

## Research Article

# A Numerical Formula for General Prediction of Interface Bonding between Alumina and Aluminum-Containing Alloys

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Interface termination between alumina and aluminum-containing alloys is discussed from a viewpoint of thermodynamics by extending the authors' previous discussion on the interface termination between alumina and pure metal. A numerical formula to predict interface bonding at alumina-aluminum-containing alloys is proposed. The effectiveness of the formula is examined by extracting information on interface termination from experimental results and first-principle calculations in references. It is revealed that the prediction by the formula agrees quite well with the results reported in the references. According to the formula, a terminating species can be switched from oxygen to aluminum, which had been actually demonstrated experimentally. The formula uses only basic quantities of pure elements and the formation enthalpy of oxides. Therefore it can be applied for most of aluminum-containing alloys in the periodic table and is useful for material screening in developing interfaces with particular functions.

## 1. Introduction

Interface bonding between oxides and metals is one of the crucial factors that determine properties of materials such as bonding strength, Schottky barrier height, sensitivity of sensors, catalytic activity, and overpotential in batteries. Metal oxides, which are composed of metals and oxygen, can have differently terminated surfaces, for example, the topmost surface being occupied only by oxygen atoms or by the metal atoms that compose the oxide. When such differently terminated surfaces form the interface with metals, bonding strength and wetting properties at the interfaces depend on surface termination species [1–5]. Electron energy level alignment between the Fermi level and oxides' valence bands (band alignment) also varies largely with surface terminating species [6–10]. Regarding alumina/metal interface, which is one of the most extensively studied systems among various oxide/metal interfaces, we have studied the thermodynamics

of interface termination and proposed a numerical formula to predict a terminating species at the interface [11]. A software program that gives predicted results according to the formula has been released [12].

Under conditions where a stable interface termination is determined by a metal in contact, alloying (mixing two or more metals) is one of the most frequently used techniques for modifying interfaces, especially for electric device applications where an electrode metal works only as an electronic conductor but is not chemically functioning. Because the choice of oxides is based on specific properties of the oxides, modification should be made on electrode metals, not on oxides. In this paper, therefore, the discussion on the thermodynamics of interface termination in [11] is extended to the interface between alumina and alloys that contain aluminum, and then a numerical formula for predicting a stable interface terminating species at alumina/aluminum-containing alloy interfaces is proposed.

This work aims to offer a new tool for predicting whether alloying with aluminum is effective or not for interface modification so that time-consuming trials and errors on each system would not be necessary. We believe that the formula proposed in this work would be of great use in material development.

## 2. Formula for Prediction

**2.1. Varieties in Termination.** The most stable phase of alumina is alpha, which has a corundum structure with hexagonal symmetry. The planes parallel to the  $c$ -axis ( $c$ -plane) have differently terminated surfaces and could be O-terminated, Al-terminated, or Al-double-layer-terminated. Because experiments on the  $c$ -plane have been mostly conducted using metal/alumina interfaces for both solid-state bonding and film growth experiments, the  $c$ -plane is considered in this study. Therefore, the interface bonding species can be either Al (M–Al–alumina, including Al-double layer) or O (M–O–alumina) when an interface is formed with a metal (M).

The interface between pure metal (M) and alumina will be terminated by either (1) M–Al–alumina (Al-termination) or (2) M–O–alumina (O-termination). Here, the influence of the coverage is neglected as discussed in the previous paper [11]. When the discussion is extended to the interface with aluminum-containing alloy (MAI), M–Al′–alumina (Al-termination, Al′ denotes terminating Al) in pure M system is replaced by (MAI)–Al′–alumina, where the atom that binds to Al′ can be either M\* or Al\* in MAI (here, M\* and Al\* denote atoms from alloys). Likewise, M–O′–alumina (O-termination, O′ denotes terminating O) is replaced by (MAI)–O′–alumina, where the atom that binds to O′ can be either M\* or Al\* in MAI. Then, there would be four different types of termination at the interface:

(alloy) | interface | alumina

(A) (MAI)—M\*—Al—alumina (Al-termination)

(B) (MAI)—Al\*—Al—alumina (Al-termination)

(C) (MAI)—M\*—O—alumina (O-termination)

(D) (MAI)—Al\*—O—alumina

Although (D) is initially derived from the O-terminated interface between (MAI) alloy and alumina, it can be regarded as Al-termination because this is the same as either (A) or (B).

**2.2. Procedure for Prediction.** Thermodynamic equilibrium among the four types of termination (A)–(D) has been considered. The equilibrium is determined by Gibbs energy difference among the terminations [11]. In our previous paper on the interface between alumina and pure metal, we use M–Al and M–O bonding energy to obtain Gibbs energy difference among different terminations for simplicity [11]. Here, for the interface between alumina and aluminum-containing alloy (MAI), we use M–Al, Al–Al, M–O, and Al–O bonding energy.

As in the previous paper, M–Al bonding energy is estimated either by the adsorption energy of Al on M (Approx-1) or by subtracting the adsorption energy of M on M from

that of Al on M (Approx-2). The subtraction is considered because the values of adsorption energy include not only the influence of chemical interaction between Al and M but also that of cohesion energy. M–O bonding energy is estimated either by the adsorption energy of oxygen on M (Approx-1) or by subtracting the dissociation energy of molecular oxygen from the adsorption energy of oxygen on M (Approx-2). The reason of adopting adsorption energy of metals to estimate M–Al or Al–Al bonding energy and that of oxygen for M–O bonding energy is as follows: values of formation enthalpy of oxides and intermetallic compounds or of mixing enthalpy include terms not only from chemical interaction but also from structural change. At the interface structural relaxation occurs more easily than in bulk and the structural term would be smaller and can be neglected for rough estimation.

