

# ATOMIC AND ELECTRONIC STRUCTURE AND CHEMISTRY OF CERAMIC/METAL INTERFACES

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## I. PROGRESS REPORT (ACCOMPLISHMENTS)

Materials containing ceramic and metal phases play a significant role in modern materials technology. Examples include dispersion hardened alloys, metal-matrix fiber-reinforced composite materials, metal-ceramic fiber-reinforced composite materials, metal-ceramic welding, oxide films and coatings on surfaces of high-temperature alloys, and microelectronic packaging. Ceramic/metal heterophase interfaces often determine macroscopic mechanical, physical, chemical or electronic properties of these materials. In structural materials, the interface must either sustain mechanical forces without failure or exhibit controlled debonding. It is widely recognized that to design and control macroscopic materials properties successfully, a fundamental understanding of the atomic-scale structure, chemical composition, and electronic structure of ceramic/metal interfaces is necessary. From a scientific standpoint, ceramic/metal interfaces represent an extreme example—of two disparate materials: an itinerant-electron conductor and a localized electron insulator<sup>1</sup>. While the theories of metal and ceramic homophase interfaces (grain boundaries) are reasonably well developed, heterophase ceramic/metal interfaces are a relatively less well-studied subject. As a result of their critical technological importance and strong fundamental interest, ceramic/metal interfaces have received a great deal of attention recently.<sup>1,2,3,4,5</sup>

### A. Experimental Results

#### 1. *Three-dimensional atom-probe microscopy as an instrument for studying ceramic/metal interfaces*

We are employing a three-dimensional atom-probe (3DAP) microscope<sup>6,7,8</sup> to study the chemical compositions of ceramic/metal interfaces on a subnanoscale, an application that exploits the unique capabilities of this instrument.<sup>9,10,11,12,13,14,15,16,17,18</sup> Before presenting our recent results, we review briefly the principles of the 3DAP microscope, which may be unfamiliar to some readers. Our instrument is the only one operated by a university-based group in the U.S.

A 3DAP microscope consists of a field-ion microscope (FIM)<sup>19</sup> that is equipped with a position-sensitive detector, as well as a special time-of-flight (TOF) mass spectrometer, which employs a reflectron lens<sup>20</sup> to obtain high mass ( $m$ ) resolution,  $m/\Delta m$ <sup>21</sup> (500 at full-width half-maximum and 250 at full-width one-tenth maximum). The location on the FIM-tip surface from which an ion is field-evaporated is inferred from the position-sensitive detection of the ion using a channel electron multiplier array (CEMA), with a gain of ca.  $10^7$  for a single ion, and its mass-to-charge state ratio ( $m/n$ ) is in turn obtained by measuring TOF values. The  $10^7$  electrons produced per incident ion are converted to light by proximity focusing the electrons created by the MCP onto a fast phosphor screen, which produces a light blip for each detected ion. Subsequently the position of the light blip on the two-dimensional phosphor screen is detected employing a specially fabricated optical detection system that correlates the position of each detected ion on the phosphor screen with its TOF; the latter yields the  $m/n$  ratio of each field-evaporated ion and therefore its chemical identity. Information concerning the third dimension is

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<sup>1</sup> We note, however, that some ceramic compounds are metallic.

obtained by dissecting an FIM tip, atom-by-atom and atomic plane-by-plane, employing the physical phenomenon of field evaporation, which permits us to investigate on a subnanoscale the bulk of a specimen. In practice we use a pulse generator operating at 1500 Hz to perform so-called pulse field-evaporation and the detection rate of ions may be in excess of  $10^5$  ions  $\text{hr}^{-1}$  using our 3DAP microscope. The position coordinates and  $m/n$  ratios of each detected ion are then plotted in 3D space to generate a three-dimensional reconstruction of the lattice that has been carefully dissected on an atom-by-atom basis. The depth resolution of a 3DAP microscope is equal to the  $\{hkl\}$  interplanar spacing along the direction being analyzed, which implies subnanometer values. The lateral resolution within a crystallographic  $\{hkl\}$  plane is ca. 0.3 to 0.5 nm, which is physically limited by trajectory effects,<sup>22</sup> while the depth resolution is not affected by trajectory effects. Figure 1 is a schematic diagram of a 3DAP microscope that indicates its essential components, without displaying the optical detection system and the reflectron lens. Figure 2 is a sample mass spectrum of a TiAl alloy containing C, Mn, Cr, W, Hf, Nb, Zr, etc., which demonstrates our ability to distinguish the isotopes of these elements from one and the high mass resolution ( $m/\Delta m$ ) of our instrument.

