Importance of open-shell effects in adhesion at metal-ceramic interfaces

Emily A. Jarvis and Emily A. Carter

Department of Chemistry and Biochemistry, Box 951569, University of California, Los Angeles, California 90095-1569

We demonstrate markedly enhanced adhesion between oxide ceramics and conducting metals via promoting open-shell electronic structure at the interface, by using a more covalent oxide or doping with early transition metals. Open-shell character suppresses closed-shell repulsions and permits local covalent and/or donor-acceptor bonding, even in the absence of a conventional reaction layer. The dramatic impact of such local bonding attractions, predicted from density-functional calculations, contradicts the idea of classical electrostatic forces dominating metal-oxide adhesion.

The need to bond dissimilar materials to one another is pervasive in modern industry and medicine. Metals and oxide ceramics must adhere well to one another, as they appear everywhere from dentistry and orthopedics (implants, fillings, and coatings) to production of specialty petrochemicals (via metal catalysts supported on oxides), to protective ceramic coatings for metal components in, e.g., turbine engines in airplanes and power plants.[1,2] Despite many empirical advances in materials design, understanding of metal-oxide adhesion at the atomic scale is incomplete; this limits predictive design of optimally adherent interfaces. Often, even the dominant attractive force between such interfaces is in dispute.

Chatain *et al.* showed that correlating the work of adhesion of a variety of metals on oxide substrates, including Al_2O_3 and SiO_2, with local metal-oxo and metal-metal bond formation provided a good fit to experimental data.[3,4] However, the same research group later refuted these predictions in favor of van der Waals and/or ''image charge'' forces dominating the interfacial interactions.[5] By contrast, recent calorimetry measurements of heats of adsorption of nonreactive two-dimensional metal islands on a ceramic substrate— Cu, Ag, and Pb on MgO(100)—suggested that localized chemical bonding (between primarily Mg ions and the metal) may serve a major role in interface adhesion.[6] Current understanding remains divided.

A common theory of ionic/metallic interfaces attributes the dominant attractive forces to global classical electrostatic effects, whereby the ionic dielectric induces an image charge in the metallic medium.[7,8] Local ionic bonding effects have been noted in *ab initio* studies of isolated metal adatoms on ceramic surfaces; however, adhesion of metallic films to ceramics is entirely different.[9] Recent density-functional-theory (DFT) studies have shown local bonding effects (metal-oxo ionic,[10–12] ''electron transfer'' directional bonding,[13] covalent,[14] and bonding at defect sites,[15]) can be significant at certain metal-oxide interfaces. Here, we stress the importance of *unoccupied* electronic states at the interface in determining nonreactive metal-oxide adhesion; we systematically correlate strong interface adhesion with empty metallic d states at the interface. In addition, we demonstrate that high ionicity (maximum charge separation) in the ceramic does *not* produce optimally adherent interfaces. Enhancing the degree of *open-shell* character at the interface can dra-

matically strengthen metal-oxide adhesion via increased covalent and *donor-acceptor* bonding accompanied by decreased closed-shell repulsion. This donor-acceptor bonding, unlike ionic and/or electron transfer (polar covalent) directional bonding mechanisms, does not require explicit charge transfer. In fact, for metal-oxide donor-acceptor bonding, the donation is from the oxygen anion to the empty acceptor states of the metal. This sharply contrasts with ionic and/or polar covalent bonding, where there is charge flow towards the more electronegative element.

We perform calculations of crystalline surfaces and interfaces within plane-wave pseudopotential density-functional theory.[16–20] The use of periodic boundary conditions allows simulation of interfaces neglecting only long-ranged relaxations. A first-principles approach has the disadvantage of being limited to several hundred atoms in computationally feasible system size, which does restrict the chemical and physical complexity of the solid-state systems that can be tackled. However, it has the advantage of not requiring *a priori* assumptions regarding the types of interactions that are permitted; thus charge transfer, polarization, and chemical bond formation are all free to occur within the self-consistent description. This flexibility is especially useful in the study of dissimilar interfaces where the detailed interactions are often collective, subtle, and poorly understood.

