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The effect of reactive element coatings on the oxidation behaviour of pure Cr and high Cr-content alloys at 900 °C

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Abstract. — The influence of various reactive element (RE) oxide coatings (Y_2O_3 , CeO_2 , La_2O_3 , CaO and HfO_2) on the oxidation behaviour of pure Cr, Fe26Cr and Ni25Cr at 900 °C in oxygen at 5×10^{-3} torr has been investigated using the ^{18}O /SIMS technique. Polished samples were reactively sputter-coated with 4 nm of the RE oxide and subsequently oxidized sequentially in $^{16}O_2$ and then in $^{18}O_2$. The effectiveness of each RE on the extent of oxidation rate reduction varied with the element used. SIMS sputter profiles showed that the maximum in the RE profile moved away from the alloy-oxide interface during the early stages of oxidation and after a certain time remained within the oxide scale, its final relative position being dependent on the particular RE. The position of the RE maximum within the oxide layer also varied with the substrate composition. For all coatings ^{18}O was found to have diffused through the oxide to the alloy-oxide interface during oxidation the amount of oxide at this interface increasing with increasing time. The SIMS data confirm that for coated substrates there has been a change in oxide growth mechanism to predominantly anion diffusion.

1. Introduction.

Chromia scales that form on pure Cr or on high-Cr content Fe-Cr or Ni-Cr alloys at elevated temperatures grow relatively slowly and usually provide good corrosion resistance. Adding a small amount of a reactive element (RE), such as Ce or Y, either in the form of alloying additions or by ion implantation or as surface coatings of their oxides, can greatly improve their oxidation resistance [1, 2]. This so-called "RE effect" also augments oxide scale adherence, decreases the amount of Cr in the alloy needed to produce a protective layer of Cr_2O_3 [3] and causes a change in the transport mechanism for oxide growth from predominantly cation to predominantly anion diffusion. These RE effects have been reviewed extensively by Whittle and Stringer [2] and more recently by Moon and Bennett [4] and Stringer [5]. Techniques such as ion implantation [6-8] and surface coating of RE oxides [9, 10] have also received much attention recently. In the present work very thin (4 ± 1 nm thick) oxide coatings of CeO_2 , Y_2O_3 , La_2O_3 , CaO or HfO_2 were reactively sputtered directly on to pure Cr, Fe26Cr or Ni25Cr substrates. The ^{18}O /SIMS technique [11-13] was employed to study the effect of such coatings on the transport properties in the oxide and to identify the oxide growth mechanism.

2. Experimental.

The Cr, Fe26Cr and Ni25Cr samples⁽¹⁾ (approximately 2.5 cm²) were prepared as described previously [12]. The samples were subsequently coated with the RE oxide to produce coatings equivalent to 4 ± 1 nm thickness [11] and were oxidized at 900 °C sequentially first in ¹⁶O₂ and then in ¹⁸O₂ at 5×10^{-3} torr pressure. The SIMS analyses were performed on oxidized samples as described previously [11, 12]. The results are presented as atomic concentration *versus* sputter time. The data were corrected for mass interferences and elemental sensitivities [12].

3. Results.

3.1 KINETICS. — A comparison of the oxidation kinetics for both uncoated and coated pure Cr and the corresponding Fe26Cr and Ni25Cr alloys shows that the extent of oxidation for the coated samples is much less than that for the uncoated samples. In the case of pure Cr and Fe26Cr the kinetics for both uncoated and coated samples agree with a parabolic rate relation with a brief short term deviation; the instantaneous parabolic rate constant for the former is greater by a factor of about 100. The extent of oxidation for the various coated Cr samples is similar, the degree of effectiveness for each element decreases in the order Ce>Y>Ca>La>Hf. The spread in oxidation extent for coated Fe26Cr is greater than that for pure Cr and the degree of effectiveness for the various RE coatings is somewhat different decreasing in the order Y>Ce>La>Hf. While for uncoated Ni25Cr parabolic behaviour is exhibited from very short times the initial deviation is quite pronounced for coated samples. The spread between the instantaneous parabolic rate constants for the uncoated *versus* the coated Ni25Cr is much less than that for pure Cr or Fe26Cr being about 15× for the alloy coated with CeO₂ and about 25× for that coated with Y₂O₃.

