FORMABILITY CRITERIA OF INTERMETALLIC COMPOUNDS CONTAINING TRANSITION METAL SYSTEMS①

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ABSTRACT Semi-empirical formability criteria of the intermetallic compounds in binary alloy systems containing one or two transition elements have been proposed, based on a modified Miedema model and the results of computation by pattern recognition method. The regularities of compound formability between the non-transition elements whose $\Phi^* < 3.8$ with transition elements can be adequately described by $\Delta\Phi^*$ and $\Delta n_{ws}^{1/3}$; when $\Phi^* > 3.8$ the effects of *spd* hybridization on compound formability are enhanced. The regularities of the compound formability between two latter transition elements can be described by $\Delta\Phi^*$ and $\Delta n_{ws}^{1/3}$ only. While the systems containing one or two early transition elements exhibit higher chemical affinity due to *spd* hybridization. These criteria may also be useful for the formability study of ternary intermetallic compounds.

Key words formability criterion intermetallic compound transition element

1 INTRODUCTION

Many intermetallic compounds exhibit outstanding mechanical or physical properties. Therefore, the prediction of new intermetallic compounds is meaningful for new materials exploration. Some achievements have been reported in this field[1, 2]. Miedema proposed to use a diagram plotted by using $\Delta\Phi^*$ and $\Delta n_{ws}^{1/3}$ as coordinates to predict the formability of binary intermetallic compounds[3, 4]. Here $\Delta\Phi^*$ denotes the electronegativity difference and $\Delta n_{ws}^{1/3}$ denotes the difference between $n_{ws}^{1/3}$ parameters (function describing valence electron density of elements). For binary systems without transition elements, a criteria $\eta = |\Delta n_{ws}^{1/3}| - 0.32|\Delta\Phi^*| < 0$ is indeed rather effective for the formability prediction. But the distinction of compound-forming systems from the systems without compound formation would become confused if binary system containing transition elements are included. Miedema considered that the *spd* hybridization between the *d* orbitals of transition elements and the *p* orbitals of non-transition elements is the origin of this confusion, he even proposed an algorithm to estimate the influence of this effect in which each element was assigned a different parameter, but it is too complicated. Besides, the discrepancy of the application of $\Delta n_{ws}^{1/3} - \Delta\Phi^*$ diagram to the binary systems with two transition elements remains unexplained.

The purpose of this work is to find definite criteria of the formability of the binary intermetallic compounds containing one or two transition elements, *i. e.*, the compounds between either one transition element and one non-transition element, or two transition elements.

2 MODEL AND METHOD OF COMPUTATION

According to basic concept of Miedema's model of alloy phases, the charge transfer be-

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tween different kinds of atoms (denoted by $\Delta\phi^*$) is the driving force of intermetallic compound formation. For the alloy system between one transition element and one non-transition element, extra chemical affinity comes from the *spd* hybridization effect. These concepts, however, cannot explain the difference of the alloying behaviors between the binary system consisting of two transition elements and that consisting of two non-transition elements.

In order to further understand the bonding behaviors between the atoms of different transition elements, quantum chemical calculation was performed for TiNi "molecule". It has been found that the occupancy of various orbitals of Ti, Ni atoms and TiNi "molecule" is as follows:

	Ni ("molecule")	Ni (atom)	Ti ("molecule")	Ti (atom)
3*d*	8.49	8.00	2.356	2.00
4*s*	1.47	2.00	0.297	2.00
4*p*	1.10	0	0.272	0

It can be seen that significant electron transfer takes place from Ti atoms (with lower ϕ^*) to Ni atoms (with higher ϕ^*), which agrees with the charge transfer concept in Miedema's model. But the quantum chemical calculation results also indicate that the *spd* hybridization occurs between the 3*d*, 4*s*, 4*p* orbitals of Ti and Ni. For example, some molecular orbitals in TiNi "molecule" are the linear combination of these atomic orbitals:

$$\Psi_6 = 0.968\phi_{\mathrm{Ni},4s} + 0.055\phi_{\mathrm{Ni},4p_z} + 0.184\phi_{\mathrm{Ti},3d_{z^2}} + 0.073\phi_{\mathrm{Ti},4p_z}$$

$$\Psi_8 = -0.046\phi_{\mathrm{Ni},3d_{xz}} + 0.696\phi_{\mathrm{Ni},4p_x} - 0.639\phi_{\mathrm{Ti},3d_{xz}} - 0.054\phi_{\mathrm{Ti},4p_x}$$

$$\Psi_{12} = 0.735\phi_{\mathrm{Ni},4p_x} + 0.780\phi_{\mathrm{Ti},3d_x}$$

$$\Psi_{14} = 0.022\phi_{\mathrm{Ni},3d_{z^2}} + 0.015\phi_{\mathrm{Ti},4p_z} - 0.810\phi_{\mathrm{Ti},4s} - 0.254\phi_{\mathrm{Ni},4p_z}$$

