Atomic Scale Studies of the Chemistry of the Cu/MgO {111} Heterophase Interface

H. Jang and D.N. Seidman
Department of Materials Science and Engineering and Materials Research Center
Robert R. Mc Cormick School of Engineering and Applied Science
Northwestern University*
Evanston, IL 60208-3108 USA

and

K.L. Merkle
Materials Science Division
Argonne National Laboratory,** Argonne, IL 60439-4838

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H. JANG and D. N. SEIDMAN
Department of Materials Science and Engineering and Materials Research Center, Robert R. McCormick School of Engineering and Applied Science, Northwestern University, Evanston, IL 60208-3108 U.S.A.

K. L. MERKLE
Materials Science Division, Argonne National Laboratory, Argonne, IL 60439 U.S.A.

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ABSTRACT

The Cu/MgO {111} heterophase interface is studied using a combination of transmission electron microscopy, high resolution electron microscopy and atom-probe field-ion microscopy techniques. Wire and foil specimens of a Cu-2.8 at.% Mg alloy were internally oxidized to produce MgO precipitates at a number density of $5 \cdot 10^{15} cm^{-3}$ with a mean diameter of ≈ 200 Å. The MgO precipitates have a semicoherent interface with the Cu matrix and they exhibit a cube-on-cube orientation relationship. The octahedral-shaped MgO precipitates were analyzed using APFIM by dissecting along a <111> direction on an atomic scale. In this manner an MgO precipitate, with a {111} plane perpendicular to the axis of the APFIM, is uncovered after the Cu matrix has been mass analyzed. It was found that the terminating {222} plane of an MgO precipitate is pure oxygen, and the second {222} plane is pure Mg.

INTRODUCTION

The structure and composition of metal/ceramic interfaces on an atomic scale is of great interest, because they frequently control the overall properties of materials [1,2]. In particular, the metal/metal-oxide heterophase system is receiving special attention due to its technological importance in electronic packaging systems and ceramic-metal composites [3,4]. The most serious limitation in the study of internal interfaces is the inadequacy of conventional techniques to provide accurate atomic scale information on the types and positions of atoms at a boundary. High resolution electron microscopy (HREM) is employed to study atomic structure near an interface by projecting atomic columns onto a two-dimensional image [5,6]. Recently, indirect spectroscopic information is obtained from HREM atomic images by comparing them with computer simulated atomic images [7,8]. Energy dispersive x-ray analysis and electron energy loss spectroscopy in analytical electron microscopy (AEM) are applied to study the interface composition [9]. However, these analyses require deconvolution of the spatial distribution from the measured signal, since the spatial resolution of the AEM is limited by the geometric diameter of the electron probe, electron scattering inside the specimen, and a minimum detection limit. Atom-probe field-ion microscopy (APFIM) is employed to investigate the chemical composition of internal interfaces on an atomic scale. The APFIM can determine the chemical identity of a single preselected atom using time-of-flight mass spectroscopy [10,11].

We present a combined TEM, HREM and APFIM study of the internal {111} interface between Cu and MgO. The results demonstrate the complete analysis of an interface in terms of both atomic structure and its chemical composition. This is the first direct experimental evidence of interface composition of a metal/metal-oxide system on an atomic scale.

EXPERIMENTS

A Cu-2.8 at.% Mg alloy was internally oxidized to form a high number density of MgO precipitates using the Rhines pack method [12]. Two forms of alloys were prepared for analysis by TEM and APFIM; i.e., a foil specimen for TEM and a wire specimen for APFIM. To obtain a high probability of finding an interface between the matrix and a precipitate, careful consideration was given to the oxidation conditions needed to obtain a high number density of MgO precipitates -- $>10^{15}$ cm^{-3}. For the TEM and HREM specimens, the twin-jet electropolisher was used with 30% nitric acid plus 70% methanol at -30°C. The APFIM specimens were electropolished to a sharply pointed tip, approximately 25 nm in diam, after an internal oxidation procedure, utilizing 100g $Na_2CrO_4 \cdot 4H_2O$ in 900 ml acetic acid. The conventional loop method was employed for electropolishing FIM tips. The tip radius was examined by TEM using a specially designed double-tilt stage holder for a wire specimen.
Hitachi H700(CTEM) and H9000(HREM) microscopes, operating at 200 kV and 300 kV respectively, were used to investigate the number density, morphology, orientation of precipitates, and atomic structure near interfaces. In order to determine the chemical composition of an interface, a straight time-of-flight atom-probe field-ion microscope was used.

