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14 June 1999

PHYSICS LETTERS A

Physics Letters A 256 (1999) 391–398

Ab initio pair potentials at metal-ceramic interfaces

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Received 29 January 1999; accepted 13 April 1999

Communicated by J. Flouquet

Abstract

A systematic approach is proposed to obtain the interfacial interatomic potentials. By inverting ab initio adhesive energy curves for the metal-MgO ceramic interfaces, We derive interfacial potentials between Ag and O^{2-} , Ag and Mg^{2+} , Al and O^{2-} , Al and Mg^{2+} . The interfacial potentials, obtained from this method, demonstrate general features of bondings between metal atoms and ceramic ions. © 1999 Elsevier Science B.V. All rights reserved.

PACS: 12.39.Pn; 68.35. – p

Keywords: Interatomic potential; Interface; Ab initio

1. Introduction

Metal-ceramic interfaces exist in a wide range of materials, e.g. metal-ceramic composites, protective coatings, and thin metal-ceramic films in electronic device. The interaction across the metal-ceramic interface critically determines the properties of these materials [1]. Principally, understanding the interaction can be done adequately using ab initio electronic calculations, and recently a number of such studies have been made using either the local density [2–5] or periodic hartree-fock [6] approximation. However, these ab initio methods require large amounts of computer time and are limited to very short period structures. In order to understand more realistic structure and properties of interface, atomistic simulations are necessary, where interatomic potentials at interface are required [7].

The metal-ceramic bond, not only has substantial ionic component but also has significant covalent/metallic character as well. The mixed bonding at interface causes great difficulty in deriving atomic potentials for the metal-ceramic systems, although various atomic potentials have had considerable success in dealing with material in which one type of bonding dominates, such as the shell model for ionic crystals and the embedded-atom model for metals. The important work on metal-ceramic bonding was done by Duffy and co-workers [8,9]. In their model, interaction between metal and ceramic is composed of short-range repulsive interactions and an attractive electrostatic image interaction [10,11], which had been applied to perfect surfaces [8]. The defect of this model is not fully atomistic and only considers ionic component of bonding, but their work has provided a valuable insight into bonding at metal-ceramic interface. The discrete classical model (DCM), an alternative method considering image

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charge effects, has developed by Finnis et al. [12,13]. DCM is fully atomistic and is not restricted to planar surfaces. However, description of interatomic forces in DCM scheme can not be easily formulated, moreover, the method requires large amounts of computer time because the charges and dipole moments on the metal atoms are obtained through solving a set of equations. On the other hand, we may have different choices for short-range repulsive interaction, for example, metal ion and ceramic ion interaction potential [8] or metal atom and ceramic ion one [14], and they cause different results [8]. To this day, little progress has been made on simulating the atomic structure of metal-ceramic interface and particularly the consequences of misfit owing to lack of accurate yet simple interfacial interatomic potential models [15,16]. So it is necessary to provide a more simple interatomic potential model for metal-ceramic interface, which is applicable for large-scale atomistic simulations and Monte Carlo simulations. The center of this paper is to provide one approach in which interfacial interatomic potentials can be obtained from the data of ab initio electronic calculation.

Smith et al. [5,17] have had used LCAO method to calculate idea adhesive energy of metal/ceramic interfaces, in that misfit dislocations, avalanches and other atomic distortions are not considered. They have established relation between energy and interfacial separation (the adhesion curve), which is similar to universal binding energy relation [18]

$$E(d) = -E_0(1 + d^*)\exp(-d^*) \quad (1)$$

where $d^* = (d - d^0)/l$, d is the interfacial separation, the parameter l is scaling constant, E^0 is ideal adhesive energy, and d^0 is equilibrium interfacial separation.

The inversion approach to constitute interatomic pair potential was proposed by Carlsson, Gelatt, and Ehrenreich (CGE) [19] in 1980, and since then the same formula has been applied with limited cases by only a couple of authors [20,21]. Recently, Bazant has developed the method to obtain parameter-free many-body potential for silicon [22]. In fact, CGE method is one kind of recursion method, and an alternative method, where möbius transformation is used, has been developed by Chen [23–25]. Cohesive energy curves were used in all above methods.

