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Atomic-Scale Studies of the Structure and Chemistry of Ceramic/Metal Heterophase Interfaces

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ABSTRACT

Atomic-Scale Studies of the Structure and Chemistry of Ceramic/Metal Heterophase Interfaces

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Materials containing metallic and ceramic phases play an important role in modern technology. The structure and chemistry, however, of ceramic/metal interfaces are not well understood. This study, therefore, was conducted to characterize fully the atomic-scale structure and chemistry of metal oxide/metal interfaces produced by internal oxidation of dilute binary and ternary metallic alloys. Ternary alloys were oxidized under conditions whereby only one of the two solute species is oxidized. The remaining solute species segregates to the ceramic precipitate/matrix interfaces.

Scanning transmission electron microscopy was used to determine the atomic structure and chemistry of the ceramic/metal interfaces. Electron energy loss and energy-dispersive X-ray spectroscopies were used to determine the chemistry and nature of bonding at the interfaces. Atom-probe microscopy was used to measure quantitatively the chemical composition of the interfaces.

Four alloys were internally oxidized: Pd-2.3 at.% Mg, Cu-2.5 at.% Mg, Cu-2.5 at.% Mg-0.8 at.% Ag, and Ag-1.5 at.% Cd-1 at.% Au. MgO precipitates are
formed in Pd, Cu and Cu(Ag) matrices and CdO precipitates are formed in a Ag(Au) matrix. In all cases, the precipitates are octahedral-shaped, bound by \{222\} planes, and maintain a cube-on-cube orientation relationship with the matrix.

Atom-probe microscopy revealed a significant level of segregation in both ternary systems. The Gibbsian excess of solute at the interface (\(\Gamma_{\text{solute}}\)) was directly calculated. The values of \(\Gamma_{\text{solute}}\) are \((4.0\pm1.9)\times10^{14}\) atoms cm\(^{-2}\) for the \{222\}MgO/Cu(Ag) and \((3.0\pm1.0)\times10^{14}\) atoms cm\(^{-2}\) for the \{222\}CdO/Ag(Au) interfaces.

Scanning transmission electron microscopy of \{222\}MgO/Cu(Ag) interfaces showed that the interfaces are semicoherent and contain misfit dislocations spaced at \(1.45\pm0.19\) nm. Double and quadruple-height steps were observed. Stand-off misfit dislocations were found at one \{111\} interplanar distance (0.208 nm) in the metal matrix. It was proven by measurements of the interface separation that the interface is terminated by oxygen ions. Silver enrichment at this interface was detected by Z-contrast imaging and by electron energy loss spectroscopy (EELS).

A study of \{222\}MgO/Cu interfaces by EELS revealed that this interface is terminated by oxygen ions and showed that copper remains metallic at the interface, introducing electronic states inside the band gap of MgO. A study of \{222\}MgO/Pd interfaces by energy-dispersive X-ray spectroscopy (EDX), however, could not reveal the interfacial chemistry due to experimental
limitations. The conditions necessary for the successful interface analysis by EDX are examined.

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LIST OF ABBREVIATIONS

ADF  annular dark field (image or detector)

AEM  analytical electron microscopy

AES  Auger electron spectroscopy

APFIM  atom-probe field-ion microscopy
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF</td>
<td>bright field</td>
</tr>
<tr>
<td>C/M</td>
<td>ceramic/metal</td>
</tr>
<tr>
<td>DB</td>
<td>diffusion bonding</td>
</tr>
<tr>
<td>EDS</td>
<td>energy-dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>EELS</td>
<td>electron energy loss spectroscopy</td>
</tr>
<tr>
<td>EFI</td>
<td>energy-filtered imaging</td>
</tr>
<tr>
<td>ELNES</td>
<td>electron energy-loss near-edge structure</td>
</tr>
<tr>
<td>FCC</td>
<td>face-centered cubic</td>
</tr>
<tr>
<td>FIM</td>
<td>field-ion microscopy</td>
</tr>
<tr>
<td>FLAPW</td>
<td>full potential linearized augmented plane wave</td>
</tr>
<tr>
<td>GB</td>
<td>grain boundary</td>
</tr>
<tr>
<td>HAADF</td>
<td>high-angle annular dark field (image or detector)</td>
</tr>
<tr>
<td>HREM</td>
<td>high resolution electron microscopy</td>
</tr>
<tr>
<td>IF</td>
<td>interface</td>
</tr>
<tr>
<td>IO</td>
<td>internal oxidation</td>
</tr>
<tr>
<td>IR</td>
<td>internal reduction</td>
</tr>
<tr>
<td>LDFT</td>
<td>local-density-functional theory</td>
</tr>
<tr>
<td>LMTO</td>
<td>local muffin-tin orbital</td>
</tr>
<tr>
<td>MBE</td>
<td>molecular beam epitaxy</td>
</tr>
<tr>
<td>ML</td>
<td>monolayer</td>
</tr>
<tr>
<td>OR</td>
<td>orientation relationship</td>
</tr>
<tr>
<td>RBS</td>
<td>Rutherford backscattering spectroscopy</td>
</tr>
<tr>
<td>REE</td>
<td>reactive element effect</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>SADP</td>
<td>selected area diffraction pattern</td>
</tr>
<tr>
<td>SCLO</td>
<td>self-consistent local orbital</td>
</tr>
<tr>
<td>SF</td>
<td>stacking fault</td>
</tr>
<tr>
<td>SIMS</td>
<td>secondary ion mass spectrometry</td>
</tr>
<tr>
<td>STEM</td>
<td>scanning transmission electron microscope or microscopy</td>
</tr>
<tr>
<td>TDS</td>
<td>thermal diffuse scattering</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscope or microscopy</td>
</tr>
<tr>
<td>UHV</td>
<td>ultra-high vacuum</td>
</tr>
<tr>
<td>UPS</td>
<td>ultraviolet photoelectron spectroscopy</td>
</tr>
<tr>
<td>WBDF</td>
<td>weak beam dark field (microscopy)</td>
</tr>
<tr>
<td>XANES</td>
<td>x-ray absorption near-edge structure</td>
</tr>
<tr>
<td>XAS</td>
<td>x-ray absorption spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
</tbody>
</table>
CHAPTER 1

INTRODUCTION

Materials containing ceramic and metal phases play a significant role in modern materials technology. Ceramic/metal (C/M) interfaces often determine macroscopic mechanical, physical, and chemical properties of these materials. It is widely recognized that to design and to control macroscopic materials properties successfully, a fundamental understanding of the atomic-scale structure and chemistry of C/M interfaces is necessary.

From the scientific standpoint, C/M interfaces represent an extreme, and the most interesting, case of a boundary between two highly dissimilar materials. While theories of metal and ceramic homophase interfaces (grain boundaries) are fairly well developed, heterophase C/M interfaces are a relatively new and less well-studied subject.

As a result of their critical technological importance and strong fundamental interest, C/M interfaces have received a great deal of attention recently [1-3]. The main effort in most experimental studies has been on observing the interface structure, determining the nature of chemical bonding at the interface, and 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. There are very few studies where quantitative measurements of solute segregation at C/M interfaces are even attempted. Judging by the omnipresence of segregation phenomena in metals and ceramics, one can state that solute segregation plays an important role in most C/M systems.

This study focuses on atomic-scale characterization of solute segregation in model C/M systems. Four systems are studied: \( \{222\} \text{MgO/Pd}, \{222\} \text{MgO/Cu}, \{222\} \text{MgO/Cu(Ag)} \) and \( \{222\} \text{CdO/Ag(Au)} \). Interfaces are created by internal oxidation of random binary or ternary alloys. The structure, morphology, and orientation of metal oxide particles are characterized by conventional transmission electron microscopy (TEM). The atomic-scale chemistry of the interfaces is determined quantitatively using atom-probe field-ion microscopy (APFIM). The atomic structure of C/M interfaces, along with some chemical information, is obtained by dedicated scanning transmission electron microscopy (STEM). These results are complemented by energy-dispersive x-ray spectroscopy (EDX) and electron energy loss spectroscopy (EELS). This combined approach enables us to address the following fundamental questions:

1. What is the solute segregation level and spatial extent at these C/M interfaces?
2. What is the structural and chemical sharpness of C/M interfaces?
3. What is the state of coherency of C/M interfaces?
4. What is the effect of solute segregation on the atomic structure of C/M interfaces?
5. What is the nature of bonding at C/M interfaces?

This thesis has the following structure:

Chapter 2 offers a concise review of the literature on C/M interfaces. Various methods of interface fabrication are discussed. Experimental techniques that have been used to study the structure and chemistry of C/M interfaces are described. A comparison of the techniques is made based on the information that these techniques can offer. Finally, the main results of the studies of C/M interfaces are presented in four subsections: (a) results of atomistic simulations and calculations; (b) dislocation structures observed at C/M interfaces; (c) nature of chemical bonding at interfaces; and (d) previous studies of solute segregation at C/M interfaces.

Chapter 3 describes a study of interfacial chemistry in two systems, {222}MgO/Cu(Ag) and {222}CdO/Ag(Au), by APFIM. It represents the first quantitative study of solute segregation at C/M interfaces. Results of a TEM investigation of metal-oxide particle size, morphology and crystallography of C/M interfaces are presented. Results of an APFIM investigation are reported. Significant levels of solute segregation is detected in both systems and the APFIM data are analyzed to extract a fundamental thermodynamic property of these interfaces – the Gibbsian interfacial excess of solute ($\Gamma_{\text{solute}}$). The APFIM results are discussed in the light of different models of interfacial segregation.

Chapter 4 reports the results of a dedicated STEM study of MgO/Cu(Ag) interfaces. Basic STEM techniques are presented. The experimental procedures
for interface preparation and STEM image acquisition are described and the main results of the STEM study are presented: (a) crystallography and defects of the interfaces; (b) dislocation structure of the interfaces; (c) chemistry of the terminating plane; and (d) evidence of silver segregation at \{222\}MgO/Cu(Ag) interface. These STEM results are compared with previous studies of atomically clean \{222\}MgO/Cu interfaces and analyzed to reveal the effect of solute segregation on the interfaces’ atomic structure.

Chapter 5 presents the results of high-resolution electron energy loss spectroscopy (EELS) study of the atomically clean \{222\}MgO/Cu interfaces. After a brief discussion of the technique and its limitations, experimental results are presented: first, a composition profile across the interface is measured; second, the electronic states characteristic of this interface are observed by energy loss near-edge structure (ELNES).

Chapter 6 summarizes a study of the \{222\}MgO/Pd interface by high-resolution energy-dispersive X-ray spectroscopy (EDS) in an analytical electron microscope (AEM). First, the conditions necessary for high-resolution EDX analysis of interfacial chemistry are analyzed. Then, the experimental procedures and main results are presented. Finally, the instrumental capabilities of the two techniques, EDX and APFIM, are compared with respect to high-resolution chemical analyses of interfaces.

Chapter 7 summarizes the main results of this thesis.

Appendices A, B, and C describe the detailed experimental procedures used to prepare and internally oxidize alloys, to prepare specimens for atom-
probe microscopy, and to prepare specimens for transmission electron microscopy, respectively.
CHAPTER 2

LITERATURE REVIEW:

CERAMIC/METAL INTERFACES

2.1 IMPORTANCE OF CERAMIC/METAL INTERFACES

Ceramic/metal (C/M) interfaces are omnipresent in modern materials. The most important examples include dispersion hardened alloys, metal-matrix fiber-reinforced composite materials, metal-ceramic welding, oxide films and coatings on the surface of high-temperature alloys, and microelectronic packaging. In all of these practical applications, C/M interfaces usually determine the mechanical strength, thermal stability, and overall performance of the material.

For example, dispersed CdO particles in silver dramatically improve spark erosion resistance of a Ag(Cd) alloy used for high-current switches [4]. The long-term stability of these materials is determined by the thermal stability of CdO precipitates, which in turn is affected by the atomic-scale structure and chemistry of CdO/Ag interfaces.

Another important example is SiC/Ti [5] and SiC/Al [6] fiber composites.
It is well established that such factors as the extent of fiber-matrix interdiffusion, formation of a reaction layer, and the use of an interfacial coating are the critical factors that control the mechanical properties of these materials.

In the case of high-temperature alloys, oxide scale decohesion is one of the major mechanisms of material failure. This effect is crucial, for example, for the performance of gas turbine components at high temperature. As discussed in recent reviews [7], scales of Cr₂O₃, Al₂O₃, and SiO₂ often spall severely from Fe or Ni-based alloys. Poor resistance to scale spallation is associated with such factors as low bond strength across the scale/metal interface, high interface stresses and stress gradients, and the presence of detrimental impurities at the interface.

Another example of the effect of C/M interfaces on material performance is integrated circuits (ICs). In this case, the effect of C/M interfaces is electrophysical. One of the main factors affecting the long-term reliability of submicron-scale ICs is the phenomenon of electromigration in Al-based or Al-Cu interconnect lines [8]. Electromigration is electron current-induced atomic diffusion. At typical operating temperatures, the dominant diffusion paths due to electromigration are through the interconnect grain boundaries (GBs). As the width of the interconnect lines decreases, a characteristic bamboo structure is developed and grain boundary circuits are interrupted. Therefore, the dominant diffusion path becomes through the interface between the metal interconnect and ceramic substrate or diffusion barrier (typically, TiN or SiO₂). As a result,
the overall long-term reliability of an IC is controlled by diffusion and void formation at substrate/interconnect C/M interfaces.

In summary, structure, bonding, and chemistry of C/M interfaces often control the mechanical properties and performance of important engineering materials. This provides an impetus for studies of the structure and chemistry of C/M interfaces at a fundamental level.

2.2 METHODS OF FABRICATION

C/M interfaces can be produced in a variety of ways, including internal oxidation, internal reduction, thin-film growth, and diffusion bonding [3]. The main advantages and disadvantages of those methods are summarized in Table 2.1.
### TABLE 2.1
Comparison between different fabrication methods of ceramic/metal interfaces, after [3].

<table>
<thead>
<tr>
<th>Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Internal oxidation or</td>
<td>– Simple</td>
<td>– Difficult to influence the crystallography</td>
</tr>
<tr>
<td>internal nitridation</td>
<td>– Produces few unique ORs</td>
<td></td>
</tr>
<tr>
<td></td>
<td>– Plenty of interfaces</td>
<td>– Difficult to control the dispersion of precipitates.</td>
</tr>
<tr>
<td></td>
<td>– Conducting specimens that are easily studied by TEM, HREM, AEM, and APFIM.</td>
<td></td>
</tr>
<tr>
<td>Internal reduction</td>
<td>– Produces few unique ORs</td>
<td>– Same as in internal oxidation</td>
</tr>
<tr>
<td></td>
<td>– Plenty of interfaces</td>
<td>– Large internal stresses</td>
</tr>
<tr>
<td></td>
<td></td>
<td>– Insulating specimens</td>
</tr>
<tr>
<td>Thin film growth</td>
<td>– Fixed interface orientation</td>
<td>– Expensive</td>
</tr>
<tr>
<td></td>
<td>– Often produces fixed OR</td>
<td>– Requires UHV environment</td>
</tr>
<tr>
<td></td>
<td>– High-quality films</td>
<td>– Unwanted diffusion reactions</td>
</tr>
<tr>
<td></td>
<td>– Atomically smooth interfaces</td>
<td>– Thermal mismatch stresses</td>
</tr>
<tr>
<td></td>
<td>– High chemical purity</td>
<td></td>
</tr>
<tr>
<td></td>
<td>– Controlled doping</td>
<td></td>
</tr>
<tr>
<td></td>
<td>– Large IFs suitable for AES, XPS, SIMS, RBS, electron microscopy techniques,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>and mechanical testing</td>
<td></td>
</tr>
</tbody>
</table>
TABLE 2.1 cont.

| Diffusion bonding | - Any desired crystallography on a macroscopic scale | - Difficult to control crystallography at the atomic scale |
|                   | - Macroscopic dimensions                           | - Difficult to control IF purity |
|                   | - Suitable for fracture mechanical tests.          | - Large residual stresses |
|                   |                                                    | - IF roughness |
|                   |                                                    | - Presence of IF voids |
|                   |                                                    | - Unwanted diffusion reactions. |

It is important to remember that fabrication of C/M interfaces does not necessarily lead to the formation of a structurally and chemically sharp boundary between the two materials. As established in recent review papers [9, 10], there are many C/M interface morphologies that are possible as a result of interactions between metal and ceramic phases. The typically observed morphologies are listed in Table 2.2. The resulting structures depend not only on the nature of components and fabrication method, but also on the processing parameters such as temperature, applied pressure, growth rate, atmosphere, and presence of impurities.
TABLE 2.2 Ceramic/metal interface morphologies, after [9, 10].

<table>
<thead>
<tr>
<th>IF type</th>
<th>IF reaction or behavior</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abrupt interface</td>
<td>Agglomeration</td>
<td>Cu/TiO₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Encapsulation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pt/TiO₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pd/TiO₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ni/TiO₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Rh/TiO₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu/TiO₂</td>
</tr>
<tr>
<td>Interface with oxide</td>
<td>Redox reaction</td>
<td>Al/Al₂O₃/TiO₂</td>
</tr>
<tr>
<td>reaction layer</td>
<td>(reactive adsorption)</td>
<td>Cr/CrOₓ/TiOₓ</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hf/HfO₂/TiOₓ</td>
</tr>
<tr>
<td></td>
<td>Ternary oxide formation</td>
<td>Ni/NiAl₂O₄/Al₂O₃</td>
</tr>
<tr>
<td></td>
<td>Oxide solid solution</td>
<td>Ni/MgO(NiO)/MgO</td>
</tr>
<tr>
<td>Interface with metallic</td>
<td>Intermetallic formation</td>
<td>Al/Ni₃Al/NiO</td>
</tr>
<tr>
<td>reaction layer</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


Internal oxidation is a popular and well-studied technique for interface preparation [11 - 13]. In particular, specimens prepared by internal oxidation have been widely utilized for studies of atomic-scale structure and chemistry of C/M interfaces by HREM, AEM, and APFIM, as discussed in Section 2.3. Most commonly, binary alloys are used for internal oxidation to produce atomically clean C/M interfaces. On the other hand, internal oxidation of ternary metallic alloys often leads to a different oxidation behavior [12]. Three distinct situations are generally observed:

1. Both solutes are internally oxidized forming two distinct simple oxide phases. Often, the solute with a higher affinity for oxygen forms small and highly dispersed particles at the early stages of oxidation. These precipitates later serve as centers for heterogeneous nucleation of the second oxide phase. Examples of this behavior are Cu(Al, Zr), Cu(Al, Hf), and Cu(Si, X), where X = Hf, Zr, Ti, or Sn [14].

2. Both solutes may oxidize in a metal matrix to form a complex oxide, such as the spinel NiAl₂O₄ in the Cu(Al, Ni) system.

3. Only one of the three elements is oxidized, while the other two remain in solid solution. Examples of this behavior include Fe(X, Al) where X = Sn, P, or Ni; Ag(Au, Mg), Cu(Ni, Al), Nb(Zr, Re), and Ta(W, Hf) alloys. The only effect of the third component, that is reported in the literature, is a diminution of the oxidation kinetics, due to the effect the third component may have on oxygen solid solubility [12].

Recently, this last mode of internal oxidation of ternary alloys was used
as a novel and elegant method to study solute segregation at C/M interfaces [15]. This research is described in details in Chapters 3 and 4 of this thesis.

2.3 EXPERIMENTAL METHODS OF INVESTIGATING THE ATOMIC-SCALE STRUCTURE AND CHEMISTRY

A wide variety of techniques have been utilized to study the structure and chemistry of C/M interfaces. The main method of structural investigation has been high-resolution electron microscopy (HREM). As the resolving power of modern HREM improved to less than 0.2 nm, it became possible to obtain direct lattice images of C/M interfaces in different orientations. A large number of experimental results has been obtained in C/M systems by HREM. They are summarized in Section 2.5. An emerging technique that also allows direct lattice imaging and can be more powerful than HREM in determining the interface structure is Z-contrast imaging in a dedicated STEM. The main reason Z-contrast imaging is not as popular as HREM is that a very small number of dedicated STEMs are currently capable of atomic-resolution imaging.

2.3.1 High-resolution electron microscopy

Interfaces produced by the methods listed in Table 2.1 usually satisfy the main conditions for HREM interface analysis with atomic resolution [16], that is:

1. The two grains on either side of an interface can be brought into a low-index orientation.
2. The interface must be viewed edge-on.
3. The interface must have no steps in the direction of the incident electron beam. In general, defects present at an interface must be confined to displacements fields that do not disturb atomic columns parallel to the electron beam [17]. Interfacial misfit dislocations do not conform to this condition. This issue is discussed in section 2.5.

The main problem, however, in determining the atomic structure of an interface from HREM images is the presence of image artifacts caused by dynamical diffraction and lens aberrations. The common approach is to use structural models of an interface as an input for image simulations that take into account the particular electron optical properties and aberrations of the microscope employed. The resulting images are then compared with the experimental ones, and a structural model is chosen that shows the best match. Based on the comparison, this model can then be refined, and used as an input for new image simulations, and then iteratively changed [18]. The key step in this iterative process is determining the goodness of fit between experimental and simulated images. Typically, this is done by a simple visual comparison that is, therefore, strongly subjective. An alternative approach to this problem is HREM image processing in order to quantify and to minimize the difference between the two images numerically by means of various correlation techniques. When consistently employed, this method is capable of revealing structural details that are not directly visible [19, 20].

2.3.2 Z-contrast
Recent advances in scanning transmission electron microscopy (STEM) have led to a great improvement of spatial resolution at the subnanometer level [21]. In combination with the chemical sensitivity of Z-contrast imaging, this method provides an opportunity to determine the structure and chemistry of C/M interfaces simultaneously using direct lattice imaging. A more detailed analysis of STEM imaging is presented in Section 4.2. To the author's knowledge, however, the only example of the application of dedicated STEM to a C/M interface is a recent study of (100)\(\alpha\)-ZrO2/Ni[111] interface [21]. Results of our work on C/M interfaces obtained by dedicated STEM are reported in Section 4.4.
2.3.3 *Energy-dispersive X-ray spectroscopy and electron energy loss spectroscopy*

Studies of C/M interface chemistry have started only recently. Most early research on model systems dealt with atomically clean C/M interfaces, while studies of technologically important materials often neglected interfacial chemistry. More recently, the understanding of the important role that interfacial chemistry plays in determining the properties of C/M interfaces has led to a number of significant studies. The main results are reviewed in Sections 2.6 and 2.7.

The main method to study chemistry of C/M interfaces has been AEM utilizing high-resolution composition analysis by EDX and bonding and electronic structure determination by EELS. These methods are complimentary in many respects [22]: EDX allows for relatively easy quantification of spectra, often with an accuracy of 5-10%. The detection sensitivity is related to the attainable electron-probe diameter. The ultimate spatial resolution of EDX analysis, however, is usually limited not by the electron-probe diameter, but by broadening of the incident electron beam by scattering. Alternatively, the spatial resolution of EELS analysis is less limited by beam broadening and approaches the incident beam diameter in the ideal case. Quantitative analysis of EELS spectra and visibility of small spectral features, however, are inferior to EDX. Our results of EELS studies of the \{222\}MgO/Cu interface and EDX studies of the \{222\}MgO/Pd interface are presented in Chapters 5 and 6 of this thesis, respectively.
The information that can be obtained from EDX and EELS analyses includes [23]: (a) interface sharpness and the presence of reaction layers; (b) solute segregation levels; (c) oxidation states of elements at the interface; and (d) charge transfer across the interface. The recently developed spatial difference method in EELS [24, 25] allows one to extract the small spectral features pertaining to the interface that may not be otherwise detectable. Chemically and electronically-specific information in the EELS spectrum is mostly contained at about 20-30 eV above the characteristic ionization edges, the region known as electron energy-loss near-edge structure (ELNES). The shape of ELNES lines is sensitive to a local atomic arrangement and thus can be used as a coordination fingerprint. This approach is the most promising method, at present, for studying the atomic-scale chemistry of C/M interfaces.

### 2.3.4 Surface analysis techniques

Important contributions have also been achieved by surface analysis techniques, such as Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS). They are limited, however, to studies of thin films and fractured surfaces, usually without structural information. In the first case, thin metal overlayers are deposited on atomically clean ceramic substrates and alteration of the electronic structure and composition of the surface as a result of metal deposition is monitored [10, 26]. This approach, therefore, can only provide information about the initial stages of ceramic-metal interactions. AEM, on the other hand, has the advantage of simultaneous structure determination
and chemical analysis of buried C/M interfaces.

2.3.5 Atom-probe field-ion microscopy

Recently, atom-probe field-ion microscopy (APFIM) has been employed to study the chemistry of C/M interfaces [15, 27, 28]. The APFIM technique is known to provide quantitative compositional analysis with unsurpassed spatial resolution [29, 30], and has been widely utilized to study interfacial chemistry [31]. The main limitation, however, in the case of C/M interfaces is the dielectric character of most ceramics. Therefore, the application of APFIM has been limited to internally oxidized specimens with highly dispersed oxide [27, 28, 32] or nitride [33] precipitates or to in situ externally oxidized metallic specimens forming thin oxide scales on their surface [34-36]. The lateral spatial resolution of APFIM analysis is determined by the size of a field limiting aperture (probe hole) and can be less than 0.5 nm. The depth resolution of analysis is limited only by the interplanar spacing of the material in the direction of analysis and can be 0.1 nm or less. APFIM analysis is equally sensitive to all elements in the periodic table, and does not require any calibration or deconvolution procedures that are common in surface analysis techniques and AEM. This makes it a powerful method of studying the chemistry of C/M interfaces, especially in systems with small precipitates, where most other techniques fail. The main experimental results are reviewed in Section 2.6. Results of the work on solute segregation at C/M interfaces are presented in Chapter 3 of this thesis.
2.4 COMPUTER SIMULATIONS AND FIRST-PRINCIPLE CALCULATIONS OF CERAMIC/METAL INTERFACES

Numerical calculations and simulations of grain boundaries (GBs) in metals and ceramics have been widely used to predict equilibrium GB structures and energies and to compare them with experiment. Interatomic interactions in ceramics can be realistically represented by simple pairwise Coulomb potentials. Therefore, relatively large systems with defects can be modeled. In metals, molecular statics, molecular dynamics, and Monte Carlo simulations are used. To simulate equilibrium structures, one has to utilize interatomic potentials. They can either be obtained empirically by fitting experimental physical properties of a particular element to simulated ones, or calculated by a first-principle method. A variety of realistic interatomic potentials for metals have been recently developed.

The situation with heterophase interfaces, however, is different. To model a heterophase interface, one has to know interatomic forces, or interaction potentials, between two or three different species. A lack of realistic interatomic force models for C/M interfaces has been the main obstacle for applying the well-developed simulation techniques to C/M interfaces [37]. Hence, mainly first-principle calculations have been employed, where only very small systems (<500 atoms) can be handled. By calculating the total energy of a system containing a C/M interface, three main problems can be addressed [3]:

1. Interface structure under constrained equilibrium conditions.
2. Effect of geometrical degrees of freedom of an interface on its energy.
3. Effect of interface chemistry on adhesive energy.

The tight-binding method was used in [38] to investigate adhesion between various transition metals and sapphire in two different orientations. It was concluded from calculations of band structure that two interactions dominate at an interface: a repulsive interaction between metal atoms and oxygen ions and an attractive interaction between metal atoms and aluminum ions. As a result, the adhesive energy is determined simply by the Al/O ratio at an interface. Aluminum ions serve as electron acceptors and charge transfer occurs from metal to aluminum ions. In this framework, the interface orientation and coordination have only a minor effect on adhesive energy. As noted in reference 3, approximations in the underlying theory of the tight-binding method make it rather qualitative and limit its predictive power. In addition, the results of this study cannot explain the strong experimental evidence for oxygen termination at Al₂O₃/Cu [39] and Al₂O₃/Nb [40, 41] interfaces. These experimental results are discussed in Section 2.6.

The most powerful group of band structure methods involves first-principle calculations in reciprocal space. These methods are the most accurate, since they use no input but the basic atomic data. All the methods assume that the total energy of the system is uniquely determined by the electron density (local density functional theory – LDFT). The most important restriction of these methods is the small size of a computational cell (<500 atoms), so that realistic
interface structures cannot be modeled, that is, only coherent interfaces are amenable to this approach.

