Acta Materialia 131 (2017) 280–295

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat

Full length article

Effects of boundary migration and pinning particles on intergranular oxidation revealed by 2D and 3D analytical electron microscopy

B. Langelier [a,*], S.Y. Persaud [b,c], A. Korinek [a], T. Casagrande [a], R.C. Newman [b], G.A. Botton [a]

[a] Department of Materials Science and Engineering, and Canadian Centre for Electron Microscopy, McMaster University, 1280 Main Street West, Hamilton, ON, L8S 4M1, Canada
[b] Department of Chemical Engineering and Applied Chemistry, University of Toronto, 200 College Street, Toronto, ON, M5S 3E5, Canada
[c] Canadian Nuclear Laboratories, 286 Plant Road, Chalk River, K0J 1J0, ON, Canada

ARTICLE INFO

Article history:
Received 22 December 2016
Received in revised form
27 March 2017
Accepted 2 April 2017
Available online 5 April 2017

Keywords:
Intergranular oxidation
Selective oxidation
STEM
EELS
FIB serial sectioning

ABSTRACT

To evaluate the beneficial effects of intergranular carbides on inhibiting stress corrosion cracking (SCC), Alloy 600 samples in the thermally-treated (TT) and solution-annealed (SA) conditions were analyzed after exposure to 480 °C hydrogenated steam. Intergranular oxidation was observed in both samples, along with diffusion-induced grain boundary migration (DIGM). Compositional mapping revealed DIGM to be more severe in 600SA, while conventional intergranular solute diffusion involving static boundaries appeared dominant in 600TT. 3D serial sectioning of the boundaries revealed strong variations in the intergranular oxide for 600TT, particularly in the depth of oxide penetration. This was attributed to Cr carbide precipitates, present due to the thermal treatment, pinning against DIGM. Immobilizing the boundary via carbide pinning reduces oxide growth by effectively starving it of the ready solute supply otherwise available to a migrating boundary. Because of this interaction between boundary migration, carbide pinning, and oxide growth, the intergranular oxidation in 600TT is highly variable and discontinuous compared to 600SA, where DIGM is unchecked and easier oxide growth produces near-uniform coverage of the boundary. This marked decrease in boundary oxide coverage likely contributes to the improved SCC resistance of 600TT. These results demonstrate the necessity of investigating such phenomena using 3D analysis methods.

1. Introduction

Alloy 600 (Ni-16Cr-9Fe) is a material historically used for steam generator tubing and other components on the primary side of water-cooled nuclear power plants. 280 °C–340 °C primary water contains added hydrogen, which reduces the potential into the range of the Ni/NiO equilibrium electrode potential; also, lithium hydroxide and, in some reactor designs, boric acid are added for pH control. Alloy 600 in the mill annealed (MA) condition has been found highly susceptible to primary water stress corrosion cracking (PWSCC) since its inception [1–14], and has since been mostly replaced by proven PWSCC-resistant alloys. Although not rendering it immune, thermal treatment of Alloy 600 at 700 °C for an extended time has been demonstrated to increase PWSCC resistance [15–19]. The major microstructural change brought on by this thermal treatment is the precipitation of intergranular Cr carbides; Cr depletion (sensitization) in the adjacent solid solution is mitigated by using an extended thermal aging time, which allows for sufficient recovery of Cr. The beneficial effects of intergranular Cr carbides have been investigated previously [15,20–23], but determining a precise mechanism by which they improve PWSCC resistance remains inconclusive.

Scott and LeCalvar proposed intergranular internal oxidation as the mechanism of PWSCC in Alloy 600 [24]. Internal oxidation is commonly reported in high temperature gaseous systems (>600 °C) in alloys with a relatively noble solvent metal, and a reactive solute alloying element [25–33]. In Alloy 600, Ni acts as a noble solvent, compared to the more reactive alloying element Cr. In conditions where the oxygen partial pressure is slightly above, at, or below the equilibrium oxygen dissociation pressure of the noble metal oxide (e.g. NiO) oxygen may diffuse into the alloy and preferentially react internally with the solute element or elements, forming discrete internal oxide precipitates. Intergranular internal oxidation of Alloy 600 in primary water would lead to embrittlement and possibly SCC

* Corresponding author.
E-mail address: langelb@mcmaster.ca (B. Langelier).

http://dx.doi.org/10.1016/j.actamat.2017.04.003
1359-6454/

under stress. Currently, intergranular oxidation embrittlement through a process analogous to internal oxidation, either through the formation of discrete internal Cr oxides or a continuous Cr oxide, is widely accepted as the mechanism of PWSCC in Alloy 600 [1–7,20–23,34–50].

Microscopy-based studies comparing intergranular oxidation in solution-annealed (SA) and thermally-treated (TT) Alloy 600 have been predominantly performed using techniques such as scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) or energy dispersive x-ray spectroscopy (EDS) [23,34,35]. These techniques are excellent for identifying nano-scale chemistry and material information. However, the specimen thickness limitation (typically < 100 nm) imposed by electron transmission inherently results in a lack of three-dimensional information. Since it is impractical to analyze numerous thin foils, TEM analysis of planar features (e.g. grain boundaries) via sampling one location in cross-section might lead to erroneous conclusions about the microstructure – especially regarding characteristics in the direction normal to the TEM foil. This is especially important with Alloy 600TT because variation in the size and distribution of Cr carbides on the grain boundary can lead to micron-scale differences in microstructure and oxidation that are not captured within any single cross-section of the boundary.

