Strong interface adhesion in Fe/TiC

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(Received 2 February 2005; in final form 17 May 2005)

As an aid to understanding the superior toughness of Ti-modified steels provided by fine Ti(C, N) particles, first-principles full-potential linearized augmented plane wave (FLAPW) density functional calculations were performed on the Fe matrix/TiC particle interface. It was found that at equilibrium a strong covalent bonding between Fe–C is formed at the interface, and the magnetic moment of the interface Fe (1.98 μB) is reduced from that of the tetragonally strained structure (2.51 μB). We then calculated with a rigid separation model the separation energy curve and the force separation law for the Fe–C debonding process at the interface, which predicts 2.45 J m⁻² for the work of separation and 30.66 [GPa] for the force maximum. We also found that the strong Fe–C bond provides an interfacial fracture strength equal to that of the pure bcc Fe matrix. A clear picture is given for the microscopic origin of this strong metal/ceramic adhesion based on density of states (DOS) considerations. For a more realistic understanding of the Fe–C bonding, structural optimization calculations were performed at each separation distance. The effect of relaxation was found to be larger at short separation distances than in the large separation region, which leads to a crossover behavior in the separation energy curve from the elastically deformed to the clearly separated regime at a critical distance (~1.75 Å), and to a discontinuity in the force separation law. Despite this large relaxation effect, the work of separation, 2.52 J m⁻², is not changed much from that of rigid separation.

1. Introduction

The ultimate goal of steel research is to design new classes of high performance steels [1] with sufficient advances in fracture toughness and strength to visibly increase component life with minimal increase in cost. To this end, the control of dispersed inclusion phases within the Fe-based matrix plays a crucial role. It has been

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demonstrated [1] that a marked increase of fracture toughness can be achieved in Ti-modified steels with controlled dispersions of Ti nitrides (primary inclusions with size \( \sim 1 \mu m \)) and carbides (secondary particles \( \leq 0.1 \mu m \)). Bulk Ti(C, N) in the NaCl(B1) structure is a well-known hard material widely used for cutting tools and wear-resistant coatings. Its electronic structure [2] is characterized by strong hybridization between Ti 3p and C (or N) 2s2p orbitals, and clear bonding and antibonding peaks appear in the density of states (DOS) that are well separated by a pseudogap. Its valence-electron number is close to the optimal value: almost all (none) of the bonding (antibonding) states are occupied. Furthermore, it was found that the pdσ bonding state possesses extremely high resistance to shear strain [2]. In spite of these understandings of bulk Ti(C, N), a fundamental understanding of the role of Ti(C, N) particles in the Fe matrix is, however, not yet clearly established.

The problem of metal/ceramic adhesion has attracted considerable and growing interest in recent years [3–16] for its broad significance for materials technology. From the theoretical side, much effort has been devoted to the \textit{ab initio} determination of the adhesion strength. It is widely believed that the adhesion strength is best described by the \textit{ideal work of separation} [8], which is the reversible work to separate the interface into two free surfaces (separation energy in the infinite separation limit, \( W_\infty \)), and \( W_\infty \) has been calculated for several metal/ceramic interfaces. [8, 11–13]. Most of these studies, however, addressed ceramic oxides, while research on interfaces between metal and conductive-ceramics [such as Ti(C, N)] is still very limited.

Recently, Dudiy \textit{et al.} [17–20] investigated the Co/Ti(C, N) interface to gain insights into metal/ceramic adhesion. Using a plane-wave pseudopotential method, they discussed the energetics and electronic structure of Co/Ti(C, N)(001) and found that strong bonding between Co and (C, N) is formed at the interface. These authors also examined layer- and orbital-projected DOS (PDOS) and compared it with bulk fcc Co(C, N). From this analysis, they argued that the antibonding states clearly seen in bulk Co(C, N) are substantially broadened in energy and space when the Co–(C, N) bond comes to the interface, due to their coupling with the delocalized metallic states of Co and that this is the most important and fundamental mechanism for the unexpectedly strong Co–C bonding at the interface. Using

\[ W_\infty = (E_{sl1} + E_{sl2} - E_{int})/2A \] (1)

