ATOMIC SCALE OBSERVATIONS OF THE CHEMICAL COMPOSITION OF A METAL/CERAMIC INTERFACE

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Introduction

The heterophase interface between a metal and a ceramic is of great practical importance because of the ubiquitousness of this interface in composite materials, thin film technology and electronic packaging systems. The nature of the chemical bond at a metal/ceramic interface is very important in determining how well these two disparate materials adhere to one another, and ultimately the performance of this heterophase interface in service. On the basic side the question of the nature and strength of the chemical bond at a metal/ceramic interface has been addressed recently from a first principles point-of-view [1,2]. In addition, much experimental effort has been expended recently employing high resolution electron microscopy (HREM) to determine the terminating plane on the oxide side of metal/metal oxide heterophase interfaces by comparing observed HREM images with computer simulated images [3-5].

In this paper we present a combined transmission electron microscopy, HREM and atom-probe field-ion microscopy (APFIM) study of a Cu/MgO heterophase interface produced by internal oxidation of a Cu(Mg) alloy. This heterophase interface is an interesting one as it consists of joining a noble free-electron metal (Cu) to a strongly heteropolar metal oxide (MgO). We demonstrate, for the first time, that by combining these three microscopies it is possible to determine the chemical identity of the terminating plane on the oxide side of a Cu/MgO {111}-type interface directly without any deconvolution of the experimental data. In particular, we demonstrate that the bonding across a Cu/MgO {111}-type interface, in a common $\langle 111 \rangle$ direction, has the sequence Cu|O|Mg|... and *not* Cu|Mg|O|... via APFIM measurements of this highly localized chemistry.

Experimental Procedures

Three different Cu(Mg) alloys were prepared by melting ASARCO copper (99.998+ at.% pure) and Johnson Matthey magnesium (99.98 at.% pure) in a graphite crucible sealed under an argon atmosphere in a quartz tube, to form small cylindrically-shaped ingots weighing ≈ 26 gm each. The particular alloy compositions prepared were Cu-0.16 at.% Mg, Cu-0.7 at.% Mg and Cu-2.8 at.% Mg; these Mg concentrations correspond to single-phase solid-solution alloys [6]. The ingots were rolled into 0.125 mm thick sheets for transmission electron microscopy (TEM) and HREM studies, or drawn into 250 μ m diameter wires for APFIM studies.

Cu/MgO internal interfaces were formed by internally oxidizing these alloy specimens utilizing the Rhines pack method [7,8]; this pack consists of a powder mixture of Cu plus Cu_2O plus Al_2O_3 (1:1:1). To realize a high probability of finding an MgO precipitate in an APFIM specimen, experiments were performed to determine the optimum Mg concentration, internal oxidation temperature and time for achieving a high number density ($>5 \cdot 10^{15} \text{ cm}^{-3}$) and small diameter precipitates ($<20 \text{ nm}$). The optimum composition is a Cu-2.8 at.% Mg alloy, at an internal oxidizing temperature of 1173 K and an oxidizing time of 1200 s for both the thin sheets and wires. Those experiments demonstrate that to achieve the desired conditions the most critical parameter is the Mg concentration, and neither the temperature nor the time of the internal oxidizing treatment appear to be especially critical.

For the TEM and HREM studies 3 mm diameter disks are punched out of the thin sheets, and a twin-jet polisher (Tenupol) employing a 30 vol.% nitric acid/70 vol.% methanol solution at 243 K is used to prepare electron transparent thin regions. The APFIM specimens are electropolished to a sharply-pointed tip with an approximately 65.8 nm radius in the region of the 111 pole, after the internal oxidation procedure, utilizing an electrolytic solution with the composition 100 g $\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$ in 900 ml of acetic acid. A stainless steel cathode in the form of a 25 mm diameter circular loop is used to electropolish the wire-shaped specimens [9]. To examine a wire-shaped specimen by TEM a specially fabricated double-tilt stage is employed for an Hitachi 700H 200 kV electron microscope [9]. This double-tilt stage is unique as it allows us to examine the same wire FIM specimen both prior to and after an atom probe study as well as at different stages of the electropolishing process [9].