Additionally, we have expended five plus person years in developing a software program, titled *ADAM*, for analyzing the experimental data obtained employing our 3DAP microscope, as just described, in a highly quantitative manner.<sup>23,24,25,26</sup> Dr. Olof Hellman is currently improving *ADAM*, as a consultant to this grant, to handle the ever larger data sets we are accumulating employing our 3DAP microscope. Most recently we have using the new LEAP<sup>2</sup> (local-electrode atom-probe) microscope at Imago Scientific Instruments, Madison, Wisconsin, which can collect data at a rate that is 300 times faster than our instrument.<sup>3</sup>

## 2. *Systematic studies of solute segregation at ceramic/metal interfaces*

Employing 3DAP microscopy, we have systematically studied the segregation of different solutes at various ceramic/metal interfaces, to search for a general rule(s) that govern solute segregation. The ceramic/metal interfaces were prepared by internally oxidizing binary or ternary metallic alloys, with one of the two solutes internally oxidized to obtain a high number density of nanoscale metal oxide precipitates, thereby yielding atomically clean ceramic/metal interfaces. The unoxidized ternary solute is made to segregate at the ceramic/matrix interfaces by decreasing the temperature of a specimen to create a significant chemical driving force for interfacial solute segregation.

The experimentally measured segregation results are summarized in Table 1, along with the properties of the segregants (the atomic volume differences between the metallic solvent and solute atoms and the associated elastic strain) and the interface (lattice misfit parameter) to which segregation occurs. It is noted that the large lattice parameter mismatch values ( $>14.8\%$ ) for the studied interfaces imply high interfacial dislocation densities, and a high density of atomic sites

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<sup>2</sup> The LEAP microscope is a 3DAP microscope that has a local electrodes that has a high-voltage pulser with a pulse frequency of  $2 \times 10^5$  Hz and can collect over 25 million atoms per hour. This is a truly revolutionary instrument as it makes the collection of statistically significant data very easy and shifts the problem to being able to analyze enormously large data sets.

<sup>3</sup> During a visit to Imago Scientific Instruments in January Stephan Gerstl (Ph.D. student on this grant) obtained a data set from a TiAl specimen.

in the vicinity of interfacial misfit dislocations are available for segregation. The quantitative measure of segregant at these heterophase interfaces is given by either the relative Gibbsian interfacial excess<sup>27,28,29,30</sup> in  $\text{nm}^{-2}$  or the number of effective monolayers.<sup>4</sup> The classical thermodynamic measure of segregation, the Gibbsian interfacial excess, has not been measurable for solid-solid interfaces at the nanoscale by alternative techniques. The total elastic strain energy per atom was calculated for the case where the solute and solvent atoms have different elastic moduli.<sup>31</sup> The results in Table 1 do not reveal a correlation of the level of segregation with elastic strain energy. For example, for Au in Ag the elastic strain energy is only  $0.11 \text{ meV atom}^{-1}$ , whereas the Gibbsian interfacial excess is  $1.65 \text{ nm}^{-2}$ , and conversely for Sb in Ag, where the elastic strain energy is  $1.2 \text{ eV atom}^{-1}$ , the Gibbsian interfacial excess is  $0.038 \text{ nm}^{-2}$ . Thus, the release of the elastic strain energy associated with the solute atom cannot be the dominant driving force for segregation.<sup>5</sup>

