Free software for general prediction of interface chemical bonding at metal – oxide interface: InterChemBond - updated

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Abstract

The updated functions of a free software for general prediction of interface chemical bonding at metal – oxide interface, InterChemBond, is reported. So far, the interface between pure metal or alloy and 19 oxides without considering interface reaction was implemented in InterChemBond. With the current update, the number of oxides available for the prediction has become 83 in total, and a new prediction mode that considers interface reactions has been implemented. The principle of the prediction for the added oxides is explained. The principles and formula for predicting interface bonding with considering interface reactions are provided as well as some dump screens of the software.

Keywords: metal – oxide interface, interface chemistry, thermodynamic equilibrium, interface reaction, prediction software

1. Introduction

Chemical bonding at metal – oxide interface is practically very important for many applications. Strong interface bonds are necessary for solid-state bonding, thermal- or corrosion-resistant coatings, and fabrication 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, the interface with metals can be terminated either by oxygen or

metal atoms. Since interface terminating species have significant influence on bonding strength, wetting [1–5], and band alignment [6–13], it should be of great use to develop a method for general prediction. So far, we have developed a method to predict interface terminating species without considering interface reactions, for metal – Al_2O_3 [14, 15], metal – ZnO [16], and metal – oxide interfaces with additional 17 oxides, BeO, MgO, SiO_2, CaO, Sc_2O_3, Cr_2O_3, Ga_2O_3, SrO, Y_2O_3, ZrO_2, CdO, In_2O_3, BaO, La_2O_3, HfO_2, Ta_2O_5, and Bi_2O_3 [17]. Most of multivalence oxides (oxides with different metal valences for the same metal, such as TiO_2, Ti_2O_3 and TiO) are excluded in the previous version because such oxides often react with a contacting metal and form oxides with reduced valance. The prediction method is applicable also for the interface between elemental semiconductors such as Si and Ge (instead of metals), and various oxides. The prediction method has been already implemented as a free web-based software, InterChemBond [18] and anyone can use the software for free of charge.

In the current update, 64 oxides including multivalence oxides are added in the prediction of the interface and the prediction that considers interface reactions are additionally implemented. This article describes the principle of the prediction for the updated functions as well as the previously implemented functions and demonstrates dump screens of each function.

2. Overview

The new top page after running InterChemBond is shown in Fig. 1. The model-1, “Interface with pure metal without considering interface reaction”, and the model-3, “Interface with alloy without considering interface reaction”, have been available in the previous version for the combinations of 19 oxides and 50 metals or elemental semiconductors. In the current updated version, the prediction of the interface between 83 oxides, including multivalence oxides, and metals and alloys (without interface reaction) is implemented. The model-2, “Interface with pure metal including interface reaction”, is added in the current updated version. In the following, the principles of the predictions for the updated functions are explained briefly as well as the functions implemented in the previous version.

2.1 Previous version

The previous version functions under condition without interface reaction, both for model-1 and model-3. The difference between model-1 and model-3 is that metal is composed of only one element (pure metal) or two (alloy). For the interface with one element, a flowchart in Fig. 2(a) has been used for the prediction, whereas that shown

in Fig. 2(b) has been applied to predict the interface bonding for alloys. Both in Fig. 2(a) and (b), the comparison of the interface bonding energy is approximated by the adsorption energy. For example, to predict the interface between pure metal M and the oxide AO, the comparison of the interface bonding energy between M-A bond (A-termination) and M-O bond (O-termination) is approximated by the comparison between the adsorption energy of A on M and that of O on M. The adsorption energy of A on M is calculated by the way described in ref. 19 and that of O on M in ref. 20. Figure 3(a) shows one example of the dump screen for the prediction of the interface bonding at Ni – Al_2O_3. Clicking the box next to "M" enables to choose a metal from the right-side periodic table surrounded by the red line. Similarly, clicking the box next to "AxOy" enables to choose an oxide from the right-bottom periodic table surrounded by the blue line, where users can select one oxide from the list of oxide appearing after clicking metal component of the oxide. After choosing both metal and oxide, clicking "Calculate" button gives the predicted result by a picture. In the case of Fig. 3(a), the predicted interface has Ni – O – Al bond at the interface (O-termination). An example of the dump screen for the prediction between an alloy and oxide is shown in Fig. 3(b). By clicking the radio button below M_A or M_B and choosing metal (or elemental semiconductor) from the periodic table for both M_A and M_B, alloy selection is done. Then, selecting oxide in the same way as for pure metal in Fig. 3(a) and clicking "Calculate" button give the predicted result by a picture. In this case, the interface between Ni(Si) alloy and Al_2O_3, which corresponds to the addition of Si in Ni, is predicted to be Ni(Si) – Si – O – Al bond (accompanied with Si interface segregation in Ni(Si) alloy). This is regarded as O-termination, although the metal species bonding to oxygen is not the main component of the alloy.

