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SPECIFIC CONTRIBUTIONS OF SIMS AND XPS TO STUDIES OF THERMAL OXIDE FILMS

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Résumé - Le SIMS donne des informations spécifiques sur la diffusion d'un tra- ceur dans un film d'oxyde en cours de croissance et sur la distribution d'im- puretés en faibles concentrations dans le film. L'état de valence de ces do- pants peut être déterminé par XPS, permettant ainsi d'expliquer leur influence sur les processus de diffusion.

Abstract - SIMS give specific informations on the diffusion of a tracer in growing oxide films and the depth distribution of impurities in low concentra- tions in the films. The valency of these dopants can be determined by XPS, thus permitting to explain their influence on diffusion processes.

The oxidation resistance of metallic alloys is determined by the growth kinetics of the oxide film and its adherence. These macroscopic properties are easily charac- terized by thermogravimetry and mechanical tests. But diffusion kinetics deduced from thermogravimetry data differ sensibly from the prediction of models, even in the case of pure single phased oxide films. The classical theory proposed for the growth of such films is based on the diffusion of atoms under the control of unidirectional stoichiometry gradients from the outer surface to the oxide-substrate interface, with diffusion coefficients measured in pure oxides at equilibrium. It does not take into account the complex structure of growing oxide films, resulting from interfacial stresses (interface with the substrate and between oxide grains): lattice deforma- tions changing the activation energy of diffusion, anisotropic crystallisation, dis- location networks, intergranular voids and cracks, all constituting short path for diffusion.

Thus analytical technics such as Secondary Ion Mass Spectrometry or Nuclear Reaction Analysis, permitting to determine diffusion profiles of marked isotropes in thin la- yers, are very useful to study the diffusion processes in thermal oxide films.

On the other hand, metallic materials always contain impurities and deliberate addi- tions, which dissolve or precipitate in the oxide film and drastically modify all its structural, mechanical and physicochemical properties. It is thus important for the optimisation of the composition of heat-resisting alloys, to characterize:
- the depth distribution of impurities in the film. The SIMS technique is perfectly suited for this purpose, because of its high sensibility,
- their eventual segregation along grain boundaries or their precipitation. The STEM is the most performant technique in this field, but ionic microscopy can also provide interesting results, avoiding the problem of making thin a film without changing its structure,
- the valence state of these foreign atoms and their influence on the electronic structure of the host lattice, which determines the concentration of point defects in the crystal and their mobility. X ray Photoelectron Spectroscopy give partial but easily accessible informations concerning this topic. However there are very few data on the insertion sites and valence states of dopants in oxides ; for instance, no data are available for important impurities such as C, S, Si.
Examples were chosen to illustrate the complementarity of specific informations obtained by SIMS and XPS.

More detailed data on the oxidation mechanism of the studied materials are given elsewhere (1 to 4). The used machines were a CAMECA SMI 300 microscope (5) and a LEYBOLD ELS 10 equipment (6). Particular conditions of experiments are given in figure captions.

I - DIFFUSION PROCESSES IN PURE NiO, Cr2O3 FILMS

The experimental procedure used in our experiments with $^{18}$O involved oxidizing the samples successively 24 h in natural oxygen, then 24 h in an atmosphere enriched with 25% $^{18}$O and finally 60 h in natural oxygen again, in order to obtain films of comparable thicknesses during the three cycles. Other cycling sequences based on the parabolic law of oxide growth might have been used. When the oxygen diffusion is negligible, the $^{18}$O profile would have a square wave form (curve A of figure 1), slightly distorted by the rugosity of interfaces (curve B). The importance of oxygen diffusion may be deduced from the unsymmetry of profiles and from the $^{18}$O/($^{16}$O+$^{18}$O) ratio in the enriched layer.