Experiments with Transmission and High Resolution Electron Microscopies

First, conventional TEM is used to determine both the number density of MgO precipitates and also the size distribution of precipitates. As found in previous investigations of fcc systems, the precipitates exhibit a cube-on-cube orientation relation with the Cu matrix [5,10]. Conventional TEM micrographs of MgO precipitates in a Cu matrix exhibit typical "coffee-bean" strain-field contrast [11]. The histogram of the diameters of the MgO precipitates is quite broad [12]. The actual diameter, however, of a precipitate is difficult to estimate from a bright-field electron microscope image, since the shape and amount of strain-field contrast depend on the direction of the electron beam relative to a specimen's crystallography [13,14]. Therefore, to determine the exact dimensions of a precipitate the Moiré fringe method is used -- it employs a double-diffraction technique [15]. For instance, we observed the parallel (111) Moiré fringes of a faceted MgO precipitate with the projected image plane close to (123). And, therefore, the shape of the fringes represents the shape of the precipitate viewed along a [123] direction. The Moiré pattern in this case is a result of the difference between the interplanar spacings of the Cu and MgO (111) lattice planes. The fringe spacing is 1.5 nm and the average size of the precipitates studied by this technique is 19.5 nm.

HREM is used to investigate the atomic structure of a Cu/MgO {111}-type interface. Axial illumination in an Hitachi H9000 HREM allows the direct observation of the configuration of atoms near an interface when proper operating conditions are met [10]. Figure 1 exhibits an HREM image (defocus value is 69.4 nm at 300 kV) of an MgO precipitate in a Cu matrix with a common [100] zone axis for both phases. (We also recorded HREM images employing a common [110] zone axis for both phases.) The diameter of this MgO precipitate is 13 nm and the octahedron exhibits truncations along {010}-type planes, indicating that the equilibrium shape has not been fully developed. The HREM images demonstrate that the orientation relationship is cube-on-cube with an octahedral-shaped precipitate that is faceted on {111} planes. The lattice misfit parameter (η) is given by $\eta = 2[(a_{\text{MgO}} - a_{\text{Cu}})/(a_{\text{MgO}} + a_{\text{Cu}})]$, where the a 's are the lattice parameters of the two phases, and its experimental value is 0.1483 in agreement with the calculated value. This lattice misfit is accommodated by a combination of localized misfit dislocations and elastic straining at Cu/MgO {111}-type interfaces.

Atom-Probe Field-Ion Microscope Experiments

For the chemical analysis of a Cu/MgO {111}-type interface a sharply-pointed atom-probe field-ion microscope specimen with a tip radius of approximately 65.8 nm, in the region of the 111 pole, is employed. TEM micrographs of an FIM specimen containing MgO precipitates show uniformly aligned MgO precipitates exhibiting a directional consistency with respect to the fiber axis of the wire. This axis is a [111] direction as determined from careful TEM tilting experiments. Hence, this observation is consistent with the known experimental results on wire textures of recrystallized Cu [16].

The same specimen was then transferred to our atom probe for a chemical analysis of a Cu/MgO (111) interface. Figure 2 is an FIM micrograph exhibiting an MgO precipitate in a Cu matrix. Note that the precipitate shows well-developed contrast features outlining its atomic scale geometry. The approximate diameter of this precipitate is 7.3 nm. The atom probe analysis is performed at a background pressure of $1.2 \cdot 10^{-8}$ Pa and a constant tip temperature of 35 K. The pulse fraction (f) -- the ratio of the pulse voltage to the steady-state dc voltage -- is maintained at 0.1, and a pulse frequency of 15 Hz is used to dissect the specimen on an atomic scale using the pulsed field-evaporation technique [17]. The detection efficiency is maintained at a constant value of 0.0062, via software in our fully computer-controlled atom probe; the steady state dc voltage is automatically increased by 10 Vdc for every 1000 field-evaporation pulses if *no* event is detected. This highly controlled procedure results in the continuous and smooth dissection, on an atom-by-atom basis [17], of a series of (111) planes as well as other planes on the surface of the approximately hemispherical FIM tip. The probe hole in the channel electron multiplier array used to view a specimen was placed at a distance from the tip such that its projected diameter covered approximately 70 atoms [18].

