A STUDY ON THE OXIDATION BEHAVIOUR OF NICKEL ALLOYS AND THE LIKELY EFFECT ON PWSCC SUSCEPTIBILITY

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ABSTRACT

Internal oxidation as the possible mechanism of primary water stress corrosion cracking (PWSCC) in Alloy 600 was studied. Alloy 600 (Ni-16Cr-9Fe), in the solution annealed (SA) and thermally treated (TT) conditions, was exposed to a hydrogenated steam environment considered to simulate primary water in nuclear plants. Atom probe tomography (APT) was used to study the oxidation behaviour in the 600 alloy at a sub-nanometer scale. Internal oxidation, both intra- and intergranularly, was observed leading to the expulsion of metallic Ni to the surface. Intergranular oxidation in Alloy 600SA resulted in embrittlement and fracture under stress. Ni was displaced away from internal oxides and the network used for expulsion of the solvent metal, Ni, to the surface was discernable at a sub-nanometer level of resolution. APT on grain boundary oxides provided further evidence for the embrittlement of Alloy 600SA by intergranular internal oxidation and lent insight into the beneficial effects of thermal treatment. Final comparisons are made between the hydrogenated steam environment and primary water with discussion on the viability of internal oxidation as the likely mechanism of PWSCC in Alloy 600.

Keywords: Alloy 600, primary water, stress corrosion cracking, internal oxidation, atom probe tomography

1. INTRODUCTION

Alloy 600 (Ni-16Cr-9Fe) was historically used for steam generator tubing and other components in the primary water circuit of pressurized water reactors (PWR) and Canada deuterium uranium (Candu) nuclear power plants due to its perceived high corrosion resistance. However, the 600 alloy was found highly susceptible to primary water stress corrosion cracking (PWSCC) and was eventually replaced by Alloys 690 and/or 800; the latter alloys exhibit higher PWSCC resistance likely due to their high Cr and/or Fe content. Primary water is relatively pure with lithium borate added in PWRs and LiOH added in Candu reactors for pH control. The temperature in the primary circuit ranges from 280 °C to 320 °C in Candu reactors and can reach 340 °C in PWRs. Hydrogen is added to primary water which reduces the potential into the range of the Ni/NiO equilibrium electrode potential. It is now well established that PWSCC susceptibility in Alloy 600 peaks in the vicinity of the Ni/NiO equilibrium electrode potential [1,2], suggesting the possibility of Cr as part of the cracking mechanism.

Scott and Le Calvar originally proposed internal oxidation as the mechanism of PWSCC in 1993 [3]. Internal oxidation is commonly observed in Ni superalloys at much higher temperatures, such as 800 °C [4–6]. The phenomenon occurs in alloys which contain a noble solvent element and a reactive solute element. In an environment where the oxygen partial pressure is within range of the dissociation pressure of the noble metal oxide, the reactive element, if below a critical concentration, can oxidize internally rather than externally; internal oxidation is also possible in situations where the oxygen partial pressure at an external oxide-metal interface is below the dissociation pressure of the noble metal oxide. Volumetric increase due to internal oxide formation produces significant internal compressive stress, which is often relieved through expulsion of the noble solvent metal to the surface [7–14]. Scott and Le Calvar proposed that in Alloy 600 the concentration of the reactive solute element, Cr, is too low to promote external oxide formation in primary water conditions near the equilibrium electrode potential of the noble
solvent metal, Ni [3]. Naturally, internal oxidation at the lower temperatures of primary water would be more subtle, with preferential intergranular oxidation more likely given that grain boundary or other short-circuit diffusion is dominant and lattice diffusion of the major alloying elements is negligible over usual laboratory timescales.

In recent years, internal oxidation as the mechanism of PWSCC in Alloy 600 has gained support in both 300 °C to 360 °C primary water environments [15-18] and 400 °C to 480 °C hydrogenated steam [10,11,19-22]. The use of high temperature hydrogenated steam to model primary water conditions was suggested by Economy et al. who found PWSCC crack growth rates in stressed Alloy 600 samples lay on one Arrhenius line extending from 300 °C primary water to 400 °C hydrogenated steam [23]. They concluded that while the conditions were accelerated in hydrogenated steam, the mechanism of cracking was likely to be similar to primary water [23]; additional oxidation phenomena may be possible in hydrogenated steam, but they likely do not influence SCC. Similar to primary water, lattice diffusion is negligible in hydrogenated steam below 480 °C over usual laboratory timescales.

