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# The application of *in situ* analytical transmission electron microscopy to the study of preferential intergranular oxidation in Alloy 600

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## ABSTRACT

*In situ* analytical transmission electron microscopy (TEM) can provide a unique perspective on dynamic reactions in a variety of environments, including liquids and gases. In this study, *in situ* analytical TEM techniques have been applied to examine the localised oxidation reactions that occur in a Ni-Cr-Fe alloy, Alloy 600, using a gas environmental cell at elevated temperatures. The initial stages of preferential intergranular oxidation, shown to be an important precursor phenomenon for intergranular stress corrosion cracking in pressurized water reactors (PWRs), have been successfully identified using the *in situ* approach. Furthermore, the detailed observations correspond to the *ex situ* results obtained from bulk specimens tested in hydrogenated steam and in high temperature PWR primary water. The excellent agreement between the *in situ* and *ex situ* oxidation studies demonstrates that this approach can be used to investigate the initial stages of preferential intergranular oxidation relevant to nuclear power systems.

## 1. Introduction

The ability to study dynamic processes in the transmission electron microscope has attracted considerable interest and attention since it was first possible to image and characterize microstructures in thin-foil specimens. There was concern that observations in thin-foil specimens may not be representative of the true microstructure. An example illustrating this point was demonstrated in the study of deformation structures in metals, as very thin specimens tended to show very few dislocations, but thicker specimens revealed the true deformation substructures. In the late 1960–70's, high voltage electron microscopes (HVEM) with accelerating voltages up to 3 MeV provided the opportunity to study “thicker” specimens than usual for conventional 100 keV transmission electron microscopes (TEM) [1]. This permitted the evaluation of more “bulk”-type microstructures, such as deformation in the vicinity of crack-tips [2,3] in metals, the assessment of the initial stages of recrystallization in metals [4], *in situ* oxidation and reduction processes [5,6], and the characterisation of various mineralogical and cementitious materials [7]. The HVEM also provided the opportunity for the design and construction of a variety of *in situ* platforms (specimen stages, gas cells) to facilitate the observation of dynamic processes in materials *in situ*. Thus, there was tremendous growth in metallurgical and materials science research concerning precipitation phenomena, phase transformations in alloys, recrystallization, initial stages of oxidation and reduction (metals/oxides),

hydrogen embrittlement, and deformation. The important caveat for *in situ* HVEM studies was the need to reproduce “bulk” behaviour – and avoid thin film effects in materials. More detailed description of the HVEM *in situ* techniques and related research are found in Swann et al. [8] and reviewed extensively by Butler [9], and Butler and Hale [10].

With improved intermediate voltage (200–400 keV) TEM designs, the developments and application of high resolution *in situ* TEM continued through the 1980–90's, particularly through the research of Sinclair, Howe and others to study the nanoscale atomic-level reactions in precipitation phenomena in materials at lower accelerating voltages [11–17].

In recent years, there has been a resurgence of *in situ* TEM to study dynamic processes in both biological and materials (particularly nanoparticle and catalyst) systems [18–20]. New specimen holder and environmental cell designs now permit evaluation of materials in a broad range of environments: liquids (including acids) with and without electrochemical control, gases, and elevated temperatures (in gas or in vacuum). Also, by modifying the holder to utilize the advanced microanalytical capabilities afforded by multiple Silicon Drift Detectors for x-ray energy dispersive (XED) spectroscopy, it is now possible to acquire elemental information from specimens in the environment of interest, which has greatly enhanced the viability and applicability of *in situ* TEM [21,22].

The ability to study more conventional wrought metals and alloys had been hampered by the preparation of specimens suitable for use in

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the new generation of *in situ* environmental chips and holders. Recent research in the Materials Performance Centre has led to the development of “hybrid” procedures for specimen preparation utilizing both electropolishing and FIB techniques [23]. With this approach, it has been possible to successfully produce relevant specimens for *in situ* liquid cell TEM studies to examine the electrochemical polarization behaviour and dissolution of MnS inclusions in H<sub>2</sub>O [24]. With the ability to produce suitable specimens, it is thus possible to exploit the benefits of combined XED and elevated temperature gas cell TEM *in situ* experiments to gain an improved understanding of the environment-sensitive materials behaviour, particularly the reactions termed “precursor phenomena” leading to materials degradation, including stress corrosion cracking (SCC) [25].

In pressurized water reactor (PWR) nuclear power systems, the environment of interest is hydrogenated primary water at approximately 300 °C with generally ~30 cc/kg H<sub>2</sub> to maintain the appropriate electrochemical conditions. Recent research [26,27] has demonstrated that the use of low pressure (atmospheric pressure) H<sub>2</sub>-steam mixtures can be used to accelerate the localised oxidation reactions that lead to the development of pronounced grain boundary (GB) migration and asymmetric composition gradients associated with preferential intergranular oxidation. Furthermore, detailed analytical electron microscopy analyses have demonstrated conclusively that localised grain boundary migration ahead of the preferential intergranular oxide penetrations are critical in the primary water stress corrosion cracking (PWSCC) “precursor” reactions [26,27].

Therefore, the ability to explore localised oxidation reactions in Alloy 600 at elevated temperature in the presence of H<sub>2</sub> containing H<sub>2</sub>O vapor offers the unique opportunity to study *in situ* the combination of oxidation and grain boundary migration phenomena important in SCC.

