Interface energy and its influence on interface fracture between metal and ceramic thin films in nanoscale

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A theoretical model about the size-dependent interface energy between two thin films with different materials is developed by considering the chemical bonding contribution based on the thermodynamic expressions and the structure strain contribution based on the mechanical characteristics. The interface energy decreases with reducing thickness of thin films, and is determined by such available thermodynamic and mechanical parameters as the melting entropy, the melting enthalpy, the shear modulus of two materials, etc. The predicted interface energies of some metal/MgO and metal/Al₂O₃ interfaces based on the model are consistent with the results based on the molecular mechanics calculation. Furthermore, the interface fracture properties of Ag/MgO and Ni/Al₂O₃ based on the atomistic simulation are further compared with each other. The fracture strength and the toughness of the interface with the smaller structure interface energy are both found to be lower. The intrinsic relations among the interface energy, the interface strength, and the fracture toughness are discussed by introducing the related interface potential and the interface stress. The microscopic interface fracture toughness is found to equal the structure interface energy in nanoscale, and the microscopic fracture strength is proportional to the fracture toughness. © 2010 American Institute of Physics. [doi:10.1063/1.3501090]

I. INTRODUCTION

The study on interface energy has attracted great attention in both experimental and theoretical aspects due to its importance in extensive fields. ¹⁻⁴ The stability of interfaces determined by interface energy affects the performance of structures and devices. Specially, the interfaces between metals and ceramics play important role in thermal barrier coatings used in aircraft and power generation turbines, and they have also extensive applications in catalytic converters, field effect transistors, anticorrosion coatings, etc. The failure of metal/ceramic interfaces may lead to the breakdown of these structures and devices. The fracture is a kind of severe interface failure mode, the fracture strength, and the fracture toughness are important parameters determining the interface fracture properties and are closely related to the interface energy. The experimental measurement of interface energy is difficult and lacking. The theoretical calculation based on the first principle, the embedded atomic method, and the molecular dynamics is complicated and time-consuming. Therefore, the scientific theoretical prediction of the interface energy and the further understanding of its influence on the interface fracture are significant. The size effect of interface energy cannot be neglected with the application of lowdimensional materials and the development of microelectromechanical systems and nanoelectromechanical systems. Study has found that the interface energy is size-dependent, $\frac{1-3}{2}$ and the size effect affects the deformation and the phase transition of nanomaterials and the stability of

In this paper, a simple theoretical model on the size-

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dependent interface energy between heterogeneous materials is developed including the chemical intrinsic interface energy and the structure interface energy, the interface energies of some metal/ceramic systems are predicted based on the model. Furthermore, the interface energy and the interface fracture strength of Ag/MgO and Ni/Al₂O₃ systems are compared with each other, and the relation between two interface quantities is discussed. Moreover, the microscopic interface fracture toughness is determined by the structure interface energy in nanoscale based on the interface potential discussion.

II. MODEL

The interface energy γ is the excess energy per unit area of a system due to appearing of the interface, and it is originated from the change in the interfacial atomic chemical bonding and the structure strain at the interface, i.e., γ includes the chemical interface energy γ_c and the structural interface energy γ_s . The chemical interface energy is larger for metal/ceramic interfaces due to the greater chemical bonding difference of two materials, and it is related to the intrinsic solid–solid interface energies of two materials γ_{c1} and γ_{c2} , respectively, thus γ_c is taken as the average value of γ_{c1} and γ_{c2} approximately. The size effect of the interface energy should be considered, which becomes obvious in nanoscale. The size-dependent intrinsic solid-solid interface energy γ_{ci} of single materials is first considered, i=1,2 denotes two materials, respectively, and the subscripts i and care elliptical in subsequent part for the simplicity of the ex-

Let γ_b be the solid–solid interface energy of single bulk materials, and $\Delta \gamma = \gamma - \gamma_b$ be the change in the interface energy in nanoscale compared to the bulk. The bulk solid–solid

interface energy γ_b is about two times of the solid-liquid interface energy γ_m of the corresponding materials. The solid-liquid interface energy $\gamma_m = 2hS_vH_m/(3V_mR)$ based on Gibbs-Thomson equation, where h is the atomic diameter of the materials, S_v is the vibrational part of the melting entropy $S_m = H_m/T_m$, H_m is the melting enthalpy, T_m is the melting temperature, V_m is the molar volume of the solids, and R is the ideal gas constant. Therefore, the bulk solid-solid interface energy can be expressed as

