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Comparison between methods for predicting maximum solid solubility of transition metals in solvent metal①

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Abstract: It is important to know the maximum solid solubility(C_{max}) of various transition metals in a metal when one designs multi-component alloys. There have been several semi-empirical approaches to qualitatively predict the C_{max}, such as Darken-Gurry(D-G) theorem, Miedema-Chelikowsky(M-C) theorem, electron concentration rule and the bond-parameter rule. However, they are not particularly valid for the prediction of C_{max}. It was developed on the basis of energetics of alloys as a new method to predict C_{max} of different transition metals in metal Ti, which can be described as a semi-empirical equation using the atomic parameters, i.e, electronegativity difference, atomic diameter and electron concentration. It shows that the present method can be used to explain and deduce D-G theorem, M-C theorem and electron concentration rule.

Key words: maximum solid solubility; function Z_f; prediction method; electronegativity difference; atomic size factor; electron concentration

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1 INTRODUCTION

The prediction of solid solubility of an alloy is a suspending but an important question. There are many microcosmic theories and good reviews published elucidating the effects of electronegativity, atomic diameter and electron concentration on the solid solubility, respectively[1, 2]. However, they are difficult to predict solid solubility though they can explain some experimental rules. Darken and Gurry[3, 4] proposed a theorem considering both atomic size and electronegativity, which greatly improved the Hume-Rothery's work (D-G ellipse theorem for short). Miedema-Chelikowsky[5] calculated the value of solid solubility by a dimensional chart with work function (Φ^*) and electron concentration($n^{1/3}$) at the boundary of Wigner-Seitz atomic cells(M-C ellipse theorem for short). ZHANG et al[6] suggested a solid solubility theory of binary transition metal alloys by establishing an ellipse equation or a parabola equation through bond parameter function and size factor. LI[7] gave the electron concentration rule when explaining the segregation of Ti_3X phase in Ti alloys. All the predictive methods mentioned above have the same two steps. At first a concentration criterion is defined by which a solute in the solvent can be determined as soluble or insoluble. Then the boundary line is determined to divide solute into soluble or insoluble and to look for the mathematical rules between the atomic parameters for solute and the solvent about the boundary line. Although it is successful in analyzing the C_{max} of some alloy systems, there are still three issues to be solved: 1) the predictive models don't reflect the effect of the concentration criterion dividing soluble or insoluble; 2) it is needed to use different fit equations according to different structural parameters for different alloy system; 3) all methods cannot calculate the value of solid solubility.

Based on the energy change in the formation of an alloy, a mathematical model was once proposed by the authors to calculate C_{max} by atomic diameter, electronegativity and electron concentration, which is successful to analyze and predict the C_{max} of transition metals in Ti, Pd, Zr and Hf[8, 9]. In this paper, it is our aim to discuss the question of the prediction using our model by taking the example of C_{max} of transition metals in Ti metal, and to elucidate the intrinsic relation among the predicting methods mentioned above.

2 MATHEMATICAL MODEL OF C_{max} AND Z_f FUNCTION

On the basis of energetics of alloys, the C_{max} can be calculated by the following equation when the solute elements solve in a certain solvent[9, 10]:

$$\ln C_{max} = a_0 + a_1 \Delta X^2 + a_2 \delta^2 + a_3 n^{2/3} \quad (1)$$

where $\Delta X = X_0 - X$, means the electronegativity difference between solute and solvent element (sub-

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script 0 means solvent, and it has the same meaning in D_0 and n_0 below); $\delta(=1-D/D_0)$ is the atomic size difference percentage between solute and solvent element. $n=(n_0+n_1)/2$ is average out-layer electrons of solute and solvent element.

For simply writing, a function[11] was defined reflecting the change of the structural parameters between the solvent and the solutes when alloys formed.

$$Z_f=a_0+a_1\Delta X^2+a_2\delta^2+a_3n^{2/3} \quad (2)$$

From Eqns. (1) and (2), one can get as follows:

$$\ln C_{max}=Z_f \quad (3)$$

The C_{max} data in this paper were read from equilibrium phase diagram to obtain the coefficient of the equation[12]. The data which the method is read is as the same as that in Ref. [11].

