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ATOMIC-SCALE STRUCTURE AND CHEMISTRY OF CERAMIC/METAL INTERFACES—II. SOLUTE SEGREGATION AT MgO/Cu (Ag) and CdO/Ag (Au) INTERFACES

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Abstract—The first quantitative measurements of solute segregation at ceramic/metal (C/M) heterophase interfaces are presented for the MgO/Cu (Ag) and CdO/Ag (Au) systems. Interfaces are produced by internal oxidation of ternary alloys. Solute segregation at C/M interfaces is induced by intermediate-temperature annealing treatments. The Gibbsian interfacial excess of solute, Γ_{solute} , at these interfaces is determined in a direct, quantitative manner by atom-probe field-ion microscopy (APFIM). These measurements are complemented in the MgO/Cu (Ag) system by a composition analysis of this interface employing electron energy loss spectroscopy (EELS). Analyses of 15 {222} MgO/Cu (Ag) interfaces by APFIM show an average segregation level of $(4.0 \pm 1.9) \times 10^{14}$ atoms/cm² or 0.22 ± 0.10 effective monolayers at 500°C. Analyses of three {222} CdO/Ag (Au) interfaces show an average segregation level of $(3.0 \pm 1.0) \times 10^{14}$ atoms/cm² or 0.22 ± 0.07 effective monolayers at 400°C. Whereas {222} CdO/Ag (Au) interfaces in unannealed specimens show no evidence of gold segregation. These results are discussed in view of recent models of interfacial segregation. © 1999 Acta Metallurgica Inc. Published by Elsevier Science Ltd. All rights reserved.

Keywords: Atom-probe field-ion microscopy; Electron energy loss spectroscopy (EELS); Binary oxide; Segregation; {222} MgO/Cu (Ag) and {222} CdO/Ag (Au) interfaces

1. INTRODUCTION

As discussed in Part I, ceramic/metal (C/M) interfaces have received a great deal of attention recently. The main effort in most experimental studies has been on observing the interface structure and chemistry and ultimately relating it to the mechanical properties of C/M interfaces. The phenomenon of solute segregation at C/M interfaces, however, has received much less attention. The ubiquity of segregation phenomena in metals and ceramics suggests that solute segregation may play an important role in C/M systems.

In the case of dispersion hardened alloys or internally oxidized alloys, it has been suggested [1, 2] that a large interfacial area of the precipitate phase would diminish the role of segregation. Experimental evidence, however, suggests that in some highly dispersed systems, small amounts of impurity elements or deliberately introduced dopants can dramatically change the morphology of the interfacial region. The effect of segregation on an alloy's properties may be twofold: i.e. segregation may cause strong decohesion at the precipitate/matrix interface and, as a result, loss of

ductility occurs through microvoid coalescence [3]. Conversely, [4], an important effect of solute segregation at a precipitate/matrix interface may be a considerable diminution of the coarsening kinetics, as a result of a shift from volume diffusion to interface controlled coarsening, yielding a much greater thermal stability of the precipitate phase. In 1971, it was found [5] that trace additions of cadmium to an Al–4 at.% Cu alloy can decrease the θ' -phase precipitate coarsening rate by a factor of five. The authors concluded that this effect is due to cadmium segregation at Al/ θ' -phase interfaces; segregation reduces the interfacial energy and, consequently, the coarsening rate, according to the classical Greenwood–Lifshitz–Wagner theory. It took over 20 years before it was proven by APFIM and AEM measurements [6, 7] that in a quaternary Al (Cu, Mg, Ag) alloy, silver and magnesium segregate to the α/Ω interface (the structure of the Ω phase was found to be almost identical to θ') with a concomitant and dramatic slowing of the aging kinetics of this alloy. Similarly, oxygen and phosphorus additions to an iron alloy were found to decrease the growth rate of Fe₄N precipitates [8], presumably as a result of segregation of O and P to Fe₄N/ α -Fe interfaces. It was later found [9, 10] by APFIM analysis that in internally nitrided Fe (Mo,

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Sb) alloys antimony segregates at semicoherent MoN/Fe interfaces, with an enrichment ratio of about 50.