$$\gamma_b = 4hS_v H_m / (3V_m R). \tag{1}$$

On the other hand, the interface energy is related to the interface stress, according to the thermodynamic definition of the interface stress f, $f = \partial G/\partial A = \partial (\gamma A)/\partial A = \gamma + A \partial \gamma/\partial A$ $\approx \gamma + A \Delta \gamma/\Delta A$, where G is the interface excess Gibbs free energy and A is the interface area. The above equation can be rearranged as $\Delta \gamma = (f - \gamma)\Delta A/A$, therefore, $\gamma - \gamma_b = (f - \gamma)\Delta A/A$ and the size-dependent interface energy can be expressed as

$$\gamma = (f\Delta A/A + \gamma_b)/(1 + \Delta A/A), \tag{2}$$

i.e., the size effect is related to the change in the interface area. Under the small strain, $\Delta A/(2A) = \Delta V/(3V)$, where V is the volume of the solid with the interface area A. Combining with the definition of the compressibility κ , $\kappa = -\Delta V/(VP)$, where *P* is the pressure difference between the inside and the outside of the solid, $\Delta A/A = -2\kappa P/3$. According to the Laplace-Young equation, for a compressible spherical particle with diameter D immersed in the liquid, P=2fA/(3V), A/V=6/D for the solid-liquid interface. For the solid-solid interface discussed here, A/V=3/D considering that two solid-liquid interfaces of particles combine to form one grain boundary or solid–solid interface, thus P=2f/D, the result is reasonable since the elastic modulus of the solid is larger than that of the liquid and the pressure difference of solidsolid is smaller than that of solid-liquid. Therefore, $\Delta A/A$ $=-4\kappa f/(3D)$, and the size-dependent solid-solid interface energy can be expressed as

$$\gamma = \gamma_b \left(1 - \frac{4\kappa f^2}{3\gamma_b D} \right) / \left(1 - \frac{4\kappa f}{3D} \right). \tag{3}$$

The expression of the intrinsic interface stress f has been obtained as^{2,9}

$$f = -\left[(3\gamma_m D_0)/(8\kappa) \right]^{1/2},\tag{4}$$

based on the similar consideration to the above discussion, where the negative sign shows the compressive interface stress, D_0 is the critical size, D_0 =3h, 2h for particles and thin films, respectively. Substituting Eq. (4) into Eq. (3), $\gamma = \gamma_b [1 - D_0/(4D)]/[1 - \gamma_b D_0/(4fD)]$. Considering the interface stress f is one order larger than the interface energy γ_b , the denominator in the above equation can be neglected.

Now the subscripts i and c are retrieved, the size-dependent intrinsic solid–solid interface energy γ_{ci} of single materials can be expressed as

$$\gamma_{ci} = \gamma_{bi} \left(1 - \frac{D_{0i}}{4D} \right), \tag{5}$$

where D is the diameter and the thickness for particles and thin films, respectively. Equation (5) is consistent with the quantum chemical calculation that surface energy is inversely proportional to the reciprocal size of a particle. For interfaces between metal and ceramic thin films, $D=t_1+t_2$ denotes the total thickness, t_1 and t_2 are the thickness of the metal and the ceramic thin films, respectively. Considering the average of two materials and substituting Eq. (1) into Eq. (5), the size-dependent chemical interface energy between two materials can be expressed as

$$\gamma_c = \frac{2}{3R} \left[\frac{h_1 S_{v1} H_{m1}}{V_{m1}} \left(1 - \frac{h_1}{2D} \right) + \frac{h_2 S_{v2} H_{m2}}{V_{m2}} \left(1 - \frac{h_2}{2D} \right) \right]. \tag{6}$$

Equation (6) shows that the chemical interface energy decreases with reducing thickness of thin films depending on some available bulk thermodynamic parameters of two materials such as the melting entropy and enthalpy.

