Full length article

An atom probe tomography study of internal oxidation processes in Alloy 600

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ABSTRACT

Internal oxidation in Alloy 600 (Ni—16Cr—9Fe) involves the inward diffusion of O, which preferentially reacts with solute elements (e.g. Cr, Fe) forming internal oxide precipitates. In this work, the internal oxidation process and its resultant metal-oxide heterostructures are systematically analyzed in 3D at the finest length scales, using atom probe tomography (APT). Internal oxidation is induced by exposure of Alloy 600 to 480 °C hydrogenated steam, with an oxygen partial pressure below the dissociation pressure of the solvent metal oxide, NiO. Following exposure, nodules of metallic Ni are observed on the sample surface, originating from material that is expelled to relieve compressive stresses generated by internal oxidation. Probing the material immediately below the surface reveals these nodules to be directly connected to their parent grains via Ni-rich metal channels. The matrix metal is intertwined with a continuous network of oxides, which are primarily $FeCr_2O_4$. The continuous interface between oxides and matrix provides the short-circuit diffusion pathways necessary for Ni expulsion. Deeper below the surface, oxides are observed as particles, rather than a continuous network, and are often aligned on matrix planes. The small oxide particles are Cr_2O_3, which is also found to be the composition at the centres of many larger $FeCr_2O_4$ oxides. This indicates that oxides first precipitate as Cr_2O_3, then later grow as $FeCr_2O_4$ when local depletion of Cr changes which phase is most energetically-favourable. Initial comparisons indicate that some fundamental findings in this work are applicable to known internal oxidation systems at lower and higher temperatures.

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1. Introduction

Alloy 600 (Ni—16Cr—9Fe) was originally used for steam generator tubing and other components in the primary circuit of nuclear power plants. Alloy 600 was found highly susceptible to primary water stress corrosion cracking (PWSCC) and was subsequently replaced by Alloy 690 (Ni—30Cr—10Fe) and/or Alloy 800 (Fe—23Cr—35Ni). Internal oxidation and selective intergranular Cr oxidation as the possible mechanism of PWSCC in Alloy 600 has been gaining traction in recent years in both 300 °C—360 °C primary water [1—6] and hydrogenated steam in the 400 °C—480 °C temperature range [7—14].

Internal oxidation is a common phenomenon observed in metal alloys at high temperatures, usually greater than 600 °C, and has been studied extensively [15—30]. It occurs in binary or ternary alloys that 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 range of the dissociation pressure of the more-noble metal oxide, the reactive element, when below a critical concentration, can oxidize internally rather than externally. Internal stress generated by the volumetric increase associated with the formation of an internal oxide is often relieved through expulsion of the noble solvent metal to the surface [13—21,31,32].

In the primary water circuit, conditions are maintained in the vicinity of the Ni/NiO standard electrode potential through the addition of hydrogen. In Alloy 600 the solute element, Cr, is not present in sufficient concentration to provide the necessary outward flux to form an external oxide. Instead, atomic oxygen can diffuse intergranularly causing embrittlement [1,2,7—9,13,14]. Unlike short-circuit diffusion at grain boundaries, lattice diffusion rates are essentially negligible in the temperature range of interest over laboratory timescales. High temperature hydrogenated steam

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as a suitable environment to simulate accelerated primary water was investigated by Economy et al. who 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 [33]. While the kinetics were accelerated in hydrogenated steam, the cracking mechanism and the role of microstructural variables was concluded to be similar to high pressure reducing water at 360 °C [33].

Scott and Le Calvar first proposed internal oxidation as the mechanism of PWSCC in Alloy 600 [34]. This mechanism was then supported by Gendron et al. who observed intergranular oxygen penetration and embrittlement to a depth of 1.5 μm in Alloy 600 after exposure to 400 °C hydrogenated steam [7–9]. Persaud et al. extended the studies using high resolution analytical electron microscopy techniques and found oxygen penetration an embrittlement to a depth of 2 μm in Alloy 600 after exposure to 480 °C hydrogenated steam [13,14]. In addition, classical internal oxidation was observed whereby Cr and Fe were internally oxidized resulting in metallic Ni expulsion to relieve internal stress [13,14]; the latter observation was first reported by Scenini et al. in electropolished Alloy 600 flat samples exposed to 480 °C hydrogenated steam [35]. Further work by Persaud et al. revealed that intragranular internal oxidation was possible in Alloys 690 and 800, even with Fe and/or Cr contents well above the "critical" contents for formation of an external protective oxide [31]. Given that lattice diffusion is essentially negligible, significant short circuits must be operating to account for the extent of intragranular internal oxidation and solvent metal transport observed previously in Alloys 600, 690, and 800. Electron microscopy work done by the same authors did not achieve the resolution necessary to study processes occurring at the atomic scale, such as development of internal solute oxides and short circuit diffusion of Ni and O.

