

Metal-Ceramic Adhesion and the Harris Functional

John R. Smith,¹ Tao Hong,² and David J. Srolovitz^{2,3}

¹Physics Department, General Motors Research and Development Center, Warren, Michigan 48090-9055

²Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan 48109-2136

³Department of Materials and Interfaces, Weizmann Institute, Rehovot 76100, Israel

(Received 28 February 1994)

The effects of a monolayer of C or S impurities on adhesion at MgO/Al and MgO/Ag interfaces were determined from first principles. Impurity effects were found to be substantial, with changes in adhesive energies ranging from 9% to 61%. All adhesion curves accurately obey the universal energy relation. The Harris functional reproduces the self-consistent results well. Given the relative simplicity of the Harris functional, these successful interfacial applications may significantly expand the size and complexity of systems which can be studied.

PACS numbers: 68.35.Wm, 68.35.Dv, 81.20.Nd

Metal-ceramic interfaces are the subject of wide-ranging research [1] because understanding them is vital to a number of technological applications such as in composites, electronic packaging systems, thin film technology, and joining. We would like to report the first computation of the effects of impurities on metal-ceramic adhesion. We find impurity effects can be substantial, and vary interestingly with the type of impurity and its location. The Harris [2,3] functional was tested against these computations, and we found that it can yield accurate results for a variety of surfaces and

interfaces. This unexpected [4–6] result points the way to reliable, first-principles computations for a broader range of applications than was hitherto thought possible.

In metal-ceramic interfaces, with and without impurities, one encounters mixtures of metallic, covalent, and ionic bonds involving a number of different elements. Only a first-principles method can be expected to give accurate results for such a complex system. Thus we have carried out fully self-consistent density functional [7,8] calculations. In terms of the self-consistent electron density $n^{\text{sc}}(\mathbf{r})$, the total energy is given by

$$E[n^{\text{sc}}(\mathbf{r})] = \sum_i \epsilon_i - \int n^{\text{sc}}(\mathbf{r}) \left\{ \frac{1}{2} \phi[n^{\text{sc}}(\mathbf{r})] + v_{\text{xc}}[n^{\text{sc}}(\mathbf{r})] \right\} d^3\mathbf{r} + E_{\text{xc}}[n^{\text{sc}}(\mathbf{r})] + E_{\text{ion}}, \quad (1)$$

where ϵ_i is the (self-consistent) eigenvalue of the i th occupied valence or conduction band state, $\phi[n^{\text{sc}}(\mathbf{r})]$ is the electrostatic potential, $v_{\text{xc}}[n^{\text{sc}}(\mathbf{r})]$ is the exchange-correlation [9] potential, $E_{\text{xc}}[n^{\text{sc}}(\mathbf{r})]$ is the exchange-correlation [9] total energy, and E_{ion} is the mutual electrostatic energy of the ion cores. Equation (1) requires the solution of Schrödinger's equation, the subsequent solution of Poisson's equation, and then iteration of the procedures until self-consistency is achieved. The difficulty of this process limits the complexity of the systems which can be treated.

The Harris [2,3] functional E^H is an approximation to $E[n^{\text{sc}}(\mathbf{r})]$ which eliminates the need to solve Poisson's equation or to iterate to self-consistency. E^H is written in terms of an input electron density distribution $n^a(\mathbf{r})$ as

$$E^H = \sum_i \epsilon_i^{\text{out}} - \int n^a(\mathbf{r}) \left\{ \frac{1}{2} \phi[n^a(\mathbf{r})] + v_{\text{xc}}[n^a(\mathbf{r})] \right\} d^3\mathbf{r} + E_{\text{xc}}[n^a(\mathbf{r})] + E_{\text{ion}}. \quad (2)$$

Here the input electron density distribution $n^a(\mathbf{r})$ is taken to be a sum of free-atom electron densities, and the ϵ_i^{out} are the output eigenvalues. The Harris functional eliminates much of the difficulty associated with Eq. (1), and Harris [2] has argued that its energy density is

accurate to correlations of order $[n^{\text{sc}}(\mathbf{r}) - n^a(\mathbf{r})]^2$. Initial tests showed that the results of Eq. (2) agree fairly well with those of Eq. (1) for diatomic molecules [10] and for cohesive properties of bulk solids [4, 11].

This excitement was dampened somewhat by reported [4–6] failures of Eq. (2) for surface properties. For example, the error in the Al(111) surface energy was found to be 78% in two [4,5] independent calculations. We will demonstrate that a different computational strategy for implementing the Harris functional yields good surface and interfacial results via Eq. (2).