The adsorption energy of Al on M (=Al on Al when M = Al) and M on M were calculated using (1), which is based on Meadima's formula [13]:

$$\begin{aligned} \Delta H_{\text{ad}}(A \text{ on } B) = & -F \times \gamma_B \times S_A + (1 - F) \times \gamma_A \times S_A \\ & + F \times \Delta H_{\text{sol}}(A \text{ in } B) - \Delta H_{\text{vap}}(A), \end{aligned} \quad (1)$$

where  $\Delta H_{\text{ad}}(A \text{ on } B)$  is the adsorption energy of  $A$  on  $B$ ,  $\gamma_A$ , and  $S_A$ , and  $\gamma_B$  and  $S_B$  are surface energy and surface area of  $A$  and  $B$ , respectively.  $\Delta H_{\text{sol}}(A \text{ in } B)$  is the heat of mixing of  $A$  in  $B$ ;  $\Delta H_{\text{vap}}$  is vaporization enthalpy.  $F$  is the portion of the area of  $A$  in contact with  $B$ , which is typically around 0.4. Here, the energy is described per mol.  $\Delta H_{\text{sol}}(A \text{ in } B)$  is calculated by the following equation:

$$\begin{aligned} \Delta H_{\text{sol}}(A \text{ in } B) = & 2V(A)^{2/3} \times \left( n(A)^{-1/3} + n(B)^{-1/3} \right)^{-1} \times N_0 \\ & \times P \times \left\{ -e(\Delta\phi)^2 + \frac{Q}{P(\Delta n^{1/3})^2} - \frac{R}{P} \right\}, \end{aligned} \quad (2)$$

where  $V(A)$  is the molar volume of metal  $A$ ,  $n(A)$ , and  $n(B)$  are the electron density of  $A$  and  $B$  at the boundary of the Wigner-Seitz cell,  $\Delta\phi$  is the work function difference between  $A$  and  $B$ , and  $P$ ,  $Q$ , and  $R$  are parameters.  $N_0$  is the Avogadro's number. The detail of the calculation and values for  $\gamma_A$  and  $\gamma_B$ ,  $\Delta H_{\text{vap}}$ ,  $V(A)$ ,  $n(A)$ , and  $n(B)$ ,  $\Delta\phi$ , and three parameters  $P$ ,  $Q$ , and  $R$  are described in [14]. The values of the calculated adsorption energy for each M–Al combination were obtained using the software [15] released by one of the authors and listed in Table 1.

The adsorption energy of oxygen on M is estimated in the following way. It has been reported [16] that the initial heat of adsorption of oxygen on some metals [17] has linear dependence on the standard enthalpy of formation [18] of the corresponding oxides with the highest oxidation state. The values of the formation enthalpy and the valence of the corresponding oxides were reexamined using other references [19, 20]. We decided to use the values from [20] to correlate the initial heat of adsorption of oxygen ( $H_{\text{ads}}$ ) with the formation enthalpy of the corresponding oxide with the highest oxidation state ( $H_{\text{form}}$ ) except Cr. The following

TABLE 1: Adsorption energy of Al and other metals (M) on M and their subtracted values.

Metal- M	Al on M Adsorption energy (kJ/mol)	M on M Adsorption energy (kJ/mol)	(Al on M) – (M on M) Energy difference (kJ/mol)
Al	270	270	0
Si	277	359	-82
Ti	384	363	21
V	400	401	-1
Cr	377	303	74
Fe	392	316	76
CO	408	335	73
Ni	407	340	67
Cu	332	265	67
Zn	299	113	186
Ga	243	227	16
Ge	258	297	-39
Zr	389	490	-101
Nb	409	582	-173
Mo	410	523	-113
Ru	454	521	-67
Rh	447	435	12
Pd	413	283	130
Ag	280	222	58
In	228	198	30
Sn	230	254	-24
La	312	358	-46
Hf	399	492	-93
Ta	433	627	-194
W	434	695	-261
Re	496	612	-116
Os	487	636	-149
Ir	474	535	-61
Pt	450	448	2
Au	325	293	32
Hg	262	60	202
Pb	215	153	62
Bi	211	169	42

numerical relationship has been obtained with the correlation coefficient of 0.977:

$$\text{Hads (kJ/mol-O)} = 0.719 \times \text{Hform (kJ/mol-M)} + 230 \text{ (kJ/mol-O)}. \quad (3)$$

We use values of Hads calculated by (3) as the adsorption energy of oxygen on M.

In Table 2, formation enthalpy of various oxides to be used for the calculation (after [20] except those in italics which are from [19]) and the calculated adsorption energy values are listed. For readers' convenience, values for metals

that were not reported in references we discuss later are also given.

In the previous paper, the following two expressions were used in order to predict whether the interface termination is either M–Al–alumina or M–O–alumina between pure metal and alumina.

Approx-1 is

$$(\text{AlonM}) - (\text{OonM}). \quad (4)$$

Approx-2 is

$$\{(\text{AlonM}) - (\text{MonM})\} - \left\{(\text{OonM}) - \frac{1}{2} (\text{O}_2 \text{ dissociation energy})\right\}, \quad (5)$$

where  $\text{O}_2$  dissociation energy = 493.07 kJ/mol [21]. Approx-2 has been proposed because the value of (AlonM) includes both chemical interaction between Al and M and cohesive energy of atomic Al, and therefore, in order to extract the term caused by only chemical interaction, subtraction of cohesive energy is necessary. The situation is the same for (OonM), where both chemical interaction between O and M and cohesive energy of atomic O are included and the subtraction of cohesive energy (=the half of  $\text{O}_2$  dissociation energy) is needed. Prediction with Approx-1 is that if (4) is positive, that is,  $(\text{AlonM}) > (\text{OonM})$ , M–Al bonding is preferred to M–O bonding and if  $(\text{AlonM}) < (\text{OonM})$ , M–O bonding is preferred. With Approx-2, prediction goes as follows: if (5) is positive, that is,  $\{(\text{AlonM}) - (\text{MonM})\} > \{(\text{OonM}) - 1/2(\text{O}_2 \text{ dissociation energy})\}$ , M–Al bonding is preferred, and vice versa.

