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Determination of the oxide scale growth mechanism using $^{18}$O-tracer experiments in combination with Transmission Electron Microscopy and nanoscale Secondary Ion Mass Spectrometry

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A B S T R A C T

Two-stage $^{18}$O/$^{16}$O exposures can be used to investigate the effect that alloying elements, secondary phases, or surface treatments have on the high temperature oxidation behaviour of certain materials. During subsequent exposures to $^{16}$O$_2$- and $^{18}$O$_2$-rich atmospheres, $^{16}$O- and $^{18}$O-rich layers are formed. Analysis of the layers using Secondary Ion Mass Spectrometry (SIMS) depth profiling allows for conclusions to be drawn about the oxide scale growth mechanism. The conclusions are, however, not entirely unambiguous due to the limited lateral resolution of the technology. Rough surface topography and the thickness variation of the oxide scale over the analysed volume add to the ambiguity of the findings. In this study, an Fe-20%Cr alloy was exposed to both $^{18}$O- and $^{16}$O-rich environments at 850 °C. Two methods were used to analyse the thermally grown Cr$_2$O$_3$ scale: (1) traditional SIMS depth profiling and (2) preparation of a cross-sectional lamellae for Transmission Electron Microscopy (TEM), which, subsequently, was analysed in a NanoSIMS. The NanoSIMS $^{18}$O and $^{16}$O elemental maps were then superimposed on the TEM image. In comparison with traditional SIMS depth profiling, the nanoSIMS elemental maps reveal detailed information about local oxide growth in different parts of an oxide scale. Moreover, a clear $^{16}$O/$^{18}$O Interface can be seen in the nanoSIMS maps, which is not the case in the sputter depth profiles. The findings of this study show that the aforementioned issues associated with sputter depth profiling can be eliminated by mapping a cross-section of an oxide scale using high resolution nanoSIMS.

1. Introduction

Two-stage $^{18}$O$_2$/$^{16}$O$_2$ experiments, in combination with analytical methods, such as Secondary Ion Mass Spectrometry (SIMS), have been used for decades in high temperature corrosion studies with the aim to investigate the oxide scale growth mechanism of metals and alloys [1–5] as well as the effect that alloying elements, secondary phases, surface treatments, and coatings have on the growth mechanism of thermally grown oxide scales [5–20]. In a study by Quadakkers et al. [7], the corrosion resistance of both Cr$_2$O$_3$- and Al$_2$O$_3$-forming alloys with yttria oxide dispersions was compared to conventional wrought model alloys with similar compositions. By utilizing the findings of this study show that the aforementioned issues associated with sputter depth profiling can be eliminated by mapping a cross-section of an oxide scale using high resolution nanoSIMS.

scale growth and improved scale adherence for steels with yttria dispersions. Cotell et al. [6,10,11], used $^{16}$O tracer experiments to study the effect ion implantation of yttrium (Y) has on the oxidation of pure chromium (Cr) in the temperature range 900–1025 °C. For the material with the highest dose of ion-implanted Y, Cr$_3^+$ flux was reduced to such an extent that the rate of O$_2^-$ transport was greater than that of Cr$_3^+$, and, consequently, the predominant growth mechanism was changed from outward growth by means of cations to inward growth by means of oxygen ions as an effect of the Y ion implantation. Also Hussey and Graham [12], Papaiacovou et al. [9] as well as Chevalier et al. [13] have shown that coating an Fe-Cr alloy with a reactive element oxide coating can change the oxide scale growth mechanism from predominantly outward cation diffusion to predominantly inward anion diffusion. Thus, clear evidence of a change in the oxide scale growth mechanism has been observed in several studies. However, the findings have sometimes been ambiguous and conclusions somewhat