Our interface adhesion energies are obtained through a series of three calculations: the isolated substrate, the isolated coating, and the combined interface. The resulting adhesion value then explicitly refers to the energy lowering as a result of interface formation relative to isolated surface formation, and is normalized by the interface area of the calculation's periodic supercell. In all surface and interface calculations, all ions within the ceramic and at the ceramic/metal interface are fully relaxed, subject to the boundary conditions of the supercell. Furthermore, to better explore the complex potential-energy landscape of the crystalline interface, we performed high-temperature annealing dynamics[21] for a variety of cases shown here. We chose lattice vectors, in a manner described previously,[1] with small lattice misfit between the coating and substrate such that the interface mismatch was ≤3% to limit unphysical strain resulting from imposed in-plane periodic boundary conditions on the somewhat incommensurate coating and substrate lattices. To further examine the effect of any remaining inter-

face strain artifacts, we performed a series of calculations using first the substrate lattice vectors and then the coating's lattice vectors for the periodic supercell, thus capturing the two most disparate possible choices. Although the detailed energetics are affected by the precise choice of lattice vectors, the overall features are similar. The specific results discussed refer to the imposed interface lattice vectors of the metal.

Our interest in the detailed interactions at metal/ceramic interfaces initially was sparked by our investigations of atomic-level mechanisms of materials failure in thermal barrier coatings (TBC's) of jet engine turbines.[1,22–24] One important interface that forms in TBC's is the result of high-temperature oxidation of a nickel alloy bond coat to produce an α-Al_2O_3/Ni alloy interface.[25] Ni/Al_2O_3 is also of interest for certain catalytic applications. Accordingly, the clean Ni/Al_2O_3 interface has been studied extensively by experiment[26–28] and various levels of theory.[24] With excess oxygen, a spinel phase $NiAl_2O_4$ can form at the pure Ni/α-Al_2O_3 interface at elevated temperature.[27,28] In the absence of excess oxygen, the interface is nonreactive and meets the general criteria to suggest it might be described reasonably by an image-charge model for interface adhesion.[29]

We studied the effect of increasing alumina film thickness on a nickel substrate; specifically, we investigated the ideal α-$Al_2O_3(0001)$/Ni(111) interface.[24] Consistent with UHV experiments, we find the nonreactive interface to be weakly adhered.[30] The variation in adhesion with increasing oxide thickness is quite interesting, however, and does not follow a simple relationship. For a monolayer alumina coating, the film exhibits both Ni-O and Ni-Al interactions. Rearrangement of the alumina film, whereby the planarity of the oxygen ions is broken, permits more pronounced Ni-O interactions than are favorable for the thicker alumina structures that maintain the hexagonal planes of oxygen, as in the corundum structure of sapphire (α-Al_2O_3). Once a bilayer of alumina is present, the planarity of the oxygen layers is maintained, and Ni-O interactions decrease. Furthermore, despite the decreased Ni-O interactions, the interface adhesion is somewhat stronger at 943 mJ/m^2, as opposed to 618 mJ/m^2 for the monolayer. Analysis of the kinetic-energy density[31] indicates this increased stabilization is related to more localized Ni-Al interactions. This is consistent with (high-temperature UHV) x-ray photoemission spectroscopy (XPS) experiments suggesting Ni-Al and Ni$_3$-Al interactions[27] but not Ni-O. For a trilayer of alumina on nickel, the interfacial adhesion decreased to nearly half the value for the bilayer case, only 456 mJ/m^2. The general "bonding" interactions of the trilayer interface were similar to those of the bilayer, but the ionic intraceramic bonding strengthened at the expense of the interfacial Ni-Al bonds. Charge transfer across the interface was very limited in all cases studied.

Alumina is a highly ionic crystal, with estimated ionic character of 60–90%,[32,33] leading to effective Al^{3+}-O^{2-} interactions. Accordingly, the interface interactions of the stable alumina structure with a late transition metal may contribute closed-shell-type O^{2-}-M repulsions. These repulsions

TABLE I. Adhesion (mJ/m^2) achieved with "M" dopant at Al_2O_3/(M-)Ni.

"M"	Ni	Al	Sc	Y	Ti	Zr
E_{ad}	1880	1490	3350	3240	3690	3210

will be most pronounced for thicker ionic films that allow highly ionic intraceramic bonding, resulting in closed-shell electronic structure. (This is consistent with the observation that thickening of the alumina layer in TBC's is correlated with increased de-adhesion at the alumina/Ni alloy interface.[25]) From a standpoint of materials design, accepting such short-ranged repulsions drastically limits the options for strengthening interfaces, especially those whose growth is not controlled, i.e., those resulting from operational oxidation. To avoid this short-range repulsion scenario, one could envision two basic approaches: (1) promoting open-shell interactions via chemical modification of the metal (alloy), or (2) promoting open-shell interactions by choosing a ceramic coating with more covalent character to its bonding. Here we consider both.