In the case of NiO film (curve D), the apparent width of interfaces on profiles (corresponding to a decrease from 90% to 10% of the $^{18}$O or $^{16}$O emissions) corresponds exactly to their average rugosities measured by talystep. The relative thicknesses of oxide formed during the three successive cycles are in good agreement with thermogravimetry data (1). The symmetry of the profile and the $^{18}$O/($^{16}$O+$^{18}$O) ratio in the enriched layer indicate that cationic diffusion is largely preponderant in the bulk of the oxide. A second maximum of $^{18}$O is often observed at the metal-oxide interface (curve C) for samples oxidized at low temperatures (600°C-800°C). It was attributed to a diffusion of the tracer in short circuits, thus permitting to explain that the diffusion kinetics have a low activation energy in this range of temperature (1).
In the case of pure chromia films developed on a 63Ni/37Cr alloy (curve E), evidence of the diffusion of the tracer can be detected on the profiles. However the diffusion of cations is more important than that of oxygen.

II - INFLUENCE OF IMPURITIES ON THE OXIDATION OF Ni

Si, Al, S, C, alkalines and alkaline earths are traditional impurities of Ni grades; they may also be introduced at the surface during polishing or thermal treatments.

We observed for instance that the oxidation kinetics of pure Ni (containing less than 50 ppm impurities in the bulk) varies of a factor 3 according to the polishing mode of the surface. This fact was connected with the important modifications of the surface rugosity, of the film crystallisation according to the strains in the Ni surfaces and of impurities introduced in the film (MORVAN J., PIVIN J.C., ROQUES-CARMES C., submitted for publication in Acta. Met.).

SIMS profiles of figure 2 show for example that various amounts of Si, Al, K enter in the oxide film according to the polishing mode. In all cases these elements tend to precipitate near the metal-oxide interface. For surfaces annealed or polished electrolytically (unstrained surfaces) the growth kinetics of the film is very heterogeneous on different grains of the substrate: the variations in the thickness of the film (and in its color) are connected with variations of a factor 10 in the Si, Al, K concentrations.

Fig. 2 - SIMS profiles of the depth distribution of some impurities in NiO films formed during an oxidation of 15 mn at 900°C in pure O₂ on Ni samples previously annealed at 1200°C in vacuum, or annealed then polished with 1 μm diamond paste. The profiles were recorded with a 5.5 kev Ar⁺ bombardment under residual vacuum; the analysed area (60 μm in diameter) was smaller than a grain of the substrate.
Experiments on Ni surfaces selectively implanted with S, C, Si (1) have shown that S, Si tend to reduce the oxidation kinetics, while surfaces implanted with C oxidise faster. Neither the $^{18}_{\text{O}}$ diffusion nor the oxide film structure are affected by these implanted impurities (1). Internal stresses in the oxide are sensibly modified by S, Si and less affected by C (2).

The valence of these impurities was determined by X.P.S. on NiO films doped with 0.5% to 2% of C, S or Si on a thickness of a few tens nm by ion implantation (Table 1 and Fig. 3). The comparison of spectra recorded a) on as implanted surfaces, b) on sputtered ones, c) after annealing at 500°C in UHV, d) after exposition to oxygen of sputtered surfaces, have shown that the results concerning the valence of the dopants are not affected by the defects induced by ion irradiation (such as the partial reduction of NiO during sputtering (7).

The results indicate that C, S, Si atoms are inserted in the lattice on Ni sites or interstitial sites as $c^{2+}$, $s^{2+}$ and $s^{4+}$ respectively. In all cases this would account for the formation of additional Ni vacancies, accelerating the Ni diffusion in the film. The correlation with the modification of the oxidation kinetics is correct for C, but the effect of S, Si on the electric equilibrium of the crystal must be minor. The modification of the tensor of internal stresses has an opposite and stronger effect.

III - INFLUENCE OF AN Y ADDITION ON THE OXIDATION OF Ni-Cr ALLOYS

Y is added in most heat-resistant alloys developing chromia or alumina films, in order to reduce the growth kinetics of these films and promote their adherence. We could demonstrate with SIMS and ionic microscopy that these beneficial effects are due to the dissolution of a few 100 ppm Y in the film, rather than to a mechanical keying of the film by internal particles of $Y_2O_3$ (3, 4). On the contrary protruding pegs of $Y_2O_3$ formed in alloys containing too large concentrations of Y promote the spalling of the film (4).

