

First-Principles Calculations of the Ideal Cleavage Energy of Bulk Niobium(111)/ α -Alumina(0001) Interfaces

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We report *ab initio* calculations of the work of adhesion for O- and Al-terminated Nb(111)/ α -alumina(0001) interfaces. Strong ionic bonds formed by Nb $4d \rightarrow$ O $2p$ electron donation account for the high adhesive strength of O-terminated interfaces. However, cleavage preferentially occurs between metal atoms at both O- and Al-terminated interfaces, and their adhesion has both covalent and ionic character. [S0031-9007(99)08432-X]

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A basic problem in materials science is to relate the strength of interfaces to their atomic and electronic structure. In particular, metal/ceramic interfaces are a class of technologically important systems whose interactions need to be understood at a fundamental quantum-mechanical level. Niobium and α -alumina (Al_2O_3 , sapphire, or corundum) form stable interfaces which are of importance both practically and as model systems for studying metal-ceramic bonding. Their mechanical adhesion is a subject of ongoing experimental interest, e.g., [1–3]. For example, an “extraordinary” adhesion has been recently reported between Nb(110) films and $\text{Al}_2\text{O}_3(11\bar{2}0)$ surfaces [3]. In special cases, including the Nb(111)/ α - $\text{Al}_2\text{O}_3(0001)$ interface, the detailed atomic structure has been revealed by high-resolution electron microscopy [4–8].

Our aim is to obtain theoretical values of the work of separation, as a step towards linking the mechanical behavior of interfaces with their structure on the atomic scale. Besides the fact that it has been well characterized experimentally, the Nb(111)/ α - $\text{Al}_2\text{O}_3(0001)$ interface is particularly suitable for theoretical study because the atomic misfit is less than 2%. It is therefore reasonable as a first approximation to ignore the misfit dislocations and to treat the interface as atomically coherent, with a short period in the plane of the interface. The application of periodic boundary conditions facilitates the use of a range of methods for calculating the total energy. Calculations have been reported based on Huckel or tight-binding [9,10] theory, and on a simple classical image charge interaction [11]. These approaches (reviewed previously in [12]) are suggestive but leave open questions—for example, the effect of treating the electronic structure self-consistently, the effect of which type of atoms terminate the interface (O or Al), and the effect of relaxing the atomic positions. The degree to which the adhesion at different interfaces can be ascribed to “ionic” bonding—i.e., electron donation from

metal to ceramic *without orbital mixing*, and “covalent” (or “metallic”) bonding in which the metal and ceramic electronic orbitals are strongly hybridized, is a question of central importance which can only be answered by *ab initio* studies. Addressing these questions, we report here the first *ab initio* calculations of the ideal work of separation W_{sep} [13] of Nb/ Al_2O_3 interfaces. This quantity is a lower bound to the energy that must be supplied to cleave the interfaces. Lattice trapping and plastic deformation may in practice mean that more energy needs to be supplied to cleave, but nevertheless W_{sep} remains a basic quantity of great experimental interest. Previous *ab initio* calculations of monolayer Nb on Al_2O_3 have been reported [14], but technical problems frustrated attempts to calculate W_{sep} for the bulk. Later the *structure* of a bulk interface was calculated in a small multilayer supercell geometry [15], but nothing could be deduced about W_{sep} or the bond strengths. We have now made calculations of W_{sep} for several different interfaces using large supercells. These calculations enable us to analyze the role of different kinds of chemical bonds at these interfaces.

The electronic structures and total energies were calculated with the free energy plane wave (PW) pseudopotential (PP) method [16]. In this method, the finite temperature density matrix is diagonalized from a Trotter factorization, which makes it an efficient *ab initio* technique for metals, in which convergence is notoriously slow. Otherwise we use conventional density functional theory in the generalized gradient approximation (GGA) [17,18]. Kinetic energy filtered and Troullier-Martins [19] forms of nonlocal PP were used. The relaxation of atomic positions has been made by steepest descents using the Hellmann-Feynman forces. A PW cutoff of 40 Ry was used in all calculations, with two k -points in the irreducible wedge of the hexagonal Brillouin zone [20].

