

**General method for predicting interface bonding at various oxide -
metal interfaces**

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Abstract

Interface termination bonding between metal oxide and metals is discussed from a viewpoint of thermodynamics. The method of interface termination prediction proposed by the authors for $\text{Al}_2\text{O}_3/\text{metal}$ and ZnO/metal interfaces is extended for general interface between metal-oxide and metals. Information on interface bonding was extracted by carefully examining experimental results and first-principles calculations in references. It is demonstrated that interface termination bonding can be predicted by extending the method to oxide-metal interfaces in general. The method uses only basic quantities of pure elements and the formation enthalpy of oxides. Therefore, it can be applied for most of metals (including elemental semiconductors) in the periodic table and metal-oxides having one stable valence. The method is implemented as a software and can be used for free of charge.

Keywords: oxide-metal interface, interface chemistry, thermodynamic equilibrium, prediction software

1. Introduction

Metal-oxide interfaces are practically very important for many applications. Strong interface bonds are necessary for solid-state bonding, thermal- or corrosion-resistant coatings, and production of composite materials. Band alignment at the metal-oxide interfaces determines the performance of electric and optical devices including solar cells. Chemical reactions at metal-oxide interfaces govern the characteristics of catalysts, fuel cells, and batteries. Oxides can have a polar surface wherein the topmost surface is occupied by only oxygen or the metal atoms constituting the oxide. Therefore, interface with metals can be terminated either by oxygen or metal atoms. Since interface terminating species has significant influence on bonding strength, wetting [1–5], and band alignment [6–13], it should be of great use in developing a method for general prediction. So far, we have developed a method to predict interface terminating species for $\text{Al}_2\text{O}_3/\text{metal}$ [14, 15], which used only very basic parameters including formation enthalpy of oxides, and successfully extended it to ZnO/metal

interfaces [16]. A system to give predicted results for the interface between various metal and Al₂O₃ or ZnO are implemented as web-based software, and anyone can use the software for free of charge [17]. One example of a screenshot of the prediction with the software is shown in Fig. 1. In this article, the prediction method is extended to the interfaces with other oxides, and to the interfaces with elemental semiconductors (instead of metals) such as Si, and Ge with various oxides. The predicted results are examined by reviewing experimental and theoretical results in references. As described below, thermodynamic equilibrium is considered only at the interface, the influence of reduction of oxides or oxidation of metals caused by interface reaction is excluded. Due to this, interfaces with oxides having only one stable valence state are considered here.

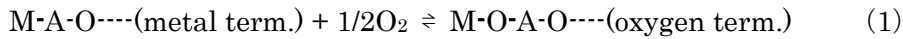
In the method, only polar interfaces in simple oxides composed of one metal component (A) and oxygen (O) will be considered. The interface between an electrode metal (M) and an oxide (AO) will be terminated either by 1) M-A-O-A (called metal termination) or 2) M-O-A-O (called oxygen termination). Thermodynamically, one of these terminations should be more stable than the other.

2. Extension of the prediction method

2.1 Interface with pure metals including elemental semiconductors

For Al₂O₃/metal interfaces, we developed the prediction method [14,15] and extended the prediction method to ZnO/metal interfaces [16]. In the prediction method, terminating species are considered in the frame of a chemical equilibrium. Here, AO / metal interfaces in general are considered.

We assume a chemical equilibrium between the two terminations as in eq. (1).



where the equilibrium constant K is represented as eq. (2).

$$K = \frac{a(M-O-A-O \cdots)}{a(M-A-O \cdots) \times \beta \cdot p(O_2)^{\frac{1}{2}}} \quad (2)$$

Here, $a(M-O-A-O \cdots)$ is the activity of oxygen-terminated interface, $a(M-A-O \cdots)$ the activity of metal-terminated one, and $p(O_2)$ is the partial oxygen pressure and β is a constant determined for each metal. The equilibrium occurs at the interface, where no oxygen gas exists, but the oxygen activity at the interface is proportional to the square root of the partial oxygen pressure [18]. The value of equilibrium constant K can be from zero to infinity. When $K > 1$, the equilibrium in eq. (1) goes to the right side (oxygen termination). K is related with the Gibbs energy ΔG of the reaction (1) through eq. (3).

$$K = \exp(-\Delta G/RT) \quad (3)$$

$$\begin{aligned} \Delta G = & \{\text{chemical potential of (M-O-A-O---) at the standard condition}\} \\ & - \{\text{chemical potential of (M-A-O---) at the standard condition}\} \\ & - \{\text{a half of oxygen chemical potential at the standard condition}\} \end{aligned} \quad (4)$$

If the equilibrium in eq. (1) goes to the right side, the interface is oxygen-terminated, and vice versa. The equilibrium constant K , which determines the direction of the equilibrium, is determined by the Gibbs energy that is a function of chemical potential for metal-termination, that of oxygen-termination and oxygen partial pressure.

