Ab initio study of Al-ceramic interfacial adhesion

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We present a small database of adhesion energies for Al/ceramic interfaces calculated using density functional methods. In total, 26 distinct interface geometries were examined, in which the ceramic component was varied amongst carbides (WC, VC), nitrides (VN, CrN, TiN), and oxides (α-Al₂O₃), while including variations in interfacial stacking sequence and ceramic termination (polar and nonpolar). We find that adhesion is smallest (largest) for those interfaces constructed from non-polar (polar) surfaces, regardless of ceramic component. Since the interfacial free energies of all interfaces are relatively small, we examine the extent to which adhesion can be described solely by contributions from the surface energies.

Interfaces between metals and ceramics play a vital role in many industrial applications:1 heterogeneous catalysis, microelectronics, thermal barriers, corrosion protection, and metals processing are but a few representative examples. Nonetheless, experimental complications associated with the study of a buried interface, and theoretical difficulties arising from complex interfacial bonding interactions have hindered the development of models capable of predicting fundamental interfacial quantities. Recently, advances in ab initio simulation techniques and the development of high resolution experimental probes have made interfacial studies more tractable, as evidenced by the appearance of several papers2–11 addressing the issue of metal-ceramic adhesion.1 However, with the exception of only one study,7 all of these focused on but one or two particular interface systems. These works have provided valuable insight into the atomic and electronic structure of several different interfaces, but the disparity of methods and approximations used (especially in the context of the ab initio calculations) can lead to difficulty in comparing results obtained by different groups and consequently inhibit a more fundamental understanding of interfacial properties.

Here we present a small database of adhesion energies for Al/ceramic interfaces compiled both from our earlier reports12–14 and new calculations on CrN(100), TiN(100), and WC(11̅2̅0). We have endeavored to be consistent in our methodology by using a uniform set of calculation parameters for all systems considered. This is significant because earlier studies have, for example, revealed discrepancies between results obtained with different exchange-correlation functionals.7,12 We have chosen to focus on Al as the metallic component because it is fairly representative of free electron metals, and it receives widespread use in practical applications ranging from microelectronics to structural materials. For ceramics, we have intentionally selected a broad class of compounds [oxides (α-Al₂O₃), carbides (WC, VC), and nitrides (VN, CrN, TiN)], and have examined various interfacial stacking sequences and surface terminations in order to make our survey as general as possible. It is hoped that such a broad sampling would facilitate predictions of interfacial properties through the identification of numerical correlations; for example, based on our results we examine the extent to which adhesion can be attributed to contributions from the surface energies alone. On the other hand, by varying the ceramic component, several of the microscopic properties relevant to interfacial adhesion change simultaneously (crystal structure, surface termination, metalloid atom), thereby complicating an analysis of trends in these underlying quantities. An analysis of these issues—although extremely important—is beyond the scope of this Brief Report, and we refer the reader instead to Refs. 15 and 16.

A fundamental quantity which influences the mechanical properties of an interface is the work of separation \( \mathcal{W}_{\text{sep}} \) (Ref. 1) (also commonly referred to as the “ideal work of adhesion”) which is defined as the energy required to break interfacial bonds and reversibly separate the interface into two free surfaces, neglecting diffusion and plastic deformation. (The degree of plastic deformation which occurs during interfacial fracture is known to depend upon \( \mathcal{W}_{\text{sep}} \).) Formally, \( \mathcal{W}_{\text{sep}} \) is defined either in terms of the surface and interfacial energies, relative to the respective bulk materials, or by the difference in total energy between the interface and its isolated surfaces

\[
\mathcal{W}_{\text{sep}} = \sigma_{1v} + \sigma_{2v} - \gamma_{12} = (E_{1}^{\text{tot}} + E_{2}^{\text{tot}} - E_{12}^{\text{tot}})/A. \tag{1}
\]

Here \( \sigma_{iv} \) is the surface energy of slab \( i \), \( \gamma_{12} \) is the interface energy, \( E_{i}^{\text{tot}} \) is the total energy of slab \( i \), and \( E_{12}^{\text{tot}} \) is the total energy of the interface system. The total interface area is given by \( A \).