So it is reasonable to consider the *spd* hybridization between atoms of different transition elements as the origin of the discrepancy in the application of $\Delta\phi^* - \Delta n_{ws}^{1/3}$ diagram to the alloy systems consisting two transition elements.

Quantum chemical calculation of AlNi "molecule" indicates that both charge transfer and *spd* hybridization take place. This is in agreement with the concept of Miedema's model.

In order to describe the factors affecting the formability of transition element-containing intermetallic compounds, it is reasonable to select the following set of atomic parameters:

(1) Miedema's original parameters: $\Delta\phi^*$ and $\Delta n_{ws}^{1/3}$;

(2) number of *d* electrons of the atoms of transition elements A and B: D_A and D_B;

(3) number of *p* electrons of the atoms of non-transition elements: P;

(4) ϕ^* of atoms of transition and non-transition elements (describing the energy levels of metallic elements, which is important to the hybridization effect between different atoms).

We will use these atomic parameters or their functions to span certain multi-dimensional space and to find the formability regularities by pattern recognition in this space.

Linear mapping and back-mapping method of pattern recognition are used for computation on 586-type microcomputer.

3 COMPOUND FORMABILITY CRITERION FOR SYSTEMS BETWEEN ONE TRANSITION ELEMENT AND ONE NON-TRANSITION ELEMENT

Fig. 1 illustrates the $\Delta\phi^* - \Delta n_{ws}^{1/3}$ diagram for the formability of binary intermetallic compounds containing one transition element and one non-transition element. It can be seen the discrepancy between these systems is not clear-out in the region with lower $\Delta\phi^*$ and $\Delta n_{ws}^{1/3}$.

By pattern recognition method, it has been found that the separation of the compound-forming systems from the systems without compound formation is very good in a three-dimensional space spanned by f_1, f_2 and f_3, where f_1 is the ϕ^* of non-transition elements, $f_2 = |\Delta n_{ws}^{1/3}| - 0.32|\Delta\phi^*|$, $f_3 = P + D$. The analysis of the distribution in this $f_1 - f_2 - f_3$ space indicates that this space can be conveniently divided into subspace by the plane $f_1 = 3.8$.

Fig. 2 shows the linear mapping of the subspace in which $f_1 < 3.8$ and $f_1 > 3.8$, respectively. The direction of mapping is onto $f_2 - f_3$

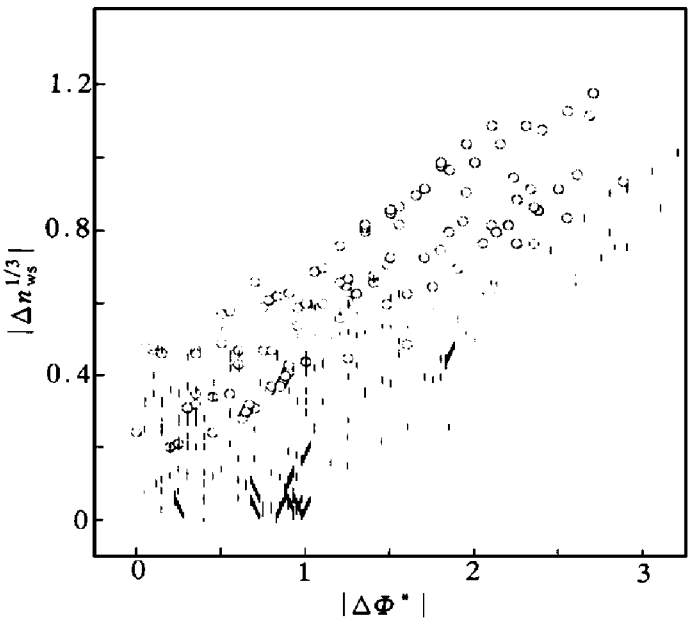

Fig. 1 $\Delta\phi^*$ —$\Delta n_{ws}^{1/3}$ diagram for compound formability in binary systems between transition elements and non-transition elements

| —compound-forming systems;
○—systems without compound formation

plane. Both regularities in Fig. 2(a) and Fig. 2 (b) are very good. It can be concluded that the regularity of the compound formability between non-transition elements whose $\phi^* < 3.8$ with transition elements can be adequately described by $\Delta\phi^*$ and $\Delta n_{ws}^{1/3}$ only (just the same as the regularity of the compound formability between two non-transition elements). This implies that in those cases the ϕ^* values of non-transition elements are too low to induce *spd* hybridization with the *d* orbitals of transition elements.