Solute segregation to interfaces between metals and scales formed during high-temperature oxidation is a relatively well-studied phenomenon [11, 12]. This process is important in the development of high-temperature alloys, since protective oxide decohesion is one of the primary reasons for high-temperature failure of these materials. Most commonly, Al_2O_3 and Cr_2O_3 oxide layers are formed on the surfaces of Fe- or Ni-based superalloys. It has long been observed that impurities including S, P, Cu, Sn, As, and Sb can segregate to a metal/scale interface and cause decohesion and exfoliation of the oxide film. Concomitantly it was also found that small additions of reactive elements such as Y, Zr, or Hf usually improve the bonding strength of the layer (the so-called REE—reactive element effect). The exact mechanism of this phenomenon is still in dispute. Several models have been proposed to explain the REE, including segregation of reactive elements to the interface leading to a direct bond strength enhancement [13] and elimination of detrimental impurities from the interface due to impurity gettering and/or site competition processes [14, 15]. Recently, an elegant interface poisoning mechanism of the REE was suggested [16, 17], where it was proposed that since in most cases oxide scales on high-temperature alloys are semicoherent, growth of the scale must involve non-conservative climb of misfit dislocations. The climb processes involve migration and annihilation of vacancies at the misfit dislocation cores. In order to reduce their elastic energy, large reactive element ions segregate to misfit dislocation cores and block the vacancy annihilation process, thereby providing for a reduced scaling rate and an improved thermal stability of the alloy. It was calculated that a fraction of a monolayer of the segregant should be sufficient to pin the misfit dislocations effectively.

Solute segregation at C/M interfaces produced by diffusion bonding was studied in Ref. [18]. The authors found that initial surface contamination by oxygen, sulfur, carbon, or chlorine greatly reduces the bonding strength in diffusion-bonded polycrystalline $\text{Al}_2\text{O}_3/\text{Nb}$ and $\text{Al}_2\text{O}_3/\text{Cu}$ systems. The diffusion-bonded $\text{Al}_2\text{O}_3/\text{Nb}$ system was studied in greater detail in Ref. [19]. Silver was deliberately introduced on to the sapphire substrates, with three different orientations, prior to UHV diffusion bonding to Nb single crystals. After the bonding, *in situ* fracture tests revealed that the bonding strength systematically decreases with increasing Ag concentration at the interface for all three orientation relationships.

Overall, there are very few studies where quantitative measurements of solute segregation at C/M interfaces are even attempted. One of the reasons for this is that ceramic materials are notoriously dif-

ficult to prepare with high purity and segregation of a specific solute to a ceramic surface or ceramic/metal interface is often masked by the segregation of trace impurities. Another reason is the experimental challenge presented by systems with nanometer-size precipitates, because of the atomic resolution needed for segregation studies at this scale.

In this paper, we present results on solute segregation at {222} MgO/Cu (Ag) and {222} CdO/Ag (Au) C/M interfaces produced by internal oxidation of ternary alloys. Our experimental approach is discussed in greater detail in Part I. The Gibbsian interfacial excess of solute, Γ_{solute} , at these interfaces is determined in a direct and quantitative manner employing atom-probe field-ion microscopy (APFIM). These measurements are complemented in the MgO/Cu (Ag) system by the use of electron energy loss spectroscopy (EELS). APFIM has been employed recently to study, on an atomic scale, the chemistry of the terminating plane of atomically clean {222} MgO/Cu and {222} CdO/Ag interfaces [20–22], thereby demonstrating the feasibility of our approach. In the present study, we microalloyed the MgO/Cu system with Ag and the CdO/Ag system with Au to obtain equilibrium Ag segregation at {222} MgO/Cu and Au segregation at {222} CdO/Ag interfaces.

Prior work on the atomic structure and chemistry of the {222} MgO/Cu [20, 23–26] and CdO/Ag (Au) [27] interfaces demonstrated that in both systems the metal oxide precipitates are octahedral shaped, with faceting on {222}-type planes of the oxide, and have a cube-on-cube orientation relationship with the metal matrix; this is for the specific internal oxidation conditions we employ. Studies by high-resolution electron microscopy (HREM) and Z-contrast scanning transmission electron microscopy (STEM) revealed semicoherent interfaces containing a network of misfit dislocations—see Part I. The lattice misfit parameter, η , is given by $\eta = 2(a_{\text{oxide}} - a_{\text{metal}})/(a_{\text{oxide}} + a_{\text{metal}})$. The value of η is 0.1512 for $a_{\text{MgO}} = 0.4212$ nm and $a_{\text{Cu}} = 0.3620$ nm, and 0.1433 for $a_{\text{CdO}} = 0.471$ nm and $a_{\text{Ag}} = 0.408$ nm.

2. EXPERIMENTAL PROCEDURE

Alloys for this study with the nominal compositions Cu–2.5 at.% Mg–0.8 at.% Ag and Ag–1.5 at.% Cd–1 at.% Au were prepared from elements with high initial purity. Interfaces in both systems were prepared by internal oxidation. For both alloys, specimens were prepared for APFIM in the form of sharply pointed tips. First, the ingots were cold swaged to 1.6 mm diameter rods; second, the swaged alloys were cold drawn into 200 μm diameter wires; third, wires were internally oxidized; finally, wire specimens were electropolished for APFIM analysis to produce sharply pointed

(<50 nm diameter) tips. The experimental procedure for the Cu-based specimens is outlined in Part I. The Ag-based specimens were oxidized in air at 650°C for 48 h. To maximize the level of gold segregation, a portion of the specimens was subsequently annealed in argon at 400°C for 24 h. For conventional TEM studies, a Hitachi H700H 200 kV microscope was utilized. The wire-shaped APFIM specimens were also examined by TEM using a specially fabricated double-tilt holder [28, 29].

