 690 was purchased from Rolled Alloys Inc. as a 1.3 mm thick sheet and used for all experiments; Table 1 gives the composition of the material. The material was cut into flat coupons measuring 1 cm by 1 cm. To ensure complete dissolution of carbides, uniform composition, and moderate grain growth, coupons were solution annealed at 1200 °C in Ar-5% H₂ gas for one hour and immediately water quenched.

Due to the high annealing temperature, coupons were initially abraded down with 400 grit paper for an extended period of time to remove a few hundred microns of the surface, which may be

depleted in Cr; different amounts of initial abrasion was also applied, though the oxidation tendency of Alloy 690 was found to be the same in all cases. Following abrasion, the coupons were ground with 800 and 1200 grit paper. Fine polishing was done using diamond paste (9 μm, 3 μm, and 1 μm) and then alumina suspension to a 0.05 μm finish. The samples were ultrasonically cleaned in ethanol and de-ionized water for 10 min each between polishing stages and dried with air. A desiccator was used to store samples until time of exposure. To further confirm that no Cr depletion had occurred, energy dispersive X-ray spectroscopy (EDX) was done on Alloy 690 samples prior to exposure to confirm that the average composition was in accordance with the values in Table 1. The EDX analysis equipment is described in Section 2.3.

2.2. Experimental methods

2.2.1. Experiment conditions for oxidation

Experiments were carried out in a tube reactor encased in a furnace, similar to the design by Scenini et al. [20–23]. A hydrogenated steam environment at 480 °C and 1 bar was used to simulate primary water conditions by maintaining an oxygen partial pressure (p_{O_2}) below the Ni/NiO dissociation pressure. Conditions were maintained well below the Ni/NiO equilibrium to allow for clear mechanistic interpretation. Determining the equilibrium dissociation pressure of oxygen ($p_{O_2,eqm}$) was done using the thermodynamic relationship for the standard molar Gibbs free energy of formation for the NiO dissociation reaction, Eq. (1).

$$p_{O_2,eqm} = \left[\exp \left(\frac{\Delta G_{f,NiO}^0}{RT} \right) \right]^2 \quad (1)$$

$p_{O_2,eqm}$ at 480 °C and 1 bar was found to be 3.0×10^{-24} bar which is consistent with the Ni/NiO equilibrium oxygen partial pressure from an Ellingham diagram at 480 °C. The desired p_{O_2} was set 30 times below $p_{O_2,eqm}$ and is controlled in the reactor by the steam dissociation reaction. Using the thermodynamic relationship for the standard molar Gibbs free energy of formation for steam at 480 °C, Eq. (2), the necessary ratio of steam to hydrogen can be determined.

$$p_{O_2} = \left[\frac{p_{H_2O}}{p_{H_2}} \cdot \exp \left(\frac{\Delta G_{f,H_2O}^0}{RT} \right) \right]^2 \quad (2)$$

The ratio of steam to hydrogen can be used to calculate the water and hydrogen flow rates required to maintain the desired p_{O_2} by performing a simple mass balance.

2.2.2. Reactor and procedures

Fig. 1 is a process flow diagram of the reactor during operation. Ultra high purity argon gas is used to purge the system of air prior to experiments. The furnace is unable to encase the ends of the tube and high temperature tapes are used to heat exposed areas. De-ionized water is pumped into the 300 °C stainless steel block using a peristaltic pump where it is mixed with hydrogen prior to entering the reactor. Hydrogenated steam is continuously refreshed. Upon exit from the reactor, the hydrogenated steam is separated by way of a condenser; hydrogen is combusted using a methane burner in a fume hood while condensed water is collected in a beaker.

A brief summary of the operating procedure is as follows:

1. The reactor's quartz tube was removed and cleaned using ethanol and deionized water. Polished samples were placed in the center of the tube and all connections were tightened.
2. The system was purged of air using ultra high purity argon gas for 1 h.

Table 1
Composition of Alloy 690 purchased from Rolled Alloys Inc. (in at.%).

Element	Composition
Ni	59.52
Fe	10.13
Cr	29.60
C	0.029
Al	0.21
Ti	0.34
Si	0.02
Mn	0.15
Cu	<0.01
P	0.003
S	0.001

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