Four types of terminations (A)–(D) for aluminum-containing alloy, as described in Section 2.1, are derived from either M–Al–alumina or M–O–alumina interface in pure metal, where (A) and (B) are derived from M–Al–alumina and (C) and (D) are derived from M–O–alumina. Therefore, in order to predict which one of terminations is realized at the interface with aluminum-containing alloy, we first predict whether M–Al–alumina or M–O–alumina is realized at the interface without aluminum in the alloy using either Approx-1 or Approx-2. Once M–Al–alumina is predicted, the second step is to predict whether the interface is (A) or (B) at the interface with aluminum-containing alloy. When M–O–alumina is predicted, the second step is to predict whether the interface is (C) or (D). Whether (A) or (B) is realized is determined by comparing the value of (AlonAl) with that of (AlonM). If  $(\text{AlonAl}) > (\text{AlonM})$ , Al–Al bonding is preferred to M–Al bonding and the termination becomes (B). Similarly, (C) or (D) is determined by the value of (OonAl) with respect to (OonM). Here, the value of (OonAl) is obtained by calculating (OonM) with  $M = \text{Al}$  and is 833.06 kJ/mol. If  $(\text{OonAl}) > (\text{OonM})$ , Al–O bonding is preferred to M–O bonding and the termination becomes (D), which is regarded as Al-termination. Here, comparison between (AlonAl) and (AlonM) or between (OonAl) and (OonM) does not need subtraction like in (5), because the

TABLE 2: Values of oxide formation enthalpy and calculated adsorption energy of oxygen on various metals (M) and related values.

		kJ/mol	kJ/mol-M	kJ/mol-O	kJ/mol-O	Energy difference (kJ/mol)
Mg	MgO	601.6	601.6	601.6	664.14	419.61
Al	Al <sub>2</sub> O <sub>3</sub>	1675.7	837.85	558.5667	833.06	588.53
Si	SiO <sub>2</sub>	910.7	910.7	455.35	885.15	640.62
<b>Ti</b>	TiO <sub>2</sub>	944	944	472	908.96	664.43
V	V <sub>2</sub> O <sub>5</sub>	1550.6	775.3	310.12	788.34	543.81
Cr	Cr <sub>2</sub> O <sub>3</sub>	1139.7	569.85	379.9	641.44	396.91
Mn	MnO <sub>2</sub>	520	520	260	605.80	361.27
<b>Fe</b>	Fe <sub>2</sub> O <sub>3</sub>	824.2	412.1	274.7333	528.65	284.12
CO	CO <sub>3</sub> O <sub>4</sub>	891	297	222.75	446.36	201.83
<b>Ni</b>	Ni <sub>2</sub> O <sub>3</sub>	489.5	244.75	163.1667	409.00	164.47
<b>Cu</b>	CuO	157.3	157.3	157.3	346.47	101.94
Zn	ZnO	350.5	350.5	350.5	484.61	240.08
Ga	Ga <sub>2</sub> O <sub>3</sub>	1089.1	544.55	363.0333	623.35	378.82
Ge	GeO <sub>2</sub>	580	580	290	648.70	404.17
Zr	ZrO <sub>2</sub>	1094.3	1094.324	547.162	1016.44	771.91
Nb	Nb <sub>2</sub> O <sub>5</sub>	1899.5	949.75	379.9	913.07	668.54
Mo	MoO <sub>3</sub>	745.1	745.1	248.3667	766.75	522.22
Ru	RuO <sub>4</sub>	239.3	239.3	59.825	405.10	160.57
Rh	Rh <sub>2</sub> O <sub>3</sub>	343.0	171.5	114.3333	356.62	112.09
Pd	PdO	85.4	85.4	85.4	295.06	50.53
Ag	Ag <sub>2</sub> O <sub>2</sub>	24.3	12.15	12.15	242.69	-1.84
In	In <sub>2</sub> O <sub>3</sub>	925.8	462.9	308.6	564.97	320.44
Sn	SnO <sub>2</sub>	577.63	577.63	288.815	647.01	402.48
La	La <sub>2</sub> O <sub>3</sub>	1793.7	896.85	597.9	875.25	630.72
Hf	HfO <sub>2</sub>	1144.7	1144.7	572.35	1052.46	807.93
Ta	Ta <sub>2</sub> O <sub>5</sub>	2046	1023	409.2	965.45	720.92
W	WO <sub>3</sub>	842.9	842.9	280.9667	836.67	592.14
Re	Re <sub>2</sub> O <sub>7</sub>	1240.1	620.05	177.1571	677.34	432.81
Os	OsO <sub>4</sub>	391.248	391.248	97.812	513.74	269.21
Ir	IrO <sub>2</sub>	274.1	274.1	137.05	429.98	185.45
Pt	PtO <sub>2</sub>	133.3	133.3	66.65	329.31	84.78
Au	AuO <sub>x</sub>	<0	<0	<0	<0	<0
Hg	HgO	90.79	90.79	90.79	298.91	54.38
Pb	PbO	218	218	218	389.87	145.34
Bi	Bi <sub>2</sub> O <sub>3</sub>	573.9	191.3	286.95	370.78	126.25

cohesive energy is canceled when (AlonAl) and (AlonM) are compared [(AlonAl) - (AlonM) = {(AlonAl) - (AlonAl)} - {(AlonM) - (AlonAl)}], as well as for (OonAl) and (OonM) [(OonAl) - (OonM) = {(OonAl) - 1/2(O<sub>2</sub> dissociation energy)} - {(OonM) - 1/2(O<sub>2</sub> dissociation energy)}]. Therefore, the expressions for each termination for aluminum-containing alloy (Approx-1) are as follows, where the flow chart for finding an expression is shown in Figure 1(a):

