

Interfacial Stoichiometry and Adhesion at Metal/ α -Al₂O₃ Interfaces

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First-principles studies of metal/ α -Al₂O₃ interfaces have revealed strong interfacial stoichiometry effects on adhesion. The metals included Al, Ni, Cu, Au, Ag, Rh, Ir, Pd, Pt, Nb, and β -NiAl. Metallic and ionic-covalent adhesive bonding effects were found in varying amounts depending on whether the interfacial stoichiometry is stoichiometric, oxygen-rich, or aluminum-rich in a qualitative way. A semiempirical but physically sensible understanding ensues for the effects of interfacial stoichiometry and reveals the underlying strong correlation of the interfacial adhesion with the physical properties of the bulk materials that join and form the interface. The metallic component of the bonding was found to be related to the ratio of $(B/V)^{1/2}$, where B and V are the bulk modulus and molar volume of the metal, respectively. In like manner, the ionic-covalent component of the bonding could be related to the enthalpy of oxide formation of the bulk metal. A unified model is proposed to describe the adhesion of metal/alumina interfaces with interfacial stoichiometry effects, and the model is also expected to be valid for other metal–oxide interfaces.

I. Introduction

ADHESION at metal/alumina interfaces is important in applications such as thermal barrier coatings for high-temperature gas-turbine engines,^{1,2} heterogeneous catalysis,^{3–5} microchip packaging,⁶ and corrosion protection.^{7–10} This has resulted in experimental and theoretical research in the fundamentals of adhesion at metal/alumina interfaces.^{11–37} It has been found^{14–16,23,38–40} that interfacial stoichiometries as well as interfacial adhesion can vary with the temperature and the environmental oxygen partial pressure. That is, the stable metal/alumina interface can vary from stoichiometric (two Al atoms for every three O atoms), to aluminum-rich or oxygen-rich.^{32–36}

Recently we (H. Li *et al.*, unpublished data) have analyzed interfacial stoichiometry effects for a series of metal/ α -Al₂O₃ interfaces via the results of first-principles computations. The metals considered included Al, Ni, Cu, Au, Ag, Rh, Ir, Pd, Pt, Nb, and β -NiAl. For each of the metal/ α -Al₂O₃ interfaces, the first-principles computations were carried out not only for the

stoichiometric interface but also for an aluminum-rich and an oxygen-rich interface.

The adhesive bonding for each stoichiometry was found (H. Li *et al.*, unpublished data) to have features common to all eleven metal/ α -Al₂O₃ interfaces. Aluminum-rich interfaces exhibit metallic bonding. On the other hand, bonding in oxygen-rich interfaces is primarily ionic, with an admixture of covalent bonding. Stoichiometric interfaces have mixed ionic-covalent and metallic adhesive bonding. It was found that the work of separation, W_{sep} , is sensitive to the interfacial stoichiometry. The work of separation, W_{sep} , of an interface is defined as the energy needed to separate the interface into two free surfaces,¹² and can be expressed by Dupré equation:

$$W_{\text{sep}} = \sigma_A + \sigma_B - \gamma_{A/B} \quad (1)$$

Here, $\gamma_{A/B}$ is the interfacial energy of the interface A/B. σ_A and σ_B are the surface energies of slabs A and B after the cleavage of the interface A/B, respectively. Oxygen-rich interfaces were found to have W_{sep} values approaching an order of magnitude larger than those of stoichiometric interfaces in some cases, with W_{sep} values of aluminum-rich interfaces lying in between. This was understood in terms of the type of bonding for each stoichiometry, as will be discussed below. It is qualitatively understood via Eq. (1) as follows. In general, α -Al₂O₃ surface energies for oxygen-rich and aluminum-rich surfaces are larger than that for the stoichiometric α -Al₂O₃ surface. Also, generally the aluminum-rich and oxygen-rich interfacial energies are smaller than the stoichiometric interfacial energy.

Most of the earlier work including our work mainly devoted to determining the effects of interfacial stoichiometry on the nature of the interfacial bonds for different metal/ α -Al₂O₃ interfaces and connecting that knowledge to the works of separation in a qualitative picture. Interfacial bonds are characterized there via first-principles results for interfacial atomic structures, electron density distributions, and local densities of electronic states, as well as with works of separation. In contrast, no correlation between interfacial adhesion and the physical properties of the bulk materials forming interface has been investigated in a quantitative and systematic way, even with a few reported relationship linking the measured adhesion data to bulk properties of host materials for the one specific interface that were most likely observed experimentally. As a matter of fact, we now understood that metal/oxide interface show stoichiometry-dependent stable structures and that the adhesion are also critically related to interfacial stoichiometry. Therefore, classifying those interfaces into different categories and analyzing their adhesion properties are truly required but can only be done with the help of a systematic theoretical approach. This is the main purpose of

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the current work. Generally, the physically sensible analytical relationships ensue between works of separation for each interfacial stoichiometry and measured bulk properties of metals and metal oxides, and provide not only enhanced understanding of interfacial stoichiometric effects but also the potential for semiempirical predictions of stoichiometry effects on works of separation for interfaces for which first-principles results are not available.