(where \( E_{int} \) is the total energy of the supercell with the interface, \( E_{sl1} \) and \( E_{sl2} \) are the total energies for the same supercell when one of the slabs is kept and the other is replaced by vacuum, and \( A \) is the interfacial area within one supercell), they calculated \( W_\infty \) for several interface geometries. For all the complex interfaces of Co/TiC, their calculated \( W_\infty \)'s are close (within 10%) to the work of adhesion from wetting experiments, 3.64 J m\(^{-2}\). For Co/TiN, their calculated values are 0.6–1.0 J m\(^{-2}\) lower than those for Co/TiC. Like others, these authors used the ideal work of separation as measures of the interface energetics. Also, Arya and Carter [21] studied bulk TiC, bulk Fe, their low index surfaces, as well as one Fe/TiC interface using a plane-wave pseudopotential method. With a careful study of stability on the TiC and bcc Fe surfaces, they selected Fe(110)/TiC(100) interface for the calculations,
which shows a lattice misfit of \( \sim 2.1\% \). Using equation (1) with \( A \) instead of \( 2A \) (they have only one interface), these authors calculated the work of adhesion by changing the number of TiC layers up to three. Their calculated work of separation is larger for 1 TiC layer (3.99 J m\(^{-2}\)) than for the others (2.57 J m\(^{-2}\) for 2 TiC layers, and 2.55 J m\(^{-2}\) for 3 layers).

In this work, to obtain some understanding of the role of the fine particles of TiC in the Fe matrix, we have performed first-principles calculations on the Fe/TiC interface, the same interface that Arya and Carter studied, but with a different orientation. Using a supercell modeled with \((\text{Fe})_4/(\text{TiC})_4/(\text{Fe})_4\) layers, we determined the electronic and magnetic structure at equilibrium. For the interface energetics, we took a different approach; instead of calculating \( W_\infty \) only, we inserted rigid separations at the interface with different separation distances and calculated the separation energies as a function of a separation distance. \( W_\infty \) is obtained as the separation energy in the infinite separation limit without using equation (1). This series of calculations serves to elucidate how the metal/ceramic interface actually behaves under separation and provides a more detailed insight about the adhesion strength than \( W_\infty \) itself. Also the force separation law can be obtained from these calculations, which is, together with the separation energy curve, a useful input for multiscale continua modeling in steel research. Finally, full structural optimizations were performed at each separation to see how the separation energy and the force separation law change with atomic relaxation.

This paper is organized as follows. Section 2 describes the methodology and the model system used in our calculations. The results of the calculations and discussion about the results are provided in section 3. Finally, we summarize our work in section 4.

2. Computational details

All calculations are performed with the highly precise all-electron full-potential linearized augmented plane wave (FLAPW) method [22, 23]. In the FLAPW method, many-body interactions between electrons are treated within either the local (spin) density approximation [L(S)DA] [24, 25] or the generalized gradient approximation (GGA) [26] in the framework of density functional theory. In the present work, we adopt GGA because it well describes many-body interactions between electrons for the bulk ground-state properties of transition metals and titanium carbides/nitrides [27, 28]. Core states were treated fully relativistically and valence states scalar relativistically. Fe 3d4s, Ti 3p3d4s, and C 2s2p electrons were treated as valence electrons, and muffin-tin (MT) sphere radii were chosen to be 2.1 (Fe), 2.2 (Ti), and 1.35 (C) atomic units (a.u.). Spherical harmonics with \( l \leq 8 \) were used inside the MT spheres to represent the charge density, potential, and augmented wave function. A cutoff of the plane-wave basis, \( K_{\text{max}} \) (in a.u.), was set so that the relation \( K_{\text{max}} R_{\text{ave}} \sim 8 \) is satisfied, where \( R_{\text{ave}} \) is the averaged MT sphere radius. In the interstitial region, a star-function is used to represent the charge density and potential with a cutoff, \( G_{\text{max}} \), of \( 2K_{\text{max}} + 2 \). The Monkhorst–Pack (MP) scheme [29], or the improved tetrahedron (IT) method [30], was applied to \( k \)-point summations, and convergence in terms of the number of irreducible \( k \)-points,
3. Results and discussion

3.1. Bulk properties of Fe and TiC, interface orientation and site preference

First, we determined the bulk properties of bcc Fe and B1 TiC with \( K_{\text{max}} = 4.0 \) for Fe and 4.3 for TiC. For \( k \)-point summations, the IT method was used with \((15, 15, 15)\) mesh points which gives \( n_k = 120 \) for both cases. To find the equilibrium lattice constant, we used a third-order polynomial to fit the total energy as a function of lattice constant, and the bulk modulus, \( B \), was obtained from its definition, 

\[
B = -V \frac{\partial P}{\partial V} = V \frac{\partial^2 E}{\partial V^2},
\]

where \( V \) is the volume of the unit cell, \( P \) pressure, and \( E \) the total energy. The results are summarized in Table 1. Our results agree well with other calculations [18, 27, 31, 32].

