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CALCULATED MIXING ENTHALPIES OF 11 IIB-IVB AND IIB-VB BINARY ALLOY SYSTEMS USING A SUBREGULAR MODEL

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Abstract

There have been no theoretical calculations of the mixing enthalpies for group B metal alloy systems using the famous Miedema theory or from first principles. Therefore such systematic calculations for the 11 group IIB-IVB and IIB-VB binary alloy systems are performed for the first time using a subregular model. The results show that the agreement between the calculations and experimental data is pretty good and could be accepted from the theoretical or experimental points of view. It can be concluded from the results that the subregular model can be used for calculating the mixing enthalpies of the group B alloy systems, at least for the IIB-IVB and IIB-VB alloy systems.

Keywords: Theoretical calculations of the mixing enthalpies; IIB-IVB and IIB-VB alloy systems; Subregular model.

1. Introduction

The mixing enthalpies (denoted by ΔH for simplicity) of group B metal alloy systems were measured experimentally very early on because the melting points for these alloys

are rather low, and the measurements of their ΔH are not too difficult. For example, Seltz and Dunkerley [1] measured the ΔH of the Bi-Sn system early in 1942. Then a lot of such measurements were performed by the Kleppa group during 1950 to 1960 [2, 3].

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Even today, some authors still measure the ΔH for such alloy systems [4 - 6]. Kopyto et al. measured the thermodynamic properties of liquid Bi-Cu-Sn alloys in 2009 [7]. To date, the ΔH for nearly all of the binary alloy systems combined the group IIB to VB metals have been measured.

There is, however, a lack of theoretical calculations especially systematic calculations of formation enthalpies for such metal systems. In principle, the ab-initio calculations could be used for calculating formation enthalpies of any metal systems, and a rather precise result for such calculation in principle could be obtained. Unfortunately, there are very few such calculations published, and we only found one paper for calculating the formation energies of group B metal alloy systems. Using high-throughput ab-initio calculations Curtarolo et al. [8] explored in 2005 the low-temperature phase diagrams for the Bi-In, Bi-Sb and In-Sb systems, and provided information about their stability at low temperatures from the experimentally observed phases in these systems. Such a situation results from the difficulties of calculating techniques, which are not easy to overcome in such theoretical calculations. And then, some approximations must be introduced in the calculations, the results obtained therefore are not always in agreement with the experimental results. The prediction of formation enthalpy at limited temperature from ab-initio calculations is still in development.

Miedema group has developed a widely used thermodynamic theory for calculating the formation energies of binary transition metal alloy systems [9-11]. Still the binary

alloy systems other than transition metal alloy systems have not been calculated by Miedema model. Our group has calculated some of these alloy systems including the alkaline metal alloys, rare earth-Mg alloys, rare earth-Al alloys, noble metal-Al alloys and rare earth-4d transition metal alloys in recent years [12 - 16]. All of the calculations used Miedema's method and formulas completely, and have proved the method can be used for the calculation of formation energies of those alloy systems.

One of the authors (Zhang Bangwei) and Jesser [17] have proposed a subregular model for calculating the formation energies for ternary alloy systems consisting of combinations of structural metals with all constituents being transition and/or simple metals. The calculations for 12 alloy systems have shown good agreement with experimental data. They therefore concluded that this subregular model is a simple and convenient method for calculating the formation energy of a ternary alloy system.

The problem is whether the subregular model could be used for calculating the mixing energies of group B metal binary alloy systems? 11 binary IIB-IVB and IIB-VB metal alloy systems (Pb-Zn, Bi-Zn, Sn-Zn, Cd-Zn, Pb-Cd, Pb-Sn, Cd-Sn, Bi-Cd, Bi-Sb, Cd-Sb and Zn-Sb) are systematically calculated in this paper.