Here it will be seen for the first time that the dependence of the metal/alumina works of separation on typical stoichiometries can be expressed in terms of a semiempirical but physically sensible analytical relationships in a quantitative way. Specifically, the works of separation are expressed in terms of the bulk properties of the metal and metal oxide. These relationships will be shown to accurately represent metal/alumina bonding for all metals considered, which in fact reveals clearly the underlying strong correlation of the interfacial adhesion with the physical properties of the bulk materials that join and form the interface.

II. First-Principles Works of Separation

W_{sep} is determined via first-principles computations^{35,36} according to:

$$W_{\text{sep}} = (E_{\text{metal}} + E_{\text{Al}_2\text{O}_3} - E_{\text{metal/Al}_2\text{O}_3})/2S \quad (2)$$

where E_{metal} and $E_{\text{Al}_2\text{O}_3}$ are the total energies of the isolated metal and α -Al₂O₃ slabs, respectively. The term $E_{\text{metal/Al}_2\text{O}_3}$ represents the total energy of the system when the metal and the α -Al₂O₃ surfaces have been allowed to come together and adhere at equilibrium separation. For the first-principles computations, the Perdew–Burke–Ernzerhof generalized gradient approximation⁴¹ (GGA) was used within the Vienna *ab initio* simulation package^{42,43} (VASP). The projector augmented plane wave method^{44,45} with a plane wave energy cut off of 500 eV and an energy convergence criterion of 10^{-4} eV is used. Readers interested in additional details about the density-functional computational details used here can read about them in Zhang and colleagues.^{33–36,46} All atoms of the system have been allowed to relax, although the stoichiometry of the metal/ α -Al₂O₃ interface is retained in the α -Al₂O₃ surface. This applies to fracture experiments, where bond separation rates are sufficiently high that the surfaces cannot relax to the ground-state stoichiometry before bonds rupture.³⁵ For the free α -Al₂O₃ (0001) surface, the ground-state stoichiometry has been shown^{47,48} to be stoichiometric. For steady-state experiments like sessile drop experiments,^{14–19} the works of adhesion, W_{ad} , can be obtained from Eq. (2) by using a stoichiometric surface for computations of $E_{\text{Al}_2\text{O}_3}$.

Here, the stoichiometric metal/alumina interface refers to an α -Al₂O₃ surface terminated by a single Al atomic layer and then joined to a metal (Al-terminated), denoted as M/(Al₂O₃)_{Al1}. The aluminum-rich case corresponds to an α -Al₂O₃ surface terminated by two Al atomic layers (Al₂-terminated), denoted as M/(Al₂O₃)_{Al2}. Finally the oxygen-rich case corresponds to the α -Al₂O₃ surface terminated by an O atomic layer (O-terminated), denoted as M/(Al₂O₃)_O. The Al₂-, O-, and Al-terminated interfaces are representative types that span the variety of expected chemistries.^{14–16,38–40}

First-principles results for W_{sep} are found in Table I. Note the smallest W_{sep} values are found for the stoichiometric interface for all the metals in general. Also in all cases the oxygen-rich interfaces have the largest values of W_{sep} . This difference due to stoichiometry is large, in some cases an order of magnitude. These can perhaps be understood in terms of the dangling bonds available from the (Al₂O₃)_O surface and not found at the (Al₂O₃)_{Al1} surface. The aluminum-rich interfaces have W_{sep} intermediate values between those for the oxygen-rich and stoichiometric interfaces, respectively.