On the other hand, the structure interface energy γ_s caused by the lattice mismatch between two materials and the dislocation strain at the interface should be considered. According to the Matthews model, 11 the initial interface energy γ_0 for a fully relaxed thin film on a substrate can be expressed as $\gamma_0 = Cb\varepsilon_0 \{\ln[D/(2b)] + 1\}/(2\pi)$, where C $= \{2[(1-\nu_1)/G_1 + (1-\nu_2)/G_2]\}^{-1}$ is the effective elastic modulus, ν is the Poisson's ratio, and G is the shear modulus, $b=(h_1+h_2)/2$ is the Burgers vector, $\varepsilon_0=(h_2-h_1)/h_1$ is the misfit strain with $h_2 > h_1$. D/2 represents the radius of the effective dislocation stress-field. Considering the semicoherent interfaces between two materials, the coherency strain ε meets partial lattice matching, and generally, the major contribution to the structure interface energy is the energy associated with the formation of dislocations that accommodates part of the misfit, 12 thus γ_s is proportional to the dislocation strain $(\varepsilon_0 - \varepsilon)$. Therefore, the structure interface energy can be expressed as $\gamma_s = \gamma_0 (1 - \varepsilon/\varepsilon_0)$, where ε is also sizedependent due to the intrinsic lattice strain of thin films compared to the corresponding bulk materials and it is determined by

$$\varepsilon = -\frac{2\kappa f}{3D},\tag{7}$$

based on the Laplace–Young equation and the isotropic assumption. The compressibility $\kappa=1/B$, where B is the volume modulus and taken as the average value of two materials. The intrinsic interface stress f refers to Eq. (4), γ_m and D_0 are also taken as the average values of two materials, respectively. Finally, the structure interface energy between two materials can be expressed as

TABLE I. The interface energies (J/m^2) of some metal/ceramic systems based on Eq. (9) and the molecular mechanics (MM) calculation (Refs. 13–15). In Eq. (9), taking D=20 nm, the other parameters are in Table II.

	Ni/MgO	Pd/MgO	Ag/MgO	Au/MgO	Cu/Al ₂ O ₃	Ag/Al ₂ O ₃	Au/Al ₂ O ₃
Eq. (9)	4.6	3.59	3	3.1	3.26	2.47	2.5
MM	4.6 (Ref. 13)	3.84 (Ref. 4)	4 (Ref. 14)	3.68 (Ref. 14)	3.24 (Ref. 15)	2.31 (Ref. 15)	2.9 (Ref. 15)

$$\gamma_{s} = \frac{G_{1}G_{2}b\varepsilon_{0}}{4\pi[(1-v_{1})G_{2}+(1-v_{2})G_{1}]} \left[\ln\left(\frac{D}{2b}\right) + 1 \right] \times \left(1 - \frac{\varepsilon}{\varepsilon_{0}}\right). \tag{8}$$

Substituting Eq. (7) into Eq. (8), the size-dependent structural interface energy can be obtained by using of some available bulk mechanical parameters of two materials such as the shear modulus and the Poisson's ratio. γ_s also decreases with reducing thickness of thin films. Combining Eqs. (6) and (8), the total interface energy γ is expressed as

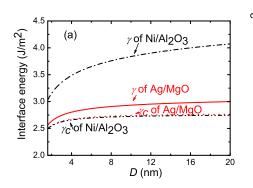
$$\gamma = \gamma_c + \gamma_s. \tag{9}$$

III. RESULTS AND DISCUSSIONS

We calculated the interface energies of some metal/ ceramic interfaces, such as Ni/MgO, Ag/MgO, Ag/Al₂O₃, etc. in terms of Eq. (9), the results are in Table I. It can be found that the predicted values based on our model are in agreement with the calculated interface energies based on the molecular mechanics. 13-15 The interface energy keeps several joules per meter square despite of size effect. Figure 1 shows the predicted interface energy of Ag/MgO and Ni/Al₂O₃ systems in the same thickness range based on the model by use of some available thermodynamic parameters. 16-24 It can be seen from the figure that the interface energy decreases with reducing thickness of thin films. We also calculate the interface energy of Ag/Ni and Ni/Co interfaces, the interface energy of metal/metal interfaces is smaller than that of metal/ ceramic interfaces. The chemical interface energy of Ag/Ni is about 0.84 J/m² at the interface thickness of 20 nm, which is very close to the experimental results of $0.76 \text{ J/m}^2.25$ The decrease in the chemical interface energy in nanoscale can explain the observed interfacial phase segregation phenomena in nanoscale Ni/Co systems. Ni and Co are miscible elements and can form alloy in bulk materials but in nanostructured Ni/Co systems they did not form the alloy as expected in their bulk phase diagram, 26 which is because that the stability of the interface increases with the decrease in the chemical interface energy and the interface may exist stably. Note that the total interface energy γ of Ag/MgO is smaller than that of Ni/Al₂O₃ at the same size [see Fig. 1(a)]. However, the chemical interface energy γ_c of Ag/MgO is slightly larger than that of Ni/Al₂O₃ [Fig. 1(b)], which implies that the interface stability of Ag/MgO is weaker and the interface may separate more easily. While the structure interface energy γ_s of Ag/MgO is smaller than that of Ni/Al₂O₃, i.e., the structural strain contribution to the total interface energy is larger for Ni/Al₂O₃, which may imply that the larger strain work needs to be overcome to separate the interface.