\{100\}MgO/Ag is one of the few interfaces that has been studied rather extensively. MgO has a cubic rocksalt structure and Ag is f.c.c. It was shown experimentally [42] that a cube-on-cube OR is observed between \{100\}MgO and \{100\}Ag. The nonpolar \{100\} plane of MgO consists of 50\% Mg and 50\% O ions. Therefore, three distinct interface configurations are possible in this orientation:

1. Silver on top of oxygen, denoted (Ag|O).
2. Silver on top of magnesium, denoted (Ag|Mg).
3. Silver above the interstices between Mg and O, denoted (Ag|::), or the lock-in configuration.

In reference 43, the \{100\}MgO/Ag interface was investigated by the full potential linearized augmented plane wave (FLAPW) method using a single monolayer of silver. The same interface was studied using the local muffin-tin orbital (LMTO) method in reference 44, and using the self-consistent local orbital (SCLO) method in reference 45. In these three cases, the 3\% misfit between the two lattices was accommodated by stretching the silver layer to match the lattice spacing of MgO (zero-misfit approximation). All three groups found that the (Ag|O) configuration is energetically preferred over (Ag|Mg) and (Ag|::) configurations. Another consistent result is that electron charge transfer across this interface is small. It was also reported that in the (Ag|O) configuration the equilibrium interface separation is about 20\% larger than the \{100\} spacing in either crystal [44]. The Ag–O bond length and force constants are similar to
those experimentally observed in Ag$_2$O. This result suggests that bonding between silver and MgO is weak and predominantly ionic. On the contrary, a similar study of {100}MgO/Ti interface in reference 44 revealed that the (Ti | O) configuration is also energetically preferred, but the interface separation is only 3% larger than the bulk {100}MgO spacing and bonding is predominantly covalent.

Using an approach similar to reference 43, the {100}CdO/Ag interface was studied in reference 46 by the FLAPW method. Like MgO, cadmium oxide has a cubic rocksalt structure and a cube-on-cube OR is usually observed in the CdO/Ag system [40]. Similarly to the {100}MgO/Ag interface, it was found that the (Ag | O) configuration is energetically preferred over (Ag | Cd) and that electron charge transfer across the interface is small. The binding energy, however, is significantly stronger, which leads to a smaller interface separation.

In a further application of the SCLO method [47], the {100}MgO/Ag and {100}MgO/Al interfaces were considered in the absence or presence of carbon or sulfur segregation at the interface. It was found that the undoped interface (Me | O) configurations have a higher adhesive energy and are energetically preferred. For these preferred configurations, the presence of impurities generally causes larger interface separations. The adhesive energy of a segregated interface is lower than for a clean one, except for carbon at a {100}MgO/Al interface. A larger interface separation can be explained by the strain effect caused by impurities. A change in adhesive energy is determined by an interplay between two factors: the impurity size misfit effect and the
additional chemical bonding it provides. The authors also concluded that for all
interfaces studied there are both ionic and covalent/metallic contributions to the
bonding.

As was proposed in reference 3, one of the most important factors
affecting bonding at C/M interfaces is interface charge. The {100} surface in a
rocksalt-structure ceramic is nonpolar, which is consistent with the low values of
electron charge transfer across the interface obtained in the abovementioned
studies. Thus, it would be most interesting to compare those results with results
on polar interfaces. In a recent study [37], both polar and nonpolar {222} and
{100}MgO/Cu, interfaces were investigated by the local-density-functional-
theory (LDFT) method. MgO also has a rocksalt structure that usually exhibits a
cube-on-cube OR with Cu [48-50]. The {222} planes in MgO are polar planes
consisting of pure oxygen or pure magnesium ions. Therefore, two interface
terminating layers are possible – oxygen or magnesium ions. It was found in
reference 37 that polar {222} interfaces are invariably preferred over nonpolar
{100} interfaces and exhibit a much higher adhesive energy and electron charge
transfer across the interface. It was also found that an oxygen-terminated {222}
interface is strongly preferred over a Mg-terminated one, which is consistent
with experimental APFIM observations [27]. These results are summarized in
Table 2.3.
Table 2.3 Properties of MgO/Cu interfaces, from [37].

<table>
<thead>
<tr>
<th>IF orientation</th>
<th>IF configuration</th>
<th>IF separation, nm</th>
<th>Adhesive energy, eV</th>
<th>Charge transfer*, e</th>
</tr>
</thead>
<tbody>
<tr>
<td>{222}</td>
<td>O-terminated</td>
<td>0.125</td>
<td>2.9</td>
<td>0.18</td>
</tr>
<tr>
<td>{222}</td>
<td>Mg-terminated</td>
<td>0.21</td>
<td>1.7</td>
<td>0.15</td>
</tr>
<tr>
<td>{100}</td>
<td>(Cu</td>
<td>O)</td>
<td>0.20</td>
<td>1.0</td>
</tr>
<tr>
<td>{100}</td>
<td>(Cu</td>
<td>Mg)</td>
<td>0.26</td>
<td>0.2</td>
</tr>
</tbody>
</table>

*Note: positive values indicate electron charge transfer from metal to ceramic, while negative values indicate electron charge transfer from ceramic to metal.

The method developed in reference 37 was also applied to polar {222} and nonpolar {100} CdO/Ag interfaces [51]. In contrast to the MgO/Cu system, the authors found that {100} interfaces in CdO/Ag system are slightly more preferred than in MgO/Cu system. This is consistent with experimental TEM observation that some CdO precipitates in internally oxidized Ag(Cd) alloy are truncated on {100} planes [52]. Preliminary results of this study in reference 51, also suggest that the adhesive energies for oxygen and cadmium-terminated {222} interfaces are similar. Experimentally, it was found by APFIM analysis [28] that O and Cd terminations at CdO/Ag interfaces produced by internal oxidation are equally probable and this is consistent with the LDFT calculations, which obtained the same adhesive energy independent of the termination.
In summary, first-principle calculations of C/M interfaces reveal the following general trends:

1. The nature and strength of bonding between metals and ceramics is determined by the character of both phases and interface geometry. One cannot generalize from one system to another.

2. Bonding at a C/M interface may involve ionic, covalent and metallic contributions.

3. Interfaces involving metals with a high affinity for oxygen generally have a higher adhesive energy than those with a low oxygen affinity.

4. The interface separation scales inversely with adhesive energy.

5. For nonpolar interfaces, configurations with metal atoms on top of oxygen ions are usually energetically preferred. One possible reason for this is easier polarizability of the oxygen ion compared to the metal ion which further lowers the electrostatic energy of the system.

6. Polar interfaces generally exhibit higher adhesive energies and electron charge transfer across the interface than nonpolar ones.

7. For polar interfaces, oxygen termination is often preferred. A feasible explanation for this effect is that a net charge on a polar ceramic plane induces an electrostatic charge in the adjacent metal layers and thus leads to stronger bonding.

8. Impurities such as sulfur reduce the adhesive energy and increase the separation of C/M interfaces.
2.5 DISLOCATION STRUCTURE OF CERAMIC/METAL INTERFACES

To predict possible dislocation structures at C/M interfaces, Bollmann’s O-lattice theory [53] has been employed. For a general commensurate interface formed by two low-index planes, there exists a periodic 2-dimensional array of O-points in the plane of interface, where lateral positions of atoms on both sides of interface are in registry. These regions of "good fit" are surrounded by areas out-of-registry, or regions of "bad fit". If a structure is allowed to relax, the regions of good fit may expand by the introduction of local misfit strains, while the regions of bad fit may localize the misfit between the two lattices into the geometrically necessary misfit dislocations that are aligned along the lines of bad fit. The misfit dislocation network may be derived by building a two-dimensional Wigner-Seitz cell around O-points in the plane of interface [54].

Figures 2.1 (a) and (b) show the predicted dislocation structure for {100} and {222} interfaces between an fcc cubic metal and a rocksalt structure oxide in a cube-on-cube OR. Both orientations are commonly observed for C/M interfaces produced by internal oxidation or by MBE. On a {100} plane, dislocation lines are parallel to <110> directions and have a Burgers vector of a/2<110>, where a is the lattice parameter. On a {222} plane, dislocation line segments are parallel to <211> directions and have a Burgers vector of a/2<110>. In both cases, dislocations have pure edge character. These models have been used to describe dislocation structures in a variety of C/M interfaces. The data on interface geometry and misfit dislocation spacing are summarized
in Table 2.4.

![Diagram](image)

**Figure 2.1.** Misfit dislocation structures predicted by O-lattice theory for (a) {100} and (b) {222} interfaces between two cubic fcc lattices in cube-on-cube orientation relationship. O-points are show by "O" symbols.
**TABLE 2.4** Experimental studies of the dislocation structure of ceramic/metal interfaces.

<table>
<thead>
<tr>
<th>System</th>
<th>Fabr.</th>
<th>OR</th>
<th>IF</th>
<th>(\eta)</th>
<th>(D_{\text{theor}})</th>
<th>(D_{\text{exp}})</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO/Cu</td>
<td>IO</td>
<td>cube-on-cube</td>
<td>{222}</td>
<td>15.4</td>
<td>1.56</td>
<td>1.68</td>
<td>[48]</td>
</tr>
<tr>
<td></td>
<td>IO</td>
<td>cube-on-cube</td>
<td>{222}</td>
<td>15.4</td>
<td>1.56</td>
<td>1.56</td>
<td>[49]</td>
</tr>
<tr>
<td></td>
<td>IO</td>
<td>cube-on-cube</td>
<td>{222}</td>
<td>15.4</td>
<td>1.56</td>
<td>1.60</td>
<td>[18]</td>
</tr>
<tr>
<td>MgO/Pd</td>
<td>IO</td>
<td>cube-on-cube</td>
<td>{222}</td>
<td>7.6</td>
<td>3.10</td>
<td>3.30</td>
<td>[48]</td>
</tr>
<tr>
<td></td>
<td>IO</td>
<td>cube-on-cube</td>
<td>{222}</td>
<td>7.6</td>
<td>3.10</td>
<td>3.12</td>
<td>[49]</td>
</tr>
<tr>
<td></td>
<td>IO</td>
<td>cube-on-cube</td>
<td>{100}</td>
<td>7.6</td>
<td>3.62</td>
<td>3.83</td>
<td>[48]</td>
</tr>
<tr>
<td></td>
<td>IO</td>
<td>twin topotaxy</td>
<td>{222}</td>
<td></td>
<td>2.10</td>
<td>2.28</td>
<td>[48]</td>
</tr>
<tr>
<td>MgO/Ag</td>
<td>MBE</td>
<td>cube-on-cube</td>
<td>{100}</td>
<td>3.2</td>
<td>6.74</td>
<td>6.53</td>
<td>[42]</td>
</tr>
<tr>
<td>MgO/Nb</td>
<td>MBE</td>
<td>epitaxy</td>
<td>{222}_{\text{MgO}}</td>
<td>10.4</td>
<td>1.5</td>
<td>2.7</td>
<td>[55]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[110]_{\text{MgO}}</td>
<td></td>
<td>[100]_{\text{Nb}}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgO/Nb</td>
<td>MBE</td>
<td>(100)_{\text{MgO}}</td>
<td></td>
<td>(110)_{\text{Nb}}</td>
<td>{100}_{\text{MgO}}</td>
<td>9.8</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[011]_{\text{MgO}}</td>
<td></td>
<td>[111]_{\text{Nb}}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CdO/Ag</td>
<td>IO</td>
<td>cube-on-cube</td>
<td>{222}</td>
<td>13.8</td>
<td>1.75</td>
<td>incoher.</td>
<td>[40]</td>
</tr>
</tbody>
</table>

\(a\) Fabr.: fabrication method. \(b\) \(\eta\): dislocation slip fraction. \(c\) \(D_{\text{theor}}\): theoretical dislocation width. \(d\) \(D_{\text{exp}}\): experimental dislocation width.
<table>
<thead>
<tr>
<th>System</th>
<th>Fabr. (^a)</th>
<th>OR</th>
<th>IF plane</th>
<th>(\eta) (^b)</th>
<th>(D_{\text{theor}}) (^c) (nm)</th>
<th>(D_{\text{exp}}) (^d) (nm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO/Cu</td>
<td>IO</td>
<td>cube-on-cube</td>
<td>[222]</td>
<td>21.0</td>
<td>1.0</td>
<td>1.0</td>
<td>[56]</td>
</tr>
<tr>
<td>NiO/Pt</td>
<td>DB</td>
<td>cube-on-cube</td>
<td>[100]</td>
<td>6.1</td>
<td>4.6</td>
<td>5.2</td>
<td>[57]</td>
</tr>
<tr>
<td>(\text{Al}_2\text{O}_3/Nb)</td>
<td>IO</td>
<td>(0001)(\text{Al}_2\text{O}_3)</td>
<td></td>
<td>(110)(\text{Nb})</td>
<td>(0001)(\text{Al}_2\text{O}_3)</td>
<td>3.2</td>
<td>7.4</td>
</tr>
<tr>
<td>(\text{Al}_2\text{O}_3/Nb)</td>
<td>MBE</td>
<td>(0112)(\text{Al}_2\text{O}_3)</td>
<td></td>
<td>(100)(\text{Nb})</td>
<td>(0112)(\text{Al}_2\text{O}_3)</td>
<td>5.5</td>
<td>2.0</td>
</tr>
<tr>
<td>(\text{Al}_2\text{O}_3/Cu) (cubic)</td>
<td>IO</td>
<td>(111)(\text{Al}_2\text{O}_3)</td>
<td></td>
<td>(111)(\text{Cu})</td>
<td>(111)(\text{Al}_2\text{O}_3)</td>
<td>9.7</td>
<td>incoher.</td>
</tr>
</tbody>
</table>

\(^a\) Fabrication methods:
- IO - internal oxidation;
- MBE - molecular beam epitaxy;
- DB - diffusion bonding.

\(^b\) \(\eta\) is a fractional misfit parameter, 
\[
\eta = 2(a_{\text{ceramic}} - a_{\text{metal}})/(a_{\text{ceramic}} + a_{\text{metal}}),
\]
where the a's are the lattice parameters.

\(^c\) \(D_{\text{theor}}\) is a dislocation spacing predicted in a particular orientation by O-lattice theory. E.g., for \{222\}\(\text{MgO/Cu}\) system \[49\] in \(<110>\) orientation assuming \(b = a/2<110>\)
\[
D_{\text{theor}} = \frac{a_{\text{MgO}}a_{\text{Cu}}}{a_{\text{MgO}} - a_{\text{Cu}}} \cdot \frac{\sqrt{3}}{2\sqrt{2}}
\]

\(^d\) \(D_{\text{exp}}\) is the spacing experimentally measured by HREM or WBDF TEM.
In most of the studies listed in Table 2.4, the structure of C/M interfaces was studied by HREM in a single projection. Therefore, only one-dimensional periodicity of the interface structure can be observed and the exact determination of the two-dimensional dislocation structure is not possible. Alternatively, the weak-beam dark-field (WBDF) TEM can be used to observe dislocation structure directly. This technique is usually limited, however, to systems with a relatively small misfit parameter for the dislocation structure to be resolved. In reference 57, the dislocation structures of [100]NiO/Pt interfaces were observed by a combination of HREM and WBDF TEM techniques. The authors demonstrated that in a simple cube-on-cube OR experimental observations are in good agreement with O-lattice theory. For more complicated OR's, however, such as in case of small deviations from a cube-on-cube OR, O-lattice theory fails to predict the size, shape, and orientation of the dislocation network.

Table 2.4 demonstrates that in most cases the observed dislocation spacing is slightly larger than the predicted one. It is suggested in the literature [17, 40, 48, 57] that the reason for this is a partial accommodation of the lattice misfit by elastic straining in the metal matrix. It has also been proposed [40] that oxygen or other impurity atoms segregated at an interface may also partially accommodate misfit.

The dislocation models predicted by O-lattice theory are based on purely geometrical considerations and do not consider the energetics of the system. As was observed by HREM and WBDF TEM techniques for the Si(Ge)/Si[111]
interface [54], the hexagonal network predicted by the O-lattice theory for \{111\} interfaces may dissociate into a network of partial misfit dislocations. For the \{100\} and \{222\} interfaces shown in Fig. 2.1, the corresponding dissociated structures are shown in Fig. 2.2. The driving force behind such transformation is a lowering of the total energy of an interface. As shown in reference 54, two different types of stacking are formed at the triple dislocation nodes in the structure displayed in Fig. 2.1 (b): intrinsic stacking faults (SFs) characterized by a sequence (...abcabc | BCABC...) and forbidden SFs (...abcabc | CABC...). The nodes of the first type may dissociate into partial misfit dislocations bounding an interfacial SF, see Fig. 2.2. The elastic energy associated with the dislocation content of an interface is proportional, to a first approximation, to the square of the Burgers vector. For a \{222\} interface, dissociated interfacial dislocations are formed by straight pure edge partial dislocations with Burgers vector $b = a/6<211>$, see Fig. 2.2 (b). Thus, the partial dislocations have a three times lower line energy than complete misfit dislocations with $b = a/2<110>$. On the other hand, the total length of dislocations is longer by the factor $\sqrt{3}$. Therefore, the dissociated structure shown in Fig. 2.2 (b) will be energetically favorable in any system with a low interfacial SF energy [54].
Figure 2.2. Dissociation of misfit dislocation structures shown in Fig. 2.1 for (a) \{100\} and (b) \{222\} interfaces. Original structures are indicated by dashed lines and the dissociated structures are shown in thick lines. O-points are indicated by "O" symbols. The shaded areas in both structures correspond to interfacial stacking faults.
For the \{100\}MgO/Ag interface, the dissociated structure shown in Fig. 2.2 (a) was proposed in reference 42. The observed dislocation spacing of 6.53 nm is in a reasonable agreement with the calculated spacing for this structure (6.74 nm).

The dissociation of misfit dislocations on \{222\}MgO/Cu interface was proposed [18] based on HREM observations and atomistic simulations. To make a conclusive decision, however, one has to observe the dislocation structure by WBDF TEM, since the spacing between dislocations in a \{222\} interface is the same for both the initial and dissociated structures.

In several C/M systems, misfit dislocations are observed that reside in the metal matrix, a few interatomic spaces away from an interface, and this is denoted the stand-off effect. There have been several attempts to explain this effect and to predict an equilibrium stand-off distance. An elasticity theory of the stand-off effect was developed in reference 58. It suggests that the driving force for the stand-off effect is the difference in elastic moduli between ceramic and metal. It is energetically favorable to shift dislocation cores into the metal to minimize the elastic strain in the ceramic phase that is usually much stiffer. An equilibrium stand-off distance is then determined by the balance between an image force that repels a dislocation away from an interface to lower the elastic strain energy in the ceramic, and an attractive coherency force that reflects an energetic advantage of semicoherent interface over a fully coherent one. Based on these assumptions, an equilibrium stand-off distance \(D_{\text{stand-off}}\) was derived using the linear elasticity theory:
\[
D_{\text{stand-off}} = -\frac{A + B}{8\pi(\alpha + 1)} \frac{b_i}{\eta};
\]  

(2.1)

where \( b_i \) is the in-plane component of a Burgers vector; \( \eta \) is a fractional lattice misfit parameter defined as

\[
\eta = \frac{2(a_1 - a_2)}{(a_1 + a_2)};
\]

(2.2)

where the \( a \)'s are the lattice parameters of the two phases. And \( A, B, \) and \( \alpha \) are constant expressions containing the elastic constants of the two materials:

\[
A = \frac{1 - \Gamma}{1 + \Gamma \kappa_1},
\]

(2.3.a)

\[
B = \frac{\kappa_2 - \Gamma \kappa_1}{\kappa_2 + \Gamma};
\]

(2.3.b)

where \( \Gamma = G_2/G_1 \) and \( \kappa_i = 3 - 4\nu_i \); \( G \)'s are shear moduli, \( \nu \)'s are Poisson's ratios, and the indices 1 and 2 refer to metal and ceramic, respectively. Finally, \( \alpha \) is the Dundurs parameter that is a measure of the elastic mismatch between two materials:

\[
\alpha = \frac{G_1(1 - \nu_2) - G_2(1 - \nu_1)}{G_1(1 - \nu_2) + G_2(1 - \nu_1)}.
\]

(2.4)
An important consequence of Eq. (2.1) is that the stand-off distance scales inversely with $\eta$. Therefore, it is expected that C/M systems with a strong elastic mismatch and a small lattice misfit will have the largest values of $D_{\text{stand-off}}$. The experimental values of $D_{\text{stand-off}}$ observed in different C/M systems are summarized in Table 2.5. To observe the correlation predicted by Eq. (2.1), Fig. 2.3 shows a plot of the stand-off distances in C/M systems versus $1/\eta$. An analysis of the data presented in Table 2.5 allows the following observations:

1. Equation (2.1) predicts only the general trend. No stand-off effect has been observed for any system with $\eta > 0.1$. Calculated values, however, seem to underestimate the observed stand-off distances. As suggested in reference 3, Eq. (2.1) is derived based on linear elasticity theory and may, therefore, underestimate the energy of misfit dislocation cores.

2. For a single C/M system, the stand-off effect may vary dramatically. In (0001)Al$_2$O$_3$/Nb, the stand-off distance varies from 0 to 1.2 nm, depending on the method of IF fabrication.

3. In some C/M systems such as {100}MgO/Ag and (0001)Al$_2$O$_3$/Nb, experiments do not exhibit the stand-off effect despite a small value of misfit. Factors such as processing conditions, oxygen partial pressure, and the presence of defects and impurities may affect the kinetics of misfit dislocation nucleation, mobility, and the resulting interface structure.

**TABLE 2.5** Stand-off distance in different ceramic/metal systems
<table>
<thead>
<tr>
<th>Interface</th>
<th>Fabrication method&lt;sup&gt;a&lt;/sup&gt;</th>
<th>η</th>
<th>$D_{\text{stand-off}}$ (nm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[222]MgO/Cu</td>
<td>IO</td>
<td>0.153</td>
<td>0</td>
<td>[48,49]</td>
</tr>
<tr>
<td>[222]CdO/Ag</td>
<td>IO</td>
<td>0.136</td>
<td>0</td>
<td>[52]</td>
</tr>
<tr>
<td>[222]MgO/Nb</td>
<td>MBE</td>
<td>0.104</td>
<td>0</td>
<td>[55]</td>
</tr>
<tr>
<td>[100]MgO/Nb</td>
<td>MBE</td>
<td>0.098</td>
<td>0.47 - 0.93</td>
<td>[55]</td>
</tr>
<tr>
<td>[222]MgO/Pd</td>
<td>IO</td>
<td>0.076</td>
<td>0.22</td>
<td>[48]</td>
</tr>
<tr>
<td>[222]MgO/Pd</td>
<td>IO</td>
<td>0.076</td>
<td>0.39 - 0.78</td>
<td>[49]</td>
</tr>
<tr>
<td>[222]MnO/Cu</td>
<td>IO</td>
<td>0.064</td>
<td>0.42</td>
<td>[56]</td>
</tr>
<tr>
<td>{100}NiO/Pt</td>
<td>DB</td>
<td>0.061</td>
<td>0.59 - 0.78</td>
<td>[57]</td>
</tr>
<tr>
<td>(0001)Al$_2$O$_3$/Nb</td>
<td>MBE</td>
<td>0.055</td>
<td>1.2</td>
<td>[55]</td>
</tr>
<tr>
<td>{0112}Al$_2$O$_3$/Nb</td>
<td>IO</td>
<td>0.032</td>
<td>0.93</td>
<td>[40]</td>
</tr>
<tr>
<td>[100]MgO/Ag</td>
<td>MBE</td>
<td>0.032</td>
<td>0</td>
<td>[42]</td>
</tr>
<tr>
<td>[222]NiO/Ag</td>
<td>external oxidation</td>
<td>0.022</td>
<td>0.47 - 0.71</td>
<td>[17]</td>
</tr>
<tr>
<td>(0001)Al$_2$O$_3$/Nb</td>
<td>MBE</td>
<td>0.019</td>
<td>0</td>
<td>[41]</td>
</tr>
</tbody>
</table>

<sup>a</sup>Fabrication methods: IO - internal oxidation; MBE - molecular beam epitaxy; DB - diffusion bonding.
Figure 2.3. Stand-off distance in ceramic/metal systems versus inverse of lattice misfit parameter, $\eta$. Open triangles are experimental data. Open circles are predictions based on Eq. (2.1). References to experimental data are given in Table 2.5.
2.6 NATURE OF BONDING AND TERMINATION OF POLAR CERAMIC/METAL INTERFACES

The attractive interaction between ceramic and metal forming an interface is the thermodynamic basis of interface stability. In turn, the type and strength of this interaction determines the atomic structure of an interface, its chemical stability, and ultimately, the mechanical behavior of the material. For this reason, studies of bonding at C/M interfaces are of both fundamental and technological importance. The nature of bonding between ceramics and metals includes the type of bonding, the bond strength, and the sign and value of charge transfer across the interface.

A variety of metal oxide/metal interfaces incorporate polar planes of the oxide, such as \{222\} planes in rocksalt structure oxides (MgO, CdO, MnO, NiO) or a basal plane of alumina. Two distinct terminations are possible at such interfaces: oxygen or metal. As discussed in Section 2.4, simulation results on this problem are very limited. Hence, a significant experimental effort was made to determine the nature of the terminating plane at polar C/M interfaces.

Despite the limited nature of chemical information obtainable by HREM, it has been the main method of determining the nature of terminating plane. Typically, HREM image simulations are used to match HREM images or through-focal series of C/M interfaces with the simulated structures having different terminations. Extensive image simulations are required to determine conclusively the nature of the terminating plane. Alternatively, as discussed in
Chapter 2.3, recently developed analytical techniques for C/M interfaces such as ELNES, APFIM, and Z-contrast STEM are capable of determining the interface chemistry more readily.

The experimental data on termination of polar C/M interfaces are listed in Table 2.6. In most cases, oxygen terminations have been reported. In an ELNES study [23] of \(\alpha\)-\(\text{Al}_2\text{O}_3\)/Cu interface produced by MBE, it was found that a direct chemical bond is established between copper and oxygen ions, and copper exists at the interface in a (+1) state. In reference 40, it was proposed that the oxygen termination of polar C/M interfaces, produced by internal oxidation, must be dominant due to a high oxygen activity. It was discovered, however, using the APFIM technique [28] that in the internally oxidized \(\{222\}\)CdO/Ag system, O and Cd terminations at \(\{222\}\) interfaces occur with equal probability. This result is also consistent with the LDFT calculations [51] discussed in Section 2.4, where it was found that the adhesive energies for oxygen and cadmium-terminated \(\{222\}\) interfaces are similar.


<table>
<thead>
<tr>
<th>Interface</th>
<th>Fabrication method\textsuperscript{a}</th>
<th>Experimental method</th>
<th>IF termination</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[222]MgO/Cu</td>
<td>IO</td>
<td>HREM/image simulations</td>
<td>O terminated</td>
<td>[49]</td>
</tr>
<tr>
<td>[222]MgO/Cu</td>
<td>IO</td>
<td>APFIM</td>
<td>O terminated</td>
<td>[27]</td>
</tr>
<tr>
<td>[222]CdO/Ag</td>
<td>IO</td>
<td>HREM/image simulations</td>
<td>O terminated</td>
<td>[40]</td>
</tr>
<tr>
<td>[222]CdO/Ag</td>
<td>IO</td>
<td>APFIM</td>
<td>O and Cd termination with equal probability</td>
<td>[28]</td>
</tr>
<tr>
<td>[222]MgO/Pd</td>
<td>IO</td>
<td>HREM/image simulations</td>
<td>O terminated</td>
<td>[49]</td>
</tr>
<tr>
<td>[222]MnO/Cu</td>
<td>IO</td>
<td>HREM/image simulations</td>
<td>O terminated</td>
<td>[56]</td>
</tr>
<tr>
<td>[100]ZrO\textsubscript{2}/Ni</td>
<td>IR</td>
<td>Z-contrast STEM</td>
<td>O-terminated</td>
<td>[21]</td>
</tr>
<tr>
<td>[222](\eta)'-Al\textsubscript{2}O\textsubscript{3}/Cu</td>
<td>IO</td>
<td>HREM/image simulations</td>
<td>O-terminated</td>
<td>[39]</td>
</tr>
<tr>
<td>[0001](\alpha)-Al\textsubscript{2}O\textsubscript{3}/Cu</td>
<td>MBE</td>
<td>ELNES</td>
<td>O-terminated</td>
<td>[23]</td>
</tr>
<tr>
<td>(01 (\bar{1})2)(\alpha)-Al\textsubscript{2}O\textsubscript{3}/Nb</td>
<td>MBE</td>
<td>HREM/image simulations</td>
<td>O terminated</td>
<td>[55]</td>
</tr>
<tr>
<td>(0001)(\alpha)-Al\textsubscript{2}O\textsubscript{3}/Nb</td>
<td>MBE</td>
<td>HREM/image simulations</td>
<td>O terminated</td>
<td>[41]</td>
</tr>
<tr>
<td>(\alpha)-Al\textsubscript{2}O\textsubscript{3}/Nb</td>
<td>DB</td>
<td>ELNES</td>
<td>Al-terminated</td>
<td>[24]</td>
</tr>
<tr>
<td>(\alpha)-Al\textsubscript{2}O\textsubscript{3}/Ni</td>
<td>DB</td>
<td>ELNES</td>
<td>Al-terminated</td>
<td>[24]</td>
</tr>
<tr>
<td>(\alpha)-Al\textsubscript{2}O\textsubscript{3}/Fe</td>
<td>DB</td>
<td>ELNES</td>
<td>Al-terminated</td>
<td>[24]</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Fabrication methods: IO - internal oxidation; MBE - molecular beam epitaxy; IR - internal reduction; DB - diffusion bonding.
In contrast to many interfaces produced by internal oxidation and MBE, a recent ELNES study [24] of $\alpha$-alumina/Me (Me = Nb, Ni, or Fe) interfaces produced by diffusion bonding in a reducing atmosphere revealed that in all three cases, the interfaces are terminated by aluminum. The authors rationalized that metal termination as being consistent with the stability of intermetallic aluminides, such as $M_3Al$, and the instability of oxides, such as FeO and NiO, at elevated temperatures in the absence of a partial pressure of oxygen. Electron charge transfer at these interfaces is from alumina to metal. As a result, direct aluminum-metal bonds are established, similar to those found in transition metal aluminides.