Łodziana and Norskov²⁸ performed density functional computations of the adhesion of a monolayer (ML) of Pd or Cu atoms on α -Al₂O₃ surfaces including aluminum-rich, oxygen-

Table I. Calculated Works of Separation, W_{sep} , for Metal (Alloy)/ α -Al₂O₃ Interfaces

Interface	Works of separation, W_{sep} (J/m ²)		
	Calculated results		
	M/(Al ₂ O ₃) _{Al2}	M/(Al ₂ O ₃) _O	M/(Al ₂ O ₃) _{Al1}
Rh/ α -Al ₂ O ₃			
Type-I	4.32 [†]	5.91 [†]	1.05 [†]
Ir/ α -Al ₂ O ₃			
Type-I	4.47 [†]	6.51 [†]	0.89 [†]
Pd/ α -Al ₂ O ₃			
Type-I	4.38 [†]	4.35 [†]	0.76 [†]
ML	5.14 [‡]	4.21 [‡]	0.99 [‡]
Pt/ α -Al ₂ O ₃			
Type-I	4.65 [†]	4.76 [†]	0.74 [†]
Ni/ α -Al ₂ O ₃			
Type-I	3.78 [§]	6.84 [§]	1.30 [§]
Type-II	4.05 [§]	6.55 [§]	1.13 [§]
Type-III	3.64 [§]	6.75 [§]	1.09 [§]
Cu/ α -Al ₂ O ₃			
Type-I	2.66 [§]	5.94 [§] , 5.62 [¶]	0.58 [§]
Type-II	2.71 [§]	5.42 [§]	0.74 [§]
Type-III	2.69 [§]	6.07 [§]	0.86 [§]
ML	3.26 [‡]	6.18 [‡]	0.91 [‡]
Au/ α -Al ₂ O ₃			
Type-I	2.31	2.78	0.29
Type-II	2.42	3.08	0.21
Ag/ α -Al ₂ O ₃			
Type-I	1.83	3.93	0.33
Type-II	1.85	4.10	0.32
Al/ α -Al ₂ O ₃			
Type-I	1.43 ^{††}	10.10 ^{††} , 8.67 [¶] , 9.73 ^{‡‡}	1.08 ^{††} , 1.36 [¶] , 1.06 ^{‡‡}
Nb/ α -Al ₂ O ₃			
Type-III	2.80 ^{§§}	9.80 ^{§§} , 10.60 ^{¶¶}	2.70 ^{§§} , 2.60 ^{¶¶}
β -NiAl/(Al ₂ O ₃) _{Al2}			
Al ₂ term–1Al	2.85		
β -NiAl–Ni ^{rich} / (Al ₂ O ₃) _{Al2}			
Oterm–8Al	3.43		

The type-I, type-II, and type-III are for the metal/ α -Al₂O₃ interfaces using different interfacial matchings and strains as discussed in H. Li *et al.* (unpublished data). The data denoted by “ML” are from the first-principles results for the adsorption of a monolayer metal atoms on alumina.²⁸ The values from GGA calculations^{29,36} are adopted for Al, Au, and Ag/ α -Al₂O₃ interfaces. [†]This work. [‡]Łodziana and Norskov.²⁸ [§]Zhang *et al.*³⁵ [¶]Batyrev and Kleinman.³⁰ ^{||}Feng *et al.*³⁶ ^{††}Zhang and Smith.³³ ^{‡‡}Siegel *et al.*²⁹ ^{§§}Batyrev *et al.*³² ^{¶¶}Zhang and Smith.³⁴ ^{|||}Li *et al.*⁴⁶ ML, monolayer; GGA, generalized gradient approximation.

rich, and stoichiometric configurations. Most of the calculated W_{sep} data for 1 ML of metal atoms on alumina are larger than those for thick metal slabs on alumina, but one can still see a similar trend of W_{sep} with interface chemistry, i.e., the Al₂- to O-, to Al-terminated cases, as shown in Table I for the ML on alumina results denoted as ML.

III. Analytical Relationships for Stoichiometry-Dependent Works of Separation

As adhesion of the metal/ α -Al₂O₃ interfaces has been shown to vary significantly with interfacial stoichiometry, it is of interest to seek an enhanced understanding and a further connection with experiment of this effect. It's difficult to carry out direct experimental probes of these stoichiometry-dependent interfacial bonds. One can attempt to develop semiempirical relationships between experimental quantities and stoichiometry-dependent works of separation, however. Armed with the knowledge of how the nature of the bonding varies with stoichiometry, one can proceed. That is, bonding is predominantly

Table II. The Electron Density Parameter at the Boundary of the Wigner–Seitz Atomic Cell, n_{ws} [Density Units (d.u.)], Estimated for the Pure Element Phase in the Metallic State^{49,50}

Metal	n_{ws}	Metal	n_{ws}	Metal	n_{ws}	Alloys	n_{ws}
Rh	5.45	Cu	3.18	Nb	4.41	β -NiAl	4.02
Ir	6.13	Au	3.87	Co	5.36	β -NiAl–Ni ^{rich}	5.36
Pd	4.66	Ag	2.52	Fe	5.55		
Pt	5.64	Al	2.69	Mn	4.17		
Ni	5.36						

For the β -Ni_{1-x}Al_x/ α -Al₂O₃ interfaces,⁴⁶ n_{ws} is approximately taken to be the average value of the parameters for pure Ni and Al to evaluate the W_{sep} of the Al₂term–1Al interface, and the n_{ws} of Ni is used to evaluate W_{sep} of the Oterm–8Al interface due to the presence of Ni-rich layer in the β -NiAl–Ni^{rich} slab (see Table I).

metallic for the aluminum-rich interfaces, ionic-covalent for the oxygen-rich interfaces, and mixed ionic-covalent and metallic for the stoichiometric interfaces.

