We employ first-principles density functional calculations to explore atomic-level interactions and predict the ideal work of adhesion at the SiO$_2$/nickel and ZrO$_2$/SiO$_2$ interfaces. We find that chemical bonding at the interface serves to strengthen significantly interfaces formed with SiO$_2$, which exhibits significant covalent bonding character, relative to those formed using more ionic oxides, such as Al$_2$O$_3$, in place of SiO$_2$. The improved strength of these interfaces due to local bonding interactions may hold materials design implications for practical applications that require optimal adhesion between metal-ceramic layered structures, including thermal barrier coatings.

I. Introduction

Achieving well-matched heterogeneous interfaces is crucial for numerous practical applications. Although matching bulk properties for the constituents of such interfaces is fairly straightforward, these properties alone cannot ensure optimal interface design. In particular, unique features relevant to thin films, amorphous structures, and the local interatomic interactions may have a significant impact on the resulting behavior—even for macroscopically thick interfaces. Unfortunately, it is these properties that are often not well-understood and generally very difficult to characterize. This prevents detailed predictive design for heterogeneous interface applications. A wealth of empirical knowledge does exist, but conclusions and trends that can be inferred from these studies are generally very conditions-dependent.

One example where optimization of interface behavior is crucial and nontrivial is in the case of thermal barrier coatings (TBCs) for jet engine turbines. TBCs serve the valuable role of protection against thermal and corrosive degradation of the superalloy turbine blades in the harsh combustion environment. Such applications require optimization of several coating and interface properties for maximum effectiveness. Among these, favorable adhesion, well-matched thermal expansion coefficients, effective thermal protection, and protection against hot oxidation/corrosion are especially vital properties that these coatings must possess. For TBCs, matching even the bulk properties over the harsh temperature and chemical potential ranges is a challenge.

A typical structure for a TBC consists of several layers. The superalloy substrate is a single-crystal alloy of primarily Ni$_3$Al in a nickel matrix. Generally, a metal alloy bond coat is deposited on the superalloy substrate: two common bond coatings are MCrAlY (where M = Ni, Fe, and/or Co) and PtAl alloys. A thin Y$_2$O$_3$-stabilized ZrO$_2$ (YSZ) film then serves as the top coat and provides the primary thermal protection for the underlying substrate. Because oxygen diffuses through ZrO$_2$ at high temperature and along cracks and grain boundaries at all relevant temperatures, the metal alloy bond coat must provide some means of oxidation/corrosion protection for the superalloy. This goal partially motivates the aluminum content in the bond-coat alloy, since alumina (Al$_2$O$_3$) provides a slow-growing oxide that effectively protects the underlying alloy from further oxidation. This layer is known as the thermally grown oxide (TGO).

The TGO layer is a site where TBC failure mechanisms are particularly concentrated. With repeated thermal cycling, the thermal barrier coating spalls. This failure can occur at the ZrO$_2$/Al$_2$O$_3$ interface but is especially prone within the Al$_2$O$_3$ TGO layer and at the interface of the metal alloy bond coat with Al$_2$O$_3$. Addition of reactive elements can improve oxidation resistance, but the role of these remains incompletely understood.

Although alumina is the preferred TGO in most current applications, other oxides may also serve in this role. Generally, a successful protective oxide must exhibit slow growth in order to (i) limit strains resulting from thermal expansion mismatch between the oxide scale and the metal alloy and (ii) avoid depletion of the oxidation element from this alloy. Chromia, alumina, and silica all exhibit potential uses in this capacity. In fact, it has been speculated that silica coatings should provide a more ideal diffusion barrier, because these generally form amorphous layers that do not allow diffusion along grain boundaries, etc. Likewise, silica should provide the slowest-growing oxide, which may be useful for limiting strain and/or dopant depletion failure of the...
bond coat alloy. Here, we use first-principles methods to investigate the potential for SiO$_2$ to substitute successfully for Al$_2$O$_3$ as the TGO.

For years it has been known that silicon might dramatically improve oxidation resistance of certain metal alloys (by the formation of an $\alpha$-SiO$_2$ scale); however, its use has been limited, since Si content tends to have detrimental effects on the mechanical properties of iron, nickel, and cobalt alloys. Nevertheless, it is possible that very low concentrations of silicon—i.e., 0.9% in the case of a steel with 20% chromium and 25% nickel—could provide maximum benefit$^{14}$ and form an underlying SiO$_2$ protective layer,$^{15}$ while still allowing good mechanical properties of the alloy. Sulfur segregation to alloy/scale interfaces has been linked with spallation at these interfaces.$^{16}$ Silica coatings on stainless steels (Incoloy 800H, which consists of $\sim$46% iron, $\sim$21% chromium, and $\sim$31% nickel,$^{17}$ as well as AISI 304, 310, and 321$^{18}$) have also been shown to provide effective sulfur protection, which may be crucial in TBC applications. The SiO$_2$ phase in these coatings was not certain but was speculated to be $\alpha$-SiO$_2$.\textsuperscript{19} In a recent test of ceramics designed to replace chromia for stainless-steel protective coatings, silica was determined to be the most effective pure ceramic that was studied; it was better than either titania or zirconia in providing corrosion resistance.\textsuperscript{20}

Silicon has been added to nickel alloys with favorable effects on both oxidation resistance and adhesion. An experimental study showed the parabolic rate constant of the oxide growth kinetics decreased for oxidation of the nickel-silicon at 900°C; the study also showed that the oxide adhesion increased for scales formed during 1100°C oxidation.\textsuperscript{20} Although amorphous silica-coated Ni-20Cr has been shown to protect the nickel from oxidation and reduce the oxidation rate, this rate reduction is not necessarily attributed to protection provided by silica. Another possible explanation is that silica may act as a reactive element to modify the growth of Cr$_2$O$_3$ on this alloy, so that the protective chromia layer forms more rapidly and the subsequent growth mechanism of that oxide is altered.\textsuperscript{21} Recent scanning transmission electron microscopy (STEM) investigations of the oxidation of a Ni-20Cr alloy showed that a thin protective silica layer forms at earlier oxidation times than had been anticipated previously. Likewise, this amorphous layer adheres to the alloy, despite the fact that the Ni-20Cr alloy contained sulfur and no reactive elements to getter this sulfur content. The authors did not observe sulfur segregation to the metal/oxide interface.\textsuperscript{22} \textsuperscript{19}

Investigation of the crystallization and phase stability of several nickel–silicon alloys, using ion-beam analysis, transmission electron microscopy (TEM), and X-ray diffractometry (XRD), has shown the formation of an epitaxial relation between Ni$_3$Si and nickel; this relation is attributed to highly favorable lattice matching.\textsuperscript{23} XRD studies of Ni$_3$Si grain growth on SiO$_2$ (formed by thermally oxidizing single-crystal Si(100)) have shown that these grains grow preferentially with the (111) planes parallel to the substrate, which was believed to reduce both interfacial and surface energies, and TEM showed the Ni$_3$Si phase to be stable up to 800°C in these grains.\textsuperscript{24} A study of the oxidation of $\sim$Ni$_3$Si and nickel–silicon–chromium alloys suggested that the initial formation of nonprotective oxides is followed by protective, amorphous silica scale formation at 700°C.\textsuperscript{25} For temperatures of $<800$°C, the chromium content seems to be beneficial in limiting the oxidation rates; at higher temperatures, this trend is reversed—chromium content increased the oxidation rates. These results led the authors to suggest that amorphous silica provides a more protective scale at high temperatures.\textsuperscript{25} In addition to oxidation resistance, it is also possible that silicon additions to nickel alloys can improve the thermal expansion coefficients of these alloys for nickel superalloy coating applications.\textsuperscript{26} Accordingly, although many details remain to be optimized, these recent studies provide some insight into the behavior of silicon content in nickel alloys.

