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Stoichiometry and Adhesion of Al/WC

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ABSTRACT

We examine the relative stability and adhesion of nonstoichiometric (polar) Al/WC interfaces and WC(0001) surfaces using Density Functional Theory as implemented in a planewave, pseudopotential formalism. Relaxed atomic geometries and the ideal work of adhesion were calculated for six different interfacial structures, taking into account both W- and C-terminations of the carbide. Based on the surface and interfacial free energies, we find that both the clean surface and the optimal interface geometry are W-terminated. However, the largest adhesion energies are obtained with the C-termination, consistent with an argument based on surface reactivity.

INTRODUCTION

Interfaces between metals and ceramics play a vital role in an increasingly large number of industrial applications[1]: heterogeneous catalysis, microelectronics, thermal barriers, corrosion protection and metals processing are but a few representative examples. However, experimental complications associated with the study of a buried interface, and theoretical difficulties arising from complex interfacial bonding interactions have hindered the development of general, analytic models capable of accurately predicting fundamental interfacial quantities.

One such quantity, which is key to predicting the mechanical properties of an interface, is the ideal work of adhesion, $\mathcal{W}_{\rm ad}$[1], which is defined as the bond energy needed (per unit area) to reversibly separate an interface into two free surfaces, neglecting plastic and diffusional degrees of freedom. Formally, $\mathcal{W}_{\rm ad}$ can be defined in terms of either the surface and interfacial energies (relative to the respective bulk materials) or by the difference in total energy between the interface and its isolated slabs:

$$\mathcal{W}_{\rm ad} = \sigma_{1v} + \sigma_{2v} - \gamma_{12} = \left(E_1^{\rm tot} + E_2^{\rm tot} - E_{12}^{\rm tot}\right)/A. \quad (1)$$

Here σ_{iv} is the surface energy of slab i, γ_{12} is the interface energy, $E_i^{\rm tot}$ is the total energy of slab i, and $E_{12}^{\rm tot}$ is the total energy of the interface system. The total interface area is given by A.

XC	Pseudopot.	a (Å)	c (Å)	c/a	V_0 (Å^3)	$\mathbf{B_0}$ (GPa)	$\mathbf{E}_{\mathrm{coh}}$ (eV)
GGA	PAW	2.932	2.849	0.972	21.21	365	16.87
	Ultra-soft	2.920	2.840	0.973	20.98	375	16.67
LDA	Ultra-soft	2.881	2.802	0.973	20.15	418	19.70
	LCAO[17]	2.88	2.81	0.977	20.18	413	17.8
Experiment[17]		2.91	2.84	0.976	20.83	329,577,434,443	16.7

Table 1: Comparison of WC bulk properties: LDA vs. GGA and ultra-soft pseudopotentials vs. the projector augmented wave method. Experimental data and another first-principles calculation (based on a linear combination of atomic orbitals) are also presented.

Although there has recently been much activity aimed at understanding metal/oxide interfaces[1, 2, 3], much less is known about metal/ceramic adhesion involving non-oxide ceramics[4]. Within this class, the transition metal carbides are a particularly notable omission, considering their exceptional hardness, strength, and corrosion resistance[5]. In this work we present, what is to our knowledge, the first theoretical investigation of *any* metal/WC interface, focusing on Al/WC. This system serves as as a convenient model of simple-metal/transition metal carbide adhesion, in that both polar and non-polar interfaces may be considered with relatively small simulation cells resulting from similar lattice geometries.

The goal of the present work is to calculate $\mathcal{W}_{\mathrm{ad}}$, optimal geometries, and the interface stability of several representative polar Al/WC interfaces within a first-principles framework in order to better understand the nature of metal/ceramic adhesion. Previous studies have shown this approach to be reliable in reproducing $\mathcal{W}_{\mathrm{ad}}$ values from experiment[1, 2, 3, 4]. A future study[6] will examine the important effects of non-polar geometries, alloying agents, and critically analyze the interfacial electronic structure.

