OXIDATION STUDIES OF ALLOY 600 IN LOW PRESSURE HYDROGENATED STEAM

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Abstract

The effect of stress on the oxidation behavior of solution-annealed Alloy 600 was investigated by exposing samples to low pressure steam environments containing hydrogen at temperatures up to 480°C. The resultant oxidized surfaces of stressed and unstressed samples were analyzed via several electron microscopy techniques. For hydrogen partial pressures greater than that corresponding to the Ni/NiO equilibrium, the strain-free surface of Alloy 600 was characterized by the presence of Ni nodules. Detailed Analytical Electron Microscopy (AEM) evaluations of the near-surface regions and grain boundaries were performed on site-specific cross-section specimen produced using the focused ion beam (FIB) technique. High resolution scanning transmission electron microscope (STEM) – energy dispersive x-ray (EDX) microanalysis revealed discrete subsurface oxides, as opposed to a continuous oxide film, thus supporting an internal oxidation process. Furthermore, preferential grain boundary oxide penetration was observed. Although no macroscopic correlation between the magnitude of the residual stress and the surface morphology was detected, local stress measurements using a recently developed FIB micro-hole drilling technique revealed residual stress variations at microscopic level. These results correlated well with the presence of intergranular and internal subsurface oxide.

Key words: Alloy 600, internal oxidation, residual stress and micro-hole drilling.

Introduction

Since the internal oxidation model was proposed as a mechanism of primary water stress corrosion cracking (PWS CC) of Alloy 600 in 1992 by Scott & Le Calvar [1], numerous laboratories have studied the properties of the oxides that form on the surfaces of Alloy 600 and 690. This model has been supported by several investigations. For instance Newman et al. [2] reported intergranular embrittlement and oxygen ingress in electropolished Alloy 600 tested in hydrogenated steam at 400°C. Delabrouille [3] confirmed deep oxygen penetration at grain boundary triple points analyzed via Secondary Ion Mass Spectroscopy (SIMS).

McIntyre et al. [4] also previously showed that Ni-18%Cr alloy exposed for a short period at 500°C at low pressure ($10^{-8}$ – $10^{-7}$ Pa) was susceptible to internal oxidation. Specifically they found Ni-enriched oxide nodules at the surface, which resembled in morphology the features formed on oxidized Ag-In model alloys used to study the internal oxidation mechanism [5]. It was also observed that these nodules grew preferentially within the grains, on micro scratches and on low energy grain boundaries (e. g. Twin GB). One of the interesting aspects of this internal oxidation is the mechanism responsible for the formation of superficial nodules, which, for the case of Alloy 600, could be a rate determining step. In the case of internally oxidized Ag-In Alloys and Pd-Ag Alloys [5-6] the volume of Ag nodules was found to be comparable to the total volume increase caused by the internal oxide. This result suggested that the material deformation around the oxide particles to accommodate the volume increase could play an important role in the Alloy susceptibility to internal oxidation. In the case of Ni-(1-5%Al) alloys internally oxidized at high temperatures (800-1100°C) this internal stress can be relieved by grain boundary sliding and the extrusion of a weak internal oxide-denuded zone adjacent to the grain boundary [7-8]. However at lower temperatures this relief mechanism may be difficult and the decrease of the stress gradient between the surface region and the internal oxidation front can occur by diffusional transport of Ni atoms to the surface [7-8]. Moreover, diffusional creep
process during the material oxidation might have been invoked for the surface formation of pure Ni nodules devoid by any oxide particles [7].

In oxidation experiments more relevant to PWSCC but in hydrogenated steam at 480°C Scenini et al. [9] showed similar surface features on electropolished Alloy 600 to those characteristic of materials susceptible to internal oxidation, such as Ag-In alloys [5]. They observed a split-ridge like grain boundary (GB) morphology and the presence of intragranular Ni-enriched nodules homogeneously distributed on the surface, which might be an evidence of creep diffusion. For this reason it was suggested that the relief of internal compressive stresses, may occur by dislocation pipe diffusion of Ni atoms to the surface [5]. In this case, the residual compressive stress could have an important role in the internal oxidation mechanism of Alloy 600 being the rate-controlling step in the internal oxidation process.