2.2. Added functions

Two types of additions have been made in this update. One is the extension of oxides available for the interface prediction. Now, the interface with one of combinations from 50 metals (including elemental semiconductors) and 83 oxides is available for the prediction. In Table 1, the list of oxides available is provided. The other type of the addition is the model addition, which is encircled by red (was shaded before the update), and became effective in Fig. 1. In this model, the interface reactions, the formation of mixed oxide of A and M, the oxidation of metal M (formation of MO), and the formation of alloys between the metal component of oxide A and the contacting metal M, MA, are considered. It might happen that the interface bonding without interface reaction is predicted after considering the interface reactions mentioned above.

3. Addition of oxide species (without considering interface reaction)

Figure 4(a) show the dump screen after the addition of oxide species, where the number of elements in black in the bottom periodic table is much larger than that in Fig. 3(a). In the previous version, only one oxide appears when an element in the bottom periodic table is clicked. However, in the current updated version, multiple oxides appear for considerable number of elements in the bottom periodic table as shown in Fig. 4(b). Therefore, a user needs to choose one of oxides among them to predict interface bonding.

The method of the prediction for the additional oxide species is exactly the same as the one for the previous one in Fig. 2(a) [17]. The majority of added oxides is multivalence, where multiple oxides with different metal valance exist. At the interface between metal and multivalence oxide, interface reaction often occurs. This is why the addition of oxide species has been implemented at the same time as the implementation of the prediction with interface reaction considered. Because the formation enthalpy of oxide per mol-O does not change much among oxides with different metal valances as seen in the third column of Table 1, the bond strength of A – O is expected not to be much different among oxides with different metal valence and therefore not to influence much on the interface bonding when the interface reaction does not occur (reduction of AO does not occur). Then, the preferred interface bonding is judged from M – O and M – A bonds. M – O bond energy is also considered not to be affected much by the difference of valence of A since bond strength of A – O may not change much by the valence of A as mentioned above. Therefore, for the prediction of the interface with different multivalence oxides, the same method as the previous one is used. It should be noted that the oxygen activity (partial pressure) at the interface could be much lower than that in ambient, and interface reaction may occur.

4. Interface with pure metal including interface reaction

When “Interface with pure metal including interface reaction” (model-2) in the top page is chosen, input screen as shown in Fig. 5, which is same as the screen for “Interface with pure metal without considering interface reaction” (model-1) appears. When metal (including elemental semiconductor) and oxide is chosen for the periodic tables, an inquiry window, asking if there is a mixed oxide phase between the selected metal and oxide exists or not, appears. A user should choose yes or no. This is because the developer of this system cannot obtain the complete set of phase diagrams for any combinations of metal and oxide.

If a mixed oxide phase exists in the phase diagram, there is no chance to form M-A bond at the interface. Therefore, the interface is always with the mixed oxide, which

means oxygen-termination. When no mixed oxide phase exists, whether the oxidation of M occurs or not is judged using the formula (1):

(Oxide formation enthalpy of metal M per mol-O) – (Oxide formation enthalpy of AO per mol-O) (1)

Here, a value for the oxide with the lowest valence of M should be used for the first term, whereas a value for the input oxide AO should be used for the second term, both of which are found in Table 1. If the value of the formula (1) is negative, which means the oxidation of M is thermodynamically stable, then, the interface bond is M – MO – AO, meaning the interface is predicted to be terminated by O atoms with the formation of MO (oxide of metal M). If the value of the formula (1) is positive, the second formula to judge whether the formation of alloy MA occurs or not, should be calculated, which is shown below.

enthalpy of solution A in M (Mixing enthalpy) +

+ {(oxide formation enthalpy of the oxide having less valence than the input oxide) – (that of the input oxide)} per mol-A atom (2)

This formula represents the energy stability of alloy (or intermetallic compound) MA formation by changing the valence of the contacting oxide AO; M + AO -> MA + AOx (x>1, meaning that the valence of A in AO increases, for example, Pt + 2SnO -> PtSn + SnO_2) The first term of the formula (2) is calculated according to ref. 19. The values of { } in the formula (2) are listed in the fourth column in Table 1. If the formula (2) is negative, the interface is predicted to be terminated with A atom with the formation of MA. When the formula (2) is positive, it means that no interface reaction occurs: no mixed oxide, no oxide of M (MO), no alloy of M (MA). Then, the prediction in model-1 in Fig. 1 is applied automatically to display the prediction results. The flowchart of the judgement with pictures showing the results is shown in Fig. 6.

