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Characterization of initial intergranular oxidation processes in alloy 600 at a sub-nanometer scale

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ABSTRACT

Intergranular oxidation in Alloy 600 exposed to 480 °C hydrogenated steam was examined at the nano-scale level with analytical electron microscopy and atom probe tomography. The fundamental processes of minor element oxidation and diffusion-induced grain boundary migration (DIGM) were explored. Intergranular oxidation was observed, with Ti and Al oxidation preceding Cr oxidation. Extensive DIGM is observed, with concentrations of minor elements far exceeding bulk values. Calculations are performed which support that the mechanism of DIGM causes large-scale segregation of minor elements. Also, discrete oxide particles ahead of the oxide front provide evidence for classical intergranular internal oxidation at temperatures below 500 °C.

1. Introduction

Alloy 600 (Ni-16Cr-9Fe) is a Ni alloy that was originally chosen for steam generator tubing and other components on the primary side of nuclear power plants due to its resistance to chloride stress corrosion cracking (SCC). However, the alloy was found to be highly susceptible to SCC in the reducing conditions of primary water (PWSCC) and was subsequently replaced in many nuclear power plants. The temperature of primary water ranges from 280 °C to 320 °C in Canada deuterium uranium (CANDU) reactors and can reach up to 340 °C in pressurized water reactors (PWR). Lithium hydroxide and boric acid are added to regulate pH, depending on the reactor design. In addition, hydrogen is added which reduces the potential of primary water into the range of the Ni/NiO electrode potential. PWSCC growth rate in Alloy 600 has been reported to peak in the vicinity of the Ni/NiO equilibrium potential [1–5], suggesting the possibility of internal oxidation. Scott and Le Calvar were first to suggest that PWSCC in Alloy 600 occurred due to internal oxidation [6], a phenomenon often observed in Ni superalloys at much higher temperatures [7–14]. Internal oxidation occurs in binary or ternary alloys which contain a noble solvent element, such as Ni, and a lower concentration of a more reactive solute element, such as Cr. In conditions where the oxygen partial pressure is in the vicinity of the dissociation pressure of the noble solvent metal oxide, the reactive element, if below a critical concentration, can oxidize internally rather

than externally [7–9,15–22]; intergranular internal oxidation can result in embrittlement and SCC.

Since the initial proposal of internal oxidation as the mechanism of PWSCC in Alloy 600, several studies have investigated the phenomenon in both 300 °C–360 °C primary water environments [23–29] and 400 °C–500 °C hydrogenated steam [17–19,30–41], a simulated primary water environment. The use of high temperature hydrogenated steam to model primary water conditions was concluded to be valid by Economy et al., who found that the time to 30% IGSCC in Alloy 600 lay on one Arrhenius line over the 300 °C primary water to 400 °C hydrogenated steam range [36]. Also, lattice diffusion is essentially negligible in hydrogenated steam below 500 °C, similar to primary water. Furthermore, experimental observation of intragranular internal oxidation has been demonstrated in Alloy 600 and other Ni alloys extending from 300 °C water to 500 °C hydrogenated steam [15,16,18,29,37,38,40,42–44]; in the latter environment, expulsion of the solvent Ni has been reported, in accordance with classical internal oxidation. The compressive stress generated during internal oxidation results in the noble solvent metal being expelled to the surface, likely diffusing along short-circuit oxide-metal interfaces [40].

Preferential intergranular oxidation of Cr and other minor impurities (e.g. Ti, Al), extending down from the sample surface, has been previously reported in primary water environments and high temperature hydrogenated steam [18,34,37–40]. The high concentration of

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Table 1
Composition of Alloy 600 purchased from Rolled Alloys Inc. in wt.% and (at.%).

Ni Bal.	Cr	Fe	Ti	Mn	Al	Cu	Co	Si	Nb	C	S	P
73.8	15.8	9.4	0.31	0.21	0.16	0.16	0.05	0.05	0.03	0.02	0.001	0.005
(71.7)	(17.3)	(9.6)	(0.37)	(0.22)	(0.34)	(0.14)	(0.05)	(0.10)	(0.02)	(0.09)	(0.000)	(0.000)

minor impurity elements at grain boundaries after exposure to representative primary water conditions is surprising given the severely hindered lattice diffusion kinetics, even with short-circuit dislocation and/or oxide-metal interface diffusion. Diffusion-induced grain boundary migration (DIGM) has been noted in Ni alloys after exposure to representative primary water conditions and high temperature hydrogenated steam and has been speculated to influence diffusion kinetics [37,38,41,44–47]. DIGM is movement of grain boundaries caused by the diffusion of reactive solute alloying elements to the grain boundary. For example, in Alloy 600 exposed to reducing steam/water, the diffusion of Al, Ti, and Cr to grain boundaries to form thermodynamically favourable intergranular oxides from adjacent grains acts as a driving force for DIGM. The mobility of the grain boundary accommodates reactive solute element diffusion from the more favourable grain and results in depletion of these solute elements in the volume between the migrated boundary and the original grain boundary plane. DIGM effectively “sweeps” reactive elements to the grain boundary, thereby increasing the overall outward intergranular flux far beyond that expected through conventional grain boundary/lattice diffusion, specifically relevant to conditions where lattice diffusion is essentially negligible. Langelier et al. and Bertali et al. have suggested that this DIGM process and minor element oxidation could play a significant role in intergranular oxidation of Alloy 600, possibly during initial stages, but further work is required to confirm such an effect [37–39,41].