We put the influence of oxygen partial pressure aside so that this term can be a constant in the range where oxides are not reduced, and oxidation of the metals does not occur. Then, the chemical potential of metal termination is approximated by the M–A bonding energy and that of oxygen termination by the M–O bonding energy as in the case of Al_2O_3 [14] and ZnO [16]. The M–A bonding energy is estimated either from the adsorption energy of A on M ($\equiv X1$), or by subtracting the adsorption energy of M on M from that of A on M ($\equiv X2$). The subtraction is used because the values of the adsorption energy include not only the influence of the chemical interaction between A and M but also that of the cohesion energy (upon adsorption, an adsorbed atom becomes a part of a solid). The adsorption energies were calculated using Meadima’s formula [19] and by using the software released by the author [20]. The M–O bonding energy is estimated either from the adsorption energy of oxygen on M (O on M, $\equiv Y1$), or by subtracting the dissociation energy of molecular oxygen from the adsorption energy of oxygen on M ($\equiv Y2$). The adsorption energy of oxygen on M is estimated in the way described in ref. 14.

Using the two types of approximation for M–A and M–O bonding energies, two comparisons are used for predicting interface termination.

Approx-1: (A on M) vs. (O on M) (= X1 vs. Y1)

Approx-2: {(A on M) – M on M} vs. {(O on M) – 1/2(O₂ dissociation energy)} (= X2 vs. Y2), where O₂ dissociation energy is 493.07 kJ/mol [21].

If (A on M) > (O on M)

and {(A on M) – (M on M)} > {(O on M) – 1/2(O₂ dissociation energy)},

interface will be A-terminated.

If (A on M) < (O on M)

and {(A on M) – (M on M)} < {(O on M) – 1/2(O₂ dissociation energy)},

then it will be O-terminated.

If the comparison results with Approx-1 and Approx-2 are different, it means that M–A and M–O bonding energies are close and can be influenced by conditions of the interface such as temperature and oxygen partial pressure. The flow of the prediction is

summarized in [Fig. 2](#).

2.2. Interface with alloys

Interface termination in oxide-alloy interfaces can be discussed by considering the effect of a second metal addition to the pure metal on the interface termination. Although, in general, metal (M) that form A-termination at metal-oxide (AO) is very limited, change from A-termination to O-termination can happen, as well as the change from O-termination to A-termination explained for Al_2O_3 [15] and ZnO [16]. The chemical equilibrium at the interface with alloy (basic metal and additive metal are represented as M_A and M_B , respectively) is determined by the amount of energy stabilization by interface bonding. Therefore, adsorption energy of A on M_A ($\equiv X1$), O on M_A ($\equiv Y1$), A on M_B ($\equiv XX1$), and O on M_B ($\equiv YY1$), should be compared as shown in [Fig. 3](#). Here, only the approximation, Approx-1, used in the interface with pure metals is used to simplify the prediction method.

3. Interface termination in references

To examine interface termination in references, oxides mostly having only one stable valence, MgO , SiO_2 , Cr_2O_3 , Ga_2O_3 , Y_2O_3 , ZrO_2 , CdO , La_2O_3 , and HfO_2 , are considered. This is because oxides with multivalence react with metals forming oxides with lower valence, which is not included in the present prediction method. In the following, the interface terminations in references are explained for each oxide-metal combination and a concise summary is given in [Table 1](#).

<MgO>

Interface with Cu has been studied by the internal oxidation of Cu (Mg) single-phase alloys with different Mg concentrations, where Mg was fully oxidized so that no Mg remained in the alloy after oxidation. O-termination has been observed by atom-probe field-ion microscopy (APFIM) [22], electron energy-loss spectroscopy (EELS) [23], high-resolution transmission electron microscopy (HRTEM) [24]. Theoretical calculations also showed O-termination [25].