APFIM data were obtained using a linear time-of-flight atom probe [30, 31]. Specimens were developed using neon as an imaging gas at 45–50 K and tilted such that the probe hole (the equivalent of a selected-area aperture in a TEM) was aligned with the 111 pole of the specimen, thus providing for data collection along a $\langle 111 \rangle$ direction. Random area analysis was utilized, since a high number density of precipitates ($> 1.0 \times 10^{21}/\text{m}^3$) made it very probable that a precipitate was randomly encountered during the course of a field-evaporation sequence. For copper-based specimens, time-of-flight spectra were recorded at a specimen temperature of 41–50 K using a pulse fraction, f , of 0.2 (f is the ratio of the pulse voltage to the steady-state d.c. voltage) and a pulsing frequency of 20 or 50 Hz. Silver-based specimens were analyzed at 42–45 K using pulse fractions of 0.15–0.25 and a pulsing frequency of 50 or 100 Hz. The ambient background pressure in the APFIM during data collection was $< 10^{-8}$ Pa. Some of the MgO/Cu (Ag) specimens, however, were analyzed at an ambient pressure of 10^{-5} Pa of Ne gas. This was done to improve the field evaporation process of MgO precipitates, as further discussed in Section 3.2. The data acquisition electronics of the APFIM system is capable of detecting up to 128 ions per pulse with 3.3 ns pulse pair resolution in the multihit mode [32].

For the EELS studies, a VG Microscopes HB501 100 kV microscope at Cornell University was utilized. A detailed description of this microscope can be found in Ref. [33]. The VG HB501 is equipped with a cold field-emission gun with a 0.3 eV energy spread and a McMullan-style parallel EELS spectrometer [34]. The energy resolution of this spectrometer is better than 0.1 eV. The microscope has also been modified to achieve high energy-drift stability (< 0.2 eV/min) and spatial-drift stability (< 0.05 nm/min). The microscope's objective lens has a 1.3 mm coefficient of spherical aberration. The minimum attainable probe size of this instrument is approximately 0.22 nm. The vacuum in the column of the microscope is better than 10^{-8} Pa, allowing for very low surface contamination levels. MgO/Cu (Ag) specimens were electropolished to produce electron-transparent thin areas and then ion milled for 10 min at room temperature to reduce surface contamination levels. EELS spectra were recorded in the image mode using a 40 μm diameter objective aperture (objective aperture semi-

angle, 10.3 mrad) and an energy dispersion of the spectrometer of 0.2 eV per channel.

3. RESULTS

3.1. Conventional transmission electron microscopy

Figures 1(a) and (b) show bright-field TEM micrographs of MgO/Cu (Ag) and CdO/Ag (Au) specimens prepared for APFIM. It was found by electron diffraction that for both systems, the wire drawing axis of the specimens is, in most cases, close to a $\langle 111 \rangle$ direction of the matrix. Therefore, for each precipitate in the cube-on-cube orientation relationship with the matrix, two of its $\{222\}$ facets are normal to the direction of analysis. This geometrical arrangement provides for the highest possible spatial depth resolution of an APFIM analysis. A schematic diagram illustrating the geometry utilized for APFIM experiments is shown in Fig. 1(c).

Clear visibility of the MgO precipitates in Fig. 1(a) allows a simple determination of the number density of precipitates. Approximating the APFIM specimen as a truncated cone, the number density of MgO precipitates in the Cu (Ag) matrix is $n_{\text{MgO}} = (1.0 \pm 0.3) \times 10^{22}/\text{m}^3$, where this value is an average for ten specimens. By assuming a regular distribution of precipitates in an alloy, the average distance between precipitates can be approximated as $(n_{\text{MgO}})^{-1/3} = 46$ nm. In a similar fashion, the number density of CdO precipitates in the Ag (Au) matrix is $n_{\text{CdO}} = (3.0 \pm 1.2) \times 10^{21}/\text{m}^3$ and the average distance between precipitates is 70 nm.

