Model Equations for Solid Solubilities in Binary Non-Transition Metal Based Alloys

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Both parabola and ellipse separating schemes are used to study the solid solubilities for the binary alloy systems based on the 18 simple metals. It has been found that the soluble elements can be separated from the insoluble ones by a parabola $y_1 = a - bx_1^2$ or an ellipse $(x_2 - m)^2/c^2 + (y_2 - n)^2/d^2 = 1$. The results show that the overall reliabilities of the solid solubilities for the 1242 binary alloys based on the simple metals are 86.4 and 89% for the parabola and ellipse regularities, respectively. The constants m , n , c and d in the ellipse equation are discussed, which can be related to some appropriate parameters for each host metal respectively.

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I. Introduction

Studying the solid solubility of binary alloy elapsed more than 60 years, but there are still unresolved problems. In the thirties, Hume-Rothery⁽¹⁾ proposed the first rule for the solid solubility. In his theory, 15% radius of host metal was used to separate the soluble elements from the insoluble elements. In the fifties, Darken and Gurry⁽²⁾ proposed the D-G graphical method to study the solid solubility. They draw an ellipse to separate the soluble region from the insoluble region. Up to the seventies, Chelikowsky⁽³⁾ proposed a new graphical method based on the pure Miedema's⁽⁴⁾ coordinates. He used this method to study the binary alloy solid solubility on 7 divalent metals. Also in Chelikowsky's method, the ellipse was used to separate the soluble region from the insoluble ones. After that, in eighties, Alonso *et al.*⁽⁵⁾⁽⁶⁾ proposed a theory to add a size factor to Chelikowsky's theory to study the solid solubility. In their theory, the first, two straight lines were used to separate the soluble elements from the insoluble ones. The second, an ellipse curve that was used commonly by other authors in the literature was used to separate the soluble elements from the insoluble ones. All these ellipses used by the above authors were not defined and the reliabilities were not very high.

From the eighties we used the bond parametric functions proposed by Chen⁽⁷⁾ and the size factor to study the solid solubility. The first, we used the bond parametric function and the size factor to study the forming ability of amorphous alloys⁽⁸⁾ and the reliability was very good. As we pointed out⁽⁸⁾, the formation of both amorphous alloys and solid solutions is affected by several factors, which, however, operate in an opposite direction. There-

fore the solid solubility of binary alloys can also be predicted by the same method using the parametric function and size factor for describing the formation of amorphous alloys⁽⁹⁾.

A further study for the solid solubilities of binary non-transition metal based alloys has been performed in this paper with the bond parametric function and size factor. The aims are that if the parabola equation is not changed when the solid solubilities for every host metal increase from 60⁽⁹⁾ to 69, especially, if the ellipse equation can be defined completely and the parameters m , n , c and d of the equation can be given, and if the overall reliabilities comparing the experimental data are still very high, i.e. approaching 90%.

II. Models

Two schemes have been used to describe the solid solubilities: one is the parabola regularity⁽⁹⁾⁻⁽¹¹⁾ and another is the ellipse regularity⁽¹⁰⁾⁻⁽¹³⁾. The difference between the two methods stems from the different representations for the electron and the size factors.

In the parabola regularity scheme, the differences between the size factors and between the electron factors for the host and solute elements are as follows:

$$x_1 = \left| \frac{R_0 - R_i}{R_0} \right| \quad (1)$$

$$y_1 = \left| \left(\frac{z}{r_k} \right)_B \left[x_{PA} - \frac{1}{3} \left(\left(\frac{z}{r_{cov}} \right)_A + 2 \right) \right] (x_{PA} - x_{PB}) \right| \quad (2)$$

where z/r_k and z/r_{cov} are the ratios of atomic valence and atomic kernel radius, and of atomic valence and covalent radius, respectively⁽⁷⁾⁽⁸⁾. The kernel radius equals approximately the positive ionic radius not including the valence

Li	Be											B		C							
Na	Mg													Al	Si	P	S				
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se						
Rb	Sr	Y	Zr	Nb	Mo		Ru	Rh	Pd	Ag	Cd	In	Sn	Sb							
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi							
			Ce	Pr*	Nd*		Sm*	Eu*	Gd*	Tb*	Dy*	Ho*	Er*	Yb	Lu*						
			Th		U		Pu*

Fig. 1 The plot of solid solubilities for the parabola regularity for the alloys based on the Mg metal. +: insoluble elements, ●: soluble elements, ■: host.