Next, for the interface orientation, we adopted the Baker–Nutting relation [35], which is often observed between bcc Fe and B1 carbides or nitrides. Since we focus on the Fe(001)/TiC(001) interface with the orientation \( (100)_{\text{bcc}} \parallel (110)_{\text{B1}} \), we used the smallest size of the in-plane cell with a fully coherent interface. Since this restriction gives a rather large lattice misfit (using the experimental lattice constants from Table 1), \( (\sqrt{2}a_{\text{Fe}} - a_{\text{TiC}})/a_{\text{TiC}} = -0.064 \) (the theoretical lattice constants give a misfit of \(-0.087\)), we determined a reasonable in-plane lattice constant by calculating the elastic energy cost for both Fe and TiC under tetragonal strain [36]: for \( \sqrt{2}a_{\text{Fe}} = a_{\text{TiC}} = 4.260 \text{Å} \), both Fe and TiC pay the same energy cost (65 meV), where the \( c \) lattice constant is 2.684 Å (Fe) and 4.437 Å (TiC). The strained coherent interface can be taken to represent the bonding behavior of the coherent patches that reside between primary interfacial dislocations in a structurally relaxed interface.

Regarding the interface geometry, we determined the site preference of Fe atoms at the TiC(001) interface by considering three types of interface positions for Fe: (a) on-top of the C site; (b) on-top of the Ti site; and (c) in the middle of the TiC square (cave site). Our two-dimensional (2D) FLAPW code [22] was applied to a film containing two layers of Fe and three layers of TiC [37]. Each Fe and TiC slab held its bulk-like structure (bct and fct, respectively), while all atoms were relaxed along

<table>
<thead>
<tr>
<th>Source</th>
<th>( a_0 ) [Å]</th>
<th>( B ) [Mbar]</th>
<th>( M ) [( \mu_\text{B} )]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Present work</td>
<td>2.831</td>
<td>1.92</td>
<td>2.17</td>
</tr>
<tr>
<td>Reference [31]</td>
<td>2.88</td>
<td>1.82</td>
<td>2.127</td>
</tr>
<tr>
<td>Reference [32]</td>
<td>2.84</td>
<td>1.86</td>
<td>2.17</td>
</tr>
<tr>
<td>Experiment [33]</td>
<td>2.86</td>
<td>1.72</td>
<td>2.12</td>
</tr>
<tr>
<td>TiC</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Present work</td>
<td>4.383</td>
<td>2.38</td>
<td>–</td>
</tr>
<tr>
<td>Reference [18]</td>
<td>4.33</td>
<td>2.52</td>
<td>–</td>
</tr>
<tr>
<td>Reference [27]</td>
<td>4.315</td>
<td>2.2</td>
<td>–</td>
</tr>
<tr>
<td>Experiment [34]</td>
<td>4.317</td>
<td>2.4</td>
<td>–</td>
</tr>
</tbody>
</table>
the c direction until the calculated atomic forces [38] were negligible (\(<0.05\,\text{eV/Å}\)). For these calculations, $K_{\text{max}} = 4.31$ and $G_{\text{max}} = 10.62$ were used, and MP scheme was applied to k-point summations with the mesh $(12, 12)$ in the 2D Brillouin zone, which gives $n_k = 21$ for the structures (a) and (b), and $n_k = 36$ for (c). From total energy comparisons, it was found that structures (a) – Fe on top of C – is by far the most stable with the relative total energies being (a) 0, (b) 2.00, and (c) 1.03 eV. For the structure (a), a strong covalent bonding was formed between Fe and C with a bond length 1.89 Å, and no clear bonding features were seen for (b) and (c).