3.2. Atom-probe field-ion microscopy

The results of a random area APFIM analysis of the interfacial chemistry of $\{222\}$ MgO/Cu (Ag) interfaces are displayed in Fig. 2 in the form of an integral profile. This profile displays the number of events of Ag, O or Mg vs the cumulative number of Cu, Mg, O, and Ag events. Therefore, the local slope of each curve corresponds to the local concentration of the corresponding element along a $\langle 111 \rangle$ -type direction. This integral profile represents the complete dissection of a single MgO precipitate several nanometers in diameter. It clearly demonstrates the Ag enrichment associated with the $\{222\}$ MgO/Cu interfaces (shown by arrows). This enrichment is quantified in Section 3.4.

An approximate depth scale of an integral profile can be reconstructed using the event frequency analysis approach (Section 3.4). The depth scale shown in Fig. 2, upper abscissa, suggests that the silver signal is somewhat delocalized in the vicinity of the $\{222\}$ interface. Two possible factors contribute to this effect. First, owing to the high dielectric constant of MgO, significant field penetration into a MgO precipitate is expected once it is uncovered during field evaporation. For larger MgO precipitates, this effect usually causes a tip to fail catastro-

Fig. 1. Bright-field TEM micrographs of (a) MgO/Cu (Ag) and (b) CdO/Ag (Au) specimens prepared for APFIM. (c) Schematic diagram illustrating the geometry of APFIM experiments. One pair of parallel {222} facets of an oxide precipitate is normal to the direction of analysis.

phically. It was found experimentally that employing imaging gas-assisted field evaporation, at an ambient pressure of 10^{-5} Pa of Ne gas, helps reduce the field-evaporation rate of MgO precipitates. Alternatively, for precipitates a few nanometers in diameter, high field-evaporation rates of magnesium and oxygen ions lead to the removal of about 10–30 ions per pulse. This effect causes a delocalization of the silver signal in the integral profile, since for a multiple event all times-of-flight are plotted sequentially from the lightest to the heaviest ions. The second explanation for signal delocalization is purely geometrical. To obtain the cleanest possible experimental situation, a precipitate must have both its front and rear interfaces completely covered by the probe hole. If, however, a small precipitate is located off-center with respect to the probe hole

then an admixture of Cu, Mg, O, and Ag signals is detected.

APFIM analyses of about 56 000 matrix atoms also demonstrate that the Ag concentration in the Cu (Ag) solid solution is 0.47 ± 0.03 at.% Ag, where 0.47 at.% is the weighted mean over 20 extended regions of solid solution and 0.03 at.% is the weighted estimate for one standard deviation. This concentration is within the primary Cu (Ag) solid-solution phase at 500°C [35]. The concentrations of magnesium and oxygen in the Cu (Ag) matrix are vanishingly small ($< 10^{-3}$ at. fr.), as is to be expected after an internal oxidation treatment.

The results of random-area APFIM analyses of the interfacial chemistry of {222} CdO/Ag (Au) interfaces are displayed in Figs 3 and 4 in the form of integral profiles. Each profile displays the num-

Fig. 2. APFIM integral profile of a MgO/Cu (Ag) specimen after internal oxidation at 950°C for 2 h and annealing at 500°C for 6 h indicating silver enrichment at {222} interfaces. Arrows indicate the positions of the two interfaces.

ber of events of Cd, O or Au vs the cumulative number of Ag, Cd, O, and Au events. Each integral profile represents the complete dissection of a single CdO precipitate several nanometers in diameter. Figure 3 shows the analysis of an unannealed specimen that was immediately quenched into water after an internal oxidation treatment. The integral profile in Fig. 3 shows *no* Au enrichment associated with a {222} CdO/Ag interface (indicated by an arrow). In contrast, Fig. 4 represents an analysis of specimens annealed at 400°C for 24 h in pure argon. At both the front and rear interfaces, a small gold enrichment is observed, which is quantified in Section 3.4.

3.3. Electron energy loss spectroscopy

For high-resolution EELS analysis of the {222} MgO/Cu (Ag) interfaces, the line-scanning mode was utilized as it takes advantage of the fact that the interfaces are atomically flat [36]. After bringing the interface edge-on, the electron beam is scanned in the *X*-direction, parallel to the interface. Each spectrum is collected from an area on the specimen of approximately $0.3 \times 7.2 \text{ nm}^2$. To obtain a compositional profile across an interface, the beam is manually moved in a stepwise manner along the *Y*-direction. This technique minimizes the radiation damage to a specimen, while maintaining the highest spatial resolution normal to the interface; it was verified experimentally that the exposure times employed and, therefore, the fluence did not result in radiation damage in the C/M interfacial region. Figure 5 displays a high-angle annular dark-field (HAADF) image of a MgO precipitate used for compositional analysis of the {222} interface. The inner collection angle of the ADF detector was 45 mrad. Figure 6(a) displays a series of EELS