3 RESULTS AND DISCUSSION

3.1 Control factors of C_{max} of transition metals in Ti element

C_{max} of transition metals in Ti can be calculated from the data listed in Table 1 by a regression analysis

Table 1 Data of C_{max}, difference electronegativity ΔX, atomic size parameter δ and electron concentration n for solvent Ti[1, 11]

Solvent	$(\Delta X)^2$	δ^2	$n^{2/3}$	C_{max}
Sc	0.04	0.008 49	2.305 2	100
Ti	0	0	2.519 8	100
V	0.01	0.005 14	2.725 7	100
Cr	0.01	0.0168 2	2.924	100*
Mn	0	0.011 19	3.115 8	30*
Fe	0.09	0.017 72	3.301 9	22
Co	0.09	0.019 58	3.482 9	14.5
Ni	0.09	0.023 59	3.659 3	11
Y	0.09	0.057 08	2.305 2	0.5
Zr	0.01	0.008 49	2.519 8	100
Nb	0.01	1.20E-05	2.725 7	100
Mo	0.09	0.001 97	2.924	100
Tc	0.16	0.005 14	3.115 8	*
Ru	0.49	0.007 28	3.301 9	25
Rh	0.49	0.007 28	3.482 9	25
Pd	0.49	0.004 21	3.659 3	31
La	0.16	0.076 42	2.305 2	1
Hf	0.04	0.006 71	2.519 8	100
Ta	0	0.000 012	2.725 7	100
W	0.04	0.001 41	2.924	100
Re	0.16	0.004 21	3.115 8	50
Os	0.49	0.007 28	3.301 9	23
Ir	0.49	0.006 16	3.482 9	15
Pt	0.49	0.003 77	3.659 3	10*

"*" is the data that are not sure from the phase diagram are not used for determining the coefficient in the equation.

program[9].

$$\ln C_{max}=5.496-2.212\Delta X^2-72.37\delta^2-0.266\,1n^{2/3} \quad (4)$$

The relation coefficient is 95.2%, which indicates the calculated value is in good agreement with the experimental one. Fig. 1 shows a comparison of C_{max} of the calculated values and the experimental ones, which also indicates that the calculated values are in accordance with the experimental ones by the fact that all data lie to the two sides of the diagonal of 45°. From the statistic values, the effect of atomic size parameter on the C_{max} of transition metals in Ti is the greatest, and then come electronegativity difference and electron concentration[9].

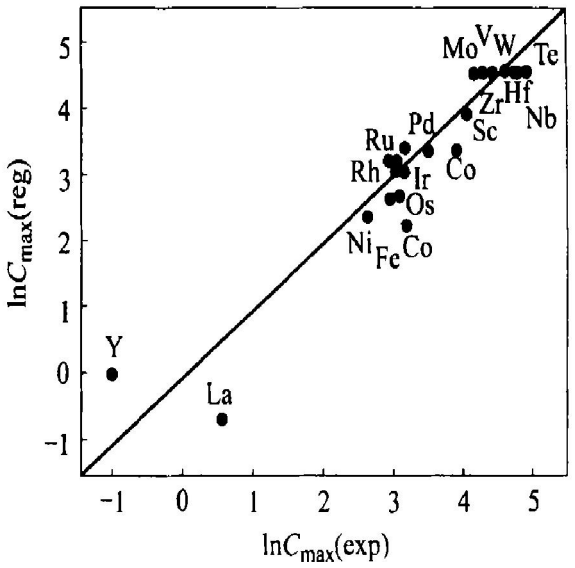

Fig. 1 Comparison between calculated and experimental values of $\ln C_{max}$ for solvent Ti

The C_{max} equation can be used to predict the C_{max} of transition metal solute in Ti. For example, put the value of the $(\Delta X)^2$, δ^2, $n^{2/3}$ listed in Table 1 into Eqn. (4), the C_{max} of Te is calculated to be about 51.5%.