In this paper, we extend inversion approach to interfaces, and construct parameter-free interfacial interatomic pair potentials. Our method is based on two assumptions: (i) the adhesive energy can be written as a sum of pair interaction energies between metal atoms and ceramic ions, and (ii) electronic structure calculations of the adhesive energy can be expressed as a function of interfacial separation. Then, the interatomic pair potentials are constructed by inverting the relation between adhesion energy and the pair potential.

In the following, Section 2 presents the derivation of the technique for the construct of the new pair potential, ϕ , from the calculated adhesive energy curve of interfacial separation. In Section 3 the resulting pair potentials for Ag/{100}MgO and Al/{100}MgO interfaces are obtained and discussed. The conclusions will be given in Section 4.

2. The inversion of interfacial atomic pair potential

For a given bicrystal interfacial structure, the total energy of the system, E , can be expressed as sum of three parts.

$$E = E_1 + E_2 + E_{12} \quad (2)$$

The first two parts are energies stored in crystal 1 and crystal 2, respectively. The last part E_{12} is the interactional energy across the interface, which can be considered as adhesive energy. We adopt the first assumption that adhesive energy can be expressed as a function of atomic distance r ,

$$E_{\text{ad}} = \sum_{i,j} \phi_{i,j}(r_{i,j}) \quad (3)$$

where $\phi_{i,j}(r_{i,j})$ is the pair potential, i,j represent two species belonged to two different crystals. To demonstrate our method, we take metal/{100}MgO system (see Fig. 1) as a prototype. These systems are of great theoretical and experimental interest [1]. For metal/{100}MgO interfaces, there are two kinds of interatomic potential $\phi_{\text{M-O}^{2-}}$ between metal atom and O^{2-} ion, and $\phi_{\text{M-Mg}^{2+}}$ between metal atom and

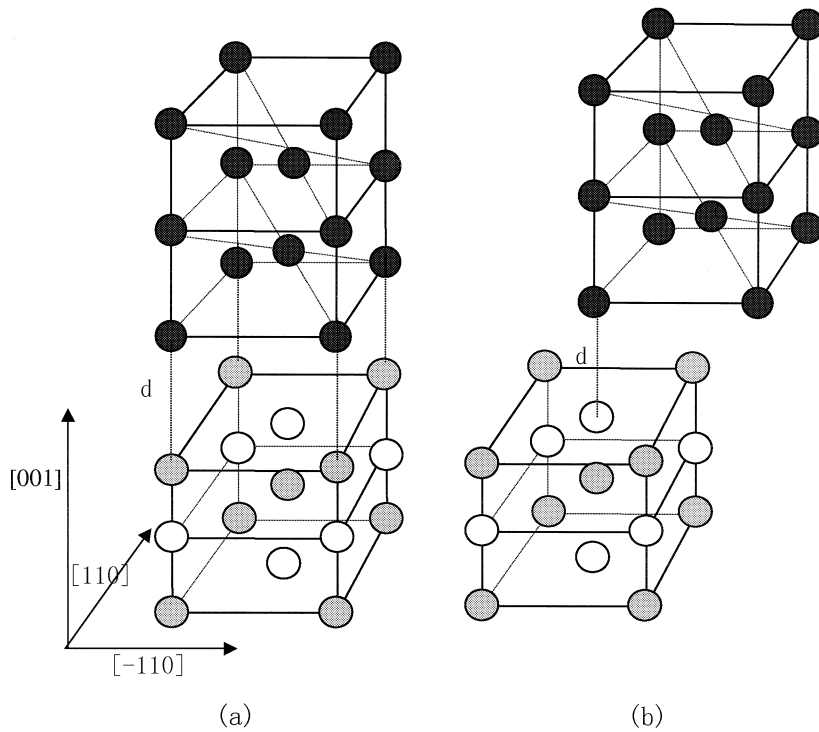


Fig. 1. The schematic figure of the *metal*/*{100}*MgO interface. The dark disks represent metal atoms, the gray disks O^{2-} ions and the white disks Mg^{2+} ions. (a) Metal atoms on the top of O^{2-} ions; (b) Metal atoms on the top of Mg^{2+} ions.