METHODOLOGY

For this study we employ Density Functional Theory (DFT)[7, 8], as implemented in the Vienna *ab initio* Simulation Package (VASP)[9]. VASP utilizes a planewave basis set for expansion of the single particle Kohn-Sham wavefunctions, and pseduopotentials for describing the computationally expensive valence electron-ion core interaction. Exchange-correlation (XC) effects can be treated within the Local Density (LDA)[10] or Generalized Gradient Approximations (GGA)[11]. Total energies were converged to 1-2 meV/atom with respect to planewave cutoff energy and $\mathbf{k}$-point sampling density. Ground state atomic geometries were obtained by minimization of the Hellmann-Feynman forces[12, 13] to a tolerance of 0.05 eV/Å or less.

To assess the importance of the W p semi-core states, we have performed comparisions on bulk WC using both ultrasoft-type[14] (with partial core corrections[15]) and Projector Augmented Wave pseudopotentials[16] (see Table 1). We find that both pseudopotentials yield results in good agreement with experiment. The bulk properties are rather more sensitive to the choice of XC functional (Table 1), as the GGA functional is in slightly better agreement with the experimental lattice constants and cohesive energy. Consequently, our calculations were performed using the GGA, in conjunction with ultrasoft pseudopotentials for W and C; a norm-conserving pseudopotential was used for Al[18].

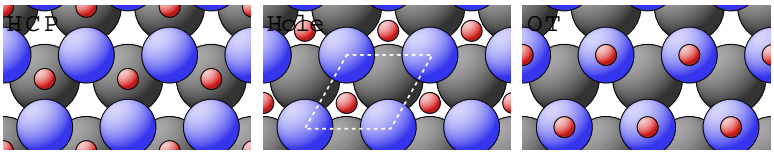

Figure 1: Three stacking sequences for the C-terminated Al/WC interface. Small spheres: Al interfacial atoms, medium-sized spheres: C atoms, large spheres: W atoms. The supercell profile along $\langle 000\bar{1} \rangle$ is shown in white.

By cleaving along the (0001) (basal) plane of hexagonal WC, one generates a polar surface terminated by either a monolayer of pure W or C. To avoid introducing spurious dipole moments, all surface and interface slabs were symmetrically terminated. As this study aims to investigate bulk-like interfaces between Al and WC, tests were performed to determine the minimum size WC slab having a bulk-like interior. After examining the workfunction, surface relaxations, and change in total energy upon making the slab incrementally thicker, we chose a (1×1) slab consisting of 9 atomic layers. An earlier study found that a 5-layer Al(111) slab was sufficiently thick[2].

Our model of the Al/WC interface uses a superlattice geometry in which the WC(0001) slab is placed between two 5-layer slabs of Al(111). This results in two identical interfaces per supercell. The free surfaces of the Al slabs are separated by 10 Å of vacuum, and all atomic coordinates are allowed to relax to their minimum force positions. To accomodate periodic boundary conditions, the softer Al slabs are expanded by 2.2% to match the in plane dimensions of the WC, while the relative orientation of the slabs is chosen to align the close packed directions: Al $[\bar{1}10](111)$ $\parallel$ WC $[11\bar{2}0](0001)$. Finally, both C- and W- terminations of the carbide were considered, along with three rigid translations (HCP, Hole, OT) as depicted in Fig. 1.

RESULTS

WC(0001)

Due to the symmetry of WC(0001), it is not possible to calculate an absolute surface energy without resorting to a thermodynamic argument. Since the stoichiometric slab has two different surfaces—one C-terminated, and one W-terminated—to extract the surface energy of one particular termination a non-stoichiometric model must be implemented, along with a generalized definition of the surface free energy, σ[19, 20, 21]:

$$\sigma = \frac{1}{2A} \left(E_{\text{slab}} - N_W \mu_W - N_C \mu_C + PV - TS \right). \tag{2}$$