(1) Aspects of Metal/Ceramic and Ceramic/Ceramic Adhesion

An absolute value of adhesion at heterogeneous interfaces is difficult to isolate via experimental means. One reason for this is the difficulty in distinguishing processes arising from different phenomena and length scales. Phase changes, chemical reactivity, and segregation of impurities also affect the measurements in realistic systems. Accordingly, measured adhesion values often comprise a variety of features, which complicates the predictive optimization of the interfaces of materials.

Traditionally, experimental measures of ceramic–metal adhesion focus on solid/liquid interfaces. This approach may provide a good estimate to solid/solid interface energetics, but it is not always the case; the assumption that the adhesion between materials is relatively constant—regardless of phase—is often unsatisfactory. A particular example where such an approximation fails is in the case of SiO$_2$/Ni, where atomic force microscopy (AFM) has shown amorphous nickel particles weakly adhere to a substrate of amorphous, submicrospheres of silica, but polycrystalline nickel particles strongly adhere to the same substrate material.\textsuperscript{27}

(2) Silica/Nickel Interface

Nickel films grown on a silica substrate have been shown to prefer the (111) orientation; this preference becomes more pronounced as the temperature increases.\textsuperscript{28} A detailed characterization of the interface is not available. As mentioned, AFM studies have shown that polycrystalline nickel particles adhere to silica substrates much more strongly than their amorphous counterparts. This observed difference in adhesion between amorphous and polycrystalline nickel on amorphous silica led Ramesh et al.\textsuperscript{29} to speculate that a silicate phase was formed at the interface of polycrystalline SiO$_2$/Ni, with perhaps Si–O$^-$–Ni$^{+}$ bonding, as indicated by infrared (IR) spectroscopy.\textsuperscript{29} It is not obvious why polycrystalline nickel would be more reactive than amorphous nickel toward SiO$_2$; indeed, one might have expected the opposite. An early study by Sangiorgi et al.\textsuperscript{30} suggested that chemical bonding of both metal–oxygen and metal–silicon varieties was required to explain the adhesion for certain nonreactive liquid metals (gold and lead) on (quartz and vitreous) silica substrates. This conclusion relied on correlations with the work of adhesion measurements. Later work that was fit instead to work of immersion suggested that the dominant interactions for interfaces between metals and ceramics with significant ionic character are instead related to van der Waals and image charge contributions.\textsuperscript{31}

Density functional theory (DFT) cluster calculations of Cu atoms and clusters on a SiO$_2$ surface (derived from a-$\alpha$-quartz) suggest that polarization is the primary attractive mechanism for the perfect SiO$_2$ surface, but that defect sites allow strong bonds to form between the metal and the ceramic.\textsuperscript{32} DFT calculations on the interactions of nickel that is deposited on SiC substrates show Ni–Si bonding;\textsuperscript{33} but the SiC crystal exhibits much more covalent bonding than SiO$_2$. Accordingly, comparisons of Ni–Si electronic properties of SiC versus SiO$_2$ substrates cannot be inferred directly. To our knowledge, no DFT simulations of the SiO$_2$/nickel interface have been reported before our work.

Most studies of metal/SiO$_2$ interfaces have investigated metal deposition on amorphous or quartz silica substrates. Crystalline silica thin-film growth on metal substrates has been achieved only recently for SiO$_2$/molybdenum interfaces.\textsuperscript{34} Generally, silica growth on metal substrates results in amorphous silica, even if a stoichiometric film is created. Studies employing scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), and XRD to investigate the interface of liquid nickel superalloys that are in contact with a silica substrate (with 25% porosity) at high temperature (1390°C) find that interfaces between oxides of the reactive elements and silica form at these high temperatures, rather than a metal/silica interface, due to the inclusion of dopants with high oxygen affinity in the alloy.

(3) Zirconia/Silica Interface

The ceramic–ceramic ZrO$_2$/SiO$_2$ interface is receiving increased attention, because of its potential use as a gate dielectric in electronic devices. Medium-energy ion-scattering studies (MEIS) have shown that ZrO$_2$ can form sharp interfaces with silica at temperatures up to 900°C (at which point silicates were formed under the conditions present in that study).\textsuperscript{36} SEM and TEM
studies have also shown good bonding with effective wetting between a ZrO\textsubscript{2} film and glass ceramics.\textsuperscript{37} Although silica has a very low solubility in YSZ, amorphous SiO\textsubscript{2} will readily form along grain boundaries of this material.\textsuperscript{38} Zirconium is effective at reducing oxides of silicon; however, a stoichiometric ZrO\textsubscript{2} film on a silicon substrate permits silicon oxidation, especially above \textasciitilde 400\textdegree–500\textdegree C.\textsuperscript{39,40} This is to be expected, because ZrO\textsubscript{2} does not provide adequate elevated-temperature oxidation protection, as also observed in TBC applications. Although SiO\textsubscript{2} growth can be problematic for electronics applications, a thin layer of this protective oxide might serve as a desirable TGO in TBCs. Binary oxides of SiO\textsubscript{2} and ZrO\textsubscript{2} can permit stabilization of the tetragonal phase of ZrO\textsubscript{2} by what were speculated to be covalent Si–O–Zr bonds.\textsuperscript{41} Tetragonal ZrO\textsubscript{2} stabilization has also been observed in zirconia–alumina nanolaminates.\textsuperscript{42} Since this tetragonal ZrO\textsubscript{2} phase is the one desired in TBC applications, this also might prove to be a useful property of SiO\textsubscript{2}–ZrO\textsubscript{2} interactions. Although generally YSZ is fairly robust against high-temperature degradation, it is prone to aging in air at moderate temperature (\textasciitilde 150\textdegree–400\textdegree C); silica (cristobalite phase at the r-ZrO\textsubscript{2} polycrystal surface) and ZrSiO\textsubscript{4} can inhibit this undesirable phenomenon.\textsuperscript{43}

To our knowledge, first-principles DFT calculations of the ZrO\textsubscript{2}/SiO\textsubscript{2} interface have not been performed elsewhere. Recent DFT calculations that predict the stability of bulk ZrO\textsubscript{2} in contact with bulk SiO\textsubscript{2} and silicon indicate that both interfaces should be (slightly) thermodynamically unstable, with the reaction of ZrO\textsubscript{2} and SiO\textsubscript{2} combining to form ZrSiO\textsubscript{4}, displaying a small negative enthalpy.\textsuperscript{44} Naturally, kinetic effects limit this reaction in practice.

Only a limited understanding of SiO\textsubscript{2} substrates with stabilized ZrO\textsubscript{2} coatings for potential TBC applications is available. The thermal conductivity of YSZ has been shown to be independent of substrate when comparing polycrystalline alumina, Al\textsubscript{2}O\textsubscript{3}(0001), the (111) and (100) faces of ZrO\textsubscript{2}, and fused quartz substrates.\textsuperscript{45} Coatings of Al\textsubscript{2}O\textsubscript{3}-stabilized ZrO\textsubscript{2} have been deposited on silica substrates, and XRD has shown that the cubic phase of ZrO\textsubscript{2} (c-ZrO\textsubscript{2}) forms at 600\textdegree C from an initially amorphous film under such conditions.\textsuperscript{46} The potential of Mullite (Al\textsubscript{2}O\textsubscript{3} and SiO\textsubscript{2}) and/or mullite with YSZ protective coatings has been investigated for protection of SiC and Si\textsubscript{3}N\textsubscript{4} for use in combustion environments; the ZrO\textsubscript{2} top coat seems to be effective in eliminating some of the unfavorable features (e.g., silica volatilization) of a SiO\textsubscript{2}-based protective coating.\textsuperscript{47} More study is needed to understand the behavior of similar multilayer coatings on metal alloy substrates; the present work is a step in this direction, where we explore the interactions at both ZrO\textsubscript{2}/SiO\textsubscript{2} and SiO\textsubscript{2}/Ni interfaces.

