Nature of Metal-Ceramic Adhesion: Computational Experiments with Co on TiC

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By means of first-principles computational experiments, the microscopic mechanism of metal-carbide adhesion is revealed. Density-functional-theory results for the Co/TiC(001) interface show the interface bonding to be dominated by Co-C bonds. The effective number of bonds is controlled by an interplay between lattice mismatch and relaxation effects. The particular strength of the Co-C bond is explained in terms of interface-induced features of the electronic states, in particular, a novel metal-modified covalent bond. The calculated adhesion strength agrees well with results of wetting experiments.

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Highly relevant in industry, the problem of metal-ceramic adhesion has attracted considerable attention in materials science in recent years. In particular, much theoretical [1–6] and experimental [7–9] effort has been directed towards rationalizing the adhesion strength in terms of the interface atomic and electronic structures. However, the major part of that work concerns the case of ceramic oxides, leaving many other important classes of metal-ceramic interfaces very poorly understood. One such class, of extreme importance in the hard-metal industry for sintering of Co-TiC(N) cerments, covers interfaces between transition metals and transition-metal carbides. This Letter reports on the first \textit{ab initio} theoretical study of a Co/TiC(001) interface, a representative case of metal-carbide systems.

While the majority of the oxides are insulating ionic crystals, the transition-metal carbides are characterized by covalent bonding mixed with metallicity and a slight ionicity [10]. Thus the mechanism of the metal-carbide adhesion is likely to differ essentially from the case of oxides. Yet it lacks understanding even at the qualitative level. Attempts to gain insight into that problem from observed trends in the wettability of carbides by liquid metals (reviewed in Ref. [11]) point at either ionic, covalent, or metallic bonding. For wetting by copper there is also a model that emphasizes dispersion forces [12], but its applicability is questioned [13]. Moreover, practically nothing can be said about the effects of the atomic coordination at the interface.

With the purpose of shedding some light upon those issues, we present first-principles computational experiments that allow us to trace how the adhesion strength originates from the specifics of the interface atomic and electronic structures. Especially interesting findings are related to the interface Co-C bonds. Those bonds are unexpectedly strong, and they play a crucial role for the energetics and atomic structure of the Co/TiC(001) interface. At the same time the strength of the Co-C bonds comes from intrinsically interfacial effects that can be clearly identified in the electronic structure.

Electron structure and total energies are calculated within the density-functional theory (DFT) [14–16], using the generalized-gradient approximation for the exchange-correlation potential in the Perdew-Wang 91 version [17]. This gives a reliable and accurate description of the ground-state properties of both transition metals [18,19] and titanium carbide [20]. The Kohn-Sham equations are solved self-consistently with the plane-wave pseudopotential method [21,22] implemented in the DACAPO code [23]. The ion cores are described by Vanderbilt ultrasoft pseudopotentials [24], with the nonlinear core corrections [25] for Co and Ti. Good absolute energy convergence, within 0.01 eV/atom, is reached with the plane-wave cutoff 26 Ry, and with the used \textit{k}-point samplings, which will be specified below.

The experimental prototypes of the Co/TiC(001) system are heteroboundary phases in the Co-TiC cerments [11] and the interface between liquid Co and TiC surface in wetting experiments [26]. In neither case the interface atomic coordination can yet be experimentally determined. However, the experimental conditions and the high, about 25%, lattice mismatch between Co and TiC make it very reasonable to assume the interface structure to be rather irregular. Thus theoretical modeling should focus on behaviors that are not particular to one ordering in the system but rather are retained from one structure to another. For extracting such general behaviors, an approach based on comparative analysis of different interface structures within a representative set of model systems is used.