Here E_{slab} is the total energy of the slab, A is the surface area, μ_W and μ_C are the chemical potentails of W and C, respectively, and N_W and N_C are the numbers of the corresponding atoms in the supercell. For typical temperatures and pressures, the PV and TS terms may be neglected. Furthermore, as the surface is assumed to be in equilibrium with the bulk, the chemical potential of the bulk carbide (μ_{WC}(bulk)), its heat of formation (ΔH), and the elemental bulk chemical potentials (μ_W(bulk), μ_C(bulk)) are related by:

$$\mu_{WC}(\text{bulk}) = \mu_W + \mu_C \tag{3}$$

$$\mu_{WC}(\text{bulk}) = \mu_W(\text{bulk}) + \mu_C(\text{bulk}) + \Delta H. \tag{4}$$

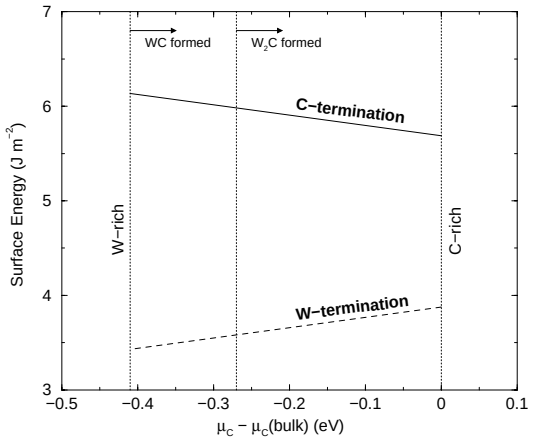

Figure 2: Surface energy vs. chemical potential for W- and C-terminated WC(0001) surfaces. Vertical lines indicate the range of stability of WC and W_2C.

Lastly, the chemical potential for each species must be less than the chemical potential in its bulk phase, $\mu_W \leq \mu_W$(bulk) and $\mu_C \leq \mu_C$(bulk), otherwise the compound would be unstable to decomposition into the elemental phases.

Using the above relationships, it is possible to rewrite Eq. 2 in terms of μ_C only:

$$\sigma = \frac{1}{2A}\left(E_{\text{slab}} - N_W \mu_{WC} + (N_W - N_C)\,\mu_C\right). \tag{5}$$

Equation 5 is plotted over the range of reasonable μ_C values in Fig. 2 for both C- and W- terminations. As shown in the Figure, our calculations predict that the W-termination has the lowest surface energy by about 2-2.5 J/m^2 over the entire range. In addition, the absolute values of both surface energies are relatively large, as one would expect from a polar surface. In particular, because the bonding in WC is partially ionic, cleaving along the basal plane breaks strong cation-anion bonds. This is energetically very unfavorable, and results in very reactive surfaces with large surface energies. As will be shown below, these reactive surfaces also impact interfacial adhesion energies.

Interface Adhesion

Our estimates of the ideal work of adhesion were calculated using two different methods. The first is based on the Universal Binding Energy Relation (UBER)[22], and involves calculating the total energy of an unrelaxed interface (formed by joining truncated bulk surfaces) as the interfacial separation is reduced from an initally large value. The optimal geometries from the UBER calculations were then used to begin a second series of calculations in which the atomic structure of each interface was optimized via minimization of the atomic forces.

Table 2 summarizes the optimal interfacial distances and $\mathcal{W}_{\text{ad}}$ values for both interfacial terminations and all three stacking sequences. Consistent with the argument that surfaces with larger surface energies are more reactive, and therefore more readily form bonds, we see that the C-terminated interfaces exhibit larger $\mathcal{W}_{\text{ad}}$ values across all stacking sequences. The HCP stacking yields the largest adhesion for both terminations, as this geometry comes closest to continuing the

		Unrelaxed(UBER)		Relaxed	
Stacking	**Termination**	$\mathbf{d_0}$ (Å)	$\mathbf{\mathcal{W}_{ad}}$ (Jm^{-2})	$\mathbf{d_0}$ (Å)	$\mathbf{\mathcal{W}_{ad}}$ (Jm^{-2})
HCP	C	1.18	7.96	1.21	6.01
Hole	C	1.03	7.88	1.11	5.40
OT	C	1.92	4.37	1.98	3.21
HCP	W	2.20	4.09	2.22	4.08
Hole	W	2.19	3.75	2.21	3.90
OT	W	2.66	1.98	2.68	1.96