Mg^{2+} ion across the interface. We set that E_O , E_{Mg} are adhesive energies for the two cases of metal atoms sit on top of the O^{2-} and Mg^{2+} ions, respectively. According to Hong et al.'s [17] calculations, the metal is uniformly stretched or compressed both in the plane parallel to interfaces so as to achieve perfect registry with ceramic substrate, therefore, E_O and E_{Mg} can be expressed as

$$E_O(d)$$

$$= \sum_{l,l'=0}^{\infty} \sum_{m,n=-\infty}^{\infty} \phi_{M-O^{2-}} \left(\sqrt{\left(d + Z_{l,l'}\right)^2 + A_{m,n}^2} \right) + \phi_{M-O^{2-}} \left(\sqrt{\left(d + Z_{l+\frac{1}{2},l'}\right)^2 + A_{m+\frac{1}{2},n+\frac{1}{2}}^2} \right) + \phi_{M-Mg^{2+}} \left(\sqrt{\left(d + Z_{l,l'}\right)^2 + A_{m+\frac{1}{2},n+\frac{1}{2}}^2} \right)$$

$$+ \phi_{M-Mg^{2+}} \left(\sqrt{\left(d + Z_{l+\frac{1}{2},l'}\right)^2 + A_{m,n}^2} \right) + \phi_{M-O^{2-}} \left(\sqrt{\left(d + Z_{l,l'+\frac{1}{2}}\right)^2 + A_{m+\frac{1}{2},n+\frac{1}{2}}^2} \right) + \phi_{M-O^{2-}} \left(\sqrt{\left(d + Z_{l+\frac{1}{2},l'+\frac{1}{2}}\right)^2 + A_{m,n}^2} \right) + \phi_{M-Mg^{2+}} \left(\sqrt{\left(d + Z_{l,l'+\frac{1}{2}}\right)^2 + A_{m,n}^2} \right) + \phi_{M-Mg^{2+}} \left(\sqrt{\left(d + Z_{l+\frac{1}{2},l'+\frac{1}{2}}\right)^2 + A_{m+\frac{1}{2},n+\frac{1}{2}}^2} \right) \quad (4)$$

and

$$\begin{aligned}
 E_{Mg}(d) &= \sum_{l,l'=0}^{\infty} \sum_{m,n=-\infty}^{\infty} \phi_{M-Mg^{2+}} \left(\sqrt{(d+Z_{l,l'})^2 + A_{m,n}^2} \right) \\
 &+ \phi_{M-Mg^{2+}} \left(\sqrt{\left(d+Z_{l+\frac{1}{2},l'}\right)^2 + A_{m+\frac{1}{2},n+\frac{1}{2}}^2} \right) \\
 &+ \phi_{M-O^{2-}} \left(\sqrt{(d+Z_{l,l'})^2 + A_{m+\frac{1}{2},n+\frac{1}{2}}^2} \right) \\
 &+ \phi_{M-O^{2-}} \left(\sqrt{\left(d+Z_{l+\frac{1}{2},l'}\right)^2 + A_{m,n}^2} \right) \\
 &+ \phi_{M-Mg^{2+}} \left(\sqrt{\left(d+Z_{l,l'+\frac{1}{2}}\right)^2 + A_{m+\frac{1}{2},n+\frac{1}{2}}^2} \right) \\
 &+ \phi_{M-Mg^{2+}} \left(\sqrt{\left(d+Z_{l+\frac{1}{2},l'+\frac{1}{2}}\right)^2 + A_{m,n}^2} \right) \\
 &+ \phi_{M-O^{2-}} \left(\sqrt{\left(d+Z_{l,l'+\frac{1}{2}}\right)^2 + A_{m,n}^2} \right) \\
 &+ \phi_{M-O^{2-}} \left(\sqrt{\left(d+Z_{l+\frac{1}{2},l'+\frac{1}{2}}\right)^2 + A_{m+\frac{1}{2},n+\frac{1}{2}}^2} \right) \quad (5)
 \end{aligned}$$

where $Z_{l,l'} = la_{MgO} + l'a_M$ is distance perpendicular to the interface between two atoms, $A_{m,n}^2 = (m^2 + n^2)a_{MgO}^2/2$ is distance parallel to the interface between atoms.