To start with, pure Al_2O_3 slabs separated by a vacuum space were constructed in a supercell with periodic

boundary conditions. The stoichiometric (0001) slab comprised seven stoichiometric layers, each layer consisting of three oxygen atoms in a plane, with an Al atom above and below the plane. This slab is therefore terminated top and bottom by Al. The vacuum space was chosen to accommodate ten (111) layers of Nb in the multilayer supercell which represented the stoichiometric (Al-terminated) interface. In the unrelaxed configuration, the Nb layer at the interface was located at the position which would have been occupied by the next Al plane in the unrelaxed bulk; this corresponds to the relative in-plane translation of the crystals which has been established experimentally. The O-terminated interface was constructed from the Al-terminated one by replacement of the two surface Al planes by Nb. An elevation of the supercell is shown in Fig. 1. For comparison, a monolayer of Nb on the O-terminated surface was also calculated by replacing the surface Al atoms by Nb on the stoichiometric Al_2O_3 slab, as in [14]. It will be helpful to introduce some notation for the surfaces we have considered. We denote by A(Al) the Al-terminated Al_2O_3 (0001) surface, and by A(O) the O-terminated Al_2O_3 (0001) surface. The surface of bulk Nb is denoted N(b), and the monolayer of Nb on A(O) is denoted by N(m)/A(O). For convenience we summarize in Table I the systems and “cleavage” planes calculated here.

When an interface is cleaved, it leaves two surfaces exposed. Its W_{sep} is defined as

$$W_{\text{sep}} = (E_1 + E_2 - E_b)/2A. \quad (1)$$

E_b is the total energy of the supercell containing the multilayered slabs; E_1 and E_2 refer to the energy of the same supercell containing a single slab of one of the pure materials, separated by vacuum from its periodic images. The area of an interface in the supercell is A and the factor 2 in the denominator accounts for the two interfaces within a supercell. The interfaces must be identical. We computed W_{sep} for both unrelaxed and relaxed structures, including pure Nb and Al_2O_3 . The results for W_{sep} in the systems we have studied are reported in Table I, and the interlayer relaxations are reported in Table II. The unrelaxed energies are useful in interpreting the nature of bonding at the

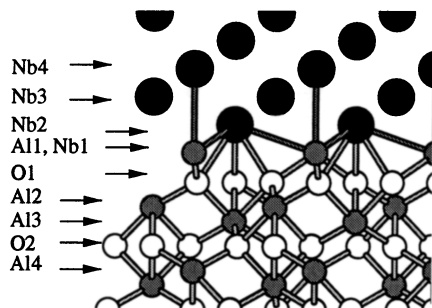


FIG. 1. Section through metal terminated interface, displaying layer labels.

TABLE I. W_{sep} (in J/m^2) for both unrelaxed (unrel) and relaxed (rel) structures.

Interface	Cleavage plane	Unrel	Rel
N(b)/N(b)	... Nb-Nb-Nb ζ Nb-Nb-Nb ...	4.9	4.2
A(Al)/A(Al)	... Al-O-Al ζ Al-O-Al ...	7.0	3.9
A(Al)/A(O)	... Al-Al-O ζ Al-Al-O ...	13.3	12.7
N(m)/A(O)	Nb ζ O-Al-Al ...	10.9	10.8
N(b)/A(O)	... Nb-Nb-Nb ζ O-Al-Al-O ...	9.3	9.8
N(b)/A(Al)	... Nb-Nb-Nb ζ Al-O-Al-Al ...	4.2	2.8
N(b)/A(O)	... Nb-Nb-Nb ζ Nb-O-Al-Al ...	4.0	3.8

interface, while the relaxed energies have thermodynamic significance.

Our calculated atomic relaxations are in line with those previously reported ([14,15], and references therein) regarding the particularly large inward relaxation of the Al plane on the stoichiometric Al_2O_3 surface. However, our calculated 10.4% relaxation of the second layer in this system is at variance with previous calculations [14,21–23], which have shown a much smaller or even negative relaxation of this layer. Our result is due to a strong lateral relaxation of the oxygen atoms in the surface plane. As each Al atom at the surface relaxes inwards it squeezes open the triangle of O atoms upon which it sits. The adjacent triangles of O atoms are thereby forced to contract, squeezing away the Al atoms below them. These lateral movements were not allowed in the calculations of [21] and [14], which only considered interplanar relaxations. We verified that artificial suppression of lateral relaxations strongly reduces the second layer relaxation, in line with other previous work (except [22], for which we have no explanation). Our fully relaxed result is more consistent with

TABLE II. Relaxation of O and Al terminated interfaces and surfaces of Al_2O_3 (0001) expressed in percent of the relevant bulk spacing. The notation of the systems is the same as in Table I.