The results in Table 1 therefore suggest that the electronic contribution to the driving force plays a significant role. It was suggested many years ago that there is also an electronic contribution to the driving force for segregation,<sup>32</sup> but it wasn't possible to calculate it realistically at that time. Recently, however, segregation of Mg (Mg is oversized by ca. 40% by volume with respect to Al) at coherent  $\alpha\text{-Al}/\text{Al}_3\text{Sc}$  heterophase interfaces has been measured employing 3DAP microscopy and a value of  $1.92 \text{ nm}^{-2}$  was determined, which is independent of aging time at  $300^\circ\text{C}$ .<sup>33</sup> Marquis et al.<sup>34</sup> demonstrate that the electronic contribution to the driving force for segregation of Mg constitutes ca. 90% of the total driving force for this situation, with the remainder being elastic strain energy. From these results we conclude that the Wynblatt-Ku equation for the driving force for surface segregation,<sup>35</sup> which does not include an electronic contribution, and therefore does not have predictive value for this problem, even though it may work in individual cases. Thus, it is our opinion that to understand fully the driving force for segregation at a ceramic/metal interface, and for interfacial systems in general, for example, first-principles density-functional theoretical approach is required.

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<sup>4</sup> The preferred metric for quantifying the level of segregation is the relative Gibbsian interfacial excess, as it is a true thermodynamic quantity for specifying the amount of segregant at a heterophase interface, whereas effective monolayers is not. We list the latter quantity simply because of its widespread use among surface scientists and some materials scientists, but its use for internal interfaces is to be discouraged.

<sup>5</sup> The classical linear elasticity expression for elastic strain energy yields the same value whether the solute atom is oversized or undersized with respect to the solvent atom.

**Table 1:** Values of the total elastic energy strain energy that may be dissipated at a ceramic/metal interface arising from the difference in atomic volumes between the solute and the solvent atoms (in this case, the segregating species and the metal matrix, respectively) and the corresponding value of the relative Gibbsian interfacial excess, as measured by 3DAP microscopy.

Ceramic/metal interface, solute, and segregation aging temperature	Atomic volume difference <sup>36</sup>	Elastic strain energy (eV atom <sup>-1</sup> )	Gibbsian interfacial excess of solute (nm <sup>-2</sup> )	Gibbsian interfacial excess (effective monolayers)*	Lattice parameter mismatch**
MgO/Cu(Sb) at 500°C	Sb in Cu 92%	6.1	2.9	0.17	15%
MnO/Ag(Sb) at 550°C	Sb in Ag 45%	1.2	0.038	0.0027	20.2%
MgO/Cu(Ag) at 500°C	Ag in Cu 44%	0.47	0.32	0.018	15%
CdO/Ag(Au) at 650°C	Au in Ag -2%	1.1x10 <sup>-4</sup>	1.65	0.12	14.8%

\*Effective monolayers are calculated relative to the atomic density of the {111} planes of the metal matrix. This is an approximation, as the experimental value for the Gibbsian interfacial excess represents an average over several different planar orientations because the proximity histogram integrates over all orientations that the precipitate makes with the matrix.

\*\*The lattice parameter mismatch is given by  $2|a_{\text{ceramic}} - a_{\text{metal}}|/(a_{\text{ceramic}} + a_{\text{metal}})$ . The larger is the lattice parameter mismatch the higher is the interfacial dislocation density.

### 3. *Nanoscale temporal evolution of a metal oxide phase*

Employing 3DAP microscopy we have been able for the first time, to ascertain the temporal evolution of internal oxidation on a subnanometer scale, and thereby to test the classical and widely accepted deterministic model of internal oxidation developed by Carl Wagner in 1959.<sup>37</sup> The Wagner model is based on the assumption that a metal oxide nucleates with its ideal thermodynamic stoichiometry, and the nucleus grows at a diffusion-limited rate governed by the oxygen diffusivity in a specific metal alloy.