Since adhesion energy's exps. (4) and (5) include two kinds of bond, it seems that recursive method can not proceed. However, if we add (subtract) Eq. (5) from Eq. (4), we can get $E^+(d)$ ($E^-(d)$) as the following expressions

$$\begin{aligned}
 E^+(d) &= \sum_{l,l'=0}^{\infty} \sum_{m,n=-\infty}^{\infty} \phi^+ \left(\sqrt{(d+Z_{l,l'})^2 + A_{m,n}^2} \right) \\
 &+ \phi^+ \left(\sqrt{\left(d+Z_{l+\frac{1}{2},l'}\right)^2 + A_{m+\frac{1}{2},n+\frac{1}{2}}^2} \right) \\
 &+ \phi^+ \left(\sqrt{(d+Z_{l,l'})^2 + A_{m+\frac{1}{2},n+\frac{1}{2}}^2} \right)
 \end{aligned}$$

$$\begin{aligned}
 &+ \phi^+ \left(\sqrt{\left(d+Z_{l+\frac{1}{2},l'}\right)^2 + A_{m,n}^2} \right) \\
 &+ \phi^+ \left(\sqrt{\left(d+Z_{l,l'+\frac{1}{2}}\right)^2 + A_{m+\frac{1}{2},n+\frac{1}{2}}^2} \right) \\
 &+ \phi^+ \left(\sqrt{\left(d+Z_{l+\frac{1}{2},l'+\frac{1}{2}}\right)^2 + A_{m,n}^2} \right) \\
 &+ \phi^+ \left(\sqrt{\left(d+Z_{l,l'+\frac{1}{2}}\right)^2 + A_{m,n}^2} \right) \\
 &+ \phi^+ \left(\sqrt{\left(d+Z_{l+\frac{1}{2},l'+\frac{1}{2}}\right)^2 + A_{m+\frac{1}{2},n+\frac{1}{2}}^2} \right) \quad (6)
 \end{aligned}$$

and

$$\begin{aligned}
 E^-(d) &= \sum_{l,l'=0}^{\infty} \sum_{m,n=-\infty}^{\infty} \phi^- \left(\sqrt{(d+Z_{l,l'})^2 + A_{m,n}^2} \right) \\
 &+ \phi^- \left(\sqrt{\left(d+Z_{l+\frac{1}{2},l'}\right)^2 + A_{m+\frac{1}{2},n+\frac{1}{2}}^2} \right) \\
 &- \phi^- \left(\sqrt{(d+Z_{l,l'})^2 + A_{m+\frac{1}{2},n+\frac{1}{2}}^2} \right) \\
 &- \phi^- \left(\sqrt{\left(d+Z_{l+\frac{1}{2},l'}\right)^2 + A_{m,n}^2} \right) \\
 &+ \phi^- \left(\sqrt{\left(d+Z_{l,l'+\frac{1}{2}}\right)^2 + A_{m+\frac{1}{2},n+\frac{1}{2}}^2} \right) \\
 &+ \phi^- \left(\sqrt{\left(d+Z_{l+\frac{1}{2},l'+\frac{1}{2}}\right)^2 + A_{m,n}^2} \right) \\
 &- \phi^- \left(\sqrt{\left(d+Z_{l,l'+\frac{1}{2}}\right)^2 + A_{m,n}^2} \right) \\
 &- \phi^- \left(\sqrt{\left(d+Z_{l+\frac{1}{2},l'+\frac{1}{2}}\right)^2 + A_{m+\frac{1}{2},n+\frac{1}{2}}^2} \right) \quad (7)
 \end{aligned}$$