The interface-model systems are chosen to balance the complexity of the realistic situations and the simplicity enforced by the computational limitations. TiC is kept in its NaCl structure and Co in the fcc structure, as in the Co-Ti(W)C systems [27]. The paramagnetic Co state is considered, a situation close to liquid Co on TiC. Co magnetism, treated elsewhere [28], does not modify our major conclusions, and the magnetic corrections to the interface energetics are well reproducible within a rigid-band approach, as for Co surfaces [29]. For simplicity, the Co(001)/TiC(001) orientation is considered. A further simplification—enforced by the computational method—is to use interface structures with rather high symmetry, at least periodic with a relatively small supercell size.
High-symmetry Co(001)/TiC(001) interface structures (Fig. 1) are generated by matching different unit cells of the TiC(001) and Co(001) surfaces, by relative rotation of those surfaces, and by adjusting the Co in-plane lattice constant. The TiC is much stiffer than Co, and thus its lattice parameters are kept as in unstrained bulk. The rotation states obtained in this way are denoted \( n \text{Co}/m \text{TiC} \), indicating that there are \( n \) surface atoms of Co per \( m \) surface atoms of Ti or C. Avoiding \((n, m)\) pairs that require large Co strain or large supercells, we confine ourselves to the \( 1 \text{Co}/1 \text{TiC}, 5 \text{Co}/4 \text{TiC}, \) and \( 8 \text{Co}/5 \text{TiC} \) rotation states, which correspond to 26\%, 12\%, and \(-1\%\) in-plane expansion of Co, respectively. Only interface translation states that retain the fourfold axial symmetry of the Co(001) and TiC(001) surfaces are considered. This gives two translation states, \( n \text{Co}/m' \text{TiC-I} \) and \( n \text{Co}/m' \text{TiC-II} \), for each \((n, m)\) pair. The rotation and translation states of all the considered model systems are summarized in Fig. 1.

The Co/TiC interfaces are modeled in a supercell geometry as periodic sequences of Co and TiC slabs, in a similar way as, e.g., in Ref. [2]. First the Co and TiC slabs are taken as ideal truncations of the corresponding bulk structures, and the inter slab distance is optimized to minimize the total energy of the system. Then all the atoms of the outermost layers of each slab are relaxed till the forces are less than 0.1 eV/Å. Most calculations are done with supercells containing three layers of each material (3 + 3 supercells). To assess the convergence with respect to the TiC surface layer, \( d_i \), defined as the distance between the outermost layers of each slab. The most illustrative examples are given by the simplest \( 1 \text{Co}/1 \text{TiC-I, II} \) systems (Fig. 1). For Co over \( C \) sites (1Co/1TiC-I) \( W_{\text{sep}} \) is an order of magnitude larger than for Co over Ti (1Co/1TiC-II). Such behavior points at a strong shortrange Co-C interaction at the interface, which indicates that there should be some strong chemical bonds between the interface Co and C atoms.

The \( 1 \text{Co}/1 \text{TiC} \) interfaces themselves are quite artificial systems because of the unrealistically large, 26\%, Co in-plane expansion required. With a more realistic strain there should be noticeably more Co surface atoms than the C sites of the TiC(001) surface can accommodate; i.e., there will be a mixture of different local configurations: Co over both C and Ti sites and also at some intermediate positions. Such mixtures are simulated by the more complex \( 5 \text{Co}/4 \text{TiC} \) and \( 8 \text{Co}/5 \text{TiC} \) interface structures (Fig. 1). The unrelaxed \( W_{\text{sep}} \) values for the complex interfaces are lower than for \( 1 \text{Co}/1 \text{TiC-I} \) because the interface incoherence introduced by the lattice mismatch restricts the number of possible Co-C bonds.

Atomic-structure relaxations are of key importance. For the \( 1 \text{Co}/1 \text{TiC} \) interfaces, and for the separated Co and TiC slabs, there are only slight changes in the structure and energetics. For the more complex interfaces the dominating relaxation effects are the changes of the Co-C and Co-Ti bond lengths at the interface (Fig. 2). Before relaxation those bond lengths are quite irregular. After relaxation, however, the Co-C distances approach 1.9–2.0 Å, close to \( d_i \) at the \( 1 \text{Co}/1 \text{TiC-I} \) interface. On the other hand, the Co-Ti distances shorter than 2.4 Å tend to increase towards that value. Strengthening of the Co-C bonds and weakening of the Co-Ti repulsion caused by the relaxation lowers \( E_{\text{int}} \) in Eq. (1) enough to give a significant increase of \( W_{\text{sep}} \) (Table I).