2. Subregular model

The key of the Miedema theory is the so called "macroscopic atoms" model [9-11]. According to the model, the interactions between i and j atoms in a binary alloy solution are just resulted from the interface

of the dissimilar atoms but not from the interior of them. The heat of mixing in a binary alloy system consists of a negative contribution from the electronegativity difference between the two constituents, which is proportional to $-(\Delta\Phi^*)^2$, and a positive contribution from their difference in electron densities, which is proportional to $(\Delta n^{1/3})^2$. In such a way, Miedema et al. obtained their key equation of the enthalpy of solution of liquid i in liquid j at infinite dilution:

$$\Delta H_{iinj}^0 = \frac{2PV_i^{2/3}}{n_i^{-1/3} + n_j^{-1/3}} \left[-(\Delta\Phi^*)^2 + \frac{Q}{P} (\Delta n^{1/3})^2 - \frac{R}{P} \right] \dots (1)$$

where V , Φ^* , and $n^{1/3}$ are the parameters, P , Q and R are the so-called constants determined by Miedema. P and Q were just determined empirically from the experimental enthalpy data. The R term is connected with hybridization of d-type wave functions with p-type wave functions if transition metals and non-transition metals become nearest neighbors in an alloy, which was determined empirically from experimental enthalpy data also by Miedema. After considering the composition in an alloy of the constituents, Miedema et al. obtained a formula of formation (or mixing) enthalpy of an alloy (equation (2.25) in [11]).

In the subregular model [17], a different equation was used for the formation/mixing enthalpy of an alloy:

$$\Delta H_{iinj} = X_i X_j (X_j \Delta H_{iinj}^0 + X_i \Delta H_{jini}^0) , \quad \dots (2)$$

where X_i and X_j are the atomic compositions of species i and j , respectively. Miedema and coworkers have

calculated the values of ΔH_{iinj}^0 for most of the binary alloy systems. The authors calculated the corresponding values which Miedema et al. have not published. So, it is rather simple for calculating the enthalpies in a binary alloy system.

It should be pointed out that the equation for the formation/mixing enthalpies of an alloy from Miedema model is similar to that of the regular model, and the equation from our model is similar to that of the subregular model. That is why we called our model for calculating ΔH of a binary alloy system as subregular model.

It must be noted that the above energy is just the chemical part resulting from the electron factors of the constituents, as described by one of the authors [18], which is the main contribution to the energy. In addition, the structural contribution to the energy of an alloy, which accounts for the difference between the valences and the crystal structure of the solute and solvent, should also be considered. However, this is expected to have only a minor effect when compared with the elastic energy contribution. Therefore, as a first approximation, this term will not be considered in the present calculations.

The elastic effect is from the difference in atomic size of the constituents. This term has not been considered in the Miedema model. Similar to the Eq. (2), the size-mismatch contribution to the formation enthalpy in a binary alloy system ΔH_{ij}^e is:

$$\Delta H_{ij}^e = X_i X_j (X_j \Delta H_{iinj}^e + X_i \Delta H_{jini}^e) , \quad \dots (3)$$

where ΔH_{iinj}^e is the elastic energy per mole of solute metal. From the classical theory of

elasticity, two formulas were obtained by Friedel [19] and Eshelby [20], which are as follows respectively:

$$(\Delta H_{inj}^e)_F = \frac{24\pi B_i \mu_j R_i R_j (R_i - R_j)^2}{3B_i R_j + 4\mu_j R_i}, \quad \dots(4)$$

and

$$(\Delta H_{inj}^e)_E = \frac{2\mu_j (V_i - V_j)^2}{3V_j + 4\mu_j \kappa_i V_i}, \quad \dots(5)$$

where B_i and κ_i are the bulk modulus and compressibility of the solute respectively, and μ_j is the shear modulus of the solvent. The values of B , μ and κ for elements have been tabulated by Gschneidner [21]. R_i and R_j are the radii for solute and solvent atoms which are represented by using half of the measured interatomic distance of elements [22]. V_i and V_j are the molar volume of solute and solvent atoms which are cited from Ref. [11].

In the subregular model, we use Cal M to indicate the formation/mixing energy only from the calculation of the chemical part, i.e. just from Eq. (2). We use Cal M+F and Cal M+E to express those for the calculations of the chemical part from equation (2) and the elastic energy calculated from Eq. (3) with the Friedel formula (4) and Eshelby Eq. (5) respectively. We will see below that only the elastic energy needs to be considered for the Sn—Zn and Bi—Sn two systems, the other 9 alloy systems just need to consider the term of Cal M.