When Cu alloy not only with Mg but also Ag (Cu + 2.5 at.% Mg + 0.8 at.% Ag) was fully internally oxidized, Ag segregation and O-termination was concluded by APFIM, EELS and scanning transmission electron microscopy (STEM) [26, 27]. From APFIM data in ref. 26, O-Ag interface is inferred.

For the interface with Pd, O-termination was observed at the interface by HRTEM using the fully internally oxidized Pd - 1.5wt% Mg alloy [24]. Theoretical calculations also suggest O-termination [28].

The interface with Ag was reported to be O-terminated from HRTEM experiment [29] and from theoretical calculations [30, 31].

For the interface with Co and Fe, O-termination is expected from theoretical calculations [32]. O-termination is expected from theoretical calculations also for Ni, Pt, and W [28].

<SiO₂>

Interface with Al and Au has been experimentally studied and O-termination for Al and Si-termination for Au have been reported [33].

<Cr₂O₃>

Only theoretical calculations for the interface with Ni, which showed O-termination, have been reported [34, 35].

<Ga₂O₃>

At the interface with Cr, the formation of Cr₂O₃ has been observed by transmission electron microscopy (TEM) [36], which means O-termination.

<Y₂O₃>

Interface with Ge has been studied with X-ray photoelectron spectroscopy (XPS) by molecular beam epitaxy (MBE) growth of Y₂O₃ on Ge and showed Ge-O-Y bonding [37], which means O-termination.

<ZrO₂>

Regarding the interface with Ni, a study on Ni film deposition on yttria-stabilized zirconia (111) by EELS revealed O-termination at Ni-ZrO₂ interface [38], while Zr-termination has been reported for the interface formed by the reduction of NiO-ZrO₂ from TEM and EELS observations [39] and for Ni-ZrO₂ composite plating, where the reduction of Zr⁴⁺ was observed by XPS [40]. In theoretical calculations, O-termination has been reported to be energetically favorable both for ZrO₂ (001) [41] and ZrO₂ (111) [42]. In ref. 43, oxygen partial pressure dependence of the stability of different terminations for different crystal orientations was discussed.

As for the interface with Cu, O-termination was observed from extended X-ray absorption fine structure (EXAFS) [44] and is suggestive from the existence of Cu ions at the interface observed by XPS [45]. With density functional theory (DFT) calculations, optimized structure was reported to be O-termination [46].

O-termination is suggestive for the interface with Co from the existence of Co ions at the interface observed by XPS [45].

At the interface with Pd, Zr-termination has been suggested from XPS measurements for ZrO₂ film on Pd (110) [47].

Zr-termination has been reported at the interface with Au in nanocomposites from

XPS measurements [48].

For the interface with Fe, O-termination is suggestive for ideal interface of ZrO (001) by DFT calculations from work of adhesion [41].

The oxygen partial pressure dependence of the interface formation energy for ZrO(001)/Si interface has been calculated by DFT method, and O-termination is suggestive to be stable for ordinal conditions [49].

<CdO>

The interface with Ag was observed to be O-terminated with CdO {222} by APFIM [50]. Theoretical calculations of the interface between Ag and CdO (001) reported O-termination (the interfacial hybridization of electrons between the Ag and O atoms) [51].

For the interface with Ag (Au) alloy, Au segregation at the interface was observed and the APFIM profile is suggestive of Cd-termination [27].

<La₂O₃>

Interface with Si was experimentally studied by depositing La₂O₃ film on Si (100) and O-termination (La-O-Si bonding at the interface) was observed by XPS [52]. Another study on La₂O₃ film deposition on Si (100) with XPS revealed the formation of La-silicate [53], which means O-termination.

As for the interface with Ge, the interface stability of Ge (111) / La₂O₃ (001) was studied by DFT calculations and O-termination was determined to be more stable [54].

<HfO₂>

Interface with Si has been studied by modeling the electric measurement (C-V characteristics) of MOS structure, where Fermi level pinning was suggested to occur due to Si-Hf bonds at the interface [55]. From the comparison between the modelling and the experiments, 20 % of Si-O-Hf and 80 % of Si-Hf bonds was suggested [56]. Another study suggested that there are a range of different interface configuration with mixed Hf-O and Hf-Si bonding [57]. Reference 58 showed that the standard interface is fully O-terminated. First-principles thermodynamics calculations reported that the interface is silica-like, which means O-termination [59].

