

Impurity Effects on Adhesion

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We report a first-principles calculation of impurity effects on adhesion. C, O, B, and S impurities all cause a pronounced decrease in the adhesive energies of the Mo/MoSi₂(001) heterophase interface. S decreases the peak interfacial strength, while C, O, and B increase it. All impurities increase interfacial spacing in proportion to their covalent radii. Impurity mechanisms are identified.

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While the technological importance of adhesion is well known [1], there have been a number of recent experimental reports that suggest that impurities can have a substantial effect on interfacial adhesion [2]. It has thus become increasingly important to gain a microscopic understanding of impurity effects in adhesion. Previous first-principles studies of adhesion between different materials have focused on impurity-free interfacial contacts [3]. In the related field of impurity embrittlement of bulk solids there have been a number of reports of quantum mechanical studies involving small clusters in the last decade [4,5]. More recently, first-principles calculations of the effects of impurities on grain boundaries have been performed [6-8].

In this Letter, the effects of impurities on the energetics of two different materials as they are brought into contact are determined. This is the first quantum mechanical calculation of impurity effects on adhesion. Our first-principles calculations are carried out with the self-consistent local orbital (SCLO) method [9,10] for electron density distributions, electronic structure, and total energies. In addition, the ideal work of adhesion (referred to as adhesive energy hereafter), the peak interfacial strength, and the full adhesion curve are determined. All of these quantities are obtained for the Mo/MoSi₂(001) interface, with and without C, O, B, and S interfacial impurities. We find that impurity effects can be quite large. A fairly simple picture of the effect of impurities on adhesive energies emerges. However, the changes in peak interfacial strengths are not simply related to changes in adhesive energies and, in fact, can be in the opposite direction.

Interfacial impurities can sit at a variety of sites at an interface depending on the atomic size and structure of the interface. Therefore, several calculations for both interstitial and substitutional impurities at the Mo/MoSi₂(001) interface were performed. All results presented here are for the lowest-energy interface. Different types of Mo/MoSi₂(001) interface compositions are possible. For example, the (001) plane in the Mo can be separated from the first Mo(001) plane in the MoSi₂ by either one or two Si planes. Again, the results presented here are only for the most stable interface.

Adhesion can be further complicated by elastic and plastic deformation [11]. In fact, the effects of plasticity can be quite large in the practical problem of interfacial strength. However, ideal adhesion parameters have been found useful for the analysis of the mechanical properties of interfaces even when there is plastic deformation [12,13]. Further, it is important to establish a base-line rigid adhesion curve so that one can quantify deformation effects. The rigid or ideal adhesion curves presented here are obtained by requiring that there be no atomic relaxation in either of the two materials as they are brought into contact. The Mo/MoSi₂ interface was chosen because MoSi₂-metal-matrix composites are some of the most promising candidates for use as high-temperature structural materials [14]. Additionally, the experimental lattice constant mismatch for the (001) planes of the two materials is less than 2%, so the interface can be treated as epitaxial, thereby simplifying the analysis [15].

Based upon available experimental and theoretical studies of impurity effects in other metallic systems, we chose the following impurities for study: C, O, B, and S. It is well known that B and C occupy the octahedral sites in bcc Fe [16]. We assume that these same sites are occupied at the Mo/MoSi₂ interface, where the local environment is very similar to that in a bcc solid. These are fourfold symmetric surface sites on the Mo(001) surface. The impurities were introduced above these sites at a monolayer coverage and at a height that was determined by minimizing the energy with respect to the separation between the clean Mo surface and the impurity monolayer. Comparison of the total energies of the impurities at interstitial and substitutional sites demonstrated that only S was substitutional, while O, C, and B were interstitial.

In order to identify the nature of the driving force for interface adhesion, the electron number density rearrangements in dopant-free and C-doped systems due to the formation of the interface are plotted in Figs. 1(a) and 1(b), respectively. For each system the self-consistent electron density distribution at large interfacial separation was subtracted from that at the equilibrium separation. The difference is nonzero only if there is electron density rearrangement due to the adhesive interac-