Scenini et al. exposed Alloy 600 to 480 °C hydrogenated steam with conditions maintained below the Ni/NiO equilibrium and reported internal oxidation resulting in metallic Ni expulsion [21]; Persaud et al. extended the studies and observed intergranular oxygen penetration and embrittlement in Alloy 600 to a depth of approximately 2 µm after exposure to similar conditions [10,11]. Also, Persaud et al. showed that oxygen penetration in thermally treated (TT) Alloy 600 was significantly shallower than in Alloy 600 in the solution annealed (SA) condition [10]. Furthermore, the intergranular oxide formed in Alloy 600TT was more Cr-dense and thicker compared to Alloy 600SA. Precipitated intergranular Cr carbides in Alloy 600TT concentrate Cr at the grain boundaries, effectively increasing the outward Cr flux intergranularly. Thermal treatment is known to increase PWSCC resistance in Alloy 600 [24-26], partly due to better formation of a relatively thick Cr-rich oxide at or near the surface of grain boundaries which limits intergranular oxygen diffusion and prevents embrittlement; it is likely that Cr carbide precipitation also imparts beneficial mechanical effects, such as suggested by Bruemmer et al. [24].

There is a general consensus that the mechanism of PWSCC in Alloy 600 is penetrative intergranular oxidation, which occurs for similar reasons as internal oxidation observed at much higher temperatures. However, the study of processes occurring at the atomic scale remain an area of interest, particularly in high temperature hydrogenated steam environments where virtually no prior work has been undertaken. Persaud et al. performed work which lent insight into the mechanism of SCC in Alloy 600 in 480 °C hydrogenated steam [10,11], but their analysis, while still high resolution, was unable to identify sub-nanometer scale processes that may be occurring. Also, given that lattice diffusion is essentially negligible in the discussed primary water-type environments for the applied test durations, significant short circuits must be operating to produce the intragranular internal oxidation and solvent metal transport observed previously in Alloy 600 and other Ni-Fe-Cr alloys. Electron microscopy work done by the authors did not achieve the resolution necessary to study processes occurring at a sub-nanometre scale, such as development of internal solute oxides and short circuit diffusion of Ni and O [10,11].

In the current study, 3-D atom probe tomography (APT) will be used to study grain boundary chemistry at a sub-nanometer scale in Alloy 600 after exposure to 480 °C hydrogenated steam with conditions maintained well below the Ni/NiO equilibrium. In addition, the process of intragranular internal oxide formation, where lattice diffusion rates are low, will be explored by APT. Although possibly not relevant to PWSCC, 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 at low temperatures. Solvent metal expulsion was first observed at a scanning electron microscope (SEM) level of resolution by Rapp et al. in Ag-In alloys exposed to air at temperatures greater than 550 °C [8,9]. However, the mechanism by which solvent metal transport occurs remains unresolved and several theories have been proposed [4,5,7,9].
2. EXPERIMENTAL METHODS

2.1 Materials and Sample Preparation

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

Samples were SA at 1050 °C in high purity Ar gas for one hour and immediately water quenched. An additional TT was applied to half the coupons at 704 °C for 24 h to precipitate Cr carbides intergranularly. A 24 hour treatment period was used because it provided sufficient time for recovery of initial chromium depletion adjacent to grain boundaries in Alloy 600 with similar C content [27].

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 minutes each between polishing stages and dried with air. A desiccator was used to preserve samples for a short period until the time of exposure.

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. [21]. Samples were exposed to a 480 °C hydrogenated steam environment for 120 h with conditions maintained well below the Ni/NiO equilibrium oxygen dissociation pressure to prevent Ni oxidation and allow for clearer study on the role of chromium and oxygen. Hydrogen and water flow rates used to promote the necessary conditions were determined through conventional thermodynamic calculations and detailed calculations can be found in previous studies by Persaud et al. [10,11].

A brief description of the system and experimental procedure is provided here; a process flow diagram with detailed procedures can be found in previous studies by Persaud et al. [10,11]. A tube reactor enclosed in a furnace was used for all exposures. Polished samples were placed in the centre of the reactor tube. High purity argon gas is used to deaerate the system prior to starting the hydrogenated steam flow. De-ionized water is pumped into the system using a peristaltic pump. Water and hydrogen are fed into a stainless steel block at 300 °C where water is vaporized and they are mixed prior to entering the reactor. The ratio of steam to hydrogen is such that the nominal oxygen partial pressure is maintained 30 times below the Ni/NiO equilibrium oxygen dissociation pressure.

2.3 Atom Probe Tomography (APT)

A local electrode atom probe (LEAP) 4000X HR (CAMECA Scientific Instruments, Madison, WI) was used for all APT analysis. Acquisition of atom probe data was conducted in ultra-high vacuum (< 4x10^{-9} Pa) with a base sample temperature of approximately 59.7K. Field evaporation of the samples was induced through the use of ultraviolet (UV) laser pulses (λ=355 nm, 40-60 pJ, 200 kHz). The UV wavelength range is reported to be the ideal in maximizing the mass resolving power when performing APT analysis on oxides [28]. A DC voltage of approximately 2-9 kV was applied to the sample at all times; the value was controlled to maintain a constant evaporation rate of 0.5% (0.005 ions per pulse).