Figure 2 shows the interface tension separation simulation of Ag/MgO and Ni/Al₂O₃ systems based on the molecular mechanics calculation²⁷ and the first principle calculation, 28 respectively. It can be seen that two stressdisplacement curves show the same shape despite of different simulation methods, and the interface tension stress σ increases first with increasing interface tension displacement Δx , then decreases after reaching the maximum stress, i.e., the interface fracture strength σ_b , vanishes finally when the interface separates, the trend is consistent with the cohesive zone model describing the interface fracture.²⁹ Differently, the interface fracture strength σ_b of Ag/MgO is lower than that of Ni/Al₂O₃, and the fracture toughness Γ_0 , i.e., the area under the σ - Δx curve, of the former is also smaller than that of the latter. Note that the fracture strength and toughness of Ag/MgO interface with the larger chemical interface energy are both smaller, i.e., the interface fractures more easily, which reflects that the stability of the interface with the larger chemical interface energy is really weaker. The smaller fracture toughness also indicates that the smaller work needs to be overcome in the fracture process, which may be related to the weaker interface adhesion ability of Ag/MgO, while the interface possess the smaller structural interface energy at the same time.

In order to further understand the intrinsic relation between the interface energy and the interface fracture properties, we calculate the interface potential energy ϕ and the



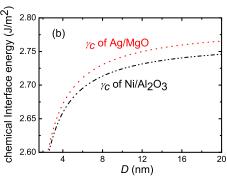


FIG. 1. (Color online) The total interface energy (a) and the chemical interface energy (b) vs the total thickness of metal/ceramic interfaces for Ag/MgO and Ni/Al₂O₃ in terms of Eqs. (6) and (9), respectively. The related parameters in the equations are in Table II.

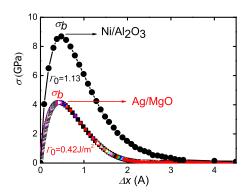


FIG. 2. (Color online) The interface tension stress vs the displacement of Ag/MgO and Ni/Al₂O₃ based on the molecular mechanics (Ref. 27) and the first principle calculations (Ref. 28), respectively.

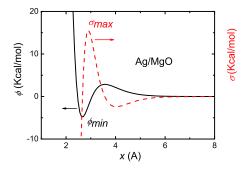


FIG. 3. (Color online) The interface potential and the stress vs the interface distance of Ag/MgO in terms of Eq. (10). The potential parameters are in Table I in Ref. 30.

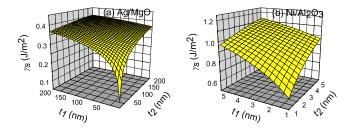


FIG. 4. (Color online) The structure interface energy vs the respective thickness of the metal and the ceramic thin films (a) for Ag/MgO and (b) for Ni/Al₂O₃ in terms of Eq. (8) with $D=t_1+t_2$. The related parameters in the equations are in Table II.

corresponding interface stress of Ag/MgO system. For metal/ceramic interfaces, ϕ refers to the modified Rahman–Stillinger–Lemberg potential as follows

$$\phi = a_0 e^{d\left(1 - \frac{x}{c_0}\right)} + \frac{a_1}{1 + e^{b_1(x - c_1)}} + \frac{a_2}{1 + e^{b_2(x - c_2)}} + \frac{a_3}{1 + e^{b_3(x - c_3)}},$$
(10)