Although Eq. (1) defines \( \mathcal{W}_{\text{sep}} \) in terms of both the surface and interfacial energies, our calculations will illustrate that these quantities do not necessarily play an equal role. We find that since \( \gamma \) is generally small for these metal-ceramic systems, the strength of the interfacial bonding (and thus \( \mathcal{W}_{\text{sep}} \)) depends to a large extent upon the reactivity of the individual surfaces, as reflected by their surface energies. As large \( \sigma \)’s indicate the presence of energetically unfavorable features such as large surface dipoles and dangling bonds, these surfaces often reconstruct or seek to passify their dangling bonds by bonding to adsorbates or, when possible, other surfaces. Hence, to first approximation, knowledge of...
the σ’s alone enables one to make a rough prediction of the strength of interfacial bonding and $V_{sep}^-$. For this study we employ density functional theory (DFT),18,19 as implemented in the Vienna *ab initio* simulation package (VASP).20 VASP uses a plane-wave basis set for the expansion of the single particle Kohn-Sham wavefunctions, and pseudopotentials21,22 to describe the computationally expensive electron-ion interaction. Sampling of the irreducible wedge of the Brillouin zone is performed with a Monkhorst-Pack grid of special k-points.23 Ground state atomic geometries for all interfaces and surfaces were obtained by minimizing the Hellman-Feynman forces to a tolerance of 0.05 eV Å⁻¹ per atom. All calculations employed the generalized gradient approximation (GGA) of Perdew and Wang.24

To ensure the precision of energies and geometries, k-point and planewave cutoff energy convergence tests were performed, resulting in total energies which were converged to within 1–2 meV per atom. The accuracy of the pseudopotential approximation was assessed by performing calculations on the bulk phases of all materials used in this study. The results of these calculations are compiled in Table I and compared with available experimental data; consistent with other GGA-DFT studies, we find excellent agreement. More detailed accounts of the pseudopotential implementations and convergence testing can be found elsewhere.12–14

As our goal was to simulate surfaces and interfaces of bulklike materials, additional checks were performed to ensure that the slabs comprising each interface were sufficiently thick to exhibit a bulklike interior. In order to accurately evaluate surface energies (see Table II) we followed the method proposed by Boettger,28 which avoids the problem of non-convergence of σ with respect to slab thickness. Large slabs of up to 15 atomic layers were used. For the polar surfaces, $\alpha$-Al₂O₃(0001)⁰, WC(0001)⁴, and WC(0001)⁵ (superscripts indicate the termination), a nonstoichiometric slab must be implemented to allow for identi-
TABLE III. Interfacial orientation relationship, polarity (P = polar, NP = nonpolar), strain, interfacial free energy (\(\gamma\)), and \(\mathcal{W}_{\text{sep}}\). The terminations of the polar ceramic surfaces are indicated with a superscript. \(\mathcal{W}_{\text{sep}}\) values correspond to the optimal stacking sequences.

<table>
<thead>
<tr>
<th>Interface</th>
<th>Orientation</th>
<th>Polarity</th>
<th>Strain (%)</th>
<th>(\gamma) (J m(^{-2}))</th>
<th>(\mathcal{W}_{\text{sep}}) (J m(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al/(\alpha)-Al(_2)O(_3)(^{\text{Al}})</td>
<td>(111)[0(\bar{1})](_{\text{Al}})</td>
<td></td>
<td>(0001)(1(0\bar{1}))(_{\text{Al}_2\text{O}_3})</td>
<td>NP</td>
<td>4.9</td>
</tr>
<tr>
<td>Al/(\alpha)-Al(_2)O(_3)(^{\text{D}})</td>
<td>(111)[0(\bar{1})](_{\text{Al}})</td>
<td></td>
<td>(0001)(1(0\bar{1}))(_{\text{Al}_2\text{O}_3})</td>
<td>P</td>
<td>4.9</td>
</tr>
<tr>
<td>Al/WC(^{\text{W}})</td>
<td>(111)[0(\bar{1})](_{\text{Al}})</td>
<td></td>
<td>(0001)(1(1\bar{2}))(_{\text{WC}})</td>
<td>P</td>
<td>2.2</td>
</tr>
<tr>
<td>Al/WC(^{\text{C}})</td>
<td>(111)[0(\bar{1})](_{\text{Al}})</td>
<td></td>
<td>(0001)(1(1\bar{2}))(_{\text{WC}})</td>
<td>P</td>
<td>2.2</td>
</tr>
<tr>
<td>Al/WC</td>
<td>(110)[0(\bar{1})](_{\text{Al}})</td>
<td></td>
<td>(1(1\bar{2}))(_{\text{WC}})</td>
<td>NP</td>
<td>0.4</td>
</tr>
<tr>
<td>Al/VN</td>
<td>(100)[0(0\bar{1})](_{\text{Al}})</td>
<td></td>
<td>(100)[0(0\bar{1})](_{\text{VN}})</td>
<td>NP</td>
<td>2.3</td>
</tr>
<tr>
<td>Al/VN</td>
<td>(100)[0(0\bar{1})](_{\text{Al}})</td>
<td></td>
<td>(100)[0(0\bar{1})](_{\text{VC}})</td>
<td>NP</td>
<td>3.2</td>
</tr>
<tr>
<td>Al/CrN</td>
<td>(100)[0(0\bar{1})](_{\text{Al}})</td>
<td></td>
<td>(100)[0(0\bar{1})](_{\text{CrN}})</td>
<td>NP</td>
<td>0.5</td>
</tr>
<tr>
<td>Al/TiN</td>
<td>(100)[0(0\bar{1})](_{\text{Al}})</td>
<td></td>
<td>(100)[0(0\bar{1})](_{\text{TiN}})</td>
<td>NP</td>
<td>5.3</td>
</tr>
</tbody>
</table>