Reconstruction of the APT data was performed using the Integrated Visualization and Analysis Software package (IVAS) v3.6.6 (CAMECA Scientific Instruments, Madison, WI), and established reconstruction algorithms [29]. For datasets that contained mostly metal with only fine oxidation the profile of the DC voltage during the experiment was assumed to be analogous to the evolution of the tip radius, and the data were reconstructed accordingly. However, for datasets containing large volume fractions of oxide, the differences in evaporation between the oxide and metal phases significantly affect the DC voltage profile. Accurate reconstruction therefore cannot be obtained using the voltage profile for such samples. In these cases, the evolution of the tip radius used for reconstruction was correlated to SEM images of tip shapes.
APT requires finely-tipped needle-shaped specimens for analysis. To prepare such samples from the grain boundaries in Alloy 600, an NVision 40 focused ion beam (FIB) instrument (Carl Zeiss, Germany) was utilized. Based on established lift-out techniques for the extraction and sharpening of APT samples, first the area of interest is identified, such as the oxidized grain boundary in Figure 1 (a). The surface of the sample targeted for extraction is then protected by depositing a layer of W. Cuts are made at 60° to the sample surface to cut out a wedge-shaped specimen, 15-20 µm long (Figure 1 (b)), which is then extracted using the FIB manipulator (Figure 1 (c)). Smaller sections of the extracted volume, approximately 3 µm in size, are then attached to Si posts using W deposition (Figure 1 (d)).

Each small volume is then sharpened into needles for APT analysis. This procedure involves identifying the region of interest by using a 30 kV Ga ion beam to mill away material along the cross-section of the sample, normal to the grain boundary in Figure 2 (a). By examining the cross-section of the sample, intra- and intergranular oxygen penetration can be observed in Figure 2 (b). When a small feature of interest is targeted for APT analysis, the tip can then be sharpened. The sharpening procedure first uses a 30 kV Ga ion beam, run in an annular pattern to produce a small pillar from the specimen, shown in Figure 2 (c). Final sharpening uses a reduced voltage of 10 kV to minimize damage from the Ga ions. This last stage of sharpening is continued until the feature of interest is within 100-200 nm of the end of the tip, shown in Figure 2 (d) for an oxidized Alloy 600SA grain boundary.

3. RESULTS AND DISCUSSION

3.1 Intergranular Oxidation

3.1.1 Alloy 600SA

A SEM image of an Alloy 600SA sample surface after exposure to 480 °C hydrogenated steam is shown in Figure 1 (a). The surface appears shiny with nodular structures distributed throughout. The nodules line up adjacent to grain boundaries. Similar surface features were observed by Persaud et al. in Alloy 600SA exposed to identical conditions [10,11]; using EDX, the nodules were confirmed to be composed of the solvent metal, Ni, expelled to the surface as a result of internal Cr and Fe oxidation [10,11]. Figure 2 (b) shows a cross-section of the Alloy 600SA grain boundary in Figure 1 (a). Oxide has penetrated to a depth of approximately 4 µm. Persaud et al. performed EDX point scans on a similar intergranular oxide in Alloy 600SA which suggested that the grain boundary oxide contained Cr but was not necessarily devoid of Fe, Ni or other impurities [10,11]; it was concluded that exclusive Cr₂O₃ formation was unlikely but higher resolution analysis was needed to determine the exact nature of the oxides. Also, Persaud et al. found evidence of intergranular embrittlement in Alloy 600SA [10,11].

Frequent fractures of the brittle intergranular oxide in 600SA during APT sample preparation prevented APT analysis of an entire oxidized grain boundary near the surface, where the oxide was thickest and most well-developed. Repeated fracture events illustrate the brittle nature of grain boundaries in Alloy 600SA due to internal intergranular oxidation. APT analysis for a sample which included the well-developed near-surface oxide adjacent to a grain boundary in 600SA is shown in Figure 3, but does not include the grain boundary itself; the oxidized metal matrix adjacent to the grain boundary is included in addition to one of the oxide-metal interfaces. The overall composition of the oxide is shown in Table 2. The oxide is heavily enriched in Cr, with a composition approaching that of Cr₂O₃. However, there is a significant Fe content of approximately 1 at. %. Fe is non-uniformly distributed in the oxide, as shown in Figure 3 (b), suggesting that in some regions of the oxide the local Fe content is significantly higher than 1 at. %; overlapping ion trajectories during evaporation make defining the exact compositions difficult.