## 2. Materials and methods

### 2.1. Material and specimen preparation

The material selected for this investigation was Alloy 600, a Ni-Cr-Fe alloy known for its corrosion resistance and SCC performance. The composition of Alloy 600 is listed in Table 1. This material was solution-annealed at 1150 °C for 30 min and water-quenched. This resulted in a fully recrystallized, coarse-grained (~200 µm) structure, which is described elsewhere [26].

Electropolished 3 mm diameter thin-foil TEM specimens for general microstructural characterisation were prepared using a Struers Tenupol 5 twin jet electropolishing unit with a Jubalo closed-cycle refrigeration system, and a 20% HClO<sub>4</sub> – 80% CH<sub>3</sub>OH electrolyte at –33 °C. These specimens were subsequently evaluated in an FEI Tecnai T20 Analytical Transmission Electron Microscope equipped with an Oxford Instruments windowless X-Max 80 TLE Silicon Drift Detector (SDD) and AZTEC analysis system for X-ray energy dispersive spectroscopy (XEDS) microanalysis.

The TEM specimens for the *in situ* experiments were prepared using an FEI Helios 660 FIB and the hybrid specimen preparation approach, which combines the conventional electropolishing and focused ion beam (FIB) techniques [23]. These specimens were examined and suitable regions were extracted for subsequent mounting on the Protochips heating Atmosphere e-Chips. HVEM *in situ* oxidation studies performed using the differentially-pumped gas reaction cell designed by Swann [5] had shown that it was important to have “thick” specimens in order to avoid/minimize surface effects and thus

generate observations that would be relevant to bulk materials behaviour. Therefore, the specimens selected for these *in situ* experiments were approximately 300 nm in thickness.

An FEI Helios 660 FIB was used for hybrid specimen extraction and for the preparation of cross-section TEM specimens from the *in situ* oxidized sample. A 250–300 nm thick specimen, approximately 25 µm by 20 µm in area, that contained a random high-angle grain boundary was extracted from the electropolished TEM specimen using an FEI Easylift™ micromanipulator. The extracted hybrid specimen was then attached to the SiN<sub>x</sub> window using Pt deposition.

### 2.2. In situ analytical TEM experiments

The *in situ* experiments were performed using the FEI Titan G2 80–200 S/TEM operated at 200 kV, with X-FEG and Super X energy dispersive x-ray spectrometers (4 SDDs). The Protochips Atmosphere environmental holder with heating chips and customized low penumbra geometry beryllium lid [21,25]. For these experiments, the specimen was tilted 20 ° and only the 2 SDDs in the direction of tilt were used for XED spectra acquisition. High-angle annular dark field (HAADF) scanning transmission electron microscope (STEM) imaging was performed with a convergence angle of 21 mrad and a HAADF inner angle of 54 mrad. The e-Cell MEMS chips used to create the *operando* environment were a pair of 300 µm thick Si wafers, with each wafer having a lithographically fabricated 300 µm x 300 µm, electron transparent SiN<sub>x</sub> window. The heating chips mounted at the upper electron beam entry side of the cell has a SiN<sub>x</sub> window thickness of 30 nm whereas the lower one is 50 nm thick. Spacers deposited onto the chips created a nominal vertical separation between the windows of approximately 5 µm. During *in situ* measurements the e-Cell was completely filled with gas at ~1 bar pressure while the temperature was closed-loop controlled by on-chip pre-calibrated heater elements. All STEM-XED spectrum imaging and analyses were performed at temperatures of 320–480 °C and under ~1 bar gas.

After the conclusion of the *in situ* experiment, a cross-section TEM specimen was extracted from the oxidized “thick” sample using the FEI Helios 660 FIB. This specimen was subsequently characterized to further analyze the extent of oxidation and grain boundary migration. Cross-sectional imaging and XED analysis of the specimen were performed in the FEI Talos F200 FEG Analytical TEM (with Super-X) and operated at 200 kV. Data analyses were performed using Gatan Digital Micrograph™ and Bruker Esprit™ software.

In order to ensure that there was no oxidation or grain boundary migration due to the elevated temperature, control experiments were performed at 320 °C in 1 bar N<sub>2</sub>.

The *in situ* H<sub>2</sub>-H<sub>2</sub>O vapor experiments were performed using a mixture of 0.5% H<sub>2</sub> in N<sub>2</sub> that was bubbled through deionized H<sub>2</sub>O (cooled to 16 °C) at 1 bar pressure with continuous H<sub>2</sub>-N<sub>2</sub>-H<sub>2</sub>O vapor flow across the specimen, which was exposed at temperatures of 320–480 °C. This H<sub>2</sub>-N<sub>2</sub> gas mixture bubbled through deionized H<sub>2</sub>O is referred to as “H<sub>2</sub>-H<sub>2</sub>O vapor” for the *in situ* experiments reported in this paper. These experimental conditions are similar to the partial pressures of O<sub>2</sub> used for *ex situ* bulk experiments performed at atmospheric pressure in a H<sub>2</sub>-steam mixture. The *ex situ* H<sub>2</sub>-steam system is described in detail in references [26–31]. The specific H<sub>2</sub>-H<sub>2</sub>O vapor mixture was selected to yield a partial pressure of O<sub>2</sub> that was more reducing than the Ni/NiO dissociation pressure (pO<sub>2</sub> Ni/NiO), so that the *in situ* observations would be relevant to previous SCC and atmospheric pressure H<sub>2</sub>-steam experiments reported in the literature [28,29].

**Table 1**  
Alloy 600 composition (wt%).

Heat No.	C	Mn	S	P	Si	Cr	Cu	Fe	Ti	Al	Ni
93510	0.047	0.23	0.002	0.005	0.30	15.42	0.01	8.94	0.34	0.19	Bal

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