The Chemical Composition of a Metal/Ceramic Interface on an Atomic Scale: The Cu/MgO {111} Interface

H. JANG AND D.N. SEIDMAN

Northwestern University, Department of Materials Science and Engineering and the Materials Research Center, Robert R. McCormick School of Engineering and Applied Science, Evanston, IL 60208

K.L. MERKLE

Argonne National Laboratory, Materials Science Division, Building 212, Argonne, IL 60439

Received September 28, 1992; Revised November 30, 1992.

Keywords: Metal/ceramic interface, internal oxidation, Cu/MgO heterophase interface, high resolution electron microscopy, atom-probe field-ion microscopy.

Abstract. The chemical composition profile across a Cu/MgO {111}-type heterophase interface, produced by the internal oxidation of a Cu(Mg) single-phase alloy at 1173 K, is measured via atom-probe field-ion microscopy with a spatial resolution of 0.121 nm; this resolution is equal to the interplanar spacing of the {222} MgO planes. In particular, we demonstrate directly that the bonding across a Cu/MgO {111}-type heterophase interface, along a $\langle 111 \rangle$ direction common to both the Cu matrix and an MgO precipitate, has the sequence Cu|O|Mg... and *not* Cu|Mg|O...; this result is achieved *without* any deconvolution of the experimental data. Before determining this chemical sequence, it was established, via high-resolution electron microscopy, that the morphology of an MgO precipitate in a Cu matrix is an octahedron faceted on {111} planes with a cube-on-cube relationship between a precipitate and the matrix; that is, $\{111\}_{\text{Cu}} // \{222\}_{\text{MgO}}$ and $\langle 110 \rangle_{\text{Cu}} // \langle 110 \rangle_{\text{MgO}}$.

1. Introduction

Metal/ceramic heterophase interfaces are currently receiving a great deal of experimental attention because they are omnipresent in a wide range of materials and structures [1–6]; for example, metal matrix composites with ceramic fibers [7], metal/ceramic nanocomposites [8], machinable ceramics, metallization of microelectronics circuit structures [9], semiconductor devices, oxide scales on metals [10], and dispersion-hardened alloys [11]. The cohesive energies of metal/ceramic interfaces have also been the focus of much theoretical effort, as ultimately the behavior of a metal/ceramic heterophase interface in service is determined by

how well these rather disparate materials adhere to one another [12–14]. In particular, on the experimental side, a great deal of energy has been expended employing high-resolution electron microscopy (HREM) to determine the terminating plane on the oxide side of metal/metal oxide heterophase interfaces by comparing HREM micrographs with micrographs computed using image-simulation techniques [15–17].

In this paper we present the results of a different approach for studying the chemical character of metal/ceramic heterophase interfaces. We employ atom-probe field-ion microscopy (APFIM) to ascertain directly—on an atomic scale—the chemical compositions of individual atomic planes in traversing Cu/MgO {111}-type

interfaces that are produced by internally oxidizing [18–25] a Cu(Mg) single-phase alloy. This is a particularly interesting metal/ceramic interface, as it involves the bonding of a noble free-electron metal (Cu) to a strongly heteropolar metal oxide (MgO). The calculated lattice misfit parameter (η) is 0.1483 for the Cu/MgO system. The heterophase interfaces formed by internal oxidation of a Cu(Mg) alloy have the following important advantages: 1) Impurity atom segregation is essentially nil—our atom probe observations substantiate this point—because of the large total interfacial area per unit volume; 2) common low-index directions between the MgO precipitates and the matrix are present that have interplanar spacings suitable for HREM; and 3) all the MgO precipitates that form have a simple octahedral shape bounded by the low-index $\{222\}$ planes. The APFIM technique is used to both supplement and complement transmission electron microscopy (TEM) and HREM observations of the same interface. Using APFIM, we demonstrate in a direct manner—without data deconvolution—that the bonding across a Cu/MgO $\{111\}$ -type interface, along a common $\langle 111 \rangle$ direction, has the bonding sequence Cu|O|Mg... and *not* Cu|Mg|O...; the spacing between the $\{222\}$ planes of MgO is 0.121 nm, and this is the APFIM spatial resolution of a composition profile along a $\langle 111 \rangle$ direction.

2. 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 high-purity graphite crucible covered with a loose-fitting graphite cap; the copper was placed on top of the magnesium in the graphite crucible to confine the magnesium vapor during melting of the two elements. Prior to using the high-purity graphite crucible, it was heated for 4 hours at 1473 K under high-vacuum conditions. The covered graphite crucible, containing the copper and magnesium charge, was placed in a quartz tube and evacuated to $1.3 \cdot 10^{-2}$ Pa, and the quartz tube was backfilled with argon gas and sealed. The small cylindrically shaped

Cu(Mg) ingots produced in this manner each weighed approximately 26 g. 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 at 1173 K [26]. The ingots were rolled into 125- μ m thick sheets for transmission electron microscopy (TEM) and HREM studies, or drawn into 152- μ m diameter wires for APFIM studies.

