



# The intergranular oxidation susceptibility of thermally-treated Alloy 600



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## ABSTRACT

The oxidation behaviour of thermally-treated Alloy 600 was studied in hydrogenated steam at 480 °C, an environment used to accelerate the oxidation reactions observed under pressurized water reactors conditions. Focused ion beam (FIB) and analytical transmission electron microscopy (ATEM) provided direct evidence of localized intergranular carbide decomposition and the formation of an intergranular Cr-rich oxide embryo. These results are in terms of the early stages of preferential intergranular oxidation and the role of carbides on grain boundary migration, carbide decomposition, and the effect of local carbon enrichments in the matrix.

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## 1. Introduction

The susceptibility of Alloy 600 to intergranular stress corrosion cracking (IGSCC) in pressurized water reactor (PWR) primary water environment is well-known and it has been a major in-service issue over the past decades [1–3]. The Internal Oxidation mechanism of Scott and Le Calvar has been proposed for IGSCC initiation [4,5] in PWR primary water environments; however, this mechanism in relation to primary water stress corrosion cracking (PWSCC) has evolved significantly since it was proposed. Internal oxidation is defined as the selective oxidation of a solute in an alloy resulting in the formation of fine discrete oxide particles [6]. However, the cause for PWSCC has been associated with the selective oxidation of Cr in the alloy [7–13] in both PWR simulated primary water as well as in accelerated SCC tests. Thus, even though selective oxidation can occur along dislocations or grain boundaries, it is not internal oxidation in the classical sense, since there is connectivity with the outer surface. Consequently, the term “internal oxidation” has been used in the past as a mechanism of SCC. A mechanistic understanding of IGSCC is key developing sound predictive models that incorporate both SCC initiation and propagation, thereby aiding the in-plant management of Alloy 600 components. Numerous parametric studies were performed over the past decades with the aim of studying the effect of temperature [14–16], cold work [15,17], residual stress [18,19] and heat treatments [20] on SCC

susceptibility of Alloy 600. In 1977, Domain et al. [20] reported an effective way to mitigate SCC by thermal treatment. Specifically, thermally-treated (TT) Alloy 600 was shown to have improved IGSCC resistance in deaerated, high-purity water than did the mill-annealed (MA) or solution-annealed (SA) material [20–22], but it was not immune. Subsequent studies demonstrated that a semi-continuous network of grain boundary (GB) carbides formed during thermal treatment could enhance SCC resistance of Alloy 600 in caustic [23] and reducing environments (e.g. hydrogenated primary water at elevated temperature) [24–27]. The main reason for this improved IGSCC resistance of Alloy 600TT was associated with the presence of grain boundary carbides, which delayed crack initiation and decreased the crack growth rate [28]. Considerable interest has been focused on the role of the Cr-rich carbides in the mitigation of IGSCC, and two main mechanisms have been proposed. The first proposed mechanism is based on the mechanical effect of intergranular carbides in affecting localised deformation whereas the second mechanism focuses on the electrochemical/chemical effects of the carbides on IGSCC and intergranular oxidation. With respect to the mechanical mechanism, Bruemmer et al. [29] proposed that intergranular carbides could serve as effective dislocation sources, promoting crack-tip blunting, thus reducing the crack growth rate and grain boundary sliding. Alternatively, carbides might create a more tortuous path for intergranular crack propagation, and, therefore, reduce the crack growth rate by mechanically interfering with crack propagation [30].

On the other hand, Was et al. [30] suggested that the oxidation of intergranular Cr-rich carbides might result in the formation of a more stable and protective Cr-rich oxide at the crack tip, hence

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reducing the oxidation rate and crack propagation rate. Dugdale et al. [32] also proposed that a more dense and protective oxide may be formed around intergranular carbides. Furthermore, Persaud et al. [11] suggested that oxidation of Cr-rich carbides at the grain boundary might impede the inward diffusion of oxygen, and consequently improve Alloy 600 SCC resistance. Although several laboratories have studied the oxidation behaviour of intergranular carbides [30,32–34], there is still little evidence of this behaviour. Burke et al. [32] in their analyses of cold-worked Alloy 600 SCC were the first to identify the presence of nanograined oxides preferentially located on the  $M_7C_3$  carbides exposed on the intergranular fracture surface and with very limited localised oxidation of adjacent metal. Thus, the effect of the semi-continuous network of grain boundary carbides on intergranular oxidation merits further analysis, since the mechanism by which intergranular carbides affect the oxidation and SCC initiation behaviour is still not fully understood.

In the last few years, several researchers observed that during PWR simulated primary water oxidation Alloy 600 and 690 grain boundaries deviate from their original position 10–20 nm (depending on exposure conditions) and became asymmetrically depleted in both Cr and Fe [36–39], and suggested that this is due to grain boundary migration. However, Bertali et al. [10,35] unequivocally demonstrated, via analytical transmission electron microscopy (ATEM) and diffraction analysis that these elemental depletions were due to grain boundary (GB) migration. In solution-annealed Alloy 600 exposed to high-temperature  $H_2$ -steam environment they identified a pronounced GB migration and suggested that this mechanism could play an important role in the early stages of IGSCC initiation. They successfully correlated the GB migration with preferential intergranular oxidation (PIO) processes. Recent experiments by the present authors were able to successfully identify and monitor the precursor phenomenon for IGSCC in PWRs [40]. They performed *in situ* analytical transmission electron microscopy (TEM) oxidation experiments using a gas environmental cell at elevated temperature, and verified the occurrence of GB migration and PIO.