The aim of this work is to improve the understanding of the roles of internal residual stresses on the oxidation of Alloy 600 in a model system that can help to understand the PWSCC mechanism occurring in PWR primary water. This study is mainly focused on the effects of residual stress on the grain boundary susceptibility to intergranular oxidation.

**Experimental Procedures**

**Material and Sample Preparation**

The material used in this work was heat HT93510 Alloy 600 produced by B&W Tubular Products Division. The chemical composition is shown in Table I. The material, originally provided in low temperature mill-annealed condition, was further solution-annealed (SA) in air for 30 minutes at 1100°C and water-quenched. The purpose of this heat treatment was to minimize the extent of intergranular carbide precipitation and produce a homogeneous microstructure with large grains to facilitate the mechanistic interpretation of the oxidation behavior. Oxidation samples (30x20x4mm³) were cut from the bulk of the material.

The samples were then plastically deformed by bending, Figure 1, in order to induce a range of residual stresses throughout the cross section. The residual stress and cold work profile was inferred from modeling using an elastic-linearly plastic constitutive law. The maximum strain was found to be 15% at the intrados and extrados and it was calculated dividing the thickness of the sample by the diameter of curvature. Although the residual stress and cold work distribution is rather complex (Figure 2(a) and (b)), the intrados is deformed in compression and is subjected to residual tensile stresses (area e of Figure 2(a)), the extrados is deformed in tension and is subjected to residual compressive stress (area a of Figure 2(a)), and no stress is present at the neutral axis (area c of Figure 2). The sample cross-sections were metallographically polished (initial mechanical grinding with SiC papers (600-4000 grit) followed by polishing with diamond paste (3 µm, 1 µm and ¼ µm) and finally 60 nm Silica Oxide Polishing Suspension (OPS)). The last polishing step was carried out to remove any superficial deformation induced by mechanical polishing (i.e. the Beilby layer) and obtain a strain-free surface representative of the bulk material. After polishing the samples were cleaned with soap and then ultrasonically cleaned in deionized water in order to remove any colloidal contamination.

**Hydrogenated Steam System**

The samples were tested in the same oxidation system used by Scenini et al. [9]; additional details concerning the operation of the system are provided in reference [9]. The main purpose of these tests was to create an environment relevant to the primary circuit of a PWR, although in steam and without the addition of B and Li. The oxidizing potential of the environment was controlled by adjusting the flow rate of steam and hydrogen. The tests were performed at 480°C in a steam-hydrogen mixture.
giving an oxygen partial pressure of $9.88 \times 10^{-26}$ atm which is about 24 times more reducing than the dissociation pressure of Ni/NiO at that temperature, for a total time of 66 hours.

**Micro-hole Drilling Technique**

The micro hole-drilling technique was employed to measure the near-surface residual stresses on the oxidized samples at microscopic scale. The method, developed by Winiarski and Withers at the University of Manchester [10], is based on measuring the strain associated with the stress relaxation when a slot or a hole is introduced on the surface using Focused Ion Beam (FIB) micromachining; the stress is then inferred by fitting the strain measured using the Digital Image correlation (DIC) technique to a Finite Element Model (FEM) [10-11].

In order to improve the surface contrast for DIC, a FIB-deposited Pt pattern was introduced around the region to be analysed; then a 2 µm in diameter- 1.5 µm depth “hole” was micro-machined. More details on the experimental configuration can be found in references [10-11].