Fig. 3. APFIM integral profile of an unannealed CdO/Ag (Au) specimen after internal oxidation at 650°C for 48 h, indicating no gold segregation at a {222} interface. An arrow indicates the position of the interface.

spectra recorded from points 1 to 5 indicated in Fig. 5(b). The most prominent ionization edge of silver used in EELS analysis is Ag-M₄₅. It has an edge onset energy of 367 eV, with the intensity maximum delayed by approximately 70 eV beyond the threshold. This shape is typical of fifth-period elements, which makes them harder to detect employing EELS. Nevertheless, line 2 in Fig. 6(a) exhibits a well-pronounced delayed-maximum edge characteristic of silver. Figure 6(b) exhibits line 2 from Fig. 6(a), after the pre-edge background was subtracted using an inverse power law fit (correlation coefficient, 0.9899). Shown in the inset in Fig. 6(b) is a calculated Ag-M₄₅ line [37]. Clearly, the edge onset is well reproduced experimentally, while the shape of the line is distorted due to the effects of plural scattering. No attempt was made in this work to obtain a quantitative analysis of the interface composition by EELS, since a reliable quantitative analysis of these interfaces has been conducted by APFIM. This qualitative evidence of silver segregation at the {222} MgO/Cu (Ag) interface obtained by EELS serves as an independent confirmation of the results of the APFIM study.

3.4. Determination of the Gibbsian interfacial excess of solute

The APFIM data presented in Section 3.2 can be used to calculate directly the value of Gibbsian interfacial excess of silver at MgO/Cu and gold at CdO/Ag interfaces. The general expression for the relative Gibbsian interfacial excess [38] of component *i* with respect to component 1 ($\Gamma_i^{(1)}$) is

$$\Gamma_i^{(1)} = \Gamma_i - \Gamma_1 \frac{C_i^\alpha - C_i^\beta}{C_1^\alpha - C_1^\beta} \quad (1)$$

where the quantities C_i^α and C_i^β are the atomic fractions of element *i* in the homogeneous regions of

Fig. 4. APFIM integral profile of a CdO/Ag (Au) specimen after internal oxidation at 650°C for 48 h and annealing at 400°C for 24 h, indicating gold enrichment at {222} interfaces. Arrows indicate the positions of interfaces.

phases α and β . The value of $\Gamma_i^{(1)}$ is independent of the position of the Gibbs dividing surface. Equation (1) is the starting point for analyzing the integral profiles displayed in Figs 2 and 4. To illustrate this point, the MgO/Cu (Ag) system is considered here. The calculations for the CdO/Ag (Au) system are similar. First, for the {222} MgO/Cu (Ag) heterophase interface the subscript i refers to Ag, the subscript 1 to Cu, α to the Cu (Ag) matrix, and β to the MgO phase. Equation (1) for this situation is

$$\begin{aligned}\Gamma_{\text{Ag}}^{(1)} &= \Gamma_{\text{Ag}} - \Gamma_{\text{Cu}} \frac{(C_{\text{Ag}}^{\alpha} - C_{\text{Ag}}^{\beta})}{(C_{\text{Cu}}^{\alpha} - C_{\text{Cu}}^{\beta})} \\ &\cong \Gamma_{\text{Ag}} - \Gamma_{\text{Cu}} \left(\frac{C_{\text{Ag}}^{\alpha}}{C_{\text{Cu}}^{\alpha}} \right) \cong \Gamma_{\text{Ag}}.\end{aligned}\quad (2)$$

The reason that $\Gamma_{\text{Ag}}^{(1)}$ reduces to Γ_{Ag} is because $C_{\text{Cu}}^{\beta} = C_{\text{Ag}}^{\beta} \cong 0$ and $(C_{\text{Ag}}^{\alpha}/C_{\text{Cu}}^{\alpha}) \cong 5 \times 10^{-3}$. Thus the problem is abridged to calculating Γ_{Ag} directly from its definition

$$\begin{aligned}\Gamma_{\text{Ag}} &= \frac{N_{\text{Ag}}^{\text{excess}}}{A} = (1/A)(N_{\text{Ag}}^{\text{vol}} - N_{\text{Ag}}^{\alpha} - N_{\text{Ag}}^{\beta}) \\ &= (N^{\text{vol}}/A) \left[C_{\text{Ag}}^{\text{vol}} - C_{\text{Ag}}^{\alpha} \xi - C_{\text{Ag}}^{\beta} (1 - \xi) \right]\end{aligned}\quad (3)$$

where $N_{\text{Ag}}^{\text{excess}}$ is the excess number of Ag atoms associated with a heterophase interface, A is the interfacial area over which this excess is determined, $N_{\text{Ag}}^{\text{vol}}$ is the total number of Ag atoms in the volume analyzed, N_{Ag}^{α} and N_{Ag}^{β} are the number of Ag atoms in the Cu (Ag) matrix and the MgO precipitate, respectively, assuming that the two phases exist up to a Gibbs dividing surface (ξ), $C_{\text{Ag}}^{\text{vol}}$ is the concentration of Ag in the volume analyzed, and N^{vol} is the total number of all elements in the same volume. The excess is defined by comparing the total number of Ag atoms in the actual system con-

taining the interface ($N_{\text{Ag}}^{\text{vol}}$), to a reference system where the two phases extend to ξ .