Layers	N(b)/A(O)	N(b)/A(Al)	A(O)	A(Al)
Nb3-Nb4	-2.4	-3.1		
Nb3-Nb2	12.2	3.6		
Nb2-Nb1	-26.3(-42 ^b)	...		
Nb2-Al1	...	-2.1		
Nb1-O1	30.4(36 ^b)	-2.2		-69.6 (-86 ^a) (-51 ^c)
O1-Al2	10.1	8.5	-7.1	10.4 (16 ^c)
Al2-Al3	-17.2	-12.9	2.4	-34.3 (-49 ^a) (-29 ^c)
Al3-O2	7.1	8.7	8.0	18.5(21 ^a)
O2-Al4	-0.9	1.7	-3.6	3.4

^aRef. [14]; ^bRef. [15]; ^cRef. [24].

the large value of 16% measured recently by x-ray diffraction [24], which is the only experimental evidence we have on this point. The same argument would account for our discrepancies with earlier Nb monolayer relaxations [14].

It is noteworthy that the largest values of W_{sep} are obtained for cleavage which leaves the A(O) surface exposed. There are three such situations: N(m)/A(O), N(b)/A(O), and A(Al)/A(O). Relaxation can increase or decrease W_{sep} , depending on the relative magnitudes of relaxation energy at the interface and at the free surfaces. In the cleavages from A(O), however, relaxation does not make a significant difference (<10%). When an A(Al) surface is created, relaxation has a more noticeable effect in reducing W_{sep} , because of the large relaxation of A(Al).

The high energies required to cleave from A(O) can be rationalized in terms of the high energy of forming the oxygen-rich A(O) surface in vacuum. In crude terms, the surface O atom has to be in an O^- rather than O^{2-} configuration in order to balance the total charge. Consider the energy released if a layer of Nb is added to an A(O) surface within a simple electronic model in which each Nb atom transfers three electrons to the surface O atoms. From the Solid State Table of Harrison [25], the Nb-4*d*-O-2*p* energy difference is 4.1 eV, therefore the energy per Nb atom from this transfer is 12.3 eV, which is just 10.0 J m^{-2} , remarkably similar to the values of 9.8 and 10.8 J m^{-2} we find for the N(b)/A(O) and N(m)/A(O) interfaces, respectively. This simple argument apparently accounts for the adhesive strength of the Nb/A(O) interface, and is suggestive of an essentially ionic interaction, with little hybridization of the electronic states between the surface O-layer and the metal. The degree to which this simple ionic picture holds true is discussed later.

For ideal cleavage of the bulk Nb-O-terminated interface, a lower W_{sep} is achieved by leaving a monolayer of Nb on the surface, N(b)/N(m)-A(O). The value of W_{sep} for this process is 3.8 J m^{-2} , much lower than 9.8 J m^{-2} required for N(b)/A(O), but comparable to W_{sep} for bulk Nb (4.2). Thus cleaving the ... Nb \uparrow Nb-O-Al-Al... is similar to cleaving bulk Nb, which has purely metallic/covalent character. Cleaving between Al planes in pure Al_2O_3 requires a large W_{sep} (7.0) which is substantially reduced by relaxation to 3.9. The effect of relaxation is much less in the case of Nb \uparrow Nb-O-Al-Al..., a reflection of the relatively small atomic relaxation (14%) that the Nb-O-Al-Al... surface undergoes. Similarly, the unrelaxed W_{sep} at the N(b)/A(Al) interface is strongly reduced from 5.0 to 2.8, again a reflection of the large relaxation at the Al-terminated Al_2O_3 surface. Experimentally, the interfaces formed with this crystal orientation are believed to be O-terminated [26]. We have a case of the "glue" being stronger than one of the components stuck together. These considerations lead us to expect this interface to fail in a ductile manner [27] as observed experimentally.

