EVIDENCE OF OXYGEN SEGREGATION AT Ag/MgO INTERFACES

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Abstract—The distribution and microstructure of MgO precipitates formed by internal oxidation of Ag/3 at.% Mg alloys have been investigated by high voltage (HVEM) and high resolution electron microscopy (HREM). The chemical composition of their phase boundaries was studied at an atomic level by electron energy loss (EELS) fine structure analyses especially at the ionization edges (ELNES). In specimens annealed in vacuum ($T = 1163$ K, total pressure about 10^{-3} Pa), oxygen occurs at the interface only, bound as MgO. However, if the samples are annealed in oxygen ($T = 673$ K, partial pressure 10^5 Pa), the spatially resolved fine structure of the energy loss O–K edge reveals an additional interface bonding part, representing an Ag₂O-like bonding state. Thus, with high oxygen activities, the interface layer between magnesia and silver consists of oxygen atoms bound partly as MgO and as Ag₂O. This segregation of excess oxygen at the Ag/MgO interfaces fits into the framework of a general structural model, which should be applicable to many metal/oxide phase boundaries. © 2000 Acta Metallurgica Inc. Published by Elsevier Science Ltd. All rights reserved.

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1. INTRODUCTION

Metal/ceramic phase boundaries are of great importance for many applications in materials science [1, 2], for instance, to thin solid films, coatings, electronic packaging, supported catalysts, and fibre-reinforced metal–matrix composites. In many dispersion-hardened materials, metal/oxide interfaces are involved in the strengthening mechanisms [3]. They are also included in microminiature electronic devices (MOS applications as, e.g. MOSFETs). Therefore, investigations into the bonding mechanisms and nanochemistry of metal/ceramic interfaces have been intensified in recent years (e.g. Refs [4–7]).

For reasons of energy, defects at interphase boundaries promote segregation of impurity atoms, which are dissolved in the bulk. Detailed knowledge of this effect is of great importance, as the solute atoms can influence the characteristics of the material [8] as observed, for instance, in the interfacial accumulation of Ag at MgO/Cu {222}, and of Sb/Zn at Ag/Mn₃O₄ [9, 10]. Furthermore, the segre-

gation of oxygen modifies the chemical composition of metal/oxide interfaces as a function of the activity of oxygen. For some systems it was shown that after internal oxidation at high oxygen partial pressures the terminal layers of the oxide lattice are close-packed oxygen planes [11–16]. On the other hand, at low oxygen activities only partly occupied oxygen layers terminate the ceramic component [13]. The system Cu/MgO, preferentially used for such investigations [5, 6, 9, 14–23], reveals that the composition of the final polar (111) magnesia plane varies from partial to full oxygen occupancy with increasing oxygen activity. Interfacial copper, however, changes its bonding state from metallic to oxidic (Cu₂O) simultaneously [7, 24]. This result is in agreement with investigations of the systems Cu/Al₂O₃ and Ag/MgO and of other oxides with palladium as the metallic component [25–29].

To investigate metal/oxide interphase boundaries, spatially resolved EDX [30], surface spectroscopy [31], high resolution electron microscopy (HREM) [5, 11–13, 21, 23, 32–34], and field-ion microscopy with atom-probe (FIP-AP) [9, 14, 15, 35] have so far been applied successfully. Electron energy loss spectroscopy (EELS) is also useful in performing such examinations, since it allows the bonding

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states of chemical elements at interfaces to be determined on a nanometre scale by analysing the near edge fine structure (ELNES) of an EELS spectrum [7, 24, 28, 29, 36, 37]. Moreover, quantitative volumetric measurements (sorption and desorption of oxygen) [25] and a special electrochemical technique applicable to the matrix metal palladium (high hydrogen permeability) have been employed [25–27]. The varying oxygen coverage at the metal/oxide interface gives rise to varying hydrogen segregation, which was studied extensively by Huang *et al.* for palladium alloys [26, 27]. There, the excess oxygen forming an oxide with the more noble matrix metal leads to irreversible trapping of hydrogen at the interface, which precedes water formation during the reduction of less noble oxides. Thus, hydrogen acts as a probe for excess oxygen. The interpretation of the experimental results finally yields the model of structural vacancies at the interface first proposed in Ref. [27] and supported by additional evidence in Ref. [25].