3.2 SIMS DATA – PURE CR. — For oxidized uncoated material the sputter profiles show that there is a discrete ¹⁸O-oxide layer on top of a ¹⁶O-layer. For samples coated with CeO₂ the position of the Ce maximum lies within the oxide scale (Fig. 1). At very short times the Ce maximum is about one quarter of the total oxide thickness from the metal-oxide interface; at longer times this changes to about two thirds of the total oxide thickness and the relative position of the maximum remains constant with time. The features of the sputter profiles obtained for the samples coated with Y₂O₃ are similar to those observed for ceria-coated samples (Fig. 2). There is a significant ¹⁸O-rich Ce and Y species, whose maximum coincides with that of the corresponding ¹⁶O species. The ¹⁸O is distributed mainly in the vicinity of the gas-oxide and metal-oxide interfaces. In the case of the lanthana- and calcia-coated samples the long term position of the RE maximum is somewhat less than halfway out in the scale from the metal-oxide interface. The Ca maximum is, however, much broader than that of the La and the Ca is distributed more uniformly throughout the scale. The sputter profiles for the hafnia-coated samples show the Hf maximum position has now dropped to about one third of the total oxide thickness from the metal-oxide interface. The ¹⁸O distribution is similar to that for the lanthana-coated samples except that there appears to be a distinct ¹⁸O-oxide layer on top of the ¹⁶O-oxide layer.

⁽¹⁾ The impurities >10 p.p.m. by weight for each material is as follows: pure Cr – O 14, Fe 14; Fe26Cr – O 42, Ni 22, W 11; Ni25Cr – C 20, Fe 31, W 100.

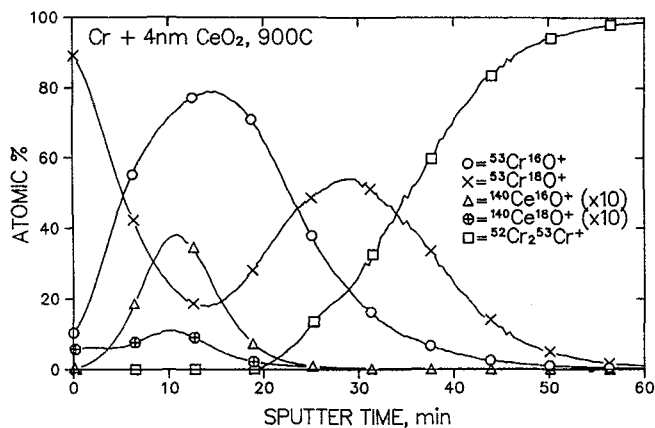


Fig. 1. — SIMS composition-depth profiles for an oxide scale formed on pure Cr coated with 4 nm CeO₂ at 900 °C in ¹⁶O₂ and then in ¹⁸O₂; oxide thicknesses were 102 and 165 nm respectively.

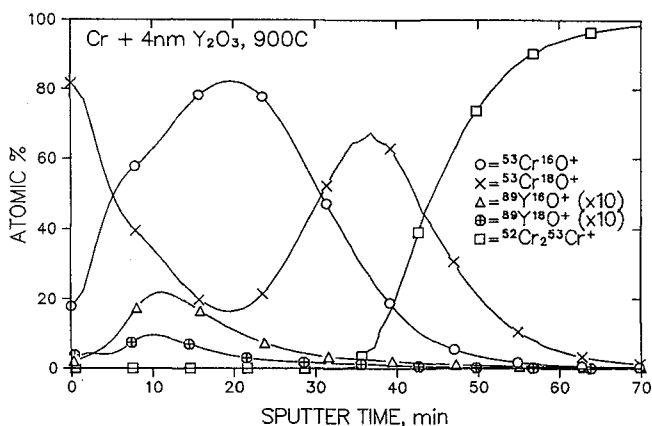


Fig. 2. — SIMS composition-depth profiles for an oxide scale formed on pure Cr coated with 4 nm Y₂O₃ at 900 °C in ¹⁶O₂ and then in ¹⁸O₂; oxide thicknesses were 104 and 178 nm respectively.

3.3 SIMS DATA – FE26CR. — As for pure Cr the SIMS sputter profiles for oxidized uncoated Fe26Cr show the presence of a distinct ¹⁸O-oxide layer on top of a ¹⁶O-oxide layer. For yttria-coated samples the Y maximum is similarly located within the oxide layer (Fig. 3) and it moves outward with time to a constant position from the alloy-oxide interface. The maxima of the significant ¹⁸O-rich Y species also coincides with the corresponding ¹⁶O-rich phase at a given time. The ¹⁸O distribution in the oxide layer is, however, different than that for coated pure Cr in that there is also a distinct maximum in the region of the Y maximum. The same comments can be applied to the SIMS results for ceria-, lanthana- and hafnia-coated substrates except that the Hf maximum is closer to the alloy-oxide interface than that of the Y.