Table 2: Unrelaxed and relaxed adhesion energies ($\mathcal{W}_{\rm ad}$) and interfacial separations ($\mathbf{d_0}$) for the six Al(111)/WC(0001) interface systems.

carbide's bulk $ABABAB\ldots$ stacking across the interface and into the metal; a similar effect was observed for the Al/α–Al_2O_3 interface[2].

Because this interface is characterized by relatively little atomic relaxation, the UBER geometries are in good agreement (to within 0.1Å) with those obtained after relaxation. Generally, allowing for relaxation increases the equilibrium separation, and in most cases reduces $\mathcal{W}_{\rm ad}$. The largest changes upon relaxation occur to the $\mathcal{W}_{\rm ad}$values for the C-termination, which change by as much as 2.5 J/m^2. This can be explained by the large relaxations present in the isolated C-terminated WC slab ($\Delta d_{12} = -22.5\%$). These relaxations are about 5 times those found for the W-termination ($\Delta d_{12} = -4.2\%$).

Interface Stability

Apart from knowing $\mathcal{W}_{\rm ad}$ for a particular interface, it is also desirable to know which interface is most stable in a thermodynamic sense. This can be assessed in a manner similar to what was done for the WC surface, by extending Eq. 5 to give the interfacial free energy, γ:

$$\gamma = \frac{1}{2A}\left\{E_{\rm int} - N_W\mu_{WC} + (N_W - N_C)\,\mu_C - N_{\rm Al}\mu_{\rm Al}({\rm bulk})\right\} - 2\sigma_{\rm Al}. \qquad (6)$$

Here $2\sigma_{\rm Al}$ is the surface energy of the two free Al(111) surfaces, and $\mu_{\rm Al}({\rm bulk})$ is the chemical potential of bulk Al. Based on this, Fig. 3 plots the interface free energy for all six interface geometries as a function of $\mu_C - \mu_C({\rm bulk})$.

Although the C-terminated HCP interface has the largest $\mathcal{W}_{\rm ad}$, its large surface energy results in the W-termination having a lower interfacial free energy, except for a small region within the C-rich regime.[1] Consequently, our calculations predict that the W-termination should be the preferred equilibrium termination.

CONCLUSIONS

We have presented one of the first *ab initio* studies of metal/carbide adhesion, focusing on the Al(111)/WC(0001) interface. We find that polar ceramic surfaces result in relatively strong adhesion, as evidenced by the large $\mathcal{W}_{\rm ad}$ values obtained for both W- *and* C-terminated interfaces.

[1] In this region WC is unstable to decomposition into W_2C.

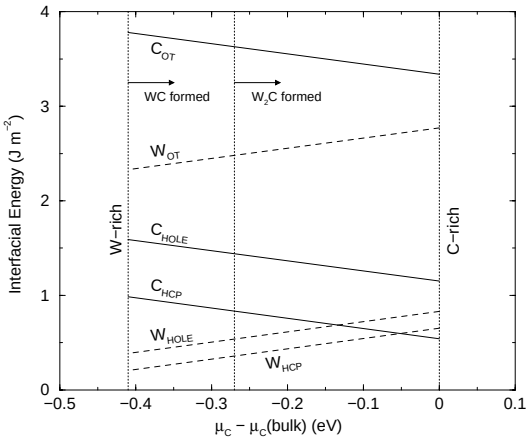

Figure 3: Interfacial free energy of the six Al/WC geometries as a function of $\mu_C - \mu_C(\mathrm{bulk})$.

Although the C-terminated interface has the greatest adhesion, its large surface energy results in the W-termination being more stable, with an overall lower interfacial free energy. A future investigation will consider the effects of a non-polar geometries, alloying agents, and will analyze the interfacial electronic structure.

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