The distribution of major alloying elements and oxygen at the metal-oxide interface is given in Figure 3 (c). Slight Fe enrichment is present at the oxide-metal interface. Ni is heavily depleted in the intergranular oxide and significantly enriched in the metal directly adjacent to the oxide. It is possible that internal intergranular oxidation has resulted in Ni being displaced to the oxide-metal interface. The intergranular internal oxide may block Ni from diffusing outward at grain boundaries. Instead, outward
Ni flow along the intergranular oxide-metal interface may coalesce with Ni being expelled along the intragranular internal oxide-metal interface directly adjacent to the grain boundaries; this process would explain the high density of Ni nodules bordering grain boundaries in Figure 1 (a) and other studies [10,11,21]. Minor element distribution at the oxide-metal interface is shown in Figure 3 (d). Mn and Al segregate to the oxide, while Cu is present in the metal and segregated to the interface.

Figure 4 (a) is APT analysis of the intergranular oxide, including the grain boundary, from deeper in the material; at this depth the intergranular oxide is 8-10 nm thick. 1D composition profiles of the major alloying elements and oxygen, in Figure 4 (b), reveal significant segregation of Cr to the grain boundary in oxidized regions. Ni is depleted in the intergranular oxide, but significant enrichment is visible adjacent to the grain boundary. Unlike the well-developed near-surface oxide in Figure 3 (a), Fe is also depleted within the intergranular oxide at this depth. 1D composition profiles for the minor elements are provided in Figure 4 (c). Al is significantly enriched in the intergranular oxide, while Ti and Mn also exhibit small degrees of enrichment. Some solute element oxidation is occurring, in addition to oxidation of Cr; previous transmission electron microscope (TEM) analysis by Persaud et al. confirms solute element oxidation of Ti at grain boundaries in Alloy 600SA and absence of minor solute elements where grain boundaries are not oxidized [10,11]. Ni enrichment, and corresponding solute depletion, occurs more favourably on the right side of the grain boundary, as shown in the 1D composition profiles in Figure 4 (b) and (c). Favourable diffusion to the grain boundary from the right grain may be due to an orientation effect or grain boundary migration.

The APT analysis volume in Figure 5 (a) is taken from an un-oxidized section of the grain boundary directly ahead of the intergranular oxide; this sample is used to investigate whether intergranular oxidation results in any change in grain boundary chemistry ahead of the oxidation front. The grain boundary is revealed by the 3D Ni+ ion density map, shown in Figure 5 (b), due to the minor changes in evaporation at the grain boundary defect. The 1D composition profiles for the major alloying elements, in Figure 5 (c), show that there is Ni enrichment and Cr depletion directly ahead of the intergranular oxide. As observed previously, there appear to be different Ni, Fe and Cr, contents directly on either side of the grain boundary indicating favourable diffusion to the grain boundary from one grain.

### 3.1.2 Alloy 600TT

Figure 6 (a) shows the surface of 600TT after exposure to 480 °C hydrogenated steam. Metallic Ni nodular structures are visible within the grains, similar to 600SA. Unlike 600SA, nodules are spaced approximately 2 µm away on either side of the grain boundaries. Also, nodules in 600TT exhibit a flat morphology, whereas nodules in 600SA generally have a mixture of flat and tall nodules; this is likely due to greater or lesser presence of surface active minor elements in Alloy 600TT. Figure 6 (b) shows a cross-section taken from 600TT across a grain boundary. Oxygen penetration has occurred to a depth of approximately 1.5 µm. The intergranular oxide is visibly thicker than 600SA and some external oxidation is present. Persaud et al. reported similar results and suggested that preferential oxidation at Cr carbides limited intergranular oxygen penetration and embrittlement in 600TT [10,11].

APT analysis of the well-developed oxide near the surface in Alloy 600TT is shown in Figure 7 (a). The analysis volume shown in Figure 7 (a) does include the grain boundary but is truncated at the bottom due to a micro-fracture as the analysis was passing through the boundary. In general, APT samples containing grain boundaries in Alloy 600TT were more durable and less likely to fracture than Alloy 600SA. Also, the intergranular well developed, near-surface oxide in 600TT was significantly thicker compared to 600SA. The 3D O+ ion density map in Figure 7 (b) allows for identification of the grain boundary due to minor changes in evaporation at the grain boundary defect. The bulk composition of the intergranular oxide in Figure 7 (a) is given in Table 3; the composition is an excellent match for Cr2O3. Minor alloying elements are present in similar amounts as the bulk 600SA intergranular oxide, shown in Table 2; however, in 600TT the near surface intergranular oxide is almost totally devoid of Fe.
The 1D concentration profiles normal to the grain boundary are shown in Figure 7 (c), for Cr and O, and Figure 7 (d), for minor alloying elements and Fe. The O level decreases slightly at the grain boundary, but is near constant. In contrast, Cr decreases significantly, approximately 8 at. %, over 3 nm on either side of the boundary. The decrease in Cr at the grain boundary corresponds to an increase in several minor alloying elements, shown in Figure 7 (d); intergranular Ti enrichment is most significant, but Al, Mn, and Fe are also present in the oxide. Similar intergranular minor element enrichment, particularly Al, was found in the oxide(s) further down the grain boundary in 600SA.