**Microstructural Characterisation**

The specimens were characterised using a variety of techniques, including light optical microscopy (LOM), scanning electron microscopy (SEM)/electron backscattered diffraction (EBSD), FIB and AEM. An FEI Quanta 650 Field Emission GUN (FEG)-SEM equipped with an Oxford Instruments X-max 50 Silicon Drift Detector (for EDX microanalysis) and an EBSD analysis system was used to assess the as-polished grain structure and oxidised surfaces. An FEI Quanta 3D Dual Beam FIB was used for the preparation of electron-transparent cross-section specimens for subsequent AEM analysis, and for micro-hole drilling analyses. Detailed AEM characterisation was performed using an FEI Tecnai F30 300kV FEG-AEM equipped with an Oxford Instruments X-max80 SDD and Aztec/INCA analysis system. Additional high resolution STEM EDX analyses were performed at 200kV using an FEI Titan G2 80-200 aberration-corrected S/STEM with an X-FEG and ChemSTEM™ technology, which has 4 SDDs for maximum sensitivity EDX spectrum imaging analysis.

**Results**

**Surface Morphology of Oxidized Samples**

The surface appearance of Alloy 600SA sample after exposure is shown in Figure 3 and is consistent with the observations of Scenini et al. [9]. The surface was characterized by homogeneously distributed intragranular features (that appear as small black spots in the light optical micrograph). A network of grain boundaries is evident in the micrograph, and a region free of the small black spots can be observed. There were no apparent macroscopic differences between the surfaces with compressive or tensile residual stress and Figure 3 can be considered representative of both regions.

SEM characterization of the Alloy 600 SA sample was performed before and after the oxidation to assess the similarities and differences in surface morphology as a function of stress. EBSD analysis allowed the determination of grains orientation and GB misorientation. The appearance of the oxidize surface is shown in Figure 4. The banded grain boundaries structure was visible over the entire surface for both the residual tensile (Figure 4(b)) and residual compressive (Figure 4(a)) stress regions; thus, it was not possible to appreciate any macroscopic difference between the 2 regions.

The observed surface morphology was very similar to the one observed by Scenini et al. [9] on Alloy 600 tested in similar conditions; it was characterized by an homogeneous distribution of intragranular Ni-enriched nodules and by a marked Nodule Free Zone (NFZ) 3-4 µm wide along the GBs. Although the surface morphology of the oxidized Alloy 600 appeared homogeneous, some localized variations in the GBs oxide morphology and in the NFZ presence were observed as shown in Fig. 5.
Analysis of the oxidized grain boundaries in this material revealed three general observations:

1. The presence of high angle grain boundaries (HAGBs) characterized by split ridge-like oxide morphology and by a marked NFZ (Figure 6(a) white arrow).
2. HAGBs characterized by crest-like oxide morphology and by the absence of a NFZ (Figure 6(b)).
3. $\Sigma 3$ GBs that appeared to behave in a similar manner to bulk material and to be immune to any oxidation (Figure 5(b) white arrow).

It is important to point out that Figure 5 was captured with the sample tilted 70° in order to better visualize the 3D morphology of the surface, and the image was digitally “flattened” using the SEM image processing software. Figure 5(b) can be considered representative for all the 3 morphologies above described.

The transition from the split ridge to crest GB oxide morphology was often noted at GB triple points (Figure 5(b)) or in correspondence of $\Sigma 3$ boundaries. This finding is in-line with the past observation of internally oxidized Alloy 600 [9], in which high-energy grain boundaries have been associated with split ridge morphology and low energy grain boundaries (e.g. $\Sigma 3$ GBs) with a crest or invisible morphology. Moreover, as clearly shown in Figure 7, it was noted that the oxidation susceptibility of high angle grain boundaries (HAGBs) sharply changed in correspondence of twin intersection. The HAGB in the top left side of Figure 7 changed its behavior from split ridge morphology to crest morphology when an intersection with a twin occurred even though the connecting boundary was also an HAGB. In the top center and left side of Figure 7, the same type of change in GB oxide morphology at a twin intersection can be seen.