Cu/MgO internal interfaces were formed by internally oxidizing those alloy specimens utilizing the Rhines pack method [20, 21]; this pack consists of a powder mixture of Cu plus Cu₂O plus Al₂O₃ (1:1:1 by volume), which is heated in a partial pressure of oxygen equal to the decomposition pressure of cuprous oxide, approximately $P_{O_2} < 10^{-2}$ Pa [21]. Figure 1 exhibits the root-mean squared-diffusion distance ($\sqrt{\langle X^2 \rangle}$) of the oxygen diffusion front (in cm) versus time (in min.) for several internal oxidation temperatures and two different Mg concentrations—0.7 and 2.8 at.% Mg—for a plate geometry. This plot was created from the experimental data presented in [21]. Figure 1 demonstrates that the time required for complete internal oxidation increases as the Mg concentration increases from 0.7 to 2.8 at.% Mg. This data also demonstrates that the time for the complete internal oxidation is about 1800 s for the foil thickness we employ, at 1173K, for the 2.8 at.% Mg alloy. The time required to internally oxidize a cylinder completely is approximately 50% of the time to achieve the same condition for a plate [27]. Therefore, an 1800 s treatment results in the complete internal oxidation of the 152- μ m diameter wires with 2.8 at.% Mg. 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 ($> 5 \cdot 10^{21} \text{ m}^{-3}$) of small-diameter precipitates (< 20 nm). There are several parameters that control the number density and the size of the precipitate in the process of internal oxidation. They are the composition of an alloy, the oxidation temperature, and oxidation time. From kinetic studies of internal oxidation, it is known that the mobility of oxygen, and the difference in the chemical affinity

Fig. 1. A plot of the root mean-squared diffusion distance ($\sqrt{\langle X^2 \rangle}$) in cm for the oxygen diffusion front versus time (min.) in Cu(Mg) alloys for two different Cu(Mg) alloys—0.7 and 2.8 at.% Mg. The curves were calculated employing data given in [21].

of oxygen for an alloying element and a matrix element are the main controlling factors in determining the number density and diameter of metal oxide precipitates. A series of experiments were carried out to obtain a suitable precipitate diameter and number density by varying those parameters. The optimum conditions for combined TEM/APFIM experiments were found to be a Cu-2.8 at.% Mg alloy, an internal oxidation temperature of 1173 K, and an oxidizing time of 1800 s for both the thin sheets and wires.

For the TEM and HREM studies 3-mm diameter disks were 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 was used to prepare electron transparent thin regions. The APFIM specimens were electropolished to a sharply pointed tip with a radius of curvature ranging from 20 nm to 80 nm, 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 was used to electropolish the wire-shaped specimens, and the electrolyte was placed in the loop to form a meniscus [28]. To examine the wire-shaped specimens by TEM, a specially fabricated double-tilt stage was em-

ployed for an Hitachi 700H 200 kV electron microscope [28]. 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 any stage of the electropolishing procedure [28].

3. Transmission Electron Microscope Results

First, conventional TEM is used to determine both the number density and size distribution of MgO precipitates in order to be certain that a precipitate is found in the small volume—approximately 10^{-21} m^3 —of an FIM tip, during the course of a pulsed-field evaporation dissection of a tip of an FIM specimen on an atom-by-atom basis. Figure 2(a) is a dark-field TEM micrograph of MgO precipitates in an internally oxidized Cu-2.8 at.% Mg alloy. Note the typical “coffee-bean” strain-field contrast effects, and the line of no-contrast perpendicular to the operating reflection g_{020} [29]. The contrast variations from precipitate to precipitate are due to the depth oscillations with the position of a precipitate in a thin foil [30]. Figure 2(b) is a bright-field micrograph in a multibeam [100] zone-axis condition. A precipitate imaged under

Fig. 2. (a) A dark-field transmission electron micrograph of MgO precipitates in a Cu matrix produced by internal oxidation of a Cu-2.8 at.% Mg alloy. The operating reflection is 020 (g_{020}), and the precipitates exhibit classical “coffee-bean” strain-field contrast. The line of no contrast is perpendicular to g_{020} . (b) A bright-field transmission electron micrograph of MgO precipitates in a Cu matrix along a [100] zone axis with a number of reflections excited—this is a so-called multibeam micrograph.

multibeam conditions reveals the shape of a precipitate without severe strain-field contrast and allows a rough estimate of the precipitate size [31]. The actual diameter of an MgO precipitate is difficult to estimate precisely from the micrographs exhibited in figure 2, since the observed shape and amount of strain-field contrast depend strongly on the diffraction conditions [29].

The moiré fringe method is a more reliable measure of the exact dimensions of a precipitate [32]. Figure 3 displays a TEM micrograph of faceted MgO precipitates, viewed along a [123] direction, that exhibit parallel $(11\bar{1})$ moiré fringes. The moiré fringe spacing is 1.5 nm, and the average diameter of the precipitates studied by this technique is 16.2 nm, with a quite broad size distribution [33].

To determine the number density of MgO precipitates, a wire specimen is used, since this simplifies the calculation of the volume corresponding to the area observed. From TEM micrographs of a wire specimen (shown in figure 10 in detail), we determined that the number density of precipitates is approximately $5 \cdot 10^{21} \text{ m}^{-3}$; this number density is high enough for the precipitates to be readily detected in the tip of an FIM specimen.

4. High-Resolution Electron Microscope Results

To investigate the atomic scale structure of a Cu/MgO {111}-type heterophase interface, and to ascertain its geometric shape, HREM observations were performed on Cu-2.8 at.% Mg specimens that had been internally oxidized, as described in section 2. 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; its calculated value is 0.1483 for $a_{\text{Cu}} = 0.362 \text{ nm}$, and $a_{\text{MgO}} = 0.42 \text{ nm}$. Axial illumination in an Hitachi H9000 HREM allows the direct observation of the configuration of atoms near an internal interface when proper operating conditions are met [34]. The high-resolution micrographs now discussed demonstrate that the MgO precipitates have an octahedral shape, with a cube-on-cube relation on the {111} planes. First, figure 4 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 the MgO precipitate and the Cu matrix. The 0.21 nm interplanar spacing of the (200) planes of this MgO precipitate, and the 0.181 nm interplanar spacing of the (200) planes of the copper matrix are indicated. Note that the projection of this precipitate on the (100) plane is an approxi-