3.2. Interface properties of Fe/TiC

To determine the interface properties more precisely and to calculate the separation energy curve, the number of superlattice layers was increased to $(\text{Fe})_4/(\text{TiC})_4/(\text{Fe})_4$ (see figure 1), where the interface geometry (a) was adopted and the 3D periodicity

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure1.png}
\caption{(Left) Supercell structure of $(\text{Fe})_4/(\text{TiC})_4/(\text{Fe})_4$ at equilibrium. Shown is the conventional unit cell. The primitive cell contains 16 atoms. (Right) Supercell structure with separation at the interface.}
\end{figure}
was continued with repeating slabs. The unit cell contained 16 atoms; since it has inversion symmetry, there are 8 types of atoms: 4 of Fe; 2 of Ti; and 2 of C. A $K_{\text{max}} = 4.13$ and $n_k = 21$ with the mesh (12, 12, 2), and the MP scheme was applied for summations over Brillouin zone. In addition to the relaxation of atomic $z$ positions, we determined the equilibrium $c$ length of the superlattice unit cell as 19.610 Å by examining the total energy of seven different $c$ lengths.

### 3.2.1. Equilibrium properties.

Using the supercell structure determined in section 3.1, we investigated the equilibrium properties of the Fe/TiC interface. Plotted in figure 2 is the valence charge density and spin density at the equilibrium optimized structure. Given in table 2 are the calculated interlayer distances and atomic magnetic moments. It is clear from figure 2 that the interface Fe atom forms a strong covalent bond with the C atom. The strong metal/ceramic adhesion found by Dudiy et al. for the Co/TiC interface [17] also occurs here at the Fe/TiC interface.

The interface bond length determined from the atomic relaxation, 1.88 Å, is very short but close to that of a separate (Fe)$_2$/TiC film calculation, 1.89 Å. This is to be compared with cementite Fe$_3$C, the most stable Fe carbide in steels: the current Fe–C interface bond length is even shorter than the shortest Fe–C bond length in Fe$_3$C, 1.96 Å [39], or shorter than our calculated Fe–C bond length of unstable B1 FeC, 2.00 Å. And the current Fe–C bond length is shorter than that of the other work on Fe/TiC [21] where, unlike the present study, the C atom is not on top of the Fe atom. We note that there is a rather extensive work on C dissolution and diffusion in Fe [40], in which the authors calculated Fe–C bond length for various C positions.

![Figure 2. (a) Valence charge density and (b) spin density contour plot on a B1 (100) section. The number in the parentheses represents the symmetry type. For charge density, the low density resulting from the metallic bonding of Fe and the high density around the nuclei are out of range for this plot; contours start from 0.047 and end at 0.14 electron/(a.u.)$^3$. For spin density, solid and dashed lines represent positive and negative contours, respectively: contours start from $\pm 0.001$ and end at $\pm 0.77$ spin/(a.u.)$^3$.](image-url)
Since these authors obtained the Fe–C bond lengths ranging from 1.75 to 2.11 Å, our result shows good agreement with those calculations. Another interesting observation is the buckling between C and Ti atoms at the interface: C atoms go up relative to Ti atoms with a distance of 0.067 Å. The charge density in the middle of the interface Fe–C bond is 0.12 electron/(a.u.)³, which is considerably higher than that of the Ti–C bond (0.07) and the Fe–Fe bond (0.06), and even higher than that of Fe₃C (0.10). Due to this strong bonding, the interface Fe atom shows a considerably reduced magnetic moment (2.00 $\mu_B$), which is a 20% reduction from the bulk value of this tetragonally strained structure (2.51 $\mu_B$), while the second Fe layer (2.46 $\mu_B$) almost recovers its bulk bct value. The second layer of Fe relaxes down toward the interface and causes an enhancement of the Fe(1)–Fe(2) bonding. The interlayer distance in the Fe block recovers its bulk value in the middle of the Fe slab.

3.2.2. Rigid separation. Now, let us focus on the character of the interface Fe–C bond. To see exactly how strong this interface Fe–C bonding is, we inserted a rigid separation at the interface, as demonstrated in figure 1, and increased the separation distance (which corresponds to normal cleavage) and obtained the separation energy curve $W(x)$ shown in figure 3 as a function of separation distance $x = (c_e - c_s)/2$, where $c_e$ and $c_s$ are the unit cell length in z-direction at equilibrium and with separation, respectively. We examined not only the interfacial separation but also two different types of Fe–Fe separation for comparison: separation inserted (i) between the interfacial and the second Fe layers and (ii) between the second and third Fe layers. Since we have two equivalent interfaces in the unit cell, the separation energy, $W_s$, is defined as half of the total energy difference between the equilibrium, $E_e$, and separated geometry, $E_s$:

$$W_s = (E_s - E_e)/2$$

The calculations were done at six different separation distances and fitted to the universal binding energy curve [41]. $W(x) = W_\infty - W_\infty x (1 + bx) \exp(-bx)$, whose obtained parameters are listed in table 3. From figure 3, the actual separation...
Table 3. The parameters obtained for the universal binding energy curve. ‘$1/b$’ gives the force-maximum separation distance, and ‘$\sigma_{\text{max}}$’ is the maximum value of the force.

<table>
<thead>
<tr>
<th>Bond</th>
<th>$W_\infty$ [eV] ([J m$^{-2}$])</th>
<th>$1/b$ [Å]</th>
<th>$\sigma_{\text{max}}$ [eV/Å] ([GPa])</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)–Fe(1)</td>
<td>2.17 (3.83)</td>
<td>0.46</td>
<td>1.74 (30.66)</td>
</tr>
<tr>
<td>Fe(1)–Fe(2)</td>
<td>3.28 (5.78)</td>
<td>0.68</td>
<td>1.77 (31.26)</td>
</tr>
<tr>
<td>Fe(2)–Fe(3)</td>
<td>2.70 (4.76)</td>
<td>0.56</td>
<td>1.77 (31.28)</td>
</tr>
</tbody>
</table>

Figure 3. (a) Separation energy per unit cell for the (001) plane cleavage. (b) Corresponding force separation law; the C(1)–Fe(1) debonding (solid line), Fe(1)–Fe(2) (dotted line), and Fe(2)–Fe(3) (dashed line). The lines were obtained by fitting with the universal binding energy curve (see text for details).
is seen to occur at the Fe(1)–C(1) interface. The calculated work of separation, 2.17 eV (3.83 J m\(^{-2}\)), is smaller than the Griffith work of Fe(1)–Fe(2) or Fe(2)–Fe(3) debonding (see table 3), and is smaller than the calculated (001) Griffith work of pure bcc Fe of 2.7 eV (5.5 J m\(^{-2}\)) [42]. However, this does not mean that the interface Fe–C bonding is weak; as is apparent from figure 3, it does resist normal separation in the same way as does the Fe–Fe bond in the small separation region. Consequently, the force maximum and its position, which are of importance in characterizing mechanical properties, also show similar values among the three types of debonding (see figure 3b and table 3), giving a comparable critical normal stress of 30 GPa. (The force separation law calculated here from first principles has been integrated with the gradient-plasticity and multiscale-continua models [43] with which to simulate the ductile fracture dynamics.)

We remark that the calculated work of separation in the present work can be compared to those of Arya and Carter [21] as mentioned in section 1. Although the current work of separation is close to that of one TiC layer case in their work, it is important to note that the present interface structure is under a large in-plane strain to make a coherent interface. Since 65 meV per layer is required to make Fe and TiC match at the interface, this energy should be released at the infinite separation, which would result in the reduction of the calculated work of separation from 2.17 eV to 2.17 \(\times 0.065 \times 12\) (12 layers in the present study) = 1.39 eV. And, this corresponds to 2.45 J m\(^{-2}\), which is very close to the 2 and 3 TiC layer cases of Arya and Carter.

The difference among the three debonding processes appears in the large separation region, and results in different \(W_\infty\) values. In addition to the covalent directional bond through 3d–3d hybridization, the Fe–Fe bond is governed by the metallic bond mediated via the sp conduction electrons, which brings features of long-range interactions. In the case of the interface Fe–C bond, this metallic-bonding feature is weaker than in the Fe–Fe bond, leading to the lack of interaction in the large separation region: the interface Fe and C atoms are bonded by the strong and short-range covalent interactions, resulting in the smaller \(W_\infty\) value than those of the other Fe–Fe bonds.

Another important factor for structural properties is the shear strength. From the charge density plot of figure 2, we can easily expect that this system would have high resistance to shear deformation or slip in the (001) plane compared to pure bulk Fe. Now, TiC has strong and highly directional bonds, which are oriented 90° with respect to each other and strongly resist shear strain. The interface Fe is pinned to the TiC surface by this directional bond along the c axis, and thus high resistance to (001) shear is clearly expected. This aspect will be addressed in future work through first-principles calculations on the same footing as the present one.