The internal oxidation of a Ag(Mn) alloy is presented in Figure 3, as obtained from 3DAP microscopy analyses, followed by the introduction of the segregant Sb from the vapor phase, prior to the final segregation anneal. Figure 4 is a compilation of proximity histograms recorded as the MnO/Ag(Sb) specimens underwent successive heat treatments. For the sake of clarity, only the Ag and Mn curves are displayed. The origin of this figure is at the MnO/Ag heterophase interface and negative distances are into the MnO precipitate and positive distances are into the Ag matrix. Firstly, note that the concentration of Mn inside of the MnO precipitates increases with increasing time and that immediately after the Ag(Mn) alloy is internally oxidized the concentration of Mn inside the precipitates is only ca. 30 at.%. Furthermore, note that the Mn concentration continuously increases with aging time when the Sb is introduced from the vapor phase, and increases further during the segregation anneal, which is used to promote segregation of Sb to the MnO/Ag interface, to a value approaching 60 at.% Mn. Concomitantly

the concentration of Ag within the MnO precipitates decreases to less than 2 at.%. An interpretation of the observed systematic decrease in Ag within the MnO precipitates is that the specimens are in different stages of metal oxide precipitate formation. During these stages, the temporal evolution of MnO precipitates involves the continuous, but slow, rejection of substitutional Ag from their volumes. Although the MnO precipitates show a stoichiometry of ca. 1:1 (Mn:O) during growth, a considerable remnant Ag concentration remains within the precipitates until the Sb segregation anneal, when the Ag concentration subsequently decreases to <5 at.%. This behavior is a consequence of the rapid interstitial diffusion of oxygen, which contrasts with the slow diffusion of substitutional Ag during the internal oxidation. Thus, paraequilibrium conditions prevail, with the kinetics controlled by the fastest moving species.<sup>38,39,40</sup> Specifically, at the temperature of internal oxidation, 900°C, the ratio of the oxygen diffusivity in silver to the silver self-diffusion coefficient is ca. 14,000.<sup>41</sup> Under these conditions, where the diffusivity of the substitutionally diffusing silver is negligible compared to that of the interstitially diffusing oxygen, paraequilibrium conditions obtain.<sup>42</sup> Under paraequilibrium conditions, the growing phase, MnO, inherits the substitutionally diffusing Ag.

Furthermore, with increasing annealing time orthoequilibrium conditions become prevalent and the MnO precipitates reject the inherited Ag atoms. Under these conditions, a low interface velocity is maintained for the growing phase, MnO, and equilibrium among the different elements is established across the interface. The experimentally observed transition from paraequilibrium to orthoequilibrium conditions during the nanoscale evolution of the MnO precipitates is an important result because it provides an atomistic explanation for the evolution of metal oxide precipitates produced by internal oxidation that is radically different from the classical and deterministic physical picture envisaged by Carl Wagner.<sup>37</sup> Specifically, our results demonstrate that one can obtain a nearly stoichiometric oxide precipitate, MnO, at the internal oxidation temperature, without the rejection of all the Ag matrix atoms from the region where it forms. This research demonstrates the power of the 3DAP microscope for following the temporal evolution of the chemistry of a physical process on a subnanoscale.

### 3. *Preparation of {222}MgO/Cu heterophase interfaces for a study of segregation of Ag or Sb at these interfaces*

### 4. **TiAl interfaces and TiAl/TiAl<sub>x</sub> interfaces**

**a. Preparation of specimens:** A critical part of our research program is the preparation of specimens that can be characterized by both 3DAP microscopy and HREM. This requires the fabrication of specimens with a high number density of carbide, boride, oxide or nitride precipitates with a mean diameter that is smaller than the radius of a field-ion microscope (FIM) tip, i.e., less than 50 nm maximum. Toward this end we have utilized specimens from three outside sources as well as processing our own specimens. Details concerning the acquired and fabricated specimens follow:



**i. TiAl specimens from GKSS Materials Research Center, Geesthacht, Germany**

A TiAl alloy was provided by Dr. Fritz Appel (GKSS Materials Research Center, Geesthacht, Germany) whose composition is Ti-45 Al-8 Nb-0.2 C-0.1 B at.%<sup>6</sup>). This alloy was extruded to a 6:1 ratio at 1250°C, heat-treated for 2 hours at 1030°C, for 0.5 h at 1330°C, and finally air cooled to room temperature. The processing of this alloy creates fine lamellae, 20-150 nm wide. In this alloy we are able to analyze chemically, employing 3DAP microscopy, a 7 nm wide titanium boride precipitate in the  $\gamma$ -phase matrix. Titanium aluminum carbides were, however, detected between the micron-sized lamellar grains and not at the  $\alpha_2/\gamma$  heterophase interfaces. Thus, this specimen did not enable us to fulfill our objective of chemically analyzing TiAl carbides between lamellae, which are thought to be critical for high-temperature strengthening. Dr. Appel also provided a TiAl alloy with  $\approx$  4 at. % carbon, which contained coarse  $\text{Ti}_2\text{AlC}$  precipitates, with hexagonal structure (H-type). The smallest H-type precipitates are, however, 200 nm in diameter, which is too large for 3DAP microscopy. Thus, neither of the alloys supplied by Dr. Appel is suitable for 3DAP microscopy although HREM observations were performed on them.

**ii. Multicomponent TiAl alloys from UES Inc., Dayton, Ohio**

Dr. Young-Won Kim (UES Inc., Dayton, OH) provided us with multi-component TiAl alloys with compositions: Ti-46.5 Al-3 Nb-1.5 Cr-0.5 Mn-1.2 (with W, Hf, Zr, B, C, O and Ti-45.9 Al-1.5 Cr-3.1 Nb-0.3 W-0.4 C - 0.2 (with B, O at concentrations. These alloys contain carbide, silicide, and boride precipitates, which are located primarily at triple junctions. We obtained detailed composition profiles of all the elements in these alloys with respect to the  $\alpha_2/\gamma$  lamellar interfaces, which reveal partitioning of Cr, Mn, C, and O to the  $\alpha_2$ -phase and Nb and Zr to the  $\gamma$ -phase. Due, however, to their duplex microstructures, containing both lamellar and equiaxed  $\gamma$  grains, and the absence of ceramic precipitates less than 50 nm in diameter, these specimens were unsuitable for ceramic/metal interface characterization by 3DAP microscopy.

**iii. Alloy K5SC from UES Inc., Dayton, Ohio and Ohio State University**

Professor Michael Mills (Ohio State University) provided us with alloy K5SC which was also prepared by Dr. Kim. K5SC has a fully lamellar structure with carbide and silicide precipitates introduced for creep strengthening above 800°C. This alloy contains a relatively high linear number density of  $0.013\text{nm}^{-1}$  of carbide precipitates (?). Although this density is still borderline for 3DAP analysis of carbide precipitates, Alloy K5SC is an excellent candidate, for analyses employing the LEAP (the local electrode atom probe) microscope (Imago Scientific in Madison, Wisconsin), whose data acquisition is two orders of magnitude faster.

**iv. Alloy processing at Northwestern University**

Specimens were synthesized in-house by an arc-melting procedure with starting materials Ti, Al, TiC, and a quaternary addition X, where X = W or Cr to obtain carbide precipitates in a

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<sup>6</sup> All alloy compositions in this proposal are in atomic percent.

single-phase  $\gamma$ -matrix TiAl alloy. This is followed by homogenization at 1200°C for seven days, and then quenching into an ice brine solution. This results in a carbon supersaturation. Next the specimens are subjected to a 24 hour anneal at 800°C, which results in a homogenous distribution of  $\text{Ti}_3\text{AlC}$  precipitates, with perovskite structure (P-type), at a number density of approximately  $7 \times 10^{17} \text{ cm}^{-3}$ , and inter-precipitate separations of the order of 10 nm. This procedure thus yields P-type carbide(X)/ $\gamma$ -matrix ceramic/metal heterophase interfaces that are analyzable by 3DAP microscopy.

