



Advanced microstructural characterization of the intergranular oxidation of Alloy 600



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ABSTRACT

Oxidation of solution-annealed Alloy 600 has been performed in a hydrogenated steam environment, which is considered to simulate PWR primary water exposure. FIB and analytical TEM characterization, coupled with detailed SEM analyses, provided unequivocal evidence of localized grain boundary migration and intergranular oxide penetrations. These localized migrations were associated with pronounced Cr and Fe depletions, highlighting the role of the grain boundaries for Cr diffusion for intergranular oxidation. These findings are discussed in relation to the early stages of intergranular oxidation, diffusion-induced grain boundary migration and subsequent SCC initiation.

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1. Introduction

The susceptibility of Alloy 600 to intergranular stress corrosion cracking (IGSCC) in pressurised water reactor (PWR) primary water environment is well-known. Amongst all the models proposed, the internal oxidation model by Scott and Le Calvar in 1992 [1] appears to be the most comprehensive. Several laboratories reported a marked dependency between crack growth rate and electrochemical potential for Alloy 600 exposed in PWR simulated primary water with the highest susceptibility in the region of the Ni/NiO equilibrium potential [2,3], where internal oxidation is more likely to occur. This model has evolved since it was first formulated, as has its role in crack nucleation and growth. However, the key parameters responsible for the general and localised “internal” oxidation susceptibility of Alloy 600 in PWR primary environment are still unclear and require elucidation to develop a mechanistic understanding of the phenomena and to assess their relative importance.

One of the major concerns regarding the internal oxidation mechanism is that the O and Cr diffusion coefficients in Ni that have been extrapolated from much higher temperature data [4–6] are four orders of magnitude lower than the one required to explain the experimentally-observed IGSCC rate in a PWR primary water environment [7]. However, the extrapolated diffusion coefficients for Cr and O do not agree with the experimentally-measured dif-

fusion coefficients in PWR conditions as reported by Fujii et al. [8] and Lozano-Perez et al. [9]. Based on these observations, the only possible explanation that can account for the discrepancy between extrapolated and measured diffusion coefficients is an enhanced Cr and O diffusivity at the lower PWR operating temperatures. In order to explain these phenomena, advanced characterization techniques have been employed by several researchers to study the intergranular oxide formed on Alloy 600 in simulated PWR primary water [9–14]. However, the factors responsible for the occurrence of preferential intergranular oxidation and enhanced O and Cr diffusivity are still unclear and under debate.

Recently, several independent observations of grain boundary (GB) migration have been reported for Alloy 600 and Alloy 690 in association with intergranular oxide penetrations [11,15,17]. A very localised (~9 nm) Cr-depleted grain boundary region was detected using atom probe tomography (APT) in an Alloy 600 specimen exposed to PWR water at 320 °C that contained an intergranular oxide [11]. The presence of a well-defined, asymmetric Cr- and Fe-depleted/Ni-rich region adjacent to a grain boundary immediately beneath the surface of an oxidised Alloy 600 specimen was also observed by Bertali et al. [17] and Lindsay et al. [18]. However, it was not possible to conclusively demonstrate that the boundaries had migrated in these studies.

The aim of this study was to investigate the initial stages of preferential intergranular oxidation with emphasis on the characterization of localised grain boundary migration and its role on the intergranular oxidation susceptibility of Alloy 600. The oxidation studies were performed at 480 °C in low pressure H₂-steam

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Table 1
Alloy 600SA composition (wt.%).

Heat no.	C	Mn	S	P	Si	Cr	Ni	Cu	Co	Fe
93510	.047	.23	.002	.005	.30	15.42	74.43	.01	.057	8.94

environment, which is considered to simulate PWR primary water environment. In fact, it has been shown by Economy et al. [19] that Alloy 600 IGSCC behaviour in steam at 400 °C does not involve changes in mechanism from 320 °C PWR primary water, and it is therefore assumed that the mechanism will be the same at 480 °C. The present paper reports a detailed microstructural investigation using high resolution field emission gun (FEG) scanning electron microscopy (SEM) and advanced analytical transmission electron microscopy (ATEM) of solution-annealed Alloy 600 exposed to H₂-steam at 480 °C, and demonstrates that grain boundary migration occurs during the oxidation process.

