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TEM INVESTIGATION OF METAL/MgO INTERFACES PRODUCED BY PRECIPITATION

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Abstract. MgO precipitates have been produced by internal oxidation of Ag-Mg, Cu-Mg and Pd-Mg alloys, respectively. Intragranular oxide particles exhibit throughout the cube-on-cube orientation relationship with respect to the metal matrix grain, and they are faceted predominantly parallel to (111) planes. Intergranular particles do not show a particular orientation relationship. The development of [111] facets during precipitate growth is attributed to the low energy of these interfaces.

1 - INTRODUCTION

Metal/ceramic interfaces determine to a large extent physical processes such as oxidation and corrosion of metals and metallic alloys, and they play a dominant role in many important technological applications. In such diverse areas as in electronic packaging, catalyst supports, protective coatings and structural metal-ceramic composites, the adhesion of metals with ceramics is a crucial point and 'interfacial engineering' is required.

However, except for systematics of wetting (see e.g. /1/), fundamental experimental data on metal/ceramic interfaces is still poor. The most simple question to ask is: what are the interfaces possessing the lowest energy in a particular metal/non-metal system? This question is even more relevant than in grain boundary research, as an interface between two stable phases may represent an equilibrium configuration with minimum energy whereas a grain boundary is never in thermodynamic equilibrium.

Similar to grain boundaries /2/, an unrelaxed planar interface can be fully described by nine geometrical parameters where $R$ (3 parameters) denotes the relative orientation between the lattices, $F$ (3 parameters) describes the rigid body translation and $g$ (3 variables) characterizes the interface orientation. Epitaxial studies as well as rotating-sphere-on-plate experiments /3,4/ are not the appropriate techniques to obtain the right answer to the above question as the normal $g$ of the substrate or plate surface is pre-selected. Also, in the so called facetting experiments, the relative orientation $R$ is fixed and the facets developed mostly represent local minima of the interfacial energy as a function of $g$. The precipitation of a second phase where precipitates have the freedom to form with minimum outer constraints seems to be the most suitable method in obtaining interfaces in or close to the thermodynamic equilibrium.

In order to produce low-energy metal/oxide interfaces, internal oxidation /5/ of a metallic alloy A-B can be applied principally to those systems where the matrix component A possesses a lower oxygen affinity than B and external oxidation of the alloy can be avoided by choosing suitable conditions. Of course, oxygen must be soluble in the alloy to a small extent. Electron microscope studies of interfaces between Al$_2$O$_3$ precipitates and Nb /6/ and interfaces between CdO particles and Ag /7/ have demonstrated that intragranular oxide particles precipitated within a matrix grain in general have a well defined orientation relationship with respect to the matrix and exhibit facets which are atomically flat. Such interfaces are ideal objects for studies using high resolution transmission electron microscopy (HRTEM) and different authors /8,9/ have investigated other internally oxidized systems preferentially using this technique.

It was realized by the authors in refs. /7,8,9/ that the oxides CdO, Al$_2$O$_3$ and NiO having a cubic crystal symmetry exhibit a cube-on-cube orientation relationship (all crystallographic planes and directions are parallel) with respect to the metal matrix. A twin-related orientation was also found for Al$_2$O$_3$ and NiO precipitates /8,9/. Surprisingly, facetting of the metal/oxide interfaces did not occur on the {100} or {110} planes as it is known for
free surfaces of CdO and NiO. Facetting of the oxide particles was observed predominantly to be parallel to the polar (111) planes. Additionally, it has been demonstrated by HRTEM studies /7/, that the terminating plane of the CdO precipitates consists of an oxygen layer, i.e. that the oxide particle is non-stoichiometric and that it would carry a net surface charge if the oxygen ions are in their normal charge state.

It is known that NiO and CdO have a considerable stoichiometry range associated with vacancies or interstials. This may be the reason for compensating e.g. charge effects. Therefore, in the present work MgO has been chosen to form precipitates in the noble metals Ag, Pd, and Cu by internal oxidation. The lattice misfit \( \delta = (a_1 - a_2)/(a_1 + a_2) \) varies in these systems to -2.7%, -7.9% and -15.3% for Ag-MgO, Pd-MgO and Cu-MgO, respectively (\( a_1 \) and \( a_2 \): lattice parameters of metal and of MgO). The orientation of the MgO crystals relative to the metal matrix and the crystallography of faceting has been investigated using conventional electron microscopy and electron diffraction. The formation of the observed interfaces is discussed with respect to kinetic and energetic arguments. Finally, problems concerning charging and non-stoichiometry of an oxide crystal inside a metal are also discussed.