This last conclusion seems to have broader applicability. In case of oxygen-terminated $\{222\}$MgO/Cu and $\{222\}$MgO/Pd interfaces [49], the authors found by HREM image simulations that the interfaces are composed of distorted structural units of Cu$_2$O and PdO, respectively. For the $\{222\}$MgO/Cu interface, it was found by first-principle LDFT calculations [37] that charge transfer occurs from copper to oxygen. Therefore, formation of directional covalent bonds between ceramic and metal at an interface appears to involve creation of interfacial structural units similar to compounds that metal and the other species (oxygen or metal) would form in the bulk. This idea correlates with a concept of grain boundary segregation, see reference 59. Different chemical bond geometries are available for a segregant at the GB that are not present in the matrix. The mechanism proposed in reference 59 implies that
when an atom reaches a grain boundary, it can form a set of bonds that are more favorable than those it can form in the bulk. The solute atom thus establishes a molecular unit which, in the ideal case, is probably similar in structure and bonding to the compound that a solute atom would try to form with the host.

In the examples considered above, strong bonding between ceramic and metal was observed that leads to the formation of semicoherent interfaces with strongly localized misfit. An opposite trend was observed for \{222\}CdO/Ag interface [40]. It was concluded from HREM image analysis that interfaces are incoherent and that the noble nature of silver implies weak adhesive forces across the interface, that mainly result from Coulomb interactions between oxygen ions and image charges induced in the metal. A recent HREM study of this interface, however, shows evidence of misfit dislocations [52]. Similarly, it was concluded from analyses of HREM images that the \{222\}η'-Al₂O₃/Cu interface is also incoherent [39]. Determining the degree of coherency of a C/M interface by HREM remains a difficult problem, since the misfit may be localized primarily in the terminating oxygen layer that is not visible in HREM images, due to the weak scattering potential of oxygen [17]. Additionally, the terminating oxygen layer in internally oxidized specimens may incorporate point defects to avoid a net electrostatic charge on the oxide precipitates.

The nature of bonding in \(\alpha\)-Al₂O₃/Cu and AlN/Cu thin film systems was studied by UPS [26]. The two ceramic substrates have dramatically different
bonding: purely ionic in $\alpha$-alumina and mostly covalent in AlN. It was found that in (0001)$\alpha$-Al$_2$O$_3$/Cu system copper binds preferentially to surface oxygen atoms, while in (0001), (01\overline{1}1), and (01\overline{1}2)AlN/Cu systems copper forms metallic bonds with aluminum.

In summary, experimental studies of bonding at C/M interface reveal the following general trends:

1. Since C/M interfaces represent the most complicated case of heterophase interfaces, bonding varies dramatically for different C/M systems. It depends on the nature of both the metal and ceramic, the chemistry of the terminating plane of the ceramic, and processing conditions such as oxygen partial pressure and substrate defects.

2. In C/M systems with unconstrained interface geometry, interfaces are usually formed on the close-packed planes of the metal and ceramic. For polar interfaces, it corresponds to interfaces with the highest charge density and therefore the strongest image interaction with the metal. Thus, these interfaces are the low-energy ones. Additionally, there is a strong tendency to align close-packed directions in both phases.

3. C/M interfaces involving reactive metals such as Nb, Al, or Fe are strongly bound by forming directional bonds between metal and one of the ceramic species. For interfaces formed in an excess of oxygen, covalent metal-oxygen bonding is usually formed with charge transfer from metal to ceramic. For interfaces formed in a reducing atmosphere, direct metal-metal bonds are
formed with charge transfer from ceramic to metal.

2.7 SEGREGATION AT CERAMIC/METAL INTERFACES

Interfacial segregation refers to the process by which a solute element becomes enriched at an interface. It occurs when the solute element diffuses through the bulk phases, encounters an interface, and becomes trapped there. Sites at the interface exist with an energy different from the adjacent lattices. Partition between these two types of sites by solutes is in accordance with statistical thermodynamic considerations, in order to minimize the free energy of the entire system. When the overall free energy has reached a minimum, the process is termed equilibrium segregation. The Gibbs adsorption isotherm defines the interfacial excess of solute \( i \) (\( \Gamma_i \)) as

\[
\Gamma_i = -\left(\frac{\partial \gamma}{\partial \mu_i}\right)_{T,P},
\]

where \( \gamma \) the is interfacial free energy and \( \mu_i \) is the chemical potential of the solute. Segregation may result either in an enrichment or depletion of solute atoms at the interface, which corresponds to either a positive or negative value of \( \Gamma_i \).
It has been long recognized that grain boundary segregation in metallic alloys critically affects many of their mechanical and physical properties. Significant knowledge has been accumulated [59-61] on the relations between grain boundary segregation and the nature of the alloy’s components, presence of additional elements, temperature, type of grain boundary, and grain boundary orientation. Segregation at heterophase interfaces, and C/M interfaces in particular, has been studied to a smaller extent. Five classes of technologically important materials involving C/M interfaces are dispersion hardened alloys, metal-matrix fiber-reinforced composite materials, oxide films and coatings on the surface of high-temperature alloys, ceramic/metal welds, and microelectronic packaging. The following paragraphs review the available experimental data on segregation in these materials.

In metal-matrix fiber-reinforced composite materials solute segregation may strongly affect the fiber/matrix cohesion and pull-out properties. This can be deleterious as a cause of unwanted separation, but can also be useful in improving the crack deflection properties [62]. In a review [63], it is reported that various fiber coatings such as carbon, graphite, or molybdenum, dramatically reduce the binding energy and sliding stress at matrix/fiber interfaces in the $\alpha$-$\text{Al}_2\text{O}_3$/TiAl and SiC/Ti systems. As a result, the overall plasticity of a composite is significantly improved.

In case of dispersion hardened alloys or internally oxidized alloys, it has been suggested [17, 40] 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 system. The effect of segregation on an alloy's properties may be dual: segregation may cause strong decohesion at the precipitate/matrix interface and, as a result, loss of ductility occurs through microvoid coalescence [62]. On the other hand [64], an important effect of solute segregation to 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 [65] that trace additions of cadmium to Al-4 at.% Cu alloy can decrease the $\theta'$ precipitation coarsening rate by a factor of five. The authors concluded that this effect is due to cadmium segregation to Al/$\theta'$ interfaces; segregation reduces the interfacial energy and, consequently, the coarsening rate, according to the Greenwood-Lifshitz-Wagner theory. It took over 20 years before it was proven by APFIM and AEM measurements [66] that in a quaternary Al(Cu, Mg, Ag) alloy, silver and magnesium segregate to $\alpha$/\(\Omega\) interface (the structure of \(\Omega\) phase was found to be almost identical to $\theta'$), indeed dramatically slowing the aging of this alloy. Similarly, oxygen and phosphorus additions to an iron alloy were found to decrease the growth rate of Fe$_4$N precipitates [67], presumably by segregation of O and P to Fe$_4$N/Fe interfaces. It was later found [68] by APFIM analysis that in internally nitrided Fe(Mo, Sb) alloys antimony segregates to MoN/Fe interfaces with an
enrichment ratio of about 50. A strong segregation level was observed for both small fully coherent precipitates and larger incoherent particles.

Solute segregation to interfaces between metals and scales formed during high-temperature exposure in an oxidizing atmosphere is a relatively well-studied phenomenon [7]. 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, Al₂O₃ and Cr₂O₃ oxide layers are formed on the surfaces of Fe or Ni-based alloys. It has long been observed that impurities including S, P, Cu, Sn, As, and Sb can segregate to a metal/scale interface and cause strong decohesion and exfoliation of the oxide film. At the same time, 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 not agreed upon in the literature. Several models have been proposed to explain REE, including segregation of reactive elements to the interface leading to a direct bond strength enhancement [69] and elimination of detrimental impurities from the interface due to impurity gettering and/or site competition processes [70]. Recently, an elegant interface poisoning mechanism of REE was introduced [71], where it was proposed that since in most cases oxide scales on high-temperature alloys are semicoherent, growth of the scale must involve nonconservative climb of misfit dislocations. The climb process involves 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 effectively the misfit dislocations.

Solute segregation at C/M interfaces produced by diffusion bonding was studied in reference 72. The authors diffusion-bonded Nb and Cu metals to polycrystalline alumina and studied the effect of bonding temperature and sputter-cleaning of the surfaces, prior to bonding, on the mechanical strength and composition of the interface. The latter was measured by AES. It was found in both systems that initial surface contamination by oxygen, sulfur, carbon, or chlorine greatly reduces the bonding strength.

The diffusion bonded Al$_2$O$_3$/Nb system was studied in greater detail in reference 73. In the first experiment, silver was deliberately introduced onto the sapphire substrates, with three different orientations, prior to UHV diffusion bonding to Nb single crystals. After the bonding, in situ fracture tests were conducted and AES of the initial and fractured surfaces performed. It was found that for any initial silver film thickness in the range 1 to 30 nm, the amount of silver on the fractured surfaces is in the range 0.3 to 0.7 monolayers. It was assumed that excess silver is removed by evaporation during bonding or diffusion into the Nb matrix, thus the amount detected corresponds to a saturated segregation layer. Mechanical measurements revealed that the bonding strength systematically decreases with increasing amount of Ag at the interface for all three orientation relationships. This was found to be in accord
with the an old idea [62, 64] that the cohesion of an interface is reduced by impurities with a larger atomic radius and a smaller heat of sublimation. The latter is true for the Nb(Ag) system. The second impurity studied at the (01$\bar{1}$0)$\text{Al}_2\text{O}_3$/Nb interface was sulfur present in the bulk Nb at a concentration of 30 at.ppm. It was made to segregate at a Nb free surface prior to bonding by \textit{in situ} annealing. As a result, AES measurements detected about 0.75 monolayer coverage at the surface. After bonding, mechanical tests indicated a very small difference (16\%) in bonding strength for interfaces with and without intentional contaminations. AES measurements showed no sulfur at the fractured surface with a sensitivity of 0.05 monolayer. Therefore, it was concluded that sulfur may also be a bond weakening element for the (01$\bar{1}$0)$\text{Al}_2\text{O}_3$/Nb interface, but the driving force for its interfacial segregation is very small. This is consistent with a thermodynamic theory discussed below, as sulfur is known to segregate very strongly to a Nb free surface.

C/M joints in microelectronic applications are usually highly controlled in terms of interfacial chemistry. One of the main problems in reducing the scale of integrated circuits (ICs) down to 0.1 $\mu$m levels is the phenomenon of electromigration [8] in Al(Cu) interconnect lines. It was observed [74, 75] that in a binary Al(Cu) alloy, Cu atoms have a much longer incubation period for electromigration damage than Al atoms. It was also found that Cu segregates to grain boundaries of this alloy. Therefore, Cu segregation at interfaces, providing the dominant paths for electromigration, can offset the catastrophic Al electromigration damage. At typical operating temperatures, the dominant
diffusion paths, due to electromigration, are through the interconnect grain boundaries. As the width of interconnect lines decreases, a characteristic bamboo grain structure is developed and grain boundary short circuits are interrupted. Therefore, the dominant diffusion path becomes along the interface between the metal interconnect and the ceramic substrate or diffusion barrier. In a recent study [76], Cu segregation at Al₂O₃/Al(Cu) interfaces was studied as a function of bulk Cu concentration and temperature. Significant levels of segregation were detected by medium energy ion scattering (MEIS), amounting to 0.2 ML of copper, while copper did not segregate to the free surface of the alloy. Assuming Langmuir-McLean behavior, the authors found an effective segregation free energy of copper at this interface equal to 0.21±0.03 eV. These results suggest that copper segregation at interconnect/substrate interfaces may play a significant role in reducing the susceptibility of the interconnect lines to electromigration damage.

Analysis of experimental data on segregation in C/M systems is thwarted by the absence of a widely accepted theory of interfacial segregation. A thermodynamic model has been developed [77] for brittle interfacial fracture of heterophase interfaces. For the case of a segregated heterophase interface, an important parameter is the change in the work of separation due to solute segregation, that is, bond weakening. For a general unstressed interface, in the context of the Langmuir-McLean model, the following equation was derived
\[ 2\gamma_{IF}^{pure} - 2\gamma_{segr}^{IF} = \Delta G_0^{IF} \cdot \Gamma_{IF} - (\Delta G_0^{S1} \cdot \Gamma_{S1} + \Delta G_0^{S2} \cdot \Gamma_{S2}); \]

where \( \gamma_{IF} \) is a work of separation; \( \Delta G_0 \) is a Gibbs free energy of segregation; \( \Gamma \) is the Gibbsian interfacial excess of solute; and the subscripts IF, S1, and S2 denote the interface and two fractured surfaces, respectively.

According to the Eq. (2.6), the effect of segregation on the bond strength of a general interface is determined by the propensity of the segregated species for surface segregation, as compared to interfacial segregation. If the tendency for surface segregation is higher than for interfacial segregation, the term on the right hand side of the equation is positive, and this is the normal case when the presence of an impurity weakens the interfacial strength. Thermodynamics, however, does not preclude the case of anomalous segregation when the strength of the interface is increased by a segregant (negative term on the right hand side). For homophase interfaces, there are well known examples [59, 61] of increased grain boundary cohesion in iron by carbon segregation and in Ni3Al by boron segregation. Data for heterophase interfaces are sparse, but one of the cases where the direct bond enhancement was suggested is the reactive element effect (REE) discussed earlier in this section. It should be noted, however, that the theory developed in [77] is qualitative and its predictive power is limited since it neglects plastic deformation process.
In conclusion, growing applications of C/M interfaces in both structural and electronic applications has motivated the recent interest in fundamental properties of such heterophase interfaces. While the atomic structure of atomically clean interfaces was studied in many systems by means of HREM, the chemistry of C/M interfaces and the atomic structure of segregated interfaces is less well studied. Judging by the paramount importance of segregation effects in metals, one can expect that understanding the mechanisms and effects of segregation in C/M systems is essential for development of many technologically important materials.
CHAPTER 3

ATOMIC-SCALE STUDY OF INTERFACIAL CHEMISTRY IN MgO/Cu(Ag) AND CdO/Ag(Au) SYSTEMS BY ATOM-PROBE MICROSCOPY

3.1 INTRODUCTION

As discussed in Section 2.7, solute segregation at ceramic/metal heterophase interfaces is known to affect the adhesion of composite interfaces because it weakens the bonding between the disparate materials that comprise such an interface. It has only been studied to some extent, however, in the case of metal/scale interfaces in high-temperature alloys. And in the case of ceramic/metal systems, with a highly dispersed ceramic phase, segregation and its effects on precipitate morphology have been observed, but not studied in detail. One of the reasons for this is that ceramic materials are notoriously difficult to prepare with high purity and segregation of a specific solute to a ceramic surface or ceramic/metal interface is often masked by trace impurities. Another reason is the experimental challenge presented by systems with
nanometer-size precipitates, because of the atomic resolution essential for segregation studies at this scale.

In this chapter, we present a novel approach to study solute-atom segregation at atomically clean ceramic/metal interfaces. Our method involves internally oxidizing ternary metallic alloys -- one solvent and two solute species at low concentrations -- fabricated from elements with a high initial purity and selectively internally oxidizing only one of the two solute species, thereby producing an atomically-clean metal-oxide phase embedded in a metallic matrix. The second unoxidized solute species must redistribute itself between the single-phase solid-solution metallic matrix and the metal-oxide phase to maintain itself in thermodynamic equilibrium in this two-phase system. Equilibrium is achieved by the unoxidized solute-species segregating to ceramic/metal interfaces. The Gibbsian interfacial excess of solute, $\Gamma_{\text{solute}}$, at this interface is then determined in a direct and highly quantitative manner employing atom-probe field-ion microscopy (APFIM). APFIM has been recently employed to study, on an atomic scale, the chemistry of the terminating plane of atomically clean \{222\}MgO/Cu and \{222\}CdO/Ag interfaces [27, 28], 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 [48-50] and CdO/Ag(Au) [52] interfaces demonstrated that in both systems
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. HREM studies revealed semicoherent interfaces containing a network of misfit dislocations. The lattice misfit parameter, \( \eta \), as defined by Eq. 2.2, is given by

\[
\eta = 2(a_{\text{oxide}} - a_{\text{metal}})/(a_{\text{oxide}} + a_{\text{metal}}).
\]

The value of \( \eta \) is 0.1525 for \( a_{\text{MgO}} = 0.4212 \) nm and \( a_{\text{Cu}} = 0.3615 \) nm, and 0.1433 for \( a_{\text{CdO}} = 0.471 \) nm and \( a_{\text{Ag}} = 0.408 \) nm.

### 3.2 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. The detailed alloy fabrication, internal oxidation, and annealing procedures are outlined in Appendix A. For transmission electron microscopy (TEM) studies, standard 3 mm diameter disk specimens were prepared. For APFIM experiments, a portion of the ingots was swaged into rods and subsequently cold-drawn into 200 \( \mu \)m diameter wires.

Interfaces in both systems were prepared by internal oxidation. The copper based alloy was oxidized employing the Rhines pack technique [11] in a 1:1:1 (vol.) mixture of Cu, Cu$_2$O and Al$_2$O$_3$ powders at 950°C for 2 h. This
condition corresponds to an oxygen partial pressure of $10^{-2}$ Pa, see Appendix A. To maximize the level of Ag segregation at $\{222\}$MgO/Cu interfaces, the specimens were subsequently annealed in argon at 500°C for 6 h. This time was chosen on the basis of the known bulk diffusivity of Ag in Cu [78] and the average distance between MgO precipitates of $\approx$46 nm; the latter was measured by TEM (Section 3.3).

The silver-based alloy was 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, an Hitachi H700H 200 kV microscope was utilized. Specimens for APFIM in the shape of sharply-pointed tips were prepared by electropolishing internally-oxidized wires. The FIM specimens were also examined by TEM using a specially-fabricated double-tilt holder [79].

APFIM data were obtained using a linear time-of-flight atom-probe [80]. Specimens were developed using neon as an imaging gas at 45 to 50 K and tilted such that the probe hole was aligned with the 111 pole of the specimen, thus providing for data collection along a $<111>$ direction. For copper-based specimens, time-of-flight spectra were recorded at a specimen temperature of 41 to 50 K using a pulse fraction, $f$, of 0.2 ($f$ is the ratio of the pulse voltage to the steady-state dc voltage) and a pulsing frequency of 20 or 50 Hz. Silver-based specimens were analyzed at 42 to 45 K using pulse fractions of 0.15 to 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 in order to improve the field evaporation process of MgO precipitates, as further discussed in Section 3.5. The data acquisition electronics of the APFIM system is capable of detecting up to 128 ions per pulse with a 3.3 ns pulse pair resolution in the multihit mode [81]. The key steps in the experimental procedure are schematically summarized in Fig. 3.1.
Figure 3.1. Schematic diagram illustrating the key steps required to produce and study solute-segregation at ceramic/metal interfaces.
3.3 RESULTS OF A CONVENTIONAL TRANSMISSION ELECTRON MICROSCOPY INVESTIGATION

TEM demonstrated that the MgO/Cu(Ag) specimens contain MgO precipitates that are morphologically identical to the ones found in the undoped MgO/Cu system [48-50]; that is, the MgO precipitates have a cube-on-cube orientation relationship with the Cu(Ag) matrix and are octahedral-shaped with faceting on {222} planes. The diameters of the MgO precipitates range from $\approx 20$ to 50 nm for the disk-shaped specimens, and $\approx 10$ to 30 nm for the wire specimens. No phases other than the solid-solution Cu(Ag) matrix and MgO were detected. Figure 3.2 is a bright-field TEM micrograph of an internally-oxidized MgO/Cu(Ag) specimen exhibiting a high number density of MgO precipitates with a mean diameter of about 20 nm. Shown in the inset is a selected area diffraction pattern recorded for a 110 zone axis. In addition to the primary reflections from the Cu(Ag) matrix, satellite diffraction spots are visible that correspond to MgO in the cube-on-cube orientation.

Figure 3.3 shows a multi-beam bright-field TEM micrograph of an MgO/Cu(Ag) specimen prepared for APFIM.
Figure 3.2. Multi-beam bright-field TEM micrograph of an internally oxidized MgO/Cu(Ag) specimen; inset, (110) selected area diffraction pattern.

Figure 3.3. Multi-beam bright-field TEM micrograph of an MgO/Cu(Ag) specimen prepared for APFIM.
It was found by electron diffraction that the wire drawing axis of the MgO/Cu(Ag) wire specimens is, in most cases, close to a $<111>$ direction of the matrix. This geometrical factor provides for the highest spatial resolution of the APFIM analysis, as discussed in Section 3.5.1. A schematic diagram illustrating the geometry utilized for APFIM experiments is shown in Fig. 3.4.

![Figure 3.4](image_url)

**Figure 3.4.** 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.
Clear visibility of the MgO precipitates in Fig. 3.3 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
10 specimens. It should be noted, however, that this value only includes the
precipitates that are retained within the volume of a specimen and are visible by
TEM. Therefore, precipitates smaller than \( \approx 5 \text{ nm} \) are excluded and this value
represents a lower bound of the actual number density. By assuming a random
distribution of precipitates in an alloy, the average distance between precipitates
can be approximated as \( (n_{\text{MgO}})^{-1/3} = 46 \text{ nm} \).

3.4 FIELD-ION MICROSCOPY

In general, refractory second phases exhibit bright image contrast in an
FIM image [29]. This is due to the fact that such phases usually have higher
evaporation fields and protrude from a specimen's surface. As a result, partially
exposed oxide precipitates can be observed on the surface of an APFIM
specimen. Figures 3.5 and 3.6 show FIM images of MgO and CdO precipitates at
the surface of copper and silver specimens, respectively. By tilting the specimen
to a position where the probe hole (selected area aperture) completely covers
the precipitate, it is possible to obtain an accurate composition analysis of the
precipitate and its rear internal interface with the matrix. This technique was
used in addition to a random area analysis, when the specimen is aligned such
that the probe hole covers the 111 pole of the matrix. A high number-density of
precipitates makes it very probable that a precipitate is randomly encountered
during the course of a field-evaporation sequence.

Figure 3.5. FIM micrograph of the surface of an MgO/Cu(Ag) tip showing small
MgO precipitates. Location of the probe hole is indicated by a circle.
Figure 3.6. FIM micrograph of the surface of a CdO/Ag(Au) tip exhibiting a large, partially exposed CdO precipitate. Location of the probe hole is indicated by a circle.

3.5 ATOM-PROBE FIELD-ION MICROSCOPY

3.5.1. (222)MgO/Cu(Ag) interfaces

Figure 3.7 shows APFIM mass spectra of the cumulative number of events versus the mass-to-charge state ratio (m/n). As hydrogen is the main background component of most ultrahigh vacuum systems, magnesium, copper and silver are present in the form of metal hydrides. It can also be seen that copper and silver are present in the spectrum in both singly and doubly-charged states, while oxygen is present as both a singly-charged ion and a singly-charged dimer. Therefore, there is an overlap of copper doubly charged
species (m/n = 31.5 amu and 32.5 amu) and oxygen dimers (m/n = 32 amu). For this reason, accurate stoichiometric ratios for the MgO precipitates cannot be measured with the current APFIM system due to its limited mass resolution. Another factor contributing to the apparent non-stoichiometry of MgO precipitates is an effect of the pulse frequency. It was found [83] that as the pulse frequency changes from 60 to 10 Hz, the apparent concentration of oxygen in MgO precipitates decreases from 50% to 15%, due to preferential field evaporation of oxygen at low frequencies as H₂O. Despite this fact, the silver signal from MgO/Cu interfaces remains unaffected and the chemistry of {222}MgO/Cu(Ag) interfaces is clearly revealed by APFIM.
Figure 3.7. APFIM mass spectra of MgO/Cu(Ag) specimens showing: (a) Cu$^{+1}$, 
(b) Cu$^{+2}$, (c) Mg$^{+2}$, (d) O$^{+1}$, (e) Ag$^{+1}$, (f) Ag$^{+2}$, and (g) H$^{+1}$ spectra.
Figure 3.7 cont.
Figure 3.7 cont.
Figure 3.7 cont.
Figure 3.7 cont.
Figure 3.7 cont.
Figure 3.7 cont.
The results of random area APFIM analyses of the interfacial chemistry of \{222\}MgO/Cu(Ag) interfaces are displayed in Fig. 3.8 in the form of integral profiles. Each 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 <111> direction.

Each integral profile represents the complete dissection of a single MgO precipitate several nanometers in diameter. The integral profiles clearly demonstrate Ag enrichment associated with the \{222\}MgO/Cu interfaces (shown by arrows). This enrichment is quantified in Section 3.6.

An approximate depth scale of an integral profile can be reconstructed using the event frequency analysis approach (Section 3.6). The depth scale shown in Fig. 3.8 (a) suggests that the silver signal is somewhat delocalized in the vicinity of the \{222\} interface. Two possible factors contribute to this effect. First, due to the high dielectric constant of MgO, significant field penetration into an MgO precipitate is expected once it is uncovered during field evaporation. For larger precipitates, this effect usually causes a tip to fail catastrophically. Alternatively, for precipitates a few nanometers in diameter high field-evaporation rates of magnesium and oxygen ions are observed such that one to about 20 ions are removed per pulse. This effect causes a delocalization of the silver signal in the integral profile, since for a multiple event all time-of-flights are plotted sequentially from light to heavy ions. The second explanation for signal delocalization is purely geometric. To obtain the cleanest possible
experimental situation, a precipitate must have both its front and rear interfaces completely covered by the probe hole. Alternatively, if a small precipitate is located off-center with respect to the probe hole then an admixture of Cu, Mg, O, and Ag signals are detected.

APFIM analyses of about 56,000 matrix atoms also demonstrates 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 twenty extended regions of solid solution and 0.03 at.% is the weighted estimate for the standard deviation. This concentration is within the primary Cu(Ag) solid-solution phase at 500°C [82]. The concentrations of magnesium and oxygen in the Cu(Ag) matrix are vanishingly small (<10⁻³ at. fr.).
Filename: 060294c.int  
Cu-2.5 at.% MgO-0.8 at.% Ag  
Internal oxidation 950°C, 2 h, Rhines pack  
Annealing in Ar, 400°C, 24 h

Figure 3.8. APFIM integral profiles of MgO/Cu(Ag) specimens showing silver enrichment at {222} interfaces. Positions of interfaces are shown by arrows.
Filename: 032294a.int
Cu-2.5 at.% MgO-0.8 at.% Ag
Internal oxidation 950°C, 2 h, Rhines pack
Annealing in Ar, 400°C, 24 h

Figure 3.8 cont.
Figure 3.8 cont.