(1) Aluminum-Rich M/ α -Al₂O₃ Interfaces

Due to the predominantly metallic bonding of aluminum-rich interfaces, one might look to relate W_{sep} to the electron density of the interface. Boer and colleagues^{49,50} once used an electron density parameter, n_{ws} , to evaluate the thermodynamic quantities of binary alloys. They defined n_{ws} as the electron density at the boundary of the Wigner-Seitz atomic cell estimated for the pure element phase in the metallic state. Those authors^{49,50} estimated n_{ws} as the ratio of experimental bulk modulus B and molar volume V of pure metals, i.e.,

$$n_{ws} = \left(\frac{B}{V}\right)^{1/2} \quad (3)$$

in which the unit of n_{ws} is defined as density units (d.u.) in Boer *et al.*⁴⁹ and Niessen and Miedema⁵⁰ as shown in Table II.

Getting back to the predominantly metallic bonding of the Al₂-terminated M/ α -Al₂O₃ interface, one might look for the adhesion to scale with the electron density parameter of the corresponding metal, i.e.,

$$W_{sep-Al_2} = An_{ws} \quad (4)$$

in which A is a scaling parameter. Indeed, Fig. 1 is a plot of the calculated works of separation, W_{sep-Al_2} , as a function of n_{ws} for Al₂-terminated interfaces. The solid line is obtained by fitting to the adhesion results for the type-I M/(Al₂O₃)_{Al₂} interfaces of Table

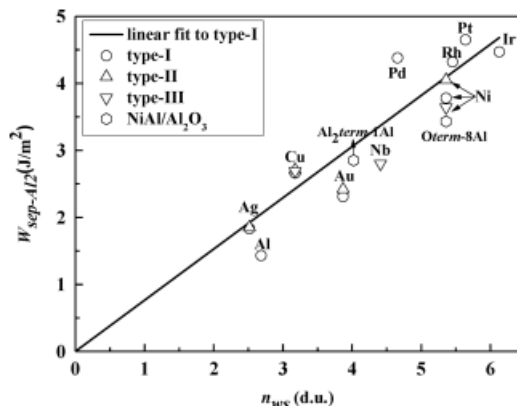


Fig. 1. Work of separation (W_{sep-Al_2}) versus electron density parameter (n_{ws}) for the aluminum-rich metal (alloy)/alumina interfaces. The W_{sep-Al_2} and n_{ws} are given in Tables I and II, respectively. The solid line corresponds to the linear fit to all the data for type-I M/(Al₂O₃)_{Al₂} interfaces. The W_{sep} corresponding to the cleavage β -NiAl/(Al₂O₃)_{Al₂} for the Al₂term–1Al interface, and β -NiAl–Ni^{rich}/(Al₂O₃)_{Al₂} for the Oterm–8Al are also plotted in the figure.⁴⁶

I, and the corresponding parameter A is estimated to be 0.76 [(J/m²)/(d.u.)]. It is very interesting to notice that there is an approximate proportionality between n_{ws} and W_{sep-Al_2} for the Al₂-terminated interfaces, even for the relatively broad range of interfaces of Fig. 1. Physically, this is due to the metallic character of the aluminum-rich interface bonding. Figure 1 shows that the higher n_{ws} is, the stronger the W_{sep-Al_2} of an aluminum-rich interface.