To investigate the effect of increasing open-shell bonding contributions to interface adhesion at the metal-ceramic interface, we introduced one-half monolayer of the early transition metals (Sc, Y, Ti, and Zr) at the Al_2O_3/Ni interface with a bilayer alumina coating. These elements were initially positioned to cover half of the fcc hollow sites, but were allowed to relax to their lowest-energy geometry over the course of the simulation. We also performed limited annealing dynamics to probe the interface structural stability; however, no new reaction products were obtained with this annealing.

Significantly improved adhesion is observed when these open d-shell elements are introduced at the interface. The adhesion values for the Al_2O_3/(M-)Ni interface for the early transition metals, with Ni and Al "dopants" also included for comparison, are shown in Table I. In the most dramatic case studied, Ti is capable of *doubling* the interface adhesion relative to Ni at this interface. Interestingly, the cost of cleaving at the ceramic/doped-metal interfaces or at the doped-ceramic/metal interfaces was the same to within $\sim$20% for each of the early transition metals. This implies that early transition-metal doping may improve both ceramic coating lifetimes on doped metal substrates as well as catalyst lifetimes for oxide supports doped with open-shell metals.

We also calculated the pure alumina and nickel ideal cleavage energetics along low-index planes in the absence of energy dissipating mechanisms. The minimum energy required for cleavage was the same to within 25% for bulk nickel, the alumina film, and at the early transition-metal-doped interface, suggesting a dramatic improvement in the cohesion of this multilayered material. This was not the case for the undoped Al_2O_3/Ni, where the interface adhesion for the thicker alumina film was *six times* weaker than cleavage within the ceramic and *eight times* weaker than cleavage within the metal. (This is consistent with scanning electron
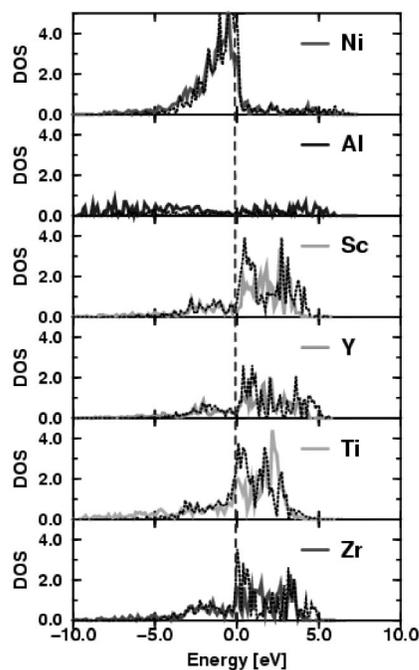
FIG. 1. This figure shows the electronic states available to the dopant atoms at the isolated metal surface (dotted lines) and at the Al_2O_3/Ni interface (gray lines). States above 0.0 eV, the Fermi level indicated by the dashed line, are conduction bands that have no occupation in the ground electronic state (zero temperature). The early transition metals (Sc, Y, Ti, Zr) have many available empty states near the Fermi level. These decrease upon interface formation, indicating donor-acceptor bonding, due to partial filling of the empty acceptor orbitals. Conversely, Ni is almost completely occupied, whereas Al has a low density of states.

microscopy images showing void formation at the alumina/metal [mostly Ni] interface formed via high-temperature oxidation of Ni_3Al alloy.[34])

These adhesion trends correlate with the ability of the dopants to accept electrons, which stabilizes the interface both by reducing interfacial closed-shell repulsions and by strengthening the interface by donor-acceptor bonding via donation from oxygen anions to the early transition-metal atoms.[35] Figure 1 displays the local density of states on a given dopant atom at the Ni(-M) surface and at the Al_2O_3/(M-)Ni interface. Although Ni has a large number of occupied states, the conduction-band states are very limited. Likewise, Al has limited states in both the conduction band and at the Fermi level. By contrast, the early transition metals all exhibit very high conduction local density of states (LDOS), indicating their open-shell nature and their ability to act as good electron acceptors; each result in similar interface stabilization values, although Ti is the most effective according to Table I. Carter and Goddard have provided a detailed orbital description of the importance of donor-acceptor metal-oxo bonding in early transition metals.[36] In addition to standard metal-metal bonding where occupied states at/near the Fermi level are important, the open-shell character of early transition metals permits donor-acceptor metal-oxo bonding. As mentioned, unlike ionic or covalent bonding, donor-acceptor bonding does not require explicit charge transfer or creating bonding-antibonding states; rather, it involves delocalization of donor lone electron pairs into empty acceptor orbitals.