Filename: 040494a.int
Cu-2.5 at.% MgO-0.8 at.% Ag
Internal oxidation 950°C, 2 h, Rhines pack
Annealing in Ar, 400°C, 24 h

Approximate depth scale, nm

Number of Mg, O, or Ag events

Cumulative number of Cu, Mg, O, and Ag events

T = 50 K
f = 0.15
ν = 50 Hz
P = 3x10⁻⁸ Pa

(c)
Filename: 040794a.int
Cu-2.5 at.% MgO-0.8 at.% Ag
Internal oxidation 950°C, 2 h, Rhines pack
Annealing in Ar, 400°C, 24 h

Figure 3.8 cont.
Cu-2.5 at.% MgO-0.8 at.% Ag
Internal oxidation 950°C, 2 h, Rhines pack
Annealing in Ar, 400°C, 24 h

Filename: 051094a.int

Number of Mg, O, or Ag events

Cumulative number of Cu, Mg, O, and Ag events

Approximate depth scale, nm

T = 50 K
f = 0.15
ν = 20 Hz
P = 3x10⁻⁸ Pa

Figure 3.8 cont.
Filename: 060694b.int
Cu-2.5 at.% MgO-0.8 at.% Ag
Internal oxidation 950°C, 2 h, Rhines pack
Annealing in Ar, 400°C, 24 h

Figure 3.8 cont.
Figure 3.8 cont.
Filename: 060694e.int
Cu-2.5 at.% MgO-0.8 at.% Ag
Internal oxidation 950°C, 2 h, Rhines pack
Annealing in Ar, 400°C, 24 h

Figure 3.8 cont.
3.5.2 \{222\}CdO/Ag(Au) interfaces

Figure 3.9 shows APFIM mass spectra of the cumulative number of events versus the mass-to-charge state ratio (m/n). Similar to a previous APFIM study of the CdO/Ag system [28, 52], silver is present in the spectrum exclusively in the singly-charged state, while cadmium is present exclusively in the doubly charged state. Hence, there is no overlap between the Ag and Cd spectra. Similar to MgO/Cu(Ag) specimens, oxygen is present as both a singly-charged ion and a singly-charged dimer with limited formation of hydrides of Ag, Cd, and O; the latter is due to the presence of residual hydrogen in the vacuum system at a partial pressure of 2×10^{-8} Pa.
Figure 3.9. APFIM mass spectra of CdO/Ag(Au) specimens showing: (a) Ag$^{+1}$, (b) Cd$^{+2}$, (c) O$^{+1}$, (d) O$_2$$^{+1}$, (e) Au$^{+1}$, and (f) Au$^{+2}$ spectra.
Figure 3.9 cont.
Figure 3.9 cont.
Figure 3.9 cont.
Figure 3.9 cont.

020296f.mn.vis

Number of events

Mass-to-charge state ratio (m/n)

180 185 190 195 200 205 210 215 220

T = 45 K
f = 0.25
ν = 50 Hz
P = 2x10^{-8} Pa

^{197}\text{Au}^{1+}
Figure 3.9 cont.

\[ T = 50 \text{ K} \]
\[ f = 0.1 \]
\[ \nu = 50 \text{ Hz} \]
\[ P = 2 \times 10^{-8} \text{ Pa} \]
The results of random area APFIM analyses of the interfacial chemistry of \{222\}CdO/Ag(Au) interfaces are displayed in Fig. 3.10 and 3.11 in the form of integral profiles. Each profile displays the number of events of Cd, O, or Au vs. the cumulative number of Ag, Cd, O and Au events. Therefore, the local slope of each curve corresponds to the local concentration of the corresponding element along a \(<111>\) direction.

Each integral profile represents the complete dissection of a single CdO precipitate several nanometers in diameter. Figure 3.10 shows the analysis of an unannealed specimen that was quenched in water after the internal oxidation. The integral profile in Fig. 3.10 shows no Au enrichment associated with a \{222\}CdO/Ag interface (indicated by an arrow). On the other hand, Fig. 3.11 represents analyses of the specimens annealed at 650°C for 24 h in pure argon. In both cases (a) and (b), a small gold enrichment at the CdO/Ag interfaces is observed, which is quantified in Section 3.6.

APFIM analyses of CdO/Ag(Au) specimens also revealed that both annealed and unannealed specimens exhibit a well-pronounced gold solid solubility in CdO precipitates. Figure 3.12 shows integral profiles across single CdO precipitates. In all cases, a significant amount of gold is present inside the precipitates, while no gold is observed at CdO/Ag interfaces. The possible reasons for this behavior are discussed in Section 3.7.
Figure 3.10. APFIM integral profile of an unannealed CdO/Ag(Au) specimen showing no gold segregation at a [222] interface. Position of the interface is indicated by an arrow.
Figure 3.11. APFIM integral profiles of CdO/Ag(Au) specimens after annealing at 400°C for 24 h showing gold enrichment at {222} interfaces. Positions of interfaces are indicated by arrows.
Filename: 031596c.int.data
Ag-1.5 at.% CdO-1 at.% Au
Internal oxidation 650°C in air, 48 h
Annealing 400°C in Ar, 24h

Approximate depth scale, nm

Number of Cd, O, or Au events

Cumulative number of Ag, Cd, O, and Au events

T = 50 K
f = 0.1
ν = 50 Hz
P = 8x10⁻⁹ Pa

Figure 3.11 cont.
Figure 3.12. APFIM integral profiles of CdO/Ag(Au) specimens showing gold solubility in CdO precipitates. Positions of interfaces are shown by arrows.
Filename: 011196c.int.data
Ag-1.5 at.% CdO-1 at.% Au
Internal oxidation 650°C in air, 48 h

T = 50 K
f = 0.20
ν = 50 Hz
P = 7x10⁻⁹ Pa

Figure 3.12 cont.
Filename: 020296a.int.data
Ag-1.5 at.% CdO-1 at.% Au
Internal oxidation 650°C in air, 48 h

Approximate depth scale, nm

Number of Cd, O, or Au events

Cumulative number of Ag, Cd, O, and Au events

T = 45 K
f = 0.15
ν = 50 Hz
P = 7x10^9 Pa

Cd
O
Au(x5)

Figure 3.12 cont.
Filename: 020296b.int.data
Ag-1.5 at.% CdO-1 at.% Au
Internal oxidation 650°C in air, 48 h

Figure 3.12 cont.
Filename: 020296c.int.data
Ag-1.5 at.% CdO-1 at.% Au
Internal oxidation 650°C in air, 48 h
Annealing 400°C in Ar, 24h

Approximate depth scale, nm

Cumulative number of Ag, Cd, O, and Au events

(e)

Figure 3.12 cont.
Filename: 020296e.int.data
Ag-1.5 at.% CdO-1 at.% Au
Internal oxidation 650°C in air, 48 h
Annealing 400°C in Ar, 24h

Figure 3.12 cont.
3.6 DETERMINATION OF THE GIBBSIAN INTERFACIAL EXCESS OF SOLUTE

The APFIM data presented in Section 3.5 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 [84] of component $i$ with respect to component 1 ($\Gamma_i^{(1)}$) is

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

where the quantities $C_i^\alpha$ and $C_i^\beta$ are the atomic fractions of element $i$ in the homogeneous regions of phases $\alpha$ and $\beta$. The value of $\Gamma_i^{(1)}$ is independent of the position of the Gibbs dividing surface. Equation 3.2 is the starting point for analyzing the integral profiles displayed in Figs. 3.8 and 3.11. 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, $\alpha$ to the Cu(Ag) matrix, and $\beta$ to the MgO phase. Equation 3.2 for this situation is
\[
\Gamma_{Ag}^{(1)} = \Gamma_{Ag} - \Gamma_{Cu} \left( \frac{C_{Ag}^\alpha - C_{Ag}^\beta}{C_{Cu}^\alpha - C_{Cu}^\beta} \right) \equiv \Gamma_{Ag} - \Gamma_{Cu} \left( \frac{C_{Ag}^\alpha}{C_{Cu}^\alpha} \right) \equiv \Gamma_{Ag}. \quad (3.3)
\]

The reason that \(\Gamma_{Ag}^{(1)}\) reduces to \(\Gamma_{Ag}\) is because \(C_{Cu}^\beta = C_{Ag}^\beta \equiv 0\) and 
\[
\left( \frac{C_{Ag}^\alpha}{C_{Cu}^\alpha} \right) \equiv 5 \times 10^{-3}. \text{ Thus the problem is abridged to calculating } \Gamma_{Ag} \text{ directly from its definition } \\
\Gamma_{Ag} = \frac{N_{Ag}^{excess}}{A} = \left( \frac{1}{A} \right) \left( N_{Ag}^{vol} - N_{Ag}^\alpha - N_{Ag}^\beta \right) = \\
\left( \frac{N_{Ag}^{vol}}{A} \right) \left[ C_{Ag}^{vol} - C_{Ag}^\alpha \xi - C_{Ag}^\beta (1 - \xi) \right] ; \quad (3.4)
\]

where \(N_{Ag}^{excess}\) is the excess number of Ag atoms associated with the heterophase interface, \(A\) is the interfacial area over which this excess is determined, \(N_{Ag}^{vol}\) is the total number of Ag atoms in the volume analyzed, \(N_{Ag}^\alpha\) and \(N_{Ag}^\beta\) 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 (\(\xi\)), \(C_{Ag}^{vol}\) is the concentration of Ag in the volume analyzed,
and $N_{\text{vol}}$ 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 containing the interface $\left(N_{\text{Ag}}^{\text{vol}}\right)$, to a reference system where the two phases extend to $\xi$.

Equation 3.4 describes a system with only one interface between the phases $\alpha$ and $\beta$. Whereas the integral profiles in Fig. 3.8 are for a system that contains two sequential parallel heterophase interfaces -- $\alpha/\beta$ and $\beta/\alpha$. An abstraction of the situation analyzed is shown in Fig. 3.13, which exhibits the nomenclature employed to analyze the data. Figure 3.13 assumes, for the purposes of generalizing the argument, that there is some solid solubility of Ag in MgO, whereas our experimental data indicates none. For the $\alpha/\beta$ (front) interface Eq. 3.4 takes the form

$$\Gamma_{\text{Ag}}^{\alpha/\beta} = N_{\text{Ag}}^{\text{excess}} / A = \left(1/A\right)\left(N_{\text{Ag}}^{\text{vol}} - N_{\text{Ag}}^{\alpha} - N_{\text{Ag}}^{\beta}\right) = \left(N_{\text{vol}} / A\right)\left[C_{\text{Ag}}^{\text{vol}} - C_{\text{Ag}}^{\alpha} \xi 1 - C_{\text{Ag}}^{\beta} [1 - \xi 1]\right] ;$$

(3.5)

where the terms are defined in Fig. 3.13.
Figure 3.13. Diagram illustrating how the Gibbsian interfacial excesses of Ag at the two interfaces are extracted from the integral profiles of Fig. 3.8 and the nomenclature employed.
Since $\langle C_{Ag}^{\beta} \rangle$ is essentially zero, Eq. 3.5 for the $\alpha/\beta$ interface reduces to

$$\Gamma_{Ag}^{\alpha/\beta} = \frac{N_{excess}^{Ag(1)}}{A} = \frac{N_{vol}^{Ag(1)} - N_{Ag}^{\alpha}}{A} =$$

$$\left( \frac{N_{vol}}{A} \right) \left[ \left\{ C_{Ag}^{vol} \right\} - \left\{ C_{Ag}^{\alpha} \right\}(\xi 1) \right]$$

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

$$A = \frac{N_{plane}^{hkl}}{\beta \rho_{hkl} \cos \phi} ;$$

where $N_{plane}^{hkl}$ is the number of atoms per $\{hkl\}$ plane, $\rho_{hkl}$ is the planar density of matrix atoms in an $\{hkl\}$ plane, $\phi$ is the angle between the interface plane and the $<hkl>$ analysis direction (in this case $\cos \phi$ is unity), and $\beta$ is the detection efficiency of the single-ion chevron detector employed in the APFIM system; $\beta$ is determined by the active area of multi channel plates (MCPs) and ranges from 0.4 to 0.6 [29, 30]. 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 $\beta$. Therefore, by combining Eqs. 3.6 and 3.7 we
obtain an explicit expression for $\Gamma_{Ag}^{\alpha/\beta}$ (or $\Gamma_{Ag}^{\beta/\alpha}$) that is independent of $\beta$ because the value of $N_{\{hkl\}}^{\text{plane}}$ is also linearly dependent on $\beta$.

The quantity $N_{\{hkl\}}^{\text{plane}}$ can be determined using event frequency analysis [85]. When a low-index direction $\langle hkl \rangle$ of an APFIM specimen is aligned over the probe hole (selected area aperture), the measured evaporation rate (number of detected ions per pulse) oscillates. This effect is explained in Fig. 3.14. The surface of an atomically sharp tip can be represented by a set of rings corresponding to a low-index pole (in our case, 111). To a first approximation, field evaporation predominantly occurs at the edges of the outermost ring, such that each succeeding layer begins to field-evaporate after the layer above it is completely removed. Figure 3.14 (a) is a plot of number of detected ions versus the cumulative number of field-evaporation pulses. Figures 3.14 (b), (c), and (d) are schematic diagrams corresponding to regions 1, 2, and 3 shown in Fig. 3.14 (a). In (b), outermost ring is small and ions pass through the probe hole and reach the detector. In (c), the ring is large and ions do not pass through the probe hole until the ring shrinks to the size shown in (d), etc. Thus, the field evaporation rate exhibits oscillations with a periodicity equal to the number of detected ions per $\{hkl\}$ plane.
Figure 3.14. Diagram illustrating oscillations in the measured field evaporation rate of an APFIM specimen aligned along a <111> direction. (a) Plot of number of detected ions versus the cumulative number of field-evaporation pulses; (b), (c), and (d), schematic diagrams corresponding to regions 1, 2, and 3 shown in (a). In (b) and (d), outermost {111} plane is small and ions pass through the probe hole and reach the detector. In (c), the plane is large and ions do not pass through the probe hole.
The event frequency analysis was performed for all specimens displayed in Fig. 3.8 and 3.11. An example is shown in Fig. 3.15 for the specimen represented in Fig. 3.8 (c). The periodicity of oscillations is disturbed by statistical fluctuations in the number of detected ions and specimen inhomogeneity. From an average spacing between maxima in Fig. 3.15, the value of $N_{\{hkl\}}^{\text{plane}}$ is 19.2. Employing the value of $\rho_{\{hkl\}}$ for a $\{111\}$Cu plane, we obtain for the $\alpha/\beta$ (front) and $\beta/\alpha$ (rear) heterophase interfaces $\Gamma_{Ag}^{\alpha/\beta} = (3.0\pm1.3)\times10^{14}$ atoms cm$^{-2}$ and $\Gamma_{Ag}^{\beta/\alpha} = (3.0\pm1.3)\times10^{14}$ atoms cm$^{-2}$. The error in $\Gamma_{Ag}$ is determined by a calculation of the propagation of errors for each quantity in Eq. 3.6. The error in $N_{Ag}^{\text{excess}}$ is calculated based on the assumption of a binomial distribution of solute atoms sampled during atom-probe analysis [86]. The error in the value of $N_{\{hkl\}}^{\text{plane}}$ is the standard error in the mean of a binomial distribution. For the $\{111\}$Cu plane one monolayer coverage equals $\rho_{Cu} d_{\{111\}Cu} N_a / M_{Cu}$, where $\rho_{Cu}$ is density of copper, $N_a$ is Avogadro’s number and $M_{Cu}$ is atomic weight of copper. This implies $1.82\times10^{15}$ atoms cm$^{-2}$ and, therefore, the measured values of $\Gamma_{Ag}$ correspond to effective coverages of $\Theta = (0.16\pm0.07)$ and $(0.16\pm0.07)$ monolayers.

Table 3.1 presents the results of the analysis of fifteen $\{222\}$MgO/Cu(Ag) interfaces that were obtained in a similar fashion.
Figure 3.15. Plot of field evaporation rate versus the total number of detected ions for the MgO/Cu(Ag) specimen presented in Fig. 3.8 (c).
**TABLE 3.1.** Levels of silver segregation at \{222\}MgO/Cu heterophase interfaces measured by APFIM

<table>
<thead>
<tr>
<th>Filename</th>
<th>IF type</th>
<th>(N_{hkl}^{plane})</th>
<th>(N_{Ag}^{excess})</th>
<th>(\Gamma_{Ag}), at cm(^{-2})</th>
<th>(\Theta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>032294a.int</td>
<td>front</td>
<td>24.7</td>
<td>6</td>
<td>4.30\times10^{14}</td>
<td>0.23</td>
</tr>
<tr>
<td>032294a.int</td>
<td>rear</td>
<td>24.7</td>
<td>6</td>
<td>4.30\times10^{14}</td>
<td>0.23</td>
</tr>
<tr>
<td>040494a.int</td>
<td>front</td>
<td>29.2</td>
<td>5</td>
<td>3.03\times10^{14}</td>
<td>0.16</td>
</tr>
<tr>
<td>040494a.int</td>
<td>rear</td>
<td>29.2</td>
<td>5</td>
<td>3.03\times10^{14}</td>
<td>0.16</td>
</tr>
<tr>
<td>040794a.int</td>
<td>front</td>
<td>21.3</td>
<td>7</td>
<td>5.82\times10^{14}</td>
<td>0.31</td>
</tr>
<tr>
<td>040794a.int</td>
<td>rear</td>
<td>21.3</td>
<td>5</td>
<td>4.16\times10^{14}</td>
<td>0.22</td>
</tr>
<tr>
<td>051094a.int</td>
<td>rear</td>
<td>20.0</td>
<td>4</td>
<td>3.54\times10^{14}</td>
<td>0.19</td>
</tr>
<tr>
<td>060294c.int</td>
<td>front</td>
<td>28.3</td>
<td>11</td>
<td>6.89\times10^{14}</td>
<td>0.37</td>
</tr>
<tr>
<td>060294c.int</td>
<td>rear</td>
<td>28.3</td>
<td>13</td>
<td>8.14\times10^{14}</td>
<td>0.44</td>
</tr>
<tr>
<td>060694b.int</td>
<td>front</td>
<td>32.0</td>
<td>6</td>
<td>3.32\times10^{14}</td>
<td>0.18</td>
</tr>
<tr>
<td>060694b.int</td>
<td>rear</td>
<td>32.0</td>
<td>6</td>
<td>3.32\times10^{14}</td>
<td>0.18</td>
</tr>
<tr>
<td>060694c.int</td>
<td>front</td>
<td>30.8</td>
<td>2</td>
<td>1.15\times10^{14}</td>
<td>0.06</td>
</tr>
<tr>
<td>060694c.int</td>
<td>rear</td>
<td>30.8</td>
<td>2</td>
<td>1.15\times10^{14}</td>
<td>0.06</td>
</tr>
<tr>
<td>060694e.int</td>
<td>front</td>
<td>20.7</td>
<td>5</td>
<td>4.28\times10^{14}</td>
<td>0.23</td>
</tr>
<tr>
<td>060694e.int</td>
<td>rear</td>
<td>20.7</td>
<td>4</td>
<td>3.42\times10^{14}</td>
<td>0.18</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td></td>
<td></td>
<td>((4.0\pm1.9)\times10^{14})</td>
<td>0.22\pm0.10</td>
<td></td>
</tr>
</tbody>
</table>

In a similar fashion, levels of gold segregation at \{222\}CdO/Ag interfaces are given in Table 3.2.
TABLE 3.2. Levels of gold segregation at \{222\}CdO/Ag heterophase interfaces measured by APFIM

<table>
<thead>
<tr>
<th>Filename</th>
<th>IF type</th>
<th>$N^\text{plane}_{(hkl)}$</th>
<th>$N^\text{excess}_{\text{Au}}$</th>
<th>$\Gamma_{\text{Au}}$ at cm$^{-2}$</th>
<th>$\Theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>022896a.int</td>
<td>rear</td>
<td>18.6</td>
<td>3</td>
<td>$2.38 \times 10^{14}$</td>
<td>0.16</td>
</tr>
<tr>
<td>031596c.int</td>
<td>rear</td>
<td>20</td>
<td>6</td>
<td>$4.16 \times 10^{14}$</td>
<td>0.30</td>
</tr>
<tr>
<td>031596c.int</td>
<td>front</td>
<td>20</td>
<td>4</td>
<td>$2.77 \times 10^{14}$</td>
<td>0.20</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td></td>
<td>$(3.0 \pm 1.0) \times 10^{14}$</td>
<td>0.22±0.07</td>
</tr>
</tbody>
</table>

3.7 DISCUSSION

It has been suggested in the literature [17, 40] 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. The experimental evidence reviewed in Section 2.7, however, shows that in some highly dispersed systems small amounts of impurity elements or deliberately introduced dopants can dramatically change the morphology of the system. In this work, the presence of ≈0.2 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 $2 \times 10^4$ cm$^2$ cm$^{-3}$. It did not, however, noticeably change the morphology of MgO.
precipitates.

The technique of internal oxidation results in 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, however, incorrect 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 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 that were quenched from the temperature of internal oxidation (650°C), 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 [87].

The observation of significant solid-solubility of gold in small CdO precipitates is surprising. While, to the author’s knowledge, no experimental data exists on the bulk solubility of Au in CdO, it is known that noble metals are very stable in contact with highly ionic ceramic materials and are often used as crucibles for ceramics fabrication [88]. Two hypotheses are proposed to explain this effect. The first idea is based on the assumption that small gold-silver clusters present in Ag(Cd, Au) solid solution may serve as preferential nucleation sites for CdO formation during internal oxidation. An analogous effect has been observed in Al-Cu-Mg-Ag alloys by APFIM [66], where Mg and
Mg-Ag co-clusters a few atoms in size serve as precursor phases for the nucleation of the Ω-phase during aging. Similarly, small ternary additions in internally oxidized Ag(Cd) alloys were found to change dramatically the CdO precipitate size and number density by providing preferential nucleation sites for the oxide during internal oxidation [89]. While the Ag-Au system exhibits a continuous series of solid solutions, experimental evidence indicates a partial ordering of the atoms in a Ag-50 at. % Au alloy [90].

An alternative explanation relies on the Gibbs-Thomson effect [91]. A classical expression for the enhanced solid solubility of component B inside a small spherical precipitate of radius \( r \) of \( \beta \)-phase placed inside a large volume fraction of \( \alpha \)-phase is

\[
\frac{X_B^\beta (r)}{X_B^\beta (\infty)} = 1 + \left[ 1 - \frac{X_B^\beta (\infty)}{X_B^\alpha - X_B^\beta (\infty)} \right] \frac{2\gamma\Omega_B}{kT\phi r},
\]

where the \( X \)'s are solid solubilities, \( \gamma \) is the interfacial free energy, \( \Omega_B \) is the atomic volume of B, \( X_B^\beta (\infty) \) refers to the solubility of B in a bulk \( \beta \)-phase \( (r = \infty) \), and \( \phi \) is a thermodynamic factor defined by

\[
\phi = 1 + \frac{\partial \ln \gamma_B^\beta}{\partial \ln X_B^\beta}.
\]

(3.8)
In our case, $B = \text{Au}$, $\alpha = \text{Ag}$, and $\beta = \text{CdO}$. Taking into account that $X_{\text{Au}}^{\text{Ag}} = 1$ and $X_{\text{Au}}^{\text{CdO}}(\infty) \ll 1$ and assuming an ideal solid solution, we can simplify Eq. 3.9 to

$$\frac{X_{\text{Au}}^{\text{CdO}}(r)}{X_{\text{Au}}^{\text{CdO}}(\infty)} = 1 + \frac{2\gamma_{\text{CdO}/\text{Ag}}\Omega_{\text{Au}}}{kT}. \quad (3.10)$$

The factor of 2 in the Eq. 3.10 is a geometrical factor characteristic of a sphere. For an arbitrarily shaped precipitate uniquely defined by a size parameter $L$, the factor is equal to a ratio of two constants, $B$ and $C$:

$$B = \frac{1}{L} \left( \frac{\partial A}{\partial L} \right) \quad \text{and} \quad C = \frac{1}{L^2} \left( \frac{\partial V}{\partial L} \right),$$

where $A$ and $V$ are precipitate area and volume, respectively. Therefore, for an octahedral precipitate with an edge length, $L$, we obtain

$$\frac{X_{\text{Au}}^{\text{CdO}}(L)}{X_{\text{Au}}^{\text{CdO}}(\infty)} = 1 + \frac{2\sqrt{6}\gamma_{\text{CdO}/\text{Ag}}\Omega_{\text{Au}}}{kTL}. \quad (3.11)$$

During the APFIM experiments, CdO precipitates are dissected along a
direction. If we define the precipitate size, \( H \), as the distance between its two opposite \( \{222\} \) facets, then \( H \) is related to \( L \) by \( H = 2L/\sqrt{6} \). Therefore,

\[
\frac{X_{\text{Au}}^{\text{CdO}}(H)}{X_{\text{Au}}^{\text{CdO}}(\infty)} = 1 + \frac{4\gamma_{\text{CdO}/\text{Ag}} \Omega_{\text{Au}}}{kTH}.
\]  

(3.12)

Experimental or theoretical data on C/M interfacial free energy are very limited. It is much more common to measure or calculate the work of adhesion, \( W \), which for C/M interfaces is typically about 1 J/m\(^2\) [3]. The only value of \( \gamma_{\text{CdO}/\text{Ag}} = 0.45 \text{ J/m}^2 \) was measured in ref. [92] by a Lifshitz-Slyozov-Wagner analysis of coarsening of CdO precipitates in Ag. To compare our experimental APFIM data with the Eq. 3.11, a conservative estimate of \( \gamma_{\text{CdO}/\text{Ag}} = 1 \text{ J/m}^2 \) was used. Figure 3.16 is a plot of the experimental values of \( X_{\text{Au}}^{\text{CdO}} \) versus the precipitate edge length \( L \). Fourteen precipitates are analyzed, ranging in size from 1.5 to 20 nm. The level of gold solubility varies between 3 and 27 at.%. The solid line in Fig. 3.16 represents the enrichment ratio from Eq. 3.11. Clearly, all the experimental data do not follow the 1/L law predicted by Gibbs-Thomson effect. Furthermore, the predicted enrichment ratios vary between 1.3 and 5 and alone they are not sufficient to explain the observed effect. Therefore, it is proposed that the observed gold solid solubility in CdO is a combination of two effects: preferential precipitation of CdO on atomic-size Ag-Au clusters present
in the initial Ag(Cd, Au) solid solution and the enhanced solid solubility of gold in CdO due to Gibbs-Thomson effect.

All the quantitative results in this chapter were obtained without data deconvolution or external calibration standards.

Figure 3.16. APFIM experimental data on Au solubility in CdO precipitates versus the precipitate edge length, L. The solid line is a prediction for the enrichment ratio based on Gibbs-Thomson effect (Eq. 3.11).
3.8 CONCLUSIONS

1. The first quantitative measurements of solute segregation at C/M heterophase interfaces are presented for MgO/Cu(Ag) and CdO/Ag(Au) systems. It is shown that data are readily analyzed to obtain the Gibbsian interfacial excess of solute.

2. After low-temperature annealings, significant segregation levels are observed in both systems. Analysis of fifteen \{222\}MgO/Cu(Ag) interfaces showed an average segregation level of \((4.0\pm1.9)\times10^{14}\) at \(\text{cm}^{-2}\) or \(0.22\pm0.10\) ML at 500˚C. Analysis of three \{222\}CdO/Ag(Au) interfaces showed an average segregation level of \((3.0\pm1.0)\times10^{14}\) at \(\text{cm}^{-2}\) or \(0.22\pm0.07\) ML at 400˚C.

3. \{222\}CdO/Ag(Au) interfaces in unannealed specimens show no evidence of gold segregation.

4. A significant level of gold solubility (3 to 27 at.%) is observed in CdO/Ag(Au) system. Analysis of 14 precipitates 1.5 to 20 nm in size shows that this phenomenon cannot be explained by Gibbs-Thomson effect alone. It is proposed that the observed gold solid solubility in CdO is a combination of two effects: preferential precipitation of CdO on atomic-size Ag-Au clusters present in the initial Ag(Cd, Au) solid solution and the enhanced solid solubility of gold in CdO due to the Gibbs-Thomson effect.

