INITIAL RESULTS ON THE AgCdO (222) INTERFACE: ATOMIC SCALE INTERFACIAL CHEMISTRY AND SEQUENCING OF ORDERED CADMIUM/OXYGEN PLANES

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Introduction

The bonding between metal-ceramic interfaces is dependent upon the crystallographic structure and chemical composition of this heterophase interface [1-4]. In the case of metal/metal oxide interfaces, the chemistry of the interface can control the properties of the bulk material. The terminating plane of a metal oxide at a heterophase interface may be a mixed cation-oxygen, pure oxygen, or pure cation plane. For example, ab initio calculations indicate that oxygen atoms in a terminating {002} plane of MgO bond to either Ag or Ti atoms in a metallic overlayer, while the composition of the terminating MgO {002} plane remains unchanged [1,3]. High resolution electron microscopy (HREM) is used to determine the crystallographic structures of metal/metal oxide interfaces [5-7]. Our recent studies of the copper/magnesium oxide (222) heterophase interface -- produced by internal oxidation of Cu(Mg) alloys -- using conventional transmission electron microscopy (CTEM), HREM, and atom-probe field-ion microscopy (APFIM) have demonstrated the atomic scale sharpness and chemical nature of the {222} terminating planes [8-10]. In particular, it is found that magnesium oxide precipitates have a cube-on-cube orientation relationship with the copper matrix, are octahedrally-shaped, and are bound by {222} planes. APFIM results demonstrate directly that the interfaces are atomically sharp, and the sequence of {222}-type planes across the interface is CuO|Mg... and not CuMgO...

In this study we present the first APFIM results on silver/cadmium oxide interfaces produced by internal oxidation of a Ag(Cd) alloy. Internal oxidation of binary metal alloys is a well-studied phenomenon, and is based upon preferential oxidation of solute atoms (B) in a dilute A(B) alloy [11-14]. Internally-oxidized silver (cadmium) alloys are used to switch medium to high currents [15], and have been the focus of studies of their strength and electrical properties [16,17]. Previous HREM investigations of silver/cadmium oxide interfaces, produced by internal oxidation, have determined that the cadmium oxide precipitates have a cube-on-cube orientation relationship with the silver matrix, are octahedrally shaped, are bound by {222} planes, and can be truncated along <100> directions [6,18,19]. (The lattice misfit parameter -- \( \eta = 2[(a_{\text{CdO}} - a_{\text{Ag}})/(a_{\text{CdO}} + a_{\text{Ag}})] \) -- between silver and cadmium oxide is 0.14.) Mader and co-workers [6,7] suggest, via HREM observations, that the terminating {222}-type plane of CdO is the oxygen plane. In this paper we present evidence that it is possible to dissect cadmium oxide precipitates on an atom-by-atom basis, via the pulsed field-evaporation technique, and thereby obtain chemical information on an...
atomic plane-by-plane scale. It is demonstrated, without any data deconvolution, that the silver/cadmium oxide interface is atomically sharp, and the sequence of planes through the (222)-type interface is AgO/Cd... and not Ag/CdO... In addition, we demonstrate that it is possible to dissect CdO (222)-type planes during the course of an analysis along a <111>-type direction, and thus examine the internal chemical composition of a metal oxide precipitate.

**Experimental Procedures**

Ag(Cd) alloys are prepared from 99.999 at.% silver and 99.999 at.% cadmium purchased from Johnson Matthey Ltd. A silver-7.3 at.% cadmium master alloy is prepared initially by arc melting the two elements together five times under an argon atmosphere. The alloy is then cold rolled into thin sheets and cut into 2 mm square pieces. Next a silver-1.7 at.% cadmium alloy is prepared from these pieces by melting them at 1473 K, with the requisite amount of silver to produce a concentration of 1.7 at.% Cd, in a graphite crucible that is sealed in a quartz tube under a pressure of argon. This alloy is further homogenized by annealing the specimens at 773 K for 24 hours. Any surface contamination is removed by filing the surface, followed by a final etching in a 1:1 solution of NH₄OH:H₂O₂. Both Ag(Cd) alloys were chemically analyzed by Ledoux Corp. to obtain the cadmium concentrations in the bulk ingots.