For the interface with Pt, oxygen partial pressure dependence on interface termination was studied by first-principles thermodynamics calculations. The study showed that both O-termination and Hf-termination are possible depending on temperatures and pressures [59].

4. Comparison with predicted results

For each combination of an oxide and a metal, calculated values of X1, X2, Y1, Y2,

XX1 and YY1, and the interface termination predictions according to the flowcharts in Fig. 1 and 2 are demonstrated in Table 2. In the table, the values of formation enthalpy of oxides, both for per oxide mole (usually in database) and for per mol-metal in oxide (mol-A), and the interface termination results from references explained in section 3 are also listed. When more than one results either for experiments or theoretical calculations have been reported, results are shown in the same column separated by “,” for the same reference, and by “;” for different reference in the table. There are some combinations for the interface not with a metal but with an elemental semiconductor such as Si and Ge. Interfaces of Si or Ge with Y_2O_3 , ZrO_2 , La_2O_3 , and HfO_2 are regarded as a model interface in high-k oxide gate stack.

In Table 2, there is a clear disagreement between prediction and results from references only for Co/ ZrO_2 and Cu/ ZrO_2 among 26 metal-oxide combinations (disagreement is less than 8 %). Concerning the interface with ZrO_2 , most interfaces are predicted as Zr-termination due to the large values of X1 (adsorption energy of Zr on metals). These large values come from large values of mixing enthalpy of Zr in metals in Miedema’s formula [19]. As seen in table 2 of ref. 60, enthalpy of alloy formation (= mixing enthalpy) calculated from Miedema’s formula tends to be much larger (sometimes twice or three times) than the experimentally obtained values for Zr. If we take this into account, X1 values for ZrO_2 would be approximately 200 kJ smaller. Then, the prediction for both interfaces Co/ ZrO_2 and Cu/ ZrO_2 becomes O-termination, which agrees with the results in references. It is considered that the disagreement for the interface with ZrO_2 is due to poor estimation of mixing enthalpy of Zr by Miedema’s formula.

Regarding the interface with alloys, only two combinations were reported [26, 27]. However, the main conclusion of the reports was solute segregation at metal-oxide interface and not much attention was paid for interface termination. Therefore, it is difficult to determine which type of interface bonding was realized in the experiments.

6. Conclusion

A method to predict an interface terminating species at oxide/metal interfaces under thermodynamic equilibrium is proposed as an extension of our previous method for Al_2O_3 /metal and ZnO /metal interfaces, which is based on thermodynamics and uses only basic parameters of metals and oxides. The predicted results are compared with both experimental and theoretical studies on interface terminating species at oxide/metal interfaces, which were carefully reviewed. Interface with oxides mostly having only one metal valence, MgO , SiO_2 , Cr_2O_3 , Ga_2O_3 , Y_2O_3 , ZrO_2 , CdO , La_2O_3 , and HfO_2 , are

discussed.

The procedure for interface prediction using the formula for pure metal (or elemental semiconductor), M, is briefly summarized as follows. First, calculate the values of the adsorption energies of metal component of oxide, A, on metal M (A on M), that of M on M (M on M), and that of oxygen on M (O on M). Second, determine the signs of the expressions [(A on M) – (O on M)] (Approx-1) and [{"(A on M) – (M on M)} – (O on M) – (493.07 kJ/mol)/2}] (Approx-2), where 493.07 kJ/mol is the dissociation energy of O₂. The interface will be A-terminated if the signs of the two expressions are positive and will be O-terminated if they are negative. If the sign of the two expressions is different, the interface termination could be condition dependent.

For alloys composed of two metals, M_A and M_B, the procedure for predicting the interface between oxide and alloys using the formula is as follows. Here, we omit a corresponding procedure of Approx-2 used for pure metal case to simplify the formula. First, calculate the values of the adsorption energies of metal component of oxide, A, on metal M_A (A on M_A) and on metal M_B (A on M_B), and that of oxygen on M_A (O on M_A) and on M_B (O on M_B). Second, compare these values and find which is the largest. When (A on M_A) is largest, the interface is predicted to be A-terminated with A-M_A bond. If (O on M_A) is largest, O-termination with O-M_A bond is predicted. A-termination with A-M_B bond is predicted when (A on M_B) is the largest, while O-termination with O-M_B bond is predicted if (O on M_B) is the largest.

