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Maximum solid solubility of transition metals in vanadium solvent①

ZHANG Jin-long(张金龙)[1], FANG Shou-shi(方守狮)[1], ZHOU Zi-qiang(周自强)[1], LIN Gen-wen(林根文)[1], GE Jian-sheng(葛建生)[1], FENG Feng(冯 锋)[2]

(1. Institute of Hydrogen Storage Materials, Shanghai University, Shanghai 200072, China;
2. Department of Mechanical, Automotive and Materials Engineering, University of Windsor, Windsor, Ont., Canada N9B 3P4)

Abstract: Maximum solid solubility (C_{max}) of different transition metals in metal solvent can be described by a semi-empirical equation using function Z_f that contains electronegativity difference, atomic diameter and electron concentration. The relation between C_{max} and these parameters of transition metals in vanadium solvent was studied. It is shown that the relation of C_{max} and function Z_f can be expressed as $\ln C_{max} = Z_f = 7.3165 - 2.7805(\Delta X)^2 - 71.278\delta^2 - 0.85556n^{2/3}$. The factor of atomic size parameter has the largest effect on the C_{max} of the V binary alloy; followed by the factor of electronegativity difference; the electrons concentration has the smallest effect among the three bond parameters. Function Z_f is used for predicting the unknown C_{max} of the transition metals in vanadium solvent. The results are compared with Darken-Gurry theorem, which can be deduced by the obtained function Z_f in this work.

Key words: solid solubility; vanadium alloys; function Z_f; electronegativity difference; atomic size parameters; electron concentration

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1 INTRODUCTION

Recently, alloys with a high density of hydrogen were enthusiastically studied not only for high-performance negative electrodes, but also for fuel cells or for other applications. Vanadium or V-based solid solution alloys with BCC structure are very attractive because of their high hydrogen absorption and desorption capacity at moderate pressure and temperature[1, 2]. Another reason is that the diffusion rate of hydrogen in vanadium is extremely high. The hydrogenation properties of vanadium have been controlled and improved by alloying with other metals[3-6].

The maximum solid solubility C_{max} of alloys is one of the basic issues of the theoretical research on phase formation. It is significant to understand the phase formation theory and improve the ability to predict extensive solid solutions, which restricts the possible adjustment range of components in vanadium alloys. It is also important for V-based solid solution alloys to apply for fuel cells and Ni-MH batteries. There are some theories to analyze the solid solubility such as Hume-Rothery's Rules, Pauling's Electronegativity Concept and Friedel's electronic theory, which respectively emphasize the effects of the electronegativity, atomic size and outer layer electron[7]. Darken and Gurry[8] proposed a method by considering both atomic diameter and electronegativity to predict the formation of solid solution alloys. However, there are some questions that can not be explained. Function Z_f has been successfully proposed to calculate the C_{max} of transition metals in Ti, Zr, Hf and Pd solvents in our previous work, which is convenient to know the relative contributions of atomic parameters[9-14]. In this paper, we shall deal with C_{max} of transition metals in vanadium by function Z_f and determine which is the main atomic factor effect on C_{max}.

2 MATHEMATICAL MODEL FOR RELATION BETWEEN C_{max} AND FUNCTION Z_f

2.1 Mathematical model

According to our previous work[9-14], there is a relation between the C_{max} of transition metals dissolved in a given solvent metal and the function Z_f.

$$\ln C_{max} = Z_f \tag{1}$$

and the function Z_f is defined as

$$Z_f = a_0 + a_1(\Delta X)^2 + a_2\delta^2 + a_3 n^{2/3} \tag{2}$$

where $\Delta X = X_0 - X$, is the electronegativity difference between solute and solvent element (subscript 0 means solvent, it has the same meaning in D_0 and n_0 below); $\delta = 1 - D/D_0$ is the atomic

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Correspondence: ZHOU Zi-qiang, Professor; Tel: +86-21-56651556; E-mail: zqzhou408@21cn.com

size difference between solute and solvent element; $n=(n_0+n_1)/2$ is the average out-layer electrons of solute and solvent element; a_1, a_2 and a_3 are the proportional coefficients and a_0 is a constant, which needs to be fixed.