Equation (3) describes a system with only one interface between the phases α and β . Whereas the integral profile in Fig. 2 is for a system that contains two sequentially parallel heterophase interfaces— α/β and β/α . An abstraction of the situation analyzed is shown in Fig. 7, which exhibits the nomenclature employed to analyze the data. Figure 7 assumes, for the purposes of generalizing the argument, that there is some solid solubility of Ag in MgO, whereas our experimental data indicate none. For the α/β (front) interface, equation (3) takes the form

$$\begin{aligned}\Gamma_{\text{Ag}}^{\alpha/\beta} &= N_{\text{Ag}(1)}^{\text{excess}}/A \\ &= (1/A)(N_{\text{Ag}(1)}^{\text{vol}} - N_{\text{Ag}(1)}^{\alpha} - N_{\text{Ag}(1)}^{\beta}) \\ &= (N^{\text{vol}}/A) \left[\langle C_{\text{Ag}}^{\text{vol}} \rangle - \langle C_{\text{Ag}}^{\alpha} \rangle \xi 1 \right. \\ &\quad \left. - \langle C_{\text{Ag}}^{\beta} \rangle (1 - \xi 1) \right]\end{aligned}\quad (4)$$

where the terms are defined in Fig. 7.

Since $\langle C_{\text{Ag}}^{\beta} \rangle$ is essentially zero, equation (4) for the α/β interface reduces to

$$\begin{aligned}\Gamma_{\text{Ag}}^{\alpha/\beta} &= N_{\text{Ag}(1)}^{\text{excess}}/A = (1/A) \left[N_{\text{Ag}(1)}^{\text{vol}} - N_{\text{Ag}(1)}^{\alpha} \right] \\ &= (N^{\text{vol}}/A) \left[\langle C_{\text{Ag}}^{\text{vol}} \rangle - \langle C_{\text{Ag}}^{\alpha} \rangle (\xi 1) \right].\end{aligned}\quad (5)$$

A value of $\Gamma_{\text{Ag}}^{\beta/\alpha}$ is calculated in a similar fashion. The requisite expression for A for an $\langle hkl \rangle$ analysis direction is

$$A = \frac{N_{\{hkl\}}^{\text{plane}}}{\beta \rho_{\{hkl\}} \cos \phi}\quad (6)$$

where $N_{\{hkl\}}^{\text{plane}}$ is the number of atoms per $\{hkl\}$ plane, $\rho_{\{hkl\}}$ is the planar density of matrix atoms in an $\{hkl\}$ plane, ϕ is the angle between the interface plane and the $\langle hkl \rangle$ analysis direction (in this case $\cos \phi$ is unity), and β is the detection efficiency of the single-ion chevron detector employed in the APFIM system; β is determined by the active area of multi channel plates (MCPs) and ranges from 0.4 to 0.6 [39]. It should be noted, however, that any measured number of ions in APFIM differs from the actual number of ions impinging on the detector by the same factor β . Therefore, by combining equations (5) and (6) we obtain an explicit expression for $\Gamma_{\text{Ag}}^{\alpha/\beta}$ (or $\Gamma_{\text{Ag}}^{\beta/\alpha}$) that is independent of β because the value of $N_{\{hkl\}}^{\text{plane}}$ is also linearly dependent on β .

The quantity $N_{\{hkl\}}^{\text{plane}}$ can be determined using event frequency analysis [40]. When a low-index direction $\langle hkl \rangle$ of an APFIM specimen is aligned over the probe hole, the measured evaporation rate (number of detected ions per pulse) oscillates. This effect is explained in Fig. 8. The surface of an atom-

Fig. 5. (a) ADF image of a MgO precipitate in the Cu (Ag) matrix used for an EELS composition profile across a $\{222\}$ interface; area of analysis is outlined by a square. (b) Approximate location of the electron probe during composition analysis. Each of the points 1–5 corresponds to a scanning area of $0.3 \times 7.2 \text{ nm}^2$ (indicated by a black rectangle).

ically sharp tip can be represented by a set of concentric planes, corresponding to a low-index pole (in our case, 111). To an excellent first approximation, field evaporation occurs predominantly at the edges of the outermost plane, such that each succeeding layer begins to field evaporate after the layer above it is completely removed. Figure 8(a) is a plot of the number of detected ions vs the cumulative number of field-evaporation pulses. Figures 8(b)–(d) are schematic diagrams corresponding to regions 1, 2, and 3 shown in Fig. 8(a). In Fig. 8(b), the topmost plane is small and ions pass through the probe hole and reach the detector. In Fig. 8(c),

the plane is larger and ions do not pass through the probe hole until the plane shrinks to the diameter shown in Fig. 8(d), etc. Thus, the field-evaporation rate exhibits oscillations with a periodicity equal to the number of detected ions per $\{hkl\}$ plane.