- (a) (OonM) < (AlonM) > (AlonAl)
- (b) (OonM) < (AlonM) < (AlonAl)
- (c) (OonAl) < (OonM) > (AlonM)
- (d) (OonAl) > (OonM) > (AlonM)

When Approx-2 is used in the first step to predict whether M-Al-alumina or M-O-alumina is realized at the interface

without aluminum in the alloy, the comparison between (OonM) and (AlonM) should be made by replacing (OonM) by {(OonM) - 1/2(O<sub>2</sub> dissociation energy)} and (AlonM) by {(AlonM) - (MonM)}. Then the corresponding expressions to (a)-(d) become as follows, where the flow chart for finding an expression is shown in Figure 1(b):

- (a') (OonM) - 1/2(O<sub>2</sub> dissociation energy) < (AlonM) - (MonM) > (AlonAl) - (MonM)
- (b') (OonM) - 1/2(O<sub>2</sub> dissociation energy) < (AlonM) - (MonM) < (AlonAl) - (MonM)
- (c') (OonAl) - 1/2(O<sub>2</sub> dissociation energy) < (OonM) - 1/2(O<sub>2</sub> dissociation energy) > (AlonM) - (MonM)
- (d') (OonAl) - 1/2(O<sub>2</sub> dissociation energy) > (OonM) - 1/2(O<sub>2</sub> dissociation energy) > (AlonM) - (MonM).

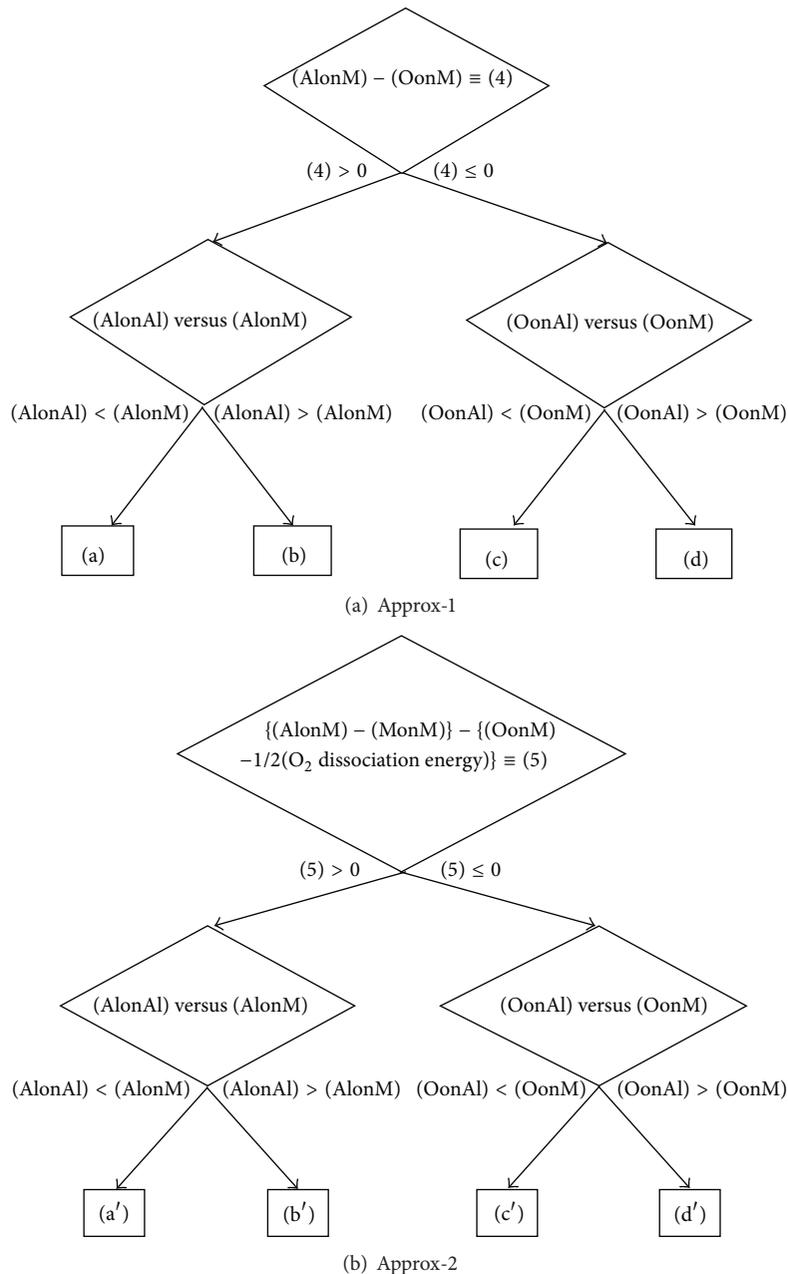


FIGURE 1: Flow chart for finding an expression that predicts termination.