In the present work, techniques of high voltage transmission electron microscopy (HVEM), high resolution transmission electron microscopy and electron energy loss spectroscopy have been used to investigate the segregation of oxygen at polar (111) interfaces between Ag and MgO precipitates produced by internal oxidation of an Ag/Mg alloy. This particular preparation method is advantageous in that flat (on an atomic scale) and low-energetic semi-coherent interfaces with a small lattice misfit of $d = 3.1\%$ are forming [4, 5, 9, 38] as the precipitates (here of MgO) are growing freely with respect to shape and orientation. Furthermore, an equilibrium between oxygen at the interface and oxygen dissolved in the matrix is easy to attain, due to the high diffusivity of oxygen in silver, even at moderate temperatures of about 700 K [39]. Therefore, only rather short annealing times in a desired oxygen atmosphere are necessary to saturate the Ag/MgO interface with an excess of oxygen [25, 40]. For the Ag/MgO system, enthalpy and entropy of the oxygen segregation as well as equations of isotherms have been determined by volumetric measurements [25], which can be used to interpret our results.

2. EXPERIMENTAL

2.1. Internal oxidation

An Ag/Mg alloy (99.9 and 99.7% purity, respectively) containing 3.0 at.% Mg was produced by arc melting. The solidified bead was then annealed in argon for 24 h at 1173 K and cold-rolled to a foil of 150 μm in thickness.

From previous investigations it is known that during the internal oxidation of this alloy, small intragranular MgO particles of about 6 nm in diameter occur, whereas some larger precipitates of 100–

400 nm are forming along grain boundaries [25, 40]. To attain a high volume fraction of the larger particles, which is more convenient for TEM investigations, internal oxidation has been performed with no previous recrystallization treatment of the alloy. Hence, the foils were annealed in air at 1173 K for 48 h, which is sufficient to ensure a complete reaction of the magnesium forming MgO precipitates. A subsequent wet chemical analysis revealed only a small evaporation loss of Mg. The precipitated MgO crystallites have formed truncated octahedra with polar $\{111\}_{\text{MgO}} \parallel \{111\}_{\text{Ag}}$ and non-polar $\{001\}_{\text{MgO}} \parallel \{001\}_{\text{Ag}}$ interfaces according to their cube-on-cube orientation relationship with the matrix.

2.2. Sorption and desorption of oxygen

In order to vary the composition of the Ag/MgO interfaces after internal oxidation, half of the Ag/MgO material was annealed for 2 h at 673 K in a pure oxygen atmosphere at a partial pressure of 10^5 Pa. This relatively low temperature was chosen to provide a high oxygen coverage at the interfaces as the segregation is exothermic there. The diffusivity of oxygen in silver is high enough to maintain the equilibrium. Under these conditions the solubility of oxygen in the matrix is only 0.001 at.% [39].

The second part of the material was annealed for 2 h at 1163 K in high vacuum (total pressure 10^{-3} Pa, which is also the upper limit for the oxygen partial pressure) to remove almost all oxygen atoms dissolved in the silver matrix during internal oxidation and, for equilibrium reasons, also those covering the Ag/MgO interfaces. Thus, even at the phase boundaries, oxygen belonging solely to the stoichiometry of MgO is expected.

2.3. Preparation of TEM samples

The preparation of TEM samples of the internally oxidized Ag/Mg foils, heat treated as described above, followed a standard route. First, 3 mm thin discs were cut from the foils by ultrasonic drilling. Being ground to a thickness of about 100 μm , the specimen was dimpled on either side to a central thickness of 20 μm by diamond tools. Final thinning to electron transparency followed via Ar-ion bombardment in a Gatan DuoMill. An ion beam at a glancing angle of 10° to the specimen is sufficient to provide a suitably extended area of less than 10 nm in thickness, close to the hole arising.