2.2 Determining of coefficients in function Z_f of vanadium binary alloys

The coefficients in function Z_f of the binary alloys for a given solvent can be fixed using a regression analysis from the known data of C_{max}, X, δ and n. The C_{max} data of the binary alloys for a given solvent can be read from the equilibrium phase diagrams[15] and the other data were read as that in Ref. [16].

For the vanadium binary alloys the data needed to determine the coefficients in function Z_f are listed in Table 1.

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

Solute	$(\Delta X)^2$	δ^2	$n^{2/3}$	C_{max}
Ti	0.01	0.006 0	2.726	100
Cr	0	0.003 9	3.116	100
Mn	0.01	0.001 4	3.302	100
Fe	0.052 9	0.004 4	3.483	47
Co	0.078 4	0.005 4	3.659	22.4
Ni	0.096 1	0.007 8	3.832	24
Y	0.16	0.111 9	2.520	0.05
Zr	0.04	0.031 1	2.726	5.2
Nb	0	0.006 5	2.924	100
Mo	0.04	0.000 9	3.116	100
Tc	0.09	0	3.302	61
Ru	0.36	0.000 2	3.483	26
Rh	0.462 4	0.000 2	3.659	18
Pd	0.36	0.000 1	3.832	37.1
Ta	0.01	0.005 4	2.924	100
W	0.01	0.001 4	3.116	100
Re	0.09	0.000 1	3.302	70
Os	0.36	0.000 2	3.483	30
Ir	0.36	0.000 1	3.659	20
Pt	0.462 4	0.000 1	3.832	12.2

3 RESULTS AND DISCUSSION

3.1 Function Z_f of vanadium binary alloys

Function Z_f of vanadium binary alloys is obtained by a regression analysis using the proposed model.

$$Z_f = \ln C_{max} = 7.316\,5 - 2.780\,5(\Delta X)^2 - 71.278\delta^2 - 0.855\,56n^{2/3} \quad (3)$$

The correlation coefficient of Eqn. (3) is 0.98. Fig. 1 shows a comparison between the calculated and experimental values of $\ln C_{max}$ for V alloys. It can be seen from Fig. 1 that the values of $\ln C_{max}$ calculated from Eqn. (3) are in good agreement with the experimental data.

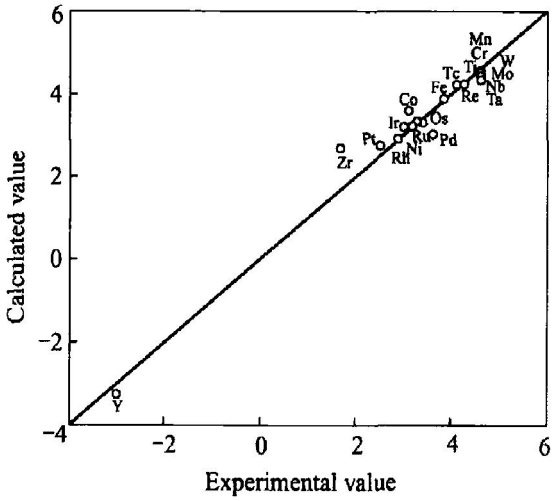

Fig. 1 Comparison between calculated and experimental values of $\ln C_{max}$

3.2 Application of function Z_f

Function Z_f can be easily used for dealing with the following questions of the C_{max} of transition metals in a given solvent.

C_{max} and function Z_f can be expressed as an equation of the three factors: electronegativity difference(ΔX), atomic size parameter δ and electron concentration n on the basis of energetics of alloys. According to the theory of regression analysis, it can determine the relative contribution by comparing the statistic values F_i.

Table 2 lists the statistic F_i of items in the Eqn. (3) by regression analysis. It is well known according to the theory of regression analysis that the larger the statistic values of the F_i items, the larger the effect of the item is. Therefore, it can be deduced from Table 2 that the factor of atomic size parameter (δ^2) has the largest effect on the C_{max} of the V binary alloy, followed by the factor of electronegativity difference; the electrons concentration ($n^{2/3}$) has the smallest effect among the three bond parameters, yet it cannot be neglected.

