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The effect of yttria coatings on the oxidation behaviour of Fe-25Al and Ni-32Al at 1100 and 1200 °C

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Abstract. — The influence of Y_2O_3 coatings on the oxidation behaviour of Fe-25wt%Al and Ni-32wt%Al has been investigated at 1100 and 1200 °C. Samples were sputter coated with 4 nm of Y_2O_3 and oxidized sequentially in $^{16}O_2$ and $^{18}O_2$. Oxide scales have been characterized using SIMS, XPS, SEM, X-ray and electron diffraction. A comparison is made between the growth of oxide on Y_2O_3 -coated and uncoated alloys. The major effects of the yttria coating at 1100 °C are to delay the formation of $\alpha-Al_2O_3$ and to increase the oxidation rate. At 1200 °C a two-layered scale is formed instead of a single layer; all of the yttrium is contained in a non-adherent outer layer.

1. Introduction.

For many years it has been known that the presence of small quantities of reactive elements such as Y can lead to improvements in the oxidation resistance of high-temperature alloys. Studies on alloys which form protective chromia scales have shown that reactive elements block outward diffusion of cations, causing scale growth to occur chiefly by inward diffusion of oxygen [1-4]. Coatings of reactive element oxides have been found to improve oxidation resistance in materials which form Cr_2O_3 or NiO scales [3]. In alumina-forming systems, the effects of reactive elements are not so clearly understood [4-8]. In this introduction, attention is directed to some of the more recent studies, based on the results of $^{16}O_2/^{18}O_2$ tracer experiments to examine the influence of Y on the growth of alumina scales.

In the absence of reactive elements, alumina scales develop by a combination of outward diffusion of cations and inward grain boundary diffusion of oxygen [9]. Conclusions of studies into the effects of Y are conflicting. In the case of alloys containing Y or Y_2O_3 additions, some authors suggest that their major effect is to block outward cation transport, causing alumina scales to grow predominantly by the inward transport of anions [10-13]. Conversely, other researchers using Y^+ ion implantation have proposed, with one exception [14], that Y can suppress or even eliminate inward diffusion of oxygen [13, 15-18]. In another paper [19], it has been noted that Al transport predominates when transition aluminas are still present, but oxygen diffusion is thought to be favoured when the $\alpha-Al_2O_3$ phase has become established. The aim of this paper is to report on the effects of thin Y_2O_3 coatings on the growth of alumina scales.

2. Experimental.

Two materials have been oxidized in this study, Ni-32wt%Al (β -NiAl) and Fe-25wt%Al (FeAl). Specimens were prepared as described previous [9]. $4(\pm 1)$ nm-thick Y_2O_3 coatings were deposited by reactively sputtering a Y target with oxygen. $^{16}O_2/^{18}O_2$ oxidation experiments were performed at oxygen pressures of 0.65 Pa at 1100 °C and 1330 Pa at 1200 °C. Subsequent SIMS and XPS analysis were carried out in a PHI model 5500 system equipped with a liquid Ga ion source and an Al K_{α} X-ray source. Additional analysis was performed in a JEOL 840A SEM and a Phillips EM 430 TEM. X-ray diffraction was done in a Scintag XDS 2000 unit using copper K_{α} radiation.

3. Results and discussion.

3.1 OXIDATION AT 1100 °C. — Oxygen uptake *versus* time curves for the early stages of oxidation of Fe-25Al and Ni-32Al at 1100 °C are plotted in figure 1. In each case, the Y_2O_3 -coated specimen gains weight more rapidly than the uncoated specimen. The effect is more pronounced for Ni-32Al than for Fe-25Al.

Fig. 1. — Oxidation kinetics at 1100 °C in 0.65 Pa oxygen for Fe-25Al and Ni-32Al with and without 4 nm-thick coatings of Y_2O_3 . ($1 \mu g cm^{-2} \simeq 5 nm Al_2O_3$).

Scanning electron micrographs show that on both coated materials, the oxides are composed of plate-like particles (Figs. 2a, b). In some areas, the scales have spalled to expose the underlying metal which has a terraced appearance (Fig. 2c). Figure 2d is an example of the

oxide morphology on uncoated NiAl after 4 h at 1100 °C. The ridged structure in this case is completely different from the plate-like morphology which is formed as a consequence of the Y_2O_3 coating. In the absence of Y_2O_3 coatings, oxidation of these two materials under such conditions results in the formation of $\alpha-Al_2O_3$ scales [20]. Transmission electron diffraction has been carried out, using stripped fragments of scale, and the oxide formed on Y_2O_3 -coated Ni-32Al has been identified as $\gamma-Al_2O_3$.

