Micromechanical testing of oxidized grain boundaries: Understanding stress corrosion cracking mechanisms

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Stress corrosion cracking (SCC) has been a concern for the nuclear industry (amongst others) for decades. At present, we lack a clear understanding of the underlying mechanisms and several models have been proposed. Some of the most accepted mechanisms rely on the fracture of a brittle phase (e.g. oxide in grain boundary), such as the Selective Internal Oxidation (SIO) model by Scott and LeCalvar [1]. Although the idea is plausible and some evidence of oxides ahead of crack tips [2] has been reported, there is no quantitative data on the brittleness of these oxides or what exact role they play in the crack propagation.

In this work, we have explored a new experimental approach which enables mechanical testing at micrometre scale. By micromachining cantilevers using a focused ion beam (FIB), highly localized regions can be tested independently [3]. We have used this approach on an Alloy 600 coupon specimen that was oxidized under simulated pressurized water reactor (PWR) primary water (1500h at 340°C). These oxidation conditions induce selective intergranular oxidation (up to 3 micrometres) in this alloy, so microcantilevers were prepared such that an oxidized grain boundary plane (at almost 90° with the exposed surface) was included in the base (See Figure 1a). Microcantilevers were triangular in cross section (1µm wide and 0.8µm deep) and 12µm long. A nanoindenter that can operate as an atomic force microscope was used to position the indenting tip near the end of the cantilever. During indentation, load-displacement data was measured. Three behaviours were observed: 1. Samples which exhibited plastic deformation and didn't fracture, 2. Samples which fractured intergranularly in a brittle manner and, 3. Samples where an intergranular crack propagated intergranularly, but no fracture was observed (see Figure 1b).

The samples which behaved as described in type 2, confirmed that the oxide was brittle in nature. It was, however, the samples which cracked but didn't fracture the ones that required further investigation. FIB 3D slicing with a voxel resolution of 3x3x9nm was performed in a Zeiss NVision 40 over a volume of 2x1x1µm containing the oxidized grain boundary plane. A 3D model was constructed and it is shown in Figure 2, revealing that a crack which followed the oxide-metal interface in one of the grains had developed, affecting most of the grain boundary plane. A few points, however, were not cracked and acted as ligands preventing fracture. In all samples examined, these points were on the top part of the oxide that formed around intergranular Cr-rich carbides.

Further (S)TEM characterization on the same grain boundary revealed that the oxide that formed around the intergranular carbide (in a Cr-depleted region) had a much higher Fe content than the "usual" Cr-rich intergranular oxide, and was also more crystalline. This could explain why that portion of the grain boundary exhibited a greater strength that ultimately prevented fracture locally. Interestingly, samples with a higher intergranular Cr-carbide density, tend to perform better in SCC test [4].

References

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Figure 1. Microcantilever containing an oxidized grain boundary plane before testing in the nanoindenter (a) and microcantilever which developed a crack but didn’t fracture (type 3) (b).

Figure 2. 3D models generated after FIB 3D slicing showing Cr carbides (red), intergranular Cr-rich oxides (Green) and open crack (dark blue). In the left image, a longer intergranular carbide is clearly visible, with a thicker oxide around it. In the right image, from another angle, the points where the crack could not propagate are indicated by white arrows.