In the following, we report results of fully self-consistent and Harris functional calculations for MgO/Al(001) and MgO/Ag(001) interfaces with and without monolayers of C and S impurities. MgO/Ag(001) was chosen for our research on impurity effects on metal-ceramic adhesion because the impurity-free interface is well studied, both experimentally [12] and theoretically [6, 13–15]. The MgO/Al(001) interface was chosen so that we could compare a metal containing d electrons (Ag) with a so-called simple metal (Al). C and S were chosen because they are representative of impurities found at interfaces. We will see that these two impurities have interestingly different effects on the adhesion.

Both Al and Ag have a relatively small lattice mismatch with MgO (3% for Ag and 4% for Al). Epitaxial interfaces have been observed [12] for MgO/Ag(001) and will likely occur for MgO/Al(001). We therefore assume epitaxial interfaces, and because MgO is much stiffer than the metals, we expanded the in-plane lattice constants of Ag and Al to match the lattice constant of MgO (4.212 Å). Trampert *et al.* [12] deposited Ag on MgO(001) using molecular beam epitaxy. Their high resolution transmission electron microscopy results indicated that the Ag atoms were on top of either Mg or O atoms, rather than above the interstices in the (001) plane of MgO. Thus we considered both translational states (metal atoms on top of either Mg or O atoms). We found that the lower energy configuration for both Ag and Al atoms was atop O atoms. This is consistent with the MgO/Ag(001) results of Refs. [13–15]. Our self-consistent results show that the adhesive energy for the atop-oxygen configuration is larger than that for the atop-magnesium configuration by 410 mJ/m² for Ag and 430 mJ/m² for Al. Schönberger, Andersen, and Methfessel [13] also reported a difference of 410 mJ/m² for MgO/Ag(001). Therefore in the remainder of this paper we consider only the lower energy, atop-O-atom configuration.

Total energy E versus interfacial spacing d is plotted in Fig. 1 for MgO/Al(001) (right panels) and MgO/Ag(001) (left panels). We will call these ideal adhesive energy curves, because at this stage we have not allowed for plastic or elastic deformations. Clean (or undoped) interfaces, as well as monolayer-impurity doped interfaces are shown. Interstitial C and S and substitutional S results are given. The interstitial site is the fourfold symmetric (“hole”) site of the metal (001) surface. In the substitutional configuration, the S replaces the surface O of the MgO. This choice was made because of the chemical similarity between O and S. Clearly there are other possible configurations, but these interstitial and substitutional configurations are a reasonable starting point. The upper panels are fully self-consistent results [Eq. (1)], while the lower panels are Harris functional results [Eq. (2)]. The curves through the computed points are from the following simple function:

$$E(d) = -E_0(1 + d^*) \exp(-d^*), \quad (3)$$

where $d^* = (d - d_0)/l$, E_0 and d_0 are the equilibrium adhesive energy per unit surface area and interfacial separation, respectively, and l is a scaling length. In Ref. [16], it is shown that Eq. (3) accurately represents the numerically derived universal binding energy relation.