Characterisation of Oxidised GB FIB Cross-Section Specimens

Several GBs located in regions subjected to either residual compressive or tensile stress were cross-sectioned using the Focused Ion Beam (FIB) to characterize their susceptibility to intergranular oxidation and to correlate it with the external oxide morphology (i.e. the presence of the NFZ, nodules, GB crest). The representative cross-sections of the three morphologies (split-ridge, crest and $\Sigma 3$ grain boundary morphology) formed with either residual compressive or tensile stress are shown in Figures 8 and Figure 9.

The FIB cross-section obtained from the residual compressive stress region (area a of Figure 2(a)) of an “crest” oxidized GB characterized by the absence of a NFZ (Figure 6(b)) is shown in Figure 8(b). The darkly-imaging feature appeared to penetrate along the grain boundary for more than 100 nm, and many homogeneously dispersed darkly-imaging particle-like features located in the near-surface region were observed (black arrow). Conversely, the GBs characterized by the same “crest” morphology but located in the residual tensile stress region (area e of Figure 2(a)) exhibited a markedly deeper intergranular penetration (more than 500 nm) as shown in Figure 8(a). Moreover, in both regions some darkly-imaging intergranular precipitates were detected along the GBs 2 µm deep (white arrows).

The FIB cross-section of a GB characterized by “split-ridge” oxide morphology (Figure 6(a)) and presence of a marked NFZ showed a complete different morphology. Figure 9(a) contains a representative SE image of this morphology. The darkly-imaging features at the grain boundary appeared to grow parallel to the surface without intergranular penetration into the bulk material. Also the proportion of homogeneously-dispersed darkly-imaging particles appeared to be much less compared to that observed for the crest-like oxidised GB. Also evident in Figure 9 (a) are several darkly-imaging intergranular precipitates.

From the SEM examination of the $\Sigma 3$ GB cross-section (Figure 9(b)) it was not possible to detect either any darkly-imaging intergranular penetrations or any layers above the GB. However, numerous
discrete darkly-imaging particles homogeneously distributed within the near-surface region of the entire cross-section were clearly visible. The GB appeared to behave in a similar way to the bulk material and was devoid from any intergranular penetrations. The apparent immunity of $\Sigma 3$ boundaries is consistent with the findings of Alexandreanu et al. [12] for Ni-16Cr-9Fe-xC alloys tested in autoclave in deaerated water and a hydrogen gas overpressure of 0.10 MPa at 360ºC. Alexandreanu et al. noted in those tests that $\Sigma 3$ boundaries did not crack even when strained up to 25% during constant extension rate tests.

AEM Analysis of FIB Cross-Section Specimens

Advanced analytical transmission electron microscopy (AEM) analyses were employed to characterize the darkly-imaging features observed by SEM in the as-FIB-ed cross-section samples. In particular, EDX spectrum imaging using the Titan S/TEM with 4 SDD systems provided fine-scale microchemical information concerning the elemental distributions within the electron-transparent cross-section samples.

Detailed characterisation of the grain boundary that contained the darkly-imaging intergranular penetration and the discretely imaging fine particles in the near-surface region, shown in Figure 10 was performed. EDX SDD spectrum images obtained using Titan “ChemiSTEM” were acquired from the three regions identified in Figure 10 and are presented in Figure 11-13. These analyses included: 1) the intergranular oxide, 2) the grain boundary region ahead the intergranular oxide tip, and 3) a surface/near-surface region. The EDX spectrum images confirmed that the darkly-imaging features were Cr-rich internal oxide precipitates. The presence of an intergranular oxide was confirmed by the Cr K$\alpha$ (blue) and O K$\alpha$ (yellow) spectrum images shown in Figure 11, which also depicts a marked asymmetric Cr depletion as well as a clear Ni enrichment with the formation of a nearly pure Ni crest on the surface on the right grain. Localized Ti and Al enrichment ahead the intergranular Cr-rich oxide tip on the right side of the GB beneath the surface was also detected.

