Understanding surface oxidation in stainless steels through 3D FIB sequential sectioning

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Abstract. Focused Ion Beam (FIB) 3D sequential sectioning has been used to reconstruct the morphology of surface oxides in 304 stainless steels in nuclear reactors in order to characterize environmental degradation. Several coupon specimens with prior cold work and oxidized under applied stress have been studied in detail. A novel statistical approach based on more than 250k individual measurements will be presented as an alternative to conventional methods.

1. Introduction

The characterization of oxide layers is a well-studied topic and in the literature, where we can find studies based on surface techniques, TEM or atom-probe tomography (APT). There is, however, a gap between the highest resolution atomic characterization with APT (which provides information on just a few nm³) and a more macroscopic approach such as SIMS or Auger depth profiling (which provides averaged information on areas of a few mm²). In this work, we demonstrate that 3D FIB sequential slicing can provide a high spatial resolution over volumes of several micrometres with minimum sample preparation.

Low potential stress corrosion cracking (LPSCC) of stainless has been identified as a potential problem for pressurized water reactors (PWRs). Although initially thought to be immune, autoclave testing under controlled environments recently confirmed that highly cold-worked stainless steels are susceptible to SCC even in PWR primary water conditions [1]. Not much later, SCC was reported in an operating PWR plant [2]. A necessary step towards understanding the mechanisms controlling SCC and the influence of cold-work is the development of better methods for characterizing oxidation at the nanoscale. It is well known that when 304 stainless steel is oxidized under PWR primary water conditions it develops a dual oxide layer with an inner layer of Cr-rich spinel and an outer layer of Fe-rich spinel [3]. If the alloy has been previously cold-worked, the oxidation process is much more complex and enhanced oxidation of twin deformation bands and high-dislocation-density regions has been observed [4]. In this work, we have focused on the inner Cr-rich oxide layer and will demonstrate that oxidation can be better described statistically, instead of by a compositional line profile or by a single diffusion coefficient.
2. Materials and methods
A nuclear grade 304 stainless steel (SUS304) was solution treated at 1060 °C for 100 min and water-quenched. The material was then unidirectionally cold-rolled to a 20% reduction in thickness (referred to as 20% CW). The surface was polished down to mirror finish with colloidal silica. Oxidation tests were performed at the INSS laboratories (Japan) in simulated PWR primary water (hydrogenated water, containing 500ppm B, 2ppm Li and 30cc STP Hd/kg H₂O dissolved H) in an autoclave for 1500 hrs at 360°C. The coupon specimens were oxidized stress-free and the tensile test specimens under a load below the yield stress of the material.

FIB sectioning was carried out on a Zeiss NVision 40 dual beam FIB instrument (2-30kV Ga+ incident beam energy with currents of 80-1000 pA). Samples were orientated such that the focused Ga+ ion beam is at normal incidence to the cross-sectional surface (x-y plane) and SEM secondary electron (SE) images were taken of each sequential 2D slice (in the x-y plane) at a tilt angle of 54. The image stretching caused by the tilt was automatically corrected by the microscope software and, therefore, all SEM images shown in this work have been tilt corrected. A beam current of 700 pA was used to carry out the sectioning, producing slices every 40nm. The 2D SE images were aligned and corrected for drift using cross-correlation of static features on the sample original surface following the method described in [5]. Then, an area containing the region of interest and with its top side coinciding with the sample’s top surface is extracted from each image and arranged as a 3D dataset.

The 3D reconstruction was carried out using Mercury Software’s Avizo .6.1. The different regions of interest appearing in the 2D images (e.g. metal, oxides) were automatically selected (using intensity thresholding methods) or manually drawn when no automated segmentation method was good enough to avoid the channelling contrast present in some SE images. The dimensions of the reconstructed volumes are typically ~20x20x5µm with a voxel size of ~11x11x40nm. The Cr-spinel segmentation was performed in a semi-automatic way, relying on intensity thresholding to separate the Cr-rich oxide from the other phases and drawing the boundaries manually when this was not satisfactory (See Figure 1).

![Figure 1](image)

**Figure 1:** (a) SEM SE image showing the cross-sectional view used to reconstruct the surface oxides. Deposited carbon appears darker at the top, while the Cr-rich oxide appears covering the top surface with a deeper oxidised region along the grain boundaries; (b) Binary mask representing the Cr-rich spinel oxide after segmentation.

3. Results
For all the four specimens characterized, a 3D model of the inner Cr-rich oxide was created (See Figure 2). The depth of oxidation was measured in over 500000 points on average per reconstructed Cr-rich spinel models and subsequently statistically analysed. The nature of the data allowed the individual analysis of features such as grains, grain boundaries (gbs) or twin deformation bands (tbds), as will be shown next.
A Cr-spinel 3D model for the sample oxidized without applied stress is shown in Figure 2a. This region includes two gbs and three grains. A similar model for the sample oxidized under applied stress is shown in Figure 2b, including three gbs and three grains. An individual histogram for these gbs can be found in Figure 3a, as an example of the kind of detailed data that can be extracted. A comparison between the oxidation behavior of the samples oxidized with and without applied stress can be found in Figure 3b. Oxidation data for each of the grains and gbs can be found in table 1.

![Figure 2: 3D model of the Cr-rich spinel oxide for the sample with 20%CW oxidized without applied stress (a) and under applied stress (b). The longer parallel bands in the top figure are oxidized deformation bands.](image)

|                  | No stress - CW | Stress and CW |
|------------------|----------------|---------------|
|                  | Average oxidation | σ | Average oxidation | σ |
| Grain 1          | 132            | 53       | 177            | 48       |
| Grain 2          | 153            | 93       | 224            | 52       |
| Grain 3          | 105            | 23       | 160            | 42       |
| Grain boundary 1 | 203            | 107      | 394            | 151      |
| Grain boundary 2 | 210            | 123      | 381            | 133      |
| Grain boundary 3 |                |          | 426            | 282      |

*Table 1: Oxidation depths in nm for each of the grains and grain boundaries in Figure 2*
4. Conclusions
Surface oxidation in a matrix of 304 stainless steel samples oxidized under simulated PWR primary water conditions has been characterized by 3D sequential FIB sectioning. The individual effect of applied stress and prior cold work has been studied. It was found that the applied stress greatly increases the oxidation depth, an effect which is magnified at grain boundaries. The technique has allowed the reconstruction of volumes containing several grains and grain boundaries with nm resolution. This remarkable spatial resolution enabled the visualization of preferential oxidation down microstructural features such as grain boundaries and deformation bands. It also produced results of high statistical significance, where a histogram of oxide depths is used to characterize surface oxidation.

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