2 - EXPERIMENTAL

High purity (5N material) Ag, Cu and Pd were each alloyed with 1 at% Mg and homogenized. Sheet material (1mm thick) of the Ag-Mg alloy was oxidized at 1173K in flowing Ar with 1 Vol% O\(_2\) which resulted in somewhat larger MgO precipitates than oxidation in air. Sheet material of Cu-Mg was internally oxidized by packing in a mixture of Cu\(_2\)O and Cu powders (Rhines pack /10/), sealing the pack in an evacuated quartz tube, and heating at 1273K. The Pd-Mg alloy was rolled down to 0.1mm and oxidized at 1273K in air. An oxidation time of 7d has been chosen for all the alloys. TEM specimens were prepared by grinding, dimpling and ion thinning using standard techniques. TEM studies were performed using a JEM 200CX transmission electron microscope, operated at 200kV and equipped with a side-entry goniometer allowing large (\( \pm 45^\circ \)) tilt angles of the specimen relative to the optical axis.

3 - RESULTS

Ag-MgO

A bright field image of intragranular MgO precipitates in Ag is shown in Fig. 1. The precipitates have a mean diameter of 10nm and do not exhibit clear facets, i.e. they are of spherical shape. However, using the reduced oxygen partial pressure, the precipitates are already larger than those produced by oxidation in air for a much longer time /11/. The size distribution of intergranular precipitates ranges from 20nm to 100nm, but they usually have no well-defined orientation relationship with respect to either of the adjacent Ag grains.

![Fig. 1: Bright field image of nearly spherically shaped MgO precipitates inside a Ag grain.](image-url)
However, in some rare cases larger intragranular particles could be observed close to Ag grain boundaries as shown in Fig. 2. Because the lattice parameters of Ag (a=0.4086nm) and MgO (a=0.4212nm) are very similar, the separation of Ag and MgO spots in the diffraction pattern could hardly be observed. However, the Moiré fringes from the (220) reflections whose normal aligns with the direction of the (220)Ag reflection (c.f. Fig. 2) indicate a cube-on-cube orientation relationship with respect to the Ag grain on the right. The four facets of the precipitate in the center which are imaged edge-on are clearly facets parallel to \( \{111\}_\text{Ag} \) and \( \{111\}_\text{MgO} \), respectively (c.f. corresponding diffraction pattern). Therefore, MgO precipitates larger than 30nm in diameter exhibit an octahedral shape where all eight facets are parallel to \( \{111\} \) planes.

Fig. 2: MgO precipitates at a grain boundary in Ag (a). The Ag grain on the right is oriented close to the [110] zone axis so that the (220) lattice planes are in the Bragg position as indicated by the diffraction pattern (b). The (220) Moiré contrast in the image of two precipitates close to the grain boundary indicates a cube-on-cube orientation relationship.

Cu-MgO

The size of MgO precipitates in Cu ranges from 50nm to 1\( \mu \)m, nearly independently on the nucleation site (intergranular or intragranular). The largest particles have been observed in the centre of the 1mm thick sample where the oxidation proceeds not so fast than in near-surface regions. Facetting of the precipitates has been observed throughout. MgO precipitates lying 50nm beneath the surface of the sample are shown in Fig. 3. The direction of the incident electron beam is parallel to the [110] zone axis of Cu and MgO, respectively and the cube-on-cube orientation relationship between matrix and precipitates is demonstrated by the corresponding diffraction pattern. Facetting is predominantly parallel to the \( \{111\} \) planes, small facets parallel to \( \{100\} \) can be observed preferentially at the smallest particles. Facets parallel to \( \{110\} \) have not been observed; the \( \{111\} \) facets lying edge-on in images with [110] incidence form a sharp edge with an angle of 109.5° (cf. Fig. 3). In accordance with the Ag-MgO system, the MgO precipitates in Cu are also octahedrally shaped.

The coarsening of MgO precipitates proceeds in an interesting way. Practically all larger (diameter > 100nm) particles possess an octahedral outer shape but with an inner core of Cu where all facets are bound by \( \{111\} \) planes. This phenomenon is illustrated in Fig. 4.
Fig. 3: TEM micrograph in [110] direction of the Cu matrix (a). The (111) and (111) facets of the MgO precipitates are imaged edge-on whereas the other (111) facets are inclined and produce a Moiré contrast. The diffraction pattern (b) indicates a cube-on-cube orientation relationship.

Fig. 4: Typical shape of coarse MgO particles in Cu. The facets are parallel to the \{111\} lattice planes, but the particle has been grown so that a Cu core is remaining.

**Pd-MgO**

The size of intragranular MgO precipitates in the centre of the Pd foil ranges from 30nm to 150nm. The very regular shape of these particles can be seen in the bright field image in Fig. 5a. Again, as in the other systems investigated the there exists a cube-on-cube orientation relationship between matrix and precipitate (cf. Fig. 5b) and facetting is observed only parallel to \{111\} lattice planes. Thus the MgO particles have a shape of an octahedron which is very regular.