5. All the quantitative results in this chapter were obtained without data deconvolution or external calibration standards.
CHAPTER 4

ATOMIC-SCALE STUDY OF INTERFACE STRUCTURE AND CHEMISTRY IN \{222\}MgO/Cu(Ag) SYSTEM BY SCANNING TRANSMISSION ELECTRON MICROSCOPY

4.1 INTRODUCTION

Specific examples provided in Chapter 2 of this thesis demonstrate that it is frequently the atomic-scale structural features and subnanometer scale chemical effects that govern macroscopic properties of heterophase materials. There have been a number of recent studies addressing the atomic structure of ceramic/metal interfaces for model systems [1, 2]. In most of these studies, the structure was established by HREM. The main problem, however, in determining the atomic structure of an interface from HREM images is the presence of image artifacts caused by dynamical diffraction and lens aberrations. The common approach is to use structural models of an interface as an input for image simulations that take into account the particular electron optical properties and aberrations of the microscope employed. The resulting images are then compared with the experimental ones, and the structural model is chosen that shows the best match. Based on the comparison, this model can
then be refined, used as an input for new image simulations, and iteratively changed [18]. The key step in this iterative process is determining the goodness of fit between experimental and simulated images. This is accomplished, typically, by a simple visual comparison that is, therefore, strongly subjective. An alternative approach to this problem is HREM image processing in order to quantify and to minimize the difference between the two images numerically by means of various correlation techniques. This process makes HREM image interpretation a rather tedious task. Alternatively, annular dark field (ADF) images can be obtained in a dedicated STEM that are, to a great extent, free from many complications of HREM images. This technique is discussed in Section 4.2.

This study is conducted to determine interfacial chemistry in C/M systems and to relate it to the atomic structure of the interfaces. Interfacial chemistry was determined quantitatively for the \{222\}MgO/Cu(Ag) and \{222\}CdO/Ag(Au) systems by APFIM, as described in Chapter 3. In this study, \{222\}MgO/Cu(Ag) interfaces prepared by internal oxidation under the same conditions as specimens described in Chapter 3, are investigated using bright field (BF) and annular dark field (ADF) imaging and electron energy loss spectroscopy (EELS) in a dedicated STEM. This study pursues the following objectives:

1. Observe the interface morphology, its structural sharpness, and presence of defects such as steps.
2. Determine chemical identity of the terminating plane.
3. Investigate the possible localization of lattice misfit into interfacial misfit dislocations. Based on the observation of local strains, make a conclusion about interfacial coherency.

4. Determine the chemical sharpness of C/M interfaces. This includes possible interdiffusion or reaction layers.

5. Detect the presence of silver at {222}MgO/Cu(Ag) interfaces.

6. Determine the depth and lateral distribution of solute at C/M interfaces.

This chapter has the following structure: Section 4.2 discusses the imaging methods available in a dedicated STEM and their interpretation; Section 4.3 describes experimental procedures; and Section 4.4 presents the main experimental results. Finally, Section 4.5 is a discussion of these results in light of previous HREM studies and atomistic simulations of {222}MgO/Cu and other ceramic/metal systems. Section 4.6 lists the principal conclusions of this study.
4.2 IMAGING BY SCANNING TRANSMISSION ELECTRON MICROSCOPY

Scanning transmission electron microscopy (STEM) has been widely utilized for characterizing materials. Recent advances in this technique are a result of the introduction of dedicated STEMs equipped with field-emission guns that led to a great improvement of spatial resolution at the subnanometer level [93]. As a result, a dedicated STEM provides a powerful tool for acquiring atomic-resolution images of crystalline materials, combined with compositional sensitivity by means of Z-contrast imaging.

Structural information can be obtained by utilizing bright-field (BF) or annular dark-field (ADF) detectors. BF STEM images are dominated by phase contrast effects similar to HREM images. Their interpretation is thus not intuitive and requires extensive use of image simulations. Increasing the collection angle of a BF detector is equivalent, due to the reciprocity theorem, to increasing the convergence angle of the incident beam in HREM [94]. It translates the first crossover of the contrast transfer function (CTF) to higher values and causes a decrease of high-frequency oscillations of the CTF present under parallel beam illumination. Therefore, the image resolution is somewhat improved. It, however, also decreases the image contrast because of averaging effects.

Image and contrast formation in the ADF detector are critically dependent on the inner collection angle of the ADF detector, as well as on the
nature of the specimen. At small collection angles, image formation is equivalent to HREM image formation under hollow-cone illumination conditions. Image resolution, therefore, is also improved; image formation, however, primarily involves beams from coherent Bragg scattering and contrast is dominated by diffraction and phase effects. These images exhibit high intensity and a strong, nonlinear thickness dependence with possible contrast reversals [95]. Chemical sensitivity under these conditions is usually lost.

When the inner detector angle is increased, coherent Bragg scattering is overtaken by thermal diffuse scattering (TDS). Analyses of ADF image formation by thermally scattered electrons was presented in references 93, 95, and 96. In the simplest form, atomic vibrations are assumed to be described by an Einstein model (a lattice of independent simple harmonic oscillators). Time-averaging the instantaneous projected potential leads to a reduction of intensity of the coherent Bragg reflections by the Debye-Waller factor. The Einstein model assumes a single atomic vibration frequency, which is not appropriate for the low-frequency (acoustic) modes that are responsible for most of the scattering [96]. Alternatively, single or multiple-phonon scattering theories are considered. It was shown in reference 97 that high-angle TDS contains a very small single-phonon contribution. To predict multi-phonon TDS, one has to perform extensive calculations [95] or to use simplifying assumptions to perform a time-averaging procedure [96, 98]. To a first approximation, the scattered intensity for each atom is proportional to the square of its atomic number (Z). This classical Coulomb limit is obtained if the collected electrons are
scattered from regions where the potential of the nucleus is not screened by the electron cloud. In practice, the screening effect reduces the Z-dependency of the scattered intensity to $Z^n$, where $n = 1.6-1.9$, depending on the ADF detector geometry [95]. This provides a basis for the chemical sensitivity of an ADF image.

Despite significant efforts, a complete theoretical description of the mechanism of incoherent ADF image formation has not yet been established. It was shown that the reduction of coherence in the ADF image originates from two factors: finite dimensions of the ADF detector that average out in-phase contributions from coherent elastically scattered electrons and partial destruction of phase relations by the TDS [95]. By analyzing the former, the authors derived the following criterion for incoherence of an ADF image:

$$\Theta_2 - \Theta_1 \gg \frac{\lambda}{\rho_{ij}},$$  \hspace{1cm} (4.1)

where $\Theta_1$ and $\Theta_2$ are the inner and outer collection angles of the ADF detector, $\lambda$ is the electron wavelength, and $\rho_{ij}$ is the distance between the two features that must be imaged incoherently.

The second condition for incoherence arises from the requirement that image formation is dominated by TDS. It imposes a lower limit on $\Theta_1$, which in
the case of a mean quadratic vibration amplitude of 0.03 Å² and a 100 kV accelerating voltage, implies that $\Theta_1 \geq 90$ mrad.

The second condition imposes a strict limitation on the ADF detector geometry. Increasing the inner collection angle $\Theta_1$ to 100 mrad or higher causes an unacceptably low image-intensity [99]. An alternative approach involves using an intermediate inner detector angle of 30 to 50 mrad. At these angles, there is a coherent contribution to the image. It was shown by image simulations in reference 98 that if a crystal is oriented along a low-index zone axis and Eq. 4.1 is satisfied, only a limited intra-column coherence is preserved, while inter-column interference becomes negligible. Thus, an entire column of atoms acts as a single scattering center. This implies that a high-angle ADF (HAADF) image is a convolution of the incident probe intensity, rather than electron wavefunction, with a specimen object function.

If a specimen is oriented along a particular zone axis, channeling of the electron beam parallel to the atomic columns leads to preservation of its shape. As a result, for sufficiently thin specimens, the spatial resolution of the collected signal is maintained throughout the specimen and ultimately approaches the incident probe diameter. In combination with atomic number sensitivity, HAADF imaging along a zone axis is denoted Z-contrast. Its capability of ultrahigh resolution with chemical sensitivity is presently unsurpassed by any other electron microscopic technique.
Since channeling conditions are easily destroyed, Z-contrast HAADF images are extremely sensitive to such factors as exact crystal orientation, surface contamination, and electron beam damage. Orientation sensitivity for HAADF images is stronger than that of conventional HREM images and requires precise positioning of the specimen. It, however, also gives rise to a strong sensitivity of the contrast to local atomic displacements, caused by atomic imperfections such as misfitting dopant atoms or dislocations [100]. HAADF images of imperfections may be complicated by short and long-range elastic strain fields. In addition, while the channeling effect provides conditions for atomic-resolution imaging, it also introduces thickness effects in the zone axis images [101]. This situation is further complicated by the fact that electrons channel for considerably different distances along atomic columns of different atomic numbers. Overall, this subject is relatively new and has not been studied in detail.

In this study, both HB 603 (Oak Ridge National Laboratory) and HB 501 (Cornell University) dedicated STEMs were employed to study the atomic structure and chemistry of [222]MgO/Cu(Ag) heterophase interfaces prepared by internal oxidation. High-resolution STEM images were acquired in both BF and ADF modes. The inner detector angle of the ADF detector was varied to reveal its effect on image contrast. The atomic structure of the interfaces was observed at different orientations, as well as imperfections present at these interfaces. The dislocation structure of the interfaces was determined. At high inner detector angles, images are analyzed to reveal evidence of silver
segregation at [222]MgO/Cu(Ag) interfaces. These observations are supplemented by high-resolution EELS compositional analysis of the interface chemistry.
4.3 EXPERIMENTAL PROCEDURE

The \{222\}MgO/Cu(Ag) interfaces for this study were prepared by internal oxidation of a ternary Cu(Mg, Ag) alloy and a subsequent low-temperature annealing treatment. The alloy preparation, internal oxidation and annealing procedures are described in detail in Appendix A. Silver segregation levels at these interfaces was measured quantitatively by APFIM, as described in Chapter 3. STEM specimen preparation was performed by electropolishing and subsequent ion milling. A detailed specimen preparation procedure is given in Appendix C.

For the STEM studies, two dedicated microscopes were utilized. The VG Microscopes HB603 300 kV microscope at Oak Ridge National Laboratory was utilized for atomic resolution imaging. The incoherent resolution of this instrument is 0.13 nm [21]. The vacuum in the column of this STEM is about $5 \times 10^{-8}$ Pa, allowing for very low surface contamination levels. Prior to the high-resolution imaging, areas of interest in the samples were flood illuminated for 20 min, to reduce the buildup of contamination when employing a highly focused electron-beam. Grayscale images (480×480 pixels) were digitally recorded with a typical acquisition time of 17 sec per frame. All images presented in this work are raw, unfiltered images with the dynamic range expanded for publication purposes. All the atomic-resolution images of \{222\}MgO/Cu(Ag) interfaces in this chapter were recorded using the HB603
For subnanometer-resolution Z-contrast imaging and EELS measurements of interface chemistry, a VG Microscopes HB501 100 kV microscope at Cornell University was utilized. This microscope is equipped with a cold field-emission gun with a 0.3 eV energy spread and it has also been modified to achieve high energy-drift stability (<0.2 eV min\(^{-1}\)) and spatial-drift stability (<0.05 nm min\(^{-1}\)). A detailed description of the microscope can be found in reference 102. BF and ADF grayscale images (256×256 and 512×512 pixels) were digitally recorded with a typical acquisition time of 10 sec per frame. The EELS experimental procedure is described in detail in Chapter 5 of this thesis. BF and ADF images of interfaces were recorded using the HB501 microscope in order to reveal the effect of objective aperture size on image resolution and contrast formation. EELS spectra were recorded to detect the presence of silver segregation at [222]MgO/Cu(Ag) interfaces.
4.4 RESULTS OF Z-CONTRAST IMAGING

4.4.1 Crystallography and defects of the interfaces

It has been shown previously [15] that MgO particles grown in a Cu(Ag) matrix, by internal oxidation, are usually octahedral-shaped and are in a cube-on-cube orientation with the matrix. The MgO precipitates are faceted on {222} planes, parallel to the {111} planes of the Cu(Ag) matrix. Since precipitates are in a cube-on-cube orientation, {222} interfaces can be imaged edge-on along two low-index zone axes – <110> and <211>. Figure 4.1 is a low-magnification STEM image of an MgO precipitate in a Cu(Ag) matrix recorded along the common [110] direction. In the BF image, Moiré fringes are visible, indicating that this precipitate is partially or completely covered by the metal matrix. Also strong strain contrast around the precipitate is visible, suggesting that most of the strain is concentrated in the metal matrix. The HAADF image (inner detector angle, 45 mrad) is virtually free of Moiré fringes and does not exhibit significant strain contrast, since at this collection angle, phase and diffraction effects are minimized. A weak bright halo, however, can be seen around the precipitate, whose origin is discussed later. Figure 4.2 is a high-magnification STEM image of a 4 nm diameter MgO precipitate in a Cu(Ag) matrix recorded along the common [211] direction. (Here and later, the diameter of a precipitate is defined as the distance between its two opposite parallel {222} facets. Therefore, for an octahedral precipitate, the diameter \(d\) is related to its edge length, \(L\) as \(d = 2L/\sqrt{6}\).) In this case, the {111} plane of the Cu(Ag) matrix is clearly resolved,
while the \{220\} fringes, spaced at 0.128 nm, are not visible due to a slight misalignment of this specimen. In both Figs. 4.1 and 4.2, the \{222\} interfaces appear flat and sharp. Figure 4.3 is an atomic-resolution HAADF image, recorded for the [110] orientation showing an atomically flat \{222\}MgO/Cu(Ag) interface.
Figure 4.1. Bright-field (BF) and high-angle annular dark-field (HAADF) images of an MgO precipitate in a Cu(Ag) matrix recorded along the common [110] direction. The BF image in (a) shows strain-field contrast in the metal matrix and Moiré fringes on the precipitate, indicating at least partial coverage of the precipitate. The HAADF image in (b) exhibits additional intensity around the precipitate that may be indicative of silver segregation at the {222}MgO/Cu(Ag) interface.
Figure 4.2. (a) Bright-field and (b) high-angle annular dark-field images of an MgO precipitate in a Cu(Ag) matrix recorded along a common <211> direction.
Figure 4.3. High-angle annular dark-field (HAADF) image of a \{222\}MgO/Cu(Ag) interface recorded along the common [110] direction. Note that this interface is atomically flat and sharp.
It was found, however, that in many cases the \{222\} interfaces contain double or quadruple-height atomic steps. Interfacial steps near the corners of the particles have previously been found for the MgO/Cu system by HREM [49]. Figure 4.4 is a [110] image of the \{222\} interface with a double-height atomic step. We define the single-height step as \(d_{\{222\}}(\text{MgO}) = 0.122 \text{ nm}\), while a double-height step is \(2d_{\{222\}}(\text{MgO}) = 0.243 \text{ nm}\). In MgO, the \{222\} planes are polar, consisting of either pure oxygen or pure magnesium ions. Consequently, two possible terminations of a polar ceramic/metal interface are possible – anion or cation. The step indicated in Fig. 4.4 has a height of \(2d_{\{222\}}(\text{MgO}) = 0.243 \text{ nm}\) and, therefore, it does not change the chemistry of the terminating plane. Figure 4.5 is an example of a quadruple-height step formed near the corner of a precipitate. Again, the height of this step is \(4d_{\{222\}}(\text{MgO}) = 0.486 \text{ nm}\) and it does not change the chemistry of the terminating plane.
Figure 4.4. HAADF image of a \{222\}MgO/Cu(Ag) interface containing a double-height step. This image is recorded along the common \langle110\rangle direction. The position of the interface is indicated by a line.
Figure 4.5. (a) BF and (b) HAADF images of a \(\{222\}\text{MgO/Cu(Ag)}\) interface recorded along the common [110] direction. Both a double and a quadruple-height atomic steps can be seen near the corner of this precipitate. The position of the interface is indicated by a line.
4.4.2 Dislocation structures of $\{222\}$MgO/Cu(Ag) interfaces

The dislocation structure of $\{222\}$MgO/Cu interfaces has been studied previously with HREM [48,49]. In both reports, periodic contrast along the interface was observed, leading to the conclusion that the interface is semicoherent containing the geometrically necessary misfit dislocations. The dislocation core structure, however, was not resolved due to resolution limitations and geometrical reasons discussed in Section 4.5. In this work, an attempt was made to determine the dislocation structure of the interfaces for a $<211>$ projection. The $<211>$ projection is rarely used as the resolving power of most microscopes is insufficient to image Cu $\{220\}$ fringes spaced at 0.128 nm. In this work, while it was possible to obtain clearly resolved Cu $\{220\}$ and Mg $\{220\}$ fringes in the bulk, the atomic structures of interfaces were not resolved in the $<211>$ projection. Therefore, the $<110>$ projection was used to determine the interfacial dislocation structure.

Figure 4.6 shows a BF and an HAADF images of a $\{222\}$MgO/Cu(Ag) interface in a $<110>$ orientation. Local bending of the atomic planes is clearly visible, and positions of regions of bad fit are marked with arrows. The average spacing between these dislocations is $1.45\pm0.19$ nm, where 0.19 nm is one standard deviation and the average value 1.45 nm is for 20 dislocations.

Misfit dislocations are also detected at interfacial steps and in the corners of precipitates. Figure 4.7 is an HAADF image of an interface containing a double-height atomic step. The positions of misfit dislocations are indicated by arrows. Shown in Fig. 4.8(a) is an HAADF image of a precipitate's corner.
addition to regular misfit dislocations, a Shockley partial dislocation with an 
(a/6)<211> Burgers vector, is observed at the junction of two facets. Extended 
along the {111} plane of the Cu(Ag) matrix is a stacking fault terminated by 
another (a/6)<211> Shockley partial dislocation at a distance of about 1.5 nm. 
Figure 4.8(b) details the atomic layer sequence associated with this defect.
Figure 4.6. (a) BF and (b) HAADF images of a [222] MgO/Cu(Ag) interface recorded along the common [110] direction. The positions of misfit dislocations are indicated by arrows. The average spacing between dislocations is 1.45±0.19 nm. The intensity of this HAADF image of MgO is too low to reveal lattice fringes.
Figure 4.7. An HAADF image of a \{222\}MgO/Cu(Ag) interface containing a double-height step. Misfit dislocations and local bending of the atomic planes are observed. Note the presence of a misfit dislocation at the double-height step.
Figure 4.8.
Figure 4.8 cont. (a) An HAADF image of the corner of an MgO precipitate in a Cu(Ag) matrix. Double-height steps are visible near the junction of the \{222\} facets. Note the contrast disturbance near the corner indicated by an arrow. (b) A schematic diagram of the image in (a) showing the \{222\} planes of MgO and Cu(Ag) and the positions of misfit dislocations. The contrast disturbance in (a) is due to a Shockley partial dislocation at the interface with Burger’s vector \((a/6)<211>\). A stacking fault is emitted into the matrix and is terminated by another Shockley partial. The stacking sequence in the matrix is indicated.

Finally, most of the misfit dislocations observed in the \{222\}MgO/Cu(Ag) system terminate at the interface, without any apparent shift of the dislocation core into the metal matrix; the latter is the stand-off dislocation effect [58]. Some sections, however, of the interfaces are found to have a terminating Cu(Ag) layer stretched along the interface to match the lattice parameter of MgO, with the core of the dislocation residing in the second Cu(Ag) layer. For the atomically flat interface shown in Fig. 4.3, Fig. 4.9 presents a schematic diagram of the interface structure with one misfit dislocation in a stand-off position. Its stand-off distance is equal to a single \{111\} spacing of the Cu(Ag) matrix.
Figure 4.9. (a) An atomically flat \{222\}MgO/Cu(Ag) interface in a \{110\} projection. (b) Schematic diagram of the misfit dislocation structure for the interface shown in (a). Note that one of the dislocations is in a stand-off position.
4.4.3 Separation of the interface and terminating plane

The clear visibility of lattice fringes and the fact that the actual atomic columns are imaged with Z-contrast, allows a precise determination of the interface separation. This quantity is important in determining the nature of bonding across an interface and may be compared to calculated values for various interface configurations [37]. Figure 4.10 (a) is an atomically flat section of a \{222\} interface and Fig. 4.10 (b) is an intensity linescan across the entire image. All the linescans were obtained using NIH Image software, Version 1.60 [103]. It is important to note that the oxygen columns are not imaged with STEM, due to their weak scattering potential. Therefore, the value measured is the distance between a terminating Cu(Ag) layer and the last Mg layer of MgO. The measurements were averaged over 14 different interfaces to produce a mean value of 0.268±0.018 nm, where 0.018 nm is one standard deviation in the mean. In Section 4.6, we compare this value with the available calculational results and show that this measurement allows us to state conclusively that the terminating layer at this \{222\}MgO/Cu(Ag) interface is oxygen, and not magnesium.
Figure 4.10. (a) HAADF image of an atomically flat {222}MgO/Cu(Ag) interface in the [110] orientation. (b) An intensity linescan across the {222} planes of MgO and {111} planes of Cu(Ag) is used to measure the interface separation.
4.4.4 Evidence of silver segregation at a \( \{222\} \text{MgO/Cu(Ag)} \) interface

In the previous work on the \( \{222\} \text{MgO/Cu(Ag)} \) heterophase interface [15] described in Chapter 3 of this thesis, silver segregation to this interface, at 500°C, was detected and quantitatively measured by atom-probe field-ion microscopy. The total amount of silver at this interface was found to be equivalent to approximately 0.2 effective monolayers, although it is most likely not confined to a single monolayer. As discussed in Section 4.2, the chemical sensitivity of Z-contrast is \( Z^n \), where \( n = 1.6-1.9 \), depending on the ADF detector geometry, and \( Z^2 \) in the ideal (unscreened) case [95]. The ratio of the squares of atomic numbers is 2.63 for the Ag-Cu pair and 15.34 for the Ag-Mg pair. Calculations in reference 95 predict that for the value of inner detector angle of 45 mrad used in this work, the parameter \( n \) is equal to approximately 1.65. Taking the worst case scenario \( (n = 1.6) \), the Z-ratio becomes 2.17 for the Ag-Cu pair and 8.89 for the Ag-Mg pair. This makes the \( \{222\} \text{MgO/Cu(Ag)} \) interface suitable for detecting silver segregation.

Chemical sensitivity of an ADF image, however, depends not only on the detector geometry, but also on the probe geometry. To illustrate this effect, BF and ADF images were recorded from the same \( \{222\} \text{MgO/Cu(Ag)} \) interface using the HB501 STEM with different objective aperture diameters, 40 and 70 \( \mu \text{m} \). This corresponds to the objective aperture semiangles of 10.3 and 18 mrad, respectively. The inner collection angle of the ADF detector was 25 mrad. The result is shown in Fig. 4.11. For the 40 \( \mu \text{m} \) diameter aperture, a well-pronounced
bright line appears at the interface in the ADF image, see Fig. 4.11 (c). An intensity linescan across the interface shown in (e) exhibits a 15% increase in intensity localized in approximately 0.8 nm wide area. For the 70 µm diameter aperture the effect is completely eliminated, see Figs. 4.11 (d) and (f). On the other hand, while no lattice fringes are visible in Fig. 4.11 (c), increasing the objective aperture diameter to 70 µm reveals the {111} lattice fringes of copper spaced at 0.208 nm. The effect of objective aperture diameter is discussed further in Section 4.6.

An additional factor to be considered in detecting silver segregation is the effect of the inner detector angle on contrast formation. Figure 4.12 displays, (a) BF, (b) low-angle ADF, and (c) high-angle ADF images, of the same {222}MgO/Cu(Ag) interface in a <110> orientation. The inner collections angles of the detector are 25 and 45 mrad in (b) and (c), respectively. Significant extra intensity is observed in the vicinity of the interface in Fig. 4.12 (b), while in Fig. 4.12 (c) the effect is not pronounced. To analyze the contrast effects quantitatively, intensity linescans were taken along a representative section of this interface. Figure 4.13 presents linescans for low (a) and high (b) collection angles. It is seen that for a small inner detection angle (25 mrad), the extra intensity reaches 30% and is spread over fifteen {111} planes in the metal matrix. The HAADF image (45 mrad detector angle) shows no more than 5% extra intensity, which is localized in 3 to 4 atomic planes. It is concluded that in the low-angle ADF images a significant contribution from strain contrast is detected. Therefore, any possible segregation effects are masked by this additional
intensity. On the other hand, HAADF images are nearly free from strain contrast and can be used to detect silver segregation.

Figure 4.14 is a HAADF image of (222)MgO/Cu(Ag) interface imaged in a <110> orientation. A significant bright halo is visible on the metal side of this interface. The intensity linescan demonstrates that a 32% increase in intensity is observed in the first two \{111\} planes, while the region of extra intensity is spread over five \{111\} planes in the Cu(Ag) matrix. This effect is believed to be due to silver segregation to this interface.
Figure 4.11.
Figure 4.11 cont. Effect of objective aperture size on bright-field (BF) and annular-dark field (ADF) STEM images. (a) and (b), BF images of a \{222\}MgO/Cu(Ag) interface recorded using 10.3 mrad and 18 mrad objective aperture, respectively; (c) and (d), ADF images recorded using 10.3 mrad and 18 mrad objective aperture, respectively; (e) and (f), intensity linescans corresponding to the rectangular areas shown in (c) and (d), respectively. Note the extra intensity at the interface in (c) that is absent in (d). Also note that \{111\} copper lattice fringes are resolved in (d), but not in (c).
Figure 4.12. (a) BF image of a [222]MgO/Cu(Ag) interface recorded along the common [110] direction. (b) Low-angle ADF image (inner detector angle 25 mrad), showing strong intensity near the interface due to strain contrast. (c) High-angle ADF image (inner detector angle 45 mrad) is insensitive to strain and shows no extra intensity.
Figure 4.13. ADF images of \{222\}MgO/Cu(Ag) interface recorded along a common [110] direction. (a) Inner detector angle 25 mrad. The intensity linescan shows a 30% increase due to strain contrast. Extra intensity is observed in about fifteen \{111\} planes into the Cu(Ag) matrix. (b) Inner detector angle 45 mrad. The extra intensity is less than 5%, indicating that the cumulative effects of strain and silver segregation are negligible.
Figure 4.14. HAADF image (inner detector angle 45 mrad) of \( \{222\}\text{MgO/Cu(Ag)} \) interface recorded along the common \([110]\) direction. Line profile taken from the rectangular area shows a 32% increase in brightness in the first and second Cu(Ag) \( \{111\} \) planes. Extra intensity is visible in five \( \{111\} \) planes. This indicates the presence of silver at this interface.
Finally, a careful examination of the STEM images shows that, in most cases, a well-pronounced additional intensity (compared to the bulk of a precipitate) is observed in the last magnesium layer of MgO. The effect can be seen, for example, at the interface exhibited in Fig. 4.10 (a). Note that an intensity linescan across the interface (see Fig. 4.10 (b)) demonstrates that the increase in intensity is 300%, with respect to the bulk MgO. Moreover, in many cases, this extra intensity is inhomogeneous and follows a quasiperiodic pattern. Figure 4.15 displays an HAADF image of the corner of MgO precipitate in a \(<110>\) projection. Modulations of intensity, parallel to the interface, can be observed in the last magnesium layer which are indicated by arrows. Measurements demonstrate that the average distance between intensity maxima is 1.6 nm, which is close to the measured spacing of the misfit dislocations (1.45 nm). To test this hypothesis, all the images were examined to check the correlation between the positions of dislocations and the atomic columns displaying extra intensity in the last Mg layer.