The APT analysis volume in Figure 8 (a) is taken from the same area as was shown in Figure 7 (a), but highlights the oxide-metal interface. 1D concentration profiles for major alloying elements and oxygen, in Figure 8 (a), reveal Fe enrichment at the oxide-metal interface, similar to the observations in Alloy 600SA in Figure 3 (c). Also significant Ni enrichment is present in the metal adjacent to the oxide with levels of Cr and Fe well below that of the bulk alloy. 1D concentration profiles for minor elements are shown in Figure 3 (d). Minor elements are distributed similarly to the Alloy 600SA, with Cu segregated to the oxide-metal interface, presumably in a metallic state, and Al and Mn preferentially partitioned in the intergranular oxide. Overall, the magnitude of the minor element concentrations is less in 600TT compared to 600SA, likely due to incorporation into precipitates during thermal treatment.

APT analysis of the near surface oxides revealed some differences with respect to grain boundary chemistry in the two heats. Alloy 600SA and Alloy 600TT were both found to undergo internal intergranular oxidation. However, the depth of oxygen penetration in Alloy 600TT was significantly less than that observed in Alloy 600SA. Also, the intergranular oxide in Alloy 600TT was thicker and enhanced diffusion of Cr to the surface due to Cr carbide precipitation allowed for some external surface oxidation adjacent to grain boundaries; the higher density and thickness of the intergranular oxide in 600TT likely aids in increasing SCC resistance compared to 600SA. Also, the intergranular oxide in Alloy 600SA was approaching that of Cr₂O₃, but was not devoid of Fe which is enriched locally in different regions of the well-developed near-surface oxide. The intergranular oxide in Alloy 600TT was a more pure Cr₂O₃ containing essentially no Fe. Cr₂O₃ is known to be protective and likely contributes to SCC resistance in Alloy 600TT; the localized mixed Fe and Cr oxides may contribute to the intergranular embrittlement observed in Alloy 600SA.

At 480 °C lattice diffusion of the metals analyzed is essentially negligible and the significant amount of Ti and/or Al diffusion to the grain boundaries observed is unexpected; transport of minor alloying impurities to grain boundaries must happen along short circuits, such as oxide-metal interfaces. The likelihood of having an Al or Ti rich intergranular oxide in Alloy 600 exposed to 300 °C to 360 °C primary water is highly improbable over usual testing times at those temperatures because the kinetics are further retarded. Therefore, absence of minor impurity intergranular oxides are one likely difference to be expected when comparing oxidation of Alloy 600SA in 480 °C hydrogenated steam and lower temperature primary water; the influence of intergranular minority impurity oxidation on SCC susceptibility remains unknown and should be studied further.

Intergranular Cr-rich oxidation in Alloy 600 has been shown to occur in 300 °C to 360 °C primary water, similar to the observations in the current work, with conditions maintained in the vicinity of the Ni/NiO standard electrode potential [15-18]. Ni metal displacement has been shown to occur in Alloy 600 in primary water ahead of the intergranular oxide [15,18]. The APT analysis volume in Figure 5 shows that Ni displacement ahead of the intergranular internal oxide is possible in 480 °C hydrogenated steam, similar to the observations in primary water; Ni displacement likely results in local stress relief at the grain boundary, but may still influence SCC and should be studied further. The similarities in intergranular chemistry, with the exception of minor element oxidation, and cause of embrittlement observed in 480 °C hydrogenated steam and lower temperature primary water suggests that the mechanism of intergranular SCC is similar in both environments.
3.2 Intragranular Oxidation

An APT analysis volume from 600TT containing a Ni nodule, as well as the internal oxide network beneath it, is shown in Figure 9. The composition of the Ni nodule, as measured by APT, is given in Table 4. It is found to be almost entirely metallic Ni (>95 at. %).

Beneath the Ni nodule, the internal oxides are present in a 3D network, and are intertwined with regions of Ni-rich metal. The networks of internal oxides and Ni-rich metal can be visualized by the isoconcentration surfaces (isosurfaces) shown for O in Figure 9 (a), and for Ni in Figure 9 (b). Having been revealed in 3D by APT, it can be seen that these Ni-rich channels are continuous throughout the volume and are present at the oxide-metal interface. Furthermore, the Ni-rich channels are directly linked to the Ni nodule. Such Ni-rich channels are likely Ni displaced away from the internal solute oxides and the compressive stress leads a connected structure and transport of metallic Ni to the surface.