When the ϕ^* values of non-transition elements are larger than 3.8, the chemical affinity of non-transition elements toward transition elements is greatly increased, as shown in Fig. 2 (b). A reasonable explanation is that in these cases the ϕ^* values of non-transition elements and those of transition elements are close to each other, so the *spd* hybridization and compound formation are enhanced.

Fig. 2 provides the formability criteria of the intermetallic compound between one non-transition element and one transition element.

4 COMPOUND FORMABILITY CRITERION FOR SYSTEMS BETWEEN TWO TRANSITION ELEMENTS

Fig. 3 illustrates the $\Delta\phi^* - \Delta n_{ws}^{1/3}$ diagram for the formability of intermetallic compounds consisting of two transition elements. It can be seen that the regularity is not very clear in the region of lower $\Delta\phi^*$ and $\Delta n_{ws}^{1/3}$.

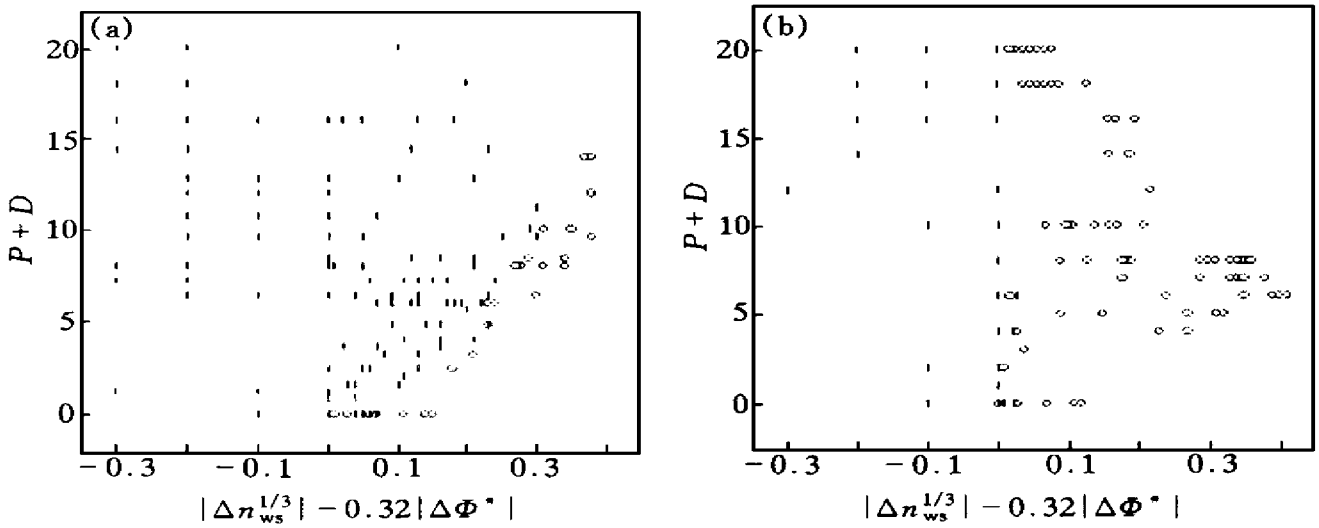

Fig. 2 Intermetallic compound formability of transition elements with non-transition elements

(a) —linear mapping from the subspace $\phi^* \geqslant 3.8$; (b) —linear mapping from the subspace $\phi^* < 3.8$;
| —compound-forming; ○—without compound formation