II. Theoretical Methods

We performed spin-polarized density functional calculations\textsuperscript{48} within the Vienna Ab Initio Simulation Package (VASP).\textsuperscript{49} In these calculations, the valence electron density is expanded in a plane-wave basis and ultrasoft pseudopotentials\textsuperscript{50} replace the core electrons and nucleus. Periodic boundary conditions allow “infinite” bulk crystals to be simulated, even though the number of unique atomic positions is limited to \textasciitilde 150 atoms in the calculations reported here. The exchange-correlation potential is approximated by the generalized gradient functional of Perdew and Wang, circa 1991 (GGA-PW91).\textsuperscript{51} The pseudopotentials used here have been described elsewhere.\textsuperscript{52–54} with the exception of the one for silicon, for which we used the standard silicon ultrasoft pseudopotential in the VASP version 4.4 database. We used two different zirconium pseudopotentials: one affords explicit treatment of the valence 5s and 4d electrons, and the other provides explicit treatment of the 4p electrons as well. The specific results in the discussion of the ZrO\textsubscript{2}/SiO\textsubscript{2} interface refer to this latter pseudopotential. Nonlinear partial core corrections to the exchange-correlation potential are included for all elements except oxygen.\textsuperscript{55}

Kinetic-energy cutoffs of \textasciitilde 340 eV for the pseudodensity and 554 eV for the augmentation density are used. The Brillouin zone is sampled with a Monkhorst–Pack grid\textsuperscript{46} of 1 \times 5 \times 5 for the SiO\textsubscript{2}/Ni interfaces and 1 \times 3 \times 3 for the ZrO\textsubscript{2}/SiO\textsubscript{2} interfaces, resulting in thirteen and five irreducible k-points, respectively. In each case, these choices of bases and k-point sampling converged the total energy (extrapolated from the free energy\textsuperscript{57}) to the meV/atom range. Two different methods for setting the partial occupancies near the Fermi level are used to enhance convergence: first-order Methfessel–Paxton smearing,\textsuperscript{58} and the tetrahedron method with corrections introduced by Blöchl et al.\textsuperscript{59} The smearing method was used in the density of states (DOS) plots that are presented later, because of the small number of irreducible k-points that are used in the larger interface supercells.

The atomic relaxations are performed using a conjugate gradient algorithm. To test whether or not our structures were converged to a favorable minimum energy atomic configuration, we performed limited high-temperature (at 1200 and 1400 K) annealing runs, using timesteps of \textasciitilde 0.35 fs for up to \textasciitilde 0.4 ps trajectories.\textsuperscript{60} Although we found no new features after annealing/quenching, it is possible that, with longer annealing runs and/or higher-temperature annealing, new reaction products could form; this is left to future work. In the atomic relaxations and molecular dynamics (MD) simulations, the positions of all atoms within the ceramic film and the top two layers of the three-monolayer (ML)-thick Ni(111) substrate are free to relax. In the ZrO\textsubscript{2}/SiO\textsubscript{2} calculations, we chose a SiO\textsubscript{2} substrate thickness of six ML, with the bottom three ML fixed to bulk values. These frozen substrate coordinates away from the interface were employed to better simulate a macroscopically thick substrate. Generally, the inclusion of \textasciitilde 10 Å of vacuum in the periodic surface and interface cells was adequate for converged total energies. Occasionally, a small artificial dipolar interaction between slab images that had non-negligible impact on the total energy (i.e., \textasciitilde 0.1 eV) was found in the direction perpendicular to the interface, which was effectively reduced by the inclusion of \textasciitilde 15 Å of vacuum. The relaxed atomic coordinates were not sensitive to these minor changes.

We define projection spheres around each atomic site for the purposes of analyzing the local s, p, and d occupation, DOS, etc. These projection radii have no impact on the charge density or energy convergence in the calculation; rather, they are simply used for post-calculation analysis purposes. The choice of the integration sphere is not unique, as we have discussed previously.\textsuperscript{61} Nevertheless, information provided by these local charge analyses can provide insight into trends and general features. For the metal-ceramic studies, we defined spheres with radii of 1.015 and 1.345 Å for Al and O in alumina, respectively; 1.08 and 1.26 Å for Si and O in silica, respectively; and 1.23 Å (and an alternative larger radius of 1.37 Å) for Ni. In the ZrO\textsubscript{2}/SiO\textsubscript{2} studies, we use a radius of 1.4 Å for Zr, 1.08 Å for Si, and 1.3 Å for O in both the SiO\textsubscript{2} and ZrO\textsubscript{2} ceramics.

The equilibrium volumes of the bulk crystals are calculated by performing a series of single-point energy calculations, while maintaining crystalline structures with perfect symmetry but uniformly expanding or contracting the lattice vectors. The resulting energy-volume relations are fit using the equation of state described by Murnaghan,\textsuperscript{53} as well as second- and third-order polynomials. Our methods of calculating surface and interfacial energies have been described previously.\textsuperscript{32,53,54} In the interface calculations, the ideal Ni lattice vectors are imposed for the SiO\textsubscript{2}/Ni interface and the ideal SiO\textsubscript{2} lattice vectors are imposed for the ZrO\textsubscript{2}/SiO\textsubscript{2} interface supercell. In both cases, the resulting misfit is \textasciitilde 2\%.

III. Results and Discussion

(1) Bulk and Surface Properties

We chose to model the \alpha-\text{quartz} phase of SiO\textsubscript{2} in our interface studies. The periodic boundary conditions imposed by our calculation necessitate a crystalline rather than amorphous silica phase, for instance, an olivine silicate layer of Ni\textsubscript{3}SiO\textsubscript{4} forms at the SiO\textsubscript{2}/Ni interface created by the hot pressing of powders at 1400\textdegree C. (See R. Drza-Halamou, L. Durand, and B. Lavelle, Mater. Sci. Eng. A, 282, 144–48 (1998).)
and the basal plane of α-quartz is the best-characterized face of crystalline SiO₂. In addition, the studies of metal adhesion on single-crystal SiO₂ have used the quartz phase,⁵⁶ and experiments have suggested that a thin layer of silica, in perhaps an α-SiO₂ phase, might form a protective layer under certain conditions.¹⁵,¹⁸ In future studies, alternative phases and faces of SiO₂ might provide additional insight. In our calculations, the equilibrium volumes of the α-quartz⁶⁸ and face-centered cubic (fcc) nickel agree with the experimental values to within 1%. Within the GGA, the c-ZrO₂ bulk volume is overestimated by < 2% with the inclusion of only s and d states on the Zr and by ~3.5% with the inclusion of p states on the Zr. As often found, the GGA overcorrects the well-known overbinding tendency of the local density approximation (LDA); hence, the equilibrium lattice vectors are slightly expanded. More detailed descriptions of the calculated bulk properties of ZrO₂, Al₂O₃, and nickel have been described previously.⁵²,⁵³

Low-pressure silica polymorphs exhibit a fairly open crystal structure. The largely covalent character of the Si–O bond allows highly directional bonding to be favored over close packing. The equilibrium volume of α-quartz (22.71 cm³/mol) lies toward the high-volume end of the silica polymorphs—between the more tightly packed, high-pressure phases such as stishovite (molar volume of 14.04 cm³) and the low-pressure stable crystal structures, such as cristobalite (molar volume of 25.76 cm³) and glass (molar volume of 27.25 cm³).⁶⁴ Hence, the α-quartz crystal structure exhibits fairly high internal compressibility.