## C. Simulation

In the simulation component of this project, our attention is restricted to chemically sharp ceramic/metal interfaces, to which our experimental HREM and 3DAP microscope studies were also directed. The atomic structure of such interfaces is influenced by a variety of factors, the most obvious of which are (i) the crystal structures of the respective phases and (ii) the lattice parameter misfit that corresponds to the interface orientation under consideration. Also critical are the interatomic interactions of each of the phases at the interface, in the bulk as well as at the interface, which determine the relaxation and the local bonding at the interface. Temperature dependence, thermodynamic and kinetic properties, and impurity segregation may also play crucial roles. Furthermore, electronic structure is important for electronic and functional material applications. Not all of these factors can, of course, be handled simultaneously with presently available simulation tools, even with the help of modern high-performance computers, and therefore careful discretion must be exercised in the selection of methods and the interfaces to which they are applied.

### 1. Simulation Methodology

Since the simulations performed in this project are intended to complement atomic-scale experimental observations of interfaces, we have restricted our consideration to atomistic methods. In view of the importance of interface lattice misfit for interface structure and properties, we have sought methods in which the interface lattice misfit can be accounted for as directly as possible. Three different simulation approaches have been developed and applied to particular interfaces. The interfaces on which results are presented below are the oxide-metal interfaces MgO/Cu, and  $\text{Al}_2\text{O}_3/\text{Nb}$ , and the carbide-intermetallic compound interface  $\text{Ti}_x\text{AlC}/\gamma\text{-TiAl}$ , with  $x = 2$  and 3. Before summarizing the results of these simulations, the motivation and general features of the three selected calculational approaches are outlined. Few atomic-scale simulations of ceramic-metal interfaces that go beyond the coherent-interface approximation have previously been attempted,<sup>43,44</sup> and the approaches employed here were all developed in work performed for this grant. They are described in more detail in a recent review article.<sup>45</sup>

#### a. Classical molecular dynamics simulation with environmentally dependent potentials:

Treatments that involve classical-potential representations of the potential energy, for example, by molecular dynamics or molecular statics, enable the simulation of interface systems with large numbers of atoms (at least of order  $10^6$  atoms) on modern parallel computers, and also enable non-zero temperatures and dynamical behavior to be simulated. The numerical efficiency of such methods is prerequisite to the proper simulation of misfit dislocation networks in typical interface systems, which often require million-atom, or even larger, computational cells.<sup>46</sup>

To ensure that the simulations are realistic, however, the physical accuracy of the employed potentials, as well as numerical efficiency, must be established. To be widely applicable, the mathematical formulation of a classical interatomic potential should ideally possess sufficient variational freedom to be able to incorporate all of the standard types of bonding, i.e., ionic, metallic, covalent and dispersion forces, as well as tractability and computationally efficiency. Oxide-metal interface systems, for example, may exhibit all of these bonding types in the vicinity of the interface. No potential scheme with all these capabilities has yet been developed, however, and compromises are necessary in practice. Metallic and covalent interactions are amenable to treatment within a unified framework (for example, the modified embedded atom method<sup>47</sup> (MEAM) or bond-order potential<sup>48</sup> (BOP) methods. The treatment of environmentally dependent electrostatic forces<sup>49</sup> requires a separate formulation, which up to now has not been combined in a self-consistent manner with either the MEAM or BOP approaches. Furthermore, dispersion forces<sup>50</sup> also require special treatment, in principle, but have received relatively little attention.

An additional complication is that typical ceramic-metal interfaces, such as those mentioned above, have at least three different atomic species (e.g., oxygen and two metallic species). Unfortunately, even the MEAM and OBOP have rarely been implemented for ternary systems, even when all components are metallic. Against this background, it seemed worthwhile to explore the development of a potential for a ternary system and apply it to a model ceramic/metal interface. Our selection of the  $\text{Al}_2\text{O}_3/\text{Nb}$  interface was dictated by the availability of first-principles calculations with which to compare our results, as well as extensive experimental data for this system.

The MEAM parameterization is a mathematically and computationally concise approach, and is highly effective in describing metallic and reasonably effective in describing covalent bonding. Since ionic charges are not explicitly included in the formulation, the applicability of MEAM to oxides is not guaranteed. Nevertheless, experience on the Al/alumina system appeared to be sufficiently encouraging to warrant application of the MEAM to Nb-alumina interfaces. Results of this application are described below, in Section 2.b.