The examination of the grain boundary beyond the intergranular oxide penetration revealed variations in Cr, Fe and Ni. A noticeable Cr and Fe depletion associated with Ni enrichment was observed along the GB for more than 500 nm (Figure 12). TEM characterisation also confirmed the presence of fine discrete Cr-rich M$_{23}$C$_6$ intergranular carbides in this material.

The third region examined (Figure 13) contained a pure metallic Ni nodule on the surface; SDD EDX spectrum images revealed a slight nickel enrichment interconnected with the surface nodule (white arrow). From the Cr and O K$\alpha$ spectrum images it was possible to distinguish two different internal oxide morphologies. Most of the Cr-rich oxide particles appeared to be interconnected and to form on preferential diffusion paths just underneath the surface nodule, whereas other discrete oxides, deeper in the bulk, seemed to be discrete and not correlated to any preferential path. Moreover, some local Fe enrichment was visible and could have been associated with the formation of a small amount of Fe-rich oxide both at the surface and in the bulk material.

Micro-hole Drilling Analysis

As previously mentioned, it is thought that residual compressive stress caused by internal oxidation, and strain localization can play an important role in the GBs oxidation behavior and be the rate-controlling step in the internal oxidation process of Alloy 600. Moreover, the high variation in internal/sub-surface oxide particles and intergranular oxide can be notably different depending on GBs surface morphology. Thus, the internal compressive stress present at different GBs may also vary. Based on these facts a GB characterized by split-ridge morphology and a marked NFZ was analysed with the micro-hole drilling technique previously described. The grain boundary analysed was in the region deformed in tension and where a residual tensile stresses was present (area b in Figure 2(a)).

Nine discrete FIB micro-hole measurements across the GB were made, as shown in Figure 14. The FIB holes were equally spaced by 8 µm in order to avoid any mutual interference on the displacement and stress calculation, while 2 holes were placed at a higher distance from the GB (40 µm) and are
intended to be representative of the bulk material. The residual stress values present in the near surface region of the oxidized Alloy 600SA are reported in Table II. The errors were calculated from fitting the strain relaxation to the computational model. The residual stresses were also graphically represented in Figure 15 Figure 16 for the X and Y direction respectively. These profiles showed high residual compressive stresses in both X and Y directions which decreased in the proximity of the GB. Specifically, in the bulk material the residual stress was more compressive than 300 MPa in both X and Y direction but near the GB it was about less than this value ($\sigma_x = -110\pm24$ MPa, $\sigma_y = -150\pm22$ MPa).

Discussion

Internal and Intergranular Oxidation Susceptibility of Alloy 600

The results of this study confirmed that solution-annealed Alloy 600 was susceptible to both internal oxidation and preferential intergranular oxidation in a low pressure hydrogenated steam environment (in particular Figure 5, Figure 6 and Figure 7) as previously postulated by Scenini et al. [9] on Alloy 600 oxidized under similar conditions. Specifically, the surface morphology of the oxidised grain boundaries (i.e., split-ridge and crest), the presence of pure metallic Ni intragranular nodules and the NFZ along the GBs, have already been reported for model alloys that are well-known to be susceptible to internal oxidation [5-6]. Similar features were also reported by Wood et al. [13] on Ni-Cr alloys tested in $H_2/H_2O$ environment at 1000ºC, although on a much larger scale. However, the most compelling evidence that Alloy 600 underwent both internal and preferential intergranular oxidation is shown in the detailed AEM characterisation of the GB cross-section specimens (Figure 10-Figure 13). The AEM results confirmed the presence of interconnected Cr-rich internal oxide particles, which form on preferential diffusional paths, as well as discrete precipitates deeper in the bulk material. Furthermore, high resolution STEM SDD EDX spectrum images also showed that the preferential intergranular oxide was mainly composed by chromium oxide astride a local enrichment of titanium and aluminum oxide.