RESULTS AND DISCUSSION

Using conventional TEM, the number density and the sizes of the precipitates were investigated. The size variation of the precipitates is quite broad, and the number density of the precipitates is high enough to find a precipitate in the small volume of an FIM tip. The typical number density of the MgO precipitates of internally oxidized Cu-2.8 at.% Mg is $\approx 5 \cdot 10^{15} cm^{-3}$ with average size of $\approx$ 200 Å in diam. A Moiré fringe technique or a multi-beam diffraction condition are employed to measure the size of the precipitates [13].
In order to study the detailed atomic structure of a Cu/MgO {111} heterophase interface, HREM observations were performed. Figure 1 shows a HREM image of an MgO precipitate (defocus value of 65.1 nm at 300 kV) in a a Cu matrix with a <110> common axis. This image shows direct evidence for a

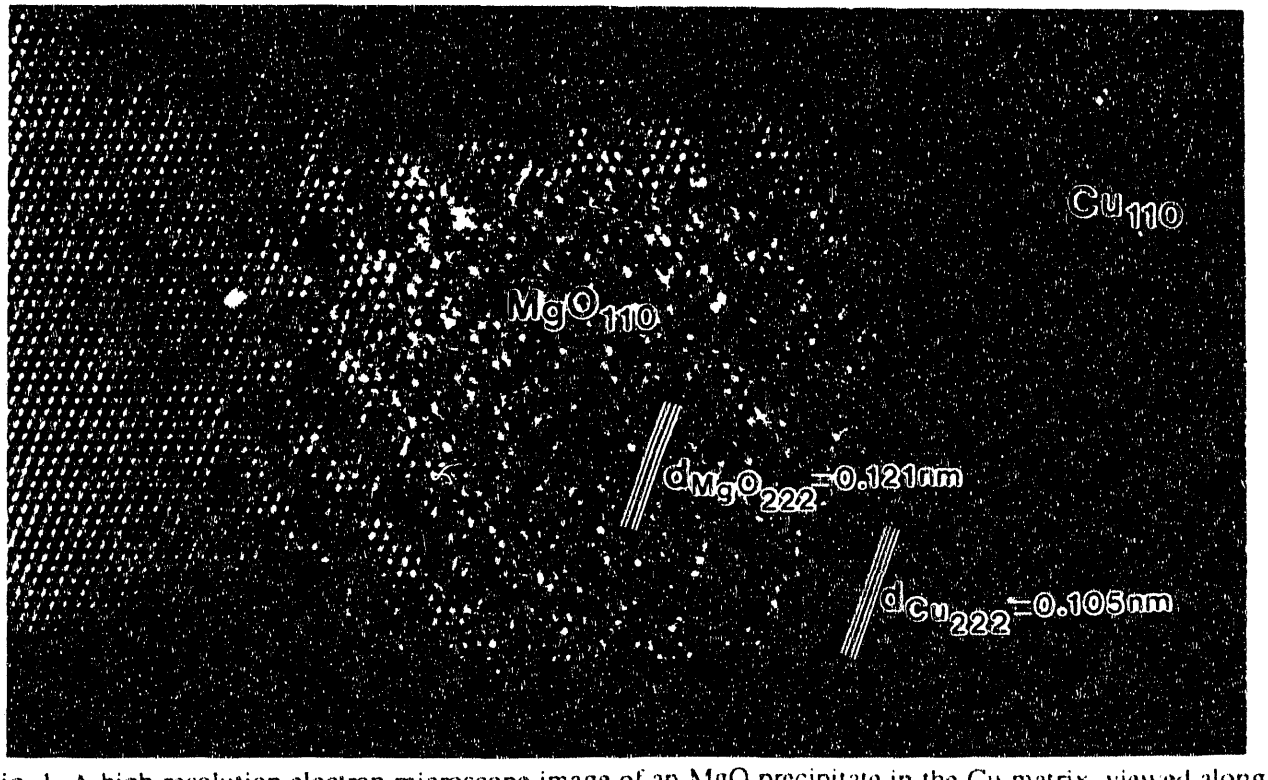

Fig. 1. A high resolution electron microscope image of an MgO precipitate in the Cu matrix, viewed along a common <110> zone axis (defocus value = 65.1 nm at 300 kV). Note that the MgO precipitate is faceted on the {111} planes, and that the truncation of the MgO precipitate by {110} planes results in a hexagonal -shaped image.