Figure 4.16 illustrates that in this case, extra intensity in the last magnesium layer is observed in the vicinity of misfit dislocations, but the precise spatial correlation between the two features is not clear. Therefore, more experimental data is needed to accept or reject this hypothesis. The origin of additional intensity in the last magnesium layer of MgO is further discussed in Section 4.6.
Figure 4.15. The corner of an MgO precipitate in a Cu(Ag) matrix. Segments of extra intensity in the last magnesium layer are indicated by arrows. The average distance between maxima is 1.6 nm.
Figure 4.16. (a) HAADF image of a \{222\}MgO/Cu(Ag) interface in <110> orientation. (b) Interface outline showing locations of misfit dislocations and the columns exhibiting extra intensity in the last Mg layer of MgO.
4.5 RESULTS OF ELECTRON ENERGY LOSS SPECTROSCOPY INVESTIGATION

For high-resolution EELS analysis of the \{222\}MgO/Cu interfaces, line mode of acquisition was used. It is discussed in detail in Section 5.2 of this thesis. This technique has the advantage of reducing the amount of electron-beam damage compared to the more commonly used point mode. The probe diameter was approximately 0.3 nm and the scanning length was 7.2 nm. Figure 4.17 displays an MgO precipitate used for compositional analysis of the \{222\} interface. Figure 4.18 displays a series of EELS spectra recorded from points 1 through 5 indicated in Fig. 4.17. The most prominent core loss peak of silver used in EELS analysis is Ag M\(_{45}\). 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 for fifth-period elements, which makes them harder to detect in EELS. Nevertheless, line 2 in Fig. 4.18 exhibits a well-pronounced delayed-maximum edge characteristic of silver. Figure 4.19 exhibits line 2 from Fig. 4.18, after background subtraction using an inverse power law fit (correlation coefficient, 0.9899) to a pre-edge background. Shown in the inset is a calculated Ag M\(_{45}\) line, from reference 104. Clearly, the edge onset is well reproduced experimentally, while the shape of the line is distorted due to the effects of plural scattering [104]. No attempt was made in this work to remove the plural scattering by deconvolution or to obtain a quantitative analysis of the
interface composition, since a reliable quantitative analysis of these interfaces has already been conducted by APFIM; see Chapter 3 of this thesis. The qualitative evidence of the silver segregation at the \{222\}MgO/Cu(Ag) interface obtained by EELS serves as an independent confirmation of the results of the APFIM study.
Figure 4.17. (a) ADF image of an MgO precipitate in the Cu(Ag) matrix used for 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 through 5 corresponds to a scanning area of 0.3×7.2 nm (indicated by a black rectangle).
Figure 4.18. EELS spectra recorded from areas 1 through 5 indicated in Fig. 4.17. Note a strong Ag M\textsubscript{45} edge appearing in line 2. Position of O K and Ag M\textsubscript{45} edges is indicated by arrows.
Figure 4.19. Ag $M_{45}$ core loss edge from a $\{222\}$MgO/Cu(Ag) interface. Inset, Ag $M_{45}$ edge shape predicted using Hartree-Slater calculations, from reference 104.
4.6 DISCUSSION

According to Bollmann’s geometric O-lattice theory, the dislocation structure of a semicoherent {111} interface between two cubic lattices must be a hexagonal net of pure edge dislocations; dislocation line segments must be parallel to the <211> directions with a Burgers vector of \((a/2)<110>\) [57]. Figure 4.20 (a) shows the misfit dislocation pattern on the \{222\} facet of an octahedral precipitate. The size of an hexagonal cell is determined by the lattice misfit parameter, \(\eta\), given by \(2(a_{\text{MgO}}-a_{\text{Cu}})/(a_{\text{MgO}}+a_{\text{Cu}}) = 15.3\%\). This corresponds to the distance between two parallel sides of a hexagon of 1.81 nm, see Fig. 4.20 (b). Since both HREM and STEM produce a two-dimensional projection of a three-dimensional object, the dislocation structure visible in an image depends on the orientation of the sample. In the <211> projection, see Fig. 4.20 (c), some segments of dislocation structure are projected end-on, giving an opportunity to determine the structure of dislocation cores, if the microscope can resolve the 0.128 nm spacing of \{220\} lattice fringes in copper. The continuous segments are, however, only 1 nm in length for the \{222\}MgO/Cu system due to the high lattice misfit. Therefore, direct imaging of dislocation cores does not seem possible in this case since a specimen of 1 nm thickness or less would not produce a reasonable image in either an HREM or a STEM.
Figure 4.20.
**Figure 4.20 cont.** Dislocation structures at \{222\}MgO/Cu(Ag) interface. (a) Misfit dislocation pattern on a \{222\} facet of an octahedral precipitate, according to O-lattice theory. (b) Dimensions and Burgers vectors of misfit dislocation pattern in (a) for \{222\}MgO/Cu interface. (c) \{222\} facet of the octahedral MgO precipitate in (a) compressed along a \(<112>\) direction. End-on dislocation segments are separated by dislocation-free regions. (d) \{222\} facet of the octahedral MgO precipitate in (a) compressed along a \(<110>\) direction. Regions of good fit are 1 nm wide. Regions of bad fit are 0.5 nm wide and contain 30° zigzag dislocation pattern. (e) An alternative model of the dislocation structure for the \{222\} interface with trigonal symmetry. (f) Schematic diagram showing decomposition of the dislocation structure in (a). Resulting structure has trigonal symmetry and consists of straight pure edge dislocations. Triangular areas at the interface are alternating regions of good fit and interfacial stacking faults (shaded areas).
Alternatively, in a <110> orientation, the dislocation structure shown in Fig. 4.20 (a) is more favorable for imaging. A projected image represents regions of good fit, separated by the regions of bad fit (see Fig. 4.20 (d)). Regions of good fit are about 1 nm wide and only contain dislocation lines lying in the plane of the image. Their Burgers vectors are parallel to the electron beam, so the local atomic displacements caused by these dislocations do not, in the first approximation, disturb the registry between the projected Cu and MgO planes. Regions of good fit are separated by a zigzag dislocation pattern with a projected width of 0.5 nm. Dislocations in this pattern are inclined 30° with respect to the electron beam, so their core structure cannot be resolved.

The predictions of O-lattice theory are in qualitative agreement with the observed periodicity at the interface. Quantitatively, the measured spacing (1.45 nm) is smaller than theoretically predicted spacing of 1.54 nm by 6%. The main discrepancy, however, between the predicted and observed dislocation structures, is a clear visibility of the atomic columns along the interface, including the regions of bad fit (see, for example, Figs. 4.4, 4.7, and 4.9). This is only possible in two cases: if the interface is incoherent or if the misfit dislocation lines are end-on. The \{222\}MgO/Cu interfaces observed in this work are obviously not incoherent. First, a Burgers circuit around any misfit dislocation shown in Fig. 4.9 does not close. Secondly, a local displacement field is clearly visible near the interface. Therefore, we can conclude that interfaces are semicoherent.
An alternative model of a \{111\} interface between two cubic lattices has been proposed in the literature [54]. It consists of a trigonal net of straight pure edge dislocations having a \<110\> line direction and a Burgers vector equal to \(\frac{a}{6}\)<211>, see Fig. 4.20 (e). As shown in Fig. 4.20 (f), this structure can be obtained by dissociation of triple nodes of the original hexagonal net into interfacial stacking faults (SFs), bound by triangles of \(\frac{a}{6}\)<211> dislocations. An analogous dislocation network was observed in simulations of \{222\}MgO/Cu interfaces [18] based on \textit{ad hoc} interatomic potentials designed to have the correct periodicity of \{222\}MgO/Cu interfaces, but otherwise not based on a detailed model of the bonding. In a recent work [105], this trigonal network was obtained at \{222\}MgO/Cu interfaces from MD calculations based on interatomic potentials derived from previous first-principle LDFT calculations. In reference 18, the author calculated the relaxed structures for both dislocation configurations and found that the trigonal structure has much smaller strain field compared to the hexagonal structure. Therefore, the trigonal structure may be energetically favorable for systems in which the gain in the elastic energy is greater than the energy of the created interfacial stacking faults. This argument is applicable to the \{222\}MgO/Cu(Ag) interface since its energy is decreased by the presence of silver at the interface, that is, Gibbsian interfacial segregation. In MD simulations in reference 105, it was found that the trigonal dislocation network is indeed the lowest energy structure for the \{222\}MgO/Cu interface at 0 K.
In principle, the trigonal and hexagonal networks are distinguishable by HREM [18], but it has proven difficult, so far, to make a definitive identification on the basis of experiment alone. Clear visibility of the atomic columns along the interface in this study, including the regions of bad fit, indicates that the dislocation lines are parallel to the beam direction, <110>. Taking into account the simulation results of references 18 and 105, it is concluded that the (222)MgO/Cu(Ag) interfaces are semicoherent and contain a trigonal network of pure edge misfit dislocations. Dislocation lines are parallel to the <110> direction and have a Burgers vector equal to (a/6)<211>.

Stand-off dislocations have not heretofore been observed at (222)MgO/Cu interfaces. According to Eq. 2.1, the equilibrium stand-off distance at the (222)MgO/Cu interface should be 0.02 nm [49]. The theoretical value [58] of stand-off distance, however, is derived based on linear elasticity theory and it does not take into account the energy contribution from the dislocation cores. In addition, the presence of 13% oversized, with respect to copper, silver atoms at the interface may affect the equilibrium stand-off position. Since only a few of the observed (222)MgO/Cu(Ag) interfaces contain stand-off dislocations at a single {111} spacing, it is suggested that “normal” configuration is slightly energetically preferred over the stand-off configuration for this system.

Double and quadruple height interfacial steps observed in this system are typical for metal-oxide precipitates grown by internal oxidation, since they are intrinsic to the growth of a precipitate by a ledge mechanism, during internal oxidation and subsequent coarsening. As noted in reference 106, this type of
imperfection possesses both ledge and dislocation character and should be
distinguished from pure ledges. The dislocation character of such steps results
from the fact that at a step, a plane of the metal oxide joins a metal plane. Since
their spacing is different, this defect is equivalent to a combination of a pure
ledge and a dislocation with a Burgers vector equal to the difference in lattice
spacing of the two phases. The authors denote this type of defect a
disconnection and note that the dislocation portion of a disconnection supports
the long-range strain field in the two lattices and thereby can also accommodate
misfit. Therefore, we can conclude that double-height steps observed at
{222}MgO/Cu(Ag) interfaces are disconnections. Their defect structure is a
combination of a pure ledge of height \(2d_{\{222\}}(\text{MgO})\) (= 0.243 nm) and a
dislocation with a Burgers vector, \(b = d_{\{222\}}(\text{MgO}) - d_{\{111\}}(\text{Cu})\) (= 0.035 nm).

The presence of steps in the structure makes observation of interfaces in
the large precipitates difficult, since if one or more steps is present in the beam
direction it makes the atomic structure of the interface unresolvable.

It is also noteworthy that all the steps observed in the {222}MgO/Cu(Ag)
system are either double or quadruple the \(2d_{\{222\}}(\text{MgO})\) height. This implies that a
single termination of these polar \{222\} interfaces is always maintained.
Otherwise, the interface separation on both sides of a step would differ. In this
work, the measured interface separation is 0.268 nm. Since oxygen layers are
invisible in STEM, the observed structure may or may not incorporate an
oxygen layer between the last Mg layer of MgO and the terminating \{111\} plane.
of Cu. First-principle calculations in reference 37 predict that an equilibrium separation of the O-terminated \(\{222\}\text{MgO}/\text{Cu}\) interface is 0.125 nm, while equilibrium separation of the Mg-terminated \(\{222\}\text{MgO}/\text{Cu}\) interface is 0.21 nm. Therefore, it corresponds to the distance between the last Mg layer of MgO and the terminating \(\{111\}\) plane of Cu of 0.247 nm for the O-terminated interface and 0.21 nm for the Mg-terminated interface. The value of interface separation measured in this work exceeds the predicted value for oxygen termination by 9\%, and the value for Mg termination by 28\%. Clearly, the experimental results are consistent with oxygen termination. The possible reasons for a 9\% discrepancy with the predicted value are discussed below.

It has been established experimentally by APFIM that the oxygen termination at atomically clean \(\{222\}\text{MgO}/\text{Cu}\) interfaces is at least strongly preferred [27]. Results of first-principle LDFT calculations of atomically clean \(\{222\}\text{MgO}/\text{Cu}\) interfaces in the zero-misfit approximation [37] also indicate that oxygen and magnesium terminations produce far different adhesive energies, 2.9 and 1.7 eV atom\(^{-1}\), thus substantiating this point. Moreover, the recent MD calculations [105] based on interatomic potentials derived from [37], indicate that the oxygen termination predicted in reference 37 in zero-misfit approximation, holds in the presence of interfacial misfit dislocations. Finally, high-resolution EELS analysis of \(\{222\}\text{MgO}/\text{Cu}\) interfaces presented in Chapter 5 of this thesis, also indicates oxygen termination of this interface. Z-contrast microscopy provides an unsurpassed accuracy in determining the interface separation, so
we conclude that (222)MgO/Cu(Ag) interfaces studied are invariably terminated by oxygen.

The value of interface separation measured in this work exceeds the theoretically predicted value [37] by 9%. It is also 29% greater than (111) spacing in Cu and 10% greater than (111) spacing in MgO. However, one cannot compare theoretical predictions for atomically clean interfaces with experimental results for interfaces with strong levels of solute segregation. The presence of 13% oversized silver atom, with respect to copper, at the interface most likely changes the value of interface separation.

The investigation of interfacial segregation by atomic resolution Z-contrast microscopy is a relatively new subject. There have been successful examples [107] of detecting segregation of solute atoms at well-defined, planar homophase interfaces (Ni and B in Ni₃Al grain boundaries). The application of Z-contrast to heterophase interfaces between metal matrix and small oxide precipitates has not heretofore been made. There is no theory at hand describing the effect of elastic strains on image contrast formation. This factor is particularly important for the system studied here, because of a 20% mismatch in the thermal expansion coefficients of Cu [108] and MgO [109] (16.5×10⁻⁶ K⁻¹ and 13.5×10⁻⁶ K⁻¹, respectively). This effect causes 0.27% elastic strain at the interface over the temperature range 1223 K–300 K, where 1223 K is the temperature of internal oxidation. As a result, in addition to interfacial strains, thermal mismatch strains are observed around precipitates. The use, however,
of a high inner collection angle of the ADF detector (45 mrad) helps keep the strain contribution to the contrast to a minimum.

Most of HAADF images in Figs. 4.1 through 4.10 exhibit little or no extra intensity at the interface, as one would expect due to the presence of silver segregation at these [222]MgO/Cu(Ag) interfaces. Moreover, there is often a systematic decrease of the copper fringe intensity near an interface, see Fig. 4.10. Several factors are contributing to this effect. First of all, one must consider the effect of objective aperture diameter demonstrated in Fig. 4.11.

It is established in the literature [93] that there is a trade-off between image resolution in STEM and image localization, or compositional resolution. STEM probe simulations in reference 93 revealed that smaller values of defocus, \( \Delta f \), or objective aperture semiangle, \( \alpha \), produce diffraction-limited probes with broad central maxima and weak tails. On the other hand, as \( \alpha \) or \( \Delta f \) increase, the central peak becomes narrower with more extended tails. The authors concluded that a good compromise between image resolution and image localization is achieved at the Scherzer incoherent imaging conditions defined by

\[
\alpha_{opt} = \left( \frac{4\lambda}{C_s} \right)^{1/4}, \quad (4.2)
\]

\[
\Delta f_{opt} = -\left( \frac{C_s}{\lambda} \right)^{1/2}, \quad \text{and} \quad (4.3)
\]
where \( C_S \) is the objective spherical aberration coefficient, \( \lambda \) is the electron wavelength, and \( d_{\text{min}} \) is the resolution limit. Imaging with \( \alpha > \alpha_{\text{opt}} \) will, therefore, suffer from compositional blurring.

The HB603 STEM used in this work is equipped with an ultra-high resolution objective pole piece with \( C_S = 1.0 \) mm. At 300 kV, this corresponds to a value of \( \alpha_{\text{opt}} \) of 9.42 mrad. An effective diameter of the objective aperture [110] used in this work is approximately 11.3 mrad, or 120\% of the Scherzer semiangle, \( \alpha_{\text{opt}} \). The spatial resolution of the ADF images recorded in this work exceeds 0.128 nm, the \{112\} interplanar spacing of copper. This value is presently unsurpassed by any other STEM. The ultrahigh resolution, however, comes at a price of the reduced compositional resolution due to larger probe tails. Therefore, the poor visibility of silver present at the \{222\}MgO/Cu(Ag) interfaces in the ADF images is attributed to signal delocalization, caused by the tails of the probe. The same effect is most likely responsible for an additional intensity (compared to the bulk of a precipitate) that was often observed in the last magnesium layer of MgO, see, Figs. 4.8 and 4.10. It was noted in reference 96 that the probe tail may give rise to spurious image intensities and lead to errors in measurements of \( Z \) for an atomic column. Therefore, one has to be

\[
d_{\text{min}} = 0.61 \lambda / \alpha_{\text{opt}} = 0.43 C_S^{1/4} \lambda^{3/4};
\]  

(4.4)
careful in interpreting the intensities of atomic-resolution ADF images. Probe simulations are necessary to evaluate the importance of this effect.

In addition to the objective aperture effect considered above, there are several geometrical factors complicating an accurate analysis of \( \{222\}\text{MgO/Cu(Ag)} \) interfaces. First, due to the triangular shape of a precipitate’s \( \{222\} \) facets, there is no region with a constant thickness of MgO along the interface. Another factor contributing to the difficulty of analysis is the presence of interfacial steps. If steps are present parallel to the beam direction, the extra intensity due to segregation is spread over a thicker region and is more difficult to detect. Finally, results of atomistic simulations [111] suggest that interfacial segregation may not necessarily be limited to a single atomic layer, and that a whole spectrum of segregation sites may exist at an interface. These sites may be found in several atomic layers parallel to the interface. Therefore, it is reasonable to expect that equilibrium silver segregation is also spread over several atomic planes of copper, making the Z-contrast less distinct.

Despite all these factors, the intensity linescan in Fig. 4.14 shows direct evidence for silver segregation. Even though Z-contrast gives only a qualitative picture, the 32% increase in intensity observed in the first two \( \{111\} \) planes of copper allows us to make an approximate estimate. If these two layers contain \( X_{\text{Ag}} \) at. fr. of silver, then we can write for the intensity from each of these layers:

\[
X_{\text{Ag}} \cdot 2.63 + (1 - X_{\text{Ag}}) \cdot 1 = 1.32, \quad (4.5)
\]
where 2.63 is a square of the ratio of the Z-numbers of Ag and Cu. This gives 
\[ X_{Ag} = 0.2 \text{ at. fr.} \] This estimate is consistent with the levels of silver segregation at 
these \( \{222\}\)MgO/Cu interfaces measured by APFIM, see Chapter 3 of this thesis.

4.7 CONCLUSIONS

In conclusion, the first dedicated STEM investigation of solute segregation 
at a ceramic/metal interface was conducted. It was found that 
\( \{222\}\)MgO/Cu(Ag) interfaces are generally flat, with some double and 
quadruple-height steps, particularly near the corners of a precipitate.

The dislocation structure of this interface was observed in a \( <110> \) 
projection. It was found that regions of good and bad fit are in agreement with 
those predicted by Bollmann’s geometric O-lattice theory. The observed spacing 
between dislocations is \( 1.45\pm0.19 \) nm, which is close to other experimental 
values in the literature for atomically clean \( \{222\}\)MgO/Cu interfaces. The clear 
visibility of the atomic columns along the interface, including the regions of bad 
fit, indicates that dislocation lines are parallel to the beam direction, \( <110> \). 
Therefore, it is concluded that the \( \{222\}\)MgO/Cu(Ag) interfaces are 
semicoherent and contain a trigonal network of pure edge misfit dislocations. 
Dislocation lines are parallel to the \( <110> \) direction and have a Burgers vector 
\( (a/6)<211> \).
Interfacial dislocations were also observed at atomic-height steps. In one case, a Shockley partial dislocation was detected at the corner of a precipitate, accommodating a rigid-body translation between two facets. To preserve the lattice continuity in the metal matrix, a stacking fault is emitted into the metal matrix terminated by a similar Shockley partial dislocation.

The distance between the terminating Cu(Ag) plane on the metal side of the interface and the last magnesium plane on the MgO side of the interface was determined and its value is $0.268 \pm 0.018$ nm. From the measurement of interface separation, it is demonstrated that the terminating layer of this polar interface is oxygen, and not magnesium. This is in agreement with our APFIM and EELS experimental results (Chapters 3 and 5) and LDFT calculations for atomically clean $\{222\}$MgO/Cu interfaces.

Under high-angle ADF imaging conditions, extra intensity is detected at the interface. It is thought that this indicates silver segregation at this interface, in agreement with our APFIM and EELS experimental results. On the metal side of the interface, extra intensity is observed in four to five atomic layers and estimates show that it corresponds to a concentration of silver of approximately 20 at.%. On the ceramic side of the interface, only the magnesium columns can be imaged in the HAADF mode. The last magnesium layer adjacent to the terminating oxygen layer, exhibits a 300% increase in intensity. On some interfaces, this intensity also varies parallel to the interface with a periodicity close to the spacing of the misfit dislocations. Due to the small extent of these features, it does not seem possible in this case to prove or reject the hypothesis
that these regions of extra intensity correlate with the position of interfacial dislocations.

Compositional sensitivity of the HAADF images in this work suffers from signal delocalization, caused by the tails of the probe. Detailed image simulations are necessary to evaluate this effect.
CHAPTER 5

CHEMISTRY AND BONDING AT \{222\}MgO/Cu INTERFACES STUDIED BY ELECTRON ENERGY LOSS SPECTROSCOPY

5.1 INTRODUCTION

Adhesion at C/M interfaces often controls the macroscopic behavior of materials containing metallic and ceramic phases, and the importance of studying bonding at C/M interfaces has been recently recognized [23]. Electron energy loss spectroscopy (EELS) offers unique opportunities to study C/M interfaces on an atomic scale, since it can provide information on chemistry and bonding of buried interfaces and is often combined with structure determination by high-resolution electron microscopy (HREM) or scanning transmission electron microscopy (STEM). The energy loss near edge structure (ELNES) is sensitive to local atomic arrangements and thus can be used as a coordination fingerprint, see Section 2.3.3 and 2.6.

In this work, high spatial-resolution EELS was used to study \{222\}MgO/Cu interfaces produced by internal oxidation. We determine the interfacial chemistry of this interface with subnanometer resolution and use
ELNES to identify electronic states pertaining to the interface.

Prior experimental work on the atomic structure and chemistry of the \{222\}MgO/Cu interfaces produced by internal oxidation demonstrated that MgO precipitates are octahedral shaped, with faceting on \{222\}-type planes of MgO, and have a cube-on-cube orientation relationship with the Cu matrix [48]. HREM studies revealed that the interfaces are semicoherent with a network of misfit dislocations. The lattice misfit parameter, $\eta$, is 0.1525 for $a_{\text{MgO}} = 0.4212$ nm and $a_{\text{Cu}} = 0.3615$ nm. As discussed in Section 2.6, the \{222\} plane in MgO is polar and contains either pure anions or cations. Thus, two terminations of the \{222\}MgO/Cu interface are possible, oxygen or magnesium. The first experimental data on this interface termination obtained by atom-probe field-ion microscopy (APFIM) [27] indicated that oxygen termination is at least strongly preferred. In a more recent work [49], oxygen termination of a \{222\}MgO/Cu interface was also suggested based on the analysis of the HREM images.

Recently, first-principle calculations based on local density functional theory (LDFT) were applied to a polar \{222\}MgO/Cu interface in the zero-misfit approximation [37]. It was found in reference 37 that an oxygen-terminated \{222\} interface exhibit a much higher adhesive energy and electron charge transfer across the interface and is, therefore, strongly preferred over a Mg-terminated one, see Section 2.6. In addition, the electronic density of states (DOS) in the vicinity of the interface was calculated for different interface configurations. These results bear direct relevance to our experimental ELNES
measurements since, in the one-electron approximation, EELS spectrum reflects the density of unoccupied states above the Fermi level [112].

5.2 EXPERIMENTAL PROCEDURE

Atomically clean \{222\}MgO/Cu interfaces for this study were fabricated by internal oxidation of a binary Cu-2.5 at.% Mg alloy for 2 h at 1223 K in a Rhines pack [11]. This procedure corresponds to oxygen partial pressure of $10^{-2}$ Pa and yields $10^{22}$ m$^{-3}$ octahedral-shaped precipitates, 10 to 30 nm in diameter. A detailed experimental procedure is given in Appendix A. Standard TEM specimens for an EELS study were prepared by electropolishing, to produce electron-transparent thin areas, followed by ion milling. Immediately after ion milling, specimens were placed in the preparation chamber of the microscope (vacuum $3\times10^{-7}$ Pa) and annealed at 423 K for 2 h to reduce surface contamination levels. Prior to examination, areas of interest were flood illuminated with electrons at a magnification of $(20–50)\times10^3$ X, to prevent buildup of surface contaminants under the highly focused electron beam, by reducing the mobility of surface hydrocarbons.

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 reference 102. 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 [113]. 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\(^{-1}\)) and spatial-drift stability (<0.05 nm min\(^{-1}\)). The minimum attainable probe size of this instrument is approximately 0.25 nm. The vacuum in the column of the microscope was better than 10\(^{-8}\) Pa, allowing for very low surface contamination levels. EELS spectra were recorded in the image mode using a 40 µm diameter objective aperture (objective aperture semiangle, 10.3 mrad) and an energy dispersion of the spectrometer of 0.2 eV channel\(^{-1}\).

5.3 RESULTS AND DISCUSSION

5.3.1 Radiation damage and acquisition of spectra

High-spatial resolution EELS analysis employs a highly focused electron-beam. This may lead to considerable electron-beam damage in a specimen, particularly for low-Z materials [104]. The radiation damage can take several forms, including disruption of chemical bonding, introduction of structural disorder and, finally, mass loss. While the first two processes directly affect only ELNES measurements, the mass loss is of concern for elemental compositional analysis, since some elements may be more susceptible to this type of damage than others. To ascertain the accuracy of EELS compositional analysis and ELNES observations, time-resolved EELS spectra were recorded from bulk Cu
and MgO. It is expected that MgO is more susceptible to electron-beam damage than Cu, due to its lower average Z-number. Figure 5.1 exhibits a series of oxygen-K spectra recorded from the same area of an MgO precipitate for a total period of 60 s. Each line is an average of several successive measurements. Background was subtracted from all spectra using an inverse power law fit to a pre-edge background. A gradual reduction of peak intensity, accompanied by a slight peak broadening, is clearly visible. To evaluate the rate of mass loss, the area under the peak was calculated for each line from 536 to 546 eV. The result is shown in Fig. 5.2 as a function of irradiation time. The rate of mass loss is negligible until a threshold time of approximately 20 s. Therefore, it is necessary to perform measurements of interface composition in a shorter time frame. The sensitivity of MgO/Cu specimens to bond disruption by the electron beam is discussed later, in Section 5.3.3.
Figure 5.1. Series of oxygen-K edge EELS spectra recorded from the same area of an MgO precipitate. A longer irradiation time leads to a considerable reduction of the peak intensity and a slight peak broadening.
Figure 5.2. Area under the oxygen-K peak shown in Fig. 5.1 (536 to 546 eV), as a function of irradiation time.
Several data collection modes can be used for high-resolution EELS analysis of interfaces. First, a focused stationary beam can be centered on an interface. This mode provides the highest sensitivity to the features present at an interface. It may also suffer, however, from specimen drift and electron-beam damage. Another popular approach is the spatial difference technique [24, 25]. It is less susceptible to beam damage, since the beam is scanned over a larger area. The collected spectra, however, typically contain a 1% to 10% contribution from an interface and the remainder is from the bulk.

In this work, the stationary mode was used for some analyses because of the high spatial-drift stability of the modified HB501 and the known mass loss onset time. In order to place the \{222\}MgO/Cu interface edge-on, the specimen was tilted to a <110> direction parallel to the electron beam, and the stationary beam was moved across an interface in a stepwise manner.

Alternatively, the line mode was used as it takes advantage of the fact that \{222\}MgO/Cu interfaces are atomically flat. 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 0.3×7.2 nm$^2$. To obtain the compositional profile across an interface, the beam is moved manually in a stepwise manner along the Y-direction. This technique minimizes the beam damage to a specimen, while maintaining the highest spatial resolution normal to the interface.

5.3.2 Composition profile across an interface

Figure 5.3 is an annular dark field (ADF) image of an MgO precipitate in a
copper matrix. It was recorded employing a \langle 110 \rangle\text{-}zone axis orientation. The \{222\}\text{MgO/Cu} interfaces are edge-on, allowing for the highest spatial resolution of the EELS analysis. Spectra were recorded at and in the vicinity of the interface in the line mode. Figure 5.4 shows an EELS composition profile across a \{222\}\text{MgO/Cu} interface. Each point on the plot corresponds to a 3 s exposure. The spatial location of each point was determined by simultaneous recording of the ADF signal. The integral intensities of the O-K, Mg-K, and \text{Cu-}L_{2,3} edges were determined by the energy window method, after background subtraction using an inverse power-law fit to a pre-edge background. The resulting intensities were converted to atomic concentrations using pure Cu and MgO as standards; MgO was assumed stochiometric at this stage.