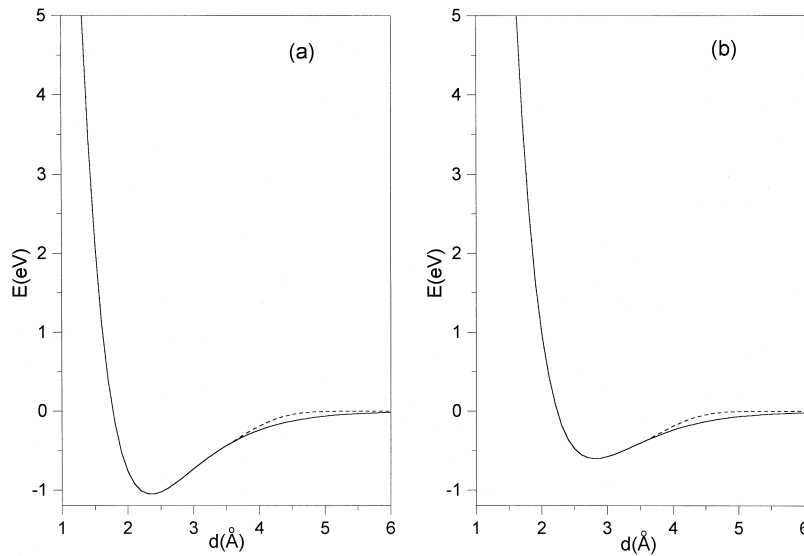


Fig. 2. The calculated adhesive energy E (per unit of surface area) vs. interfacial separation d for Ag/{100}MgO interface. The solid line corresponds to the case before cutoff, while the dashed corresponds to the case after cutoff. (a)Metal atoms on the top of O^{2-} ions; (b)Metal atoms on the top of Mg^{2+} ions.

where

$$E^+ = E_O(d) + E_{Mg}(d) \tag{8}$$

$$E^- = E_O(d) - E_{Mg}(d) \tag{9}$$

$$\phi^+ = \phi_{M-O^{2-}} + \phi_{M-Mg^{2+}} \tag{10}$$

$$\phi^- = \phi_{M-O^{2-}} - \phi_{M-Mg^{2+}} \tag{11}$$

Hence, the composite adhesive energy E^+ (E^-), can be represented by the sum of several one-component pair potentials ϕ^+ (ϕ^-). The following objective, given the value of E^+ and E^- as a function of d , is to invert relation (6) and (7) to find pair potential ϕ^+, ϕ^- . Then, pair potential $\phi_{M-O^{2-}}$ and $\phi_{M-Mg^{2+}}$ can be obtained from

$$\phi_{M-O^{2-}} = \frac{\phi^+ + \phi^-}{2} \tag{12}$$

$$\phi_{M-Mg^{2+}} = \frac{\phi^+ - \phi^-}{2} \tag{13}$$

Eqs. (6) and (7) can be substantially written in terms of a nonlinear transformation as:

$$E(d) = \left[\phi(d) + \sum_p T_p \phi(d) \right] \tag{14}$$

and the transformation operator T_p is defined by

$$T_p \phi(d) = n_p \phi \left(\sqrt{(d+l_p)^2 + a_p^2} \right) \tag{15}$$

l_p and a_p are fixed value for a given bicrystal interface, n_p is atomic pair numbers with the same l_p and a_p . Following the CGE's method [19],

$$\begin{aligned} \phi(d) &= \left(1 + \sum_p T_p \right)^{-1} [E(d)] \\ &= \left(1 - \sum_p T_p + \sum_p \sum_q T_p T_q - \dots \right) [E(d)] \end{aligned} \tag{16}$$

Thus we have central result of the section, in which pair potential $\phi(d)$ is expressed in terms of composite adhesive energy $E(d)$. Then, Pair potential $\phi_{M-O^{2-}}$ and $\phi_{M-Mg^{2+}}$ between metal atoms and ions can be obtained from expressions (12), (13), and

they can be expressed in term of adhesion energy E_0 and E_{Mg} .