The formation of discrete intergranular internal oxide particles, as originally proposed by Scott [6], has not yet been observed in Alloy 600. As a result, the mechanism of PWSCC in Alloy 600 has, thus far, been classified as continuous intergranular preferential or selective Cr oxidation embrittlement, which occurs because of conditions being near the Ni/NiO equilibrium electrode potential or oxygen dissociation pressure, analogous to internal oxidation. Intergranular internal oxidation, as originally proposed, may still be possible well ahead of the intergranular oxide front as a precursor to the formation of the continuous preferential intergranular oxide; however, this possibility has not been investigated extensively. In general, the initial processes occurring during intergranular oxidation of Alloy 600 in primary water, possibly minor impurity segregation and/or discrete internal oxide precipitation, are not yet well understood.

The mechanism of PWSCC in Alloy 600 is suggested to be continuous preferential intergranular Cr oxidation, which occurs for similar reasons as internal oxidation observed at much higher temperatures. However, the study of initial oxidation processes at a sub-nanometer scale remains an area of interest, particularly in high temperature hydrogenated steam environments. Under such conditions, no prior work has been undertaken other than the observation of minor impurity oxidation [18,29,37–39,41]. Analytical transmission electron microscopy (TEM) work by Persaud et al. [17,18,41] and Bertali et al. [37–39] has provided insight into intergranular oxidation of Alloy 600 in 480 °C hydrogenated steam, but their analysis was unable to conclusively verify how early-stage oxidation processes occur. Further understanding of the intergranular oxide and related microstructure can be provided by atom probe tomography (APT). APT relies on spatial and elemental measurement of ions that are successively field-evaporated from a small volume of material, with the data able to be reconstructed into a 3D model of that material volume. APT has typically been limited to conductive materials (i.e. metals and alloys), but the implementation of pulsed-laser atom probes has opened up the

technique to studying non-conducting materials, such as oxides [48–52]. This analysis technique couples high spatial and elemental resolution, and offers the ability to study intergranular oxidation at the near atomic-scale. In the current study, APT and TEM are used to examine grain boundary chemistry in Alloy 600, after exposure to 480 °C hydrogenated steam with conditions maintained well below the Ni/NiO equilibrium oxygen dissociation pressure. Analysis using information gathered from a combination of these two high resolution techniques are performed to verify whether DIGM is a plausible explanation for the segregation and formation of minor impurity (i.e. Ti and/or Al) intergranular oxides. Examinations are also conducted well ahead of the continuous preferential intergranular oxide front, which show that formation of discrete internal oxide precipitates is possible in Alloy 600 at 500 °C and below.

2. Experimental methods

2.1. Materials and sample preparation

A 1.3 mm thick Alloy 600 sheet obtained from Rolled Alloys Inc. was used for all exposures; the composition of the material is given in Table 1. Flat coupons were cut from the sheet measuring 1 cm by 1 cm. All coupons were solution annealed (SA) at 1050 °C in high purity Ar gas for one hour and immediately water quenched.

Flat coupons were ground using 400, 800, and 1200 grit paper. Following this, step-wise fine polishing was done using diamond paste (9 µm, 3 µm, and 1 µm) and alumina suspension to a 0.05 µm finish. 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 preserve samples for a short period until the time of exposure.

The geometry and surface finish chosen for the present study are meant to simplify material conditions to allow for easier study of initial oxidation processes in ideal conditions, not necessarily representative of in-service steam generator tubing. Future work will involve examination of geometry and surface cold work effects on SCC susceptibility, intergranular oxidation, and diffusion of alloying elements.

2.2. Experimental conditions and procedures

Experiments were carried out in an atmospheric pressure reactor at Surface Science Western, London, ON, Canada. The reactor was based on the design in work previously done by Scenini et al. [19]. Samples were exposed to a 480 °C hydrogenated steam environment for 120 h with a pre-determined oxygen partial pressure that set conditions well below the Ni/NiO equilibrium oxygen dissociation pressure (on the Ni-metal side). The oxygen partial pressure was set such that conditions were maintained approximately 30 times below the Ni/NiO equilibrium oxygen dissociation pressure, which prevented Ni oxidation and allowed for a clearer study on the role of minor impurity alloying elements, chromium and oxygen. It should be noted that “reactive elements” described in the present study are minor alloying elements in Alloy 600 that are more reactive than the noble Ni base metal. Hydrogen and water flow rates used to promote the necessary conditions were determined through conventional thermodynamic calculations; detailed calculations can be found in previous work by the authors [17,18].

The chosen experimental conditions are meant to simulate

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