The calculated bulk modulus is quite dependent on the extent of the potential energy surface that is sampled. Even more important than the fact that the SiO₂ structure is not “space-filling,” the internal compressibility of SiO₂ is not primarily related to a uniform decrease in bond lengths while maintaining the perfect crystal structure, as is often assumed in calculated bulk moduli estimates. Instead, distortion of the silica tetrahedra, where bond angles change but bond lengths do not, and especially contributions from rotations of the silica tetrahedra primarily account for the ease of initial compressibility and the resulting low observed bulk modulus. We find that a calculated value near the observed estimates of 38.7(± 1.0) GPa,⁶⁴ can be attained only by allowing internal relaxations and restricting sampling to very near the equilibrium volume. Excluding such distortions results in an almost fourfold overestimate of the bulk modulus (148.1 GPa versus 38.7 GPa) when sampling the region within 5%–7% of the equilibrium volume.

The surfaces of Ni(111) and ZrO₂(111) have been described previously.⁵²,⁵³,⁶⁶ Although SiO₂ is a material of great technological importance, the perfect crystalline surfaces often are not the surfaces of interest; instead, polycrystalline and amorphous surfaces tend to dominate practical applications. Nevertheless, the basal (0001) plane of α-quartz is perhaps the best-characterized crystalline SiO₂ surface. It is likely that this clean surface will undergo several reconstructions. These reconstructions are excluded if the periodic boundary conditions do not permit a unique surface area that is large enough to accommodate such effects. We did not perform a detailed study of surface reconstructions. However, we did start with a surface, i.e., cleavage between the two oxygen layers, that would permit similar long-range reconstructions to those that have been modeled using empirical potentials,⁷₃ and that also allows us to model stoichiometric, nonporal surface slabs.

Experimental reflection electron energy loss spectroscopy (REELS) studies of the SiO₂(0001) surface indicate two primary defects: oxygen vacancies and a “tridimensional disorder,” which refers to an amorphization defect in the crystal structure.⁶⁷ Low-energy electron diffraction (LEED) studies have also shown that a reconstruction occurs at a temperature of ~600°C, whereby the reconstruction periodic area is 84 times larger than the original surface.⁶⁸ Current direct ab initio methods cannot model such large length scales. However, work is under way to couple length scales and develop efficient and accurate linear-scaling electronic structure theories.⁷⁰ ⁷¹ Such methods eventually should allow more complete studies of these SiO₂ surface reconstructions, as well as small-percentage component contaminants, etc.

We found that the surface energy of the relaxed, unstructured (0001) surface of α-quartz was very well converged by a thickness of six stoichiometric SiO₂ units, ~10 Å. Even a much thinner slab of only three stoichiometric SiO₂ units provided a surface energy within 1% of the converged value. The calculated surface energy of 2.30 J/m² is likely to be a significant overestimate, because the in-plane boundary conditions are those of the bulk hexagonal cell and exclude long-ranged reconstructions that would otherwise serve to reduce the surface energy. A previous estimate of the (0001) surface energy of α-quartz, using a self-consistent tight-binding method, is nearly twice as large, at 4.49 J/m².⁷² The accuracy of this estimate suffers both from similar exclusion of long-ranged reconstructions and limited self-consistency (and other approximations) in the electronic structure calculation. A recent study used ab initio and empirical methods to study the basal plane of α-quartz, but they did not report energetics. They found that formation of three- and six-membered ring surface reconstruction structures represented local minima using the same initial cleavage conditions as those used here.⁷³

(2) SiO₂(0001)/Ni(111) Interface

Matching the surfaces of Ni(111) with SiO₂(0001) requires only a 1.3% imposed misfit for a unique interface area of 21.44 Å². This misfit results in very minor unphysical strain imposed by the periodic boundary conditions. Since we are modeling the thickening of SiO₂ on a nickel substrate, we chose to impose the bulk lattice vectors of the metal. This means that the SiO₂ films initially were formed using the perfect α-quartz atomic coordinates expanded in the interface plane by 1.3% to present a commensurate lattice to that of the substrate. Over the course of the simulation, these coordinates were permitted to relax to a more energetically favorable configuration; however, little change in the SiO₂ structure is observed on relaxation, further confirming the minimal imposed lattice strain.

We studied the effect of increasing thickness of the stoichiometric silica film on the SiO₂/Ni interface. For all thicknesses, the relaxed SiO₂ films maintain a structure very similar to the initial (bulklike) coordinates. Minor relaxations serve to stabilize the interface, i.e., the interfacial oxygen relaxes to a more favorable Ni–O–Ni interaction; however, no phase changes or dramatic rearrangements are observed. We find similar interactions for silica coatings three, six, and nine ML thick on a Ni(111) substrate. The adhesion energy is similar in the three cases, with a calculated adhesion of 1.29 J/m² for the 3-ML coating, 1.37 J/m² for the 6-ML coating, and 1.37 J/m² for the 9-ML coating. These differences correspond to at most a 0.1 eV difference, for the three different silica film thicknesses studied, in the interface total energy subtracted from the sum of the isolated slab (coating and substrate) energies. Effectively, the calculated adhesion remains constant for these silica films ranging from 5 to 15 Å thick. Accordingly, this estimate for the ideal work of adhesion should also apply to films of macroscopic thickness, since the 6- and 9-ML silica films exhibit regular, bulklike behavior within the center region of the film. Likewise, plastic energy dissipation mechanisms are not likely to contribute significantly for a silica coating, further supporting the relevance of the simulated interface to the macroscopic SiO₂/Ni interface. The periodic cell corresponding to the 6-ML silica coating on Ni(111) is shown in Fig. 1.

In addition to similar calculated adhesion values, the local atomic and electronic structure at the interface is fairly similar for the silica films that are ≥ 5 Å thick. Table I displays the Ni–O and Ni–Si bond lengths formed across the interface, as well as the Si–O bond lengths of the interfacial Si. This table also displays the site-projected charge difference for the atoms involved in interfacial bonding, at the interface relative to the charge projected onto those atoms in an isolated surface with the same atomic coordinates as the interface (i.e., where the other side of the interface has been “instantaneously” removed). In all cases, these atomic sites experience a relative reduction in the interface environment, with
oxygen showing the most dramatic change (an increase of \(-0.25\) e in electronic charge).

For reference, the bond lengths in NiO are 2.09 Å, Ni–Si bonds in the \(\text{L}1_2\) NiSi structure are \(\sim2.48\) Å,\(^{23}\) and the Si–O bonds in \(\alpha\)-quartz are 1.61 Å. Hence, the Ni–Si and Ni–O bond lengths at the interface are significantly shorter than those in the respective bulk crystals, by 0.1 Å in the case of Ni–O and by \(\geq0.2\) Å for Si–Ni. Concurrently, the last row in Table I shows that the Si–O bonds at the interface are weakened (stretched) to accommodate the Ni–Si and Ni–O (Si–O–Ni) bonding interactions. This straining of intracermic bonding to maximize interfacial bonding is indicative of strong, favorable local bonding interactions at this interface.