5. Conclusion

A free software for general prediction of interface chemical bonding at metal – oxide interface, InterChemBond, is updated. In addition to the previous prediction for the interface between pure metal or alloy and 19 oxides without considering interface reaction, the number of oxides available for the prediction has increased up to 83 in total, and a new prediction model that considers interface reactions has been implemented in the current update. The principle of the prediction for the added oxides is explained. The principles and formula for predicting interface bonding with considering interface reactions are provided as well as some dump screens of the software.

Although the prediction method uses simple approximations and is very rough, the

method can be applied for many combinations of metal – oxide interface in general. The number of combinations, 50 metals and {(50·49)/2} alloys (combinations of a base metal and additional metal) and 83 oxides, is 105,825 in total. Therefore, the software should be helpful for screening materials.

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Table 1 List of oxides available for the predictions and enthalpy values used for the formula for the predictions

metal component of oxide	oxide	formation enthalpy [kJ/mol-O]	difference of formation enthalpy between AO and $A_{1-x}O$ [kJ/mol-A]
Li	Li_2O	-597.9	-
Be	BeO	-580.1	-
Na	Na_2O	-414.2	-
Mg	MgO	-601.6	-
Al	Al_2O_3	-558.6	-
Si	SiO_2	-455.4	-
K	K_2O	-361.5	-
Ca	CaO	-634.9	-
Sc	Sc_2O_3	-636.3	-
Ti	TiO_2	-472.0	-
	Ti_3O_5	-491.9	-124.2
	Ti_2O_3	-507.0	-59.4
	TiO	-519.7	-240.8
V	V_2O_5	-310.1	-
	V_3O_5	-386.6	-131.0
	V_2O_3	-406.3	-34.9
	VO	-431.8	-177.6
Cr	CrO_2	-299.0	-
	Cr_2O_3	-379.9	-28.2
	Cr_3O_4	-382.8	-59.5
Mn	MnO_2	-260.0	-
	Mn_2O_3	-319.7	-40.5
	Mn_3O_4	-347.0	-16.9
	MnO	-385.2	-77.4
Fe	Fe_2O_3	-274.7	-
	Fe_3O_4	-279.6	-39.3
	FeO	-272.0	-100.8
Co	Co_2O_3	-80.8	-
	Co_3O_4	-222.8	175.9
	CoO	-237.9	-59.1
Ni	NiO	-240.1	-
Cu	CuO	-157.3	-
	Cu_2O	-168.6	-73.0
Zn	ZnO	-350.5	-
Ga	Ga_2O_3	-363.0	-
Ge	GeO_2	-290.0	-
	GeO	-261.9	-318.1
As	As_2O_5	-185.0	-
	As_2O_3	-444.9	204.9
Rb	RbO_2	-139.4	-
	Rb_2O_2	-236.0	-42.8
	Rb_2O	-339.0	-66.5

metal component of oxide	oxide	formation enthalpy [kJ/mol-O]	difference of formation enthalpy between AO and $A_{1-x}O$ [kJ/mol-A]
Sr	SrO	-592.0	-
Y	Y_2O_3	-635.1	-
Zr	ZrO_2	-550.3	-
Nb	Nb_2O_5	-379.9	-
	NbO_2	-398.1	-153.6
	NbO	-405.8	-390.4
Mo	MoO_3	-248.4	-
	MoO_2	-294.5	-156.2
Tc	Tc_2O_7	-159.1	-
	TcO_2	-228.9	-99.1
Ru	RuO_2	-152.5	-
Rh	Rh_2O_3	-114.3	-
Pd	PdO	-85.4	-
Ag	Ag_2O_2	-12.2	-
	Ag_2O	-31.1	3.4
Cd	CdO	-258.4	-
In	In_2O_3	-308.6	-
Sn	SnO_2	-288.8	-
	SnO	-280.7	-296.9
Sb	Sb_2O_3	-240.1	-
Cs	Cs_2O	-345.8	-
Ba	BaO	-548.0	-
La	La_2O_3	-597.9	-
Hf	HfO_2	-572.4	-
Ta	Ta_2O_5	-409.2	-
W	WO_3	-281.0	-
	WO_2	-294.9	-253.2
Re	Re_2O_7	-177.2	-
	ReO_3	-204.8	-5.8
Os	OsO_4	-98.5	-
Ir	IrO_2	-137.1	-
	Ir_2O_3	-67.5	-173.0
Pt	PtO_2	-66.7	-
	PtO	-70.0	-63.4
Au		0.0	-
Hg	HgO	-90.8	-
Tl	Tl_2O_3	-131.0	-
	Tl_2O	-178.7	-107.2
Pb	PbO_2	-138.7	-
	Pb_3O_4	-179.6	-37.9
	PbO	-219.0	-20.5
Bi	Bi_2O_3	-191.3	-