In principle, the interface termination depends on the temperature and the partial pressure of oxygen. Therefore, these influences should be taken into account for more accurate and precise prediction. Furthermore, Gibbs energy of interface termination, which should depend on crystal orientations of metal and oxide in contact, is approximated with the very simple and brief way in this method. However, it has been demonstrated that the predictions of interface termination mostly agree with the reported experimental results and explain the results of theoretical calculations. Hence, the prediction method should be useful for screening materials for developing interfaces since the method is based on thermodynamics, and uses only basic parameters of metals and oxides, being applicable to various oxide-metal combinations. The prediction procedure is implemented as a web-based software in InterChemBond [17], where users can obtain predicted results by choosing a metal and an oxide from the periodic table as soon as this manuscript is opened to the public.

Conflict of interest

The authors declare no potential conflict of interests.

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Table 1 Summary of reported interface terminations between oxides and metals in references.

Table 2 Calculated values of the adsorption energies of metal component of oxide, A, on metal M_A (A on M_A), that of oxygen on M_A (O on M_A), the subtracted values of $\{(A \text{ on } M_A) - (M_A \text{ on } M_A)\}$ and $\{(O \text{ on } M_A) - 1/2(O_2 \text{ dissociation energy})\}$, and the adsorption energy of A on metal M_B (A on M_B) and that of oxygen on M_B (O on M_B). Values of oxide formation enthalpy for per oxide mole (usually in database) and for per mol-metal (mol-M) are also listed. The predicted results for each combination using these values are shown together with experimental and theoretical results from references.

Fig.1 An example of screenshot for the prediction of interface bonding at Al_2O_3 and Ni(Si) alloy in the current InterChemBond system.

Fig.2 Procedure to predict interface termination between oxide (AO) and pure metal (M).

Fig.3 Procedure to predict interface termination between oxide (AO) and alloy (M_A+M_B).

Table 1 Summary of reported interface terminations between oxides and metals in references.

oxide(AO)	orientation of oxide	metal(M)	interface termination		
			experiment	theory	reference
MgO	{111}	Cu	O		22
	{222}	Cu	O		23
	(1-11)	Cu	O		24
	(111), (100)	Cu		O	25
	{222}	Cu(Ag)	O		26, 27
	(1-11)	Pd	O		24
	(001)	Pd		O	28
	{100}	Ag	O		29
	{100}	Ag		O	30
	(001)	Ag		O	31
	(100)	Co		O	32
	(100)	Fe		O	32
	(001)	Ni		O	28
	(001)	Pt		O	28
SiO ₂		Al	O		33
		Au	Si		33
Cr ₂ O ₃	(0001)	Ni		O	34
	(0001)	Ni		O	35
Ga ₂ O ₃		Cr	O		36
Y ₂ O ₃		Ge	O		37
ZrO ₂	(111)	Ni	O		38
		Ni	Zr		39
		Ni	Zr		40
	(001)	Ni		O	41
	(111)	Ni		O	42
	(100)	Ni		O, Zr	43
		Cu	O		44
		Cu	O		45
	(-111)	Cu		O	46
		Co	O		45
		Pd	Zr		47
		Au	Zr		48
	(001)	Fe		O	41
(001)	Si		O	49	
CdO	{222}	Ag	O		50
	(001)	Ag		O	51
	{222}	Ag(Au)	Au-seg		27
La ₂ O ₃		Si	O		52
		Si	O		53
	(001)	Ge		O	54
HfO ₂		Si	O, Hf		55, 56
		Si	O, Hf (exp + calc)		57
		Si		O	58
		Si		O	59
		Pt	O, Hf (exp + calc)		59

Table 2 Calculated values of the adsorption energies of metal component of oxide, A, on metal M_A (A on M_A), that of oxygen on M_A (O on M_A), the subtracted values of $\{(A \text{ on } M_A) - (M_A \text{ on } M_A)\}$ and $\{(O \text{ on } M_A) - 1/2(O_2 \text{ dissociation energy})\}$, and the adsorption energy of A on metal M_B (A on M_B) and that of oxygen on M_B (O on M_B). Values of oxide formation enthalpy for per oxide mole (usually in database) and for per mol-metal (mol-M) are also listed. The predicted results for each combination using these values are shown together with experimental and theoretical results from references.