Below the nodule there exist localized regions where Cr and Al-rich oxides segregate (marked (2) and (3) respectively in Figure 9 (b)). Composition results for these regions show that they are near-stoichiometric Cr₂O₃ and Al₂O₃ (see Table 4), given that some “loss” of O is typical for APT of oxide materials [30-32]. Previous TEM analysis of these intragranular internal oxides by Persaud et al. led to the conclusion that the oxides were a mixture of Cr and Fe oxides, probably depleted in Cr₂O₃ which was unlikely to form due to the low Cr content of Alloy 600 [10,11]. Current APT analysis finds that the oxides which make up the majority of the continuous internal oxide network (marked (4) in Figure 9 (b)) have a composition approaching FeCr₂O₄ spinel.

The Nabarro-Herring creep mechanism may apply to the current case, whereby a vacancy gradient is created between the internal oxidation front and the stress-free alloy surface [4,5,7]. Vacancies then diffuse from high concentration, the alloy surface, to the oxide-metal interface and a counter flow of solvent metal (i.e. Ni) atoms diffuses from the oxide-metal interface to the surface. The Nabarro-Herring creep mechanism for solvent metal transport has been applied successfully to several alloys at high temperature, including dilute binary Ni-Cr and Ni-Al alloys [4,5,7]. However, short circuit dislocation pipe diffusion may also apply, as proposed by Guruswamy et al. in Ag-In alloys exposed to air at 773 K and above [9]. For the current case, the percent volume increase due to internal Cr and/or Fe oxidation can be calculated from APT data; detailed calculations can be found in an upcoming paper by the authors [33]. Average volume expansion is 44.2 ±9.9%. With such an enormous increase in internal volume, the production of dislocations in the Ni-rich metal is likely. Increased dislocation density will accelerate solvent metal transport and inward oxygen diffusion.

Figure 10 is an APT dataset deep in the internally oxidized zone, close to the bulk metal. As it is sampled from a deeper section of the material, the oxides present within the volume have had less time to develop, compared to the large 3D network of oxides in Figure 9. Thus the APT data presented in Figure 10 represents an earlier stage in internal oxide formation. Examination of internal oxide composition reveals that there is also a discrepancy in composition between the large and small oxide particles. 2D composition maps are provided in Figure 10 for the elements of interest, Ni (b), O (c), Cr (d), and Fe (e). Ni enrichment is again visible at the oxide-metal interface, see (1) in Figure 10, and solute elements are depleted as Ni is displaced from the growing internal oxides. There are sub-regions within the large oxides that are enriched in Cr and O, and depleted in Fe, see (2) in Figure 10. The fine oxides located further down in the dataset are enriched only in Cr and O, and lean in Fe (see (3) in Figure 10).
The areas of O, Cr, and Fe enrichment from Figure 10 are visualized in 3D by isosurfaces for those corresponding elements, and are shown in
Figure 11. The Cr-rich regions are seen to make up the core of the larger oxides. A proxigram from one of the Cr-rich core isosurfaces is shown in

Figure 11 (b). In the centre there exists a Cr-rich oxide, where Fe is deficient; the composition is close to that of Cr₂O₃. Surrounding the core is a region of relative Fe-enrichment; the composition of the oxide in this region approaches that of FeCr₂O₄. Departing from the oxidized region, the Cr, Fe, and O contents all decrease, and Ni becomes enriched. In this case, the metal-oxide interface can appear quite diffuse.
due to both trajectory overlap, and the non-uniform nature of oxide particles being measured by the proxigram, as it is expanded to greater distances from the original interface.

The presence of a Cr$_2$O$_3$ core to the FeCr$_2$O$_4$ oxide shows that initial oxide formation begins with Cr$_2$O$_3$ precipitation. This finding is confirmed by examination of the fine oxide particle compositions, shown in
Figure 11 (c). The proxigram in

Figure 11 (c) reveals that only Cr-enrichment is associated with the O distribution, while, in contrast, Ni and Fe segregate away from the oxide. Internal oxidation can therefore be seen to begin by preferential oxidation of Cr. The growth of Cr$_2$O$_3$ results in Cr depletion in the surrounding matrix, thereby enriching
the area in Ni and Fe. This is further evident in the proxigram for the Fe-rich region from

Figure 11 (d), which reveals how Fe enrichment is associated with depletion in O and Cr, and a slight enrichment in Ni. It should be noted that these Fe-rich regions are on the periphery of the large oxide, which is consistent with the Fe solute being rejected from the initial Cr₂O₃ oxides.

Expulsion of metallic Ni has never been observed in Alloys 600, 690 or 800 when exposed to 300 °C to 360 °C primary water. Lattice diffusion kinetics at the lower temperatures of primary water would likely
not support solvent metal expulsion for normal test durations, even in the presence of short circuits. However, intergranular penetration of oxygen has been observed by Lozano-Perez et al. in electropolished Alloy 600 after exposure to 360 °C primary water for 4840 h with conditions on the NiO side of the Ni/NiO phase boundary [15]; Ni metal enrichment was reported ahead of the internal intergranular oxide. These results suggest that while the kinetics would not support diffusion of the solvent metal to the surface, Ni metal can be displaced by penetration of oxide in primary water, similar to the results in the current study.