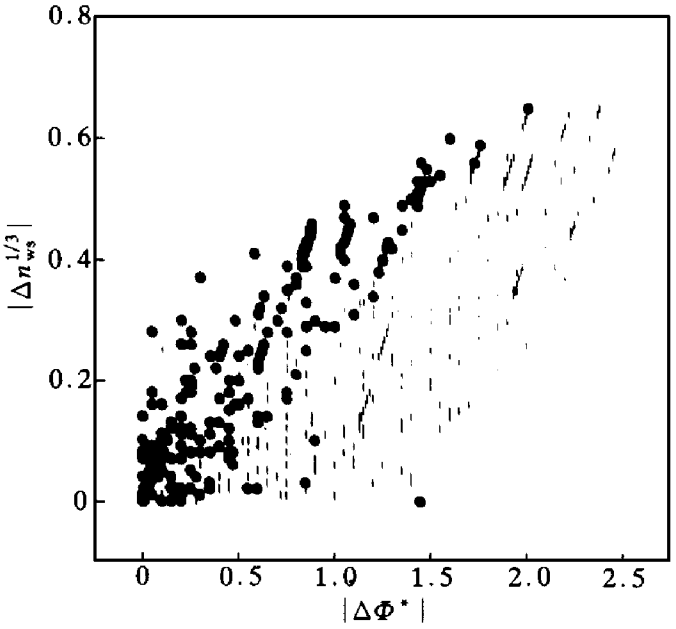

Fig. 3 $\Delta\phi^*$ —$\Delta n_{ws}^{1/3}$ diagram for compound formability in binary systems between transition elements

| —compound-forming systems;
● —systems without compound formation

By pattern recognition, it has been found that the regularity in a multi-dimensional space spanned by D_A, D_B, $|\Delta n_{ws}^{1/3}| - 0.32|\Delta\phi^*|$ and $D_A + D_B$ is very good. And the following subspaces can give very good linear mappings for clear-out separation:

(1) subspace whose $D_A \geqslant 5$ and $D_B < 5$, or $D_B \geqslant 5$ and $D_A < 5$;

(2) subspace whose $D_A \geqslant 5$ and $D_B \geqslant 5$;

(3) subspace whose $D_A < 5$ and $D_B < 5$.

Take the subspace (2) as an example, Fig. 4 illustrates the linear mappings of the three subspaces. The directions of the linear mappings are all onto the place with $D_A + D_B$ and $|\Delta n_{ws}^{1/3}| - 0.32|\Delta\phi^*|$ as coordinates.

It is interesting to note that the compound formability between two latter transition elements can be described by $\Delta\phi^*$ and $\Delta n_{ws}^{1/3}$ only. It means that in those cases the influence of *spd* hybridization is not significant, while the systems containing one or two early transition elements exhibit higher chemical affinity due to *spd* hybridization.

Fig. 4 provide effective criterion for the intermetallic compound formability in binary systems between two transition elements.

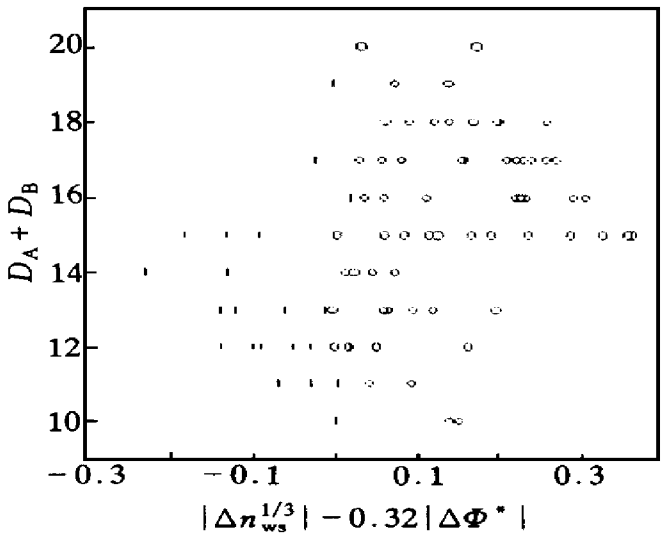

Fig. 4 Intermetallic compound formability of systems with two transition elements

(Linear mapping of subspace $D_A \geqslant 5$, $D_B \geqslant 5$)

| —compound-forming systems;
○ —systems without compound formation

5 PROSPECT

The formability of ternary intermetallic compound is an important but difficult research topic for ternary alloy phase diagram prediction. The criteria of formability for binary intermetallic compounds can be used as a starting point of this research. It is interesting to discuss the relationship between the formability of ternary intermetallic compound $A_xB_yC_z$ and the criteria of compound formability of A-B, A-C and B-C systems. A preliminary statistical study indicates that all known ternary intermetallic compounds $A_xB_yC_z$ correspond to at least two binary systems with compound formation.

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