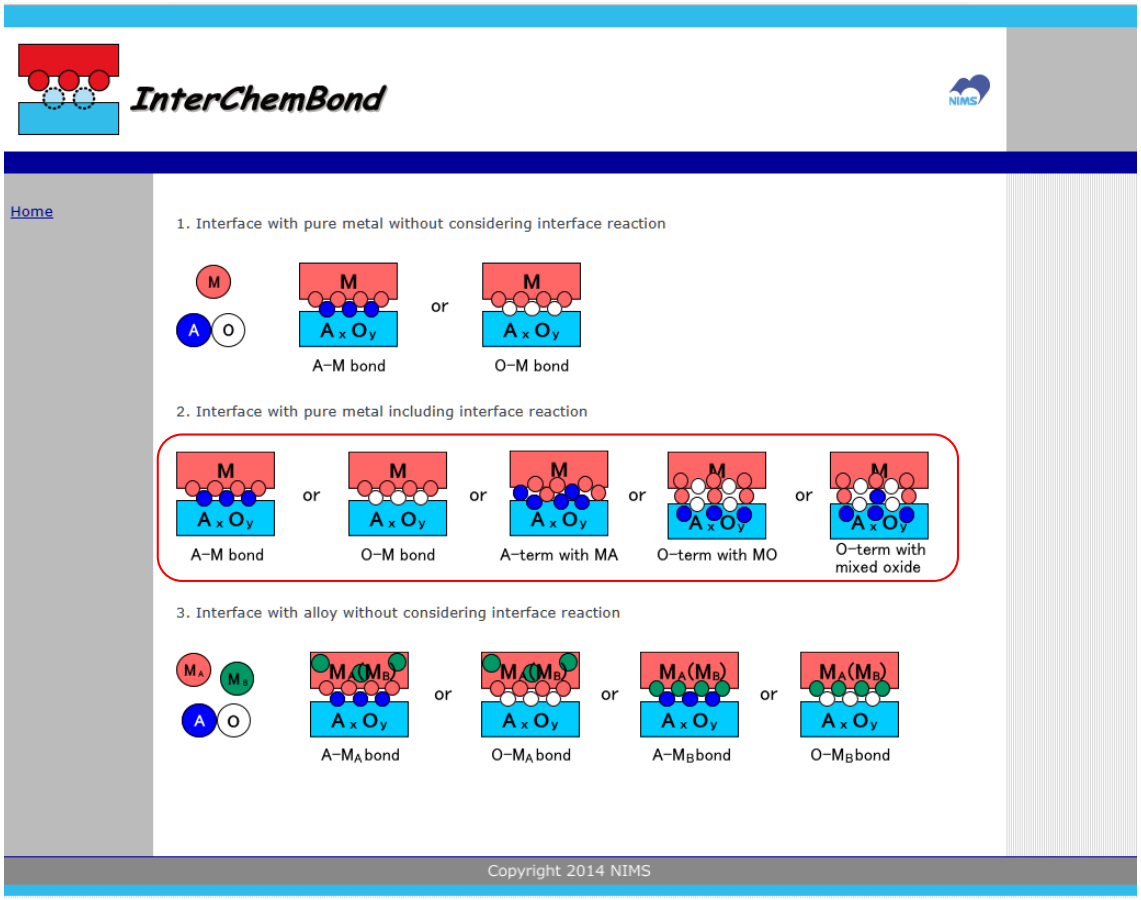
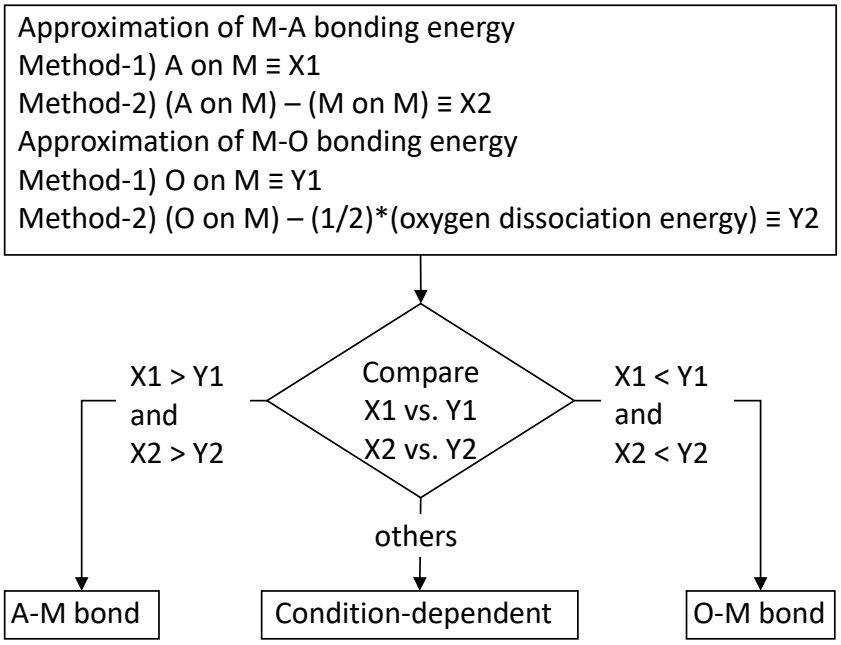