There is a particularly interesting finding: a C atom located under an interstitial of Co (5Co/4TiC-I and

![Image](https://example.com/image)

**FIG. 1.** Interface-model systems: position of the first Co layer with respect to the TiC surface layer. (a) 1Co/1TiC-I: Co over C; (b) 1Co/1TiC-II: Co over Ti; (c) 5Co/4TiC-I; (d) 5Co/4TiC-II; (e) 8Co/5TiC-I; (f) 8Co/5TiC-II.

<table>
<thead>
<tr>
<th>Interface</th>
<th>( d_i ) (Å)</th>
<th>( W_{\text{sep}} ) (J/m²)</th>
<th>Unrel</th>
<th>Rel</th>
</tr>
</thead>
<tbody>
<tr>
<td>1Co/1TiC-I</td>
<td>1.85</td>
<td>4.42 (4.47)</td>
<td>4.18</td>
<td>(4.27)</td>
</tr>
<tr>
<td>1Co/1TiC-II</td>
<td>2.4</td>
<td>0.68 (0.47)</td>
<td>0.46</td>
<td>(0.37)</td>
</tr>
<tr>
<td>5Co/4TiC-I</td>
<td>2.06</td>
<td>2.74</td>
<td>3.28</td>
<td></td>
</tr>
<tr>
<td>5Co/4TiC-II</td>
<td>2.08</td>
<td>2.60</td>
<td>3.25</td>
<td></td>
</tr>
<tr>
<td>8Co/5TiC-I</td>
<td>2.10</td>
<td>2.66</td>
<td>3.25  (3.45)</td>
<td></td>
</tr>
<tr>
<td>8Co/5TiC-II</td>
<td>2.10</td>
<td>2.67</td>
<td>3.22</td>
<td></td>
</tr>
</tbody>
</table>
Co bonding

8Co/5TiC(1) goes very deep into Co after relaxation. The displacement is up to 45%-60% of the TiC interlayer distance, until the Co-C bond length reaches 2.0 Å. Such a relaxation creates new Co-C bonds, with a concomitant reduction of the Ti-C bonds.

For all the considered complex Co/TiC interface models, the relaxed \( W_{\text{sep}} \) values are close to the adhesion work from wetting experiments [26], 3.64 J/m\(^2\) (at 1500 °C), only about 10% smaller. The value for the 8Co/5TiC-I interface with 5 + 5 supercells, \( W_{\text{sep}} = 3.45 \text{ J/m}^2 \), is even closer to the experimental value.

To understand the nature of the interfacial Co-C bond, those bonds are compared with the bonds in bulk CoC and TiC. The latter are dominated by \( \sigma \) hybridization between the metal \( d \) orbitals and the C-2\( p \) orbitals [32,33]. Among the 3\( d \)-transition-metal carbides, TiC has the largest cohesive energy, because its Fermi level lies between energies of the bonding and antibonding states. CoC is unstable experimentally but has been studied in DFT [32]. The cohesion in CoC is weaker than in TiC, due to substantial filling of the Co-C antibonding states. This trend is reproduced in our calculated cohesive energies: 7.3 and 5.8 eV/atom for TiC and CoC, respectively. However, the interface Co-C bonds are much stronger than both the Co-C and Ti-C bulk bonds. The calculated value of the TiC(001) surface energy, 1.84 J/m\(^2\) (unrelaxed), implies that the work required to cleave the 1Co/1TiC-I (Co over C) interface (Table I) is about 20% larger than the value for the TiC crystal along the (001) plane (3.68 J/m\(^2\)). Moreover, there are twice as many Ti-C bonds per unit area of the (001) plane in bulk TiC as Co-C bonds at 1Co/1TiC-I. Thus the interface Co-C bonds are about twice as strong as the bulk Ti-C bonds.