Fig. 3. A $(11\bar{1})$ moiré fringe pattern of a faceted MgO precipitate with the image plane close to (123) . The operating reflection for this micrograph is $11\bar{1}(\mathbf{g}_{11\bar{1}})$. The shape of the fringes represents the shape of the precipitate viewed along a $[123]$ direction. The strain-field contrast pattern near the MgO precipitates displays a different shape compared to the pattern seen in Fig. 2; this demonstrates that the contrast changes according to the orientation of the specimen relative to the electron beam.

mately square-shaped figure; two of the sides are, however, slightly curved—the rounding effect at the corners is probably due to the anisotropy of the interfacial free energy on a Wulff plot [35]. The truncation of an octahedron by the $\{100\}$ -type planes gives rise to squares of different dimensions; this is the truncation due to the intersection with the surfaces of the specimen. Second, figure 5 is a HREM image (defocus value of 65.1 nm at 300 kV) recorded employing a common $[110]$ zone axis for an MgO precipitate in a Cu matrix. This micrograph shows quite clearly that the projection of this precipitate on a (110) plane has an hexagonal-shape, although it is not a perfect hexagon because of moiré thickness effects resulting from the inclined $\{111\}$ planes; the hexagonal shape arises from the truncation of an octahedron by $\{110\}$ -type surfaces, when they do not pass through its apex. The 0.242 nm interplanar spacing of the (111) planes of this MgO precipitate, and the 0.209 nm interplanar spacing of the (111) planes of the copper matrix are indicated. The diameter of this MgO precipitate is 10 nm. Third, figure 6 is an HREM image (defocus value of 44

Fig. 4. A high-resolution electron microscope image of an MgO precipitate in the Cu matrix viewed along a $[100]$ zone axis; the defocus value is 69.4 nm at an operating voltage of 300 kV. The 0.21 nm interplanar spacing of the (200) planes in the MgO precipitate is indicated on the precipitate, and the 0.181 nm interplanar spacings of the (200) planes in the Cu matrix is indicated on it. The atomic columns in both the precipitate and the matrix exhibit the same crystallographic orientation relationship—the cube-on-cube orientation.

nm), also recorded employing a common $[110]$ zone axis, and exhibiting a diamond-shaped MgO projection on the (110) plane; this shape is a result of the truncation of an octahedron by a $\{110\}$ -type surface passing through its apex. To illustrate these observations, figure 7 displays the octahedral shape of an MgO precipitate, as deduced from the HREM images, with the major crystallographic planes indicated. This figure also includes the possible two-dimensional projections of an octahedron created by $\{001\}$ or $\{110\}$ surface truncations. The $\{111\}$ -type faceted planes seen in figures 4 to 7 can be made even flatter by a post-internal-oxidation annealing treatment under high-vacuum conditions [34, 36]. The number density, however, is lower, and the precipitate diameter greater—30 to 300 nm—when this post-internal-oxidation treatment is employed; therefore, we restricted the present experiments to short internal oxidation times; no post-vacuum annealing treatments were employed. Those HREM images

Fig. 5. A high-resolution electron microscope image of an MgO precipitate in the Cu matrix viewed along a common [110] zone axis; the defocus value is 65.1 nm, and the operating voltage is 300 kV. The MgO precipitate is faceted on {222}-type planes, and the truncation of the MgO precipitate by (110) surfaces of the specimen results in a hexagonal-shaped image. This is additional evidence for a cube-on-cube orientation relation between the two phases. The 0.242 nm interplanar spacing of the (111) planes in the MgO precipitate is indicated on the precipitate, and the 0.209 nm interplanar spacings of the (111) planes in the Cu matrix is indicated on it.

also demonstrate that the orientation relationship is cube-on-cube¹ with the Cu matrix, as found in previous investigations [17, 34, 36], with an octahedral-shaped precipitate that is faceted on {111} planes.

Figure 8 is an HREM micrograph recorded employing a common [110] zone axis (defocus value of 65.1 nm at 300 kV) that exhibits misfit dislocations at the interface between an MgO precipitate and the Cu matrix. The average spacing between the observed misfit dislocations is approximately 1.32 nm, as estimated from figure 8. Thus the lattice misfit between the MgO precipitate and the Cu matrix appears to be accommodated almost completely by localized misfit dislocations; although some residual elastic straining may also be present at Cu/MgO {111}-type interfaces. It is interesting to note that in spite of the large value of η (14.83%) the

Fig. 6. A high-resolution electron microscope of an MgO precipitate in the Cu matrix viewed along a common [110] zone axis; defocus value is 44 nm, and the operating voltage is 300 kV. The truncation of an MgO precipitate by (110) surfaces of the specimen results in a diamond-shaped image, as is expected when (110) planes pass through the apex of an octahedron.

precipitate is semi-coherent with the matrix [34, 36]. Since the interface contains a 2-[D] hexagonal network of misfit dislocations that would, in general, be inclined to the viewing direction, a detailed contrast analysis would be necessary to determine the degree of misfit localization. The spacing between misfit dislocations (S_D) is given by $|\mathbf{b}|/\alpha$, where $\mathbf{b}$ is the Burgers vector of the edge dislocations in Cu (0.256 nm), and α is the fractional lattice parameter mismatch with respect to Cu (0.16). Thus, the value of S_D in the {111}-type plane is 1.6 nm along a $\langle 110 \rangle$ -type direction. The projection of this S_D onto the {110}-type plane, along $\langle 112 \rangle$ -type direction, is given by $\sqrt{3}/2$ and is equal to 1.38 nm.² Therefore, the fractional difference between the calculated misfit dislocation spacing (1.38 nm) and the observed spacing (≈ 1.32 nm) is small.