If (d) or (d') is satisfied, the interface between alumina and pure metal M is O-terminated, whereas the interface with M alloyed with Al is Al-terminated. This is the key to switch interface termination species from oxygen to aluminum by adding Al to metals that satisfy (d) or (d'). Whether this switching of interface termination species occurs or not is governed by the adsorption energy of oxygen on M and Al. As in the expressions (d) and (d'), when the adsorption energy of oxygen on Al is larger than that on M, Al-O bonding is preferred at the interface and type (D) termination, that is, Al-termination, is formed. On the other hand, it is clear that switching Al-terminated interface to O-terminated one

by alloying with Al is impossible from the expressions (a)–(d). It should be noted that the systems where different termination is predicted in the first step using by either Approx-1 or Approx-2 are limited only to Ru, Rh, Ir, Pt, and Hg (predictions for these systems are M-Al-alumina with Approx-1 and M-O-alumina with Approx-2). Furthermore, aluminum-containing alloys of these metals are predicted to be Al-terminated whether interface termination is predicted as M-Al-alumina or M-O-alumina in the first step (termination (A) or (D)). Therefore, we may be able to use Approx-1 in the first step for predicting the interface in aluminum-containing alloy.

TABLE 3: Binding energies of Al 2p in Ti-Al compounds prepared in various conditions compared to those in alumina on Cu and Ni related metals as references.

	Preparation conditions	Binding energy (eV)			Termination	Reference
		Al 2p <sub>3/2</sub> or Al 2p (ox)	Al 2p <sub>3/2</sub> or Al 2p (MAI)	Al 2p <sub>3/2</sub> or Al 2p (ox) – (MAI)		
Cu <sub>9</sub> Al(111)		74.90	72.58	2.32	Al	[24]
Cu(111)		74.11		1.53	O	[10]
NiAl(110)		74.91	72.47	2.44	Al	[10]
Ni(111)		74.11		1.64	O	[10]
TiAl(111)	$1 \times 10^{-5}$ Pa, 923 K	75.5	72.2	3.3		[25]
Ti <sub>45</sub> -Al <sub>55</sub>	$1 \times 10^{-5}$ Pa, 923 K	75.5	72.3	3.2		[26]
Ti <sub>55</sub> -Al <sub>45</sub>	$<5 \times 10^{-8}$ Pa, ~873 K	74.9	71.6	3.3		[27]
Ti <sub>3</sub> Al	$1 \times 10^{-5}$ Pa, 923 K	75.5	72.3	3.2		[26]
TiAl	$1.3 \times 10^{-5}$ Pa, 673–873 K	74.4	71.7	2.7		[28]
Ti <sub>45</sub> -Al <sub>55</sub>	10 Pa, 423 K & 623 K	75.2	72.57	2.63		[29]
TiAl	air, 573–673 K	74.9	72.3	2.6		[30]

In summary, to find a type of interface bonding in aluminum-containing alloy (MAI), interface termination at alumina-corresponding pure metal (without aluminum in the alloy) should be first examined. Then, if the interface with pure metal is Al-terminated, values of (AlonM) and (AlonAl) are to be compared. For O-terminated interface with pure metal, values of (OonM) and (OonAl) should be compared. This procedure gives the type of interface bonding in aluminum-containing alloy from expressions (A)–(D). After looking for M that satisfies (AlonAl) > (AlonM) (M = Ga, Ge, In, Sn, Hg, Pb, Bi in Table 1), we found that there is no M with (OonM) < (AlonM). Therefore, there is no M that satisfies expression (B).

It should be noted that the values of (OonM) are derived from the standard formation enthalpy of corresponding oxide, which is defined at 1 bar pressure. Because both oxidation and reduction of metal can occur in the same system at different oxygen pressure, a terminating species would vary with oxygen pressure, especially for metals with relatively small standard formation enthalpy values.

There is one more thing to be noted. In all the above discussion, the possibility of alumina reduction is excluded. However, if the oxide formation enthalpy of metal M per mol-O is larger than that of alumina, formation of oxide with M and reduction of alumina should occur, which is expected for M = La, Hf in Table 2.

### 3. Termination in Aluminum-Containing Alloys in References

*3.1. Experimental Results.* There are only a limited number of references that handle interface termination between alumina and aluminum-containing alloys. We have investigated interface termination using NiAl(110) and Cu-9Al(111) [10] and showed that Al 2p XPS peak is a good measure to judge a type of termination. If Al 2p peak has a component between that for Al<sub>2</sub>O<sub>3</sub> and metallic Al, the component is attributed to the interface and the interface is Al-terminated. For NiAl(110),

the shoulder in Al 2p peak in oxidized substrate has been known [22], which were attributed to Al that binds the substrate and alumina film using calculation and STM [23].

Although other references did not discuss interface termination, by examining the reported Al 2p XPS spectra, a type of interface termination can be estimated in the above way. For FeAl, a similar shoulder in Al 2p peak as in NiAl and Cu-9Al was reported [31], which indicates that the interface between FeAl and alumina formed by the oxidation of FeAl was Al-terminated though the authors of the paper did not mention it. In addition to NiAl(110), when NiAl(111), a different orientation of the same intermetallic, was oxidized, a similar shoulder in Al 2p was reported [32].