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speculative. Major sources of errors are the roughness of the oxide scale as well as uneven sputtering that creates a non-flat analysis area in the sputter crater [21]; this is a particular problem for thin oxide scales. A study by Fontana et al. [8] used $^{18}$O tracer experiments to investigate the effect $\text{La}_2\text{O}_3$ and $\text{Y}_2\text{O}_3$ coatings have on the $\text{Fe-22Cr-0.5Mn steel}$ Crofer 22 APU. A significant improvement in oxidation resistance was observed for the reactive element coated materials, however, the $^{18}$O tracer experiments did not indicate a change in growth direction as was observed in other studies [9,10,13,22]. Moreover, Prescott et al. [23] used $^{18}$O tracer experiments to study transport in $\alpha$-$\text{Al}_2\text{O}_3$ scales on $\text{Fe-Al and Ni-Al alloys}$. It was shown that the scale growth process varied in different locations: either predominantly by means of metal outward diffusion or oxygen inward diffusion. Such local variations in the predominant growth direction may be very difficult to observe due to the often too large areas analysed using SIMS sputter depth profiling (lateral resolution often in the micron range or, in the best cases, a few hundreds of nanometres [24,25]). In the case of SNMS analysis, which is recommended for quantitative analysis, the lateral resolution is in the mm range [26]. Also Jedlinski et al. [27] concluded that only analytical methods that have respectable sensitivity and resolution can be used as a source of reliable information on the growth mechanisms of non-uniform, ridged scales. Since the area analysed often is in the micrometre range, it is important that the oxide scale grows homogeneously. In order to form a more homogenous oxide scale, samples used for $^{18}$O tracer experiments did not indicate a change in growth direction as was observed in other studies [9,10,13,22]. Moreover, Prescott et al. 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University of Gothenburg. NanoSIMS images were acquired at 256 × 256 pixel resolution, and the field of views ranged from 8 × 8 μm to 10 × 10 μm. A medium primary ion beam aperture D1 = 3 was used to achieve high spatial resolution images of the oxide interface at approximately 50 nm spatial resolution [33]. ES3 was used to achieve sufficient mass resolving power (MRP) to avoid possible isobaric interferences. The OpenMIMS plugin (Harvard University) was used to process NanoSIMS images.

3. Results

The Cr2O3 scale formed on the model alloy after 168 h at 850 °C is approximately 1–2 μm in the TEM image in Fig. 3. The oxide grain size at the metal-oxide interface is very fine, in contrast to the crystals formed at the surface, which are almost in the μm-range.

In the TOF-SIMS sputter depth profiles in Fig. 4, it can be seen that the oxide scale formed during the second stage (16O) is located at the surface of the Cr2O3 scale. Furthermore, it can be seen that the 16O concentration levels off toward the metal-oxide interface. The oxide scale formed during the first stage (18O) is, in contrast, located at the metal-oxide interface (assuming that the interface is located at the position where the total oxygen signal decreases) and decreases toward the surface of the sample.

Fig. 5 shows the 16O and 18O maps acquired using NanoSIMS on the TEM lamella from the 168 h sample (the same sample as in the TOF-SIMS depth profiles in Fig. 4). It can be seen in the figure that the oxide scale formed during the second exposure stage (16O) is located at the gas-oxide interface, whereas the initial oxide scale formed during the first stage (18O) is located at the metal-oxide interface. The 16O and 18O maps in Fig. 5 also show that local differences in oxide scale growth took place. In some areas, very little increase in oxide scale thickness is observed during the second stage (48–168 h) whereas, in other areas, large 16O-rich grains were formed during the second exposure stage.

The data from the 16O and 18O maps in Fig. 5 can be used to plot line scans through the oxide scale (see Fig. 6). From these line scans, it can be seen that the area where the 16O and the 18O signals overlap is very small (100–300 nm), especially compared to the TOF-SIMS sputter depth profiles in Fig. 4. Furthermore, in Fig. 6 an 16O-gradient can be observed within the 18O-rich oxide layer. Such a gradient is not seen for the isotope 18O within the 16O-rich layer.

Fig. 7 shows the 16O and 18O maps acquired using NanoSIMS on a TEM lamella from the Fe20Cr sample that was exposed for 500 h. Similar to the results for the 168 h sample (Fig. 5) the oxide scale formed during the second exposure stage (16O) is mainly located at the gas-oxide interface whereas the oxide scale formed during the first stage (18O) is located at the metal-oxide interface. Compared to 168 h more
The intensity for $^{18}\text{O}$ (green), $^{16}\text{O}$ (blue), and $^{16}\text{O}$ plus $^{18}\text{O}$ (black) is plotted as a function of sputter time. (For the colour figure the reader is referred to the web version of this article.)

5. Conclusions

In this study, an Fe20Cr model alloy was exposed for a total of 168 and 500 h in a two-stage $^{16}/^{18}\text{O}$ exposure at 850 °C. The thermally grown Cr$_2$O$_3$ scale on the 168 h sample was analysed using two methods: (1) traditional TOF-SIMS depth profiling and (2) $^{16}/^{18}\text{O}$ mapping of a cross section of the thermally grown Cr$_2$O$_3$ scale using high resolution NanoSIMS. Both techniques indicated that the dominant growth mechanism for the oxide layer was by means of chromium outward diffusion. This was very clear in the NanoSIMS maps. The NanoSIMS line scans and maps showed that a smaller part of the oxide scale growth is due to oxygen ion inward diffusion (mixed growth). Furthermore, the NanoSIMS maps also showed that there is strong local variation in oxide scale growth (individual grains grow differently). After 500 h the NanoSIMS map showed clearly that oxygen ions diffuse along grain boundaries toward the metal-oxide interface. The findings in this study show that much more reliable and detailed data can be generated from two-stage $^{16}/^{18}\text{O}$ exposures by mapping a cross section of the sample using high resolution NanoSIMS than by using sputter depth profiles.