The C_{max} equation of transition metals in Ti binary alloy can also be helpfully used to judge the veracity of C_{max} data in phase diagram. For example, the C_{max} of Cr in Ti was 100% by the phase diagram measured by Ralph Hultgren, which is a large departure comparing to the calculated value (32.4%) by Eqn. (4). As a result, it is doubted that the high temperature part of the phase diagram by Ralph Hultgren might be incorrect for two reasons. One is that the liquidus of that phase diagram is drawn with broken lines, which indicates it is not exact. And the temperature in the middle of solidus curve is a horizontal line about 1 673 K, which indicates it will be a two-phase area according to the phase law, but it is a single-phase marked by Ralph Hultgren. So it contradicts with the phase law. The other is that the structure of the Ti-40% Cr binary alloy annealed at 1 523

K and then water quenched has been proved two-phase by electron probe[9]. C_{max} of Cr in Ti is 33% estimated by the horizontal line in the phase diagram, which is comparable with the calculated value.

3.2 Relation between model of C_{max} and other predicting methods for solid solubility

3.2.1 Relation between model of C_{max} and Darken-Gurry ellipse theorem

Darken and Gurry[3, 4] distinguished the solid solubility by an ellipse which is centered on the point of atomic diameter and electronegativity of solvent element and two half-axis are ±15% of atomic size and ±0.4 electronegativity of solvent, respectively. They pointed out that the elements within the ellipse had larger solid solubility than the ones outside the ellipse. Fig. 2 shows such D-G ellipse for Ti binary alloys, in which the values near the elemental signs are the C_{max} data of the solute in Ti element. It is found that C_{max} of the transition metals Mo, W, Cr, V, Nb, Mn, Ta, Zr, Hf and Sc in the ellipse in Ti element are more than 10%, which is in agreement with D-G theorem. But C_{max} of many transition metals outside the ellipse such as Fe, Co, Ni, Ru, Rh, Pd, Os, Ir and Re are also greater than 10%, which is in disagreement with D-G theorem. So, D-G theorem seems not to be the best to elucidate the rule of transition metals solved in Ti element. It is also found that there exists different criterions to distinguish the solid solubility for different objects. For example, the values of C_{max} of many solutes in Mg or Al are greater than 5% within the ellipse while in solvent Ag element is greater than 10%[3]. Thus, D-G ellipse cannot reflect the concentration criterion and cannot predict the value of solid solubility. Fortunately, the C_{max} equation can solve the above questions and offer a theoretical proving for D-G theorem.

The predictive method mentioned above has

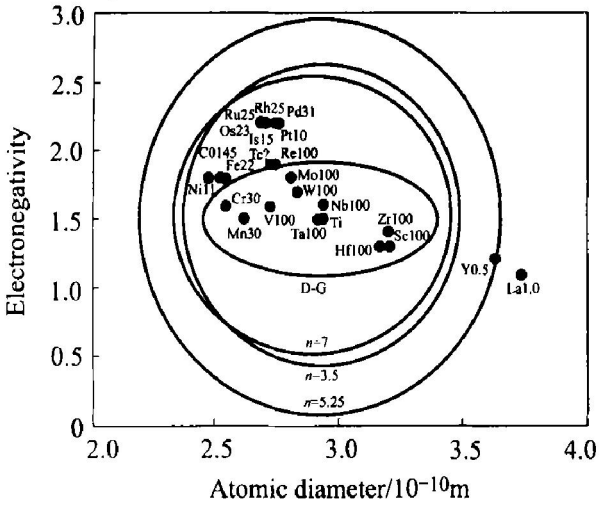

Fig. 2 D-G ellipse of $\ln C_{max}$ for solvent Ti vs electron concentration(C_{max0}= 10%)

two steps. At first a concentration criterion was defined by which a solute in the solvent can be determined as soluble or insoluble. Then the boundary line was determined to divide solute into as soluble or insoluble and to look for the mathematical rules between the atomic parameters for solute and the solvent about the boundary line. Having the C_{max} equation, it is easy to realize the two steps just by making a solution for the equation $Z_{f0}= \ln C_{max0}$.

According to the C_{max} equation, when C_{max} is equal to C_{max0}, it is easy to obtain an ellipse equation by making a transposition:

$$Z_{f0}= C_{max0}= \ln a_0+ a_1\Delta X^2+ a_2\delta^2+ a_3 n^{2/3} \quad (5)$$

$$\frac{(X_0- X)^2}{[Z_{f0}- a_0- a_3 n^{2/3}]/a_1}+ \frac{(D_0- D)^2}{D_0^2[Z_{f0}- a_0- a_3 n^{2/3}]/a_2}= 1 \quad (6)$$

It shows the following points from Eqn. (6).

