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STRUCTURE OF METAL-OXIDE INTERFACES

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Résumé - Ce travail présente quelques résultats relatifs à la structure des interfaces Ni/NiO et Ti/TiO2 formées lors de l'oxydation thermique des deux métaux étudiés. Ces deux systèmes métal-oxyde ont été choisis car ils correspondent aux deux principaux modes de croissance des couches d'oxyde contrôlés soit par la diffusion cationique (Ni/NiO) soit par la diffusion anionique (Ti/TiO2).

Abstract - This work presents some results on the structure of Ni/NiO and Ti/TiO2 interfaces formed by thermal growth of an oxide scale. These two metal-oxide systems were chosen because they correspond to the main mechanisms of oxide growth controlled by cationic diffusion (Ni/NiO) or anionic diffusion (Ti/TiO2).

The detailed study of the metal-oxyde interfaces is of some importance to a better understanding of growth mechanisms of oxide scale during oxidation of metals or alloys and factors affecting oxide scale integrity. The aim of this work is to present some results concerning the Ni/NiO and Ti/TiO2 interfaces. These two systems were chosen because they correspond to the two main diffusion mechanisms involved in oxide scale growth /1,2/: - outward cationic diffusion for Ni/NiO system - inward anionic diffusion for Ti/TiO2 system

I - EXPERIMENTAL PROCEDURES

Specimens 10 x 5 x 1 mm were cut from high purity polycrystalline Ni or Ti sheets; a stable equilaxed microstructure with a nearly uniform grain size of 200 μm for Ni specimens and 100 μm for Ti specimens was obtained by high temperature annealing at 1050°C (Ni specimens) or 875°C (Ti specimens) for 24 hours followed by a slow furnace cooling. "In situ" TEM oxidation of Ni or Ti thin foils was studied between 450°C and 850°C at pO2 = 10^-2 Pa for a duration up to 2 hours. Thick specimens were oxidized at temperatures between 750°C and 950°C at pO2 = 2.5 10^4 Pa for a duration between 2 hours and 50 hours.

Prior to oxidation runs, the specimens were mechanically polished up to 1000 grade SiC paper; all Ti specimens were chemically polished in HNO3-HF; in the case of Ni, mechanically polished and electrolytically polished specimens were used. Two different kinds of TEM observations were performed on oxidized specimens: i/ Examination of microstructure of oxide scale. ii/ Examination of metal and oxide scale structure and metal-oxide interface from thin foils prepared
by the transverse sectioning method so that the mean interface plane is parallel to the electron beam /3,4/. Ion-beam thinning was performed with 6-keV Ar ions, a specimen current of about 80 μA and an incidence between 15° et 10°; thinned parts of about 30 μm may be observed and revealed the microstructure of the complete oxide scale and subjacent metal. TEM examinations were carried out by using Philips EM 300 G or Jeol JEM 200 CX microscopes.

II - "IN SITU" TEM OXIDATION

From "in situ" TEM oxidation, nucleation and growth of the oxide were studied and metal-oxide mutual orientations determined as a function of temperature and test time. During the first stages of oxidation, numerous different metal-oxide mutual orientations were observed for both Ni and Ti specimens. But, as the oxidation time increases some of these mutual orientations become predominant and are always observed independently of test temperature or duration. These predominant mutual orientations are reported in Table I for Ni/NiO and Table II for Ti/TiO₂; as it will be discussed later, these orientations always correspond to those expected from calculations based on Bollmann's model of crystalline interfaces /5-7/.

** Table I - Predominant Ni/NiO mutual orientation relationship **

<table>
<thead>
<tr>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td>N.1</td>
<td>001</td>
<td>100</td>
<td>001</td>
<td>100</td>
</tr>
<tr>
<td>N.2</td>
<td>110</td>
<td>111</td>
<td>110</td>
<td>111</td>
</tr>
<tr>
<td>N.3</td>
<td>001</td>
<td>110</td>
<td>111</td>
<td>111</td>
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<tr>
<td><strong>N.4</strong></td>
<td>110</td>
<td>111</td>
<td>101</td>
<td>111</td>
</tr>
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</table>

** Antiparallel orientation to N.1 **

** Table II - Predominant Ti/TiO₂ mutual orientation relationships **

<table>
<thead>
<tr>
<th>Relation</th>
<th>(hkl) Ti</th>
<th>[uvw] Ti</th>
<th>(hkl) TiO₂</th>
<th>[uvw] TiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>T.1</td>
<td>001</td>
<td>110</td>
<td>100</td>
<td>010</td>
</tr>
<tr>
<td>T.2</td>
<td>110</td>
<td>111</td>
<td>001</td>
<td>110</td>
</tr>
</tbody>
</table>

* The relationship must be read : (hkl) [uvw] _Me_ / (hkl) [uvw] _OX_

The relationships T.1 and T.2 are very close together, the relationship T.2 may be deduced from T.1 by a TiO₂ lattice rotation of 2.49° around 001 TiO₂. In addition, Fig. 1 shows that in the case of Ti/TiO₂ system a fine (101) twinning of TiO₂ nucleus is observed when the test temperature is higher than 700°C.
Fig. 1 - Twinned TiO$_2$ nucleus formed after 10 min oxidation at 750°C.