In a similar dopant study at the ZrO_2/Ni interface, we find Ti and Zr to be the most effective of the early transition metals in increasing adhesion, although the stabilization relative to Ni only resulted in at most a 45% improvement (for Zr). These results follow from our open-shell interpretation. We find c-ZrO_2 to be less ionic than Al_2O_3, thereby intrinsically exhibiting more covalent behavior; thus the ZrO_2/Ni interface is improved less dramatically than Al_2O_3/Ni by introducing open-shell metal dopants.

As mentioned earlier, a less ionic ceramic coating might also limit closed-shell repulsions and promote interfacial bonding. Accordingly, we investigated the α-SiO_2(0001)/Ni(111) interface, as a function of increasing SiO_2 thickness. SiO_2 is a more covalently bonded crystal than either Al_2O_3 or ZrO_2,[37] with an estimated covalent character of $\sim 50\%$.[38] The key feature distinguishing this case from that of Al_2O_3 or ZrO_2 on Ni is that the trend of increasing preference for intraceramic ionic bonding at the expense of interface adhesion is not observed. In fact, the adhesion of silica films to nickel remains relatively constant even for films several times thicker than the trilayer alumina coating. Our calculated adhesion at these SiO_2/Ni interfaces is nearly *three times* stronger than the trilayer Al_2O_3/Ni adhesion. Although charge transfer is also very limited across the SiO_2/Ni interface, covalent-type bonding is more pronounced.

Our interface studies display limitations of a classical image charge description of adhesion for an ionic dielectric in contact with a conducting metal. At short range (~ 2 Å), previous electrostatic models assumed strong repulsions,[39] i.e., infinite in the case of hard spheres or exponential for a more realistic description of electronic repulsions. In the opposite limit, the semi-infinite ionic material should induce an interface adhesion energy roughly on the order of its own surface energy, since the energetic "cost" of forming the surface is compensated in the interfacial environment by an effective continuance of the ionic lattice via induced images in the metal.[39] Our results show that the short-ranged electronic wave-function interactions can be tailored to contribute strong local bonding *attractions*, significantly strengthening the interface even in metal-ceramic couples where a first-order approximation suggests closed-shell *repulsions*. Availability of empty metallic d states correlates with our calculated increase in adhesion at metal-ceramic interfaces doped with early transition metals. Alternatively, empty oxygen states, resulting from partially ionic oxides with $\sim O^-$ rather than O^{2-} electronic structure, enhance late transition metal-oxide adhesion relative to oxides with closed-shell oxygen electronic structure.

Interestingly, some observations used previously to support the image-charge adhesion picture may be explained instead through the local bonding effects discussed here. Tasker and Stoneham correlate the ability of a given oxide to be wet by metals with the oxide's capability of forming (charged) defects.[39] We posit that these wetted oxides are also the more covalently bonded crystals, leading to signifi-

cantly enhanced interface "bonding" interactions via open-shell effects. For instance, nonreactive liquid metals wet NiO but not alumina. In contrast to the highly ionic nature of alumina, recent experimental evidence from reflection high-energy electron diffraction studies of the (100) NiO surface shows a best fit for only 30% ionic character.[40] The simple formal charge picture of Ni^{2+} and O^{2-} in this crystal misrepresents its true electronic structure. Instead, a local electronic structure of Ni^+-O^- is more appropriate, where closed-shell O^{2-}-M repulsions with nonreactive metals will be significantly reduced, compared to a highly ionic lattice such as Al_2O_3.

We suggest *open-shell* interfacial bonding may be tailored to dominate adhesion at metal/oxide interfaces. The observed TBC performance improvements with doped-metal-alloy bond coats may be a direct result of such interfacial bonding. Moreover, many widely used catalysts are (nearly) closed-shell metals on highly ionic ceramic supports operating at elevated temperatures. Open-shell tailoring of metal supported catalysts may enhance their durability via increased local adhesion to suppress Ostwald ripening/sintering, thus maintaining the high surface area necessary for optimum catalytic activity. Naturally, collective effects at heterogeneous interfaces remain important, and any blanket statement can be cause for suspicion. Nevertheless, our results support the importance of open-shell bonding for strong interface adhesion—even for nonreactive couples. Traditional formal charge treatments used to predict and rationalize the behavior of complex materials provide an incomplete picture. Open-shell character in metals and deviation from full ionicity in ceramics provide the quantum glue to dramatically strengthen interfaces between dissimilar materials.

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