It is clearly visible in Fig. 5.4 that an oxygen signal is present at the interface, while the Mg signal is negligibly small. Once again, this indicates that this polar interface is oxygen-terminated. The 90\% width of the compositional profile is approximately 0.7 nm and is determined by the spatial resolution of analysis, which is in turn controlled by the initial probe diameter and beam broadening inside the specimen.
Figure 5.3. (a) Annular dark field image of an octahedral-shaped MgO precipitate in a Cu matrix recorded employing a <110>-zone axis. The area used for EELS analysis is outlined by a square. (b) Enlarged view of the area used for EELS analysis. Points correspond to the 0.3 nm probe diameter used. Spectra were recorded in the line mode, with each line acquired from a rectangular area 0.3×7.2 nm², parallel to the interface, indicated by a white rectangle.
Figure 5.4. EELS composition profile across a \{222\}MgO/Cu interface showing integrated edge intensities for Mg-K, O-K, and Cu-L\(_{2,3}\) edges, normalized to the bulk Cu and MgO signals. The oxygen intensity at the interface is notably higher than magnesium, proving that this polar interface is O-terminated. The spatial resolution of the analysis is better than 1 nm and is limited by incident probe diameter and beam broadening inside the specimen.
This direct observation of oxygen termination of the $\{222\}$MgO/Cu interface is in agreement with previous experimental and calculational results discussed in Section 5.1. It is also consistent with the experimental observation of oxygen termination of the $\{222\}$MgO/Cu(Ag) interfaces by Z-contrast imaging in Chapter 4 of this thesis.

5.3.3 Electronic states and the nature of bonding at an interface

The most prominent core-loss edges of Cu, O and Mg are Cu-L$_{2,3}$, O-K, and Mg-K, with edge onset energies of 931, 532, and 1305 eV, respectively [104]. Therefore, no peak overlap problem exists in the MgO/Cu system. On the other hand, separate spectra must be recorded for each edge. To avoid accumulation of radiation damage in a single area of analysis, each edge was recorded in a new location along the interface in a stationary or line mode. While it was determined that no mass loss occurred using exposure time $< 20$ s (see Fig. 5.2), it was found that the shape of ionization edges was much more sensitive to electron-beam damage. In all of the ELNES measurements, when the probe was placed at an interface, only the first spectrum recorded from this area had a shape distinctly different from the corresponding bulk spectrum. If the probe remained stationary over the same area, each successive spectrum did not retain this distinct shape. This effect is believed to indicate that the electronic states characteristic of the $\{222\}$MgO/Cu interface are very sensitive to bond disruption caused by the electron beam. Therefore, collection times of 3 or 4 s were used to observe the interfacial states. This also serves to explain the
poor signal-to-noise (S/N) ratios in the spectra collected from an interface, as compared to bulk lines used for reference, for which much longer total exposure times were used. From all the spectra, the background was subtracted using an inverse power-law fit to a pre-edge background. Figure 5.5 exhibits the Cu-L\textsubscript{2,3} edge recorded at the interface and in the bulk copper. Notably, copper retains the basic shape of the edge, although the near-edge structure is different from the bulk. Figure 5.6 exhibits the O-K edge recorded in a similar fashion. The edge collected at the interface appears much broader, with a well-pronounced pre-peak on the bulk edge onset. The pre-peak extends approximately 6 eV on the low-energy side. Finally, Fig. 5.7 exhibits the Mg-K edge recorded in four different locations: in the bulk MgO, at the interface, as determined by the maximum transverse gradient of intensity in the ADF image, and 0.2 and 0.4 nm away from the interface on the copper side. In the first three cases, the edge retains the shape characteristic of bulk MgO, while in the last case, the S/N ratio is too low to determine the edge shape. Therefore, it is concluded that no distinct features characteristic of the \{222\}MgO/Cu interface are observed in the Mg-K edge.
Figure 5.5. Cu-L$_{2,3}$ edge recorded at a $\{222\}$MgO/Cu interface and well away from the interface, in the bulk Cu.
Figure 5.6. O-K edge recorded at a {222}MgO/Cu interface (thick solid line) and in bulk MgO (thin solid line). Spectra are scaled to match the post-edge background. The dotted line is a spatial difference spectrum. The shaded rectangle marks the bulk MgO bandgap.
Figure 5.7. Mg-K edge recorded in four different locations: in the bulk MgO, at the interface, as determined by the maximum transverse gradient of intensity of the ADF detector, and 0.2 and 0.4 nm away from the interface on the copper side.
Interpretation of the observed near-edge structure of Cu-L$_{2,3}$ and O-K edges is somewhat facilitated by the fact that the electron energy loss edges and near-edge structure are closely analogous to those observed in x-ray absorption spectroscopy (XAS) and x-ray absorption near-edge structure (XANES). XAS of copper compounds has been a subject of several experimental studies [114-116], while XANES of the oxygen-K edge in MgO was calculated in reference 117.

Since it was found that copper at the [222]MgO/Cu interface is bound to oxygen, XAS studies of copper oxides, CuO and Cu$_2$O, are of particular interest. It was noted in reference 114 that transition metal oxides such as TiO$_2$, Cr$_2$O$_3$, FeO, NiO, and CuO, show prominent sharp peaks at the metal L absorption edges. For historical reasons, these features are often called "white lines." The origin of white lines in those compounds is a resonance, or a strong correlation, between a 2p electron ejected to an empty 3d band, and a core hole thus created in the 2p level [115]. This resonant state can be described as a pseudoparticle denoted a core exciton. On the other hand, copper in Cu$_2$O has a formal oxidation state (+1) described by the electron configuration (Ar)3d$^{10}$. The fully occupied d-band suggests that no white line is expected. It is, however, observed experimentally. It was proposed in reference 114 that the origin of the white line in the XAS spectra of Cu$_2$O is a particular linear O-Cu-O coordination of copper in Cu$_2$O that narrows the copper bands and gives rise to
resonance effects. This idea was supported in reference 116 by comparing the experimental XAS spectra with the band-structure calculations. The majority of other monovalent copper compounds do not exhibit a white line. Therefore, the shape of the Cu-L$_{2,3}$ edge observed in this work indicates that the d-band of copper is essentially full and the amount of charge transfer from copper to MgO is small, i.e., copper remains metallic at the interface. This conclusion is consistent with the band-structure calculations in reference 37, where it was found that the amount of charge transfer for an O-terminated [222]MgO/Cu interface is 0.18 e atom$^{-1}$.

The pre-peak observed in the oxygen-K edge indicates that empty electronic states are introduced inside the band gap of MgO. While this spectral feature is small and is difficult to quantify due to poor S/N ratio, it is believed that the energy width of this pre-peak may be large enough to remove the band gap between the filled and empty oxygen states and to give rise to a partial metallization of the terminating oxygen layer at the interface. This result is also consistent with band-structure calculations. The calculated layer projected local densities of state for the O-terminated [222]MgO/Cu interface in reference 37 exhibit a decrease, and eventually a collapse, of the MgO bandgap towards the interface.

Notably, the Mg-K edge at the interface shows no difference in fine structure. This is consistent with an O-terminated interface and implies that the
disturbance of electronic states in MgO in the vicinity of the interface is confined to the terminating oxygen layer.

The observation of metallic copper and a partial metallization of the terminating oxygen layer at the [222]MgO/Cu interface is strikingly different from the model of bonding developed in reference 23 for the (0001)α-Al2O3/Cu(111) interface. It was concluded in reference 23, on the basis of ELNES observations of Cu-L2,3 and O-K edges, using the spatial difference technique, that the interface is O-terminated and copper is in a +1 state and is bound directly to oxygen. The observed spatial difference spectrum of Cu-L2,3 exhibited a white line similar to the one found in Cu2O. While one certainly cannot generalize from one system to another, it should be noted that when Cu atoms at an interface are coupled to the broader bands of bulk Cu, one would expect the structural (O-Cu-O) and electronic configurations giving rise to the white lines in Cu2O to be lost.

One potential pitfall of the spatial difference technique is that only a small fraction of the signal collected from an interface is actually emitted by the interface. The scanning area used in reference 23 for the spatial difference technique was 10×12 nm². As noted above, the electronic states pertaining to the interface are probably confined to a monolayer thickness on each side. It was also concluded in reference 23 that Al atoms are not involved in the bonding, which is localized to a terminating oxygen layer. Assuming a 0.4 nm thick
interface layer, only 4% of the signal is emitted from the interface. In addition, if energy drift is present in the EELS detector, shift of just a single detector channel produces sharp, derivative-like features in the difference spectrum on the onsets of ionization edges, which is a basis of the energy difference method [24]. The last point is illustrated in Fig. 5.8. A spectrum of bulk Cu-L\textsubscript{2,3} edge was shifted by 0.5 eV and subtracted from the original spectrum. The difference spectrum exhibits a sharp feature on the onset of the bulk Cu ionization edge (936 eV) that is reminiscent of the Cu\textsubscript{2}O spectrum (inset, from reference 115). Therefore, care must be used when employing the spatial difference technique to take into account these factors. On the other hand, a direct observation of interface electronic states in this work does not involve any spectra manipulation. The analysis is limited, however, to very short times (<4 s) due to the strong susceptibility of interface electronic states to electron-beam damage.
Figure 5.8. Effect of the energy drift in the EELS detector on the spatial difference spectrum. Spectrum of bulk Cu (thin solid line) was shifted by 0.5 eV (filled circles) and subtracted from the original spectrum. The difference spectrum (thick solid line) exhibits a sharp, derivative-like feature on the onset of the bulk Cu ionization edge that is reminiscent of the Cu$_2$O spectrum (inset).
5.4 CONCLUSIONS

1. Interface chemistry was measured by EELS for the \( \{222\}\text{MgO/Cu} \) interface, produced by internal oxidation. This interface is atomically sharp and chemically abrupt and is terminated by oxygen, in accordance with previous experimental data and band-structure calculations. The 90% width of the composition profile is 0.7 nm. The spatial resolution of analysis is determined by the initial probe diameter and beam broadening inside the specimen.

2. Electronic states characteristic of this interface were observed by placing a stationary electron beam, 0.3 nm diameter, directly at the interface, or by scanning the beam along the atomically flat interface. The interfacial electronic states are demonstrated to be highly sensitive to electron-beam damage, which required a collection time of the spectra of 4 s or less.

3. The shape of the Cu-L\(_{2,3}\) edge observed at this interface indicates that the d-band of copper is essentially full and the amount of charge transfer from copper to MgO is small, \( i.e., \) copper remains metallic at the interface. This is consistent with the results of band-structure calculations.

4. The pre-peak observed in the oxygen-K edge at the interface indicates that empty electronic states are introduced inside the band gap of MgO. It is believed that this pre-peak indicates a partial metallization of the terminating oxygen layer at the interface. This result is also consistent with band-structure calculations, predicting a collapse of the MgO bandgap near the interface.
5. The Mg-K edge at the interface shows no difference in fine structure. This is consistent with an O-terminated interface and implies that the disturbance of electronic states in MgO in the vicinity of the interface is confined to the terminating oxygen layer.
CHAPTER 6

CHEMISTRY OF \{222\}MgO/Pd INTERFACES STUDIED BY ENERGY-DISPERSIVE X-RAY SPECTROSCOPY

6.1 INTRODUCTION

Among the techniques employed to investigate interfacial chemistry, energy dispersive x-ray spectroscopy (EDX) and electron energy loss spectroscopy (EELS) are among the most widely used. Both techniques provide an advantage for recording spectra, while concurrently obtaining bright or dark field TEM or STEM images and crystallographic information via selected area electron diffraction patterns. As discussed in Section 2.3.3, the two techniques are complimentary in many respects and have provided valuable information on chemistry and bonding at C/M interfaces. An EDX detector with an ultrathin window can detect light elements down to boron (Z = 5) and typically has a minimum mass fraction detectability of 0.1 to 0.2 wt.%. This combination enables researchers to reach ultimately a spatial resolution of 1 nm for chemical analyses in ideal cases [118]. The generation of characteristic x-rays, however, is strongly Z-dependent and, therefore, the analyses of light elements and
compounds imposes additional problems. The data processing of x-ray spectra involves consideration of several possible sources of error [119].

In this chapter, we present an attempt to study the chemistry of the \{222\}MgO/Pd interfaces, produced by internal oxidation, using high-resolution EDX. We first discuss the requirements to reduce the errors involved in investigating the chemistry of heterophase interfaces employing EDX. Secondly, the chemical composition of the \{222\}MgO/Pd interface is measured by EDX. Finally, the data are analyzed to reveal practical limitations on high-spatial resolution EDX analysis of interfacial chemistry in C/M heterophase systems.

6.2 CONDITIONS OF HIGH-RESOLUTION ENERGY-DISPERSIVE X-RAY ANALYSIS OF INTERFACES

Quantitative EDX analysis involves the elimination of all sources of spurious x-rays and a complicated procedure to analyze quantitatively x-ray spectra [119]. X-ray signals that are artifacts can be produced in a TEM’s illumination system and specimen stage region, as well as from the x-ray detector itself. Secondly, the quantification of x-ray spectra requires an absorption correction, a fluorescent correction, accurate specimen thickness measurements, background subtraction to obtain genuine intensities, and the determination of the so-called k-factor (or Cliff-Lorimer factor) [120].

In addition, there are several important requirements and constraints for investigating interfacial chemistry using EDX. The first concern is the specimen
geometry with respect to the incident electron beam and EDX detector. To achieve high spatial resolution, the interface should be planar (or at least have no steps in the direction of the incident beam) and should be positioned parallel to the incident electron beam. For the same reason, the EDX detector has to be located at the extended plane of the interface to avoid obtaining a mixed signal from adjacent grains [121]. These geometrical requirements demand the careful orientation and positioning of the interface to be analyzed. To achieve these conditions, a rotation-tilt TEM specimen holder is preferred to avoid the time-consuming efforts necessary to meet these geometrical requirements with the more commonly employed double-tilt TEM sample holder. Finally, careful analysis of interfacial chemistry in a specimen is possible only when the interface plane extends over the entire thickness of a specimen in the area of analysis. Figure 6.1 displays the ideal arrangement of an interface with respect to the incident electron beam and EDX detector. When collecting a series of x-ray spectra, the electron probe should be moved normal to the interface plane, that is, along the edge of a specimen with a constant thickness. If these conditions are not considered prior to collecting x-ray spectra, serious errors can be introduced into the compositional chemical analysis.
Figure 6.1. An ideal arrangement of a heterophase interface and x-ray detector for high-resolution EDX analysis. The heterophase interface (between the $\alpha$ and $\beta$ phases) should be planar and parallel to the incident electron beam direction, and the x-ray detector has to be located at the extended plane of the interface.
The second consideration, important for the study of a heterophase interface, is that the spatial resolutions obtainable in the two different materials can be dramatically different. In the first approximation, the spatial resolution of analysis is calculated [119] from the equation,

\[ R = \left( d^2 + b^2 \right)^{1/2} \]  \hspace{1cm} (6.1)

where \( R \) is the spatial resolution as defined by the probe diameter at the bottom surface of a specimen, \( d \) is the probe diameter at the top surface of a specimen, and \( b \) is the beam broadening within a specimen. In Eq. 6.1, both \( d \) and \( b \) are assumed to have a Gaussian distribution. The initial electron probe, however, only has a Gaussian shape when it is properly limited by probe-forming apertures [122]. Furthermore, the assumption that the Gaussian shape of a probe is preserved after traversing the specimen is only valid for thick specimens and neglects diffraction and channeling effects. Nevertheless, Eq. 6.1 gives a reasonable explanation of the major factors controlling \( R \). Since \( R \) represents the electron-beam diameter on the exit surface of a specimen, it overestimates the spatial resolution. A better estimate of \( R \) was proposed [123] that averages the beam diameter at the entrance and exit surfaces and is given by
\[ R = \frac{d + \left( d^2 + b^2 \right)^{1/2}}{2} \]  

(6.2)

The beam broadening, \( b \), within a specimen, however, is material dependent. Using a single-scattering model, \( b \) can be expressed [123] as

\[ b = 7.21 \times 10^5 \left( \frac{\rho}{A} \right)^{1/2} \frac{Z}{E} t^{3/2} \]  

(6.3)

where \( t \) is the thickness in cm, \( \rho \) is the average density, \( A \) is the average atomic weight, \( Z \) is the average atomic number of a specimen, \( E \) is the beam voltage in eV, and \( b \) is given in cm.

An alternative method to evaluate beam broadening employs Monte Carlo simulations. An advantage of this method is that it takes into account multiple scattering events. Monte Carlo simulations of the beam broadening effect were performed for two materials, MgO and Pd, as a function of specimen thickness and energy of the incident electron beam (100 and 200 keV). The results are presented in Table 6.1. Simulations were performed using a Monte Carlo code developed by D. C. Joy (University of Tennessee) [129].

**TABLE 6.1** Electron beam broadening in MgO and Pd as a function of specimen thickness and accelerating voltage obtained by Monte Carlo simulations.
<table>
<thead>
<tr>
<th>Specimen thickness (nm)</th>
<th>Beam broadening in MgO (nm)</th>
<th>Beam broadening in Pd (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100 kV</td>
<td>200 kV</td>
</tr>
<tr>
<td>10</td>
<td>0.37</td>
<td>0.18</td>
</tr>
<tr>
<td>50</td>
<td>4.17</td>
<td>2.08</td>
</tr>
<tr>
<td>100</td>
<td>11.78</td>
<td>5.89</td>
</tr>
<tr>
<td>200</td>
<td>33.31</td>
<td>16.66</td>
</tr>
<tr>
<td>300</td>
<td>61.23</td>
<td>30.61</td>
</tr>
<tr>
<td>500</td>
<td>131.74</td>
<td>65.86</td>
</tr>
</tbody>
</table>
Table 6.1 demonstrates that beam broadening is approximately a factor of two greater for Pd than for MgO. Figure 6.2 is a schematic diagram of the electron beam broadening effect for an MgO/Pd heterophase interface, illustrating that the broadening effect in Pd is significantly bigger. The mixing of two x-ray signals from different materials cannot be avoided, in general, and the deconvolution of such a mixed signal is fairly complicated. If the scattering characteristics of the two phases involved ($\alpha$ and $\beta$) are dramatically different, geometrical models cannot be applied and Monte Carlo simulations should be used. To reduce signal mixing from two adjacent grains, the specimen should be as thin as possible. A very thin specimen, however, is easily damaged by the highly focused electron beam. Also, since a thin specimen requires long exposure times to collect a statistically significant x-ray signal, especially in the case of ceramics which are often low-Z materials, drift of both the specimen and electron beam represents a serious problem. Furthermore, study of heterophase interfaces is often conducted for matrix/precipitate systems, where the specimen preparation stage commonly adds to complications. Achieving very small thicknesses in such systems may lead to the fall-out of precipitates or to a non-uniform thickness across the interface, which makes signal deconvolution virtually impossible.
Figure 6.2. Electron beam broadening for a [222]MgO/Pd heterophase interface. Near the interface the beam broadening is asymmetric and requires a rigorous deconvolution procedure to obtain accurate interfacial chemistry.
The third and the most frequently encountered difficulty in the quantitative EDX study of a thin film is the determination of the k-factor (or Cliff-Lorimer factor). Within the so-called "thin film criterion," the specimen is considered to be infinitely thin, so that x-ray absorption within a specimen can be neglected. In many practical cases, however, errors introduced by this assumption can be significant. In reality, the k-factor is not a constant and is a function of a specimen's thickness. In addition, even for a very thin specimen, absorption does not only occur in the specimen, but also in contamination layers on a specimen's surface and on a detector's window [124]. It is, therefore, indispensable to measure accurately the thickness of the region from which the x-ray signal is collected. For a precise measurement of the specimen thickness the convergent beam electron diffraction (CBED) technique is typically used, since it yields a value that is accurate to ±2%. Without careful consideration of the above points the measurement of interfacial chemistry via EDX can yield erroneous results.

6.3 EXPERIMENTAL PROCEDURE

The [222]MgO/Pd specimens for this study were prepared by internal oxidation of a Pd-2.3 at.% Mg alloy. The alloy was fabricated from elements with a high initial purity by arc melting in an argon atmosphere. TEM specimens, 150 to 200 µm thick, were internally oxidized in air for 24 h at 1000°C and electropolished to produce electron-transparent thin areas. The detailed alloy
preparation, internal oxidation, and TEM specimen preparation procedures are provided in Appendices A and C.

For the compositional analysis of a \{222\}MgO/Pd heterophase interface by EDX, an Hitachi HF2000 analytical electron microscope was employed. The electron source of this 200 kV microscope is a cold field-emission type with an energy spread of 0.2 eV and a minimum probe diameter of 1 nm. The Link Analytical Pentafet EDX detector is separated from the TEM by an ultrathin window. The electropolished specimens were ion milled before insertion into the microscope to minimize the formation of a surface oxide. To reduce the hydrocarbon contamination, the specimen was flood illuminated for approximately 15 minutes with a spread electron beam at a magnification of $20 \times 10^3$ X, in order to prevent hydrocarbon migration induced by the local heating of the specimen by a highly convergent electron-beam. For accurate compositional analyses, the experimental requirements of EDX for interfacial studies, as discussed in the section 6.2, were carefully fulfilled.
6.4 RESULTS

Initially, a highly stochiometric MgO single crystal was studied to obtain the k-factor between Mg and O experimentally. Thin electron transparent areas were produced by crushing a \{100\}MgO single crystal in liquid nitrogen. A series of EDX spectra were obtained from the specimen as a function of specimen thickness. The latter was measured by the CBED technique and the contamination of the specimen was not serious while performing these experiments. Figure 6.3 displays a TEM micrograph of an MgO single crystal, where each labeled point (a, b, c, d, e, f, g, h, i, and j) corresponds to a different thickness. Figure 6.4 exhibits the variation of the k-factor as a function of specimen thickness for each of the labeled points in Figure 6.3. The k-factor varies by a factor of 2 for the thickness range 24 to 420 nm. This result indicates that the k-factor changes as a function of thickness of the sample and that an absorption correction is necessary. The k-factor, however, did not change significantly for a specimen thicknesses of less than 50 nm, demonstrating that it is within the thin-film criterion.
Figure 6.3. TEM micrograph of a highly stochiometric MgO single crystal. The specimen was obtained by cleavage at liquid nitrogen temperature to produce wedge-shaped thin areas. The thickness of the sample was measured at the points marked 'a' through 'j' employing the CBED technique.
Figure 6.4. Experimental variation of the k-factor as a function of specimen thickness for the MgO single crystal shown in Fig. 6.3. Error bars are ±3σ for the counting statistics. The k-factor does not change significantly for a specimen thickness of less than 50 nm.
Finally, a compositional analysis across a [222]MgO/Pd interface was performed. The probe diameter on the top surface of the specimen was approximately 5 nm. This value was determined by measuring the diameter of the area on the specimen damaged by the highly focused electron beam. It was also confirmed by the contamination spot method. This diameter (5 nm) is not at the ultimate capabilities of the microscope employed. A further decrease, however, in probe diameter would have lead to an unacceptably low image-intensity and a very poor x-ray signal from the weakly-scattering MgO phase. The specimen thickness near the interface was 38 nm and it was a constant across the interface. Figure 6.5 shows an octahedral-shaped MgO precipitate in a Pd matrix that is faceted on {222}-type planes. It was previously shown by TEM [48] that MgO precipitates produced in a Pd(Mg) alloy by internal oxidation exhibit a cube-on-cube orientation relationship with the Pd metal matrix. The specimen was oriented to a <110> direction parallel to the beam axis in order to place the heterophase interface plane edge-on. It has been previously demonstrated [48], and confirmed by TEM observations in the present study, that the [222]MgO/Pd interface obtained by internal oxidation is atomically or nearly atomically sharp. Therefore, the image of the specimen displayed in Figure 6.5 serves as an ideal test specimen [125] to examine the spatial resolution/analytical sensitivity relationship for an interface between two dissimilar materials.
Figure 6.5. A TEM micrograph of an octahedral-shaped MgO precipitate in a Pd matrix recorded employing a <110> zone axis. The \{222\}MgO/Pd interface appears very sharp from the micrograph. Points of high-resolution EDX analysis are indicated by circles (not to scale). The probe diameter is about 5 nm and the spacing between two spots near the interface is maintained at 4 nm.
For data processing, the value of $k_{\text{Mg/O}}$ was obtained from our experiments and $k_{\text{Mg/Pd}}$ and $k_{\text{O/Pd}}$ were calculated using the ratio method [119]. Figure 6.6 displays the composition profiles, thus obtained, across a \{222\}MgO/Pd heterophase interface. It is seen from this figure that the compositional profile is not sharp at this interface and is broader on the Pd-side than on the MgO-side; the 90%-width of the compositional profile is about 17 nm. This observation does not mean that this interface is actually chemically diffuse, but rather it reflects the fact that the incident beam diameter and beam broadening effect inside the thin foil strongly affect the results of a high-resolution EDX analysis. The broader profile for Pd is due to a stronger beam-broadening effect than for MgO, as was predicted by the Monte Carlo simulations. In the next two sections, the factors affecting spatial resolution of EDX analysis are analyzed to compare the experimental profile with the ultimate capabilities of the microscope for the system studied.
Figure 6.6. The composition profile across a $\{222\}$MgO/Pd interface obtained by EDX. The combination of probe diameter and beam broadening effects leads to the generation of an apparently chemically "diffuse" profile for an atomically or nearly atomically sharp interface.
6.5 SPATIAL RESOLUTION OF ENERGY DISPERSIVE X-RAY ANALYSIS

Based on Eq. 6.1, the two contributions to the spatial resolution of microanalysis – incident probe diameter and beam broadening effect – can be analyzed by considering relationships between probe diameter, probe current, specimen thickness, beam broadening effect, and counting statistics. An analytical model for calculation of the total x-ray generation from a thin sample has been discussed in references 119 and 125. The sample is in the form of a thin film, so x-ray absorption within the sample is neglected. Other simplifying assumptions are that x-ray fluorescence, backscattering, and electron-energy loss prior to ionization are negligible. In addition, the effects of diffraction and generation of fast secondary electrons are ignored.

The total number of x-rays produced per incident electron from an element i (i = Mg) in the MgO sample [125] is

\[ I_i = \frac{\omega_K P_{K\alpha} N_a \rho Q t C_i}{A}; \]  

(6.4)

where \( \omega_K \) is the K-fluorescence yield, \( P_{K\alpha} \) is the fraction of K-shell ionizations emitted as \( K\alpha \), \( N_a \) is Avogadro’s number, \( \rho \) is the density of MgO (3.58 g cm\(^{-3}\)), \( Q \) is the ionization cross-section, \( t \) is the specimen thickness, \( C_i \)
= 0.6 is the weight fraction of Mg in MgO, and \( A \) is the atomic weight of Mg (24 \( g \cdot mol^{-1} \)). The ionization cross-section is calculated [119, 125] from

\[
Q = 6.51 \times 10^{-20} \left[ \frac{n_s b_s \ln(c_s U)}{E_c^2 U} \right];
\]  

(6.5)

where \( n_s = 2 \) is the number of electrons in the K-shell, \( b_s \) and \( c_s \) are constants evaluated as 0.35 and 2.42, respectively [125], \( E_c = 1.253 \) is the ionization potential for the K-shell in keV [130], and \( U = E_0/E_c \) is the overvoltage \( (E_0 = 200 \text{ kV} \) is the incident electron beam energy). The value of \( Q \) calculated from Eq. 6.5 for the \( MgK_\alpha \) line and a 200 kV incident electron beam is \( 1.08 \times 10^{-21} \text{ cm}^2 \).

This number corresponds to a \( MgK_\alpha \) x-ray yield \( (I_i) \) of \( 4.8 \times 10^{-6} \) x-rays electron\(^{-1} \) for a 38 nm thick MgO specimen.