The site-projected charge differences between the surface and interface environments all display significant increases in electronic charge at the interface. This too is indicative of chemical bonding effects at this interface. Because all atomic sites experience some electron gain, it is unlikely that ionic effects are dramatic. Instead, this charge increase on each atomic site is indicative of the formation of localized covalent-type bonds. Such bond formation is also consistent with the “straining” of intracermic bonding, mentioned above, to permit close covalent bonding across the interface.

Although it might have been expected, we find no direct correlation between interface adhesion and the isolated surface energies of the ceramic. If a simple relationship were to hold, the ceramics with higher surface energy should adhere more strongly than those with lower energy, since the surface energy of the ceramic is a positive contribution to \(W_{\text{ad}}\), according to the Dupré equation.\(^{74}\) It is interesting to compare our predicted most stable surface energies of several ceramics with the subsequent calculated metal–ceramic adhesion energies for interfaces formed by joining those surfaces with the Ni(111) surface. The 3-ML \(\alpha\)-SiO\(_2\)(0001) slab, as mentioned earlier, is effectively converged with respect to surface energy, and results in a surface energy of 2.3 J/m\(^2\). For \(\alpha\)-Al\(_2\)O\(_3\), we predict a surface energy of 1.4 J/m\(^2\) for the 3-ML film and a converged (0001) basal plane surface energy of 1.5 J/m\(^2\).\(^{53}\) The most stable ZrO\(_2\) surface energy for both tetragonal and monoclinic zirconia (\(t\)-ZrO\(_2\) and \(m\)-ZrO\(_2\), respectively) was estimated to be \(\sim1.2\) J/m\(^2\).\(^{66}\) (For comparison, our GGA estimate of the Ni(111) surface energy is 1.9 J/m\(^2\).\(^{53}\)) The calculated ceramic/nickel adhesion is 1.4 J/m\(^2\) for SiO\(_2\), \(<0.5\) J/m\(^2\) for Al\(_2\)O\(_3\), and \(<1.0\) J/m\(^2\) for ZrO\(_2\). If it followed that higher surface energy structures result in greater interface adhesion, the Al\(_2\)O\(_3\) film should have adhered more strongly than the ZrO\(_2\); instead, our calculated adhesion values for these two ceramics exhibit the reverse ordering. There is not a straightforward relation between surface energies; specific energetics of the interface—in particular, interface stabilization via local bonding interactions—are crucial to consider when explaining calculated adhesion trends.

Table II gives some sense of comparison between the local bonding interactions at the interfaces of nickel with three MLs of Al\(_2\)O\(_3\),\(^{53}\) ZrO\(_2\),\(^{52}\) and SiO\(_2\), respectively. Similar to Table I, we

---

**Table I. Structural and Electronic Properties of the SiO\(_2\)/Ni Interface for Three, Six, and Nine Monolayers of SiO\(_2\)\(^\dag\)**

<table>
<thead>
<tr>
<th>Coating thickness</th>
<th>Ni–O bond length (Å)</th>
<th>Ni (e)</th>
<th>O (e)</th>
<th>Ni–Si bond length (Å)</th>
<th>Ni (e)</th>
<th>Si (e)</th>
<th>Si–O bond length (Å)</th>
<th>Ni (e)</th>
<th>O (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 ML</td>
<td>2.00, 2.06</td>
<td>0.038, 0.033</td>
<td>0.230</td>
<td>2.25</td>
<td>0.142</td>
<td>0.087</td>
<td>1.62, 1.64, 1.66</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 ML</td>
<td>1.99, 2.06</td>
<td>0.025, 0.027</td>
<td>0.247</td>
<td>2.25</td>
<td>0.143</td>
<td>0.085</td>
<td>1.61, 1.62, 1.66</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9 ML</td>
<td>1.98, 2.06</td>
<td>0.033, 0.029</td>
<td>0.259</td>
<td>2.25</td>
<td>0.146</td>
<td>0.084</td>
<td>1.61, 1.62, 1.66</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^\dag\)Interfacial bond lengths (Å) and the maximum site-projected charge differences (e), between the atoms involved in bonding in the interface environment and the corresponding atoms at an isolated surface, are indicated. Positive values indicate an increase in electronic charge at the interface.

---

**Table II. Comparison of the (Shortest) Interfacial Bond Lengths and the Maximum Site-Projected Charge Differences (between the Atoms Involved in Bonding in the Interface Environment and at an Isolated Surface) at the Interface of Ni(111) with Three ML of the Oxide Ceramics\(^\ddagger\)**

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Ni–O bond length (Å)</th>
<th>Ni (e)</th>
<th>O (e)</th>
<th>Ni–X bond length(^\ddagger) (Å)</th>
<th>Ni (e)</th>
<th>X (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(_2)O(_3)</td>
<td>2.37</td>
<td>0.00 (0.02)</td>
<td>0.03</td>
<td>2.32</td>
<td>0.13 (0.20)</td>
<td>0.04</td>
</tr>
<tr>
<td>ZrO(_2)</td>
<td>2.02</td>
<td>(0.15)</td>
<td>0.17</td>
<td>2.88</td>
<td>(0.18)</td>
<td>0.05</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>2.00</td>
<td>0.04 (0.09)</td>
<td>0.23</td>
<td>2.25</td>
<td>0.14 (0.24)</td>
<td>0.09</td>
</tr>
</tbody>
</table>

\(^\ddagger\)No atomic site exhibits charge loss in the interface environment. Projection radii for ZrO\(_2\) are described elsewhere.\(^{52}\) Charge on Ni shows the values obtained using 1.23 Å (1.37 Å) projection radii. \(^\ddagger\)X is Al, Zr, or Si.
report the bond lengths and the corresponding charge projected onto each of the two atomic sites in the bond relative to the projected charge on those atoms immediately on interface cleavage. One important feature in this table is the weak Ni–O interactions of the Al₂O₃/Ni interface; i.e., the Ni–O “bond” is much longer than that formed with the other two oxides, and neither the O nor the Ni experience a dramatic change in projected charge relative to the isolated surface environment. Conversely, the Si and O in the SiO₂/Ni interface experience the greatest charge increases, relative to the cations and oxygens of the other oxides, and also form the shortest bonds with Ni. Specific choices of integration radii do affect the reported “charge gain”; nevertheless, the more favorable Ni–Si and Ni–O interactions in silica (short bonds and “shared” charge gain) and the unfavorable Ni–O interactions in alumina are consistent with the calculated adhesion trends.