cube-on-cube orientation relation between the matrix and the precipitates, as found in previous investigations [5,14]. The shape of an MgO precipitate in a HREM image, however, depends on the orientation of the precipitate since the truncation of an octahedral-shaped precipitate appears differently in a two-dimensional projection [13]. Thus the HREM image for a <100> common direction shows a square shape, instead of a diamond shape as occurs for a <110> direction [15]. The HREM image also exhibits misfit dislocations at the interface between MgO and the Cu matrix. The spacing between misfit dislocations is approximately 1.67 nm, and the lattice misfit is accommodated by a combination of localized misfit dislocations and elastic straining at {111} interfaces [13]. It is interesting to note that in spite of the large value of the misfit parameter (η = 14.83%) the precipitate is semicoherent with the matrix.

For an atomic scale chemical analysis of a Cu/MgO {111} interface, the sharply pointed tip was prepared via electropolishing. The MgO precipitates demonstrate directional consistency with respect to the axis of the wire. The axial direction of the wire turned out to be along the <111> direction as determined by TEM tilting experiments, and it is a preferred axial orientation in FCC materials after drawing. The same specimen is transferred to the APFIM for chemical analysis of a {111} interface [15]. Figure 2 is an FIM micrograph showing an MgO precipitate in the well developed Cu matrix. The approximate diameter of the precipitate is 7.3 nm. The specimen is analyzed by APFIM parallel to the {111} plane of the Cu matrix, until the probe hole passes the interface between the Cu matrix and an MgO precipitate. Figure 3 shows an integral profile of the cumulative number of Mg and O ions versus the cumulative number of Cu plus Mg plus O ions. It was obtained by performing a random analysis along a <111> direction of the Cu matrix. It is seen from this integral profile that the matrix is essentially pure Cu up to the Cu/MgO {111} interface. Note carefully that the outer most {222} plane of ions of the MgO precipitate consists solely of oxygen ions, and the second {222} plane consists solely of Mg atoms. This specimen failed catastrophically after the second {222} plane of the MgO had been field evaporated. The depth resolution of the integral profile is equal to the interplanar spacing along the <111> direction in the MgO precipitate -- 0.121 nm. The crystal structure of MgO is NaCl type (rock-salt structure) and the composition of point defect free {222} planes alternates from 100 at.% oxygen to 100 at.% magnesium as one travels along a <111> direction from the Cu matrix to a common <111> direction in the MgO precipitate. Thus the experimental results for this precipitate demonstrate directly -- that is, without deconvolution -- that the bonding across a Cu/MgO {111} interface has the sequence CuIOIMg -- and **not** CuIMgIO.

