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Oxygen and sulphur influence upon segregation at a nickel-chromium alloy surface (*)

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Résumé. — On a étudié par spectroscopie Auger les phénomènes de ségrégation apparaissant lors de l'oxydation et du recuit sous vide de la face (111) d'un alliage Ni-30 % Cr. Les résultats obtenus avec une surface propre et une surface recouverte de soufre indiquent un enrichissement en chrome oxydé lorsque la température permet la mobilité des atomes. Cette ségrégation est plus marquée en présence de soufre.

Abstract. — Segregation phenomena induced by oxygen on a (111) face of a nickel-chromium alloy (30 % Cr) during oxidation and following vacuum annealing have been studied by Auger Spectroscopy. Both with a clean and a sulphur-covered surface, the results show a chromium enrichment provided the temperature allows sufficient mobility of surface atoms. Sulphur enhances this segregation.

In order to investigate the mechanisms of protective scale formation during oxidation, segregation phenomena induced by oxygen on a (111) face of a Ni-30 % Cr single crystal and their relation to the binding energies of oxygen with the various constituents have been studied by Auger Spectroscopy.

The measurements were carried out with a CMA spectrometer in a vacuum of about 10^{-9} torr on two kinds of surfaces : the first one cleaned by argon ion bombardment followed by flash heating up to 800 °C, the second one covered with sulphur segregated from the volume by a 15 min. anneal at 700 °C. In both cases, the samples were progressively exposed to oxygen up to 350 Langmuirs at room temperature and at 400 °C, and then vacuum annealed for 2 min. at increasing temperatures. After each treatment, intensities, shapes and chemical shifts of the Auger peaks were used to monitor the evolution of surface bonds. Furthermore, surface (≈ 6 Å) and volume (≈ 20 Å) could be distinguished by using the low- and high-energy peaks taking into account the escape depth of these electrons.

In order to show the segregation of metal atoms, we have drawn (Fig. 1) the ratio of the peak heights corresponding to the chromium $L_3M_{2,3}M_{2,3}$ (489 eV) and the nickel L_3VV (848 eV) transitions. Thus, we can follow the relative concentration of the components at the alloy surface during the different treatments.

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Fig. 1. — Evolution of the chromium to nickel peak height ratio during oxidation at room temperature (a) and at 400 °C (b) followed by vacuum annealing of a clean (1) and a sulphur-covered (2) NiCr surface.

On figure 1, both during oxidation and vacuum annealing, the different curves indicate surface enrichment in the element with the greatest affinity to oxygen, i.e. chromium. This result is in agreement with several studies concerning oxidation of metal alloys [1-3].

Enrichment is possible if metal atoms have sufficient mobility. At room temperature, the low mobility of surface atoms explains the slight enrichment observed, involving only two or three top atomic layers (Fig. 1a). At 400 °C, the mobility of atoms is enhanced leading to the extension of segregation to the volume (Fig. 1b).

The evolution of the surface chemical bonds has been characterized by the chemical shift of chromium (36 eV) and of oxygen peaks, by the appearance of a peak at 46.4 eV when three-dimensional chromium oxide nucleation occurs [4] and by the change in shape of the nickel (61 eV) peak.

During room temperature oxidation of the clean sample, oxygen is chemisorbed on the metal atoms near the surface (Cr : 36.0 eV $\rightarrow$ 34.3 eV ; O : 515.5 eV). During annealing, nickel is reduced by chromium at 400 °C : this is in agreement with previous results obtained by ESCA [3]. Simultaneously, the available oxygen allows chromium segregation and three-dimensional oxide formation (Cr : 33.7 eV and peak appearance at 46.4 eV ; O : 513.5 eV). At 550 °C, the segre-

gation phenomenon diminishes with the beginning of the oxide dissociation ; at 700 °C chromium is totally reduced (Cr : 36.0 eV) and oxygen is no longer detected at the surface.

During oxidation at 400 °C, nickel and chromium oxides are formed over a larger depth enhancing the stability of the system (Cr : 36.0 eV $\rightarrow$ 33.2 eV and 46.4 eV ; O : 513.0 eV). The reduction and dissociation phenomena are then retarded during the anneals : at 700 °C, chromium is not yet totally reduced and oxygen is still present in the analysed volume although in a smaller amount.

On the other hand, figure 1 suggests a more pronounced segregation process at the sulphur-covered surface. This phenomenon is particularly marked in the case of oxidation at 400 °C (Fig. 1, curve 2). Figures 2 and 3 represent under these conditions the chromium (489 eV), nickel (848 eV), oxygen and sulphur peak heights evolution for the two types of surfaces.

One can notice that during the oxidation of the sulphur-covered surface (Fig. 3), the oxygen peak height increases quickly in the same time as nickel and sulphur peak heights diminish. Furthermore, the energy position of the chromium and oxygen peaks indicate a strong chromium oxidation at the surface (Cr : 36.0 eV $\rightarrow$ 33.0 eV and enhanced peak at 46.4 eV ; O : 512.5 eV).

The comparison of the sulphur amounts coming up to the clean and to the sulphur-covered surfaces during the vacuum annealing (Figs. 2 and 3), suggests that sulphur remained at the alloy oxide interface during oxidation. While oxygen interaction with a sulphur-covered nickel surface results in a SO₂ desorption [5], the oxidation of a sulphur-covered chromium surface is controlled by sulphur remaining at the metal-oxide interface [6]. Thus, in spite of the larger nickel concentration in the bulk alloy, the same behaviour as for sulphur-covered chromium could be expected since the topmost layers are highly enriched in chromium [7]. Therefore, chromium migrates toward the surface during oxidation giving rise to an oxide layer while sulphur remains at the

Fig. 2. — Evolution of Auger peak heights during oxidation at 400 °C followed by vacuum annealing of a clean NiCr surface.

Fig. 3. — Evolution of Auger peak heights during oxidation at 400 °C followed by vacuum annealing of a sulphur-covered NiCr surface.

alloy-oxide interface. This layer thickness can be calculated from the sulphur signal attenuation and is found to be $\approx 12 \text{ \AA}$ thick for a 300 Langmuirs oxygen exposure.

Room temperature oxidation of the sulphur-covered surface results in nickel and sulphur signal attenuation, together with oxygen signal increase and chromium oxide layer formation (Cr : 36.0 eV $\rightarrow$ 33.5 eV and peak at 46.4 eV ; O : 513.0 eV). The calculated layer thickness is here about 5 $\text{\AA}$.

In conclusion, our work shows an oxygen-sulphur antagonism whose effect is to maintain the sulphur at the alloy-oxide interface during oxidation. Sulphur acts there like a barrier reducing oxygen diffusion towards the volume and therefore favouring chromium oxide formation. In addition, during the vacuum anneals, the maximum of segregation and the onset of oxygen removal take place at lower temperatures for the sulphur-covered than for the clean surfaces. This could indicate that the presence of sulphur favours the chromium oxide dissociation.

Similar behaviour of sulphur has been reported by other authors for oxidation of Ni-Fe [8] and Fe-Cr-Ni [9] alloy surfaces : sulphur is pushed away from the surface during oxidation and favours oxygen removal during the vacuum annealing.

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