With respect to the environmental exposure conditions used in this study, a paper to be presented at this conference by Lindsay et al. [14], shows that the phenomenology of SCC in low pressure hydrogenated steam appears to be similar to PWSCC. From a more practical point of view, there are significant similarities between the present work and what reported in the literature for Alloy 600 oxidized in simulated PWR primary water. For instance, the presence of Cr-depleted and nickel enriched region ahead the oxide tip along with the asymmetric Cr depletion on the right-hand side of GB (Figure 11 and Figure 12) have been observed also in SCC and corrosion tests performed in nominal PWR primary water at 340ºC [15-16]. The sharp changes in the HAB preferential oxidation susceptibility occur at twin intersections (Figure 7) is consistent with observations by Alexandreanu et al. [12] for 325ºC autoclave SCC tests.

These observations suggest that this environment can be relevant to the PWR primary water. The greater temperature used in the present work (480ºC) in respect to the typical primary circuit temperature (325ºC), was used in the experiments to accelerate the oxidation process by two orders of magnitude according to the activation energy proposed by Economy and Jacko [17].

The correlation between the GB surface morphology and the preferential intergranular penetration susceptibility suggests that the mechanism accounting for the GB oxide formation might be dissimilar on GBs with different character. It is postulated that the formation of a thin and continuous Cr$_2$O$_3$ oxide layer above certain GBs (Figure 9(a)) may be attributes to fast Cr diffusion to the surface along the grain boundaries. This rapid diffusion may enable more oxide formation on the alloy surface at the grain boundaries. The oxide can then develop sideways, above the adjacent grains, probably incorporating the internal oxide particles formed just beneath the surface by coalescence. When the external thin oxide layer is formed, it could eliminate direct access of the external environment to the alloy, protecting it from further internal oxidation and intergranular oxide penetration. The layer can
then grow both in thickness and sideways and form a continuous and protective Cr$_2$O$_3$ layer above the entire surface. However, it may take much longer time for this layer to be formed. In which case, and when the Cr diffusivity at the grain boundaries is not fast enough for the formation of a thin external oxide layer, intergranular penetration can easily occur as it can be seen in Figure 8.

Stress Generation due to Internal and Intergranular Oxidation and its Relief Mechanism

Preferential intergranular oxide penetration readily occurred on certain GBs in addition to internal oxidation. Similar penetration was detected in earlier studies on Ni-Cr Alloys (tested in 1 atm of oxygen at 800-1000°C and in H$_2$/H$_2$O environment at 1000°C [13]) as well as on diluted Ni-Al Alloys [7-8] (although having a very different morphology), and stress generation due to volume increase was given as possible explanation for the intergranular penetration occurrence. In fact, when internal and intergranular oxide grows, the resulting volume increase leads to internal compressive stresses and to the development of a biaxial tensile stress in the adjacent alloy region just ahead the oxidation front. These stresses could induce the continuous formation of ultrafine cavities and other defects, which can ”open up” the boundary ahead the intergranular oxide and enhance its growth as a thin and continuous band. Therefore, the material deformation around the oxide to accommodate the volume increase and the mechanism responsible for the stress-relief could play an important role in the Alloy susceptibility to internal oxidation and preferential intergranular penetration. At high temperatures (1073-13073K) this internal stress could be relieved by grain boundary sliding and the extrusion of a weak internal oxide-denuded zone adjacent to the grain boundary [7-8].

However, at lower temperature this mechanism can be difficult and the stress-relief can occur by diffusional creep process of solvent atoms (Ni) to the surface. The surface morphology, characterized by a large amount of intragranular nodules and grain boundary ridges (Figure 5 to Figure 7) mainly composed by pure metallic Ni as confirmed from the AEM analyses (Figure 11 and Figure 13), suggest that the stress-relief mechanism might occur in a similar manner to the one proposed by Guruswamy et al. [5]. With the initial deformation of the region just ahead the oxidation front, the resulting increased dislocation densities and consequent countercurrent Ni/vacancy flow by pipe diffusion. The proposed mechanism is also supported by the slight nickel enrichment interconnected with the surface nodule (Figure 13) and penetrating in the bulk in an oblique direction in parallel with the interconnected internal oxide particles, which might be an evidence of the pipe diffusion mechanism accounting for the relief of stress.