oxide	metal-A M_A	metal-B M_B	formation enthalpy of oxide [kJ/mol]	formation enthalpy of oxide [kJ/mol-A]	adsorption energy [kJ/mol]						prediction	experiment	theory
					Aon M_A	Oon M_A	Aon M_A - M_A on M_A	Oon M_A - 493.07/2	Aon M_B	Oon M_B			
					X1	Y1	X2	Y2	XX1	YY1			
MgO	Cu		601.6	601.6	223	346.47	-42	99.935	-	-	O	O	O
	Cu	Ag			223	346.47	-42	99.935	160	242.69	O-Cu	O	
	Pd				324	295.06	41	48.525	-	-	Mg, O	O	O
	Ag				160	242.69	-62	-3.845	-	-	O	O	O
	Co				291	446.36	-44	199.825	-	-	O		O
	Fe				257	528.65	-59	282.115	-	-	O		O
	Ni				295	409	-45	162.465	-	-	O		O
	Pt				376	329.31	-72	82.775	-	-	Mg, O		O
W		307	836.67	-388	590.135	-	-	O		O			
SiO2	Al		910.7	910.7	359	833.06	89	586.525	-	-	O	O	
	Au				395	<0		102	<0	-	-	Si	Si
Cr2O3	Ni		1139.7	569.85	313	409	-27	162.465	-	-	O		O; O
Ga2O3	Cr		1089.1	544.55	363	641.44	136	394.905	-	-	O	O	
Y2O3	Ge		1905.3	952.65	389	648.7	92	402.165	-	-	O	O	
ZrO2	Fe		1094.324	1094.324	588	528.65	272	282.115	-	-	Zr, O		O
	Co				622	446.36	287	199.825	-	-	Zr	O	
	Ni				629	409	289	162.465	-	-	Zr	O; Zr	Zr, O; O
	Cu				529	346.47	264	99.935	-	-	Zr	O	O
	Pd				660	295.06	377	48.525	-	-	Zr	Zr	
	Au				566	<0		273	<0-493.07/2			Zr	Zr
CdO	Ag		258.4	258.4	112	242.69	-110	-3.845	-	-	O	O	O
	Ag	Au			112	242.69	-110	-3.845	159	<0	Cd-Ag	Au-seg	
La2O3	Ge		1793.7	896.85	435	648.7	138	402.165	-	-	O		O
	Si				459	885.15	100	638.615	-	-	O	O; O	
HfO2	Si		1144.7	1144.7	444	885.15	85	638.615	-	-	O	O, Hf	O
	Si				444	885.15	85	638.615	-	-	O	Hf, O	
	Pt				671	329.31	223	82.775			O	Hf, O	