1) Eqn. (6) is an ellipse when $Z_{f0}- a_0- a_3 n^{2/3} = k$, which the central coordinate is a point (X_0, D_0) and the long, the short axis are $(\frac{k}{a_1})^{1/2}$ and $D_0(\frac{k}{a_2})^{1/2}$, respectively. The D-G equation can be obtained just letting $(\frac{k}{a_1})^{1/2}= X \pm 0.4$ for abscissa and $D_0(\frac{k}{a_2})^{1/2}= D_0 \pm 15\%$ for vertical coordinate, which are the conditions for D-G equation coming into existence. The method mentioned above can also be considered as a theoretical identification on D-G equation.

2) The shape and size of the ellipse drawn by Eqn. (6) is influenced by the value of $Z_{f0}- a_0- a_3 n^{2/3}$. The effect of n on the shape and size of the ellipse is listed in Table 2 and shown in Fig. 2. Fig. 3 shows the effect of the soluble criterion on the shape and size of ellipse for Ti binary alloys. From Figs. 2, 3 and Table 2, the C_{max} theory is in agreement with the experiment that C_{max} of all elements in ellipse are greater than 10% while smaller than 10% for the elements outside the ellipse if 10% is taken as the criterion to determine the value of solid solubility. That is to say, D-G theorem can be seen as a special example of C_{max} equation which omitting the effect of item $n^{2/3}$.

3) If k cannot be taken as a constant, the C_{max} equation will not be an ellipse. So, only when the effect of the change in $n^{2/3}$ can be omitted can an ellipse be used to fit the data of C_{max}.

3.2.2 Relation between model of C_{max} and Miedema-Chelikowsky ellipse theorem

Miedema-Chelikowsky estimated the value of solid solubility by a dimensional chart with parameters $n^{1/3}$ and Φ^* that are related with electronegativity. Fig. 4 illustrates such M-C ellipse of Ti al-

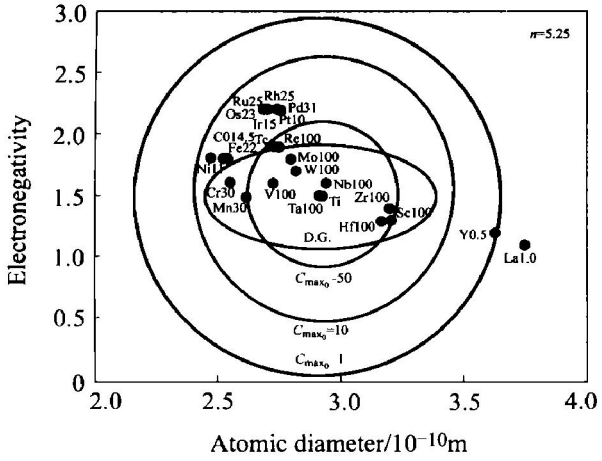

Fig. 3 D-G ellipse of $\ln C_{max}$ for solvent Ti vs characteristic concentration(n= 5.25)

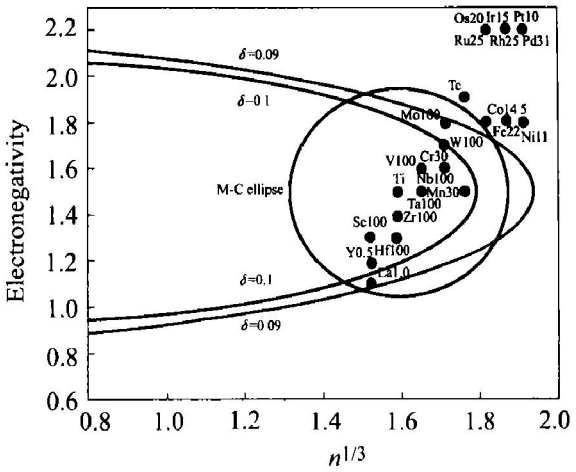

Fig. 4 Effect of δ on M-C ellipse for solvent Ti(C_{max0}= 50%)

