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The effect of residual stress on the Preferential Intergranular Oxidation of Alloy 600

G. Bertali*, F. Scenini, M.G. Burke

Material Performance Centre, The University of Manchester, Manchester, UK

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ABSTRACT

Alloy 600 was exposed to H_2-steam to simulate the oxidation that occurs in high temperature water where this alloy is known to be susceptible to SCC. Analytical electron microscopy was employed to characterize the early stages of oxidation to aid in developing an understanding of the stress corrosion cracking behaviour of this alloy. The oxide consisted of sub-surface Cr_2O_3 particles, preferential intergranular oxidation and formation of surface Ni nodules. The measurements of residual stresses at the microscopic level using a recently-developed FIB micro-hole drilling technique revealed a correlation between local stress variations at the grain boundaries and the oxide morphology.

1. Introduction

It is well-recognised that Primary Water Stress Corrosion Cracking (PWSCC) of Alloy 600 is one of the major challenges for nuclear power plant operation. Extensive research has focused on PWSCC crack growth rates measurements to develop empirical models for crack growth, and thereby aid in assessing the life of real components as well as develop safety cases [1]. However, the initiation stage of PWSCC are undoubtedly the most important to study [2] because SCC can be undetected for several decades before of a rapid fracture. Over the years, several mechanisms have been proposed, such as Hydrogen-based mechanisms [3,4], film/rupture dissolution models [5] and oxidation mechanisms such as the "selective internal oxidation" (SIO) model proposed by Scott and Le Calvar in 1992 [6,7]. This latter that has been considered the most likely mechanism to account for both the initiation and propagation stages of SCC, though this model has evolved significantly since it was first formulated in more than two decades ago. Over the past several years, detailed microstructural investigations conducted by several laboratories have demonstrated the occurrence of preferential intergranular oxidation after exposure in high-temperature and high-pressure environment in Alloy 600 [8–14], as well as in once thought immune Alloy 690 [15]. More recent studies by Bertali et al. [16,17] and Persuad et al. [18] using the same experimental apparatus devised by Scenini et al. [19] revealed marked preferential intergranular oxidation susceptibility for both Alloy 600 and 690 in high-temperature low-pressure H_2-steam environment. Although this environment might be considered irrelevant to pressurize water reactor (PWR) primary water environment, past studies by Economy et al. [20] showed a monotonic dependence between the two media suggesting that the same cracking mode is active in both environments despite differences in density and temperature. It is therefore believed by the present authors and other groups [16–19] that by studying the high-temperature oxidation behaviour of Ni-based alloy in this more user friendly low-pressure environment it is possible to identify the precursor events associated to the early stages of PWSCC crack initiation.

A common observation associated with the low-pressure internal oxidation of Ni-Cr alloys tested at 1000 °C in gases of several O_2 partial pressures was found to be the formation of nodules of precipitate-free Ni on the surface during the oxidation process and the transport of Ni to the surface was enhanced under application of external load [21]. Wood et al. [22] also observed the formation of Ni-rich nodules in dilute Ni-Cr alloys (1–5% Cr) when tested in a controlled Ni-NiO oxide pack at 800–1100 °C. Few years later McIntyre et al. [23] noticed similar features also on Ni-18%Cr alloy tested at 500 °C in vacuum chambers at low pressures (10^{-4}–10^{-7} Pa). These nodules, detected from several laboratories, were similar in morphology to those that formed on Ag-In alloys, which were widely used in the past as model alloys to study internal oxidation

* Corresponding author.
E-mail address: Giacomo.bertali@postgrad.manchester.ac.uk (G. Bertali).

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

Heat No.	C	Mn	S	P	Si	Cr	Ni	Cu	Co	Fe	Ti	Al
93510	0.047	0.23	0.002	0.005	0.30	15.42	bal	0.01	0.057	8.94	0.34	0.19

phenomena [24]. Nodules similar to those reported by McIntyre et al. [23] were also observed by Scenini et al. [19] on the surface of Alloy 600 exposed in hydrogenated steam at 480 °C, suggesting that this material might also exhibit some type of internal oxidation. The presence of a split-ridge like grain boundary (GB) morphology and homogeneously distributed intergranular nodules were attributed to the relief of internal compressive stress by dislocation pipe-diffusion controlled creep of Ni atoms to the surface [24]; with the compressive stress being the driving force as well as an accelerating factor for Ni diffusion and extrusion. More recently, Bertali et al. [16,17] showed that the oxidized surface morphology of Alloy 600 exposed in hydrogenated steam at 480 °C can locally vary.

Despite the detailed work carried out to date, there is still the need to identify the precursor events associated to the early stages of PWSCC crack initiation and to improve the understanding on the role of stress on the intergranular oxidation susceptibility of Alloy 600. These aspects were addressed in the present paper on Alloy 600 exposed to hydrogenated steam at 480 °C, an environment that aimed to simulate and accelerate primary water conditions. Advanced analytical microstructural examination was carried out at the oxidized surface and grain boundaries using high-resolution scanning electron microscope (SEM), analytical electron microscope (AEM). The results were correlated with the stress variation at the microscopic level locally measured using the recently developed micro-hole drilling technique [25,26].