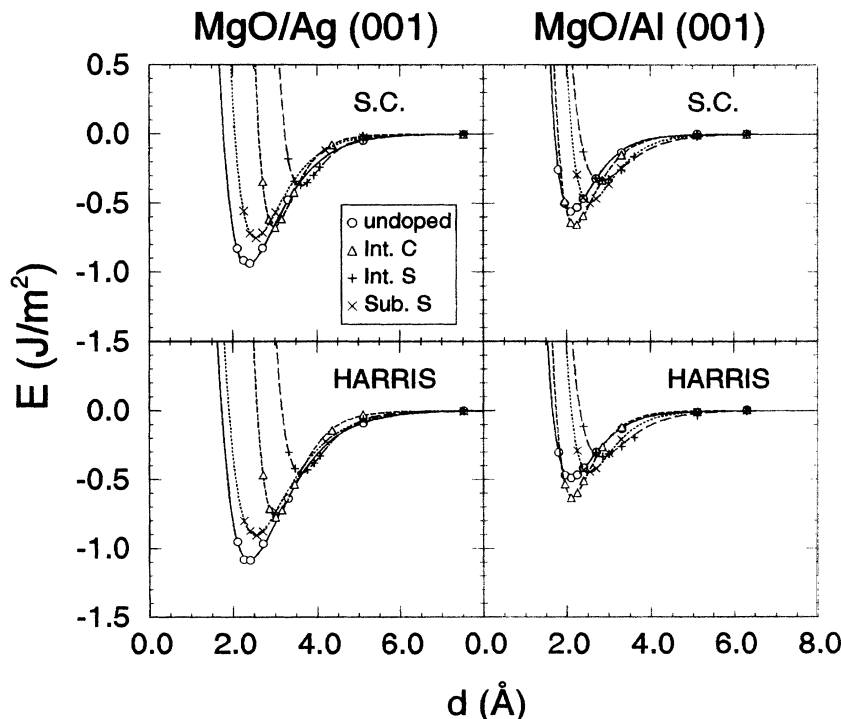


FIG. 1. Adhesive energy E versus interfacial separation d . The right panels show results for MgO/Al(001) and the left panels MgO/Ag(001). The upper panels contain fully self-consistent results [Eq. (1)], while the lower panels contain Harris functional results [Eq. (2)]. Impurity free (undoped) interfaces as well as interstitial C and S and substitutional S doped interfaces at the monolayer level are shown. The ideal adhesive energies E_0 referred to in the text are the negative of the values of E at the minima of the curves.

The universal binding energy relation has been shown earlier [16] to apply also to energetics of bimetallic adhesion, diatomic molecules, chemisorption, equations of state of nuclear matter, and equations of state of all classes of solids. Note first that the universal binding energy relation passes accurately through the computed points for all cases shown in Fig. 1.

Second, note the equilibrium adhesive energy E_0 (see Fig. 1 and Table I), of the undoped MgO/Ag is 400 mJ/m² larger than that of MgO/Al. [Interestingly, our computed Ag(001) surface energy is 490 mJ/m² larger than our Al(001) surface energy.]

Third, we see that impurity effects can be quite strong in metal-ceramic interfaces, as we found earlier [17] for Mo/MoSi₂ interfaces. Note that typically the impurities decrease E_0 , which is consistent with experimental data [18,19] on a variety of materials and impurities. The size of this effect can be large: E_0 is reduced by 61% for a monolayer of interstitial S in MgO/Ag. Interstitial C in MgO/Al actually increases E_0 . An increase of adhesion due to impurities is not typical, but it has been seen experimentally [18] in some cases. We feel this may be due to the fact that Al is stretched to become epitaxial with MgO, perhaps providing some extra volume for a small impurity like C to be inserted interstitially with a minimum of strain energy. (In general, strain energy would tend to decrease E_0 , whereas chemical bonds formed between the impurity and the two surfaces tend to increase E_0 .)

Next note that the self-consistent curves (upper panel) are in striking agreement with the Harris functional results (lower panel). The curves appear quite similar at all interfacial spacings d and the ordering of the energy curves is the same for both methods. This accuracy for a variety of materials and interfacial spacings is evidence of a remarkable stability of the Harris functional. Table I shows that the agreement in equilibrium interfacial separations d_0 is typically within a few hundredths of an Å. The difference between self-consistent and Harris functional E_0 values in Table I is on average 10%, while the predicted changes in

E_0 due to impurities differ by only 3.5%. Such higher accuracies for energy changes due to atomic restructuring are not unusual for first-principles approaches. Good Harris functional results for several Si bulk crystal structures have been reported [20]. Our results now suggest that the Harris functional also provides reliable results for surfaces and interfaces [21]. Because of the relative simplicity of this approximation, the way is now opened to the relatively accurate treatment of significantly more complex systems.

Note in Table I that our Harris functional error for the Al(001) surface energy is <1%, as compared to 78% reported [4,5] for Al(111). Why is the accuracy achieved here using the Harris functional so much better than that found by earlier authors [4,5]? The accuracy of our surface and interfacial results, relative to those obtained in earlier studies, may be due to the differences in computational strategies. The earlier approach [4,5] was to determine the surface energy by subtracting the energy of the bulk single crystal from the thin-film energy. Surface energies are obtained as a small difference between large numbers (total energies). It is therefore important to compute the two total energies in the same way, which promotes cancellation of errors when the energies are subtracted. This is difficult to do when separate calculations are done for systems with and without surfaces [22]. In the present study, we performed all calculations on a single system, determining the total energy as a function of interfacial spacing. We took care to use the same basis sets, the same direct-space mesh, etc., for all spacings. This is likely the reason that the present Harris functional results are more accurate than those previously reported.

In summary, we found that impurity effects at the monolayer level can be substantial. Changes in equilibrium adhesive energies ranged from 9% to 61%. In all but one case, C and S impurities decreased the adhesive energies of both MgO/Al and MgO/Ag. For interstitial C in MgO/Al, the adhesive energy was increased. All metal-ceramic adhesion curves, with and without impurities, accurately obeyed the universal energy relation. Good agreement was obtained between fully self-consistent results and those obtained via the Harris functional. The remarkable accuracy of the Harris functional approach and the concomitant decrease in computational resources required to apply it, relative to other local density functional methods, opens the path to applying *ab initio* methods to significantly more complex systems than were previously thought possible.