Employing the technique outlined above and the value of $\rho_{\{hkl\}}$ for a $\{111\}_{\text{Cu}}$ plane, we obtain for the α/β (front) and β/α (rear) heterophase interfaces shown in Fig. 2, $\Gamma_{\text{Ag}}^{\alpha/\beta} = (6.9 \pm 2.1) \times 10^{14} \text{ atoms/cm}^2$ and $\Gamma_{\text{Ag}}^{\beta/\alpha} = (8.1 \pm 2.3) \times 10^{14} \text{ atoms/cm}^2$. The error in Γ_{Ag} is determined by a calculation of the propagation of errors for each quantity in equation (5). The error in $N_{\text{Ag}}^{\text{excess}}$ is calculated based on the

Fig. 6. (a) EELS spectra recorded from areas 1 to 5 indicated in Fig. 5. Note a Ag-M₄₅ ionization edge appearing in line 2. Arrows indicate positions of O-K and Ag-M₄₅ edges. (b) Ag-M₄₅ ionization edge from a {222} MgO/Cu (Ag) interface. (Inset) Ag-M₄₅ edge shape predicted using Hartree-Slater calculations, from Ref. [37].

assumption of a binomial distribution of solute atoms sampled during atom-probe analysis [41]. The error in the value of $N_{\{hkl\}}^{\text{plane}}$ is the standard error of the mean of a binomial distribution. For the {111}_{Cu} plane one monolayer (ML) coverage equals $\rho_{\text{Cu}} d_{\{111\}\text{Cu}} N_{\text{a}} / M_{\text{Cu}}$, where ρ_{Cu} is the density of copper, N_{a} is Avogadro's number and M_{Cu} is the atomic weight of copper. This implies 1.82×10^{15} atoms/cm² and, therefore, the measured values of Γ_{Ag} correspond to coverages of $\Theta = 0.37 \pm 0.11$ and 0.44 ± 0.12 effective ML. The analysis of 15 {222} MgO/Cu (Ag) interfaces indicates an average segregation level Γ_{Ag} of $(4.0 \pm 1.9) \times 10^{14}$ atoms/cm²

or $\Theta = 0.22 \pm 0.10$ effective ML at 500°C; these results are summarized in Table 1. The analysis of three {222} CdO/Ag (Au) interfaces indicates an average segregation level Γ_{Au} of $(3.0 \pm 1.0) \times 10^{14}$ atoms/cm² or $\Theta = 0.22 \pm 0.07$ effective ML at 400°C; these results are summarized in Table 2.

4. DISCUSSION

As seen in Tables 1 and 2, the measured segregation levels at both {222} MgO/Cu (Ag) and {222} CdO/Ag (Au) interfaces amount to approximately 0.2 effective ML coverage. The microscopic in-

Fig. 7. Diagram illustrating how the Gibbsian interfacial excesses of Ag at the two interfaces are extracted from an integral profile, Fig. 2, and the nomenclature employed.

terpretation of these quantities is not straightforward, since APFIM experiments and Monte Carlo simulations on grain boundaries demonstrate unambiguously [42–50] that interfacial segregation is not necessarily limited to a single atomic layer and a whole spectrum of segregation sites, exhibiting both attractive and repulsive binding energies, may exist at an interface, and that these sites may be found in several atomic layers parallel to an interface. Therefore, it is reasonable to expect that equilibrium solute segregation at C/M interfaces may also be spread over several atomic planes of the matrix and the values of coverage represent an integral total over a number of different segregation sites.

As discussed in Section 1, it has been suggested in the literature that in systems with a highly dispersed second phase, the role of interfacial segregation is diminished due to the large ratio of the interfacial area to the volume. Notably, in this

Fig. 8. Diagram illustrating oscillations in the measured field evaporation rate of an APFIM specimen aligned along a $\langle 111 \rangle$ direction. (a) Plot of number of detected ions vs the cumulative number of field-evaporation pulses; (b–d), schematic diagrams corresponding to regions 1, 2, and 3 shown in (a). In (b) and (d), the topmost $\{111\}$ plane is small and ions pass through the probe hole and reach the detector. In (c), the topmost plane is larger and ions do not pass through the probe hole.

work the presence of ≈ 0.2 effective ML of silver at $\{222\}$ MgO/Cu interfaces does not deplete the matrix of solute, even though the ratio of the interfacial area to the volume is $2 \times 10^4 \text{ cm}^2/\text{cm}^3$. This level of segregation did not, however, noticeably change the morphology of MgO precipitates.