There are XPS studies on the oxidation of TiAl and Ti<sub>3</sub>Al, but well resolved Al 2p spectra were not reported. However, we are able to estimate the interface termination difference by examining the reported Al 2p binding energies in the following way. In Table 3, Al 2p binding energy values of alumina and of intermetallics taken from references [10, 24–30] are listed. In the case of Cu and Ni systems, where all the data come from our laboratory under the same energy calibration conditions, differences of Al 2p<sub>3/2</sub> values in alumina (Al 2p<sub>3/2</sub> (ox)) with respect to the ones in M–Al (Al 2p<sub>3/2</sub> (MAI)) for Al-terminated samples (2.3–2.4 eV) are clearly different from those for O-terminated ones (1.5–1.6 eV). For Ti systems, the energy difference between Al 2p (ox) and Al 2p (MAI) falls in two categories, one 3.2–3.3 eV and the other 2.6–2.7 (in the references, Al 2p<sub>3/2</sub> and Al 2p<sub>1/2</sub> were not resolved). The smaller energy difference appears to suggest O-termination, while the larger one is for Al-termination. If we examine the preparation conditions for all these experiments in Table 3, it seems that the suggested terminating species is dependent on the oxidation potential during the interface formation. In the case of lower oxygen pressure and/or higher temperature (=lower oxidation potential), larger energy difference, that is, Al-termination, appears to be realized. The interface termination deduced from reported experiments is schematically summarized in Table 4.

TABLE 4: Schematic representation of interface terminating species at interfaces with alumina reported in experiments.

Mg										
Ca	Sc	Ti*	V*	Cr*	Mn	Fe*	CO*	Ni*	Cu*	Zn
		TiAl <sup>‡</sup>				FeAl <sup>†</sup>	COAl	NiAl <sup>†</sup>	Cu(Al) <sup>†</sup>	
Sr	Y	Zr	Nb*	Mo	Tc	Ru	Rh	Pd	Ag <sup>‡</sup>	Cd
Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

\* O-term.

† Al-term.

‡ Oxygen pressure dependent.

**3.2. Theoretical Results.** To the authors' knowledge, there is no reference that calculates the stability of interface termination at alumina/aluminum-containing alloy (including intermetallics) by first-principle calculations. The references that discuss the chemical potential of Al,  $\Delta\mu_{\text{Al}}$ , as a parameter in the thermodynamic study of interface termination for alumina-Ni, Cu, Ag, and Au [33–35] interfaces handle Al-containing intermetallics. Their conclusion is that an interface terminating species changes from oxygen to aluminum according to the increase of the chemical potential of Al in metals as schematically shown in Figure 2. This  $\Delta\mu_{\text{Al}}$  is a function of both oxygen partial pressure and aluminum activity  $a_{\text{Al}}$  in metals. The figure assumes that alumina is more stable than oxide of metal M, MO. Here, using Figure 2, we discuss the influence of aluminum activity under constant oxygen partial pressure, where alumina is stable. From the right to the left in the figure, metal composition changes from pure metal to Al intermetallics. On the border B at the right side in Figure 2, the interface is not  $\text{Al}_2\text{O}_3/\text{M}$  (pure metal) but  $\text{Al}_2\text{O}_3/\text{MO}_x$  (metal oxide). When  $a_{\text{Al}}$  is larger than that at the border B, the interface is O-terminated. If mixed oxide phase MAIO exists, the border C appears in the figure and the interface with alumina would be  $\text{Al}_2\text{O}_3/\text{MAIO}_x$  instead of  $\text{Al}_2\text{O}_3/\text{MO}_x$ . The interface  $\text{Al}_2\text{O}_3/\text{MAIO}_x$  is regarded as O-terminated from a bonding point of view, because M–O bonding, not M–Al, exists at the interface. On the border A at the left side in Figure 2,  $\text{Al}_2\text{O}_3$  reduces to Al metal that forms an intermetallic compound MAI, such as  $\text{Cu}_3\text{Al}$  and  $\text{Ni}_3\text{Al}$ , and the interface is  $\text{Al}_2\text{O}_3/\text{MAI}$ , not  $\text{Al}_2\text{O}_3/\text{M}$ . Therefore, the reference tells us that the interface between MAI (M = Ni, Cu, Ag and Au) and alumina is Al-terminated.

#### 4. Comparison between Prediction and Results in References

Here, we examine the prediction derived from the proposed expressions for each system and compare with the results deduced from the reported results.

In Table 5, the prediction for pure metal (M), the examination of the expression described in Section 2.2 (both Approx-1 and Approx-2), and the resulting prediction for aluminum-containing alloy (MAI) are listed for various metals. The results from the experimental references are also shown in the table. For M on which experimental results both for M and MAI are available (M = Fe, Ni, Cu), the interface is terminated by oxygen for pure M. Therefore, the termination for MAI should be either (C) or (D). Because (OonM) is