At first glance, it might seem incorrect for all atomic sites to experience a “reduction” in the interface environment, such as is indicated in Tables I and II. In fact, this is not contradictory. As mentioned earlier, the projection radii for the atomic sites are not designed to be space filling—this would result in entirely unphysical results for open crystal structures and especially for surface and interface supercells that contain a vacuum region. Rather, the projection spheres indicate a region around each atomic site where the electron density reasonably can be associated with that particular site. This means that there is electron density unaccounted for in the interstitial regions; likewise, there is some flexibility in a “reasonable” choice of integration spheres. Of course, ionic and covalent bonding effects contribute to the charge difference. The general charge increase in the interface environment is primarily related to more localized electron density in the interface environment, in contrast to the surface exponential decay that is exhibited by insulating ceramics and the power-law decay of the electron density away from the surfaces of conducting metals.²⁵

Figure 2 displays a cross section of the electron density difference between the interface and the sum of the densities of the isolated surfaces (with the same atomic structure as the interface, i.e., where the other side of the interface has been “instantaneously” removed) for the 9-ML silica coating on the Ni(111) substrate. The lighter regions correspond to a decrease in electron density, and the darker regions represent an increase in electron density in the interface environment, with each contour corresponding to 6.7 × 10⁻² e/Å³. The total charge-density difference is conserved, i.e., equal to zero, within 1 × 10⁻⁶ e/Å³. Although Figs. 2(a) and (b) may appear to experience only charge gain, recall that these panels only display a specific perpendicular two-dimensional cut near an interfacial bonding region. For regions that do not intersect bonded forms across the interface, there is a slight decrease in the delocalized density spilling into the vacuum region relative to the two surfaces. The gray background represents effectively no change (within 1 × 10⁻³ e/Å³). Relevant nuclear positions are indicated by arrows, with these positions periodically repeating along the interface. Generally, the density perturbations appear fairly minor and highly localized to the interface region. Figure 2(a) displays a cut near interfacial Ni–O bonding. Significant gain in the charge density on the O site is not apparent, which allows us to exclude dramatic NiO ionic bonding, although Table I shows an increase in electronic charge of 0.25 e on the O site. This increase is partially due to overlap with the Ni, because of the short (1.98 Å) bond that is formed between the Ni and O at the interface. Such a short bond suggests that strong Ni–O closed-shell repulsions are not present, as is also suggested by what appear to be minor charge density perturbations at the interface. Figure 2(b) displays a similar cut near an interfacial Ni–Si bond. A local Ni–Si bonding region, i.e., density buildup between the Ni–Si nuclei, is apparent in Fig. 2(b). The features in both plots suggest that covalent bonding, rather than charge transfer, may account for the site-projected charge increases on all atoms in the interface environment and the dramatic energetic stabilization that results from interface formation.

Fig. 2. Cross-sectional slice of the charge density difference between the SiO₂/Ni interface and the sum of the isolated SiO₂ and Ni slabs (a) near the Ni–O bonding region and (b) near the Ni–Si interfacial bond. Locations of the relevant nuclei are indicated by arrows. Same gray scale is used in all plots. Light regions indicate charge density loss; dark regions correspond to charge density gain at the interface relative to the sum of the isolated surfaces.
the surface states; these features disappear in the interface environment. This region does not correspond to typical surface gap states of the SiO$_2$(0001) surface; instead, these are features unique to the unrelaxed atomic coordinates of the cleaved SiO$_2$ film. Likewise, the lone-pair states near 0.0 eV of the surface O are a strong feature of the third panel in Fig. 3. Perhaps more interestingly, new occupied states, whose position is indicated by the dashed line near $\sim 6.5$ eV, appear in the interface environment. These new interface states show contributions from mixed Ni $s$ and $d$ states and O $p$ states in the Ni–O bond and Ni states of primarily $s$ character, with states of mixed $s$ and $p$ character on the Si, for the Ni–Si bonds, indicating localized Ni–O and Ni–Si bonding of covalent nature. Naturally, this feature is not present in any of the isolated surface local DOS projections.

Figure 4 displays the local DOS for the atoms involved in Ni–O and Ni–Al interactions (corresponding to the Ni, O, and Al of the Al$_2$O$_3$ row in Table II) at the Al$_2$O$_3$/Ni interface and in those corresponding cleaved surfaces. In contrast to the significant modification of the local DOS in the SiO$_2$/Ni interface, these plots for the Al$_2$O$_3$/Ni interface display less dramatic modifications. No additional new states appear on interface formation, unlike the case of SiO$_2$/Ni. The primary change to the local DOS in this interface structure is a shift to lower energy of the O and Al states in the interface environment. This is due to nickel screening of the Madelung potential imposed by the ceramic film and does not indicate local bonding interactions. These local DOS offer further confirmation to conclusions drawn from Table II, where Al$_2$O$_3$/Ni was anticipated to exhibit the weakest Ni–O bonding interactions.

The increased Ni–O bonding in SiO$_2$/Ni, relative to Al$_2$O$_3$/Ni, is likely to provide a major contribution to the three-times-larger adhesion calculated for the SiO$_2$/Ni interface over the Al$_2$O$_3$/Ni interface. In TBC applications, one mechanism that leads to spallation of the ceramic coating is void formation at the interface; in particular, the local electronic structure of the interface oxygens is modified significantly. The fairly strong may enhance failure at this site in TBCs. Increased local bonding at the SiO$_2$/Ni interface might inhibit such void formation and provide a preferable layer for oxidative protection, at least from a microscopic standpoint. Phase transitions and diffusion mechanisms are also crucial aspects of the macroscopic behavior of the coating. Based on our calculations, we suggest forms of silica-based TGO coatings could improve the lifetime of TBC operation by inhibiting oxide growth, void formation, and subsequent spallation. Such applications are also likely to require favorable ZrO$_2$–SiO$_2$ interactions; otherwise, the preferred failure site would merely be translated to an outer interface of the TBC. Accordingly, we investigate this ceramic/ceramic interface in the next section.

(3) ZrO$_2$(111)/SiO$_2$(0001) Interface

Achieving a small misfit when matching the surfaces of $\alpha$-quartz(0001) with ZrO$_2$(111) requires a fairly large unique interface area (83.62 Å$^2$). The periodic cell for a 3-ML ZrO$_2$(111) coating on SiO$_2$(0001) is shown in Fig. 5. The interface matching chosen for the $c$-ZrO$_2$(111)/SiO$_2$(0001) interface imposes a mismatch of only 1.9%. Maintaining a low misfit is crucial, because energy-dissipating mechanisms such as slip planes are not permitted by the periodic boundary conditions imposed with the calculation supercell. Similar to the surface terminations studied in the ZrO$_2$(001)/Si–Al$_2$O$_3$(1102) interface study of Christensen and Carter, the SiO$_2$ and ZrO$_2$ surfaces are both oxygen-terminated to create stoichiometric, nonpolar surfaces. Such surfaces should result in a lower bound estimate for interface adhesion and reactivity: there is no strong chemical potential or polarity driving force to promote adhesion and/or new phase formation at the interface, and O–O bonding is not expected.

We find that the adhesion energy at this $c$-ZrO$_2$(111)/$\alpha$-SiO$_2$(1001) interface is quite high: $\sim 2.8$ J/m$^2$ for the thickest ZrO$_2$ film studied (3 ML, $\sim 7.5$ Å thick). This value is more than a factor of 2 larger than the calculated adhesion at the ZrO$_2$/Al$_2$O$_3$ interface with a ZrO$_2$ film of similar thickness! Likewise, it is larger than the surface energies of either the SiO$_2$(0001) or ZrO$_2$(111) films. Local interfacial bonding interactions account for this dramatic increase in adhesion at the interface of ZrO$_2$ with SiO$_2$, relative to that with Al$_2$O$_3$. As we shall see, the ZrO$_2$/SiO$_2$ interface exhibits dramatic rearrangement of the atomic coordinates at the interface; in particular, the local electronic structure of the interfacial oxygens is modified significantly. The fairly strong
covalent nature of the Si–O bond provides an explanation for this, with the local electronic structure of O in bulk SiO₂ being better approximated by O⁻ than O²⁻, hence permitting additional bonding with increased coordination. As mentioned earlier, because of the complexity of the interface supercell, the interface structures we have found likely represent local minima on the potential-energy surface. However, finding more stable minima would only serve to increase the interface adhesion energy; hence, the comparisons to ZrO₂/Al₂O₃ and the results discussed here merely indicate the nearest neighbor across the interface, where atoms are labeled according to the unique atomic sites on either side of the interface; i.e., Si(1) corresponds to the fourth unique silicon interfacial site, O(Si-1) corresponds to the first of four unique O sites associated with the SiO₂ side of the interface, O(Zr-1) corresponds to the first of seven unique interfacial O sites associated with the ZrO₂ side of the interface, etc. (see Fig. 5).