2. Experimental procedures

2.1. Material and sample preparation

The Alloy 600 used in this study was provided from B&W Tubular Products Division via Westinghouse. The composition of this material is reported in Table 1. This material, originally provided in a low-temperature mill-annealed condition, was subsequently solution-annealed (SA) and water-quenched in order to minimize the extent of intergranular carbide precipitation and produce a coarse-grained recrystallized microstructure to facilitate the mechanistic interpretation of the oxidation behaviour. The material was heat-treated in air in a preheated furnace at 1100 °C for 30 min and then water-quenched to room temperature within 10 s. The SA Alloy 600 was then sectioned to remove the near-surface material (several millimetres in thickness), and the oxidation coupons were then sliced so that the surfaces of interest were located several millimetres away from the original heat-treated (oxidized) surface. In this way any pre-oxidation that occurred during the heat-treatment would not affect the subsequent oxidation experiments.

Rectangular oxidation coupons (20 × 15 × 1 mm³) of SA Alloy 600 were cut from bulk material using a diamond edge-cutting disk. The coupons were metallographically polished with 3 μm diamond paste. In order to remove any superficial deformation induced by mechanical polishing and to obtain a surface free from any residual stress, one surface was further polished with a colloidal silica polishing suspension (60 nm). The surface after colloidal silica polishing is representative of the bulk material (free of surface deformation). After polishing, the samples were ultrasonically cleaned in deionized water to remove any colloidal silica contamination and then dried in hot air.

Table 2
Summary of the experiments carried out in the H₂-steam system.

Test #	Material	Time (h)	Ratio steam/H ₂	Pressure O ₂ (pO ₂) (atm)	Dissociation pressure Ni/NiO (pO _{2Ni/NiO}) (atm)	Ratio (pO ₂ Ni/Ni)/(pO ₂)	Purpose
1	600SA	15	62.16	9.88 × 10 ⁻²⁶	2.34 × 10 ⁻²⁴	23.70	Map oxidation stages
2	600SA	20	62.16	9.88 × 10 ⁻²⁶	2.34 × 10 ⁻²⁴	23.70	Map oxidation stages
3	600SA	120	62.16	9.88 × 10 ⁻²⁶	2.34 × 10 ⁻²⁴	23.70	Map oxidation stages
4	600SA	120	N/A	N/A	2.34 × 10 ⁻²⁴	Pure H ₂ environment	Effect of H ₂ on the oxidation

2.2. Hydrogenated-steam oxidation system

The oxidation experiments were conducted in a low-pressure H₂-steam environment at temperatures up to 480 °C for different exposure times at a water flow rate of 1.8 mL/min and a steam-to-H₂ ratio of 62.16, which correspond to an oxygen partial pressure of 2.34 × 10⁻²⁴ atm. This system had previously been employed in past oxidation experiments on Ni-based alloys [16–18,20,21], and it had been shown to accelerate the oxidation of the alloys whilst maintaining the appropriate thermodynamic conditions with respect to the Ni/NiO transition that are relevant to those conditions to PWR primary water at operating temperatures. Therefore, the main reason for the selection of this system was the ability to perform oxidation tests relevant to the PWR environment in a relatively rapid and simple manner. The oxidation system used for the experiments allowed the oxygen partial pressure over the Ni/NiO transition [16] to be set by adjusting the hydrogen and steam flow rate. Additional details concerning the operation of the system are provided in reference [16,20].

A total of 4 oxidation experiments were conducted, and the experimental conditions for each test as well as the test purpose are reported in Table 2.

2.3. Microstructural characterization

The specimens were characterized prior to and after oxidation using a variety of complementary microstructural analysis techniques including FEG-SEM, focused ion beam (FIB) microscopy, and analytical TEM (AEM). The as-polished pre-exposure and post-exposure (oxidized) samples surfaces were evaluated using a Zeiss Ultra 55 FEG-SEM equipped with an Oxford Instruments Energy Dispersive X-ray (EDX) INCA analysis system. An FEI Quanta 3D Dual Beam FIB/SEM was used for the preparation of cross-section specimens for subsequent analysis. The cross-section specimens of as-polished and oxidized Alloy 600 coupons were initially analysed using an FEI Magellan 400 XHR FEG-SEM and an Zeiss Ultra 55 FEG-SEM using the InLens detector and a BSE detector at high (20 kV) and low accelerating voltage (3–5 kV).

The cross-section specimens of the oxidised coupons containing grain boundaries were extracted from the bulk coupons using the TEM lift-out technique, mounted on grids, and subsequently thinned using the FIB. This technique has been widely used for TEM sample preparation [22–24]. In order to characterise the general Alloy 600 microstructure, including type and extent of precipitation, conventional TEM specimens were prepared from

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