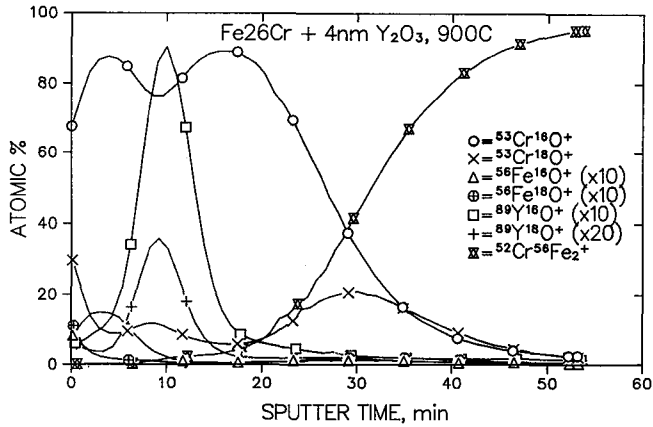


Fig. 3. — SIMS composition-depth profiles for an oxide scale formed on Fe26Cr coated with 4 nm Y₂O₃ at 900 °C in ¹⁶O₂ and then in ¹⁸O₂; oxide thicknesses were 109 and 43 nm respectively.

3.4 SIMS DATA – Ni25Cr. — The oxide scale on uncoated Ni25Cr consists of a layer of ¹⁸O-oxide on top of a layer of ¹⁶O-oxide. In the case of Ni25Cr coated with either CeO₂ (Fig. 4) or Y₂O₃ the Ce and Y maxima lie within the scale being at about 60% of the total oxide thickness from the alloy-oxide interface in both instances. The position of the maximum does not appear to change at longer times. Once again there is a considerable component of ¹⁸O-rich Ce or Y species in the oxide layer. The ¹⁸O distribution for the ceria-coated samples show maxima in the vicinity of the gas-oxide and alloy-oxide interfaces and in the region of the Ce maximum as observed for coated Fe26Cr samples. For the yttria-coated samples, however, there is no apparent ¹⁸O maximum associated with the Y maximum.

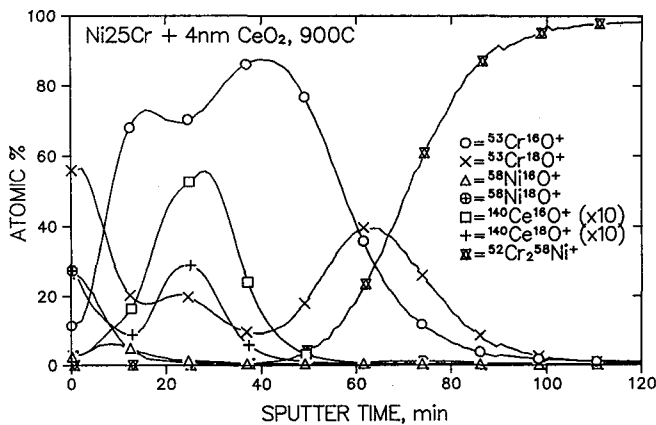


Fig. 4. — SIMS composition-depth profiles for an oxide scale formed on Ni25Cr coated with 4 nm CeO₂ at 900 °C in ¹⁶O₂ and then in ¹⁸O₂; oxide thicknesses were 250 and 151 nm respectively.

4. Discussion.

The oxidation behaviour of pure Cr and of the alloys Fe26Cr and Ni25Cr coated with various RE oxides and oxidized at 900 °C has shown that such coatings are effective in significantly reducing the extent of oxidation of the base material. These results are in agreement with other data [9, 10, 14], which have demonstrated that RE additions can radically reduce oxidation rates in high Cr-containing alloys. In the present instance the level of RE required is relatively low (4 nm), which is equivalent to 1×10^{16} atoms cm^{-2} . Such a level is much less than that afforded by other coating techniques such as the sol-gel or nitrate-converted oxide methods, but similar to that produced during ion implantation.