Fig. 2. — SEM micrographs of Fe-25Al and Ni-32Al after oxidation at 1100 °C in 0.65 Pa oxygen. a) Fe-25Al coated with 4 nm Y_2O_3 after 2 h oxidation; b) and c) Ni-32Al coated with 4 nm Y_2O_3 after 4 h oxidation; d) uncoated Ni-32Al after 4 h oxidation.

The coated specimens have been analyzed by SIMS and depth profiles for positive species are presented in figure 3. In each case, the gas was changed from $^{16}O_2$ to $^{18}O_2$ at the mid-point of the experiment. Both materials give rise to SIMS profiles which exhibit similar features. Firstly, the outermost portion of the scale, close to the gas-scale interface, is rich in ^{18}O . In figure 3a the oxygen concentrations tail off gradually due to the roughness of the oxide (Fig. 2a). Secondly, the maximum Y^+ signal is detected in the vicinity of the broad substrate-scale interface. The most likely explanation of these results is related to the effects of Y on the conversion of transition alumina to $\alpha-Al_2O_3$, since Y is reported to delay the transformation process [19,21].

Transition aluminas are reported to have high defect densities [22] and to grow by cation diffusion [21]. They often exhibit whisker types of morphology [23]. Oxide morphologies (Figs. 2a, b) and diffraction data confirm that such phases are indeed formed at 1100 °C and SIMS profiles, with high ^{18}O levels in the outer portions of the scales, are not inconsistent with the assumption that such scales have grown by cation diffusion. The sputtered layer of Y_2O_3 has remained at the original interface and may be thought of as an inert marker in these short experiments. Previous experiments on uncoated specimens [20] have revealed that Ni-32Al develops a ridged structure of $\alpha-Al_2O_3$ which grows mainly by outward diffusion of Al whereas oxide on Fe-25Al grows by a mechanism involving outward transport of Al and inward, short circuit diffusion of oxygen.

Fig. 3. — Positive SIMS profiles obtained from Fe-25Al and Ni-32Al coated with 4 nm Y_2O_3 after oxidation at 1100 °C in 0.65 Pa oxygen. a) Fe-25Al oxidized for 1 h in $^{16}O_2$ followed by 1 h in $^{18}O_2$; b) Ni-32Al oxidized for 2 h in $^{16}O_2$ followed by 2 h in $^{18}O_2$. Sputtering was by 25 keV gallium ions.

3.2 OXIDATION AT 1200 °C. — Morphologies of oxides formed on Ni-32Al after 24 h and Fe-25Al after 12 h oxidation are presented in figure 4. Both oxides have been identified as $\alpha-Al_2O_3$ by electron and X-ray diffraction. The scale on Y_2O_3 -coated Ni-32Al consists of two layers of oxide. The outer layer is composed of flakes and is non-adherent and fragmented (Fig. 4a). The inner layer has not spalled as badly as the outer layer, although there are some areas where the metallic substrate is exposed (Fig. 4b). The morphology of the inner layer is very similar to that of oxide formed on uncoated Ni-32Al under the same conditions (Fig. 4c). In such scales, the ridge structure has almost fully coalesced and there is no evidence of cracking or spalling.

A two-layered oxide is also formed on Y_2O_3 -coated Fe-25Al. The outer scale is extremely convoluted (Fig. 4d) and has detached completely, the inner scale is also badly spalled revealing the substrate (Fig. 4e). Oxides on this material are typically less adherent than those on Ni-32Al; the oxide on uncoated Fe-25Al also spalls and is similar in morphology to the inner oxide layer. The presence of a few needles and whiskers of Al_2O_3 is noted on both the inner and outer layers (Fig. 4d). On both alloys, the metallic substrate is exposed in places where both layers of oxide have become detached. Its morphology is marked by angular impressions where oxide grains have been in contact, and by large voids with smooth sides and bases. Such features have been observed for uncoated Fe-25Al (Fig. 4f), so they cannot be attributed to the presence of Y_2O_3 ; however, as such voids are present beneath transition alumina at 1100 °C it is possible that the Y_2O_3 coating accelerates their formation, perhaps by promoting cation transport before transformation to $\alpha-Al_2O_3$.

Since differences in oxide morphologies are observed for both Ni-32Al and Fe-25Al, such

Fig. 4. — SEM micrographs of Ni-32Al and Fe-25Al after oxidation at 1200 °C in 1330 Pa oxygen. a) and b) Ni-32Al coated with 4 nm Y_2O_3 after 24 h oxidation; c) uncoated Ni-32Al after 24 h oxidation; d) and e) Fe-25Al coated with 4 nm Y_2O_3 after 12 h oxidation; f) uncoated Fe-25Al after 12 h oxidation.

changes must result from application of the Y_2O_3 coating. Alloyed Y or dispersed Y_2O_3 is reported to affect scale microstructures, although it is more usual for scales to become columnar grained and less convoluted [24-26].