The authors would like to acknowledge, with thanks, useful conversations with Dr. Michael W. Finnis. This work was supported by the U.S. Office of Naval Research under Grant No. N00014-91-J4019. The authors wish to also thank the San Diego Supercomputer Center for support. D.J.S. gratefully acknowledges the hospitality of The Weizmann Institute of Science and the partial support of the Michael Visiting Professorship.

TABLE I. Ideal adhesive energies E_0 and equilibrium interfacial spacings d_0 for (001) interfaces. E_0 is in J/m² and d_0 is in Å. The subscripts int and sub refer to interstitial and substitutional impurity configurations, respectively.

	Self-consistent		Harris	
	E_0	d_0	E_0	d_0
Al/Al	1.020	2.02	1.030	1.99
MgO/Al	0.550	2.13	0.490	2.11
MgO/C/Al	0.660	2.19	0.630	2.13
MgO/S _{int} /Al	0.340	2.80	0.320	2.87
MgO/S _{sub} /Al	0.500	2.57	0.450	2.54
MgO/Ag	0.950	2.34	1.080	2.38
MgO/C/Ag	0.670	2.99	0.770	3.00
MgO/S _{int} /Ag	0.370	3.61	0.450	3.60
MgO/S _{sub} /Ag	0.750	2.54	0.900	2.52

- [1] See, e.g., *Proceedings of the International Symposium on Metal-Ceramic Interfaces*, edited by M. Rühle, A.H. Heuer, A.G. Evans, and M.F. Ashby [Acta Metall. Mater. Suppl. **40** (1992)].
- [2] J. Harris, Phys. Rev. B **31**, 1770 (1985).
- [3] W. Matthew, C. Foulkes, and R. Haydock, Phys. Rev. B **39**, 12520 (1989).
- [4] A.J. Read and R.J. Needs, J. Phys. Condens. Matter **1**, 7565 (1989).
- [5] M.W. Finnis, J. Phys. Condens. Matter **2**, 331 (1990).
- [6] M.W. Finnis, Acta Metall. Mater. **40**, S25 (1992).
- [7] The self-consistent local-orbital method we use is described fully by J.R. Smith, J.G. Gay, and F.J. Arlinghaus, Phys. Rev. B **21**, 2201 (1980).
- [8] W. Kohn and L. Sham, Phys. Rev. A **140**, 1133 (1965).
- [9] S.H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980); D.M. Ceperley and B.J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
- [10] F.W. Averill and G.S. Painter, Phys. Rev. B **41**, 10344 (1990).
- [11] H.M. Polatoglou and M. Methfessel, Phys. Rev. B **37**, 10403 (1988).
- [12] A. Trampert, F. Ernst, C.P. Flynn, H.F. Fischmeister, and M. Rühle, Acta Metall. Mater. **40**, S227 (1992).
- [13] U. Schönberger, O.K. Andersen, and M. Methfessel, Acta Metall. Mater. **40**, S1 (1992).
- [14] P. Blöchl, G.P. Das, H.F. Fischmeister, and U. Schönberger, in *Metal-Ceramic Interfaces*, edited by M. Rühle, A.G. Evans, M.F. Ashby, and J.P. Hirth (Pergamon, Oxford, 1990) pp. 9–14.
- [15] A.J. Freeman, C. Li, and C.L. Fu, in *Metal-Ceramic Interfaces* (Ref. [14]), pp. 2–8.
- [16] A. Banerjee and J.R. Smith, Phys. Rev. B **37**, 6632 (1988), and references therein. See also P. Vinet, J.H. Rose, J. Ferrante, and J.R. Smith, J. Phys. **1**, 1941 (1989).
- [17] T. Hong, J.R. Smith, and D.J. Srolovitz, Phys. Rev. B **47**, 13615 (1993).
- [18] J.R. Smith and T.V. Cianciolo, Surf. Sci. Lett. **210**, L229 (1989).
- [19] D. Korn, G. Elssner, H.F. Fischmeister, and M. Rühle, Acta Metall. Mater. **40**, S355 (1992).
- [20] H.M. Polatoglou and M. Methfessel, Phys. Rev. B **41**, 5898 (1990).
- [21] These results support the use of the Harris functional by O.F. Sankey and D.J. Niklewski, Phys. Rev. B **40**, 3979 (1989).
- [22] After submission of our manuscript, we became aware of work to be published by J.C. Boettger, Phys. Rev. B (to be published). Boettger provides evidence in support of our arguments about possible inaccuracies associated with subtracting total energies from separate thin film and bulk computations.