3. Results

The experimental measured data are quoted from Hultgren et al [Sn—Zn, Cd—Zn, Cd—Sn, Pb—Cd, Zn—Sb, Bi—Zn, Cd

—Sb, Bi—Cd, and Bi—Sb] [23], Bourkba et al [Sn—Zn and Pb—Sn] [24], Tod et al Pb—Zn] [25], Beggerow [Cd—Sn] [26], Bourkba and Hertz [Pb—Sn] [27], and Badawi et al, [Pb—Sn] [28].

3.1. Comparison of the enthalpies for the whole range of composition

Figure 1(a, b) compares the calculations with experimental data for all of the 11 IIB—IVB and IIB—VB group metal systems. From Fig.1(a, b), one can see the following features.

The agreement between calculations and measured data is very good for the six alloy systems of Pb—Sn, Bi—Cd, Bi—Zn, Pb—Zn, Bi—Sb and Cd—Sb. Considering the experimental scatter of calorimetric measurements, one can say that such agreement is near perfect for these six alloy systems. The subregular model is a very simple approach to theoretical calculation for ΔH , which just needs to use the parameters of the elemental metals, but a very good result can be obtained from it, which indicates that this theoretical approach catches the key for calculating the enthalpies of an alloy system.

For three other alloy systems (Zn—Sb, Pb—Cd and Cd—Zn), the agreement from Cal M is not so very good, but still rather good or reasonable. In other words, the calculated results can be accepted.

Only for the two alloy systems of Sn—Zn and Cd—Sn, the errors of the Cal M from the experimental data are rather large. When considering the elastic term, Cal M+F (for the Sn—Zn alloy system) or Cal M+E (for the Cd—Sn alloy system) can improve the