2.4. Microstructural and nanochemical analyses

HVEM investigations were carried out using a JEOL JEM 1000-06/71 high voltage transmission electron microscope operating at 1 MV. In this way, a large specimen area has been analysed to yield a

detailed survey of the distribution of the MgO precipitates along the grain boundaries of the Ag matrix. High resolution transmission electron microscopy studies were then performed in a Philips CM 20 FEG operating at 200 kV and equipped with a post-column electron energy filter (Gatan Imaging Filter GIF 200) for EELS analyses. The thermally assisted field emission gun enables an energy resolution of the EEL spectra of 0.8–1 eV, which were usually acquired at a dispersion of 0.5 eV per channel. This yields information on the chemical bonding state of the elements of interest by analysing the ELNES of the relevant ionization edges, which can be attributed to transitions of core-shell electrons into unoccupied states above the Fermi level [41]. With respect to the Ag/MgO interface to be examined either point analyses were made, or series of EEL spectra along a line across a well developed (111) matrix/particle interface have been recorded in the scanning transmission (STEM) mode, with the electron probe (diameter about 2 nm) digitally scanned by the Gatan Digiscan model 688.

To obtain chemical information from the interface area, i.e. to extract the interface specific part of the ELNES, the spatial difference technique [28] was applied: as the spectrum of the interface also contains information from the adjacent matrix and precipitation areas (the probe diameter is larger than the thickness of the interface layer) this

method requires reference spectra of the precipitation areas in addition to the interface spectrum. Subtracting the suitably scaled (to prevent unphysical negative counts) and background-eliminated reference spectra from the interface spectrum provides information as to the interfacial atoms, particularly, their chemical environment or oxidation state, which may differ from that of the bulk material. This spectrum processing was carried out using the Gatan ELP software.

3. RESULTS

3.1. Size and distribution of the MgO precipitates

To characterize the MgO precipitates formed, the internally oxidized Ag/MgO foils were first investigated by HVEM. Large MgO particles preferentially localized at the grain boundaries of the Ag matrix occurred in addition to much smaller oxide precipitates in the bulk according to Ref. [25]. Figure 1 presents a HVEM bright-field image of the Ag/MgO material typical of both sets of specimens, annealed in vacuum and annealed in oxygen. Large MgO particles of typically 100 nm in diameter along the grain boundary (middle) are clearly shown by their light contrast. These precipitates grown by ripening processes have a size suitable for EELS analyses of the Ag/MgO interface (see below). Although the Ag matrix recrystallized

Fig. 1. HVEM image of large MgO precipitates located at a grain boundary of the Ag matrix.

during internal oxidation, a small grain size of only a few micrometres was achieved. The foils had been deformed plastically by cold rolling and precipitation. The HREM image of Fig. 2 shows that numerous small MgO precipitates, typically of about 5 nm in diameter (occurring already within both grains of Fig. 1) have formed in the silver bulk. They are imaged by their diffraction contrast. Because of the high oxygen affinity of magnesium, even a single molecule of MgO can build up a stable nucleus. Due to the large interfacial area, these particles provide the large part of the total amount of oxygen atoms segregating at the Ag/MgO phase boundaries. However, for an EELS analysis of the interface, these precipitates are less suited as they are smaller than the average foil thickness. Figure 2 also shows that the atomic planes cross the Ag/MgO interface continuously with no misfit dislocations forming, i.e. the small magnesia crystals are terminated by a completely coherent interface. There is no reaction zone forming along these boundaries.

3.2. EELS analyses of the Ag/MgO interfaces

After annealing in oxygen and vacuum, respectively, the chemical composition of the Ag/MgO phase boundaries was investigated by interpreting the interface-related features in the spatial resolved

EELS spectra. In particular, the O–K ionization edge was analysed in order to determine the bonding state of oxygen across the interface on a nanometre scale to find out whether an oxidized Ag interlayer has formed, or not. Thus, both kinds of heat treatment (cf. Section 2.2) were compared.