Solvent metal expulsion was first observed at a SEM level of resolution by Rapp et al. in Ag–In alloys exposed to air at temperatures greater than 550 °C [15,21]. Several studies have shown that the volume of solvent metal accumulated on the surface is equivalent to the volume increase due to internal oxide precipitation [15–17,19]. Thus, the driving force for noble solvent metal expulsion is undoubtedly the compressive stresses generated during the formation of internal solute oxides. However, the mechanism by which solvent metal transport occurs remains unresolved. Several theories have been proposed, and demonstrated to be valid depending on the environment of exposure and the material, such as extrusion through mechanical action [16,17], Nabarro-Herring diffusional creep or diffusion via oxide-metal interfaces [16–19,22], and dislocation pipe diffusion [15,17–19]. However, in Alloy 600 such mechanisms have not yet been evaluated. Studying an internally oxidized zone in Alloy 600 at a sub-nanometer scale would allow the clarification of the mechanism of solvent metal expulsion.

In the current work, intragranular internal oxidation will be examined using atom probe tomography (APT). APT can provide a sub-nanometer level spatial resolution and excellent elemental sensitivity for nano-scale volumes of material, and will be applied here to study the mixed metal and oxide microstructure of internally oxidized Alloy 600. Being traditionally used to analyze metallic specimens, the application of APT to oxides is not as straightforward. Issues with APT of oxides and oxide-metal mixtures stem from their typically non-conducting nature [36], and the potential for large evaporation field differences between oxides and metal leading to pronounced aberrations in ion flight trajectories and local magnification [37,38]. However, the use of laser-pulsed APT has been shown to yield an improvement in spatial and chemical quantification of oxides [36,39,40]. Yet issues still persist with APT analysis of oxides, even with laser pulsing. Many authors

have reported an apparent loss of O for bulk oxide materials studied by APT [41–44], which has not been unambiguously explained. Furthermore, while laser pulsing may decrease the effective difference in evaporation field of oxides embedded in a metal matrix, thus reducing ion trajectory aberrations [45], it does not necessarily remove them entirely. Therefore, APT analysis of oxides and oxide-metal mixtures still requires careful interpretation of results. Nevertheless, APT has still been successfully applied to a variety of bulk oxide materials [41,44,46], oxide nanoparticles in ODS alloys [40,45,47,48], and corrosion products [42,43,49–52]. When applied to the study of oxidation/corrosion, most recent studies have primarily focused on surface oxidation [49,50] or grain boundary oxidation [42,43,51–53]. Other than the studies by Kluthe et al. [37,38] on internal oxidation of Mg in Ag–Mg, intragranular internal oxidation has not been as thoroughly analyzed by means of APT.

The current study therefore examines Alloy 600 samples exposed to a 480 °C hydrogenated steam environment, considered to simulate accelerated primary water conditions in a nuclear power plant. The process of intragranular internal oxide formation, where lattice diffusion rates are low, will be explored by APT. Transport of the solvent element, Ni, to the surface to relieve internal stress will also be investigated to provide further insight into the mechanism of short circuit diffusion in Alloy 600, and likely other Ni–Fe–Cr alloys, at low temperatures; in the absence of significant lattice diffusion it can be assumed that solvent metal diffusion to the surface occurs exclusively via short circuits. Final remarks will be made on the applicability of the current work to oxidation in lower temperature primary water and to classical internal oxidation processes at higher temperatures.

2. Experimental methods

2.1. Materials and sample preparation

A 1.3 mm thick Alloy 600 sheet was purchased from Rolled Alloys Inc. and used for all exposures; Table 1 reports the composition of the material. Flat coupons were cut from the material measuring 1 cm by 1 cm.

Coupons were solution annealed (SA) at 1050 °C in high purity Ar gas for one hour and immediately water quenched. Half the coupons underwent an additional thermal treatment (TT) at 704 °C for 24 h to promote intergranular precipitation of Cr carbides. A 24 h treatment period has been shown to allow sufficient recovery of initial chromium depletion adjacent to the grain boundaries in Alloy 600 with similar C content [54]. The purpose of concentrating Cr at grain boundaries is to increase the outward flux of Cr to promote external rather than internal oxidation at grain boundaries; the beneficial effects of thermal treatment on the PWSCC susceptibility of Alloy 600 has been reported frequently in literature [55–59]. Detailed work has been done previously by the present authors evaluating and comparing the likely intergranular PWSCC susceptibility of Alloy 600SA and Alloy 600TT in 480 °C hydrogenated steam using high resolution electron microscopy [14]; the intragranular oxidation phenomena were reported to be similar regardless of heat treatment. In the current work, analysis focuses exclusively on samples of Alloy 600TT.

Prior to exposure coupons were ground using 400, 800, and

Table 1
Composition of Alloy 600 samples.

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