On the SiO₂ side of the interface, all Si and O interfacial sites form favorable bonds, except in the case of Si(2), where the nearest interfacial atom is a distant (3.33 Å) Zr atom. This Si(2) is also the only atomic site on the SiO₂ side of the interface that does not gain projected charge in the interfacial environment. The more open interface region, corresponding to O atoms that were originally associated with the SiO₂ and ZrO₂ slabs, respectively.

![Fig. 5. Periodic cell of the 3-ML ZrO₂(111) coating on SiO₂(0001). In the SiO₂ region the Si atoms are represented by light-orange, larger spheres, and the O atoms are indicated by dark-orange, smaller spheres. In the ZrO₂ region, the Zr atoms are shown as light-blue stick-spheres, and the O atoms are indicated by red spheres. Substrate and coating slabs away from the interface are shaded, and the periodically unique atomic coordinates at the interface are indicated as “Interface atoms.” Local details of interface bonding are presented in Table III. Interface atoms referenced to in Table III include (i) Si₁₋₃₋₄₋₅, the orange spheres in the interface region; (ii) Zr₁₋₇₋₅₋₆, the blue spheres in the interface region; and (iii) Oₙ₋₇₋₈, the red spheres in the interface region, corresponding to O atoms that were originally associated with the SiO₂ and ZrO₂ slabs, respectively.](#)

Table III. Site-Projected Charge Differences between Atoms at the SiO₂/ZrO₂ Interface and Those Atoms in the “Instantaneously” Cleaned Surfaces†

<table>
<thead>
<tr>
<th>Site</th>
<th>Charge (e)</th>
<th>Bonded to</th>
<th>Bond length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si₁₋₃₋₄₋₅</td>
<td>0.17</td>
<td>O(Zr-3)</td>
<td>1.64</td>
</tr>
<tr>
<td>O(Si₁₋₃)</td>
<td>0.36</td>
<td>Zr(3)</td>
<td>2.05</td>
</tr>
<tr>
<td>Si₂₋₃</td>
<td>-0.03</td>
<td>(Si₃₋₅₋₆)</td>
<td>(3.33)</td>
</tr>
<tr>
<td>O(Si₂₋₃)</td>
<td>0.20</td>
<td>Zr(4)</td>
<td>2.13</td>
</tr>
<tr>
<td>Si₃₋₅₋₆</td>
<td>0.21</td>
<td>O(Zr-6)</td>
<td>1.59</td>
</tr>
<tr>
<td>O(Si₃₋₅₋₆)</td>
<td>0.33</td>
<td>Zr(1)</td>
<td>2.12</td>
</tr>
<tr>
<td>Si₄₋₅₋₆</td>
<td>0.19</td>
<td>O(Zr-7)</td>
<td>1.61</td>
</tr>
<tr>
<td>O(Si₄₋₅₋₆)</td>
<td>0.36</td>
<td>Zr(7)</td>
<td>2.02</td>
</tr>
<tr>
<td>Zr₁₋₇₋₅₋₆</td>
<td>0.01</td>
<td>O(Si-3)</td>
<td>2.12</td>
</tr>
<tr>
<td>O(Zr₁₋₇₋₅₋₆)</td>
<td>0.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr₂₋₅₋₆</td>
<td>-0.15</td>
<td>(Si₃₋₅₋₆)</td>
<td>(3.33)</td>
</tr>
<tr>
<td>O(Zr₂₋₅₋₆)</td>
<td>0.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr₃₋₅₋₆</td>
<td>0.05</td>
<td>O(Si₁₋₃)</td>
<td>2.05</td>
</tr>
<tr>
<td>O(Zr₃₋₅₋₆)</td>
<td>0.56</td>
<td>Si₁₋₃</td>
<td>1.64</td>
</tr>
<tr>
<td>Zr₄₋₅₋₆</td>
<td>0.05</td>
<td>O(Si₂₋₃)</td>
<td>2.13</td>
</tr>
<tr>
<td>O(Zr₄₋₅₋₆)</td>
<td>0.38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr₅₋₇₋₆</td>
<td>-0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(Zr₅₋₇₋₆)</td>
<td>0.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr₆₋₇₋₆</td>
<td>-0.10</td>
<td>(Si₃₋₅₋₆)</td>
<td>(3.47)</td>
</tr>
<tr>
<td>O(Zr₆₋₇₋₆)</td>
<td>0.63</td>
<td>Si₃₋₅₋₆</td>
<td>1.59</td>
</tr>
<tr>
<td>Zr₇₋₆₋₇</td>
<td>0.10</td>
<td>O(Si₄₋₅₋₆)</td>
<td>2.02</td>
</tr>
<tr>
<td>O(Zr₇₋₆₋₇)</td>
<td>0.59</td>
<td>Si₄₋₅₋₆</td>
<td>1.61</td>
</tr>
</tbody>
</table>

†Bond lengths and interfacial atoms involved in those bonds are also indicated. Atoms are labeled according to the unique atomic sites on either side of the interface, i.e., Si₁₋₃₋₄₋₅ corresponds to the fourth unique silicon interfacial site, O(Si₁₋₃) corresponds to the first of four unique oxygen sites associated with the silica side of the interface, O(Zr₁₋₇₋₅₋₆) corresponds to the first of seven unique interfacial oxygen sites associated with the zirconia side of the interface, etc. Cases with bond lengths in parentheses merely indicate the nearest neighbor across the interface, where the long length suggests a conventional “bond” is not formed with this coordination.
structure of the SiO₂ does not allow for complete interfacial bonding for all atoms from the ZrO₂ side of the interface. This can be seen in that O₂ (Zr-3) –O₂ (Si-2), O₂ (Zr-3), and O₂ (Zr-5), as well as Zr (5) (and effectively Zr (6)), do not gain coordination from the SiO₂ surface in the relaxed interface structure. Nevertheless, even the O sites that do not experience any increased coordination display significant charge gain (0.25–0.38 e) in the interface, relative to the surface. The O sites that do experience increased coordination, by forming bonds with Si at the interface, experience an even larger (0.56–0.63 e) increase in local charge as a result, consistent with the electropositive nature of silicon. This occurs somewhat at the expense of the Zr to which the O are bonded for Zr (2) and Zr (6) positions, which are bonded to O₂ (Zr-7) and O₂ (Zr-6), respectively.

Table IV shows the lengths of the interface bonds formed at the ZrO₂/Al₂O₃ and the ZrO₂/SiO₂ interfaces and the bulk crystal equilibrium bond lengths of several corresponding oxides. In both ceramic/ceramic interfaces, bond lengths near the optimum values for bulk α-quartz, α-Al₂O₃, and t- or m-ZrO₂ are formed across the interface. Bond lengths alone cannot explain the more than twofold increase in adhesion of the ZrO₂/SiO₂ interface, relative to ZrO₂/Al₂O₃. The charge difference evaluated in the ZrO₂/Al₂O₃ study was very small, with maximum differences of ~0.05 e on the interfacial Zr and 0.06 e on the zirconia O. We cannot compare these charge differences directly with those we computed for the ZrO₂/SiO₂ interface, because the integration spheres were chosen in a very different manner. Qualitatively, the values of Table III indicate that the charge redistribution at the ZrO₂/SiO₂ interface is significantly greater, with some sites experiencing differences that are a factor of 10 larger than those reported for the ZrO₂/Al₂O₃ interface!