Fig.1 The dump screen of the top page of the current InterChemBond system, which gives predictions for various metal – oxide interfaces.

(a)



(b)

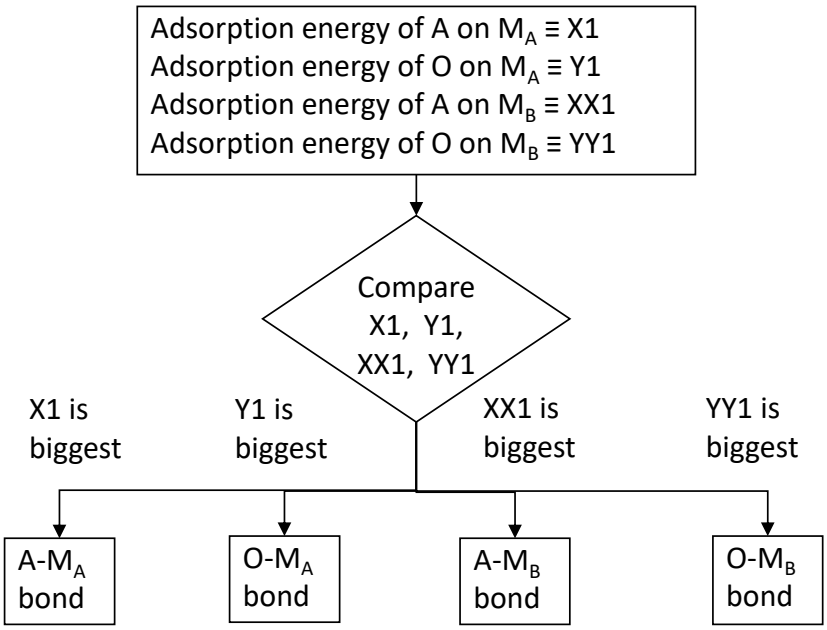


Fig.2 Procedure to predict interface termination between oxide (AO) and pure metal (M) (a). Procedure to predict interface termination between oxide (AO) and alloy (M_A+M_B) (b).