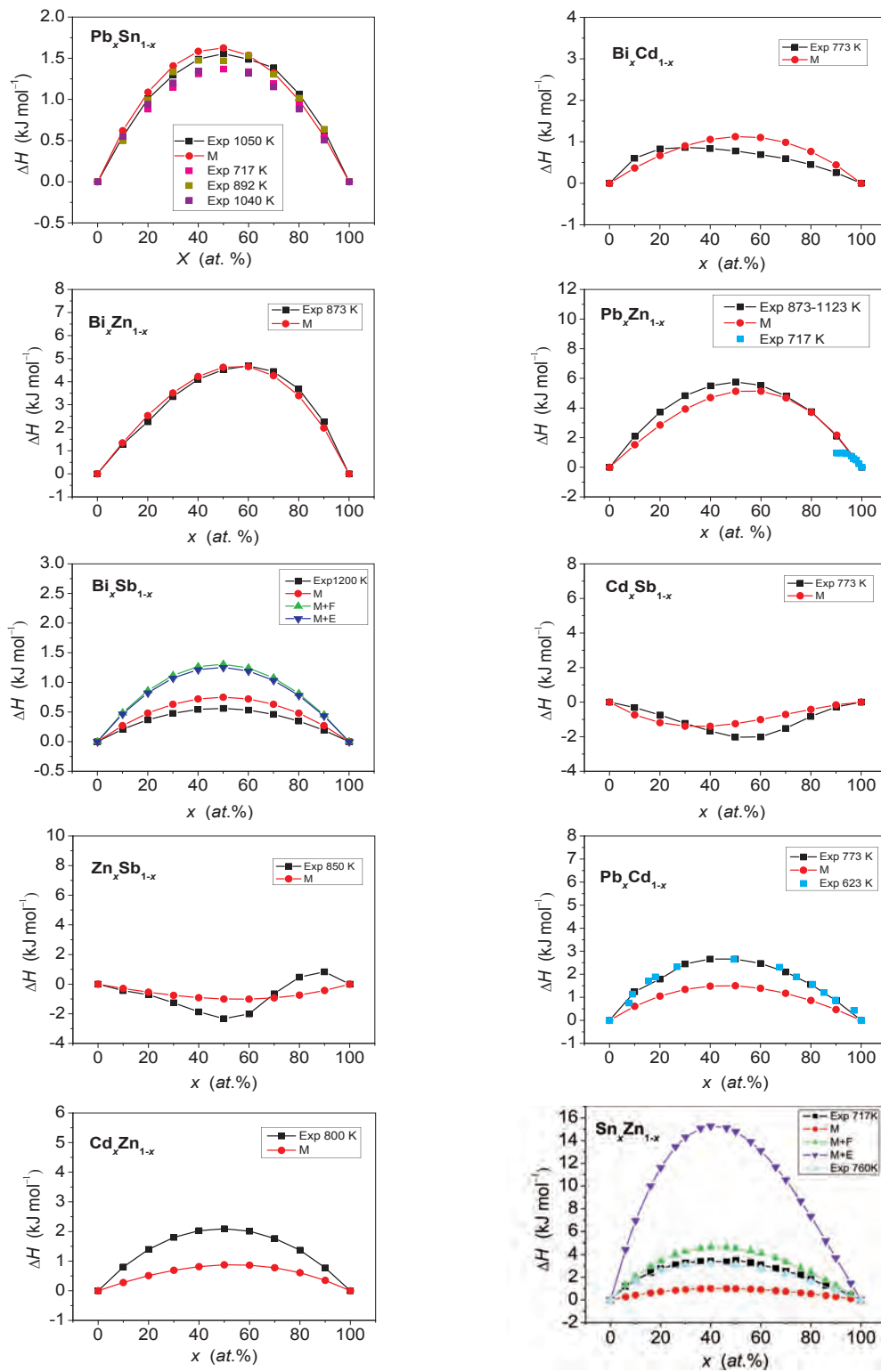


Figure 1a. The calculations of mixing enthalpies compare to the experimental data for 10 binary IIB–IVB and IIB–VB alloy systems. The citations for the experimental data indicated in the text.

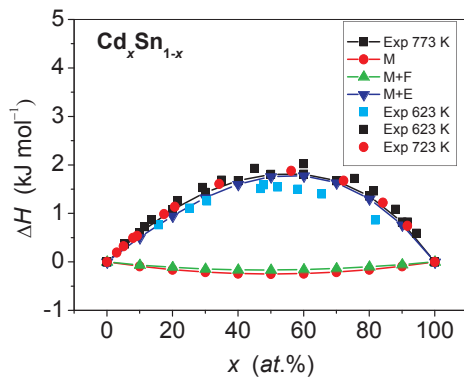


Figure 1b. The calculations of mixing enthalpies compare to the experimental data for the last one binary alloy systems.

agreement, and the agreements for these two alloy systems become very good, which can be seen obviously from the last figures in Fig. 1a. and Fig 1b. In other words, for these two alloy systems, Cal M can't calculate precisely their mixing enthalpies, but the elastic energies must be considered.

In the plot of the Bi–Sb alloy system in Fig. 1a, the two curves for the Cal M+F and Cal M+E are also indicated. This just shows that the error will be increased when the elastic term is also considered, so we only need to use the Cal M term. Such a situation

is the same for all of the nine alloy systems except the last two systems of Sn–Zn and Cd–Sn as mentioned above. This is similar to the formation enthalpies calculated by the subregular model for various ternary alloy systems [17].

3.2. Calculation errors

In general, there are some errors between the calculated results and experimental data. We have calculated them. $|\overline{\Delta H_{\text{Exp}}}|$, and $|\overline{\Delta H_{\text{M}}}|$ represent the average values of experimental data and of calculation results for all of the alloys of an alloy system respectively. The ratio of average error between calculations and measured data $|\overline{\Delta H_{\text{Exp}}} - \overline{\Delta H_{\text{M}}}| / |\overline{\Delta H_{\text{Exp}}}|$ for all of the alloys of every alloy system can be obtained. The results are shown in the Table 1. It can be seen that the ratio of average error is less than 12 % for 4 alloy systems (Cd–Sn, Bi–Zn, Pb–Sn and Pb–Zn). The ratios are from 30 % to 47.6 % for all of the other 7 systems. The maximum mixing enthalpy and size factor for every alloy system also show in the Table.

Table 1. Maximum mixing enthalpy, size factor and average errors of the present calculations for the 11 binary IIB–IVB and IIB–VB alloy systems, in kJ/mol.