Considering that the chemical bonding of the stable β -Ni_{1-x}Al_x/ α -Al₂O₃ interfaces is also primarily metallic in both the Al₂term–1Al and Oterm–8Al interfaces,⁴⁶ the corresponding works of separation are also given in Table I and plotted in Fig. 1. In a simple approximation, the n_{ws} for the β -NiAl alloy is taken to be the average value of the parameters for pure Ni and Al to evaluate the W_{sep} of the Al₂term–1Al interface via Eq. (4). The n_{ws} of Ni is used to estimate the adhesion of the Oterm–8Al interface due to the presence of Ni-rich layer in the β -NiAl–Ni^{rich} slab (Table II),⁴⁶ Fig. 1 shows that the works of separation for both the β -NiAl/(Al₂O₃)_{Al₂} and β -NiAl–Ni^{rich}/(Al₂O₃)_{Al₂} interfaces also follow Eq. (4) very well, with the same scaling parameter A . In fact, an approximate proportionality between surface energies of metals and electron density parameters was also observed by Boer and colleagues.^{49–51} This is consistent with the picture that both the surface energies of metals and adhesive energies for interfaces between metals and aluminum-rich α -Al₂O₃ (0001) surface involve predominantly metallic bonding. Therefore, it is reasonable to expect that Eqs. (3) and (4) are appropriate for estimating adhesion of other aluminum-rich M/ α -Al₂O₃ interfaces. At this time, the physical meaning of the scaling parameter A is not understood. However, as the correlation exhibited in Fig. 1 covers many metal/ α -Al₂O₃ systems, it is speculated to be closely linked with the metallic bonding of the Al₂-terminated interfaces as well as the character of electronic structure of the aluminum-rich α -Al₂O₃ (0001) surface.

(2) Oxygen-Rich M/ α -Al₂O₃ Interfaces

For the oxygen-rich, clean α -Al₂O₃ (0001) surface, through Mulliken population analyses,^{47,52} it is found that one of the surface O atoms per surface unit cell carries an electronic charge of only –0.58, compared with –1.0 for an O atom in the bulk oxide. This leads to unsaturated dangling bonds on the O-terminated α -Al₂O₃ surface. As discussed earlier, strong ionic-covalent interfacial bonds form for the oxygen-rich M/ α -Al₂O₃ interface, and this is the primary reason why W_{sep} of such M/(Al₂O₃)_O interfaces are always the largest in comparison with those of the aluminum-rich and stoichiometric interfaces.

This feature of the metal–O interaction at the oxygen-rich interface is similar to that found in the corresponding metal oxides. This is suggestive that the work of separation of the O-terminated interface, W_{sep-O} , might be expected to correlate with the experimental enthalpy of formation of the bulk metal oxide per oxygen atom, $|EOF|$ (Table III), in the following way:

$$W_{sep-O} = C + D|EOF| \quad (5)$$

here, C and D are scaling parameters. Indeed, the W_{sep-O} correlate with the $|EOF|$ of metal oxides well as shown in Fig. 2. By fitting all the adhesion data for the type-I M/(Al₂O₃)_O interfaces in Table I, the C and D are estimated to be 3.87 J/m² and 1.01

Table III. Experimental Enthalpies of Formation [EOF in eV/(O Atom)] of Metal Oxides

Metal oxide	EOF [eV/(O atom)]	Metal oxide	EOF [eV/(O atom)]	Metal oxide	EOF [eV/(O atom)]
Rh ₂ O ₃	–1.23	CuO	–1.68	NbO	–4.35
IrO ₂	–1.29	Au ₂ O ₃	–0.01	CoO	–2.46
PdO	–1.20, –0.89	Ag ₂ O	–0.32	Fe ₂ O ₃	–2.85
PtO ₂	–0.87	Al ₂ O ₃	–5.79	MnO	–3.99
NiO	–2.49				

The data are derived from Kubaschewski *et al.*⁵³ and Lide.⁵⁴

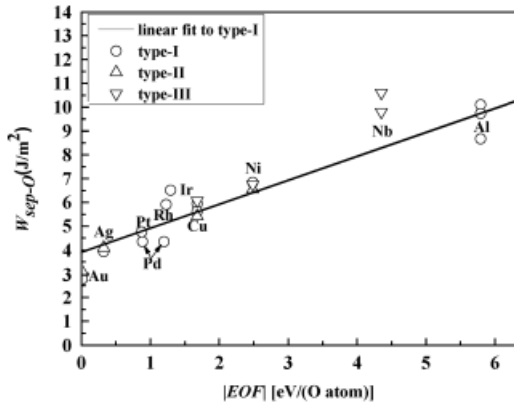


Fig. 2. Work of separation ($W_{\text{sep-O}}$) versus enthalpy of formation ($|EOF|$) for the oxygen-rich metal/alumina interfaces. The $|EOF|$ are listed in Table II. All $W_{\text{sep-O}}$ are taken from Table I, and the solid line is a linear fit to all the adhesion results for type-I $M/(Al_2O_3)_O$ interfaces.

$[(J/m^2)/(eV/O \text{ atom})]$, respectively. Figure 2 shows that the $W_{\text{sep-O}}$ of an interface increases with the increasing of $|EOF|$ of the corresponding metal oxide. This is consistent with the physical picture that the metal–oxygen interaction is important for the adhesion of oxygen-rich interfaces. Note, however, that $W_{\text{sep-O}}$ via Eq. (5) is $\geq 3.87 \text{ J/m}^2$, even for small $|EOF|$. This is likely due to Al–O–metal effects beyond simple metal–O effects.