The SIMS results for uncoated samples show that cation diffusion has been predominant. Similar results were obtained when the coating thickness was insufficient [11]; in such cases the RE was concentrated at the alloy-oxide interface. The RE has acted as a marker confirming predominant cation diffusion as the operative oxidation mechanism. A coating level of 4 nm on pure Cr, Fe26Cr and Ni25Cr substrates is sufficient to cause a change in oxidation mechanism from cation predominant to anion predominant diffusion as demonstrated by the position of the RE within the scale. The effectiveness of the different RE species varies. In general Ce and Y are the most effective under the present experimental conditions, providing the lowest oxidation rate and being concentrated in the scale closest to the gas-oxide interface. This agrees with previous work [15, 16] on the oxidation of Cr implanted with a dose of 2×10^{16} atoms Y cm^{-2} .

The SIMS results for all coated samples show that inward ^{18}O diffusion through the ^{16}O -layer has occurred during oxidation as shown by the appearance of ^{18}O -containing species at the substrate-oxide interface. For coated pure Cr the amount of oxide formed at the metal-oxide interface is greater, implying a greater predominance for anion diffusion in this case. This again provides support for a change in oxidation mechanism as indicated by the position of the RE within the oxide layer. A further feature shown in the profiles is the significant ^{18}O -rich RE species coincident with the corresponding maximum for the ^{16}O -rich species. This suggests that in passing through the scale some of the ^{18}O has exchanged with the ^{16}O in the RE.

In the case of both Fe26Cr and Ni25Cr there is also a maximum in the $^{53}\text{Cr}^{18}\text{O}^+$ profiles in the same region indicating that there has been some ^{18}O -oxide formation probably along oxide grain boundaries. This does not, however, always appear to be the case for pure Cr. There is a definite indication of a small maximum for the yttria-coated (Fig. 2) and for one of the lanthana-coated specimens. It is believed that the amount of oxide formed in grain boundaries in the vicinity of the RE maximum is less for oxides formed on pure Cr and its appearance in the SIMS profiles is masked in some instances by the much larger ^{18}O maxima at the gas-oxide and metal-oxide interfaces.

While the SIMS data indicate that the RE resides in a discrete zone within the oxide scale for pure Cr, Fe26Cr and Ni25Cr they do not indicate its precise location or distribution. Comparison with the results of other work on the structure and location of Y within scales on Cr implanted with Y [15, 16] suggests that the RE is located at oxide grain boundaries, perhaps as discrete particles and as ions [14]. Segregation of Y to oxide grain boundaries has also been observed in Cr_2O_3 formed on Y-implanted stainless steel [6]. TEM/EDX, EELS and diffraction carried out on thin oxide formed on a ceria-coated Fe26Cr sample shows that the Ce segregates to form CeCrO_3 particles within the scale [17]. Ce segregation at grain boundaries has also been demonstrated for chromia formed on Ce-implanted Ni30Cr; the Ce-rich phase is believed to be CeCrO_3 [8]. Electron Spectroscopic Imaging (ESI) of the thin oxide formed on lanthana-coated Fe26Cr at short times also demonstrates the segregation

of La to regions of high disorder such as oxide grain boundaries [18]. It is concluded that the grain boundary diffusion of Cr cations is retarded by this RE segregation such that the mobility of oxygen anions exceeds that of the cations. The degree of RE effectiveness may be a function of the ease with which a binary phase of the form (RE) CrO₃ could be formed. The reason that Ce, Y and La are the most effective REs may be because they can form such binary oxides more readily. Ca and Hf would be expected to form such phases with difficulty.

5. Conclusions.

A significant reduction in the extent of oxidation of pure Cr, Fe₂₆Cr and Ni₂₅Cr at 900 °C has been achieved by applying 4 nm-thick coatings of CeO₂, Y₂O₃, La₂O₃, CaO and HfO₂ to the substrate surface prior to oxidation. ¹⁸O/SIMS analysis of sputtered oxide scales show that a RE maximum occurs within the scale and that ¹⁸O diffusion has taken place. These results suggest that a change in oxidation mechanism has occurred from predominantly cation to predominantly anion diffusion. The extent to which each RE is effective varies, yttria- and ceria-coatings providing the greatest reduction in oxidation rate in all cases. It is believed that the RE concentrates at oxide grain boundaries, both as a binary oxide of the form (RE) CrO₃ and in ionic form. Cr cation diffusion is impeded, while oxygen diffusion is allowed to continue.

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