***b. First principles density functional calculations for heterophase interfaces with large misfit:*** As mentioned above, typical interface systems, with misfit parameters of the order of a few percent, require consideration of large computational cells. For such systems, the calculation of interface properties with first-principles (electronic structure) methods is prohibitive. If misfit is defined as  $\epsilon_m = (a_1 - a_2) / a_2$ , where  $a_1$  and  $a_2$  are lattice parameters parallel to the interface of the two phases, the inverse misfit,  $n_m = 1/\epsilon_m$ , is a convenient measure of cell size. The nearest integer to  $n_m$  is proportional to the cell size, or the spacing of misfit dislocations, of an interface that is the closest periodic approximant to the true heterophase interface, which is likely not precisely periodic. The assumption of two-dimensionally periodicity is nevertheless in most instances an excellent approximation.

The smallest values of the inverse misfit observed for real heterophase interfaces are of order  $n_m = 5$  or 6. For such minimal values, the periodic-unit-cell size, when only a relatively small number of atomic layers on either side of the interface are considered, may include of the

order of a few hundred atoms. Although this is still a formidably large cell size for electronic structure calculations, its treatment is feasible in some cases, with modern high-performance computers. Using plane-wave pseudopotential methods, calculations were performed<sup>51</sup> for the {222}MgO-Cu interface, for which  $n_m = 7$ . The calculations employed cells as large as 497 atoms, with 3.5 MgO layers and 5 Cu layers. Unlike simulations with classical potentials, the first-principles calculations are restricted to static interfaces at zero temperature. Such calculations, however, are of high accuracy, and electronic-structure information is also provided.

***c. First principles density functional calculations for general heterophase interfaces:***

Except for interfaces with the smallest values of  $n_m$ , first-principles calculations cannot be applied directly to misfitting interfaces. Since small values of  $n_m$  are the exception, as mentioned above, it is desirable to develop methods that enable the treatment of more general interfaces (with relatively small misfit), while still exploiting the accuracy of first-principles methods. These considerations motivate a formulation in which the interface energy is expressed as

$$\gamma = \gamma_{\text{coh}} + \Delta\gamma,$$

where  $\gamma_{\text{coh}}$  is the interface energy for the coherent interface and  $\Delta\gamma$  is a correction. For most chemically sharp interfaces, the coherent-interface energy can be readily calculated with first-principles methods by employing a relatively small unit cell.<sup>52</sup> The correction  $\Delta\gamma$  includes three parts, the coherent strain energy,  $\Delta\gamma_{\text{strain}}$ , the local relaxation at the interface,  $\Delta\gamma_{\text{relax}}$ , and a stoichiometric correction,  $\Delta\gamma_{\text{stoic}}$ . The strain term  $\Delta\gamma_{\text{strain}}$  involves the energy of a uniform strain, and is relatively straightforward to calculate. The local relaxation and interface bonding term is the most challenging, because it requires, in principle, the relaxation for a structure with a large periodic spacing in the interface plane. We approximate this term as an average over properties of coherent interfaces (such as that employed to calculate  $\gamma_{\text{coh}}$ ) with different parallel translation states. The correction can then be calculated with a small unit cell. The stoichiometric correction  $\Delta\gamma_{\text{stoic}}$  accounts for the fact that the interface stoichiometry of the coherent and the incoherent (or semicoherent) interfaces are different. For the interfaces to which we have applied this formulation,  $\Delta\gamma_{\text{stoic}}$  is numerically small, and is therefore neglected.

## **2. Applications**

***a. {0001}Al<sub>2</sub>O<sub>3</sub>/Nb<sup>53</sup>:*** As mentioned, the selection of this interface to test the accuracy of the MEAM treatment was motivated by the availability of extensive results of first-principles calculations from previous work. Both experimental data and results of first principles calculations were employed in the data base for fitting the MEAM potential. The fitting data, however, refer only to pure systems and binaries, but not to results for the interface itself, so that interface simulations with the MEAM potential represent new predictions. The MEAM potentials for the Al-O-Nb system were applied to the three possible interface terminations of alumina, namely the oxygen termination, and the single and double Al layer terminations. Cleavage energies and interlayer spacings were obtained. These results were compared with two first principles calculations.<sup>54</sup> The agreement was encouraging.