Figure 9 demonstrates the atomic mismatch across a Cu/MgO {111} heterophase interface using a hard-sphere model. Misfit dislocations appear in this hard-sphere model at approximately the correct spacing, without employing atomic relaxations, as expected, since six interatomic distances in MgO correspond (within

Fig. 7. A schematic drawing of an MgO precipitate with the major crystallographic directions indicated. The precipitate has an octahedral shape, and is faceted on $\{111\}$ planes. The relationship between the MgO precipitate and the Cu matrix is cube-on-cube. It also shows possible two-dimensional projections of an octahedrally shaped MgO precipitate by a series of truncations: (a) truncated by $\{001\}$ specimen surfaces; (b) truncated by $\{110\}$ specimen surfaces.

0.56%) to seven interatomic distances in copper. This is clearly seen in figure 9, which is a side view of the Cu/MgO $\{111\}$ heterophase interface along a $\langle 110 \rangle$ direction.

5. Atom-Probe Field-Ion Microscope Results

For a chemical analysis of a Cu/MgO $\{111\}$ -type interface, a sharply pointed atom-probe spec-

Fig. 8. A high-resolution electron microscope image exhibiting a semicoherent interface between an MgO precipitate and the Cu matrix. The presence of misfit dislocations at an interface is indicated by black arrows. The average distance between misfit dislocations is estimated to be approximately 1.32 nm from this micrograph. The image was recorded with a common $[110]$ zone axis at a defocus value of 65.1 nm, and an operating voltage of 300 kV.

imen with a tip radius of approximately 65.8 nm, in the region of the (111) pole, is employed. Figure 10 is a TEM micrograph of an FIM specimen containing MgO precipitates. From this TEM micrograph, it is seen that the FIM specimen contains 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 [37]; it is noted, however, that recrystallized Cu can exhibit several different textures— $[100]$, $[111]$, $[112]$ —depending on the amount of plastic reduction, the alloying element, and annealing temperature [37]. Note that the number density of MgO precipitates is high enough that the pulsed field-evaporation of this specimen is likely to result in the random intersection of the surface of the FIM tip with a precipitate. This is a crucial point, since if the number density of precipitates is not high enough then the probability of finding an MgO precipitate in the volume of

Fig. 9. Hard-sphere model of a heterophase interface between Cu and MgO. An open circle represents an atom in the first $\{110\}$ and a circle with an X sign in its centre represents an atom in the second $\{110\}$ plane (side view). The black arrows indicate the presence of the geometrically necessary misfit dislocations.

an FIM tip is essentially nil. Alternatively, it is possible to use a combination of TEM and careful electrochemical backpolishing techniques to place a preselected metal oxide precipitate in the field-of-view of a field-ion microscope image [28, 38].

Figure 11 is a schematic drawing illustrating the relationship between an MgO precipitate and the chevron ion detector in the atom probe [39a]. The MgO precipitate sits in an FIM specimen such that a $\{222\}$ -type plane is parallel to the channel electron multiplier array containing a circular probe hole; that is, for instance, a (222) bounding plane of an octahedral-shaped MgO precipitate is parallel to a (111) plane of the Cu matrix. The distance from the probe hole to the FIM is typically between 4 and 6 cm, and the distance from the FIM tip to the chevron ion detector is approximately 2.24 m; the chevron ion detector consists of two channel electron multiplier arrays in series to yield a gain of $\approx 10^6$ for a single ion [39b]. The projected diameter of the probe hole on the surface of the FIM tip is varied by changing the distance between the FIM specimen and the channel electron multiplier array [39a]. In the cases to be discussed (see figures 12 to 16), this distance was adjusted such that the projected diameter of the probe hole is less than the diameter of a precipitate. A pulsed

Fig. 10. A transmission electron micrograph of a Cu field-ion microscope specimen containing a high number density of MgO precipitates. The MgO precipitates are all aligned in the same direction with respect to the matrix—that is, along a $\langle 111 \rangle$ -type direction; thus, a $\{111\}$ -type plane of a MgO precipitate is parallel to a corresponding $\{111\}$ -type plane of the Cu matrix.

dissection process consists of applying a series of pulse voltages (V_p) on top of a steady-state imaging voltage (V_{dc}), as this results in the dissection of a specimen on an atom-by-atom basis; pulsed field-evaporation is a highly controllable process that has been successfully employed to observe individual point defects—vacancies and self-interstitial atoms—in the bulk of specimens [40], as well as small precipitates in metal alloys [41–45]. As illustrated in figure 11, all the atoms in the cylinder of material with the diameter D are analyzed—that is, their mass-to-charge state ratios are determined—on an atom-by-atom basis. For the geometry illustrated in figure 11, *no* matrix correction to the composition of a precipitate is required; alternatively, if the diameter of a precipitate is smaller than the projected diameter of the probe hole on a precipitate, then there is a *potential* correction to a precipitate's composition. In the case of MgO precipitates, there is no solid solubility of Cu in MgO; hence, even if Cu is detected while dissecting a precipitate, this is Cu from the matrix and not from the precipitate; the problem of a possible matrix contribution to a precipitate has been dealt with in some detail elsewhere [46].