Alloy system	Maximum enthalpy	Size factor, %	$ \overline{\Delta H_{\text{Exp}}} $	$ \overline{\Delta H_{\text{Exp}}} - \overline{\Delta H_{\text{M}}} $	$ \overline{\Delta H_{\text{Exp}}} - \overline{\Delta H_{\text{M}}} / \overline{\Delta H_{\text{Exp}}} , \%$
Pb–Zn	5.136	25.64	4.232	0.4898	11.57
Bi–Zn	4.69	12.33	3.3978	0.1817	5.35
Sn–Zn	3.496	12.33	2.5916	0.7732	30.07
Cd–Zn	2.903	10.38	1.5602	0.5856	37.5
Pb–Cd	2.659	14.07	1.966	0.8771	44.61
Pb–Sn	1.557	12.1	1.1622	0.0766	6.59
Cd–Sn	1.089	1.95	1.3614	0.0708	5.2
Bi–Cd	0.863	1.95	0.659	0.2554	38.7
Bi–Sb	0.561	6.7	0.41	0.1397	34
Cd–Sb	–2.026	4.7	1.1808	0.4912	41.6
Zn–Sb	–2.332	5.7	1.175	0.559	47.57

The definition of the size factor for an alloy system is, $\frac{|R_i - R_j|}{\frac{1}{2}(R_i + R_j)}$ where R_i and R_j are the radii for solute and solvent atoms, which are represented by using half of the measured interatomic distance of elements [22].

4. Discussion

If the calculated results versus the experimental values of the mixing enthalpies for the 11 IIB—IVB and IIB—VB binary alloy systems are plotted onto one figure, then the errors are illustrated very clear, as shown in Fig. 2. The fine linear line $y = x$ represents exact (100 %) agreement between the calculations and measured data, and the two outer thick lines indicate the defined data zone, with an error range of ± 1.0 kJ/mol-. It can be seen that all of the data are located within in the area with few data points located very close to the border. Comparing a similar figure (Fig. 2.31 in Ref.

[11]) for the formation enthalpies for compounds of a transition metal and a polyvalent non—transition metal made by Miedema et al. themselves, it is easy to find that the present calculations of mixing enthalpies compared to the experimental data for the 11 IIB—IVB and IIB—VB binary alloy systems are somewhat superior to those from Miedema's original model. In particular, the scatter in the Fig. 2 in Ref. [29] for the formation enthalpies of the 260 intermetallic compounds calculated by Zhang et al. using original Miedema model is larger than that in the present Fig. 2. Therefore, we may say that the present calculations are somewhat superior to those for all transition metals calculated by the original Miedema model.

From the calculated values of the size factor for 11 alloy systems are shown in Table 1, it can be seen that the general trend of size factor with mixing enthalpy is similar, i.e. the size factor is large, the value of the maximum enthalpy is large too. However,

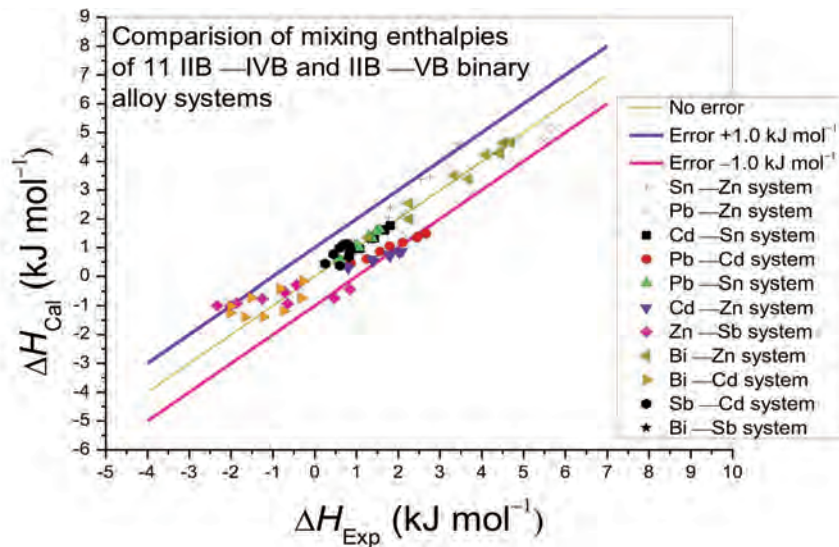


Figure 2. Comparison of mixing enthalpies of ΔH_{cal} and ΔH_{Exp} for 11 IIB—IVB and IIB—VB binary alloy systems. The citations for the experimental data indicated in the text.