Fig. 2 The plot of solid solubilities for the parabola regularity for the alloys based on the Cd metal. +: insoluble elements, ●: soluble elements, ■: host.

Table 2 Theoretical results of parabola and ellipse regularities for the solid solubilities of binary alloys based on the 18 simple metals.

Regularity	Soluble solutes			Insoluble solutes			Summary		
	Total	Correct	Reliability, %	Total	Correct	Reliability, %	Total	Correct	Reliability, %
Parabola	162	141	87	1080	932	86.3	1242	1073	86.4
Ellipse	162	139	85.8	1080	968	89.6	1242	1107	89.1

correct, the reliability can be calculated. Table 2 shows the calculated results. It can be seen that the reliabilities for the soluble and insoluble elements are 87 and 86.3%, respectively. The overall reliability for the solid solubilities of binary alloys based on the 18 non-transition metals, therefore, is 86.4%. This result is comparable to that for the 2460 binary alloys based on the 23 transition, 13 rare-earth and 3 actinide metals with the same scheme⁽⁹⁾⁻⁽¹¹⁾, and is in good agreement with the experimental data.

2. Ellipse regularity

In Fig. 3 a plot of the electron factor y_2 versus size factor x_2 is shown for most of the elements in the period table, in which each point of coordinates corresponds to individual element. With the experimental data of solid solubilities, another kind of plots of solid solubilities for the alloys based on the 18 simple metals can be obtained. As the same as in Section III.1 we have found from the plots that the soluble elements are located close to the host metal, and the insoluble ones are located away from it for every host metal. The soluble region can be separat-

ed obviously from the insoluble one also. Similarly, the best dividing line can be defined with the least-squares fitting procedure. Now it is an ellipse curve for every host element. The interior of the ellipse is the soluble region, and the outside is the insoluble region. All of the ellipse are similar shapes, i.e., the major axis runs parallel to the y axis and minor axis runs parallel to the x axis though the size of them are dependent on the host metals. Figures 4 and 5 show the typical plots of solid solubilities. The equation of the ellipse is given by

$$\frac{(x_2 - m)^2}{c^2} + \frac{(y_2 - n)^2}{d^2} = 1 \quad (6)$$

where x_2 and y_2 are the electron, size factors for each host metal respectively, which represent in eqs. (3) and (4). m , n , c and d are constants, which are shown in Table 3.

The reliability of the ellipse regularity for the solid solubilities of alloys based the 18 non-transition host metals can be calculated. The results are shown in Table 2 too. The results show that the reliabilities for the soluble and insoluble elements are 85.8 and 89.6%, and the overall reliability is 89%, which is comparable to that for the 2691

Fig. 3 The plot of the electron factor y_2 vs size factor x_2 for most of the elements in the period table.

Fig. 5 The plot of solid solubilities for the ellipse regularity for the alloys based on the Bi metal. +: insoluble elements, •: soluble elements, ■: host.

Fig. 4 The plot of solid solubilities for the ellipse regularity for the alloys based on the Ag metal. +: insoluble elements, •: soluble elements, ■: host.

alloys based on the 23 transition, 13 rare earth and 3 actinide host metals with the same scheme^{(9)–(12)}. This result is in excellent accord with the experimental data.

IV. Discussion

1. Constants a and b

How to explain and understand the constants in the equations for the regularities is very important. According to the same analyzing procedures as in Refs. (9)–(11), it has been found that the a and b in the parabola eq. (5) are related to the cohesion energy $E^{(26)}$ and the parameter EmR_0^3 for every pure host metal respectively. μ is the shear modules of the host metal⁽²⁷⁾ and R_0 is the atomic radius⁽¹⁵⁾. From the results of Figs. 6–8 in Ref. (9), we do have such kinds of correspondences for every host metal.

2. Constants m , n , c and d

First, the constants m and n are discussed. m and n are the coordinates of the center point for the ellipse. Generally speaking, the coordinate point for each host metal is not far from the center of the ellipse. From this we believe that m and n should be dependent on the coor-

Table 3 Parameter m , n , c , and d of ellipse equation for 18 simple metals.