*Intergranular* precipitates have a diameter up to 500nm and in general they are polycrystalline as it can be seen from Fig. 6. Facetting of these particles can be observed on a small scale where the facet length scales with the size of the MgO micrograins of the precipitate. Because of these small dimensions the orientation of these facets could not have been determined yet.
The cube-on-cube orientation relationship between MgO precipitates and the fcc metals found in the present study was expected because it was also observed in earlier investigations of the internally oxidized systems Ag-MgO \(^{12}\), Ag-CdO \(^{7}\) and Pd-NiO \(^{9}\) where the oxides have the rock salt structure. Since the oxides are very stable and a reorientation of the growing precipitate can be excluded, the orientation relationship must be fixed when the stable nucleus is formed. The cube-on-cube orientation is also observed throughout in numerous investigations on epitactic systems of fcc metallic films on fcc substrates and it is also the densest populated orientation detected by sphere-on-plate experiments \(^{3,4}\) on fcc systems. Thus, independently on nucleation mechanisms and on the lattice misfit this simple orientation relationship must lead to an exceptional low-energy configuration in fcc systems.

The precipitate facetting is known as having been developed during growth. In the case of high temperature oxidation, i.e. close to the melting temperature of the metal, the matrix constraint is considered to be small as discussed elsewhere \(^{13}\). Therefore, the shape of oxide precipitates should not be determined by the elastic strain.
energy. This is certainly different for metal precipitates produced by internal reduction of mixed oxides (for example /14/) where the matrix constraint may be a dominant factor influencing the precipitate morphology. The shape of oxide precipitates in metals must thus be controlled by the two remaining factors: (i) the energy, which is minimized by the development of large facets having the lowest interfacial energy in the system and (ii) the kinetics of particle growth which leads to facets which grow fastest parallel to the interface plane. In principle, interfaces of minimum energy will be developed after a very long annealing time, but the oxidation time used in the present study may be not long enough to justify this argument. However, the growth kinetics themselves may give a strong support for the development of low-energy interfaces. This has been discussed earlier with respect to the facetting of Al₂O₃ precipitates in Nb and CdO particles in Ag, respectively /13/. Therefore, it is concluded that the lowest energy configuration of fcc metal/fcc oxide interfaces produced under the conditions used in the present study is realized when the relative orientation is n = <111>.

Results on the Ag-MgO system /7/ as well as hydrogen trapping experiments in Pd-MeO systems /15/ (Me: Al, Zr) strongly suggest that the MgO crystallites are also bound by (111) planes consisting of oxygen. The oxide crystal will have no residual dipole moment, but it would be non-stoichiometric and charged if the oxygen ions are in their normal charge state /16/. Both, the non-stoichiometry and the charge could be avoided if (i) the crystal contained a compensating concentration of Mg interstitials or O vacancies /16/, or (ii) if the outermost oxygen layer is only partly occupied. Sharp (111) facets were observed at very small MgO octahedrons with an edge length of 35nm, and it is calculated that this corresponds to an oxide composition of 49.4at% Mg and 50.6at% O which can not be compensated by point defects in pure MgO. On the other hand, an approximately 50% coverage of the terminating (111) oxygen layer where the interface would be composed out of equal parts of Mg and O, would not be in agreement with the different trapping behavior of hydrogen at metal/oxide interfaces in an environment of oxygen-excess and metal-excess, respectively /15/. This result can only be explained by a practically complete coverage of either oxygen or metal ions. Therefore, we conclude that the MgO crystallites are indeed non-stoichiometric which is, however, only ascribed to their surface composition and which is in close similarity to the situation of a free crystal surface with an adsorbed O layer in an oxygen-excess environment.

The oxide crystals are composed out of initially neutral Mg atoms dissolved in the metal matrix and out of O atoms diffusing from the sample surface. The oxygen-excess, responsible for the terminating O layer may give rise to a surface charge. However, this charge could be diminished or removed if the oxygen ions at the interface carried less ionic charge than the O²⁻ ions of the usual ionic model. An electron transfer essentially from the terminating oxide plane to the metal has indeed been observed in ab initio electronic structure calculations for a Ag/MgO interface parallel to the (100) plane /17/; the charge transfer amounts to 0.1e⁻ per Mg-O pair in the usually neutral (100) plane. It can be speculated that the charge transfer may be much larger for a polar metal/oxide interface. An answer to this question can only be given by using an ab initio approach to the problem of bonding at polar metal/oxide interfaces similar to the calculations performed by Blöchl et al. /17/. Finally, it is noted that even a charged crystal can be stabilized within a metal when both crystals come into close proximity as shown by Finnis et al. /16/.

REFERENCES

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