The same specimen exhibited in figure 10 was transferred to our atom probe for a chemical analysis of a $\{111\}$ -type interface. Figure 12 is an FIM micrograph exhibiting an MgO precipitate in the Cu matrix. The heterophase interface of the MgO precipitate is parallel to the (111) planes of the Cu matrix; this is consistent with the HREM observations, and it also implies that

Fig. 11. The geometry employed for analyzing a Cu/MgO interface, with the plane of the channel electron multiplier array containing the probe hole parallel to a $\{222\}$ plane of the MgO precipitate. The projected diameter of the circular probe hole on the surface of the field-ion microscope tip is indicated by the letter D. The pulsed field-evaporated ions pass through the probe hole in the channel electron multiplier array on their journey to the chevron ion detector; the latter consists of two channel electron multiplier arrays in series with an overall gain of 10^6 for an individual ion. The distance from the field-ion microscope tip to the channel multiplier array is typically between 4 cm and 6 cm, while the distance to the chevron ion detector is ≈ 2.24 m. The APFIM spatial resolution of a composition profile across a Cu/MgO $\{111\}$ interface—along a common $\langle 111 \rangle$ direction—is determined by the interplanar spacing of the $\{222\}$ planes of an MgO precipitate—0.121 nm. This schematic diagram is *not* to scale.

the exposed plane of the precipitate is a $(222)_{\text{MgO}}$ plane. The approximate diameter of this precipitate is 7.3 nm.³ Note the projection of the probe hole onto the FIM image at approximately 10 o'clock near the 111 pole. Figure 13 is a series of FIM micrographs recorded at various stages of a pulsed field-evaporation dissection sequence of this MgO precipitate; the actual dissection process is on an atom-by-atom basis, and these six FIM images are simply representative of this process. Image 1 is at the beginning of the pulsed-field dissection process of this precipitate, and by image 6 the MgO precipitate has been completely removed; the black arrow heads point at the MgO precipitate. It is emphasized that both the MgO precipitate and the Cu matrix are simultaneously removed by this technique—see figure 11. Also note that individual atoms within the MgO precipitate are resolved at different stages of its dissection; furthermore, the

Fig. 12. A field-ion microscope image of an MgO precipitate in a Cu matrix. The plane of the MgO precipitate is parallel to the (111) planes of the Cu matrix. The diameter of the MgO precipitate in this figure is approximately 7.3 nm. The Ne gas is at $8 \cdot 10^{-4}$ Pa gauge pressure, and the tip temperature is 40 K.

precipitate exhibits well-developed contrast features outlining its atomic scale geometry.

Figure 14 is a histogram of the number of events versus the mass-to-charge state ratio of a Cu specimen containing an MgO precipitate; the ordinate is a logarithmic scale, while the abscissa is a linear scale. This mass spectrum is dominated by the Cu peaks due to the presence of both singly (Cu^{1+}) and doubly (Cu^{2+}) charged Cu ions; the two peaks for each charge state are due to the two naturally occurring isotopes of Cu with the masses 63 and 65 amu. Also note the presence of singly and doubly charged O ions—those peaks are due to the isotope with the mass 16 amu—as well as singly charged Mg ions from an MgO precipitate. The presence of a peak due to singly charged hydrogen ions is also present; this peak is from the ambient pressure in the atom probe. This atom-probe analysis was performed at a background pressure of $1.2 \cdot 10^{-8}$ Pa and a constant tip temperature of 35 K.

For the analysis of a specimen containing MgO precipitates, the pulse fraction (f)—the ratio of

Fig. 13. A series of FIM images showing the pulse dissection of a specimen containing a 7.3 nm diameter MgO precipitate in a Cu matrix; the (222) plane of the MgO precipitate is parallel to the (111) planes of the Cu matrix. Individual atoms within a (222) plane of the MgO precipitate are resolved during the course of this pulsed dissection process. These six micrographs were recorded at various stages of the pulsed dissection process, and the actual dissection is on an atom-by-atom basis. The Ne gas is at $8 \cdot 10^{-4}$ Pa gauge pressure, and the tip temperature is 40 K.

Fig. 14. An atom-probe field-ion microscope mass spectrum of an internally oxidized Cu/MgO specimen. The ordinate is the number of events plotted on a logarithmic scale, while the abscissa is the mass-to-charge state ratio of the pulsed field-evaporated ions. This spectrum was recorded at a background pressure of $1.2 \cdot 10^{-8}$ Pa employing a pulse fraction (f) of 0.1; f is the ratio of the pulsed field-evaporation voltage (V_p) to the steady-state voltage (V_{dc}) on a field-ion microscope specimen. The hydrogen ion signal is from the background pressure in the atom probe.

V_p to V_{dc} —is maintained at 0.1, and a pulse frequency of 15 Hz is used to dissect the specimen on an atomic scale [39, 46, 47]. The detection efficiency—that is, the ratio of the ions detected to the number of field-evaporation pulses—is maintained at a constant value of 0.0062, via software in our fully computer-controlled (Macintosh II fx) APFIM [39]; the value of V_{dc} is automatically increased by 10 V_{dc} for every 1,000 field-evaporation pulses if *no* event is detected. This highly controlled procedure results in the continuous and smooth dissection [39, 46, 47] of a series of (111) planes, as well as other planes on the surface of the approximately hemispherical FIM tip. The central (111) plane exhibited in figure 12 is placed under the probe hole, and the ions collected therefore correspond to a “boring” along a [111] direction. For this geometry the APFIM spatial resolution of a composition profile across a Cu/MgO (111) interface is determined by the interplanar spacing of the (222) planes of an MgO precipitate. 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 a small number of atoms [47–50].

Figure 15 is an integral profile of the cumulative number of Mg or O ions versus the cumulative number of Cu plus Mg plus O ions [51]. It was created by performing a random area analysis along the [111] direction of the Cu matrix. The Cu signal on the ordinate is omitted for clarity because of the large difference between its value and the Mg or O values. The projected diameter of the probe hole on the tip is smaller than the diameter of the MgO precipitate uncovered; this implies that no correction to the data is required [46]. It is seen from this integral profile that the matrix is essentially pure Cu up to the Cu/MgO (111) interface; 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 concentration of $\approx 10^{-3}$ at. fr. oxygen; in addition, only one Mg event was detected for a bulk concentration of $\approx 9 \cdot 10^{-5}$ at. fr. magnesium. Note carefully that 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 APFIM depth resolution of this integral profile is equal to the interplanar spacing along the [111] direction in the MgO precipitate— $d_{222} = a_{\text{MgO}}/(2\sqrt{3}) = 0.121$ nm. The crystal structure of MgO is NaCl-type (rock-salt structure), and, therefore, the compositions of point-defect free (222) planes alternate 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 (see figures 9 and 11). Thus, the experimental results for this precipitate demonstrate directly—that is, *without* data deconvolution—that the bonding across a Cu/MgO (111) interface has the sequence Cu|O|Mg|... and *not* Cu|Mg|O|.