The technique of internal oxidation results in a ceramic/metal interface with a low interfacial free energy. The conventional wisdom suggests that solute–atom segregation at such interfaces is negligible. This idea is incorrect, however, as the Gibbsian interfacial excess of solute is determined by the first derivative of the interfacial free energy with respect to the chemical potential of the solute, and not by the absolute value of the interfacial free

Table 1. Levels of silver segregation at $\{222\}$ MgO/Cu heterophase interfaces measured by APFIM; Θ has the units effective monolayers

#	IF type	$N_{\text{Ag}}^{\text{plane}}_{\{hkl\}}$	$N_{\text{Ag}}^{\text{excess}}$	Γ_{Ag} (atoms/cm ²)	Θ
1	front	24.7	6	4.30×10^{14}	0.23
2	rear	24.7	6	4.30×10^{14}	0.23
3	front	29.2	5	3.03×10^{14}	0.16
4	rear	29.2	5	3.03×10^{14}	0.16
5	front	21.3	7	5.82×10^{14}	0.31
6	rear	21.3	5	4.16×10^{14}	0.22
7	rear	20.0	4	3.54×10^{14}	0.19
8	front	28.3	11	6.89×10^{14}	0.37
9	rear	28.3	13	8.14×10^{14}	0.44
10	front	32.0	6	3.32×10^{14}	0.18
11	rear	32.0	6	3.32×10^{14}	0.18
12	front	30.8	2	1.15×10^{14}	0.06
13	rear	30.8	2	1.15×10^{14}	0.06
14	front	20.7	5	4.28×10^{14}	0.23
15	rear	20.7	4	3.42×10^{14}	0.18
Average				$(4.0 \pm 1.9) \times 10^{14}$	0.22 ± 0.10

Table 2. Levels of gold segregation at {222} CdO/Ag heterophase interfaces measured by APFIM; Θ has the units *effective* monolayers

#	IF type	$N_{\{hkl\}}^{\text{plane}}$	$N_{\text{Au}}^{\text{excess}}$	Γ_{Au} (atoms/cm ²)	Θ
1	rear	18.6	3	2.38×10^{14}	0.16
2	rear	20	6	4.16×10^{14}	0.30
3	front	20	4	2.77×10^{14}	0.20
Average				$(3.0 \pm 1.0) \times 10^{14}$	0.22 ± 0.07

energy. The results presented herein on Ag segregation at {222} MgO/Cu interfaces and Au segregation at {222} CdO/Ag interfaces substantiate the latter point of view.

In unannealed CdO/Ag (Au) specimens, which were rapidly quenched from the temperature of internal oxidation (650°C) to room temperature, the absence of gold segregation at {222} CdO/Ag interfaces is consistent with the well-known fact that GB segregation in metals is maximized over a fairly narrow temperature range. For GB segregation in Ag-based alloys, a typical range is 280–450°C [51].

5. CONCLUSIONS

The first quantitative measurements of solute segregation at C/M heterophase interfaces are presented for the MgO/Cu (Ag) and CdO/Ag (Au) systems. It is shown that the data are readily analyzed to obtain the Gibbsian interfacial excess of solute. After low-temperature annealing treatments to induce heterophase segregation, significant segregation levels are observed in both systems. The analysis of 15 {222} MgO/Cu (Ag) interfaces indicates an average segregation level of $(4.0 \pm 1.9) \times 10^{14}$ atoms/cm² or 0.22 ± 0.10 *effective* monolayers at 500°C. The analysis of three {222} CdO/Ag (Au) interfaces indicates an average segregation level of $(3.0 \pm 1.0) \times 10^{14}$ atoms/cm² or 0.22 ± 0.07 *effective* monolayers at 400°C, whereas {222} CdO/Ag (Au) interfaces in *unannealed* specimens exhibit *no* evidence of interfacial gold segregation. All the APFIM quantitative results in this section are obtained without data deconvolution or external calibration standards; the naturally occurring isotopic abundances provide an absolute internal calibration standard. The presence of silver at the {222} MgO/Cu (Ag) interfaces is confirmed by the high-resolution EELS compositional profile across an interface using the Ag-M₄₅ line. This qualitative evidence of silver segregation at the {222} MgO/Cu (Ag) interface obtained by EELS serves as an independent confirmation of the results of the APFIM study.

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