Now, the question is: ‘why is the interface Fe–C bonding so strong?’ To answer this, let us examine the projected DOS (PDOS) onto the interface atoms depicted in figure 4. Despite the strong covalent Fe–C bonding and strong metal/ceramic adhesion realized at the interface, each PDOS resembles remarkably well the bulk one – meaning that the interface electronic structure can retain its original bulk features to a considerable extent. This retention of the bulk features at the interface, which deters embrittlement, arises from the special role of the interface Fe 3d_{3\sigma^2-\pi^2}
state in the current interface structure. In figure 5, the interface PDOS is further decomposed into the specific Fe 3d_{3z^2-r^2} and C 2p_z orbitals, which are relevant to the pdσ hybridization. We can see clear evidence of strong hybridization with several resonance peaks in their PDOS. The 3d_{3z^2-r^2} PDOS is significantly different from the

Figure 4. Projected DOS onto the interface atoms. Left panels are for majority spin, while right minority. The corresponding bulk PDOS (bct Fe or fct TiC) is also shown by gray line. Fermi energy is set at 0 eV.

Figure 5. Projected DOS onto the Fe(1) 3d_{3z^2-r^2} and C(1) 2p_z orbitals. Some of the clear resonance peaks due to the pdσ hybridization are indicated by arrows.
bulk one, while the other 3d orbitals (not shown) and even the C 2p₂ orbital retain more or less their bulk features [44]. The e₉ orbitals of Fe are less important in promoting bcc cohesion than the t₂g orbitals since in the stretching direction of the e₉ orbitals there are no bcc nearest neighbor atoms. In this sense, the 3d₃½₋₁½/₃C₀r² orbital can change its features from the bulk rather freely, and provide an optimal situation for strong pdσ hybridization which appears in the bulk Ti–C, without much affecting the bcc cohesive energy – except for the magnetic energy cost (the occupied minority states in the 3d₃½₋₁½/₃C₀r² orbital are increased and the majority states decreased as a result of the pdσ hybridization). Thus, the C(1) 2p₂ state need not greatly change its PDOS from the bulk in forming the pdσ bond with Fe(1), and is still able to keep optimal features for the strong Ti–C bonds.

3.2.3. Separation with relaxation. In order to gain more realistic and physical insights into the Fe/TiC interfacial bonding, we performed the full structural optimization at each separation distance to see how the separation energy changes from that of the rigid separation case. Figure 6 shows the separation energies for all the three types of separation with relaxation. In the case of rigid separation, the separation was seen to occur at the Fe(1)–C(1) interface; the relaxed results also show that the actual separation does occur there. In the small separation region, all the three processes behave exactly the same, but at large separation distances, the separation at the Fe(1)–C(1) has the lowest energy implying that it is the ground state at a given separation distance among the three separations. Thus, we restrict ourselves henceforth to the separation at the Fe(1)–C(1) interface only.

Plotted in figure 7 are the separation energy and the force separation law with atomic relaxation as a function of separation distance. For better fitting accuracy, we inserted three more separations, 1.75, 1.85, and 1.96 Å. As is clear from the figure,
the separation energies change remarkably upon relaxation. The effect of relaxation is larger at small separation distances (<1.75 Å) than at large separation distances (>1.75 Å). At small separations, the separation energy is well-fitted with a parabola, \( W(x) = ax^2 \) with \( a = 0.57 \) [eV/Å²], whereas at large separation distances it follows a universal binding energy curve [41] as in the rigid separation case, but with a different \( a_{\text{max}} (= 2.00 \) [eV/Å] = 35.3 [GPa]). The idea of rigid and relaxed separation was applied to other systems such as \( \alpha \)-Al₂O₃, Al, and Si [45, 46], and the same behavior in the separation energy was observed.