The aim of the present study is to investigate the initial stages of PIO for thermally-treated Alloy 600 in an environment known to accelerate PWSCC without changing the oxidation behaviour of the material [10,35], and compare this with published results obtained for solution-annealed Alloy 600 tested under identical conditions [35]. The focus of the present investigation is to assess and understand the effect of the intergranular carbides on localised grain boundary migration and grain boundary pinning, carbide oxidation/decomposition and the role of carbon deriving from the carbide oxidation/decomposition.

## 2. Experimental procedures

### 2.1. Material and sample preparation

The material used in this study was Alloy 600 manufactured by B&W Tubular Products Division and supplied by Westinghouse (heat #93510). The material was provided in the low-temperature mill-annealed condition, and the bulk composition is reported in Table 1. The material was solution-annealed (SA) in air at 1100 °C for 30 min and subsequently water-quenched to room temperature within 10 s in order to minimize the extent of intergranular carbide precipitation. The recrystallized coarse-grained (200–400  $\mu\text{m}$ ) microstructure facilitated the investigations in this study. The material in the SA condition was exactly the same as used in previous by the present authors [10,35]. Some of the solution-annealed material was thermally-treated (TT) in air at 700 °C for 15 h and subsequently water-quenched to produce a semi-continuous network of Cr-rich carbides along the grain boundaries.

Rectangular oxidation coupons ( $20 \times 15 \times 2 \text{ mm}^3$ ) of TT Alloy 600 were cut from the heat-treated block of material and metallographically polished with 3  $\mu\text{m}$  diamond suspension solution. The specimens for this study were extracted several mm away from the oxidized surface, so any pre-oxidation that occurred during the heat-treatment would not affect the test specimens. The final polishing step was performed using an Oxide Polishing Suspension (OPS) solution, which enabled the removal any superficial deformation induced by mechanical polishing. This is important as it is known that a superficial deformed layer will have an impact on the oxidation behaviour of the alloy [41,42]. The OPS polishing procedure produced a strain-free surface so that it can be considered to be representative of the bulk material.

### 2.2. Hydrogenated steam oxidation system

The oxidation experiments were conducted in a low-pressure (1 bar)  $H_2$ -steam environment at temperatures up to 480 °C at a water flow rate of 1.8 mL/min,  $H_2$  flow rate of 35 mL/min and a steam-to- $H_2$  ratio of 62.16. This system, which has been used over the past decade for oxidation experiments on Ni-based alloys [10,35,43], has been shown to accelerate the oxidation of the alloys while maintaining the appropriate thermodynamic conditions with respect to the Ni/NiO transition. It is well-known that the maximum SCC susceptibility of Alloy 600 occurs at a potential of +80 mV vs. Ni/NiO transition, which also corresponds to the window of potential where commercial pressurized water reactor (PWR) operate [43,44].

The oxidation tests were conducted for 120 h at 480 °C in low pressure (1 bar)  $H_2$ -steam environment at an  $O_2$  partial pressure of  $9.9 \times 10^{-26}$  atm, which is 24 times lower than the Ni/NiO dissociation pressure at the test temperature. The conditions chosen for this study were identical to those reported in a recent publication by the present authors [34]; additional details concerning the operation of the system are provided by Scenini et al. [45], who originally developed the low pressure  $H_2$ -steam system [45], and also reported by Persaud et al. [11] who used a replica of this system.

### 2.3. Microstructural characterization

The specimens were characterized prior to and after oxidation using complementary microstructural analysis techniques including field emission gun (FEG) scanning electron microscopy (SEM), focused ion beam (FIB) microscopy, and analytical transmission electron microscope (AEM). A Zeiss Merlin FEG-SEM equipped with an Oxford Instruments X-max 150 silicon drift detector (SDD) and an Oxford Instruments Extreme 100 windowless SDD for energy dispersive X-ray (EDX) microanalysis was used to characterize the as-polished specimen surfaces before and after exposure. An FEI Helios NanoLab 660 DualBeam FIB was used to prepare site-specific cross-section TEM specimens in order to evaluate the oxide and its penetration depth at selected high-angle grain boundaries (HAGBs) and to perform 3D “slice-and-view” analyses. A Through-Lens Detector (TLD), Mirror Detector (MD) and In-Column Detector (ICD) at high (20 kV) and low accelerating voltage (3–5 kV) were employed for electron imaging. Cross-section specimens were then extracted from the coupons using the TEM lift-out technique and thinned using the FIB to electron transparency. In order to characterize the baseline material microstructure, including type and extent of precipitation, several conventionally-prepared samples were examined with TEM. These were 3.0 mm diameter disc samples obtained from the thermally-treated Alloy 600 were electropolished in 20%  $HClO_4$  – 80%  $CH_3OH$  at –33 °C using a Struers Tenupol equipped with a Jubalo closed cycle refrigeration system. Initial AEM characterization of the TEM specimens

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