Intragranular internal solute oxide formation has been reported to occur in Ni-Fe-Cr alloys in 315 °C to 360 °C primary water [34,35]. Olszta et al. reported the presence of an intragranular penetrative Cr-rich internal oxide in Alloy 690 exposed to 360 °C for 1000 h with 25 cm³ H₂/kg H₂O added to maintain conditions at the Ni/NiO stability line [34,35]. Olszta et al. proposed that the flux of Cr to the surface is not sufficient to form continuous external Cr₂O₃ intragranularly and a penetrative internal oxide network can develop by oxygen diffusion through the non-protective porous oxide [34,35]. The depth of oxygen penetration was approximately 50 nm to 150 nm depending on surface cold work. Olszta et al. suggested that oxygen diffusion is accelerated by diffusion down a dislocation substructure [34,35], similar to Guruswamy et al. in Ag-In alloys exposed to air at temperatures greater than 773 K [9]. The large compressive stress imparted by intragranular volume increase due to internal oxidation suggests that dislocation pipe diffusion is also responsible for some of the short-circuit diffusion observed in the current work.

4. CONCLUSIONS

- Intergranular embrittlement of Alloy 600SA by internal oxidation penetration to a depth of up to 4 µm is observed after exposure to 480 °C hydrogenated steam for 120 h.
- Intergranular oxidation in Alloy 600TT penetrates to a shallower depth of approximately 1.5 µm compared to Alloy 600SA. APT allowed for analysis at a sub-nanometer scale and revealed that unlike 600SA, the intergranular oxide in 600TT is thick, devoid of Fe, and has less minor impurities, such as Al and Ti.
- Internal oxidation and stress relief through solvent metal expulsion were studied using APT for the first time. Ni-rich channels are formed adjacent to growing internal oxides which, under sufficient compressive stress, form an inter-connected network at the oxide-metal interface allowing for transport of Ni to the surface; the enormous increase in volume suggests that dislocation pipe diffusion likely also assists in accelerating diffusion processes.
- APT analysis of the intragranular internal oxide at greater depth in three dimensions revealed the process of internal solute oxide formation. Cr₂O₃ cores are formed initially and grow until the surrounding matrix becomes Cr-depleted. At this point, FeCr₂O₄ formation becomes favourable.
- Internal intergranular oxidation is likely the mechanism of embrittlement in 480 °C hydrogenated steam and lower temperature primary water; some minor differences are expected given the accelerated kinetics at 480 °C, such as intergranular minor impurity segregation. Intragranular oxidation phenomena exhibit some resemblance, but the severely hindered lattice kinetics in 300 °C to 360 °C primary water results in similarities being subtle.

5. ACKNOWLEDGEMENTS

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6. REFERENCES


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

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Ni</th>
<th>Fe</th>
<th>Cr</th>
<th>C</th>
<th>Mn</th>
<th>S</th>
<th>Si</th>
<th>Cu</th>
<th>Al</th>
<th>Ti</th>
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</tr>
</thead>
<tbody>
<tr>
<td>600 (wt. %)</td>
<td>Bal.</td>
<td>9.4</td>
<td>15.8</td>
<td>0.02</td>
<td>0.21</td>
<td>0.001</td>
<td>0.05</td>
<td>0.16</td>
<td>0.16</td>
<td>0.31</td>
<td>0.05</td>
<td>0.03</td>
<td>0.005</td>
</tr>
<tr>
<td>600 (at. %)</td>
<td>Bal.</td>
<td>9.6</td>
<td>17.3</td>
<td>0.09</td>
<td>0.22</td>
<td>0.001</td>
<td>0.10</td>
<td>0.14</td>
<td>0.34</td>
<td>0.37</td>
<td>0.05</td>
<td>0.02</td>
<td>0.005</td>
</tr>
</tbody>
</table>

### Table 2: APT measured composition from the grain boundary oxide for 600SA shown in Figure 3. Error estimates are 1 sigma from counting error.

<table>
<thead>
<tr>
<th>Composition (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
</tr>
<tr>
<td>0.17 ±0.01</td>
</tr>
</tbody>
</table>

### Table 3: APT measured composition from the grain boundary oxide for 600TT shown in Figure 7. Error estimates are 1 sigma from counting error.