The generally small magnitude of \(\gamma\) is insensitive to the choice of metallic component, with \(\gamma < 2\) or less. The data are bracketed by horizontal error bars giving the range of possible \(\sigma\) listed in Table II. While the \(\mathcal{W}_{\text{sep}}\) data on the whole follow a roughly linear trend with respect to \(\sigma\), all but one of the data points fall to the right of the line. This reveals that bonding at these interfaces is on average weaker than in the respective bulk systems. The one system falling to the left of the line, and therefore having a negative \(\gamma\), involves the oxygen-terminated \(\alpha\)-Al\(_2\)O\(_3\) surface, which has the largest surface energy and \(\mathcal{W}_{\text{sep}}\). In an earlier paper\(^{12}\) we argued that the strong bonding at this interface could indicate the possibility of fracture within the Al rather than at the metal-ceramic junction, were the interface subjected to a tensile stress.

With the exception of TiN, the rocksalt-structured carbides and nitrdes (CrN, VN, and VC) exhibit the largest dependence of \(\mathcal{W}_{\text{sep}}\) upon the surface energies. These three systems have the smallest interfacial energies, only 0.03–0.18 J m\(^{-2}\), and their \(\mathcal{W}_{\text{sep}}\) s cluster in a nearly linear fashion along the bottom left of Fig. 1, close to the \(\gamma = 0\) line. Presumably, the smallness of \(\gamma\) for these interfaces can be explained by similarities between bulk and interfacial bonding, since both bulk components exhibit some degree of metallic bonding. We note that two earlier studies\(^{44,45}\) involving (Al/Ag/Ti)/\(\text{MgO}\) observed a similar dependence of \(\mathcal{W}_{\text{sep}}\) upon metallic surface energies. For Al/TiN, which is some-
what of an outlyer with respect to the other rocksalt ceramics, the \( \gamma \) contribution is larger, 0.62 J m\(^{-2}\), possibly due to the relatively large interfacial strain of 5.3%.

Figure 1 also illustrates that those interfaces involving \( \alpha\)-Al\(_2\)O\(_3\) and WC(1\(\overline{1}\)20) have \( \gamma_{\text{sep}} \)'s which are not as well described by surface energies alone (i.e., \( \gamma \) effects are more important). For the \( \alpha\)-Al\(_2\)O\(_3\) interfaces, as with TiN, a possible explanation for this behavior could be strain effects, which are also significant (4.9\%) for this system. In addition, the mainly ionic bonding in bulk \( \alpha\)-Al\(_2\)O\(_3\) differs substantially from that found in Al. While for the WC system the strain is low (0.4\%), and differences in the respective bulk bonding are less pronounced (WC is metallic), this model implements an incoherent, misfit geometry characterized by irregular bonding across the interface.

In summary, we have presented a small \textit{ab initio} database of adhesion energies for nine Al/ceramic interfaces, surveying several different interface terminations and bonding sites.

We show that the surface energies play a dominant role in determining the work of separation for these systems, as the interfacial energies are generally much smaller in comparison. In most cases, and in particular for those systems involving the cubic carbides and nitrides, \( \gamma_{\text{sep}} \) can be described largely in terms of surface energies alone. Exceptions to this rule arise mainly for systems characterized by relatively large interfacial strain or incoherent interfacial bonding. Knowledge of the surface energies could therefore serve as a reasonable starting point for the estimation of interfacial strength.

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46 We take CrN to be in its room-temperature paramagnetic state.
47 The Al/WC(1\(\overline{1}\)20) system contains a misfit: a (4\(\times\)1) surface of WC(1\(\overline{1}\)20) is interfaced to a (5\(\times\)1) Al(110). The large supercell needed for this calculation made a superlattice geometry impractical, and the interface was formed at only one surface of the WC.