III - OXIDE SCALE AND SUBJACENT METAL MICROSTRUCTURE

The examination of detached thin oxide film, both parallel and transverse sections made a detailed characterization of oxide scale and subjacent metal microstructure possible, particularly, transverse sections appears to be very useful for such a study. Surprisingly, transverse sections reveal that the microstructure of NiO and TiO$_2$ scales are very similar. A typical scale microstructure developed on Ni oxidized at 750°C for 24 hours is shown in Figure 2. This figure reveals a duplex microstructure made of an external subscale of columnar oxide grain normal to the metal-oxide interface and an internal subscale with an equiaxed microstructure. Large intergranular porosity may be observed within the external subscale; on the contrary, internal subscale always appears to be compact with a very fine grain size.

Fig. 2 - Transverse section through NiO scale formed after oxidation at 750°C for 24 hours.

Similar features are observed on TiO$_2$/Ti transverse section. However, as for the oxide nucleus, an intense twinning of TiO$_2$ grains are gene-
rally observed. The occurrence of this twinning is particularly evident from Figure 3 showing a parallel section of TiO₂ scale formed on Ti substrate oxidized at 750°C for 50 hours.

Fig. 3 - Parallel section of TiO₂ scale developed on Ti substrate oxidized at 750°C for 50 hours.

These examination reveal also an intense dislocation activity in the oxide and the metal directly adjacent to the metal-oxide interface (figures 4 a-b).

![Image of dislocations](image)

0.1 μm (a) 0.2 μm (b)

Fig. 4 - a/ Dislocation in NiO grain at the Ni/NiO interface b/ Dislocation in Ti substrate adjacent to the Ti/TiO₂ interface.

IV - METAL-OXIDE INTERFACE

The observation of metal-oxide interface is generally difficult the grain size of oxide directly adjacent to the metal substrate being very small; the grain size of TiO₂ internal subscale does not exceed
0.1 m and in the case of NiO internal subscale, the grains size is very dependant of surface preparation and temperature. Only Ni specimens oxidized at 950°C with a NiO grain size of about 0.8 m at the Ni/NiO interface made some observations of the interface (figures 5a,b) possible. In this case, the interface is irregular and all the NiO grains show an important curvature turned towards the Ni substrate. This curvature may be attributed to the interfacial tension, however preferential intergranular diffusion on interfacial reaction may also lead to the formation of a curved interface; for the larger NiO grain a faceted interface is generally observed (Fig. 5 a).

![Image](a)

![Image](b)

**Fig. 5 -** Ni specimens oxidized at 950°C for 24 hours
a/ Faceted NiO grain - NiO dark field
b/ Intrinsic dislocations located at the Ni/NiO interface

Only some observations show a near periodic distribution of interfacial defects (Fig. 5b), which are believed to be secondary interface dislocations but unfortunate attempts to determine the Burgers vectors of these defects were unsuccessful. Moreover, diffraction from the interface and observation of Moire fringes confirm that there is an epitaxial relationship between Ni and adjacent NiO grains; the most commonly observed relationship corresponds to the parallel orientation (relation N.1 of Table II), relations N.3 and N4 were also found, but for several grains the Ni/NiO mutual orientation is complex and does not correspond to coincidence between crystallographic directions of high atomic density. In such cases, it may be assumed that non crystallographic factors such that stresses associated to oxide growth can affect the metal-oxide mutual orientation; this can explain the high dislocation activity near the interface.

V - DISCUSSION

The studies and experimental observations on metal-oxide interfaces are in very limited number /3,8-11/ and the transverse sectioning methods were only applied to Ni specimens oxidized at 1000°C /8-9/. The present work shows the complexity of the microstructure of oxide scales developed during the oxidation of Ni and Ti at temperatures lower than 1000°C. However the observation of strong epitaxial relationship between Ni and NiO and the occurrence of TiO2 twinning
allows us to assume that a first approach of these interface may be done by using the geometrical model of crystalline interface initially developed by Bollmann /5/. The calculations were made with the aid of a general computer program adapted to the studied systems which are characterized by a large misfit between the metal and oxide lattices. For the Ni/NiO interface, these calculations show that the more stable orientation is the parallel one (relation N.1. Table I); this orientation corresponds to the smallest value of $\Sigma_2$ det $(I - A^{-1})$

where $A$ is the linear homogeneous transformation relating Ni and NiO lattices. Thus, this mutual Ni/NiO corresponds to the greater size of "O" lattice which is a f.c.c. lattice with a lattice parameter of about 22.5 Å; this very small value explains the difficulty to observe secondary dislocations lying at the Ni/NiO interface. Indeed, the other relationships lead to smaller "O" cells or to smaller Burgers Vectors so that the observations of intrinsic dislocations must be more difficult.

For Ti/TiO$_2$ interface, the calculation shows that the observed predominant relationships do not correspond to special orientations; according to Bonnet /7/, the sign of the main deformations indicates that no minimum of $\Sigma_2$ det $(I - A^{-1})$ can be found for the Ti/TiO$_2$ system. However, if the twinning of TiO$_2$ is introduced in the calculation, a special orientation corresponding to three negative main deformation may be found. This is in good agreement with our experimental observations and those of Flower and Swann /12/ who observed TiO$_2$ twinning by "in-situ" HVEM oxidation of Ti thin foils in an environmental cell.

In addition, it should be noticed that the observations of oxide scale microstructure and subjacent metallic substrate lead to a better understanding of oxide scale growth. This is particularly obvious from the similarity of microstructure of NiO and TiO$_2$ which enable us to believe that the diffusion processes through the oxide scale is much more complex than generally assumed. This study also shows that the O - lattice model may be applied to complex system such as metal-oxide with large lattice misfit.

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