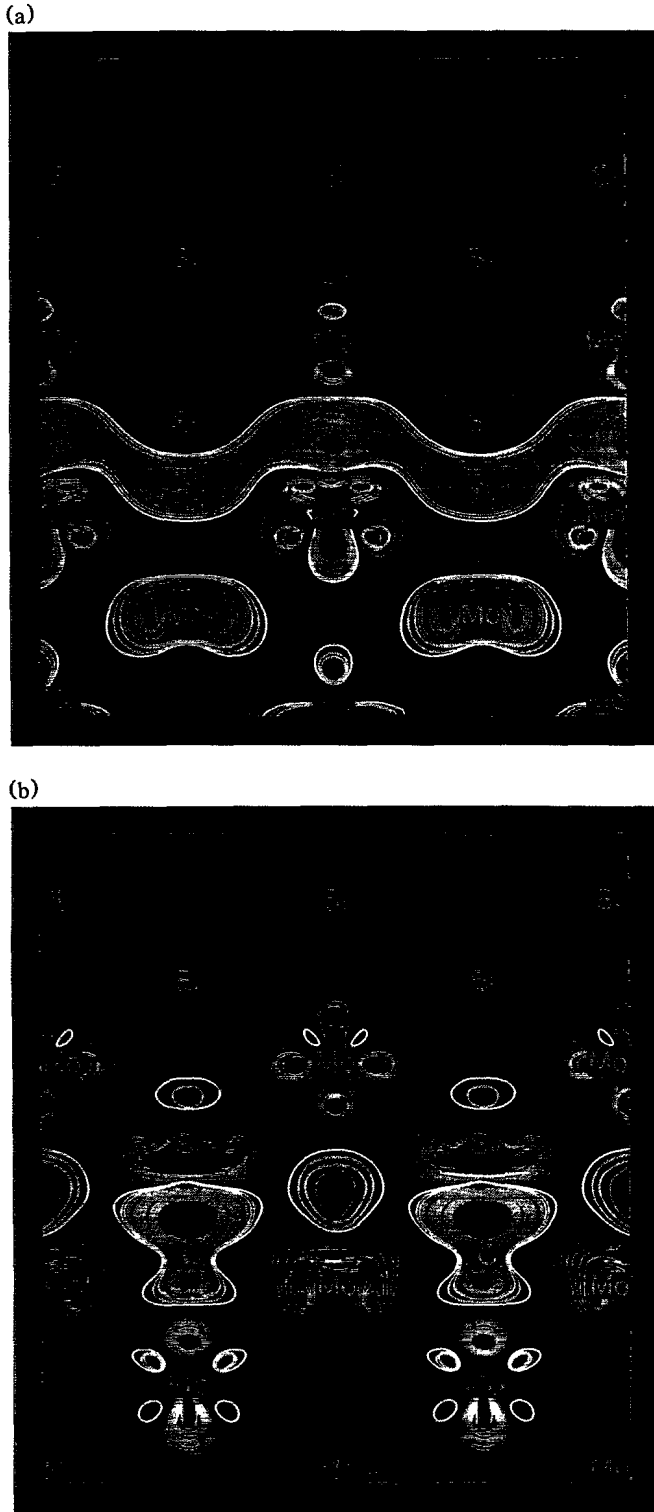


FIG. 1. (a) Mo/MoSi₂ and (b) Mo/C/MoSi₂ charge-density rearrangements due to adhesion plotted on a plane perpendicular to the interface running diagonal across the (square) surface unit cell. Blue and purple are used to denote negative contours in the order of increasing value (less negative), while positive contours are represented by yellow, red, and pink in the order of increasing value.

tion. One can see that metallic screening has limited the electronic rearrangement to within one or two atomic layers of the interface in either material. In the carbon-free systems, the electrons accumulate between the MoSi₂ and Mo atoms at the interface, indicating adhesive interfacial bonding, as would be expected based upon the Hellmann-Feynman [17] theorem. The electron accumulation between atoms is reminiscent of covalent bonding in diatomic molecules. This parallel between the diatomic molecular bond and the bimetallic interfacial bond has been pointed out earlier [18-20]. Note the relatively large accumulation of electrons between the surface atoms of the Mo film and the second-layer Mo atoms in the MoSi₂ film. The contour plots for the C-doped film show that the introduction of C into the interface significantly reduces that accumulation, presumably reducing the strength of that adhesive bond. There is a relatively large accumulation of electrons around the C atoms. This is due to chemical bonds formed across the interface by the C atoms and to a compression or strain attributable to the interstitial nature of the C.

Much of the physics noted in the electron density results is mirrored in the energetics. The calculated energy (E) per unit surface area as a function of interfacial separation (d) is shown in Fig. 2 for all the systems. In all cases, d is the distance between the plane through the nuclei of the surface atomic layer of the Mo film and the plane through the nuclei of the surface Si layer of the MoSi₂ film. Let us concentrate on the impurity-induced equilibrium adhesive energies and spacings, which are indicated by the minima of the curves. It is evident that all of the impurities reduce the adhesion and increase the equilibrium interfacial separation. This is a strong effect,

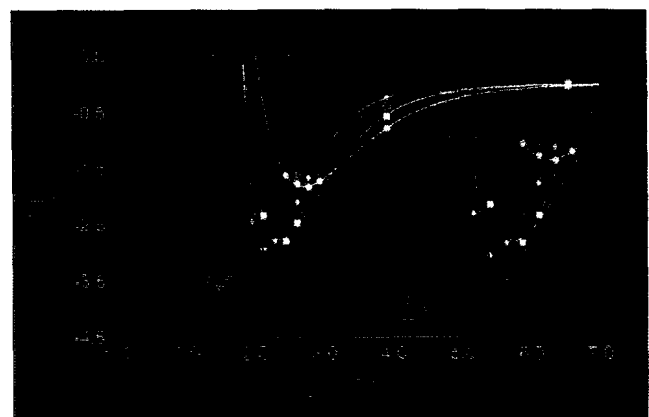


FIG. 2. The calculated energy E (per interface) of the system vs interfacial separation d between Mo and MoSi₂. The orange O's, fuchsia Δ 's, dark blue \diamond 's, light blue \square 's, and pink O's correspond to dopant-free, C-, O-, B-, and S-doped MoSi₂, respectively. Lines through the points correspond to the universal binding energy relation (UBER) [20], with the parameters determined by fitting to all of the data points shown. Inset: The details of the fit in the vicinity of the minimum points.

leading to a decrease in adhesive energies by nearly a factor of 2 in the case of the S-doped interface.