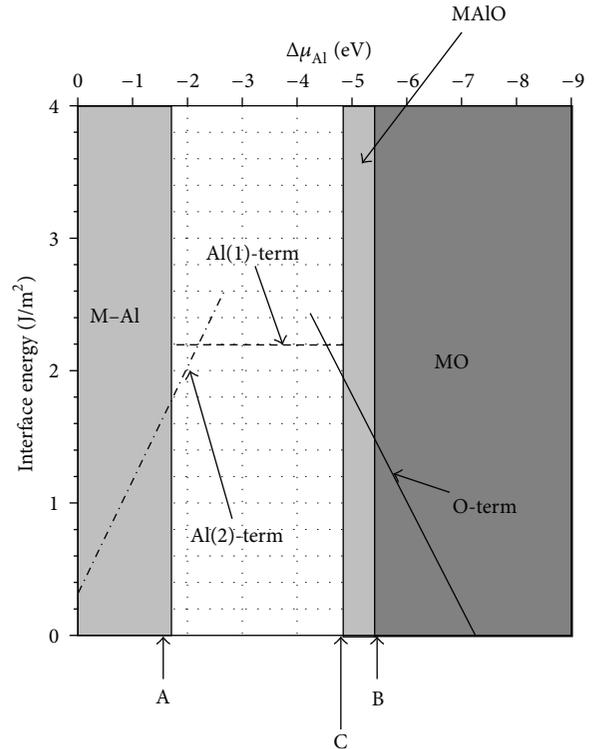


FIGURE 2: Schematic diagram of interface energy and preferred interface termination as a function of  $\Delta\mu_{\text{Al}}$  (chemical potential of Al) for M with intermetallic compound (MAI) and oxides (MO) formation taken into account. On the left side of the border A,  $\text{Al}_2\text{O}_3$  reduces to Al metal. On the right side of the border B, the interface is not  $\text{Al}_2\text{O}_3/\text{M}$  (pure metal) but  $\text{Al}_2\text{O}_3/\text{MO}_x$  (metal oxide). When  $a_{\text{Al}}$  is larger than that at the border B, the interface is O-terminated. If mixed oxide phase MAIO exists, the border C appears in the figure and the interface with alumina would be  $\text{Al}_2\text{O}_3/\text{MAIO}_x$  instead of  $\text{Al}_2\text{O}_3/\text{MO}_x$ .

smaller than (OonAl), expression (d) or (d') applies. This means that our formula predicts Al-termination for MAI (M = Fe, Ni, Cu). The experimental results agree with this prediction. In Section 2.2 it is noted that switching O-terminated interface with pure M to Al-termination by adding Al in M should be possible. Our experiments on alumina/Ni, NiAl, Cu, and Cu-9Al interfaces [10] actually demonstrated the above idea of termination switching. The experiment clearly showed that O-terminated interface with

TABLE 5: The interface prediction for pure metal (M), examination of interface type and interface prediction for aluminum-containing alloy, and experimental results on interface termination in references.

M	Predicted interface termination for pure metal (M)	Predicted interface type for MAI		Predicted interface termination for alloy (MAI)	Experimental results from references
		Approx-1	Approx-2		
Si	O	C	C	O	
Ti	O	C	C	O	Al, O
V	O	D	D	Al	
Cr	O	D	D	Al	
Fe	O	D	D	Al	Al
CO	O	D	D	Al	
Ni	O	D	D	Al	Al
Cu	O	D	D	Al	Al
Zn	O	D	D	Al	
Ga	O	D	D	Al	
Ge	O	D	D	Al	
Zr	O	C	C	O	
Nb	O	C	C	O	
Mo	O	D	D	Al	
Ru	Al, O	A	D	Al	
Rh	Al, O	A	D	Al	
Pd	Al	A	A	Al	
Ag	Al	A	A	Al	
In	O	D	D	Al	
Sn	O	D	D	Al	
La	O	—	—	Al <sub>2</sub> O <sub>3</sub> reduction	
Hf	O	—	—	Al <sub>2</sub> O <sub>3</sub> reduction	
Ta	O	C	C	O	
W	O	C	C	O	
Re	O	D	D	Al	
Os	O	D	D	Al	
Ir	Al, O	A	D	Al	
Pt	Al, O	A	D	Al	
Au	Al	A	A	Al	
Hg	Al, O	A	D	Al	
Pb	O	D	D	Al	
Bi	O	D	D	Al	

pure Ni and pure Cu changed to Al-terminated with NiAl and Cu-9Al.

For M = Ti, where the expression (c) or (c') is satisfied, our formula predicts O-termination. In the experimental reports, both O-termination and Al-termination appear to be obtained depending on the conditions (oxygen potential) for the interface formation as discussed in Section 3.1. Al-termination, which is in disagreement with the prediction, was obtained under low oxygen pressure at high temperature. Under such condition, adsorbed oxygen is known to dissolve into bulk Ti [36]. For Ti, although (OonAl) < (OonM), it appears that dissolution of oxygen at the interface into Ti occurs, resulting in Al-termination. The dissolution of oxygen into metal or alloy is highly dependent on a kind

of metals or alloy and is not taken into account in the prediction formula. Among Si, Ti, Zr, Nb, Ta, and W, which satisfy expression (c) or (c'), similar behavior as for Ti is expected for Zr, Nb, and Ta, because these three metals dissolve considerable amount of oxygen according to the phase diagrams.

One more thing to be noted is that all the metals that satisfy expression (c) or (c') have a mixed oxide phase described as MAIO in Figure 2, Al<sub>2</sub>O<sub>3</sub>·SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>·TiO<sub>2</sub>, 2Al<sub>2</sub>O<sub>3</sub>·ZrO<sub>2</sub>, 1/2(Al<sub>2</sub>O<sub>3</sub>·Nb<sub>2</sub>O<sub>5</sub>) (=AlNbO<sub>4</sub>), 1/2(Al<sub>2</sub>O<sub>3</sub>·Ta<sub>2</sub>O<sub>5</sub>) (=AlTaO<sub>4</sub>), 2Al<sub>2</sub>O<sub>3</sub>·6WO<sub>3</sub> (=Al<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub>).

As mentioned in Section 3.2, interface for these metals could be Al<sub>2</sub>O<sub>3</sub>/MAIO (border C in Figure 2), which contains Al-O-M-O- bonding at the interface and hence is regarded