2. Experimental procedures

2.1. Material and sample preparation

The Alloy 600 used in this study was manufactured by B&W Tubular Products Division and supplied by Westinghouse. This material was provided in the low-temperature mill-annealed condition, and the bulk composition is reported in Table 1. The material was subsequently solution-annealed (SA) in air at 1100 °C for 30 min and water-quenched to room temperature within 10 s in order to produce a coarse-grained, fully recrystallized microstructure and minimize intergranular carbide precipitation. Oxidation coupons of dimensions $30 \times 20 \times 4\,mm^3$ were cut from the heat-treated plate several millimetres away from the oxidized surfaces where any pre-oxidation and consequent solute depletion (e.g. of Cr) might have occurred.

The samples were plastically deformed by bending in order to induce a range of plastic strain levels and residual stresses throughout the cross-section. The bent sample was then sliced longitudinally to obtain two samples with identical variation of stress and strain through the section. The residual stress was calculated from modelling using an elastic-linearly plastic constitutive law, whereas the maximum extent of plastic strain was calculated from the sample geometry (i.e. dividing the sample thickness by its diameter of curvature). From the knowledge of the maximum strain it was therefore possible to calculate the strain variation through the thickness of the samples during bending. The assumption was that the strain is linearly dependent on the position through the thickness and that the neutral axis where the strain is zero is exactly half way through the thickness of the sample. Thereafter, from the constitutive law (elastic/linearly plastic), the stress distribution was calculated through the thickness; this stress represented the maximum stress present in the sample after bending and before unloading. The unloading phase was modeled by applying a bending moment equal in magnitude but opposite sign to the loading one. The unloading stress that is generated by the unloading bending moment was assumed to vary linearly with the thickness of the sample and that it is zero at the neutral axis. This is a realistic assumption considering that upon unloading it is only possible to recover the elastic energy (i.e. there is linearity between stress and elastic strain). Finally, the stress distribution through the thickness of the sample once the beam was unloaded was calculated from an arithmetic addition of the stresses generating during loading and during unloading phases. This yielded the residual stress variation through the thickness as predicted by the theory [25].

The maximum strain calculated, assuming that the neutral axis was in the middle of the sample, was ±15%. The calculated residual stress and CW profile are shown in Fig. 1, four different regions and the neutral axis were defined:

A: “extrados” region deformed in tension (10% < CW < 15%) and subjected to residual compressive stress;

B: region deformed in tension (0% < CW < 10%) and subjected to residual tensile stress;

C: Neutral axis (assumed to be in the centre);

D: region deformed in compression (0% < CW < 10%) and subjected to residual compressive stress;

E: “intrados” region deformed in compression (10% < CW < 15%) and subjected to residual tensile stress.

The cross-sections of the sliced samples were metallographically polished with diamond paste (3 μm and 1 μm). The samples were subsequently cleaned (soap and water) and then ultrasonically cleaned for 15 min in deionized water. A final polish using 60 nm Silica Oxide Polishing Suspension was performed in order to remove any superficial deformation induced by mechanical polishing, and to obtain a strain-free surface; otherwise it is known that a superficial deformed layer will have an impact on the alloy oxidation behaviour [26,27]. After final polishing, the samples were ultrasonically cleaned in deionized water to remove any colloidal silica contamination, and then dried in a stream of air.

2.2. Hydrogenated steam system

The polished coupons were tested in a low-pressure H_2-steam environment at temperatures up to 480 °C for 66 h at a water flow rate of 1.8 mL/min and a steam-to-H_2 ratio of 62 which correspond to an oxygen partial pressure of 2.34×10^{-24} atm. This oxidation system was originally developed by Scenini et al. [19] and subsequently used by several laboratories [16–18]; it had been shown to accelerate the oxidation of the alloy whilst maintaining the appropriate thermodynamic conditions with respect with the Ni/NiO transition that are relevant to those conditions to PWR primary water at operating temperatures. The main purpose of these tests was to assess the effect of the H_2-steam environment on SCC precursor phenomena that can provide insight for primary circuit SCC in a PWR. This model environment, however, contains no addition of Boron or Lithium. Additional details concerning the operation system are provided in references [16,18,19].

2.3. Micro-hole drilling technique

The micro-hole drilling technique was employed to measure the residual stress at microscopic level in the near-surface region of the specimens. This method, developed by Winiarski and Withers [28], is mainly based on a full-field, multi-axial computation technique, which allows the determination of residual stresses using the hole-drilling method with Digital Image Correlation (DIC) [28,29]. When a hole is micro-machined into the surface using the Focused Ion Beam (FIB) microscope the strain associated with the stress relaxation can be measured using the DIC technique. The residual