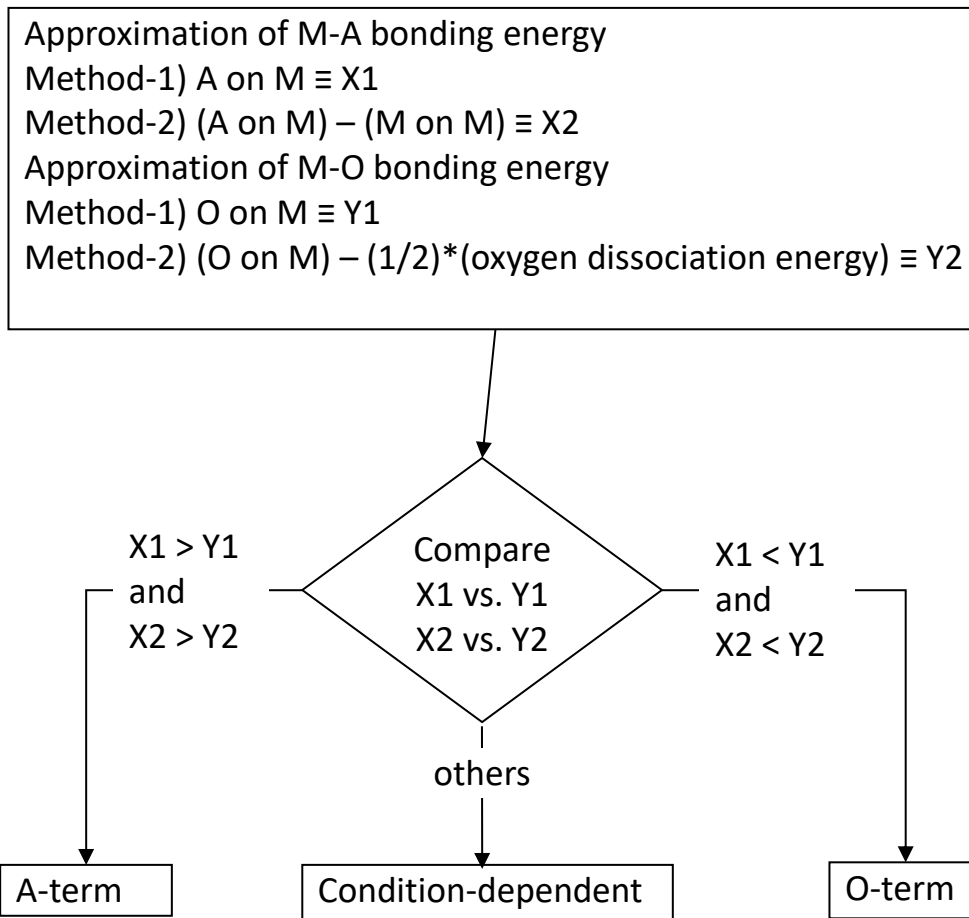


Fig.2 Procedure to predict interface termination between oxide (AO) and pure metal (M).

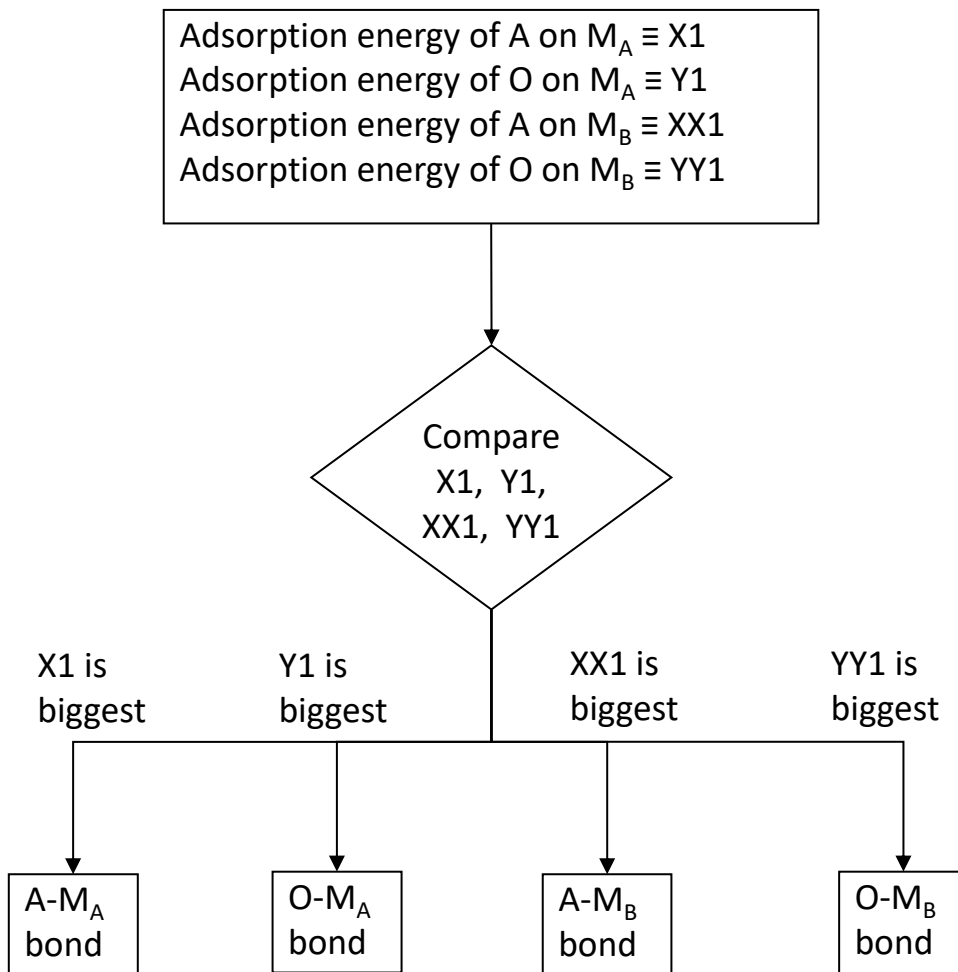


Fig.3 Procedure to predict interface termination between oxide (AO) and alloy (M_A+M_B).