The total number of x-rays detected from a specimen is evaluated from

\[
N = I_i \cdot \left( \frac{i \tau}{e} \right) \cdot \left( \frac{A_{\text{det e}}}{4\pi R^2} \right) = \frac{\omega K P_{K\alpha} N_a \rho \rho Q \tau C_i i \tau A_{\text{det e}}}{4\pi R^2 e A};
\]  

(6.6)

where \( i \) is the specimen current, \( \tau \) is the exposure time, \( e \) is the charge on an electron, \( A_{\text{det e}} \) is the active area of the detector (0.3 cm\(^2 \)), \( e \) is the Si(Li) detector
efficiency [131] for the \( \text{MgK}_\alpha \) line (0.604), and \( R = 4 \text{ cm} \) is the specimen-to-detector distance. Therefore, for the values \( \omega_K = 0.0265 \) and \( P_{K\alpha} = 0.989 \) (reference [130]), and a typical collection time (\( \tau \)) of 100 sec, Eq. 6.6 becomes

\[
N = \text{const} \cdot i \cdot t = 8.56 \cdot 10^{17} \cdot i \cdot t ;
\]  (6.7)

where \( i \) is in amps and \( t \) is in cm. If the x-ray count is maintained at a statistically significant level of \( N_{\text{min}} = 1000 \) (which is equivalent to a relative random quantification error of 9.5% [125]), it results in the following inverse relation between \( i \) and \( t \)

\[
i = \frac{N_{\text{min}}}{8.56 \cdot 10^{17}} \cdot t^{-1} = 1.17 \cdot 10^{-15} \cdot t^{-1}
\]  (6.8)

or

\[
\ln(i[A]) = -34.4 - \ln(t[cm]).
\]  (6.9)

The total probe current is, in turn, related to the probe diameter. This relation was modeled in reference [126], and the results presented therein can be approximated for a typical field-emission source by
\[ \ln(d_{nm}) = 8.07 + 0.36\ln(i[A]). \]  

(6.10)

Combining Eq. 6.9 with Eq. 6.10 we finally obtain

\[ \ln(d_{nm}) = -4.34 - 0.36\ln(t\,[cm]) = 1.46 - 0.36\ln(t\,[nm]). \]  

(6.11)

A relationship between specimen thickness, \( t \), and beam broadening, \( b \), can be obtained from the results of the Monte Carlo simulations displayed in Table 6.1. A linear approximation to the \( \ln(b) \) vs. \( \ln(t) \) relationship via a least-squares method for an MgO film and a 200 kV electron beam yields,

\[ \ln(b_{nm}) = -5.18 + 1.51\ln(t\,[nm]). \]  

(6.12)
6.6 DISCUSSION: LIMITATIONS OF ENERGY-DISPERSIVE X-RAY SPECTROSCOPY FOR THE STUDIES OF INTERFACIAL CHEMISTRY

By combining Eqs. 6.11 and 6.12 with Eq. 6.1, the effect of specimen thickness on the spatial resolution can be examined. This relationship is presented in Figure 6.7. The spatial resolution, R, is indicated by solid lines and contributions from probe diameter and beam broadening are denoted by dashed lines. The relationship between specimen thickness, t, and electron beam broadening, b, follows the well-known $t^{3/2}$ power law for a single-scattering model (Eq. 6.3). On the other hand, the requirement to maintain the x-ray signal, N, at a constant value, leads to an inverse relationship between specimen thickness and probe diameter; that is, for a thinner specimen, a larger probe diameter must be utilized to produce the same x-ray count. Notably, the interplay of the two parameters in Eq. 6.1 leads to a lower limit on the spatial resolution, if the x-ray signal must be maintained at a statistically significant value.
Figure 6.7. Variation of probe diameter, $d$, beam broadening effect, $b$, and spatial resolution of EDX analysis, $R$, as a function of specimen thickness, $t$, for an MgO specimen. The amount of beam broadening is found from Monte Carlo simulations. The probe diameter is calculated based on the requirement of maintaining the x-ray signal from the specimen, $N$, at a constant value of 1,000 or 10,000 counts.
The highest calculated spatial resolutions in MgO obtained from the model outlined above are about 1.5 nm for an x-ray count of N = 1,000 and 2.5 nm for N = 10,000. Similar calculations were conducted for a thin palladium sample. The relationships between Pd specimen thickness, beam broadening, and initial beam diameter necessary to generate the Pd\(_{L\alpha}\) x-ray count of 1000 are

\[
\ln(d[nm]) = -4.67 - 0.36 \ln(t[cm]) = 1.13 - 0.36 \ln(t[nm]) \quad (6.13)
\]

and

\[
\ln(b[nm]) = -4.19 + 1.50 \ln(t[nm]). \quad (6.14)
\]

The width of a composition profile across an atomically sharp heterophase interface was calculated in reference [127]. The width of the profile, \(L\), is related to the spatial resolution, \(R\), as \(L = R / \sqrt{2}\). This relationship is derived assuming that the specimen thickness and the amount of beam broadening are the same on both sides of an interface. While the former condition is satisfied for the \{222\}MgO/Pd interface studied, the latter is obviously not correct. Nevertheless, we can approximate the resulting spatial resolution as \(L = (R_{\text{MgO}} + R_{\text{Pd}}) / 2\sqrt{2}\). This value is plotted in Fig. 6.8 as a function of specimen thickness, \(t\).
Figure 6.8. Approximate width, $L$, of the EDX composition profile across a [222]MgO/Pd interface as a combination of the spatial resolutions in the respective phases, $R_{\text{MgO}}$ and $R_{\text{Pd}}$. The contributions to spatial resolution from beam broadening, $b$, and the initial beam diameter, $d$, are displayed as dashed lines. The amount of beam broadening is found from Monte Carlo simulations. The probe diameter is calculated based on the requirement of maintaining the x-ray signal from the specimen, $N$, at a constant value of 10,000 counts.
Figure 6.8 illustrates an additional difficulty associated with the analysis of a heterophase interface between two materials with disparate Z-numbers. The optimal spatial resolution from each phase is achieved at different specimen thicknesses. If the thickness is kept constant across an interface, the resulting profile represents a compromise between the optimal conditions for the two phases. As a result, the best attainable width of the composition profile is about 1.8 nm for the minimum x-ray signal from the specimen, N = 10,000. The predicted value of L, however, for the specimen thickness of 38 nm employed in this study, is about 2.4 nm. Whereas the experimental profile across a \{222\}MgO/Pd interface shown in Figure 6.6 has a 17 nm 90%-width on the MgO side of the interface. The reasons for this discrepancy may be the simplifying assumptions mentioned above, as well as the ignored effects of incident beam convergence, microscope instabilities, and specimen drift. In particular, beam tailing (beam tailing is a degradation in spatial resolution manifested as long, low-concentration tails in the composition profile) in low-Z materials, such as MgO, is often observed due to fast secondary electron generation, while in high-Z materials, such as Pd, the multiple scattering effect becomes significant [127]. The general trend, however, is well-known: improvement in the spatial resolution of microanalysis invariably reduces the x-ray signal at the expense of analytical detectability limit [119, 125, 127]. The case of the \{222\}MgO/Pd system considered here is particularly unfavorable, because of a large difference in Z numbers between the two phases. The same effect, however, will affect EDX compositional analysis of any heterophase interface.
Recent improvements of dedicated STEMs have decreased the minimum attainable electron probe size to 0.13 nm [21]. It is unlikely, however, that the spatial resolution of EDX analysis in a STEM will approach this limit, since the problems of low x-ray detector efficiency and incident beam broadening are inherent in the method and cannot be fully overcome.

On the other hand, the EELS signal intensity usually far exceeds that of the EDX signal because of the high collection efficiency (20 to 50%) of an electron spectrometer, compared with about 1% for the EDX detector [128]. In addition, EDX suffers from a low (<2%) x-ray fluorescence yield for light elements (Z<11). Moreover, the spatial resolution of EELS analysis is higher than that of EDX, as discussed in Chapter 5. Therefore, the combination of strong signal levels, particularly for light elements, with improved spatial resolution, makes EELS a more favorable method for high-resolution compositional analysis of C/M interfaces. Obtaining quantitative compositional analysis from EELS data, however, remains a difficult problem.

Finally, the APFIM technique used in this work to characterize the [222]MgO/Cu(Ag) and [222]CdO/Ag(Au) interfaces, provides quantitative chemical analysis directly on an atomic scale. Determining the interface composition is straightforward and does not require any calibration or deconvolution of data. The lateral spatial resolution of APFIM analysis is determined by the diameter of the probe hole (selected-area aperture) and it can be less than 0.5 nm. On the other hand, the depth resolution of APFIM analysis is determined by the interplanar spacing of the material analyzed in the
direction of analysis and it can be 0.1 nm or less. Recent examples of the quantitative compositional analysis of C/M interfaces [15, 27, 28, 52] by APFIM illustrate the capabilities of the technique.
6.7 CONCLUSIONS

1. Light-element (small Z) quantitative analysis employing energy dispersive x-ray spectroscopy (EDX) has long been considered a difficult problem. The counting statistics of high-resolution EDX analysis imposes a strict limitation on the attainable spatial resolution of analysis because of a lower limit on the intensity of the detected x-ray signal. In the case of a low-Z phase, such as MgO, this limitation appears to dominate over the minimum achievable probe diameter.

2. Application of the EDX technique to a [222]MgO/Pd interface demonstrates that the measured compositional profile is not sharp at this interface and the profile on the Pd-side is broader than on the MgO-side; the 90%-width of the compositional profiles is about 17 nm. This observation does not mean that this interface is actually chemically diffuse, but rather it reflects the fact that the incident beam diameter and beam broadening effects inside the specimen strongly affect the results of a high-resolution EDX analysis. The broader profile for Pd is due to a stronger beam-broadening effect than for MgO, as is predicted by the Monte Carlo simulations.
CHAPTER 7

SUMMARY

Growing applications of ceramic/metal interfaces in both structural and electronic applications have motivated the recent interest in fundamental properties of such heterophase interfaces. While the atomic structure of atomically clean interfaces was studied in many systems by means of HREM, the chemistry and bonding of ceramic/metal interfaces and the atomic structure of segregated interfaces is less well studied.

This study was conducted to characterize the atomic-scale structure and chemistry of metal oxide/metal interfaces produced by internal oxidation of dilute binary and ternary metallic alloys. Binary alloys were internally oxidized to produce atomically clean interfaces. While ternary alloys were internally oxidized under conditions whereby only one of the two solute species was oxidized. The remaining solute species segregated to the ceramic precipitate/metal matrix interfaces.

Scanning transmission electron microscopy was used to determine the atomic structure and chemistry of the ceramic/metal interfaces. Electron energy loss spectroscopy and energy-dispersive X-ray spectroscopy were used to
determine the chemistry and nature of bonding at the interfaces. Atom-probe microscopy was used to measure quantitatively the chemical composition of the interfaces.

Four alloys were internally oxidized: Pd-2.3 at.% Mg, Cu-2.5 at.% Mg, Cu-2.5 at.% Mg-0.8 at.% Ag, and Ag-1.5 at.% Cd-1 at.% Au. MgO precipitates were formed in Pd, Cu and Cu(Ag) matrices and CdO precipitates were formed in a Ag(Au) matrix. In all cases, the precipitates were octahedral-shaped, bound by \{222\} planes, and maintained a cube-on-cube orientation relationship with the matrix.

The first quantitative measurements of solute segregation at C/M heterophase interfaces were performed for MgO/Cu(Ag) and CdO/Ag(Au) systems by atom-probe field-ion microscopy. It is shown that the data are readily analyzed to obtain the Gibbsian interfacial excess of solute. All the quantitative results were obtained without data deconvolution or external calibration standards.

After low-temperature annealing treatments, significant segregation levels were observed in both systems. Analysis of 15 \{222\}MgO/Cu(Ag) interfaces showed an average segregation level of \((4.0\pm1.9)\times10^{14}\) at cm\(^{-2}\) or 0.22\(\pm\)0.10 effective monolayers at 500°C. Analysis of three \{222\}CdO/Ag(Au) interfaces showed an average segregation level of \((3.0\pm1.0)\times10^{14}\) at cm\(^{-2}\) or 0.22\(\pm\)0.07 effective monolayers at 400°C. While \{222\}CdO/Ag(Au) interfaces in unannealed specimens exhibited no evidence of gold segregation.
A significant level of gold solubility (3 to 27 at.%) was observed in CdO/Ag(Au) system. Analysis of 14 precipitates 1.5 to 20 nm in size showed that this phenomenon cannot be explained by Gibbs-Thomson effect alone. It is proposed that the observed gold solid solubility in CdO is a combination of two effects: preferential precipitation of CdO on atomic-diameter Ag-Au clusters present in the initial Ag(Cd, Au) solid solution and the enhanced solid solubility of gold in CdO due to the Gibbs-Thomson effect.

The first dedicated STEM investigation of solute segregation at a ceramic/metal interface was conducted. It was found that {222}MgO/Cu(Ag) interfaces are generally flat, with some double and quadruple-height steps, particularly near the corners of a precipitate.

The dislocation structure of {222}MgO/Cu(Ag) interfaces was observed in a <110> projection. It was found that regions of good and bad fit are in agreement with those predicted by Bollmann’s geometric O-lattice theory. The observed spacing between dislocations is 1.45±0.19 nm, which is close to other experimental values in the literature for atomically clean {222}MgO/Cu interfaces. The clear visibility of the atomic columns along the interface, including the regions of bad fit, indicates that the dislocation lines are parallel to the electron beam direction, <110>. Therefore, it was concluded that {222}MgO/Cu(Ag) interfaces are semicoherent and contain a trigonal network of pure edge misfit dislocations. The dislocation lines are parallel to the <110> direction and have a Burgers vector (a/6)<211>.
Interfacial dislocations were also observed at atomic-height steps. In one case, a Shockley partial dislocation was detected at the corner of a precipitate, accommodating a rigid-body translation between two \{222\} facets. To preserve the lattice continuity in the metal matrix, a stacking fault is emitted into the metal matrix terminated by a similar Shockley partial dislocation.

The distance between the terminating Cu(Ag) plane on the metal side of the interface and the last magnesium plane on the MgO side of the interface was determined and its value is 0.268±0.018 nm. From the measurement of interface separation, it was demonstrated that the terminating layer of this polar interface is oxygen, and not magnesium. This is in agreement with our APFIM and EELS experimental results and LDFT calculations for atomically clean \{222\}MgO/Cu interfaces.

Under high-angle ADF imaging conditions, extra intensity was detected at the \{222\}MgO/Cu(Ag) interface. It was proposed that this indicates silver segregation at this interface, in agreement with our APFIM and EELS experimental results. On the metal side of the interface, extra intensity was observed in four to five atomic layers and estimates showed that it corresponds to a concentration of silver of approximately 20 at.\%, in agreement with our APFIM results. On the ceramic side of the interface, only the magnesium columns can be imaged in the HAADF mode. The last magnesium layer adjacent to the terminating oxygen layer, exhibits a 300% increase in intensity. At some \{222\}MgO/Cu(Ag) interfaces, this intensity also varied parallel to the interface with a periodicity close to that of the misfit dislocations. Due to the
small extent of these features, it was not possible in this case to prove or reject
the hypothesis that these regions of extra intensity correlate with the position of
interfacial dislocations. The presence of silver at \{222\}MgO/Cu(Ag) interfaces
was also detected by EELS employing a probe approximately 0.3 nm in
diameter.

Compositional sensitivity of the HAADF images in this work suffered
from signal delocalization, caused by the tails of the probe. Detailed image
simulations are necessary to evaluate this effect.

Interface chemistry was measured by EELS for the \{222\}MgO/Cu
interface produced by internal oxidation. This interface was found to be
atomically sharp and chemically abrupt and was terminated by oxygen, in
accordance with previous experimental data and band-structure calculations.
The 90\% width of the composition profile was 0.7 nm. The spatial resolution of
analysis is determined by the initial probe diameter and beam broadening inside
the specimen.

Electronic states characteristic of this interface were observed by placing a
stationary electron beam, 0.3 nm diameter, directly at the interface, or by
scanning the beam parallel to the atomically flat interface. The interfacial
electronic states were demonstrated to be highly sensitive to electron-beam
damage, which required a collection time of the spectra of 4 s or less.

The shape of the Cu-L_{2,3} edge observed at this interface indicated that the
d-band of copper is essentially full and the amount of charge transfer from
copper to MgO is small, that is, copper remains metallic at the interface. This is
consistent with the results of our band-structure calculations.

The pre-peak observed in the oxygen-K edge at the interface indicated that empty electronic states are introduced inside the band gap of MgO. It is believed that this pre-peak indicates a partial metallization of the terminating oxygen layer at the interface. This result is also consistent with band-structure calculations, predicting a collapse of the MgO bandgap near the interface.

The Mg-K edge at the interface showed no difference in fine structure. This is consistent with an O-terminated interface and implies that the disturbance of electronic states in MgO in the vicinity of the interface is confined to the terminating oxygen layer.

Application of the EDX technique to a \{222\}MgO/Pd interface demonstrated that the measured compositional profile is not sharp at this interface and the profile on the Pd-side is broader than on the MgO-side; the 90%-width of the compositional profiles was about 17 nm. This observation does not mean that this interface is actually chemically diffuse, but rather it reflects the fact that the incident beam diameter and beam broadening effect inside the specimen strongly affect the results of a high-resolution EDX analysis. The broader profile for Pd was due to a stronger beam-broadening effect than for MgO, as was predicted by the Monte Carlo simulations.

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APPENDIX A

ALLOY FABRICATION, INTERNAL OXIDATION AND
ANNEALING TREATMENTS

Alloys for this study were fabricated from elements with high initial purity. Cu(Mg) and Cu(Mg, Ag) alloys were prepared from 99.999 wt.% Cu, 99.99 wt.% Mg, and 99.9999 wt.% Ag purchased from Johnson Matthey Inc. First, master alloys with the compositions Cu-5 at.% Mg and Cu-5 at.% Mg-1.6 at.% Ag were prepared by arc melting in one atm of high-purity argon gas. The arc melter of Northwestern University’s Materials Research Center was used. The initial materials (0.5 to 2 mm size), total amount about 10 g, were placed in a copper hearth, in such a way that the Mg chips were covered by copper shot. This helped prevent excessive evaporation of Mg during melting. The base pressure in the melting chamber before backfilling with argon was <10^-4 Pa. The ingot, in the form of a button, approximately 20 mm diameter, was flipped 5-6 times and remelted to insure the homogeneity of the master alloy. The ingot was then sand-blasted to remove surface scale, cold rolled to <200 μm thick sheet, cut into 5mm×5mm chips, and remelted with the requisite amount of copper to produce the final nominal compositions: Cu-2.5 at.% Mg and Cu-2.5 at.% Mg-0.8 at.% Ag. At this stage, ingots of two different shapes were
produced: buttons approximately 20 mm diameter were prepared for subsequent cold rolling, while cylindrical ingots 6×6×25 mm³ were prepared for subsequent cold swaging and drawing. An identical arc melting procedure was used for both ingots.

A Pd(Mg) alloy was prepared from 99.999 wt.% Pd and 99.99 wt.% Mg purchased from Johnson Matthey Inc. First, a master alloy with the compositions Pd-4.6 at.% Mg was prepared by arc melting in one atm of high-purity argon gas. The arc melter of Northwestern University's Materials Research Center was used. The initial materials (0.5 to 2 mm size), total amount about 10 g, were placed in a copper hearth, in such a way that the Mg chips were covered by palladium chips. This helped prevent excessive evaporation of Mg during melting. The base pressure in the melting chamber before backfilling with argon was <10⁻⁴ Pa. The ingot, in the form of a button, approximately 20 mm diameter, was flipped 5-6 times and remelted to insure the homogeneity of the master alloy. The ingot was then sand-blasted to remove surface scale, cold rolled to <200 µm thick sheet, cut into 5mm×5mm chips, and remelted with the requisite amount of palladium to produce the final nominal composition: Pd-2.3 at.% Mg.

A Ag(Cd, Au) alloy was prepared from 99.9999 wt.% Ag, 99.9999 wt.% Cd and 99.9 wt.% Au, purchased from Johnson Matthey Inc. First, a master alloys with the composition Ag-7.5 at.% Cd was prepared by arc melting in 1 atm of high-purity argon gas. The base pressure in the melting chamber before
backfilling with argon was $<10^{-4}$ Pa. The ingot in the form of a button, approximately 20 mm diameter, was flipped 5-6 times and remelted to insure the homogeneity of the master alloy. The ingot was then sand-blasted to remove surface scale, cold rolled to $<500$ µm thick sheet, and cut into 2mm×2mm chips. These chips were placed in a graphite crucible with the requisite amount of silver and gold to produce the final nominal composition: Ag-1.5 at.% Cd-1.0 at.% Au. The crucible was placed in a 12/8 mm or 12/10 mm quartz tube, evacuated to a base pressure of $<1$ Pa, flushed four times with high-purity argon, backfilled with argon to approximately 0.5 atm, and then sealed. The melting was conducted in a resistance heated furnace at 1000°C for 0.5 h. The crucible was furnace-cooled to improve homogeneity of the ingot and to reduce thermal stresses.

From both Cu and Ag-based alloys, two types of specimens were prepared, disk and wire. From the Pd-based alloy, only disk specimens were prepared. Disk specimens for TEM, HREM, and STEM were prepared by cold-rolling the ingots to 150-200 µm thick foil and then punching out standard 3 mm diameter TEM disks from the foil. Wire specimens were prepared in two stages. First, the ingot was cold swaged to 1.6 mm (0.063”) diameter rod; the swagger in the Metallography Laboratory of the Materials Science and Engineering Department was used. For some of the alloys prepared, especially with higher solute concentration, an intermediate annealing was necessary to improve the alloy’s plasticity and to prevent its jamming in the swagger. In this case, after passing through 5 or 6 swaging dies the cylindrical ingot was sealed
in a quartz tube filled with argon and annealed. Cu-based alloys were annealed at 900°C for 2 h, while Ag-based alloys were annealed at 700°C for 2 h. Second, the swaged alloys were cold drawn into 200 μm diameter wires. No intermediate annealing was necessary at this stage. To pass the end of a wire through each succeeding die, the ends were filed or electropolished to a sharp point using standard wire polishing procedures (see Appendix B). To prevent wire from jamming in the dies a TFE release agent dry lubricant, manufactured by Miller-Stephenson Chemical Co., was used. Typically, an initial cylindrical ingot of approximately 10 g weight yields 6 to 10 m of 200 μm diameter wire and 10-40 standard 3 mm diameter TEM disks.

Copper-based disk and wire specimens were internally oxidized using the Rhines pack technique [11] in a mixture of Cu, Cu₂O and Al₂O₃ powders (1:1:1 vol.) at 950°C for 2 h. Al₂O₃ powder was added to the mixture to prevent it from sintering into a monolith, at the temperature of internal oxidation. Figure A.1 shows a schematic diagram of the Rhines pack. Since chemical equilibrium is established between Cu and Cu₂O, these conditions correspond to an oxygen partial pressure of 10⁻² Pa at 950°C [132]. To maximize the level of Ag segregation at MgO/Cu interfaces, the specimens were sealed in a quartz tube with high-purity argon and annealed at 500°C for 48 hr. During the annealing stage, a small amount of 99.9 wt.% pure Cu powder was added to the quartz tube to serve as an effective getter for any residual oxygen or water vapor.
Silver-based disk and wire specimens were placed in an open-ended quartz tube and internally oxidized in air at 650°C for 48 h. To maximize the level of Au segregation at CdO/Ag interfaces, some CdO/Ag(Au) specimens were sealed in a quartz tube with high-purity argon and annealed at 400°C for 24 h. Palladium-based disk specimens were placed in an open-ended quartz tube and internally oxidized in air at 1000°C for 24 h.
Figure A.1. Rhines pack technique used to internally oxidize Cu-based alloys.
Copper and silver-based wire specimens were electropolished for APFIM analysis to produce sharply pointed (<50 nm diameter) tips. The electrolyte composition for copper-based alloys was 30 wt.% sodium dichromate in glacial acetic acid, while the electrolyte for silver-based alloys was 2 vol.% perchloric acid in 2-buthoxyethanol (ethylene glycol monobutyl ether). During the first stage (beaker polishing), a horizontal stainless steel or platinum loop, 1 mm thick and 25 mm in diameter, was used as a cathode. A wire specimen was immersed to ≈10 mm depth in the electrolyte, and polished at stepwise decreasing voltages. For copper-based samples, polishing was continuous at 40, 25, and 10 V dc for about 60 s at each voltage. For silver-based specimens, the voltage had to be applied in short pulses (0.1 to 1 s long) to allow for dissolution of a black reaction product on the surface of a specimen. This can be done manually or using a pulse generator; voltages of 40, 25 and 15 V dc were subsequently used. The final sharpness of the specimen was such that the location of its end was indistinguishable with a naked eye. At the second stage (loop polishing) the cathode was a vertical 3 mm diameter platinum loop made
of 200 µm diameter wire. The loop was mounted under an optical microscope, such that its center was in focus. A droplet of electrolyte was placed on the loop; it was small enough to be retained on the loop by surface tension. The end of a tip (about 2 mm long) was immersed into the droplet at zero voltage. The voltage was turned on and a specimen was quickly withdrawn from the electrolyte. This "sweeping" action was repeated until the end of the tip was sufficiently thin. As a rule of thumb, a specimen was sharp enough for an APFIM experiment if its end was indistinguishable in the optical microscope at a magnification 200x. The voltages used for copper-based specimens at this stage were 10, 4 and 2 V dc, and for silver-based specimens 15 and 10 V dc, sequentially. After polishing, the specimens were rinsed in ethanol using one of two techniques. The first technique involved immersing the tip in a small beaker with ethanol and slowly stirring it for 30-60 s, repeated twice. The second technique involved pouring a small trickle of ethanol down a vertically held specimen, for 10-20 s, repeated twice. In both cases, any violent motion had to be avoided to prevent a tip from bending. A schematic diagram of the beaker and loop polishing procedures and specimen rinsing is shown in Fig. A2.
Figure A.2. A schematic of (a) beaker polishing, (b) loop polishing and (c) specimen rinsing procedures for APFIM.
Copper-based disk specimens for electron microscopy studies were prepared using electropolishing and a subsequent ion milling procedure. Electropolishing of TEM and STEM specimens was performed using a methanol-30 vol.% nitric acid electrolyte. A Tenupol 10 twin jet polishing unit was used under the following conditions: electrolyte temperature, -15 to -34°C; voltage, 12 V dc; current, 100 mA at -15°C, 200 mA at -34°C (current density 12 to 24 A cm²); average polishing time, 1 min at -15°C, 6 min at -34°C. Typically, flow rate settings of the Tenupol unit between 6 and 10 were used. Polishing should result in a uniform thinning towards the center of a disk with a hole at the center no larger than 0.2 mm diameter. Specimens were then rinsed in four subsequent solutions, at least 60 s in each one: methanol, ethanol 1, ethanol 2, and triply distilled water. While the first three treatments were aimed at removing the electrolyte from the surface, the last solution served to remove the washed out MgO precipitates that would have otherwise settled on the surface and introduced experimental artifacts. The high surface tension of water helped to remove the precipitates effectively. Finally, specimens were dried on filter paper for at least 60 s.
For conventional TEM studies, ion milling was performed using a Teddington Ion Tech unit under the following conditions: temperature, 20 °C; argon pressure, 4·10⁻³ Pa; angle with respect to a specimen's surface, 10°; voltage, 4 kV; current, 0.3 mA; and duration, 10 min.

For the dedicated STEM studies performed at ORNL, an E. A. Fischione Instruments Model 3000 argon gun mill was utilized under the following conditions: temperature, 20 °C; argon pressure, 4·10⁻² Pa; angle with respect to a specimen's surface, 12°; voltage, 1.5 kV; current, 3.0 mA; and duration, 10 min. Specimens were immediately placed into the preparation chamber of the microscope at a base pressure of <10⁻⁸ Pa and kept overnight to reduce their degassing rate. Prior to examination, areas of interest were flood illuminated with electrons at a magnification of (20–50)×10³ X, to prevent the buildup of surface contaminants under the highly focused electron beam, by reducing the mobility of surface hydrocarbons.

For the dedicated STEM studies performed at Cornell University, a BAL-TEC RES010 ion milling unit was used under the following conditions: temperature, 293 K; argon pressure, 8·10⁻³ Pa; angle with respect to a specimen's surface, 15°; voltage, 1.5 kV; current, 3.0 mA; and duration, 10 min. Specimens were immediately placed in the preparation chamber of the microscope (vacuum 3×10⁻⁷ Pa) and annealed at 423 K for 2 h to reduce surface contamination levels. Prior to examination, areas of interest were flood
illuminated with electrons at a magnification of \((2-5)\times10^3\) X, to prevent the buildup of surface contaminants under the highly focused electron beam, by reducing the mobility of surface hydrocarbons.

Palladium-based disk specimens for analytical electron microscopy studies were prepared using electropolishing and a subsequent ion milling procedure. Electropolishing of TEM specimens was performed using an acetic acid-25 vol.% perchloric acid electrolyte. A Tenupol 10 twin jet polishing unit was used under the following conditions: electrolyte temperature, 20°C; voltage, 30 V dc; average polishing time, 10 min.

Ion milling of palladium-based specimens was performed using a Teddington Ion Tech unit under the following conditions: temperature, 20 °C; argon pressure, \(4\times10^{-3}\) Pa; angle with respect to a specimen's surface, 15°; voltage, 4 kV; current, 0.5 mA; and duration, 15 min.