TEM samples are prepared from the silver-1.7 at.% cadmium ingot by cold rolling it into sheets with a thickness of 100 μm, and then punching out 3 mm diameter disks from the sheets. The disks are oxidized in air at 843 K for 14.5 hours. Then the internally oxidized disks are jet polished, to obtain electron transparent specimens, using a solution of 10% perchloric acid in glacial acetic acid at 35 Vdc, and finally rinsing the disks in ethyl alcohol. Conventional transmission electron microscopy images are obtained using an Hitachi 700H electron microscope, and high resolution electron microscopy images are obtained employing an Hitachi HF 2000.

The remaining silver-1.7 at.% cadmium ingot is swaged into a rod and drawn into 200 μm diameter wires. The same internal oxidation conditions used for disks are used for the wire specimens. The internally oxidized wires are electrolytically sharpened to a point using a platinum loop as a cathode. The electrolyte is 2% perchloric acid in a 2-butoxyethanol solution used at 40 Vdc; this procedure results in sharp tips -- <10 nm diameter -- with no preferential electropolishing of the CdO precipitates or the heterophase interfaces. CTEM analysis is performed using the Hitachi 700H; the sharply-pointed wires are held in a double-tilt stage that was specifically designed to hold one cm long wire specimens [20]. Field-ion images are obtained at 40 K employing a neon partial pressure of 7x10⁻⁵ Pa. A tip is aligned in the APFIM such that the probe hole covers the 111 pole of an exposed cadmium oxide precipitate. Time-of-flight (TOF) mass spectra are obtained with the specimen maintained at a temperature (Ta) of 30 K, employing a pulse fraction (f) of 0.1 -- f is the ratio of the pulse voltage to the steady state dc imaging voltage -- at a background vacuum of better than 1.33x10⁻⁸ Pa in the atom probe.

**Results and Discussion**

Truncated octahedrally-shaped CdO precipitates are formed with a cube-on-cube orientation relationship, on the (222) planes of CdO, with respect to the silver matrix; cadmium oxide has a NaCl-type structure and the (222) planes alternate between all cations or all anions. Figures 1 and 2 are taken along <001> and <110> zone axes respectively. Moiré fringes between the silver matrix and CdO precipitates are clearly present in two directions, as are coherency strain fields along <111> directions. The precipitates are truncated along the <001>-type directions by (002)-type planes. In Figure 3 the silver matrix diffraction pattern along the <110>-type direction clearly shows satellite and double diffraction spots. The (222) facet planes of the octahedra are approximately 10 nm in length, while the
total length along the <001> direction is approximately 20 nm. The hexagonal shape of a CdO precipitate is easily seen in a HREM image (Fig. 3), indicating a {002} truncation.

The APFIM results are presented in Fig. 4 in the form of an integral profile; that is, the cumulative number of Ag or Cd or O events versus the cumulative number of Ag plus Cd plus O events. This integral profile contains two CdO precipitates that are labeled oxide 'A' and oxide 'B'. The first CdO precipitate, labelled 'A', is completely exposed and we obtain atoms from only the oxide and no signal from the silver matrix that precedes it. In this precipitate, planes of cadmium, oxygen, and silver are distinguishable, and eleven ordered planes of pure cadmium and pure oxygen are clearly sequenced -- see Fig 4. Note for this sequence of 11 planes that the first few pairs of oxygen/cadmium planes have a stoichiometry ratio of approximately 1:1, and that this ratio becomes less than unity with increasing depth. A solid line with a slope of 0.5 is indicated in Figure 4 -- this is for the ratio of O/(Cd+O) or Cd/(Cd + O); note well that the slope for the pure oxygen or pure cadmium planes is equal to unity. The cadmium and oxygen planes follow an ordered sequence through the interfacial region -- labeled "Back Face of Oxide'A'" in Fig. 4 -- until only silver events are detected. The presence of a silver signal along with the cadmium or oxygen planes is attributed to the position of the cadmium oxide precipitate with respect to the probe hole. If the probe hole covers an area away from the center of a triangularly-shaped (222) face of a cadmium oxide precipitate (see Fig. 5), as opposed to the center of this triangle, then the cylinder of precipitate analyzed intersects a 222 interface -- during the course of the pulsed-field dissection process -- that makes an angle of 70.5° with respect to the topmost (222) plane. Therefore, the cylinder of atoms analyzed intersects a portion of the silver matrix as it traverses the CdO/Ag heterophase interface, and silver atoms are detected that are intermingled with the cadmium and oxygen atoms. To avoid this effect the position of the probe hole must be in the geometric center of the topmost triangularly-shaped (222) plane, see Fig. 5(b), so that the cylinder of CdO precipitate analyzed intersects a parallel (222) plane at the bottom of the precipitate. Oxide precipitate 'A' is Cd rich mainly due to a deviation from stoichiometry near the center of the precipitate. The overall Cd:O ratio is 1.29; that is, this precipitate is hypostoichiometric with respect to oxygen.