Another indication of the strength of the interface Co-C bonds is the described relaxation effects, i.e., that the Co-C bond lengths tend to their optimal values at the expense of the Ti-C bonds. The drastic difference between the interface and bulk Co-C bonds is an important stabilizing mechanism for the Co/TiC interfaces, which allows strong interface chemical bonding to coexist with low interface chemical reactivity, preventing CoC layer formation.

The strength of the Co-C interface bond manifests itself in several ways in the electron structure. Figure 3 displays the electron density for the 1Co/1TiC-I interface compared to bulk CoC, identifying a chemical bond between the interface Co and C atoms with an electron density about 40% higher than in the bulk Co-C or Ti-C bonds. The same applies to the densities of the Co-C bonds at the 5Co/4TiC and 8Co/5TiC interfaces (not shown). Such density distributions indicate the predominantly covalent character of the interface Co-C bonds.

Figure 4 shows the main components of the local density of states (LDOS) for the 1Co/1TiC-I interface and the bulk CoC and TiC. The latter (Figs. 4c and 4d) have separate LDOS regions of bonding and antibonding states. In the interface LDOS (Fig. 4a) the formation of interface Co-C bonding states shows a C-\( sp \) LDOS feature in an intermediate region between the C-\( sp \) LDOS peaks of bulk CoC and TiC, respectively. The Ti-C bonding states are partially suppressed. Figure 4b demonstrates that already in the subsurface layers of the Co and TiC slabs the LDOS is almost the same as in the corresponding bulk materials (Fig. 4d).

The strength of the interface Co-C bonds is too large to be explained by some change in the filling of the Co-C

FIG. 2. Unrelaxed (diamonds) and relaxed (filled circles) bond lengths (in Å) for different symmetry-independent Co-C and Co-Ti atomic pairs.

FIG. 3. Valence-electron density for the (100) cuts of the 1Co/1TiC-I interface (5 + 5-supercell) compared to bulk CoC (outside the ionic cores). The consecutive contours change by a factor of \( \sqrt{2} \), and the units are electrons/Å\(^3\). The dashed line is at 0.5 electrons/Å\(^3\).

FIG. 4. The calculated local density of states projected onto the atomic orbitals is shown for (a) the interface layers of 1Co/1TiC-I, (b) one layer away from the same interface, (c) Co and C in bulk CoC and for Ti in bulk fcc Ti, and (d) the corresponding bulk phases of Co and TiC.
bonding and antibonding states. There are interface-specific qualitative changes in the character of those states. These changes can be understood by analyzing how a bulk-type Co-C bond is modified when it is transferred into the interface environment. In bulk CoC the Co-C antibonding states are mainly localized around the Co atom, giving a sharp peak in the Co-d LDOS (Fig. 4c). At Co/TiC, around the interface Co atom there is a large concentration of metallic states from the surrounding Co, with energies all over the energy interval of the Co-C antibonding states. Under such conditions the Co-C antibonding states become delocalized in space and energy, in the same way as Co atomic states are delocalized into metallic states in bulk Co. Delocalization of the Co-C antibonding states reduces their antibonding effect and also provides more space for accumulation of the bonding states along the Co-C bond, resulting in a strong metal-modified covalent bond (Fig. 3). This picture makes the interface LDOS (Fig. 4a) show no pronounced resonances from the Co-C antibonding states and have Co-d components as in bulk Co (Fig. 4d) rather than as in bulk CoC (Fig. 4c).

In summary, extensive electron-structure calculations demonstrate that the main mechanism of the interface adhesion between Co and TiC(001) is the strong covalent Co-C bonds. The number of those bonds is lowered by the lattice mismatch, but this lowering is partially compensated for by creation of new bonds and strengthening of the existing ones upon the structure relaxation. The strength of the interface bonds is a manifestation of a novel intrinsically interfacial effect in the electronic structure: delocalization of the Co-C antibonding states due to coupling with the Co metallic states.

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