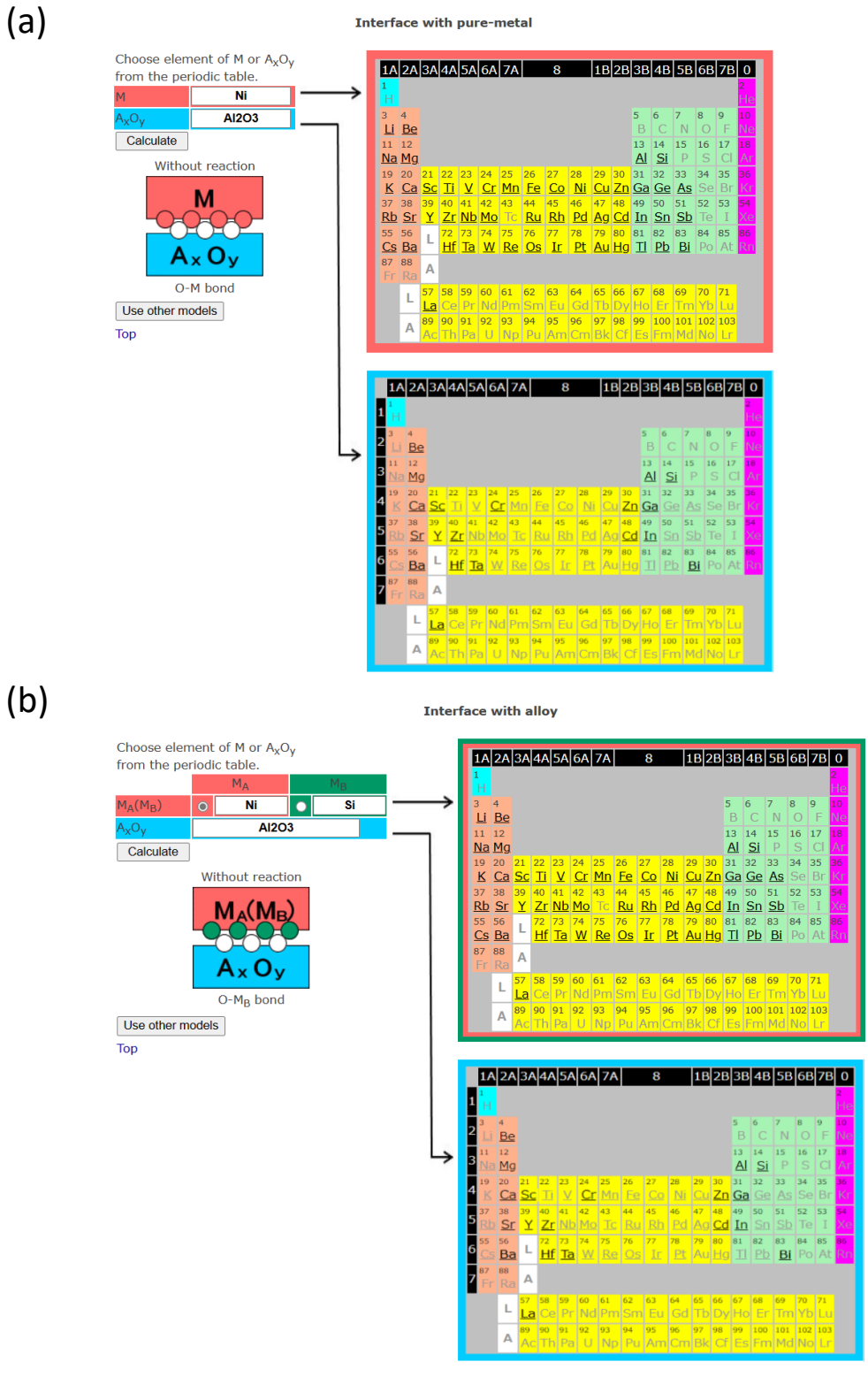


Fig.3 An example of dump screen for the prediction of bonding at Ni – Al_2O_3 interface (a) and at Ni(Si) alloy – Al_2O_3 interface (b) in the previous InterChemBond system.