A useful way to investigate the nature of the bonding is via the Mulliken populations and bond orders. These

can be obtained by projecting the self-consistent wave functions onto the local basis of pseudoatomic orbitals [28], with a spillage of typically less than 1%. We calculate the bond orders using the definition of Mayer [29]. The results are shown in Table III. The magnitude of the bond orders is an indication of the strength of covalent or metallic bonding as compared to ionic bonding; in a pure ionic bond the bond order would vanish. In interpreting Mulliken charges and bond orders caution is needed. Because of the arbitrariness of the basis set, no significance should be attached to absolute numbers which should rather be interpreted as an indication of trends. With this caveat, several effects can be deduced from Table III. Consider first the charges. Whether we consider the monolayer Nb or bulk Nb on oxygen terminated alumina [A(O)], there is a remarkable consistency in the charge transferred from the metal. For N(m)/A(O) the Nb has a charge of +1.04, which is equal to the sum of the charges +0.77 and +0.27 on the top two layers of Nb(b) in contact with A(O). Thus the ionic bond formed at the Nb/A(O) interface spreads through two layers of Nb. The surface oxygen atoms carry charges of -0.84 and -0.86, respectively. For comparison, with this basis set the Mulliken charge of bulk oxygen in alumina is -1. With the terminating layer of Al, on the other hand, the charge on the oxygen is slightly greater (-0.93) and the charges on the Al (+1.50) and the Nb in the adjacent layer (+0.37) indicate greater ionicity of the Al. The bonding in bulk alumina and N(m)/A(O) was previously interpreted as ionic by inspection of the energy resolved charge densities [14] on the monolayer. However, energy resolved charge densities give no such clear picture for N(b)/A(O). Fortunately, the Mulliken charges now tell us clearly that the interaction with the surface O atoms is similarly ionic in each case.

Turning to the bond orders, the Nb-O1 bond order in the monolayer system N(m)/A(O) is 0.93, an indication that a degree of Nb-4*d*-O-2*p* hybridization does indeed occur. In the bulk N(b)/A(O) interface, the Nb1-O1 bond-order is reduced to 0.60, consistent with the *outward* relaxation of Nb1, but the net bond-order at the interface is maintained through a weaker bond-order (0.3) with the second layer of Nb atoms. It is interesting that the Nb1-Nb4 (nearest neighbors) bond-order in the N(b)/A(O) is 0.78, somewhat reduced from the same in bulk Nb (1.04). This is in line with the reduction in the W_{sep} in going from cleaving bulk Nb to cleaving ... Nb-Nb-Nb \uparrow Nb-O-Al-Al... In the latter case we are cleaving essentially a weakened metallic bond, due to the Nb1-O1 ionic interaction. Similarly, in the N(b)/A(Al) interface, we see a relatively small Al1-Nb4 bond order (0.48), also consistent with the small W_{sep} for that interface.

In summary, we have presented for the first time *ab initio* calculations of the ideal work of separation of Nb(111)/ Al_2O_3 (0001) interfaces. Mulliken charges and bond orders enable us to rationalize the bonding across

TABLE III. Table of Mulliken populations and bond orders.

Mulliken pop.	N(m)/A(O)	N(b)/A(O)	N(b)/A(Al)	Nb(111)
O1	-0.84	-0.86	-0.93	...
Nb1/Al1	1.04	0.77	1.50	-0.07
Nb2	...	0.27	0.37	0.00
Bond order				
O1-Nb1/Al1	0.93	0.60	0.50	...
O1-Nb2	...	0.30	0.34	...
Nb1/Al1-Nb4	...	0.78	0.46	1.04

the interface. The O-terminated interfaces form strong bonds with a high degree of ionic character. A very similar picture is expected to hold for other O-terminated interfaces, such as Nb(110)/Al₂O₃(11 $\bar{2}$ 0) in which the Nb atoms occupy Al-lattice sites. Our calculations provide a microscopic explanation of their high adhesive strength, as recently experimentally reported [3]. We predict that cleavage preferentially takes place between metal atoms, whose bonding has both ionic and metallic/covalent character influenced by the proximity of the interfacial O atoms.

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