there are some obvious exceptions, e.g. the Pb—Cd, Pb—Sn and Bi—Cd system are very clearly out of order. So, we may have the conclusion that the size factor is not the deciding factor for the magnitude of ΔH for the IIB—IVB and IIB—VB alloy systems.

The mixing enthalpies for 9 of the 11 alloy systems are positive, but those for the other two alloy systems of Cd—Sb and Zn—Sb are negative. What does this mean? Or how do we understand the sign of the mixing enthalpy for an alloy system? The formation enthalpy of an alloy system depends on the interaction between atoms of constituents. The positive mixing enthalpy means the reaction is endothermic during mixing a solution from constituents, indicating the instability of the alloy with respect to phase separation into its constituents. This situation occurs when the interaction between like atoms in the system is strong, but one between unlike atoms is rather weak. In contrast, the negative mixing enthalpy indicates the reaction is exothermic during mixing a solution from constituents, and the alloy/solution becomes stability with respect to phase separation into its constituents. From the view point of alloy phase diagram, the former case indicates that miscibility gaps usually form in such systems, or belongs to the so-called a pure eutectic type of phase diagram (type I phase diagram hereafter). And for the latter case, at least one intermediate compound should be formed in the alloy phase diagram (type II phase diagram hereafter).

All of the phase diagrams for 8 alloy systems exhibiting significant positive mixing enthalpies either have miscibility gaps in the liquid phase or form pure eutectic

phase diagrams, and the two phase diagrams of Cd—Sb and Zn—Sb systems with negative mixing enthalpies have more than one intermetallic compound. The only exception is the alloy system of Cd—Sn, its enthalpy is positive, but its phase diagram forms an intermediate phase, belonging to type II. Such an example can also be found in alloy systems other than the IIB—IVB and IIB—VB systems. For example, Cu—Ni has a positive ΔH but is not eutectic and has no miscibility gap in the liquid phase. This exception obviously tells us that the sign of enthalpies does not depend completely on the type of phase diagrams, in other words, they do not exactly correspond though they are closely related. The exact appearance of the phase diagram is not solely determined by ΔH but also from the entropy of mixing, ΔS . Figure 3 shows such relationship between the mixing enthalpies and the alloy phase diagrams for the 11 binary IIB—IVB and IIB—VB metal alloy systems. The solid line indicates that the alloy phase diagram of an alloy system formed by the two metals connected with the line is type I. And the dash line just indicates the type II phase diagram. The numbers on the lines are the maximum mixing enthalpies of the alloy systems of the two metals connected by the line, in kJ/mol. The information on phase diagrams has been taken from Ref. [30]. We can see from Fig. 3 that there is only one exception of the Cd-Sn alloy system, its ΔH is positive but its phase diagrams is belonging to type II.

Some authors discussed the relationship between the sign of the formation enthalpy and the phase diagram for an alloy system. For example, Vassilev [31] discussed very

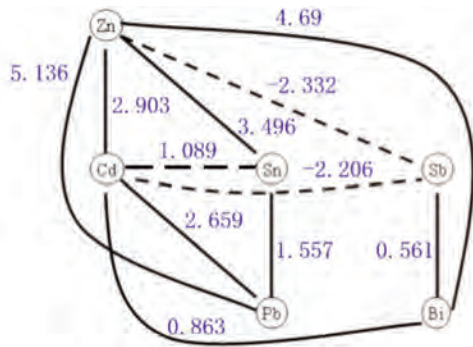


Figure 3, Relationship between the ΔH and alloy phase diagrams for the binary IIB-IVB and IIB-VB metal alloy systems. The numbers on the lines are the maximum mixing enthalpy of the respective alloys, in kJ/mol. The explanation see the text.

recently the enthalpies of alloy systems for Bi, Sn, Zn, In and elements of IVth and Vth periods with the phase diagrams and size factors of the alloy systems. He found as a rule (with some exceptions) miscibility gaps form in systems exhibiting significant positive enthalpies of mixing (assessed by means of the Miedema method). Also, he found as a general trend for such alloy systems that existing intermediate

compounds are observed in systems having negative Miedema enthalpies of mixing. These points of view are similar to our above analysis.