Figure 16 is an integral profile along a [111] direction across a Cu/MgO (111) interface in another octahedral-shaped MgO precipitate. In this case, no Mg events were detected in the matrix, while 7 oxygen events were detected out of a total of 815 events, and this implies a bulk concentration of $<10^{-3}$ at. fr. magnesium and $8.6 \cdot 10^{-3}$ oxygen. Once again, there is an abrupt transition from an essentially pure Cu matrix to a (222) plane in the precipitate that is 100 at.% oxygen, and the second (222) plane is 100 at.% magnesium (again the tip failed catastrophically). The depth resolution is 0.121 nm for this profile, just as it is in figure 15. Thus, once again, the experimental results for this precipitate demonstrate directly that the bonding across a Cu/MgO (111) interface has the sequence Cu|O|Mg|... and *not* Cu|Mg|O|....

6. Conclusions and Discussion

1. Three different Cu(Mg) alloys—0.16, 0.7 and 2.8 at.% Mg—were internally oxidized to find an alloy composition, annealing temperature and time that yields a high number density ($5 \cdot 10^{21} \text{ m}^{-3}$) of small (<20 -nm diameter) MgO precipitates.

2. A transmission electron microscope study of internally oxidized field-ion microscope specimens of those alloys demonstrated that the num-

Fig. 15. Integral profiles across a Cu/MgO {111} interface detected during a random area analysis along a [111] direction. The cumulative number of Mg or O ions detected is plotted versus the cumulative number of Cu plus Mg plus O ions detected. 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 $1.2 \cdot 10^{-8}$ Pa. The Cu signal—not exhibited—disappears at the Cu/MgO {111} interface, and the signal is 100 at.% oxygen until that {222} plane has been completely removed by the field-evaporation process; the next {222} plane is found to be 100 at.% magnesium. This result indicates directly that the sequence of {111}-type planes across this heterophase interface is Cu|O|MgO|... The depth resolution for this chemical composition profile is $a_0/(2\sqrt{3})$, 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 have *not* undergone any deconvolution process.

ber density and diameters achieved for the 2.8 at.% Mg alloy are suitable for performing atom-probe field-ion microscope studies to determine the Cu/MgO interfacial chemistry on an atomic scale. The optimum internal oxidation conditions for our experiments are a time of 1,800 s at 1,173 K for the Cu-2.8 at.% Mg alloy.

3. A high resolution transmission electron microscope study of MgO precipitates in a Cu matrix along the [100] or [110] axial directions demonstrates that the precipitates have the morphology of an octahedron with the facets corresponding to {111} planes. The orientation relationship between an MgO precipitate and the Cu matrix is cube-on-cube; that is, $\{111\}_{\text{Cu}} // \{222\}_{\text{MgO}}$ and $\langle 110 \rangle_{\text{Cu}} // \langle 110 \rangle_{\text{MgO}}$.

4. The MgO precipitates are semicoherent with the Cu matrix, even though the lattice misfit parameter (η) is 0.1483; η is given by $2[(a_{\text{MgO}} - a_{\text{Cu}})/(a_{\text{MgO}} + a_{\text{Cu}})]$ where the a 's are the lattice parameters of the two phases. Misfit

dislocations are detected at the Cu/MgO {111}-type heterophase interface, with an average spacing of 1.32 nm. The calculated spacing between the misfit dislocations is 1.38 nm, and since the observed spacing is 1.32 nm, this implies that the fractional difference in these spacings is small. This suggests that the misfit between the MgO precipitate and the Cu matrix is accommodated mainly by dislocations.

5. The MgO precipitates are readily detectable by field-ion microscopy. A recrystallization texture of the Cu wires is fortuitously [111], hence the MgO precipitates sit in a Cu matrix such that a {111}-type facet of the octahedral-shaped precipitates is perpendicular to the [111] fiber axis of the wires. This implies that a random area analysis of the precipitates along a [111] direction, via the pulsed field-evaporation technique, results in the uncovering of Cu/MgO {111}-type heterophase interfaces.

6. The Cu matrix is found, via atom-probe

Fig. 16. Another integral profile across a Cu/MgO {111} interface detected during a random area analysis along a [111] direction. The cumulative number of Mg or O ions detected is plotted versus the cumulative number of Cu plus Mg plus O ions detected. 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 $1.2 \cdot 10^{-8}$ Pa. The Cu signal—not exhibited—disappears at the Cu/MgO interface, and the signal is 100% oxygen until that plane has been completely removed by the field-evaporation process; the next {222} plane is 100% magnesium. This result indicates directly that the sequence of planes across this heterophase interface is Cu|O|Mg...

field-ion microscopy, to be almost 100 at.% Cu, with only trace amounts of oxygen ($<10^{-3}$ at. fr.) and magnesium ($<10^{-4}$ at. fr.) after an internal oxidation treatment. No evidence was found for impurity atoms at the Cu/MgO {111} heterophase interface. This implies that impurity atoms are unnecessary to stabilize the Cu/MgO {111}-type interface.

7. Atom-probe field-ion microscopy analyses reveal that the sequence of atoms across a Cu/MgO {111} interface is Cu|O|Mg|... and *not* Cu|Mg|O|.... Thus, the terminating {222}-type plane for a MgO precipitate in a Cu matrix is oxygen, and not magnesium. This result is achieved *without* any deconvolution of the experimental data. The resolution of the composition profile perpendicular to the interface is equal to the interplanar spacing of the {222}_{MgO}-type planes, and this value is 0.121 nm.