Table 2 Effect of C_{max0} and electron concentration on Darken-Gurry ellipse

C_{max0}	n	Axis(D) for D-G ellipse		Axis(X) for D-G ellipse	
		Max.	Min.	Max.	Min.
10	3.5	3.48	2.38	2.58	0.42
10	7	3.44	2.34	2.5	0.5
1	5.25	3.676	2.184	2.957	0.043
10	5.25	3.463	2.397	2.540	0.460
50	5.25	3.234	2.626	2.094	0.906
D-G ellipse		3.37	2.49	1.9	1.1

loys. It can be seen from Fig. 4 that C_{max} of many solute elements in Ti within the ellipse are greater than 10% but some solute elements(Y, La) are not while some solute elements outside the ellipse also greater than 10%, which indicates there exists a big deviation to analyze C_{max} for Ti alloys by M-C theorem.

C_{max} equation can be applied to explain M-C theorem. By transposition from Eqn. (5), one can get

$$\frac{\Delta X^2}{(Z_{f0}-a_0-a_2\delta^2)/a_1}+\frac{n^{2/3}}{(Z_{f0}-a_0-a_2\delta^2)/a_3}=1 \quad (7)$$

Eqn. (7) is an ellipse when($Z_{f0}-a_0-a_2\delta^2$) is constant that affects the shape and size of the ellipse. It neglects the effect of atomic size parameter δ which cannot be ignored from the analysis in 3.2.1. That is the reason why there exists a big deviation to analyze C_{max} for Ti alloys by M-C theorem. However, if the concentration criterion of C_{max} adjusts to 50%, the fitting results will be remarkably improved. That is to say, all C_{max} of solute elements except Y and La in the ellipse are larger than 50% while all data outside the ellipse are less than 50%.

3.2.3 Relation between model of C_{max} and rule of electron concentration

LI[7] emphasized that the electron concentration is the controlling factor when explaining the separation of Ti_3X phase in Ti alloys after he found out the values of the atomic diameter and electronegativity of solute elements are very close. He pointed out an electron concentration rule that intrinsic electron concentration was 2.12 when Ti_3X phase formed in Ti alloys, which is important for the researchers in that field. It is easy to understand from the C_{max} equation proposed above. When the values of the atomic diameter and electronegativity of solute elements are very close to the ones of Ti, it means that the value of both electronegativity difference ΔX and atomic size parameter δ are approximately equal to zero, which makes it obvious that the value of C_{max} will be controlled by electron concentration from Eqn. (1). Moreover, the value of C_{max} will decrease with the increase of electron concentration. It is in agreement with the results deduced by LI[8]. It should be noted that the values of atomic diameter and electronegativity of the solute elements in this paper are no longer close to the ones of Ti, so it is necessary to predict the value of C_{max} of transition metals in Ti by Eqn. (1).

3.2.4 Relation between model of C_{max} and rule of bond parameter functions

ZHANG et al[6] proposed a theory of solid solubility by drawing the boundary line of soluble or insoluble by bond parameter functions and size parameter. Though it is successful for some alloy systems, there are two questions: 1) it cannot make sure to use which bond parameter functions that including Y-coordinate by a function of valence diameter ratio and electronegativity when predicting C_{max} of unknown elements; 2) the solid solubility equation may be parabola(eg for Zr and Ni alloys)

or ellipse(eg for Ti alloys). It cannot make sure to use which one to predict new C_{max} of unknown solvents. It is proved that C_{max} equation can be applied to Ti, Zr, Hf and Pd binary alloys with the same form and all of the relation coefficients are over 90%, which indicates more intrinsic of solid solubility than ZHANG's theory.

4 CONCLUSIONS

1) The mathematical model of C_{max} is a new predicting method to calculate the maximum solid solubility of transition metals in a certain solvent and to estimate the relative contributions of electronegativity difference, atomic diameter and electron concentration.

2) C_{max} model can rationally explain the rules of Darken-Gurry theorem, Miedema-Chelikowsky theorem and electron concentration, which are proved to be the special examples of C_{max} equations by neglecting some certain items.

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