SIMS images indicate how $\alpha\text{-Al}_2\text{O}_3$ scales develop on coated and uncoated materials. Images from oxidized Ni-32Al are shown in figure 5. The $^{18}\text{O}^-$ image (Fig. 5a) of a tapered cross-section of the uncoated side shows that new oxide is formed in the outer portion of the scale and also in the grain boundaries all through the scale and at the metal-scale interface. On the Y_2O_3 -coated side, the inner and outer layers of oxide are very clearly distinguishable in the SIMS maps from a tapered section. The fragmented outer oxide is rich in ^{16}O (Fig. 5b), low in ^{18}O (Fig. 5c), and all the detectable Y is incorporated in this layer (Fig. 5d). The inner oxide is ^{18}O -rich (Fig. 5c) and resembles the image obtained from the uncoated side (Fig. 5a) as expected from observations of scale morphologies. ^{18}O -rich inner layers seem to grow mainly where the outer ^{16}O -rich layer has cracked or spalled. In places where the outer layer remains intact, such as the left hand side of figures 5e, f, g, the inner layer contains a greater proportion of ^{16}O (Fig. 5e). As seen in figures 5d,g, Y is located mainly at the outer and inner surfaces of the outer oxide layer. Figure 5h is a Y^+ map of the surface in plan view. The top right hand corner represents an area of inner oxide; the remaining area represents the outer oxide. It can be seen that the Y is contained in the outer oxide layer and that it has coalesced into small particles less than 100 nm in size.

Fig. 5. — Series of SIMS images for Ni-32Al oxidized at 1200 °C, first in $^{16}\text{O}_2$ for 12 h and then in $^{18}\text{O}_2$ for 12 h: a) $^{18}\text{O}^-$ image from a $4\times$ tapered cross-section of the uncoated material; b), c) and d) $^{16}\text{O}^-$, $^{18}\text{O}^-$ and Y^+ images, respectively, from a $2.5\times$ tapered cross-section of the 4 nm Y_2O_3 coated material; e), f) and g) $^{16}\text{O}^-$, $^{18}\text{O}^-$, and Y^+ images, respectively, from another area of the tapered section of 4 nm Y_2O_3 coated material; h) Y^+ image of the outer surface of the 4 nm Y_2O_3 coated material. In all images, regions rich in the particular element or isotope appear white.

The nature of the Y-containing oxides on both Ni-32Al and Fe-25Al is uncertain. XPS analysis of the top surface of the outer oxide layer on Fe-25Al confirmed the presence of Y at a level $\sim 1\text{at}\%$, and the Y peak position showed it to exist in oxidized form. Other workers have identified mixed oxide particles such as YAlO_3 and $\text{Y}_3\text{Al}_5\text{O}_{12}$ in Al_2O_3 scales [25-27]

and some researchers [28] believe that Y-containing, oxygen conducting oxides are formed on alumina grain boundaries. Another possibility is merely that Y-containing oxide is still present as Y_2O_3 and that the thin uniform sputtered layer has been broken up and formed small islands by surface diffusion to minimize surface energy and contain essentially all the Y_2O_3 in the original 4 nm layer. Surface coatings are often broken up and incorporated in developing scale providing there is a component of outward scale growth [3].

It is pertinent to note, however, that Quadackers *et al.* [29] have reported that ion implantation of Y has an adverse effect on the oxidation behaviour of alumina-forming Fe-20Cr-5Al. This material performs better when it contains additions of metallic Y or Y_2O_3 dispersion [28]. Similarly, Jedlinski [30] has found that implanted Y is only effective up to a point where the stresses generated in scale growth cause cracking of the alumina and permit inward transport of oxygen. Work with Cr and Cr-based alloys [31] has shown that 4 nm-thick CeO_2 sputter coatings are effective in blocking cation transport in Cr_2O_3 , but we have recently found that coatings much thicker than this are not beneficial to the oxidation resistance of Al_2O_3 -forming alloys.

4. Summary.

Thin sputtered coatings are ineffective in improving the oxidation resistance of Ni-32Al and Fe-25Al. They delay the transformation to $\alpha-Al_2O_3$ and fail to reduce oxidation rate or to improve scale adherence. In the case of Al_2O_3 -forming materials, it appears that Y_2O_3 coatings, or Y implants, do not confer the same beneficial effects of Y alloying or Y_2O_3 dispersions. If Y limits cation diffusion in Al_2O_3 scales, then a layer of Y-free oxide will form beneath the outer, Y-containing layer. The growth of this inner oxide proceeds, much as it would on a Y-free alloy as there is no reservoir of Y below the outer oxide. Consequently the Y can only affect the early stages of oxidation and can offer no protection if the scale should crack or spall.

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