Acknowledgments

This research is supported by the U.S. Depart-

ment of Energy Office of Basic Energy Sciences grant No. DEFG02-89ER45403. It also utilized central facilities of the National Science Foundation funded Materials Research Center at Northwestern University. We wish to thank Drs. X.W. Lin and W.A. Chiou for help with specimen preparation and high-resolution electron microscopy, respectively, and Mr. David Chan for useful discussions. Dr. K.L. Merkle was supported by the U.S. Department of Energy, BES-Materials Science under contract #W-31-109-ENG-38.

Notes

1. That is, $\{111\}_{\text{Cu}}//\{222\}_{\text{MgO}}$ and $\langle 110 \rangle_{\text{Cu}}//\langle 110 \rangle_{\text{MgO}}$.
2. This was calculated for the smallest angle (30°) between a $\langle 110 \rangle$ -type direction and a $\langle 112 \rangle$ type direction.
3. The diameter of a precipitate is calculated by first determining the local radius (R) in the region of the 111 pole, and then calculating a liner distance (λ) on the surface using the Pythagoras formula. The expression for λ is $(2nd_{111}R)^{1/2}$, where n is the number of 111 planes between the 111 pole and a neighboring pole used to determine R , and d_{111} is the interplanar spacing of {111}.

copper matrix planes. The value of λ provides a length scale for measuring a precipitate's diameter.

References

1. *Metal-Ceramic Interfaces: Proceedings of an International Workshop*, edited by M. Rühle, A.G. Evans, M.F. Ashby and J.P. Hirth (Pergamon, Oxford, 1990).
2. *Proceedings of the International Symposium of Metal/Ceramic Interfaces*, edited by W. Mader and M. Rühle, Acta Metall. Mater. **40**, supplement (1992).
3. *Proceedings of the International Congress: Intergranular and Interphase Boundaries in Materials*, Colloq. Phys. (Paris) **51**, Colloque C1, Supplément au No. 1 (1990).
4. *Proceedings of the International Conference on the Structure and Properties of Internal Interfaces*, J. Phys. (Paris) **46**, Colloque C1, Supplément au No. 4 (1985).
5. *Proceedings of the Interface Science and Engineering '87 Conference*, J. Phys. (Paris) **49**, Colloque C5 Supplément au No. 10 (1988).
6. *Proceedings of the International Congress: Intergranular and Interphase Boundaries in Materials*, Thessaloniki, Greece, Materials Science Forum, 126–128 (1993).
7. G. Petzow, T. Suga, G. Elssner and M. Turwitt, in *Sintered Metal-Ceramic Composites*, edited by G.S. Upadhyaya (Elsevier, Amsterdam, 1984), p. 3.
8. H. Gleiter, Nanostructured Mater. **1**, 1 (1992).
9. *Electronic Packaging in Materials Science*, edited by E.A. Geiss, K.N. Tu, and D.R. Uhlmann, Mat. Res. Soc. Symp. Proc. **209** (1985).
10. H. Schmalzried, Ber. Bunsenges. Phys. Chem **87**, 551 (1983); (a) G.L. Kellogg, Surf. Science **171**, 359 (1986).
11. J.L. Meijering and M.J. Druyvesteyn, Philips Research Reports **2**, 81 (1947).
12. A.J. Freeman and Chun Li, in *Metal-Ceramic Interfaces: Proceedings of an International Workshop*, edited by M. Rühle, A.G. Evans, M.F. Ashby and J.P. Hirth (Pergamon, Oxford, 1990), pp. 2–8; (a) Chun Li and A.J. Freeman, Phys. Rev. B **43**, 780 (1991).
13. P. Blöchl, G.P. Das, H.F. Fischmeister and U. Schönberger, in *Metal-Ceramic Interfaces: Proceedings of an International Workshop*, edited by M. Rühle, A.G. Evans, M.F. Ashby and J.P. Hirth (Pergamon, Oxford, 1990), pp. 9–14; (a) U. Schönberger, O.K. Andersen and M. Methfessel, Acta Metall. Mater. **40**, S1 (1992).
14. M.W. Finnis, A.M. Stoneham and P.W. Tasker, in *Metal-Ceramic Interfaces: Proceedings of an International Workshop*, edited by M. Rühle, A.G. Evans, M.F. Ashby and J.P. Hirth (Pergamon, Oxford, 1990), pp. 35–44.
15. R. Gronsky, Ultramicroscopy **24**, 155 (1988).
16. M. Rühle, K. Burger and W. Mader, Microsc. Spectrosc. Electron. **11**, 163 (1986); (a) G. Necker and W. Mader, Phil. Mag. Letts, **58**, 205 (1988); (b) W. Mader, Z. Metallkde. **80**, 139 (1989); (c) W. Mader and B. Maier, Colloq. Phys. (Paris) **51**, Colloq. C1, 867 (1990).
17. W. Mader and G. Necker, in *Metal-Ceramic Interfaces: Proceedings of an International Workshop*, edited by M. Rühle, A.G. Evans, M.F. Ashby and J.P. Hirth (Pergamon, Oxford, 1990), pp. 222–233.
18. C.S. Smith, Min. and Met. **11**, 213 (1930); (a) *idem, ibid.* **13**, 481 (1932); (b) *idem*, J. Inst. Metals **46**, 49 (1931).
19. K.W. Fröhlich, Z. Metallk. **28**, 368 (1936).
20. F.N. Rhines, Trans. AIME **137**, 246 (1940).
21. F.N. Rhines, W.A. Johnson and W.A. Anderson, Trans. AIME **147**, 205 (1942).
22. C. Wagner, Z. Elektrochem. **63**, 772 (1959).
23. G. Böhm and M. Kahlweit, Acta Metall. **12**, 641 (1964); (a) M. Kahlweit, Prog. Chem. Solid State **2**, 134 (1965).
24. R.A. Rapp, Corrosion-Nat. Assoc. Corr. Eng. **21**, 382 (1965).
25. J.L. Meijering, in *Advances in Materials Research*, edited by H. Herman (J. Wiley & Sons, New York, 1971), vol. 5, pp. 1–81.
26. M. Hansen and K. Anderko, *Constitution of Binary Alloys*, 2nd ed. (McGraw-Hill, New York, 1958), pp. 594–596; (a) R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, and K.K. Kelley, *Selected Values of the Thermodynamic Properties of Binary Alloys* (American Society for Metals, Metals Park, Ohio, 1973), pp. 750–755.
27. J.H. Swisher and E.O. Fuchs, Trans. Metall. Soc. AIME **245**, 1789 (1969).
28. B.W. Krakauer, J.G. Hu, S.M. Kuo, R.L. Mallick, A. Seki, D.N. Seidman, J.P. Baker and R.J. Loyd, Rev. Sci. Instrum. **61**, 3390 (1990); (a) B.W. Krakauer and D.N. Seidman, Rev. Sci. Instrum. **63**, 4071 (1992).
29. M.F. Ashby and L.M. Brown, Phil. Mag. **8**, 1083 (1963).
30. M. Wilkens in *Modern Diffraction and Imaging Techniques in Materials Science*, edited by S. Amelinckx, R. Gevers, G. Remaut and J. Van Landuyt (North Holland, Amsterdam, 1970) p. 5.
31. R. Hattenbauer and F. Haider, Scripta Metall. Mater. **25**, 1173 (1991).
32. W. Kesternich, Mat. Res. Soc. Symp. Proc. **62**, 229 (1986).
33. D.J. Pedder, E.D. Boyes, and G.C. Smith, Metal Science J. **12**, 437 (1976).
34. K.L. Merkle, Ultramicroscopy **37**, 130 (1991); in *Metal-Ceramic Interfaces: Proceedings of an International Workshop*, edited by M. Rühle, A.G. Evans, M.F. Ashby and J.P. Hirth (Pergamon, Oxford, 1990), pp. 242–249; K.L. Merkle, M.I. Buckett, and Y. Gao, Acta Metall. Mater. **40**, S249 (1992).
35. C. Herring, in *Structure and Properties of Solid Surfaces*, edited by R. Gomer and C.S. Smith (The University of Chicago Press, Chicago, 1953) Ch. 1; (a) C. Herring, Phys. Rev. **82**, 87 (1951).
36. P. Lu and Cosandey, Acta Metall. Mater. **40**, S259 (1992).
37. C.S. Barrett and T.B. Massalski, *Structure of Metals*, 3rd ed. (McGraw-Hill, New York, 1966), pp. 568–569.
38. B.W. Krakauer and D.N. Seidman, Rev. Sci. Instrum. **63**, 4071 (1992); (a) D. Chan, D.N. Seidman and K.L. Merkle, unpublished research.
39. (a) T.M. Hall, A. Wagner and D.N. Seidman, J. Phys. E: Sci. Instrum. **10**, 884 (1977); (b) J.L. Wiza, Nuc. Instrum. Meth. **162**, 587 (1979).
40. D.N. Seidman, J. Phys. F: Metal Phys. **3**, 393 (1973); (a) A.S. Berger, D.N. Seidman and R.W. Balluffi, Acta Metall. **21**, 123 & 134 (1973); (b) D.N. Seidman, in *Radiation Damage in Metals*, edited by N.L. Peterson