The current work aims to reveal the effects of Cr carbide formation on intergranular internal oxidation by means of multi-scale 2D and 3D electron microscopy and atom probe tomography (APT). Samples of Alloy 600 in both the SA and TT conditions are systematically analyzed and compared, following exposure to high temperature hydrogenated steam to promote internal oxidation. This environment is regarded as an accelerated primary water environment, originally stemming from the work of Economy et al. [14]. Several other studies have since demonstrated the similarities in intergranular oxidation and embrittlement in Alloy 600 extending from 300 °C primary water to 500 °C hydrogenated steam [1–7,20–23,34–50]. Earlier works by the authors have characterized the intragranular internal oxidation using APT [47], as well as both intragranular and intergranular oxides by STEM-EELS/EDS [34,35]. This study further utilizes STEM-EELS to identify the local intergranular chemistry in 600SA and 600TT in two-dimensional sections, but also uses tomography to expand the analysis to 3D, based on focused ion beam (FIB) serial sectioning and scanning electron microscopy (SEM) imaging. This approach reveals the influence of Cr carbide precipitation on intergranular oxide penetration, and the mechanisms by which it acts, which are reported with respect to changes observed in intergranular oxidation between the two alloys.

2. Experimental methods

2.1. Materials and sample preparation

Alloy 600 sheet was obtained from Rolled Alloys Inc. and used for all exposures. The material composition is given in Table 1. Flat 10 mm × 10 mm coupons were cut from the 1.3 mm thick sheet, and were solution annealed at 1050 °C for 1 h in high purity Ar gas, then immediately water quenched.

An additional thermal treatment was applied to half the coupons at 704 °C for 24 h to precipitate Cr carbides intergranularly. A 24 h treatment period allowed sufficient time for recovery of initial chromium depletion in the solid solution adjacent to grain boundaries [51]. Alloys with these two thermal histories: solution-annealed (designated 600SA), and solution-annealed and thermally-treated (designated 600TT) will be analyzed and compared in this work.

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

Flat coupons were ground using SiC paper, and then polished using diamond paste. The final polish was performed using a 0.05 μm alumina suspension. Samples were cleaned between polishing stages by 10 min ultrasonic treatments in ethanol and deionized water.

2.2. Experimental conditions and procedures

Experiments were carried out in an atmospheric pressure reactor based on the design in work previously done by Scenini et al. [42]. Samples were exposed to a 480 °C hydrogenated steam environment for 120 h. Conditions were maintained at an oxygen partial pressure 30 times below the Ni/NiO equilibrium oxygen dissociation pressure, which prevented Ni oxidation and allowed for clearer study on the role of chromium and oxygen. The chosen conditions are considered to simulate the conditions of primary water, but are more reducing; the water/hydrogen electrochemical potential in-service is in the vicinity of (slightly below or slightly above) the Ni/NiO equilibrium electrode potential. Hydrogen and water flow rates fed to the reactor were determined through conventional thermodynamic calculations, detailed in previous work by the authors [34,35]. In addition, a process flow diagram with detailed procedures can be found in a previous study by the authors [34,35].

2.3. Scanning transmission electron microscopy (STEM)

Samples were prepared for STEM analysis by performing a standard lift-out procedure using an NVision40 (Carl Zeiss, Germany) SEM equipped with a FIB column. Samples at the grain boundaries were protected with W deposition prior to extraction, and attached to Cu half-grids also using W deposition. Thinning of the specimens to electron transparency was conducted using the Ga ion FIB at successively lower voltages of 30 kV, 10 kV, and 5 kV. Additional details on the FIB lift-out procedure for these samples are provided in Ref. [35].

STEM analysis was conducted with an aberration-corrected FEI Titan 80–300 (FEI Company, The Netherlands) at an accelerating voltage of 300 kV, using a high-angle annular dark field (HAADF) detector. Composition mapping was performed using EELS and a GIF Tridiem 865 spectrometer (Gatan Inc., USA). The convergence half-angle was 8 mrad and the collection half-angle was 15 mrad.

2.4. Atom probe tomography (APT)

APT samples were also prepared by FIB lift-out. Specimens were welded to pre-sharpened Si posts using W deposition, and sharpened into needles of <100 nm tip radius using an annular Ga ion beam at 30 kV [52]. The final milling step was performed at 10 kV, and involved sharpening the tip such that the region of interest was placed at the tip apex.

APT analysis was performed using a Cameca LEAP 4000X HR atom probe (Cameca Instruments, USA) operating in laser-pulsing mode ($\lambda = 355$ nm, 200 kHz, 75 pJ/pulse). The specimen temperature was ~59 K, and the analysis chamber vacuum was 3–4 $\times 10^{-11}$ Torr. A target evaporation rate of 0.005 ions/pulse (0.5%) was maintained by varying an applied DC voltage, ranging from ~0.5–6.0 kV. Reconstruction and analysis of APT data was done