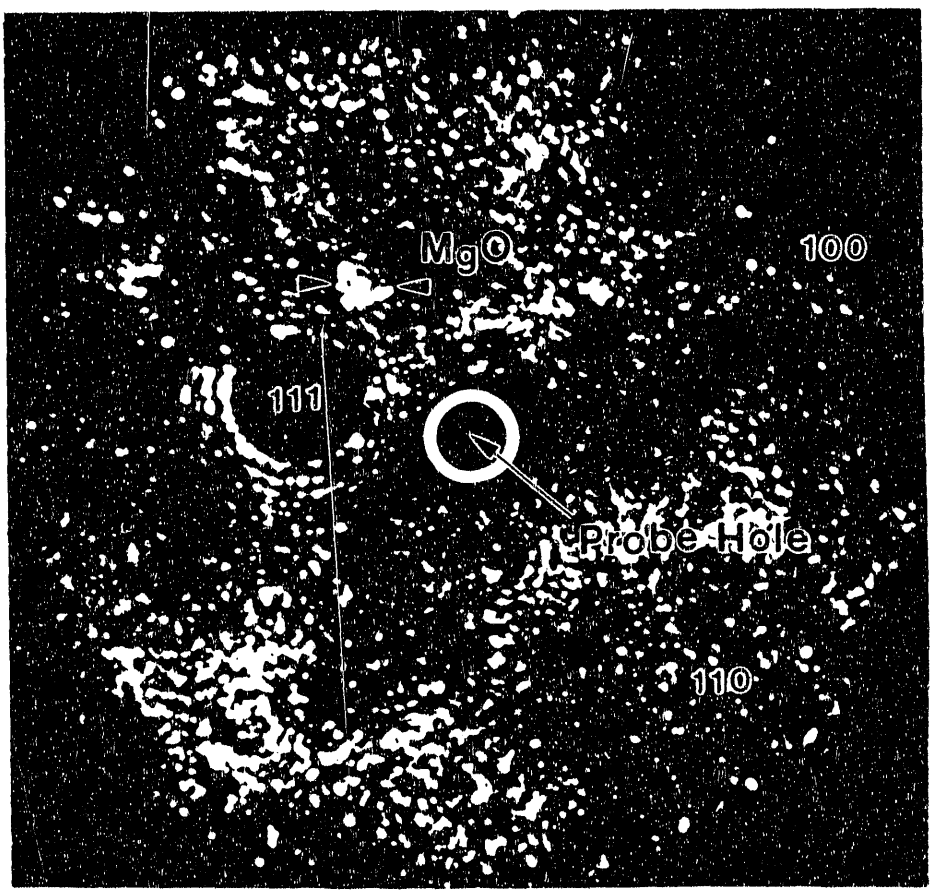

Fig. 2. A field-ion microscope image of an MgO precipitate in a Cu matrix. The diameter of the MgO precipitate in this figure is approximately 7.3 nm. The Ne gas is at $6 \cdot 10^{-6}$ Torr and the tip temperature is 40 K.

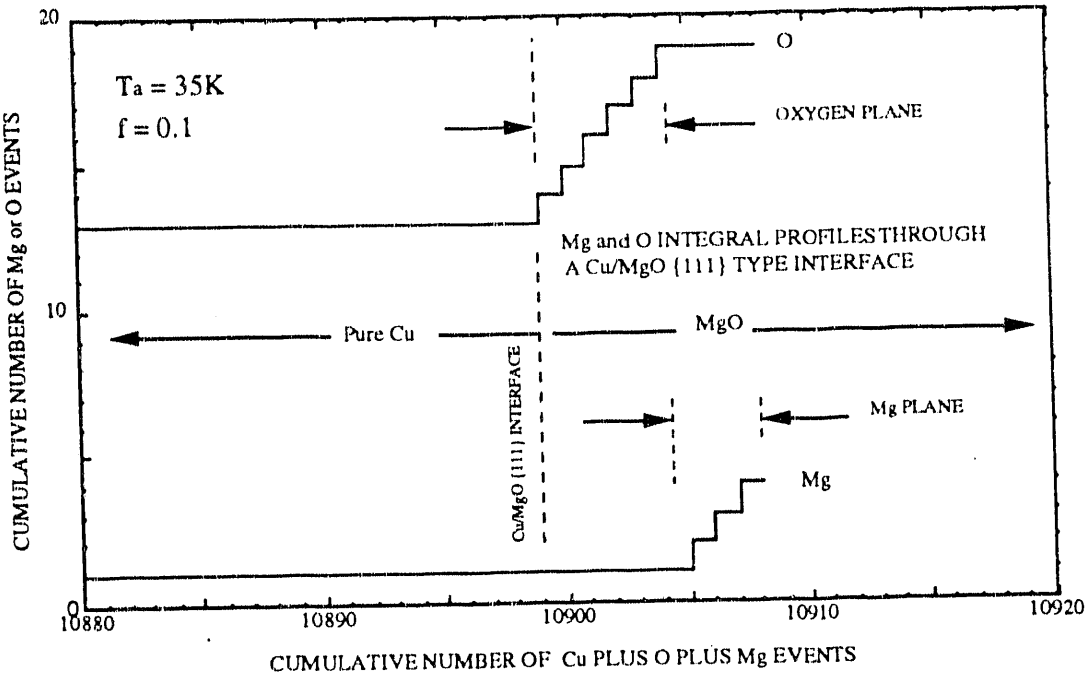

Fig. 3. Integral profiles across a Cu/MgO {111} interface detected during a random area analysis along a <111> direction. The data were collected for a specimen temperature of 35 K, a pulse fraction of 0.1, a pulse frequency of 15 Hz, and a background pressure of $8 \cdot 10^{-11}$ Torr. The Cu signal -- not exhibited -- disappears at the Cu/MgO {111} interface and then the signal is 100 at.% oxygen until that {222} plane has been completely removed by the field evaporation process, and then the next {222} plane is found to be 100 at.% magnesium.

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