- and S.D. Harkness (American Society for Metals, Metals Park, Ohio, 1976), pp. 28–57; (c) D.N. Seidman, *Mater. Res. Soc. Symp. Proc.* **138**, 315 (1989); (d) D.N. Seidman, *Mater. Res. Soc. Symp. Proc.* **139**, 25 (1989).
41. S.S. Brenner, *Surf. Sci.* **70**, 427 (1978); (a) S.S. Brenner and M.K. Miller, *J. Metals* **35** (3), 54 (1983).
 42. R. Wagner, *Field-Ion Microscopy* (Springer-Verlag, Berlin, 1982), Ch. 4, pp. 80–99.
 43. P. Haasen, *Metall. Trans. A* **16A**, 1173 (1985); (a) P. Haasen and R. Wagner, *Ann. Rev. Mater. Sci.* **15**, 43 (1985).
 44. T. Sakurai, A. Sakai and H.W. Pickering, *Atom-Probe Field-Ion Microscopy and Its Applications* (Academic Press, New York, 1989), chap. 6, pp. 202–235.
 45. D. Blavette and P. Auger, *Microsc. Microanal. Microstruct.* **1**, 481 (1990).
 46. R. Herschitz and D.N. Seidman, *Acta Metall.* **32**, 1141 & 1155 (1984).
 47. S.M. Kuo, A. Seki, Y. Oh, and D.N. Seidman, *Phys. Rev. Lett.* **65**, 199 (1990); (a) J.G. Hu and D.N. Seidman, *Phys. Rev. Lett.* **65**, 1615 (1990); (b) D.N. Seidman, *Mater. Sci. Eng.* **A137**, 57 (1991).
 48. J.G. Hu, Ph.D. thesis, Northwestern University, Evanston, IL (1991).
 49. J.G. Hu and D.N. Seidman, *Scripta Metall. Mater.* **27**, 693 (1992).
 50. B.W. Krakauer, Ph.D. thesis, Northwestern University, Evanston, IL (1993).
 51. H. Jang, D.N. Seidman and K.L. Merkle, *Scripta Metall. Mater.* **26**, 1493 (1992).