(3) Stoichiometric M/α -Al₂O₃ Interfaces

The chemistry of the stoichiometric metal/alumina interfaces falls in between the aluminum-rich and oxygen-rich cases. It contains one Al layer between the adhered metal atoms and the oxygen layer. The single layer of Al atoms does not make the Al-terminated metal/alumina interface metallic like the aluminum-rich interface. The $M/(Al_2O_3)_{AlI}$ interfaces in fact show a mix of metallic and ionic-covalent bonding. Based on the above discussion of the adhesion of the aluminum-rich and oxygen-rich interfaces, especially the two models described by Eqs. (4) and (5), one might reasonably expect that a combination of n_{ws} and $|EOF|$ could be used to describe the works of separation,

$W_{\text{sep-AlI}}$, for the $M/(Al_2O_3)_{AlI}$ interfaces. Therefore $W_{\text{sep-AlI}}$ is formulated by the following equation:

$$W_{\text{sep-AlI}} = En_{ws} + F|EOF| \quad (6)$$

By fitting all the stoichiometric adhesion results from first-principles calculations in Table IV, the scaling parameters E and F are estimated to be 0.13 $[(J/m^2)/(d.u.)]$ and 0.15 $[(J/m^2)/(eV/O \text{ atom})]$, respectively. One can see the expression of Eq. (6) for the stoichiometric interface is not a simple linear combination of those expressions of Eqs. (4) and (5) for aluminum-rich and oxygen-rich interfaces because of the relatively large constant (3.87 J/m^2) of Eq. (5) not found in Eq. (6). Again it is suggested that Al–metal–O interactions are not captured by n_{ws} and $|EOF|$.

In order to check the validity of the model, results from Eq. (6), from first-principles calculations, and from experimental measurements are given in Table IV. It should be pointed out that the metals in Table IV are not only of fcc structure, but also hcp (Co), bcc (Fe and Nb), and complex (Mn).⁵⁷ The results are also compared in Figs. 3 and 4 for clarity. The above results show clearly that there is a correlation described by Eq. (6), and this model reproduces well the variation of works of separation, no matter whether comparing to the first-principles calculations for the Al-terminated metal/alumina interfaces or to experimental measurements.

Comparing the scaling parameters obtained for the differently terminated interfaces, the parameter multiplying the n_{ws} term in Eq. (6) is smaller than the equivalent term in Eq. (4), i.e., $E < A$. This is consistent with the physical picture that the metallic bonding in the aluminum-rich interface is stronger than that of the stoichiometric interface. Likewise, the coefficient for the $|EOF|$ term in Eq. (6) is also smaller than the corresponding parameter in Eq. (5), i.e., $F < D$, which is consistent with the picture that the ionic-covalent bonding is stronger in the oxygen-rich interface.

Models^{19,55,58–61} have been proposed to estimate the adhesion of Al-terminated metal/alumina interfaces, although none treated the effects of interfacial stoichiometry. Chatain *et al.*¹⁹ proposed a phenomenological expression for estimates of W_{sep} of the Al-terminated $M/(Al_2O_3)_{AlI}$ interfaces, as follows:

$$W_{\text{sep}} = -\frac{c}{N^{1/3}V_{\text{Me}}^{2/3}} [\Delta\bar{H}_{O(\text{Me})}^\infty + \frac{2}{3}\Delta\bar{H}_{Al(\text{Me})}^\infty] \quad (7)$$

Table IV. Calculated Works of Separation for Stoichiometric $M/(Al_2O_3)_{AlI}$ Interfaces, $W_{\text{sep-AlI}}$