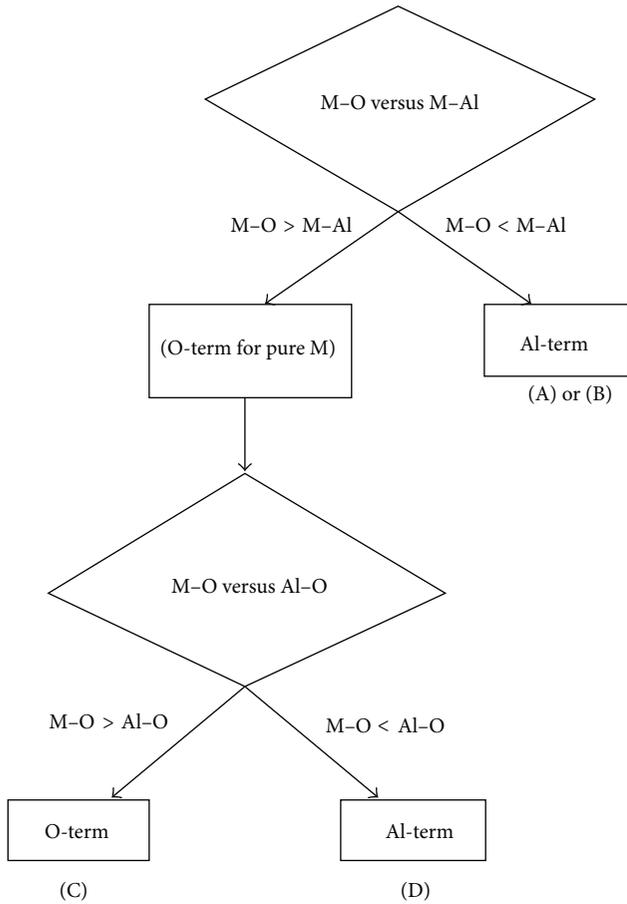


FIGURE 3: Flow chart for predicting a termination type among (A)~(D) in the text.

as O-termination in this paper. When the formation enthalpy of metal oxide increases, approaching that of alumina, the position of borders B and C shifts toward left side in Figure 2, while the position of border A is not influenced by oxide formation enthalpy but mainly by the strength of M–Al bonding (if the M–Al bonding is stronger, the position of border A moves toward right side).

The features shown in Figure 2 in the theoretical study are based on thermodynamics and are common among all the systems calculated. Therefore, we can expect the features to be universal for any metal. Then, when the interface is Al-terminated, alumina is expected to be in equilibrium with aluminum-containing alloys or intermetallics under oxygen partial pressure that metal is not oxidized. This guides the practically useful technique to switch interface bonding from an originally O-terminated interface to Al-termination by adding Al in a metal M. The exception of the application of this technique is the case where  $(\text{OonAl}) < (\text{OonM})$  (expression (c) or (c') is satisfied). Interface bonding for metals that satisfy expression (c) or (c') would be process-dependent in practice, because the thermodynamic stability of Al-terminated and O-terminated interface is very close for metals that satisfy both  $(\text{OonAl}) < (\text{OonM})$  and (formation enthalpy of oxide of metal M)  $<$  (formation enthalpy of

$\text{Al}_2\text{O}_3$ ). For such case, prediction is possible by observing which one of metal elements is preferentially oxidized in Al-containing alloys or intermetallics. If Al is preferentially oxidized, the interface would be Al-terminated, whereas the preferential oxidation of M would result in O-terminated.

It should be noted that if MO is more stable than  $\text{Al}_2\text{O}_3$ , interface Al/MO instead of  $\text{Al}_2\text{O}_3/\text{M}$  should be formed under thermodynamic equilibrium. Among metals we consider in Table 2, Mg, La, and Hf correspond to the case.

By incorporating the discussion on Figure 2 into the expressions presented here, we can make an algorithm to find interface termination in Al-containing alloy as in Figure 3. This algorithm guides a novel method to control interface termination; for a metal with  $(\text{OonM}) < (\text{OonAl})$ , an interface that exhibits O-termination in pure metal can be switched to Al-termination by alloying the metal with Al. It also concludes that a stable Al-terminated interface cannot be formed for metals with  $(\text{OonM}) > (\text{OonAl})$  under equilibrium conditions if oxygen partial pressure is not low enough to reduce  $\text{Al}_2\text{O}_3$ . Therefore, for such metals, utilizing a quenching process is necessary to obtain Al-terminated interfaces. One example of a quenching process is depositing Al on metals followed by oxidation without sufficient annealing, which avoids atomic diffusion needed to reach thermodynamically stable O-termination.

The influence of oxygen partial pressure is not taken into account in (1) and (3), which are used to calculate the adsorption energies of Al on M and oxygen on M, respectively. On the other hand, the strengths of M–O and Al–O bonds should depend on the oxygen partial pressure. Therefore, prediction by this method is not accurate, especially for easily reduced metals. However, it provides a guide for termination, which we believe is quite useful for material development.

## 5. Conclusions

Interface bonding between alumina and aluminum-containing alloy (MAI) has been investigated. A method to predict an interface terminating species is proposed by extending the prediction method already proposed for the interface between alumina and pure metals. In the method, to find the most stable interface termination, the interface bonding energies of differently terminated interfaces, which are estimated using the adsorption energy of Al on base-metal M and that of M on M, and the adsorption energy of oxygen on M and Al are compared. In the algorithm for prediction, interface termination at alumina-pure metal interface should be first examined. Then, if the interface with pure metal is Al-terminated, values of  $(\text{AlonM})$  and  $(\text{AlonAl})$  are compared. For O-terminated interface with pure metal, values of  $(\text{OonM})$  and  $(\text{OonAl})$  should be compared. This procedure gives the type of interface bonding in aluminum-containing alloy according to the expressions (a)–(d) or (a')–(d') in the text. Based on the algorithm, it is also revealed that O-terminated interface can be switched to Al-terminated one by adding Al to pure metal M.

The predicted results are compared with those deduced from experimental studies. The agreement is very good. For aluminum-containing alloys where there is little difference

between (OonM) and (OonAl), termination type would be dependent on temperature and oxygen partial pressure and these influences should be taken into account for more accurate and precise prediction. However, for most of metals, the formula for prediction proposed here should be very effective and useful for material screening in developing interfaces because the method is based on thermodynamics and uses only basic parameters of metals and oxides.

## Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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