3. Pair potentials for Ag – Mg²⁺, Ag – O²⁻, Al – Mg²⁺, Al – O²⁻

In Ag/{100}MgO and Al/{100}MgO interface systems, Hong et. al. [17]. have calculated adhesive energy curves for the case of metal atoms on the top of O²⁻ ions and Mg²⁺ ions, respectively. They use four points method to decide expression (1), and their results are much larger than those of other calculations [7] for Ag/{100}MgO. Here we do not want to pursue precision of pair potentials, and we directly adopt their results. The results are shown in Figs. 2 and 3.

If we directly adopt $E(d)$ as inverting mother function, Eq. (16) will be not converged for the case of interface. This is because $E(d)$ decreases too slowly as d increases. To avoid embarrassment, we must modify tail of $E(d)$ as Bazant do [22]. The reasons are the following: (i) these are problems inherent to inversion process, which, in spite of being exact, stretches the assumption of a volume-independent potential to unphysical extreme. Because inversion amounts to solving in order of decreasing

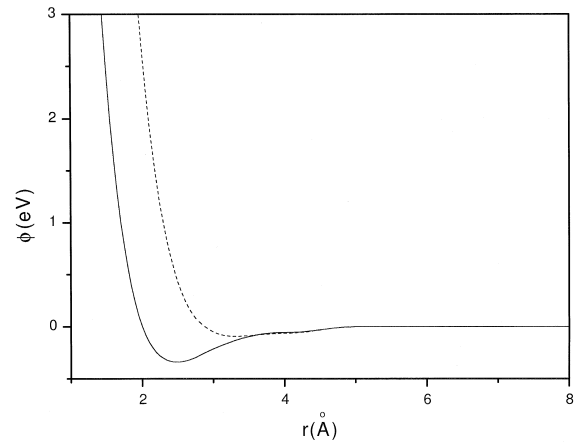


Fig. 4. The inverted pair potential $\phi_{Ag-O^{2-}}$ (solid line) and $\phi_{Ag-Mg^{2+}}$ (dashed line) for Ag/{100}MgO interface.

distance from infinite separation, the tail of potential comes from unscreened interactions between atoms in a low density gaseous phase [22]. It is obviously unreasonable that the same tail is then used to describe long range in a bulk crystal, which is presumably screened by the presence of closer atoms; (ii) we forgo the requirement that the potential exactly reproduce the entire adhesive energy curve, and focus on condensed volumes typical of solid and liquid

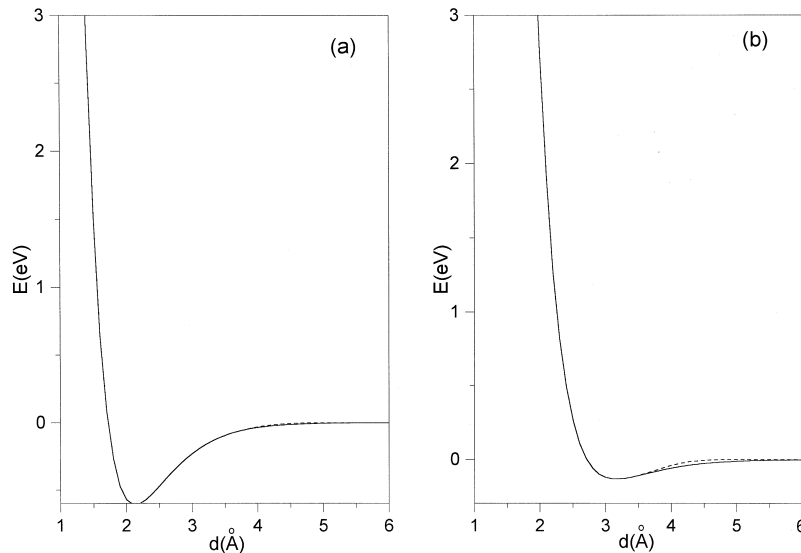


Fig. 3. The calculated adhesive energy E (per unit of surface area) vs. interfacial separations d for Al/{100}MgO interface. The explanations are same as Fig. 2.