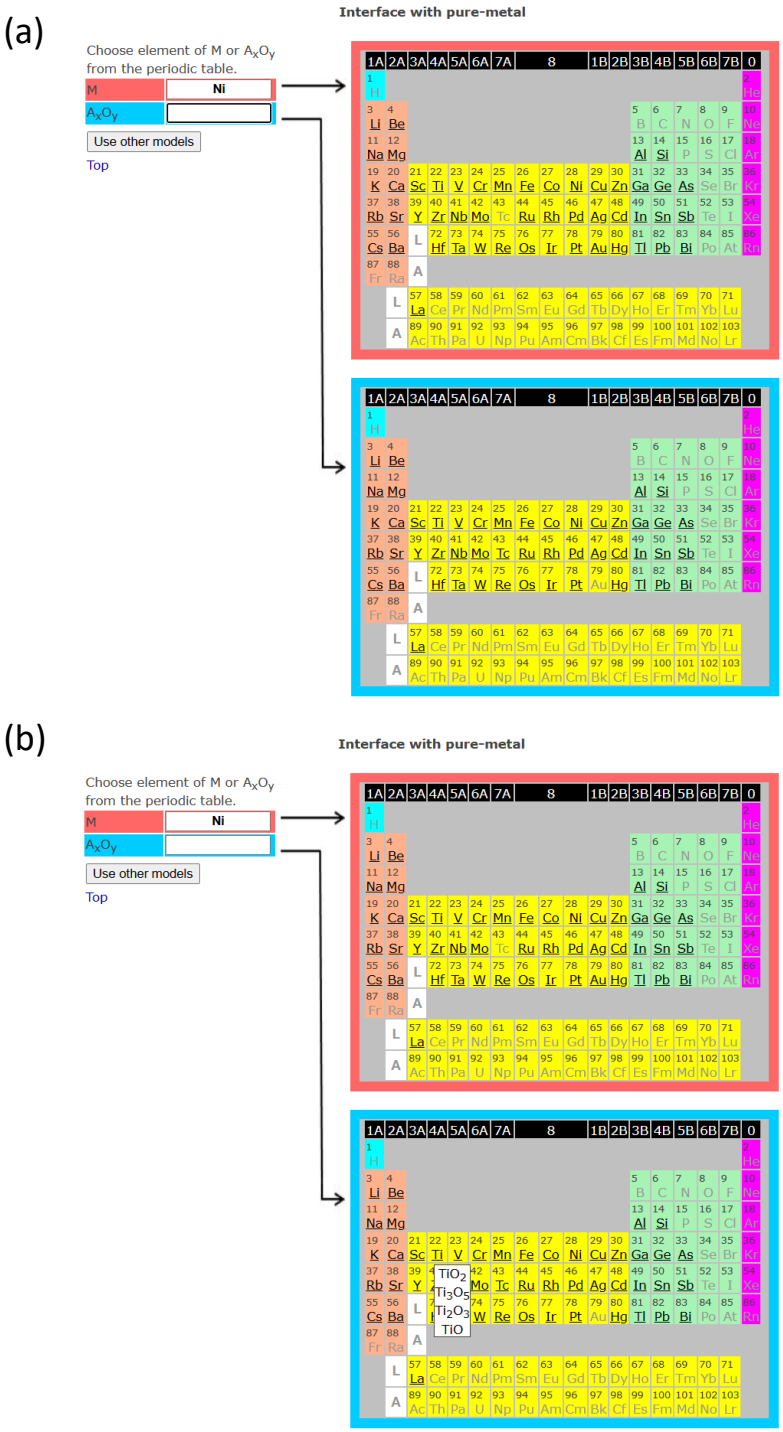


Fig.4 An example of dump screen of the input of metal and oxide for the prediction in the current updated InterChemBond system (a). The number of available elements for oxides (letter in black) increased compared to Fig. 3(a). An example of dump screen for oxide choice among multivalence oxides (b).