In the region denoted oxide 'B', the field evaporation process proceeds from the pure silver matrix through the AglCdO heterophase interface and reveals that oxygen is the first (222) plane to be uncovered, and cadmium is the second (222) plane detected. (Unfortunately, the tip failed several planes later.) This portion of the integral profile demonstrates directly that the chemical sequence across a AglCdO {222}-type heterophase interface is AglOICd... and not AglCdO...

Conclusions

Atom-probe field-ion microscopy is employed to demonstrate directly that the terminating (222)-type plane of CdO is oxygen and not cadmium for the AglCdO (222) heterophase interface; that is, the sequence of {222} planes is AglOICd... and not AglCdO...

It is also demonstrated that APFIM is capable of determining the internal chemical composition of CdO precipitates on an atomic scale. For example, eleven ordered planes of cadmium and oxygen are clearly resolved for an analysis along a <111>-type direction. In addition, field evaporation through a metal/metal oxide interface is possible without failure of the specimen. The atomic resolution of the composition profile is directly related to the interplanar spacing. In this case, it is 0.136 nm and 0.118 nm in cadmium oxide and silver, respectively, along the <111> direction. The present results on the AglCdO (222)-type heterophase interface are similar to those found for the CulMgO (222)-type heterophase interface [8-10], in that the terminating (222)-type planes in both cases are atomically sharp and consist solely of oxygen atoms. For both metal/metal oxide interfaces this result is obtained without any data deconvolution.
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References

FIG. 1. Octahedrally-shaped CdO precipitates shown along a <001> silver zone axis. Moiré fringes are clearly seen in two directions.

FIG. 2. CdO precipitates shown along a <110> silver zone axis. In addition to Moiré fringes, coherency strain fields are seen along <111> directions. The precipitates are approximately 20 nm in length along the <001> direction.

FIG. 3. A high resolution electron micrograph of CdO precipitates in a silver matrix shown along a <110> zone axis. The cube-on-cube orientation relationship between CdO and Ag is clearly seen, as are Moiré fringes in two directions. Note the hexagonal shape of the precipitates for this projection, indicating a {002} truncation.
FIG. 4. An integral profile of atoms taken along a [111] direction. In oxide precipitate 'A' eleven ordered planes of 
cadmium and oxygen are observed. The interfacial region between oxide 'A' and the silver matrix also follows an 
ordered sequence. Because the trailing \{222\}-type interface makes an angle of 70.5° with respect to the leading 
interface (see Fig. 5) silver is detected in this region. In oxide precipitate 'B' the order of \{222\} planes is \text{AgO} \text{Cd}... 
and not \text{AgCdO}..., and therefore the terminating \{222\} plane is oxygen in CdO.

FIG. 5. Schematic of a truncated octahedrally-shaped CdO precipitate in a silver matrix: (a) [001] projection and (b) 
[110] projection. If the probe hole is positioned towards the corner of a triangularly-shaped \{222\} plane, then this off-
centered cylinder intersects an adjacent \{222\} plane that makes an angle of 70.5° with respect to the top \{222\} plane. 
Consequently, silver atoms are detected and intermingled with the cadmium and oxygen events as the off-centered 
analyzing cylinder crosses the CdOAg interface.