Figure 3 is an integral profile of the cumulative number of Mg or O ions versus the cumulative number of Cu plus Mg plus O ions of another MgO precipitate uncovered during a random area analysis. The projected diameter of the probe hole on the tip is smaller than the diameter of the MgO precipitate; this implies no correction to the data is required because of a matrix contribution to the precipitate's composition. It is seen from this integral profile that the matrix is essentially pure Cu; prior to the Cu/MgO (111) interface only 13 oxygen events were detected out of a total of 10,899 Cu plus O plus Mg events for a bulk oxygen concentration of $\approx 10^{-3}$ at. fr. O; in addition, only one Mg event was detected for a bulk Mg concentration of $\approx 9 \cdot 10^{-5}$ at. fr. Mg. Note carefully that the the outermost (222) plane of ions of the MgO precipitate consists *solely* of oxygen ions, and the second (222) plane consists *solely* of magnesium ions. (At this point the specimen failed catastrophically, presumably because the evaporation field of a magnesium ion is considerably lower than that of an oxygen ion.) The depth resolution of this integral profile is equal to the interplanar spacing along the $\langle 111 \rangle$ direction in the MgO precipitate -- $(d_{222})_{\text{MgO}} = a_0/(2\sqrt{3}) = 0.121$ nm, where a_0 is the lattice parameter of MgO (0.420 nm). We have obtained the same result for other octahedral-shaped precipitates by also analyzing along $\langle 111 \rangle$ -type directions across Cu/MgO {111}-type interface planes. The crystal structure of MgO is NaCl-type (rock salt structure) and, therefore, the compositions of point-defect free {111}-type planes alternate from 100 at.% oxygen to 100 at.% magnesium as one travels along a $\langle 111 \rangle$ -type direction from the Cu matrix to a common $\langle 111 \rangle$ -type direction in the MgO precipitate. Thus our experimental results demonstrate directly -- that is, *without* data deconvolution -- that the bonding across a Cu/MgO {111}-type interface has the sequence Cu|O|Mg|... and *not* Cu|Mg|O|... .

Conclusions

We have demonstrated that it is possible to determine directly the chemical composition of a metal/ceramic heterophase interface on an atomic scale by using a combination of conventional transmission and high resolution electron microscopies to locate and determine the structure of a metal/ceramic interface. And then using atom-probe

field-ion microscopy measurements to ascertain the chemical identities of the ions at a heterophase interface as a function of atomic position across an interface. The first application of this approach is made to a Cu/MgO {111}-type interface that was created by the internal oxidation of a Cu-2.8 at.% Mg alloy at 1173 K for 1200 s. The depth resolution of the composition profile, across this interface in a $\langle 111 \rangle$ direction, is equal to $a_{\text{MgO}}/(2\sqrt{3}) = 0.121$ nm, where a_{MgO} is 0.420 nm. In conclusion, the terminating plane of MgO at a Cu/MgO {111}-type interface is shown to be oxygen and *not* magnesium via very direct atom probe field-ion microscope studies.

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FIGURE 1. High resolution electron microscope micrograph of an MgO precipitate in a Cu matrix viewed along a [100] zone axis for both phases employing axial illumination; this image was recorded at a defocus value of 69.4 nm at an operating voltage of 300 kV. Atomic columns both in the MgO precipitate and the Cu matrix show the same crystallographic orientation -- cube-on-cube. This MgO precipitate has a diameter of 13 nm.

FIGURE 2: Field-ion microscope image of an MgO precipitate in a Cu matrix. The (111) plane of the MgO precipitate is parallel to the (111) plane of the Cu matrix. The diameter of the MgO precipitate is approximately 7.3 nm. The neon imaging gas is at $8 \cdot 10^{-4}$ Pa gauge pressure and the temperature of the field ion microscope specimen is 40 K.

FIGURE 3: An integral profile across a Cu/MgO (111) interface detected during a random area analysis; this profile was recorded at a specimen temperature of 35 K, a pulse fraction of 0.1, and a pulse frequency of 15 Hz. The plot is the cumulative number of Mg or O ions detected versus the cumulative number of Cu plus Mg plus O ions detected. The Cu signal -- not exhibited -- disappears at the Cu/MgO (111) interface and then the signal is 100 at. % O until the first (222) plane has been completely removed by the field evaporation process, and then the next (222) plane is 100 at. % Mg. This result indicates directly that the sequence of planes across this (111) heterophase interface is CuO|Mg... . The depth resolution for this chemical composition profile is $(d_{222})_{MgO} = a_0/(2\sqrt{3})$, where a_0 is the lattice parameter of MgO (0.420 nm), and is equal to 0.121 nm. The data displayed in this integral profile has *not* undergone any deconvolution process. Note that the number of oxygen events detected before the Cu/MgO (111) interface is reached is 13 out of a total number of 10,899 events (Cu plus Mg plus O); and the number of Mg events detected before this same interface is reached is 1 out of a total of 10,899 events (Cu plus Mg plus O); thus, the respective concentrations of oxygen and magnesium in the Cu matrix are $\approx 10^{-3}$ at. fr oxygen and $\approx 9 \cdot 10^{-5}$ at. fr. magnesium.