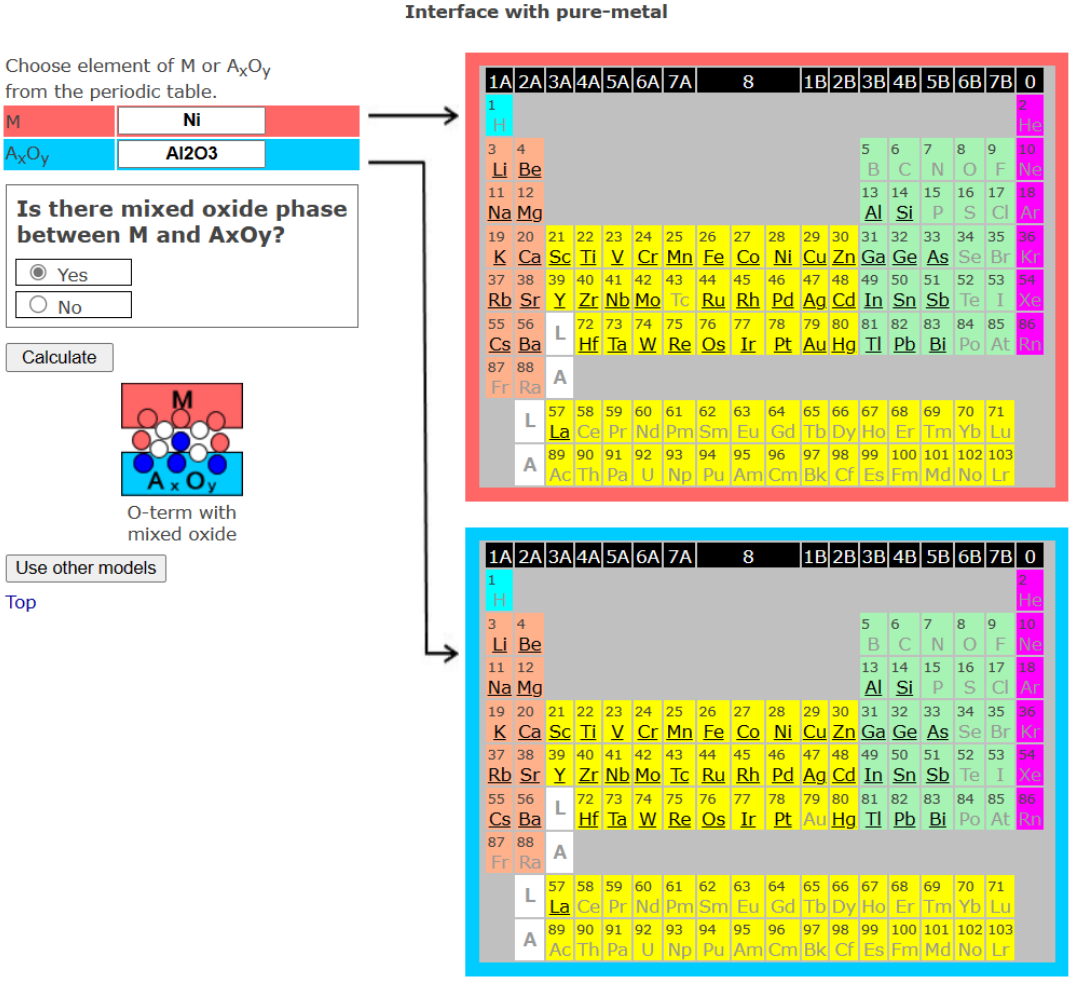


Fig.5 An example of dump screen for the prediction of bonding at Ni – Al_2O_3 interface including interface reaction under the existence of mixed oxide in the currently updated InterChemBond system.

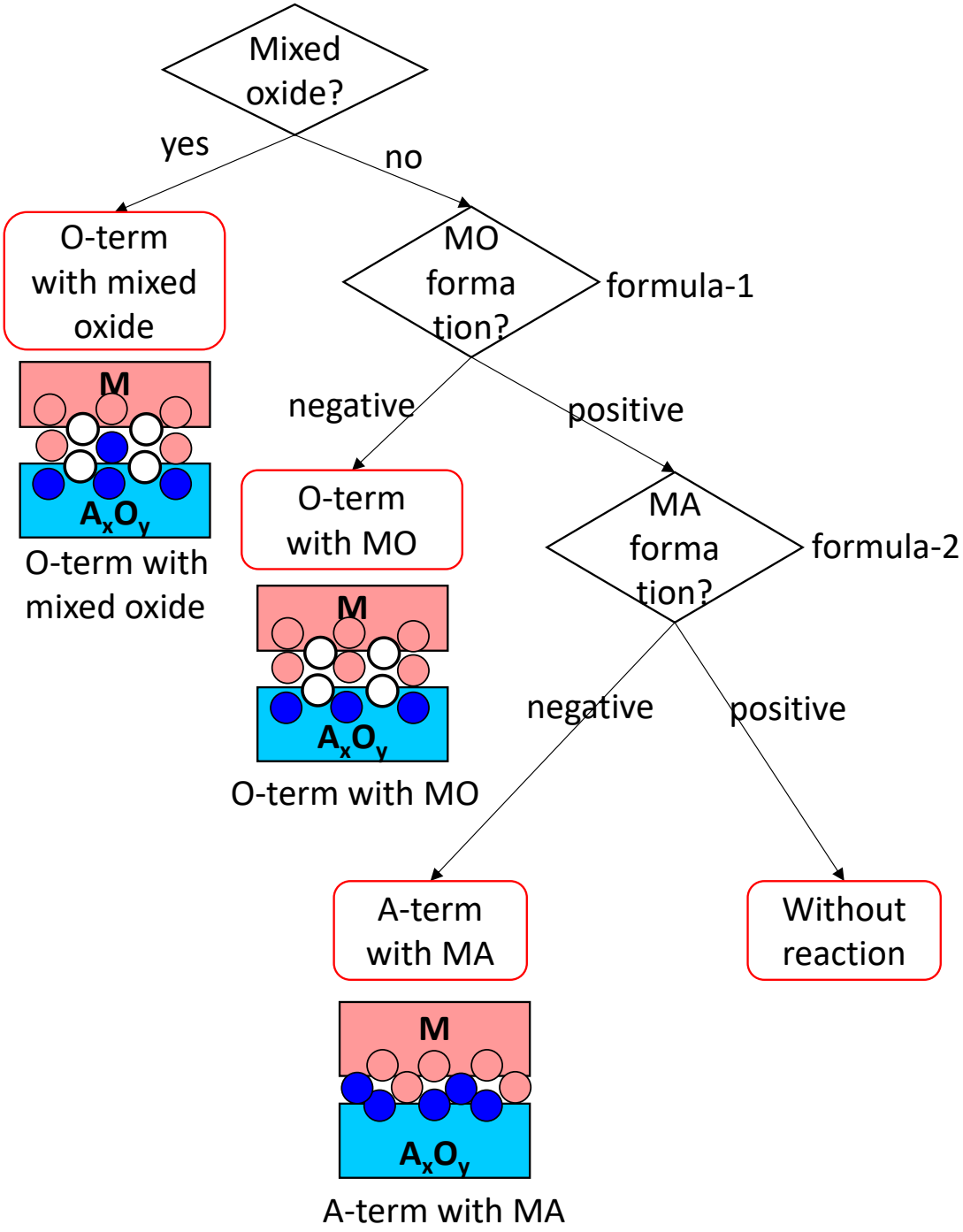


Fig.6 Flowchart of judgement and results representations.