<table>
<thead>
<tr>
<th>Composition (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
</tr>
<tr>
<td>0.05 ±0.01</td>
</tr>
</tbody>
</table>

### Table 4: APT measured compositions from the regions in Figure 9. Error estimates are 1 sigma from counting error.

<table>
<thead>
<tr>
<th>Region</th>
<th>Composition (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
</tr>
<tr>
<td>(1) Ni Nodule</td>
<td>95.3 ±0.03</td>
</tr>
<tr>
<td>(2) Al oxide</td>
<td>0.73 ±0.06</td>
</tr>
<tr>
<td>(3) Cr oxide</td>
<td>0.31 ±0.01</td>
</tr>
<tr>
<td>(4) Oxide Network</td>
<td>5.45 ±0.03</td>
</tr>
</tbody>
</table>
Figure 1: SEM images of the typical FIB extraction procedure for grain boundary samples, shown for 600SA. The steps are as follows: (a) selection of grain boundary area, (b) milling of sample wedge for extraction, (c) extraction of the wedge, (d) fixing wedge sections onto pre-sharpened needles.
Figure 2: SEM images of the typical FIB sharpening procedure for grain boundary samples, shown for 600SA. (a) Examining wedge cross-section to reveal the oxidized boundary, (b) detail of cross-section shown in (a), (c) sample following milling, (d) APT sample following final sharpening.
Figure 3: APT analysis volume of the near-surface intergranular oxide in Alloy 600SA. (a) is a 3D atom map showing Ni, CrO ions, and 50 at.% O isosurface. (b) is a 2D composition map from a 20nm thick cross-section, showing Fe concentration. (c) and (d) are proximity histograms (proxigrams) from the lower isosurface shown in (a), with 1D concentration profiles plotted for (c) Ni, O, Cr, and Fe and (d) minor impurities, Cu, Al, and Mn. Error bar estimates are 1 sigma from counting error where the error is calculated from each bin used to make the profile.
Figure 4: APT analysis volume of a thinly-oxidized grain boundary in Alloy 600SA. (a) is a 3D atom map showing Ni, CrO ions, and 6 at. % O isosurface. (b) and (c) are 1D concentration profiles normal to the grain boundary, showing (b) Ni, O, Cr, and Fe, and (c) Al, Mn, and Ti. Error bar estimates are 1 sigma from counting error where the error is calculated from each bin used to make the profile.
Figure 5: APT analysis volume of a grain boundary in Alloy 600SA, directly ahead of the intergranular oxide penetration. (a) is a 3D atom map showing Ni ions, (b) is a 3D Ni ion relative-density temperature map, (c) is a 1D concentration profile normal to the grain boundary, for Ni, Cr, and Fe. Grain boundary location is indicated by arrows in (a) and (b).
Figure 6: SEM images of Alloy 600TT showing (a) the sample surface, and (b) a FIB cross-section of an oxidized grain boundary.
Figure 7: APT analysis volume of an oxidized grain boundary in 600TT. (a) is a 3D atom map showing Ni, CrO ions, and 30 at% O isosurface, (b) is a concentration map for O, (c) and (d) are 1D concentration profiles normal to the grain boundary, for (c) O and Cr, and (d) Ti, Al, Mn, and Fe. Grain boundary location is indicated by arrows in (a) and (b). Error bar estimates are 1 sigma from counting error where the error is calculated from each bin used to make the profile.
Figure 8: APT analysis volume of a grain boundary oxide in 600TT. (a) is a 3D atom map showing Ni, CrO ions, and 40 at. % O isosurface, (b) and (c) are proxigrams from the surface shown in (a), with 1D concentration profiles plotted for (b) Ni, O, Cr, and Fe and (c) Cu, Al, and Mn. Error bar estimates are 1 sigma from counting error where the error is calculated from each bin used to make the profile.
Figure 9: APT analysis volume of a Ni nodule and the underlying internal oxide network, showing (a) Ni (green) and CrO (red) ions with isosurface for 20 at. % O, (b) O ions (teal) with isosurfaces for (1) 80 at. % Ni, (2) 20 at. % Al, and (3) 40 at. % Cr, and (c) 2D concentration map for Ni from a 10 nm cross-section.
Figure 10: (a) APT analysis volume of internal oxides, showing Ni (green) and CrO (red) ions with isosurface for 20 at. % O. (b)-(e) are 2D composition maps from 10 nm thick cross-sections for (b) Ni, (c) O, (d) Cr, and (e) Fe. Labels indicate examples of (1) Ni enrichment adjacent to the oxide, (2) Cr-rich, Fe-lean features within the oxides and (3) within the metal, and (4) Fe-rich features at the edges of oxide particles.
Figure 11: a) APT analysis volume of internal oxides, with isosurfaces for 10 and 20 at. % O, 20 at. % Fe and 33 at. % Cr. (b)-(d) are proxigrams corresponding to interfaces marked in (a), showing Ni, O, Cr, and Fe concentration profiles. Error bar estimates are 1 sigma from counting error where the error is calculated from each bin used to make the profile.