In the above calculations, only coherent interfaces were treated, and misfit was neglected. To facilitate the parametrization, previous work on the binary Al-O system was adopted without modification. Since the alumina lattice constants of this previous parametrization are slightly different from experiment, the lattice constant misfit for the  $\{0001\}\text{Al}_2\text{O}_3\text{-Nb}$  interface that is incorporated into our ternary MEAM potential does not coincide with the experimental one. As a result, the simulation of the  $\{0001\}\text{Al}_2\text{O}_3\text{-Nb}$  interface, and other interface orientations, will require an adjusted potential. Some further discussion on this point is given in the proposed new work section.

**b.  $\{222\}\text{MgO/Cu}$ <sup>55,56</sup>:** The inverse misfit for this interface,  $n_m = 7$ , is small enough to allow treatment at the first-principles level (local density approximation; gradient corrections, however, were not employed). The calculations were performed with the FEMD code<sup>57</sup>, with optimized pseudopotentials that enabled employment of a relatively small cutoff energy (47 Ry). An alternative possibility is the VASP code<sup>58</sup>, which is slightly more efficient, and is being used in new applications. In addition to the large cell (up to 497 atoms) calculations, which were performed to determine the structure of the relaxed misfitting interface, with its trigonal misfit dislocation network, small-cell calculations of the coherent interface were performed to elucidate how the interface electronic structure varies with the parallel translation state.

All of the completed results correspond to the oxygen termination; relaxation of the Mg-terminated interface are not yet converged.<sup>59</sup> A remarkable feature of the results for the oxygen-terminated interface is that the terminating oxygen layer shows a puckering that is comparable to that of the Cu layer at the interface; the MgO layers below the terminating layer are quite rigid. In effect, the layer of oxygen at the interface becomes part of the metal, because of overlap of the metallic wavefunctions and metal-induced gap states. The relaxed misfit dislocation network shows the expected trigonal symmetry, although in principle a hexagonal symmetry is possible.<sup>60</sup>

**c.  $\text{Ti}_3\text{AlC}/\gamma\text{-TiAl}$ <sup>61</sup>:** Carbide precipitates in a TiAl matrix improve its high-temperature strength, particularly creep resistance, and are therefore under investigation as a possible ingredient in high-temperature structural alloys based on titanium aluminide. Properties of the precipitate interfaces with the  $\gamma\text{-TiAl}$  matrix merit attention because of the role they play in nucleation and growth, mechanical properties as well as precipitate stability against coarsening. Our calculations have focused on the two ternary carbides  $\text{Ti}_3\text{AlC}$ , with perovskite structure (P-type) and  $\text{Ti}_2\text{AlC}$ , with hexagonal structure (H-type). The P-type precipitate faces with  $\langle 100 \rangle$  orientation have misfits of  $-0.036$  and  $-0.021$ , and the H-type precipitate platelets parallel to  $\langle 111 \rangle$  has misfits of  $-0.73$  and  $-0.067$ , with the host. Electron microscopy observations show the former to be coherent, and the latter incoherent. Since the misfits of this interface are too small ( $n_m > 15$ ) for these interfaces to be treated by the ‘exact’ first-principles approach used for MgO-Cu, we have applied instead the more approximate first principles formulation, which involves relatively small unit cells. The results of calculations for the predominant interface orientations of the two types of interface [P(100)-TiAl(100), and H(0001)-TiAl(111)] show that the differences in interface properties are determined not only by the disparity in the misfits but also by the marked contrast in the interface bonding. The bonding at the P(100)-TiAl(100) interface is strong because (100)TiAl layers have precisely the same structure in both the host and the precipitate phases, and the coherent interface may therefore be considered ‘pseudomorphic’. The preferred interface termination for the H-phase, which is a (0001)Ti layer opposite a (111) TiAl

layer of the host shows much weaker bonding, at least in part because of Ti-Ti and TiAl bond length frustration across the interface.

#### E. List of Publications

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