Interfaces	Works of separation, $W_{\text{sep-AlI}}$ (J/m ²)				
	By Eq. (6)	By Eq. (7)	By Li's model	Experimental data	By first-principles
Rh/(Al ₂ O ₃) _{AlI}	0.87	0.95	1.21		Type-I 1.05 [†]
Ir/(Al ₂ O ₃) _{AlI}	0.97	0.82	1.36		Type-I 0.89 [†]
Pd/(Al ₂ O ₃) _{AlI}	0.72,0.77	0.81	1.03	0.74 [‡]	Type-I 0.76 [†]
Pt/(Al ₂ O ₃) _{AlI}	0.85	0.53	1.25	0.90 [§]	Type-I 0.74 [†]
Ni/(Al ₂ O ₃) _{AlI}	1.04	1.16	1.19	1.19 [‡]	Type-I 1.30 [¶]
					Type-II 1.13 [¶]
					Type-III 1.09 [¶]
Cu/(Al ₂ O ₃) _{AlI}	0.65	0.58	0.70	0.49 [‡]	Type-I 0.58 [¶]
					Type-II 0.74 [¶]
					Type-III 0.86 [¶]
Au/(Al ₂ O ₃) _{AlI}	0.48		0.86	0.27 [‡]	Type-I 0.29 ^{††}
				0.56 [¶]	Type-II 0.21 ^{††}
Ag/(Al ₂ O ₃) _{AlI}	0.36	0.20	0.56	0.32 [‡]	Type-I 0.33 ^{††}
					Type-II 0.32 ^{††}
Al/(Al ₂ O ₃) _{AlI}	1.20		0.60	0.95 [‡]	Type-I 1.08 ^{§§} , 1.36 ^{¶¶} , 1.06 ^{¶¶}
				1.13 ^{‡‡}	
Nb/(Al ₂ O ₃) _{AlI}	1.20		0.98		Type-III 2.70 ^{†††} , 2.60 ^{‡‡‡}
Co/(Al ₂ O ₃) _{AlI}	1.04	0.98	1.19	1.14 [‡]	
Fe/(Al ₂ O ₃) _{AlI}	1.12	0.84	1.23	1.21 [‡]	
Mn/(Al ₂ O ₃) _{AlI}	1.12	1.05	0.93	0.86–1.29 [‡]	

First-principles calculations and model estimations using Eqs. (6) and (7), and Li's model⁵⁵ are all listed. Experimental results are also provided for comparison, which correspond to works of adhesion, (W_{Ad}), for the $M/(Al_2O_3)_{AlI}$ interfaces as discussed in the paragraph below Eq. (2). [†]This work. [‡]Chatain *et al.*¹⁹ [§]Saiz *et al.*¹⁴ [¶]Zhang *et al.*³⁵ ^{¶¶}Li.⁵⁶ ^{††}Feng *et al.*³⁶ ^{‡‡}Lipkin *et al.*⁵⁶ ^{§§}Zhang and Smith.³³ ^{¶¶}Batyrev and Kleinman.³⁰ ^{¶¶¶}Siegel *et al.*²⁹ ^{†††}Batyrev *et al.*³² ^{‡‡‡}Zhang and Smith.³⁴

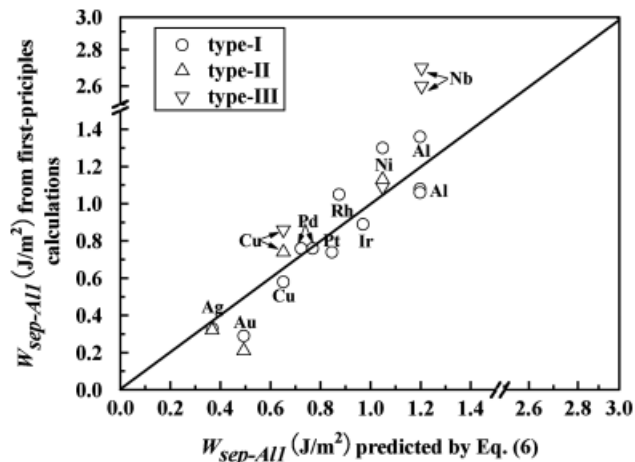


Fig. 3. $W_{\text{sep-AlI}}$ from first-principles calculations versus $W_{\text{sep-AlI}}$ predicted by Eq. (6) for the stoichiometric metal/alumina interfaces. All the data are listed in Table IV.

in which the empirical constant c was estimated to be 0.22, N is Avogadro's constant, and V_{Me} is the molar volume of the metal Me. $\Delta\bar{H}_{\text{O}(\text{Me})}^{\infty}$ and $\Delta\bar{H}_{\text{Al}(\text{Me})}^{\infty}$ are the enthalpies of mixing at infinite dilution of oxygen and aluminum atoms in the bulk metal Me, respectively.

Li⁵⁵ regarded the $W_{\text{sep-AlI}}$ as a function of the electron density parameter n_{ws} , although no straightforward expression was given. From Table IV, it is observed that most of the results obtained here and Chatain and colleagues' model predictions agree well with experimental data, while there are several large discrepancies for Li's model, such as the Pd-, Pt-, Cu-, Au-, Ag-, and Al-related systems. Considering the mixed ionic-covalent and metallic character of chemical bonding at the $\text{M}/(\text{Al}_2\text{O}_3)_{\text{AlI}}$ interfaces, the electron density parameter n_{ws} is not sufficient to describe the adhesion of the stoichiometric interface. The contribution from the metal–oxygen ionic-covalent bonding has to be considered, even though it is not as large.