As is well known, the first goal of the Miedema theory was used for analyzing the sign of predicted and experimental enthalpies of formation for liquid alloys at the equiatomic composition in binary systems involving two metals with pronounced p character in the wave functions of their conduction electrons. Using the values of Φ^* and $n^{1/3}$, they really obtained a good separation between the positive and negative mixing enthalpies for such alloy systems with a very few exceptions by drawing a straight line in the Fig. 2.5 in Ref. [11]. However, they only used the experimental enthalpies from Heltgren et al. [23], and some data of mixing enthalpies have not yet been included in the book for the 11 IIB-IVB and IIB-VB binary alloy systems. So, we draw a similar figure for the 11 B-group metal alloy systems, as shown in Fig. 4. It can be seen

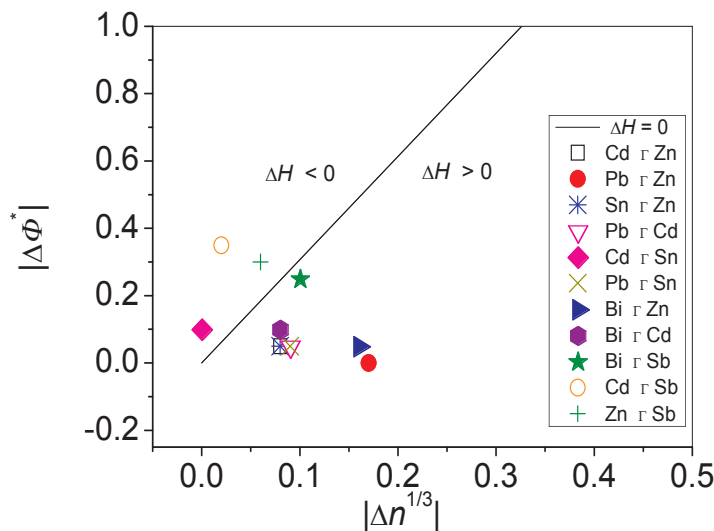


Figure 4, Separation of the sign of ΔH for the 11 IIB-IVB and IIB-VB binary alloy systems.

that except for the alloy system of Cd—Sn located in the “wrong” area ($\Delta H < 0$ area), all of the points of data for the 10 alloy systems are located in their “correct” areas. The alloy system of Cd—Sn is in the area of $\Delta H < 0$ just because its enthalpies are positive, which shows that the plot drawn by the two Miedema coordinates of $\Delta\Phi^*$ and $\Delta n^{1/3}$ cannot separate the signs of ΔH for the IIB—IVB and IIB—VB alloy systems exactly.

5. Conclusion

Using a subregular model which is different and rather simple compared to the original Miedema formula of formation enthalpy, the mixing enthalpies of 11 IIB—IVB and IIB—VB binary alloy systems have been calculated, which have not previously been calculated systematically either by Miedema model or by theoretical methods from the first principle.

The agreements between the calculations and experimental data of mixing enthalpies for the 11 IIB—IVB and IIB—VB binary alloy systems are very good or reasonable. The subregular model therefore can be used to calculate the mixing enthalpies for alloy systems of group B metals, at least for the IIB—IVB and IIB—VB binary alloy systems.

Analyzing the results for the IIB—IVB and IIB—VB binary alloy systems has shown that the signs of enthalpies are closely related to the type of phase diagrams, though such relationship is not exact. The sign of enthalpy of an alloy system is decided by the interactions between the atoms in the alloy system. Usually, when the interactions between similar atoms in an alloy system are

rather strong, its phase diagram would have miscibility gaps in liquid phase or be a pure eutectic type. The mixing enthalpies would be positive. Otherwise, when the interactions between dissimilar atoms in an alloy system are strong, its phase diagram would have intermediate phase(s), and negative enthalpy occurs.

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