3.2.1. Specimens annealed in oxygen. A typical series of EEL spectra along a line across an Ag/MgO interface with a large amount of segregated oxygen (annealed in O₂ at 673 K for 2 h) is demonstrated in Fig. 3. Crossing the phase boundary from the MgO crystal to the Ag matrix at steps of about 2 nm the K-ionization edge of oxygen disappears, with the M₄₅ edge of silver appearing. These EEL spectra prove that at the interface both shape and onset of the O–K edge change significantly with respect to the MgO side. As these typical fine-structure features of an ionization edge in an EEL spectrum depend on the environment of the target O atom, the bonding state of oxygen at the interface is different from that in MgO.

The bonding state of oxygen at the Ag/MgO phase boundary has been analysed in more detail by separating the EEL spectrum of MgO from that measured at the interface, as done in Fig. 4. This figure shows the background-subtracted O–K edges of MgO (below) and Ag₂O (above) from standards together with an interface region, extracted from the middle part of Fig. 3 (curve “interface”). The

Fig. 2. HREM image of intragranular coherent MgO precipitates in internally oxidized Ag/MgO.

Fig. 3. Set of EEL spectra along a 50 nm line across the Ag/MgO interface (sample annealed in oxygen).

ELNES of this interface-related spectrum is similar to that of MgO as the larger part of the measuring probe sees the oxygen from the precipitate. However, on the low energy side of the first peak

there is a small energy shoulder. This change in the bonding state of oxygen directly at the interface is more pronounced if the normalized spatial difference method is used, i.e. by subtracting the O-K

Fig. 4. O-K ELNES at the interface of a sample annealed in oxygen compared with those of Ag_2O and MgO, difference spectrum: interface minus MgO.

Fig. 5. O-K ELNES at the interface of a sample annealed in vacuum compared with that of MgO, difference spectrum: interface minus MgO.

edge of MgO from that recorded at the interface, presented as the “difference” curve in Fig. 4. The difference spectrum clearly shows two neighbouring peaks—a positive one and a negative one—at 532 and 539 eV, respectively, marked by lines in the figure. These energies just correspond to the characteristic 1s–2p transitions of oxygen in Ag₂O and MgO, respectively, used as reference standards.

3.2.2. Specimens annealed in vacuum. Using the same method as described above, the bonding state of oxygen has been investigated at the Ag/MgO phase boundary of a vacuum annealed material (at 1163 K for 2 h) by taking sets of EEL spectra across the interface between large MgO precipitates and the Ag matrix. Background-subtracted O-K edges of MgO and a typical edge taken from the interfacial region are shown in Fig. 5. The O-K ELNES of the Ag/MgO interface now reveals almost the same characteristic features as that of MgO. The onset and peak energies are identical. In particular, the interface spectrum no longer displays a hump in front of the MgO main peak at 539 eV. Even the difference spectrum (interface minus MgO), also shown in Fig. 5, does not indicate any oxygen at the interface bound in a way different from MgO.

4. DISCUSSION

After annealing an Ag/MgO specimen in vacuum, the bonding state of oxygen at the Ag/MgO interface is the same as in MgO. Therefore, only oxygen atoms belonging to the stoichiometry of MgO are present at the phase boundary. This is not the case after annealing the Ag/MgO sample in oxygen. The

O-K ELNES, observed at the Ag/MgO interface, now reveals a second bonding part of oxygen in addition to the features of MgO, which is characterized by a shoulder near the energy (≈ 532 eV), where the O-K ELNES of Ag₂O has its first maximum.

In a first approximation (i.e. neglecting the special energy distribution of the unoccupied states in the conduction band), the edge onset depends on the core electron energies. The behaviour is elucidated in Fig. 6 for Ag₂O and MgO (bonding energies taken from Ref. [42]). As oxygen is rather weakly bound in Ag₂O ($\Delta E = -0.24$ eV), its bonding state is not easy to distinguish from that of free oxygen by EELS fine structure analysis due to the limited energy resolution of the spectrometer. This problem does not arise for MgO due to the much larger difference in the 1s electron energies ($\Delta E = -5.90$ eV). Therefore, it is difficult to decide

Fig. 6. Comparison between the bonding energies of oxygen in Ag₂O and MgO.

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