Details of the oxygen isotope distribution within the oxide scale can be observed. Grain boundaries observed in the STEM image correlate well with $^{16}\text{O}$-rich areas.

4. Discussion

Both the TOF-SIMS sputter depth profiles and the NanoSIMS maps from the TEM lamellas showed that the oxide scale is rich in $^{16}\text{O}$ at the gas-oxide interface and poor in $^{16}\text{O}$ at the metal-oxide interface. This indicates that the oxide layer, formed during the second stage (48–168 h and 168–500 h respectively), grew predominantly by means of outward cation diffusion. This is in good agreement with the literature where several studies have shown that thermally grown oxide scales formed on Fe-Cr alloys as well as other Cr$_2$O$_3$-forming alloys predominantly grow by outward diffusion of cations at elevated temperature \cite{8,13,14,34}. However, for the hypothetical case of inward lattice diffusion of oxygen ions the TOF-SIMS profiles are expected to look very similar to the one in Fig. 4. This was schematically described by Reddy et al. \cite{35}. In contrast, the NanoSIMS oxygen line scans and maps (Figs. 5 and 6) showed a clear interface between the $^{16}\text{O}$- and the $^{18}\text{O}$-rich oxide layers which clearly contradicts the interpretation of lattice diffusion of oxygen ions. The smeared out $^{16}/^{18}\text{O}$ interface in the TOF SIMS depth profiles (Fig. 4) is due to a thin Cr$_2$O$_3$ scale (1–2 μm thick) and a rather rough surface in combination with large variations in scale thickness (see Fig. 3). With the high lateral resolution of the NanoSIMS this problem is eliminated. The advantage of this method is, however, not only to reduce or eliminate artefacts such as $^{16}\text{O}$/18O overlapping. The results presented in this work also show that additional information regarding the oxide scale growth mechanism can be obtained when TEM data is combined with NanoSIMS $^{16}/^{18}\text{O}$ mapping. This becomes obvious in Fig. 7. The $^{16}\text{O}$ rich layer on the oxide surface provides evidence of oxide growth by metal cation diffusion as discussed above; moreover, areas identified as grain boundaries in the STEM image are enriched in $^{16}\text{O}$. This matches well to an interpretation that undoped Cr$_2$O$_3$ grows by metal cation transport and oxygen inward transport (along grain boundaries). Although this has been speculated earlier, to the authors’ knowledge, this is the first direct experimental evidence of oxygen transport along grain boundaries. Also for the 168 h sample oxygen ion inward diffusion along grain boundaries is believed to be part of the oxide scale growth mechanism. The line scans in Fig. 6 show that $^{16}\text{O}$ had diffused toward the metal-oxide interface forming an $^{16}\text{O}$ gradient within the $^{18}\text{O}$-rich layer. Due to the much shorter diffusion time for the 168 h sample compared to the 500 h sample, the $^{16}\text{O}$ signal within the grain boundaries was most probably not high enough in order to be able to see $^{16}\text{O}$-enrichment at the grain boundaries in the NanoSIMS map. It is predicted that the more detailed information gained by TEM/NanoSIMS will be very valuable in order to gain new insights into the oxidation mechanisms of the studied material.
Fig. 5. $^{16}$O and $^{18}$O nanoSIMS maps of the TEM lamella shown in Fig. 3 that was prepared from the Fe20Cr model alloy exposed for 168 h (48 h in Ar-20% $^{18}$O$_2$ containing 1% H$_2$$^{18}$O + 120 h in Ar-20% $^{16}$O$_2$ containing 1% H$_2$$^{18}$O) at 850 °C.

Fig. 6. NanoSIMS line scans (b, c, and d) at three different areas shown in a) of the Cr$_2$O$_3$ scale formed on the Fe20Cr model alloy exposed for 168 h (48 h in Ar-20% $^{18}$O$_2$ containing 1% H$_2$$^{18}$O + 120 h in Ar-20% $^{16}$O$_2$ containing 1% H$_2$$^{18}$O) at 850 °C.
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