In fact, the amount of local strain, or increase in the equilibrium spacing d , is simply related to the covalent radius [21] of the impurities, as seen in Fig. 3. The interfacial spacing is, to a good approximation, a linear function of the covalent radius of the atoms of the impurity layer. This suggests a rather simple picture of the effects of impurities. That is, the impurities act as spacers at the interface, pushing the two surfaces apart. This stretches the bonds across the interface, weakening them and thereby decreasing the adhesive energy. This is consistent with Fig. 2 and, e.g., the apparent weakening of the Mo-Mo bond across the interface seen by the lowering of the electron density in that bond shown in Fig. 1(b) as compared to Fig. 1(a).

A complete picture of the impurity effects on adhesion is not that simple, however. Consider now the peak interfacial strength [maximum force per unit (cross-section) area], which is twice the derivative of the energy curves with respect to interfacial spacing. The peak interfacial strengths for the impurity-doped interfaces are the following: S, 20.6; B, 40.8; O, 50.2; and C, 59.0 in GPa. The interfacial strength of the impurity-free interface is 39.6 GPa. While B increases the interfacial strength slightly, O and C impurities significantly strengthen the interface, despite the fact that all of the impurities examined decreased the adhesive energy. The shapes and, in particular, the widths of the energy versus separation curves shown in Fig. 2 are not simply related to the well depths. There is an interesting grouping of the minima of the impurity curves in Fig. 2: The minima for B, O, and C fall near the maximum slope (force) region of the impurity-free Mo/MoSi₂ curve, while the minimum for the S curve lies in a lower force region of that curve. A clearer understanding of this interfacial strength behavior requires additional results on other impurities and materials.

Experimental measurements of the effects of impurities on adhesion have all been focused on peak interfacial strengths, as opposed to adhesive energy measurements. Hartweck and Grabke [16] examined the effects of C, N,

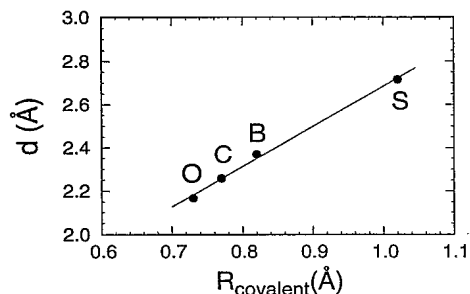


FIG. 3. Interfacial separation d between Mo and MoSi₂ vs covalent radius [21] of impurities.

S, and P on adhesion between two polycrystalline Fe surfaces. They found increased peak interfacial strengths for all four impurities. On the other hand, Buckley [22] found that O, S, and H₂S all decreased the adhesive strengths between two single-crystal Fe surfaces. Perhaps it is not surprising that there is some disagreement, since such measurements are quite difficult. In the related field of impurity embrittlement of bulk solids (see, e.g., Rice and Wang [13]), C is known as a cohesion enhancer in steels, while S is known as an embrittler. While Mo/MoSi₂ is a different interface, these steel results are not inconsistent with our results that C produced the largest increase in interfacial strength and S led to the largest decrease in interfacial strength.

Although there are no quantum mechanical calculations of impurity effects on adhesion in the literature, a number of quantum mechanical studies on embrittlement of bulk solids have been reported [4-8]. The first cluster calculations which provided energies and forces are due to Painter and Averill [5]. They reported that S, B, C, N, O, H, and Be increased the cohesive energies of their six-atom Ni clusters. They also found that B, C, N, and O increased the maximum restoring force, the cluster analog to the peak interfacial strength at a solid interface, while they reported that S and Be decreased the maximum restoring force. While we find a decrease in adhesive energies for the solid Mo/MoSi₂ interface when S, B, C, O, and Nb are introduced, our peak interfacial strength results do parallel their maximum-restoring-force results. The differences in the binding energy results may be due to application to different metals. We believe that they are more likely due to the difference between a six-atom cluster and a solid. Indeed, Fu and Painter [8] found that H lowered the (100) cleavage energy and strength of a FeAl crystal. The grain boundary calculations of Olson and co-workers [7] suggested that P and S decreased bonding strength at grain boundaries in Fe, whereas C and B increased the bonding strength. On the other hand, Goodwin, Needs, and Heine [6] found that substitutional Ge and As increased the (111) cleavage energy of Al.

In conclusion, our calculations have shown that all the impurities considered decreased the adhesive energy of the Mo/MoSi₂ system. A simple picture emerged in which the impurities increased the spacing between the Mo and MoSi₂ crystals, thereby stretching bonds and lowering the Mo-MoSi₂ cohesive energy. Impurity effects on peak interfacial strengths were not that simple, however. The impurities C, O, and B increased the interfacial strength, while S decreased it. A complete understanding of this interesting strength result must await investigations of impurity effects in other materials.

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