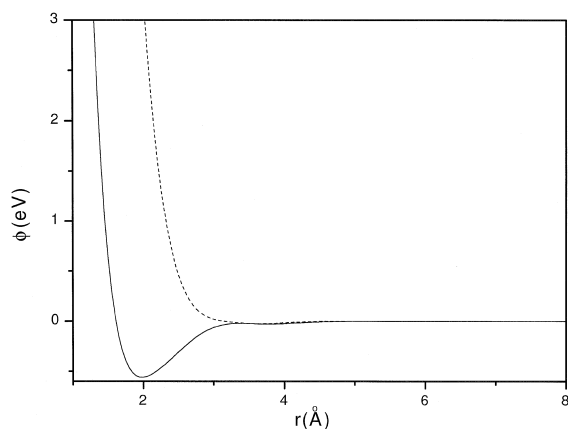


Fig. 5. The inverted pair potential $\phi_{\text{Al}-\text{O}^{2-}}$ (solid line) and $\phi_{\text{Al}-\text{Mg}^{2+}}$ (dashed line) for Al/{100}MgO interface.

environments, whose exact energies can be persevered with any choice of tail for the potential. Thereupon, we modify $E(d)$, and force energy curve $E(d)$ to be zero for $d \geq 4.5 \text{ \AA}$ without disturb energies within neighborhood of the equilibrium bond length, where metal-ceramics bonds are well defined. For example, modified results are shown in Figs. 2 and 3.

Figs. 4 and 5 show the results the inversion of calculated adhesive energy of Ag/{100}MgO and Al/{100}MgO. As demonstrated in Figs. 4 and 5, the potential between metal and O^{2-} ion has a larger bonding energy (the depths of the minima) than that between metal atom and Mg^{2+} ion. This result is as expected from the simple picture that the Ag and Al atoms form a stronger bond with O ions than with Mg ions. The potential between Ag atom and Mg^{2+} ion has modest bond strength. Al atom has extremely weak bonding with Mg^{2+} ion, because $\phi_{\text{Al}-\text{Mg}^{2+}}$ has very shallow minima. Bond length(positions of the minima) of Ag and O^{2-} is smaller than that of Al and O^{2-} . These differences perhaps is due to lack of inner d -shells in Al which are present in Ag.

Duffy et al.'s potential model [8] only incorporate ionic effects of the chemical bonding at ceramic-metal interface, but other bonding effects, such as covalency and metallicity, are omitted. Obviously, our pair potentials mix the contributions of all different components of bond including ionic component and covalent/metallic. The evaluation of the potential model is difficult since there have been few

experiments describing the atomic arrangement and we have to rely, in part, on a comparison with previous electronic structure calculations. We believe our pair potential will give results which are in agreement with electronic structure calculations, since potentials directly obtained from ab initio data. Clearly, our potentials are more reasonable than those in Vitek's method [15] which assumed phenomenological parameterized potentials, and will be more likely applied to calculations of the properties of systems far equilibrium.

4. Summary

In conclusion, we have presented an inverting technique to obtain effective interfacial interatomic potentials. By inverting ab initio adhesive energy curves for the metal-MgO ceramic interfaces, we have demonstrated general features of bondings between metal atoms and ceramic ions. The technique provides a feasible approach to obtain the interfacial interatomic potentials by fitting ab initio databases and it is not restricted to metal-ceramic interface only, so its main idea will find no difficulty in applying to other kinds of interface. We hope that this method will lead to interfacial potentials with improved transferability, more important, we expect it can throw light on studying technological important interfaces and the effect of temperature on metal-ceramic adhesion via molecular dynamics. Applying the pair potential model to study the structure and mechanic properties of metal-ceramic interface will be reported in our further work,

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