Considering that the volume of nickel nodules was found to be comparable to the total volume increase caused by internal/intergranular oxidation and assuming that the nickel nodules are extruded from the bulk material in order to release the compressive stresses caused by the oxide formation, a correlation between the stress and the surface morphology (the presence of a Nodule Free Zone) might exist. Scenini et al. [9] proposed that the residual compressive stresses, that are assumed to be the driving force for Ni diffusion, might not be constant but decrease and reverse at the GBs. From the stress profile obtained with the micro-hole drilling technique (Figure 15 and Figure 16) the superficial residual compressive stresses, in both x and y direction, reduce markedly next to the GB and become roughly half the stress measured in the bulk of the grains. This suggests that a fast relief of the compressive stresses along the GB occurred. The fast relief of the compressive stresses at the GB should lead consequently to a lower biaxial tensile stress ahead the oxidation front and to a lower susceptibility to preferential intergranular penetration. This is confirmed by the GB cross sectioning, which revealed the low susceptibility to intergranular penetration of GBs characterized by the NFZ (Figure 9(a)).

On the other hand, when the stress relief at the GB is not fast enough to accommodate the volume increase, the higher compressive stress can generate a biaxial tensile stress ahead the oxidation front, which can support stress assisted oxidation and thus enhance the occurrence of intergranular oxide (Figure 8). Once the intergranular oxide is formed it would also help to reduce more the grain boundary transport of Ni to the surface leading to higher compressive stresses near the GB with resultant increased biaxial tensile stress and higher dislocation density. A portion of this high
compressive stress is then relived by pipe diffusion of nickel atoms to the surface with the formation of nodules also on the GB itself (Figure 6(b)).

**Residual Stress and Cold Work Effects on the Intergranular Susceptibility**

The intergranular oxide penetration measured via FIB-produced cross-sections was very dependent on the sign and magnitude of residual stress. In particular, it was noted that the oxide penetrated along the GB to a maximum depth of 200 nm in locations subjected to a compressive residual stress. Conversely, when a tensile residual stress was present, the GB penetration was in excess of 500 nm. The increased depth of preferential intergranular penetration in the tensile region might be associated in part to the stress-assisted diffusion of Cr to the GB and the opposite vacancy migration away. In fact Cr is expected to diffuse faster to grain boundaries under a tensile stress (higher amount of defects and vacancy) increasing consequently the intergranular oxidation rate.

Moreover, in presence of a tensile stress the O solubility in the material is markedly increased and its diffusivity is affected by the hydrostatic (triaxial) stress gradient present in the host metal [18]. Oxygen in fact, locally diffuses from compressive or low tension zones towards those in high tension. In the current case, when a residual tensile stress is present a stress gradient is generated between the surface and only in the bulk material a hydrostatic stress can be present. This stress gradient is ultimately responsible for the enhanced oxygen diffusion along the grain boundary and for the phenomenon of stress assisted preferential intergranular oxidation.

It is also important to point out that in order to introduce the residual stress the sample was plastically bent, and therefore a considerable amount of cold work is present in the specimen, especially at the intrados and extrados (see figure 2 (b)). Therefore, also the effect of cold work on the intergranular oxidation susceptibility has to be taken into account and it has an additive effect to the phenomena described above, even when a compressive residual stress would hinder intergranular oxidation.

