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# The effect of rare-earth impurities on the oxidation resistance of chromium*

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A systematic study has been made of the effects of Group III and rare-earth impurities on the thermal oxidation of chromium. The elements were introduced by ion-implantation to depths of about 30 nm with doses in the range $5 \times 10^{14}$ to $5 \times 10^{16}$ ions $cm^{-2}$. A number of the samples were annealed after implantation, to eliminate effects arising from radiation damage, and were subsequently oxidized for 30 min in dry oxygen at 750 °C. Impurity distributions were determined both before and after oxidation by means of Rutherford back-scattering of $\alpha$ particles, to correlate oxidation effects with the migration of impurities. Comparison of the oxygen uptake for the variously implanted samples was made by using deuteron bombardment and the $^{16}O$ (d, p) $^{17}O$ and $^{16}O$ (d, p) $^{17}O^*$ nuclear reactions. Impurity analysis was carried out also by using a Cameca ion microprobe analyser. Initial studies designed to eliminate the effects of radiation damage, involving the implantation of $Cr^+$ ions over a range of doses and energies, indicated that annealing at 750 °C was necessary to overcome the effects of bombardment-induced damage.

For unannealed chromium samples the oxidation rate was found to be reduced (by 60–90%) by all of the implanted species. For annealed samples all rare-earth implants produced approximately 60% reduction in oxidation while lead and tin caused small increases. Ion microprobe analysis of samples implanted with $Pr^+$, $Ho^+$ and $Ce^+$ indicated that the $Ho^+$ and $Ce^+$ ions had to some extent diffused away from their initial implant sites and that this resulted in a smaller effect on the oxidation rate compared with the relatively immobile Pr which caused a 93% reduction in oxidation. The possible existence of a diffusion barrier associated with a perovskite oxide structure ($ABO_3$) was not supported by X-ray diffraction measurements which did, however, indicate two unidentified peaks. These peaks may be associated with the formation of some other binary oxide.

Scanning electron microscope studies of $Ca^+$ and $Dy^+$ implanted samples indicated that the implanted oxide is smoother and more uniform than on the unimplanted chromium. It was also found to be very hard and adherent and was difficult to abrade away with 14 μm diamond paste.

These results suggest a number of possibilities: (1) a mixed oxide compound may be present, possibly a spinel or modified perovskite, blocking the migration paths for $Cr^+$ ions; (2) rare earth atoms or oxide precipitates may act as sinks for vacancies created by $Cr^+$ out-diffusion; (3) the rate of vacancy formation and oxygen in-diffusion may be controlling factors (there is some evidence for this from the depth distributions of the implanted layers, oxygen moving through without altering the profiles); (4) the presence of a rare earth in the oxide or at the metal–oxide interface may alter the plasticity or grain size and thus relieve stress in the oxide, or it may improve the ductility of the metal.

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