This crossover behavior can be easily understood: for separation distances less than a critical separation (1.75 Å), the quantum mechanical potential energy barrier...
between the surfaces is low, and the interfacial atoms can tunnel through the barrier and move toward each other to restore bonding upon relaxation, which results in an elastically elongated system without a clear separation. Beyond the critical separation, however, the potential barrier between the two surfaces is too high for the atoms to restore bonding, and Fe and TiC remain separated with a well-defined separation distance. Thus it may be inferred that the actual breaking of the Fe–C bond occurs near 1.75 Å. This is confirmed in figure 8, in which the normalized interlayer distances between Fe(1)–C(1), Fe(1)–Fe(2), and Fe(2)–Fe(3) are given. As is clear from the figure, all the distances quickly restore their equilibrium values after a critical separation except that of Fe(1)–C(1), which grows larger. And, due to this crossover behavior of the separation energy, the force separation law has a discontinuity at a critical separation, where the force has a maximum value, $\sigma_{\text{max}}$ (see figure 7b). The position of $\sigma_{\text{max}}$, 1.75 Å, is significantly shifted from that of rigid separation case in which $\sigma_{\text{max}}$ appears at 0.46 Å. In addition, $\sigma_{\text{max}}$ is increased from its rigid separation value by 4.64 GPa. We note that despite this large relaxation effect, the work of separation remains almost the same even under relaxation ($W_\infty = 2.21 \text{ [eV]} = 3.9 \text{[J m}^{-2}]$, which is also reduced to 2.52 J m$^{-2}$ due to lattice misfit). This is because the work of separation is obtained at the infinitely separated limit, and the relaxation effect is very small at large separation distances.

4. Summary

We performed extensive first-principles FLAPW calculations on the Fe(001)/TiC(001) interface, and determined the equilibrium and separation properties. At equilibrium, a strong covalent bond is formed between the interface Fe and C. Due to this strong covalency, the magnetic moment of interface Fe is significantly
reduced from its bct value. In order to see how strong the Fe–C interfacial bonding is, we performed rigid separation calculations, and obtained the separation energy curve and the first-principles force separation law. These calculations, along with a detailed investigation of the PDOS, revealed: (1) The Fe–C bond is governed by short-range interaction coming from pdσ hybridization. (2) At small separations, the Fe–C bond resists normal separation in the same way as does the Fe–Fe bond. The difference appears in the large separation region resulting in different $W_\infty$ values due to the different metallicity in the bonds. (3) The actual separation occurs at the Fe–C interface with $W_\infty = 3.83 \text{ J m}^{-2}$, which is significantly reduced to $2.45 \text{ J m}^{-2}$ due to lattice misfit. The force separation law was also obtained and has been integrated into gradient plasticity and multiscale continua models. (4) The Fe 3d$_{32-\sigma}$ orbital at the interface plays a dominant role in this strong metal/ceramic adhesion because it is rather free to change from the bulk and enables other interface states to retain their original bulk features. This allows the interfacial C 2p$_z$ to keep its bulk character and the optimal features of the strong Ti–C bonds in forming the pdσ bond with the interface Fe.

To gain a more realistic understanding of the Fe–C interfacial bonding, a full structural optimization was performed at each rigid separation, and the results also show that the separation occurs at the Fe–C interface. The detailed study of the Fe–C interfacial separation revealed that the relaxation effect is more vivid in the small separation regime than at large separation distances, which leads to a crossover behavior in the separation energy curve: the separation energy curve is well fitted by a parabola at small separation distance (\(<1.75 \AA\)), and follows a universal binding energy relation in the large separation region (\(>1.75 \AA\)). This crossover behavior was reflected in the force separation law, which has a discontinuity at the critical separation, 1.75 Å, at which the actual breaking of the Fe–C bond occurs. In spite of this large relaxation effect, $W_\infty$ does not change much from that of rigid separation because the relaxation effect is small at large separation distances, and $W_\infty$ is obtained in the infinite separation limit.

Acknowledgements

The authors are grateful to Y.N. Gornostyrev, O.Y. Kontsevoi, and C.F. Woodward for their fruitful discussions. This work was supported by the ONR (grant No. N00014-01-1-0953) under the Naval Materials by Design Grand Challenge and by grants of computer time at the NAVO and ERDC Supercomputing Centers.

References

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[36] The Poisson effect was fully taken into account. At each \( a \) (in-plane lattice constant), the \( c \) constant was found by minimizing the total energy.
[42] The calculated (001) separation of pure bcc Fe shows very similar behavior to the Fe(2)–Fe(3) debonding process.
[44] Loosely hybridizing with Ti(1) atoms, Fe(1) can keep a bcc-like environment, while strongly hybridizing with the Fe(1) 3d\(_{z^2}\) orbital C(1) keeps a B1-like environment.