where x is the interface atomic distance, the other parameters are the potential parameters given by Chen-Mobius inversion method based on the *ab initio* calculation. ³⁰ Considering two kinds of atomic pairs Ag/Mg and Ag/O across the interface, the potential parameters are all approximately taken as the average values of the both for the simplicity of the calculation. The interface stress $\sigma = \partial \phi / \partial x$. Figure 3 shows the calculated interface potential of Ag/MgO based on Eq. (10), the absolute value of the minimum potential energy $|\phi_{\min}|$ or the interface adhesive energy is 4.77 kcal/mol, i.e., 1.77 GPa after the unit conversion, that is 0.47 J/m² after multiplying by the corresponding interface distance. $|\phi_{\min}|$ almost agrees with the microscopic interface fracture toughness Γ_0 of Ag/ MgO (0.42 J/m²) based on our molecular mechanics simulation as shown in Fig. 2, and also roughly agrees with the calculated structural interface energy γ_s , 0.41 J/m² as shown in Fig. 4(a), based on our analytical model when the thickness of Ag and MgO thin films are both 200 nm. For $\text{Ni}/\text{Al}_2\text{O}_3,~\Gamma_0$ is 1.13 $~\text{J/m}^2$ (Fig. 2), which also agrees with γ_s at D=11 nm as shown in Fig. 4(b) corresponding to the scale of the first principle calculation. Therefore, the structural interface energy in nanoscale corresponds to the microscopic interface fracture toughness or the interface adhesive work. Moreover, the larger γ_s or the fracture toughness is, the higher is the strength, since that the larger $|\phi_{\min}|$ is, the higher the maximum stress σ_{max} is, the result is in agreement with the previous discussion.

Figure 3 also shows the interface stress of Ag/MgO, it can be seen that the maximum stress σ_{max} , i.e., the fracture strength, is 15.44 Kcal/mol, that is 5.7 GPa after the unit conversion, which is close to the calculation result based on the our molecular mechanics as shown in Fig. 2. In fact, the calculation in Fig. 2 is based on the same interface potential, but is more accurate. On the other hand, the structure interface energy is much smaller than the chemical interface energy, e.g., γ_c is 3.16 J/m², more than one order of γ_s (0.41 J/m²) for Ag/MgO at the same thickness. The chemi-

TABLE II. The related parameters in the equations. h=2r with the atomic radius r. h is taken as the average value of both elements for MgO, and taken as the bond length for Al₂O₃. For ceramics, $V=M/\rho$ with the molar mass M and the density ρ , $B=2G(1+\nu)/[3(1-2\nu)]$. For metals, $S_v=S_m$, for ceramic semiconductors, $S_v=0.4S_m$ (Ref. 16).

	Ag	Au	Ni	Pd	Cu	MgO	Al_2O_3
h (nm) (Ref. 17)	0.3194	0.3188	0.2754	0.304	0.2806	0.3376 (Ref. 17)	0.324 (Ref. 23)
H_m (kJ/mol) (Ref. 18)	11.3	12.55	17.47	17.6	13.05	90 (Ref. 20)	111.4 (Ref. 24)
T_m (K) (Ref. 18)	1234	1337.58	1726	1825	1357.6	3073 (Ref. 21)	2326 (Ref. 24)
S_n (J/mol/K) (Ref. 18)	9.157	9.383	10.122	9.644	9.613	11.7 (Refs. 20 and 21)	19.157 (Ref. 24)
V_m (cm ³ /mol) (Ref. 18)	10.3	10.2	6.59	8.9	7.1	11.26 (Ref. 21)	25.49 (Ref. 24)
G (GPa) (Ref. 19)	30.3	26	76	43.6	48.3	130 (Ref. 22)	150 (Ref. 24)
ν (Ref. 19)	0.367	0.42	0.312	0.39	0.343	0.18 (Ref. 22)	0.22 (Ref. 24)
B (GPa) (Ref. 19)	103.6	171	177.3	187	137.8	160 (Ref. 22)	217.86 (Ref. 24)

cal interface energy should also be related to the total fracture energy, and may contribute to the plastic dissipation, how it affects the fracture behavior has yet to be discovered.

IV. CONCLUSION

In summary, a theoretical model about the size dependence of the interface energy between two thin films with different materials is developed. The interface energy decreases as the thickness of thin films decreases, and the size effect depends on the atomic diameter, the melting enthalpy, the shear modulus of two materials, etc. The theoretically predicted interface energy is in agreement with the results based on the molecular mechanics calculation. The comparison of the interface energy and the interface fracture strength of Ag/MgO and Ni/Al₂O₃ systems indicates that the fracture strength is higher for the interface with the larger structure interface energy, the former corresponds to the maximum of the first order derivative of the interface potential, and the latter corresponds to the microscopic interface fracture toughness.

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