(4) All Stoichiometries of $\text{M}/\alpha\text{-Al}_2\text{O}_3$ Interfaces

Combining the results for the interfaces of different terminations, a simple, semiempirical relationship ensues for the work

of separation, applicable to all the metals and interfacial stoichiometries:

$$W_{\text{sep}} = an_{\text{ws}} + b|\text{EOF}| + c \quad (8)$$

The nature of the chemical bonding of metal/ $\alpha\text{-Al}_2\text{O}_3$ interfaces underlying Eq. (8) is now clear. The coefficients a – c are different for the different stoichiometries. However, the above comparisons with results of experiments and first-principles computations demonstrate clearly that there does exist a group of (a – c) parameters to describe the adhesion of metals with $\alpha\text{-Al}_2\text{O}_3$ for stoichiometric, aluminum-rich, and oxygen-rich interfacial stoichiometries. It is reasonable to expect that the model has some applicability to other interfaces between metals and oxides.

IV. Conclusions

Through analyses of interfacial stoichiometry, atomic relaxation, electronic structure, chemical bonding, and adhesion between $\alpha\text{-Al}_2\text{O}_3$ and a series of metals including Al, Ni, Cu, Au, Ag, Rh, Ir, Pd, Pt, Nb, and $\beta\text{-NiAl}$, one can conclude the following. Chemical bonding is found to be metallic for the aluminum-rich interfacial stoichiometry, primarily ionic with some covalent contributions for the oxygen-rich stoichiometry, and of mixed ionic-covalent and metallic for the stoichiometric interfaces. Simple empirical relationships were identified. It was found that the metallic component of bonding scales with $(B/V)^{1/2}$, where B is the bulk modulus and V is molar volume of the metal. Similarly, it was found that the ionic-covalent component of bonding is equal to a constant plus a term that scales with the enthalpy of oxide formation $|\text{EOF}|$ of the metal. A linear combination of a constant, $(B/V)^{1/2}$, and the enthalpy of oxide formation, both of the latter of the metal, provides a unified relationship to evaluate the works of separation for all the stoichiometries: aluminum-rich, oxygen-rich, and stoichiometric metal/ $\alpha\text{-Al}_2\text{O}_3$ interfaces. This relationship is consistent with the results of first-principles calculations and experimental measurements for all three potential stoichiometries of the eleven metal/ $\alpha\text{-Al}_2\text{O}_3$ interfaces. These analytic functions of a constant, $(B/V)^{1/2}$, and $|\text{EOF}|$ suggest also that Al-metal–O interactions are important contributors to stoichiometric effects in bonding at these interfaces. In general, higher surface energies and lower interfacial energies lead to the higher works of separation found for O-rich and Al-rich interfaces.

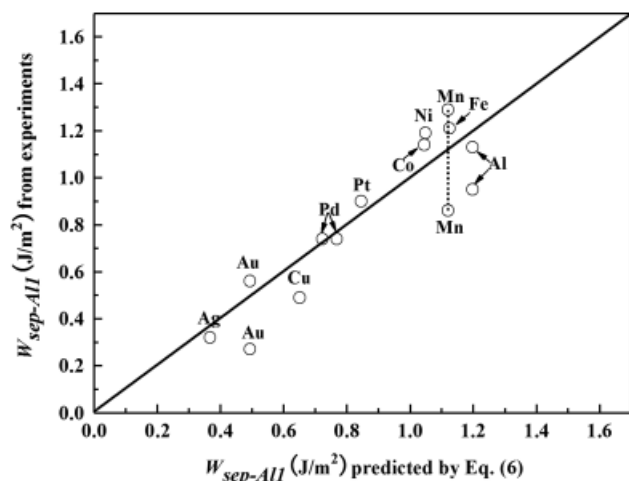


Fig. 4. $W_{\text{sep-AlI}}$ by experimental measurements versus $W_{\text{sep-AlI}}$ predicted by Eq. (6) for the stoichiometric metal/alumina interfaces. The slope of solid line is unity. All the data are listed in Table IV, and the short vertical dotted line designates the range of experimental data¹⁷ for the $W_{\text{sep-AlI}}$ of $\text{Mn}/(\text{Al}_2\text{O}_3)_{\text{AlI}}$. Experimental data correspond to the work of adhesion (W_{ad}) for the $\text{M}/(\text{Al}_2\text{O}_3)_{\text{AlI}}$ interfaces as discussed in the paragraph below Eq. (2).

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