It was supposed that Y atoms are inserted in the lattice on Cr sites as $y^{3+}$. They would associate one or several Cr vacancies in order to suppress the distorsion of the lattice induced by their large size (35% over that of $Cr^{3+}$ ions). SIMS profiles of $^{18}_{\text{O}}$ in the films and XPS study of the electronic structure of the oxide doped with 5% Y give some confirmations of these hypothesis :

- the diffusion of oxygen is preponderant in $Cr_2O_3$ doped with Y contrarily to pure $Cr_2O_3$ (see Fig. 1 and 4). The diffusion fluxes of Cr and O become comparable and $^{18}_{\text{O}}$ is distributed throughout the film,
- the valence of Y is $3^+$ (see Table 1),
- the core levels of O, Cr atoms are not modified, but a shoulder is observed on the O2s peak towards higher binding energies (Fig. 5) indicating that O atoms are more highly bond. Note also that the peak of uncoupled d electrons decreases because the amount of $Cr^{3+}$ ions with a (3d)$^3$ configuration decreases, while the amount of $Y^{3+}$ ions with a (4d)$^0$ (5s)$^0$ configuration increases (Fig. 5).

The suppression of the oxidation kinetics seems to be only due to a decrease of the Cr diffusion ; the O diffusion becomes preponderant despite the stronger bonds exchanged by these atoms with Y neighbours.
TABLE 1

<table>
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<tr>
<th>SAMPLE</th>
<th>O1s*</th>
<th>Cr 2p 3/2</th>
<th>Ni 2p 3/2</th>
<th>DOPANT LEVEL</th>
<th>DOPANT ENERGY</th>
<th>BONDS</th>
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<td>NiO + 10^{16} C 100 kev</td>
<td>530.1</td>
<td>854.7</td>
<td>285.0</td>
<td>Ni-O</td>
<td>C-C</td>
<td>Cr-O</td>
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<tr>
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<td>854.3</td>
<td>153.3</td>
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<tr>
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<td>854.3</td>
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<td>Ni-O, Y_{2-0}</td>
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</tr>
<tr>
<td>Pure NiO</td>
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<td>Ni-O</td>
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<td>576.9</td>
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<td>Pure Cr_{2}O_{3}</td>
<td>530.7</td>
<td>576.8</td>
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<td></td>
<td>Cr_{2}O_{3}</td>
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</table>

* Slight shifts of binding energies (0.1 to 0.6 eV) due to charges accumulations were corrected by referencing all energies to the known O1s levels in NiO, Cr_{2}O_{3}.

Fig. 3 - Part of the XPS spectrum recorded on NiO implanted with 10^{16} C/cm^2 of E = 100 keV, after removal of 80 nm by sputtering with Ar^+ ions. Conditions of XPS analysis were: Mg Ka radiation, constant pass energy of 50 eV, recording time of 1000 s.

Fig. 4 - SIMS profile of the depth distribution of an ^{16}O tracer in the Cr_{2}O_{3} film formed at 800°C on 63Ni/37Cr doped with 9.10^{15} Y/cm^2 of 100 keV. The Y concentration in the film is about 300 ppm (3).
Fig. 5 - Part of the XPS spectrum recorded on Cr$_2$O$_3$ doped with $10^{16}$ Y/cm$^2$ of $E = 100$ keV, after sputtering 30 nm. The conditions of analysis are the same as for Fig. 3. The differences in the intensities of O$_2$s peaks (at 22 eV), O$_2$p peak (at 5.3 eV) is due to a difference in the analysed areas. Their slight shift of 0.1 eV is due to a difference in charge accumulation. The peak at 2.2 eV is relative to uncoupled Cr3d electrons.

REFERENCES