Table IV. Lengths of Interfacial Bonds Formed at the ZrO₂/Al₂O₃ and ZrO₂/SiO₂ Interfaces, and Bulk Crystal Equilibrium Bond Lengths of Several Corresponding Oxides

<table>
<thead>
<tr>
<th>Material(s)</th>
<th>Bond length (Å)</th>
<th>Zr–O</th>
<th>Zr–Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO₂/SiO₂</td>
<td>1.59–1.64</td>
<td>2.02–2.13</td>
<td>3.33–3.47</td>
</tr>
<tr>
<td>ZrO₂/Al₂O₃</td>
<td>1.91</td>
<td>2.09</td>
<td>2.98, 3.05</td>
</tr>
<tr>
<td>α-Al₂O₃</td>
<td>1.87</td>
<td>2.10</td>
<td>2.98, 3.05</td>
</tr>
<tr>
<td>α-SiO₂</td>
<td>1.61</td>
<td>2.22 (c), ~2.06 (m), ~2.10 (f)</td>
<td></td>
</tr>
</tbody>
</table>

*Letters in parentheses (c, m, and f) denote cubic, monoclinic, and tetragonal, respectively.*
types of cations, the resulting electronic structure indicates the interfacial O atoms are reduced in the interface environment and become more ZrO$_2$-like.

IV. Conclusions

In previous studies, we investigated the ideal interfaces formed between Al$_2$O$_3$/Ni and ZrO$_2$/Al$_2$O$_3$. Both interfaces exhibited weak adhesion; this was especially dramatic in the case of thicker Al$_2$O$_3$ films on the metal substrate. We postulated that an inherent atomic-level weakness of such interfaces was due to closed-shell repulsions. For Al$_2$O$_3$/Ni, these arise from the O anions and the nearly filled d shell of the Ni; in the case of ZrO$_2$/Al$_2$O$_3$, the significant ionic character to the bonding in both oxides results in effectively closed-shell O anions. To minimize such effects at these interfaces, we investigated the effect of doping the Al$_2$O$_3$/Ni

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**Fig. 6.** Electron density difference plots for 2D slices perpendicular to the ZrO$_2$/SiO$_2$ interface for (a) a Zr–O bond, (b) a Si–O bond, and (c) a Zr–O bond formed with no increased O coordination on the Si. Same gray scale used in all plots.
interface with early transition metals, which have open $d$ shells. These modifications to the local electronic structure of the interface dramatically increased interface adhesion. We also speculated that closed-shell repulsions at heterogeneous interfaces might be alleviated with modification of the O anion electronic structure in the oxide. To this end, we have investigated the interfaces of nickel and ZrO$_2$ with a more covalently bonded oxide, SiO$_2$.

We presented the detailed interactions that occur at an interface between the late transition metal (nickel) and a ceramic with significant covalent character in its bonding (SiO$_2$). The significantly increased interface adhesion of the SiO$_2$/Ni interface, compared with the Al$_2$O$_3$/Ni interface (three times stronger!), appears to arise from local bonding of predominantly polar covalent character. In particular, the Ni–O interactions, which appear repulsive in Al$_2$O$_3$/Ni, are more favorable with SiO$_2$. The more covalent nature of SiO$_2$ results in reduced repulsions between the Ni $3d$ shell and the O atoms in SiO$_2$, as well as more covalent Ni–O bonding. We speculate that the increased local bonding and adhesion for the SiO$_2$ coating should inhibit void formation at this interface, relative to those formed with more ionic oxides that exhibit repulsive Ni–O interactions.

Our investigation of the ZrO$_2$/SiO$_2$ interface shows stronger bonding than that exhibited by the interface of zirconia with the more ionic Al$_2$O$_3$ substrate. The stoichiometric ZrO$_2$ does not reduce the SiO$_2$, as might be expected for a ZrO$_{2-x}$ oxide; however, the interfacial O ions that are associated with both the SiO$_2$ and ZrO$_2$ sides of the interface do exhibit electronic structures that are more similar to bulk O ions in ZrO$_2$. Increased ionic character to the interfacial O-cation bonding permits less rigid geometric requirements for these interfacial bonds, which minimizes strain at the interface. The “amorphous” bonding (in that the Si–O and Zr–O bond lengths are not uniform) across the interface serves to increase local coordination of both Si and Zr, thus resulting in a large ZrO$_2$/SiO$_2$ ideal work of adhesion. We find very strong bonding at this interface, as might have been anticipated from SEM and TEM studies of ZrO$_2$ films on glass ceramics and the slight negative enthalpy for SiO$_2$ reacting with ZrO$_2$.

At elevated temperatures, it can be expected that both the SiO$_2$/Ni and the ZrO$_2$/SiO$_2$ interfaces will be somewhat reactive. The heats of formation per mole of O indicate that the most stable oxide of Ni is over 200 kJ less stable than SiO$_2$, while SiO$_2$ is only ~50 kJ less stable than ZrO$_2$ per mole of O. Our results for the interface of nickel with SiO$_2$, as well as with Al$_2$O$_3$ and ZrO$_2$, suggest that chemical bonding provides a significant source of interface strengthening, even at 0 K and in the absence of a new reaction phase. Nonreactive interfaces can form weak, strained bonds with minimal internal bonding strains within the ceramic and/or metal; in the case of stronger interface interactions, interface bonding may be sufficiently favorable even to allow for slight straining of the intracermic or intrametal bonding, as seen at the SiO$_2$/Ni interface.
Although many TBC performance goals have been understood for decades, optimizing the performance of these coatings for particular applications remains an active area of research. As mentioned earlier, silica coatings have shown very favorable oxidation/corrosion protection on certain alloys, and mullite coatings display promise in protecting silicon carbide and silicon nitride ceramics. To our knowledge, silica or mullite coatings have not been well-studied for nickel-based superalloy applications with YSZ thermal protective coatings. Of course, temperature effects are likely to play an important role, and SiO2 phase changes under extreme thermal cycling may limit practical applications of such protective oxide. However, in TBC applications, the YSZ top coat will provide some thermal protection to both the underlying oxides and the metal alloy substrate, hence limiting the extreme temperatures to which the SiO2 might be exposed. The favorable local adhesion at these interfaces suggests such coatings might exhibit improved resistance to debonding, void formation, and subsequent spallation under thermal cycling conditions.

Acknowledgment

The authors thank Prof. Rick Garfunkel for helpful discussions regarding the suitability of SiO2 as a low-oxygen-mobility oxide.

References

Emily A. Jarvis currently is sponsored by the American Chemical Society to serve as a Congressional Science Fellow in the U.S. Senate through the American Association for the Advancement of Science. Dr. Jarvis earned her doctorate while working in Professor Emily Carter’s research group at UCLA. Her research employed density functional calculations to investigate atomic-level aspects of materials failure and to suggest chemical modifications designed to improve materials performance. In particular, this work focused on enhancing adhesion at metal/ceramic interfaces for high-temperature applications. Dr. Jarvis’ research received several awards, including the Materials Research Society Gold Award and the UCLA Physical Chemistry Dissertation Award.

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