**Conclusions**

From the examination of Alloy 600 oxidized at 480°C in low pressure hydrogenated steam the following conclusions can be drawn:

- Advanced AEM characterisation of FIB-produced cross-section specimens demonstrated that Alloy 600 underwent both internal and intergranular preferential oxidation.
- Local stress measurements using a recently-developed FIB micro-hole drilling technique revealed stress variations at microscopic level. These results were correlated with the presence of intergranular and internal subsurface oxide. In particular, it was shown that the residual compressive stress decreased at the GB devoid of preferential oxidation and internal oxidation.
- As a consequence of internal and intergranular preferential oxidation, compressive stresses are generated within the surface of the samples, which may be the driving force for Ni nodules formation on the surface of the sample. The high rate of Ni transport to the surface might be explained in terms of pipe-diffusion-controlled creep and the slight bulk Ni enrichment interconnected with the nodule strongly supports this mechanism.
- The presence of residual tensile stress enhances the intergranular oxidation susceptibility of Alloy 600.
- A correlation between the oxide morphology and the GB character was identified, suggesting that the GB character can play a fundamental role on the intergranular oxidation susceptibility of Alloy 600SA.
References


Tables

Table I: Alloy 600SA composition (wt. %).

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Table II: Residual stress values calculated with the micro-hole drilling technique.

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Figures

Figure 1: (a) Bent sample used for the oxidation studies.

Figure 2: Residual stress (a) and cold work (b) profile on the sample cross-section after relaxation.

Figure 3: LOM image of Alloy 600SA after exposure to low pO\textsubscript{2} at 480°C for 66 hours.
Figure 4: Secondary electron (SE) image of the oxidized surface of the Alloy 600SA specimen in the compressive (a) and tensile (b) region.
Figure 5: (a) SE image of oxidized Alloy 600SA with random high angle and $\Sigma 3$ GBs; (b) More detailed image showing 2 high angle GBs and 1 $\Sigma 3$ GB (arrowed).

Figure 6: (a) SE image of a GB triple point region with 3 oxidised grain boundaries 1 of which (white arrow) was characterized by split ridge morphology and a NFZ; (b) SE image of a HAGB characterized by a crest morphology of oxidized Alloy 600SA.

Figure 7: SE image showing the oxide morphology of both HAGBs and $\Sigma 3$ boundaries.
Figure 8: FIB SE images of a cross-section obtained through an oxidised GB characterised by the crest morphology (a) in the tensile region; and (b) in the compressive region.

Figure 9: (a) FIB SE images of GB cross-section characterized by (a) a split ridge oxide morphology; and (b) a non preferentially oxidised surface ($\Sigma 3$ boundary).
Figure 10: Titan STEM-HAADF image of the preferential intergranular oxidation with areas identified that were subsequently analysed using SDD EDX.

Figure 11: (a) STEM-HAADF image of region 1 in Figure 9, and corresponding SDD-EDX spectrum images for (b) Cr, (c) Fe, (d) Ni, (e) O, (f) Al, (g) Ti showing the qualitative distribution of elements in the vicinity of an oxidised grain boundary with oxide penetration and an internally oxidised near-surface region. Note the presence of the coarse Cr-rich intergranular oxide, and the discrete Al-Ti-enrichments associated with the oxidised boundary.
Figure 12: (a) STEM-HAADAF image of region 2 in Figure 9, and corresponding SDD-EDX spectrum images for (b) Cr, (c) Ni and (d) Fe showing the qualitative distribution of elements along the grain boundary beneath the intergranular oxide penetration.

Figure 13: (a) STEM-HAADAF image of region 3 in Figure 9, and corresponding SDD-EDX spectrum images for (b) Cr, (c) Fe, (d) Ni, (e) O, (f) Al, and (g) Ti showing the qualitative distribution of elements in the vicinity of an intragranular oxide penetration and an internally oxidised near-surface region.
Figure 14: SE image of the oxidized Alloy 600SA area analysed with the micro-hole drilling technique.

Figure 15: Oxidized Alloy 600SA mapped residual stress of each hole in the x direction as a function of distance from the GB.
Figure 16: Oxidized Alloy 600SA mapped residual stress of each hole in the y direction as a function of distance from the GB.