Evidence of sulphur-enriched grain boundaries in a chromia scale

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The addition of sulphur to a wet CO_2 environment can improve the quality of the resulting oxide scale and reduce its penetration by carbon, thereby slowing alloy carburisation [1]. Yu et al. [1] previously hypothesised that sulphur penetrates the oxide scale via grain boundary diffusion, suggesting that preferential occupation at grain boundary sites by sulphur decreases the probability of carbon ingress via grain boundary diffusion [1]. However, there has been no evidence to date showing sulphur penetration along oxide scale grain boundaries.

In a recent study of an Fe-20Cr alloy [2], evidence of carbon penetration along the grain boundaries of a passivating chromium oxide scale was provided by atom probe tomography (APT). Here, APT has been utilised to observe oxide grain boundaries in the chromia scale grown on an Fe-20Cr alloy during exposure to Ar-20%CO_2-20%H_2O-0.5%SO_2 for 10 min at 650 °C. The scale-alloy interface was captured in an atom probe tip, a thin slice revealing the x-z plane, shows the alloy on the left and oxide on the right, Figure 1. The oxide is chromia, but contains a thin layer of Fe-rich oxide parallel to the alloy surface, at a distance of roughly 40 nm. Sulphur was present both on the alloy and gas side of the Fe-rich layer, however, carbon was found only in the outer oxide layer. The distributions of carbon and sulphur are shown to correlate with chromia grain boundaries. This contribution will discuss the transport processes leading to the microstructure of Figure 1.

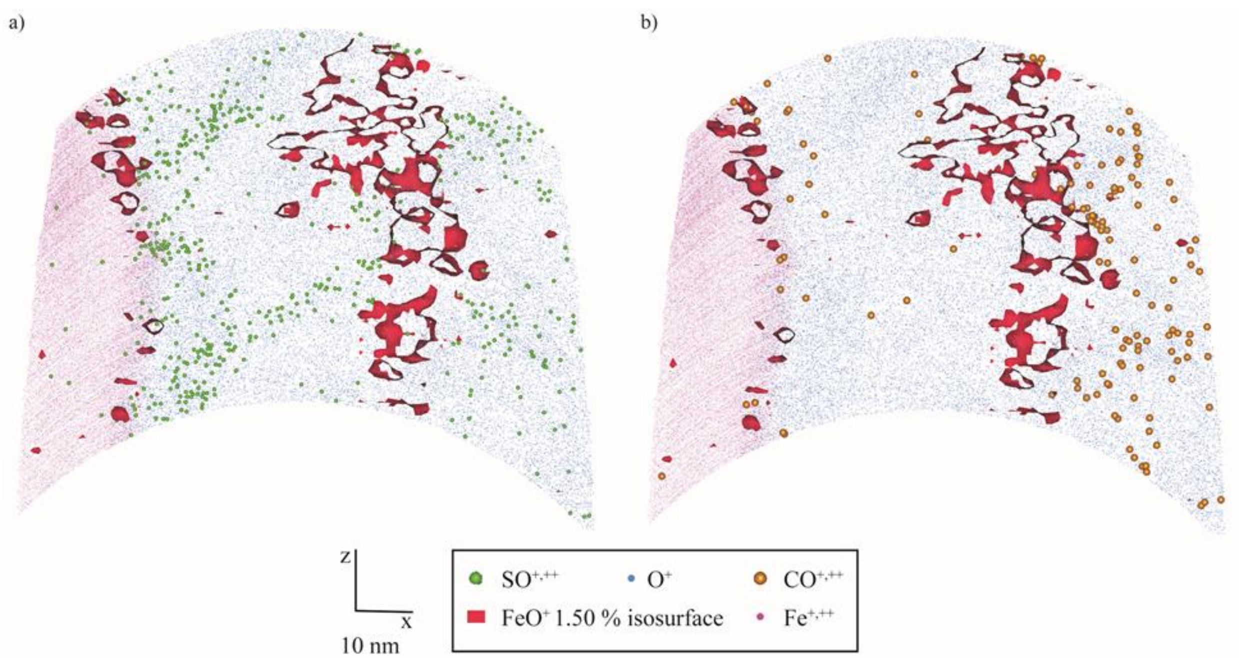

Figure 1: a) and b) are the same 4 nm section extracted from an atom probe dataset, where the Fe-20Cr substrate can be seen on the left of each image. a) shows the SO^+ and SO^{++} ions, which are distributed throughout the inner and outer oxide grain boundaries. b) shows the CO^+ and CO^{++} ions, which are situated predominantly within the outer section of the oxide scale.

1. Yu, C., J. Zhang, and D.J. Young, *Corrosion Behaviour of Fe - Cr - (Mn, Si) Ferritic Alloys in Wet and Dry CO2 - SO2 Atmospheres at 650 °C.* Oxidation of Metals, 2017.
2. Young, D.J., et al., *Penetration of protective chromia scales by carbon.* Scripta Materialia, 2014. **77**(0): p. 29-32.