	Li	Be	Mg	Al	Ca	Cu	Zn	Sr	Ag	Cd	In	Sn	Sb	Ba	Au	Tl	Pb	Bi
m	1.50	1.15	1.54	1.49	2.05	1.36	1.38	2.05	1.45	1.56	1.78	1.41	1.38	2.00	1.48	1.50	1.52	1.45
n	0.00	2.05	1.05	1.20	0.30	3.50	2.20	0.15	1.65	2.10	2.30	2.05	2.35	0.10	3.50	1.75	2.00	2.20
c	0.50	0.15	0.30	0.16	0.25	0.26	0.15	0.30	0.35	0.36	0.38	0.21	0.22	0.20	0.35	0.36	0.28	0.15
d	0.40	2.00	1.35	0.50	0.30	4.10	2.00	0.40	2.05	1.10	1.30	1.65	1.35	0.50	3.50	1.75	2.00	2.10

Fig. 6 Correspondences between constant m and R_0 for the 18 simple host metals.

Fig. 8 Correspondences between constant d and E for the 18 simple host metals.

Fig. 7 Correspondences between constant n and y_2 for the 18 simple host metals.

Fig. 9 Correspondences between constant c and $(\mu R_0^3)^{-1/2}$ for the 18 simple host metals.

dinates, i.e. the size and electron factors of the host elements,

$$m \propto R_0 \quad (7)$$

$$n \propto y_2. \quad (8)$$

From the results shown in Figs. 6 and 7 the values of m and n for the 18 simple elements do depend on the values of R_0 and y_2 for every host metal in a broad manner, respectively.

To elucidate the meaning of c and d clearly, let m and n equal zero, the ellipse equation then becomes

$$\frac{x^2}{c^2} + \frac{y^2}{d^2} = 1. \quad (9)$$

It can be seen from the equation that d is the major axis of the ellipse. Its physical meaning is the maximum tolerant electron factor difference between the solute and solvent elements for the soluble region when the size factor

difference between them is zero. From the view point of alloying effect for an alloy system, it means that the total energy of the alloy system only comes from the energy caused by the electron factor difference between the two constituents while the elastic distortion energy caused by the size factor difference is zero. It is easy to imagine that the energy caused by the electron factor difference must be dependent on the cohesive energy E of a host element. Therefore,

$$d \propto E. \quad (10)$$

From the results shown in Fig. 8, the values of d for the 18 simple elements are really related to E of every host metal.

c is the minor axis of the ellipse, which indicates that c is equivalent to the maximum tolerant size factor difference between the solute and solvent elements for the soluble region when the electron factor difference is zero. Now it means that the total energy of the alloy system

only comes from the energy caused by the size factor difference while the energy caused by the electron factor difference is zero. The solid solubility for this alloy system would be very small when the size factor difference is greater than this maximum tolerant size factor difference. In this case we have derived a formula, eq. (4) in Ref. (9), i.e. the maximum tolerate size factor difference Δx is

$$\Delta x \propto (\mu R_0^3)^{-1/2} \quad (11)$$

where μ is the shear modules of the host metal, R_0 is its atomic radius. Therefore, c can be given by

$$c \propto (\mu R_0^3)^{-(1/2)} \quad (12)$$

From the results shown in Fig. 9, really, such kind of correspondence between c and $(\mu R_0^3)^{-(1/2)}$ for all of the 18 simple elements can be found.

3. Adaptability of the Chelikowsky's assumption

As mentioned in Section II, Chelikowsky has assumed that the solute is assigned to be of the insoluble class if there are no experimental data as well as no phase diagram. In this case, our results for the ellipse regularity show that the overall reliability is 86.8% when the solute elements having experimental data and phase diagram are only considered, and is 95.3% when the solute elements having no experimental data and no phase diagrams take into account, for the parabola regularity, these values are 85.7 and 88.2%, respectively. The error are 8.5 and 2.5% respectively steamed from the assumption for the two regularity, which are not large to the total reliability and are reasonable. We have therefore proved once more for the 18 simple host metals that this assumption can be adapted.

V. Conclusions

The systematic studies of the solid solubilities for simple host metals have not been yet carried out in the literature up to date. Such kind of research has performed successfully with the schemes incorporating the bond parametric function and size factor in 1242 binary alloys based on the 18 non-transition host metals.

Not only a parabola but an ellipse equation for separating the soluble region from the insoluble region in the plots of solid solubilities have been obtained with somewhat different parameters acting as abscissa and ordinate, respectively, to construct the plots. The overall reliabilities of the parabola and ellipse regularities are 86.4 and 89%, which indicate that the schemes are very effective for predicting the solid solubilities of alloys for the 18 host metals.

The constants a and b in the parabola equation and m , n , c and d in the ellipse equation can be defined with the appropriate parameters for the pure host metals.

The assumption that the solute is assigned to be of the insoluble class if there are no experimental data as well as no phase diagram has been proved once more for the 18 simple host metals.

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