The values of the unknown C_{max} of some transition metals solved in vanadium can be predicted by Eqn. (3). Table 3 lists the prediction values and the fiducial range of C_{max} of some transition metals solved in vanadium whose maximum solid solution limits are not sure from the phase diagram.

Function Z_f can explain the rules of D-G theo-

Table 2 Values of statistic items in Eqn. (3)

a_i	Reg. coefficient a_i	Statistic F_i
a_0	7.316 5	0
a_1	− 2.780 5	17.349
a_2	− 71.27 8	276.41
a_3	− 0.855 56	6.191 7

Table 3 Prediction values of C_{max} and their atomic parameters

Solute	$(\Delta X)^2$	δ^2	$n^{2/3}$	Prediction value	
				$\ln C_{reg}$	C_{max}
Sc	0.09	0.031 1	2.520	2.693 ± 0.696 2	14.78 ± 2.006
Tc	0.09	0	3.302	4.241 ± 0.696 2	69.49 ± 2.006
La	0.25	0.140 6	2.520	− 5.556 ± 0.696 2	0.003 863 ± 2.006
Hf	0.09	0.027 4	2.726	2.781 ± 0.696 2	16.13 ± 2.006

rem, which is proved to be the special examples of C_{max} equation by neglecting some certain items[12]. According to the C_{max} equation, when C_{max} is set to C_{max_0}, it is easy to get a Z-F ellipse equation:

$$Z_{f_0} = \ln C_{max_0} = a_0 + a_1 \Delta X^2 + a_2 \delta^2 + a_3 n^{2/3} \quad (4)$$

$$\frac{(X_0 - X)^2}{[Z_{f_0} - a_0 - a_3 n^{2/3}]/a_1} + \frac{(D_0 - D)^2}{D_0^2[Z_{f_0} - a_0 - a_3 n^{2/3}]/a_2} = 1 \quad (5)$$

Eqn. (5) is an ellipse when $Z_{f_0} - a_0 - a_3 n^{2/3} = k$, that the central coordinate is point (X_0, D_0) and the long and short axis are $[k/a_1]^{1/2}$ and $D_0[k/a_2]^{1/2}$ respectively. We can obtain the D-G theorem just by letting $[k/a_1]^{1/2} = X \pm 0.4$ for abscissa and $D_0[k/a_2]^{1/2} = D_0 \pm 15\%$ for vertical coordinate, which is the conditions for D-G theorem coming into existence.

Thus, D-G ellipse of V binary alloys can be expressed as

$$\frac{(1.6 - X)^2}{0.4^2} + \frac{2.72 - D^2}{0.408^2} = 1 \quad (6)$$

The shape and size of the ellipse drawn by Eqn. (5) are influenced by the value of $Z_{f_0} - a_0 - a_3 n^{2/3}$. The effects of n on the shape and size of Z-F ellipse equation of V binary alloys when $C_{max_0} = 50\%$ are expressed as Eqn. (7).

$$\frac{(1.6 - X)^2}{1.224\,4 - 0.307\,71 n^{2/3}} + \frac{(2.72 - D)^2}{0.353\,37 - 0.088\,804 n^{2/3}} = 1 \quad (7)$$

$$\frac{(1.6 - X)^2}{0.405^2} + \frac{(2.72 - D)^2}{0.217^2} = 1 \quad (8)$$

D-G theorem can be seen as a special example of Z-F ellipse equation in which omitting the effect of item $n^{2/3}$ is omitted by comparing Eqn. (6) with Eqn. (7).

D-G ellipse that the minor axis is $D_v \pm 15\%$ (abscissa) and the major axis is $X \pm 0.4$ (ordinate) is shown in Fig. 2. The center of the ellipse is at (2.72, 1.6) that stands for the atomic diameter and electronegativity of vanadium respectively. C_{max} of most transition metals (Ta, W, Nb, Mo, Ti, Cr, Mn, Fe, Re, Tc) in vanadium in the ellipsoid are larger than 50%, which is in agreement with the D-G method. But C_{max} of other transition metals (Co, Ni) are less than 50%, which is not in agreement with D-G method. C_{max} out of the ellipsoid (La, Y, Sc, Hf, Zr, Os, Ru, Ir, Rh, Pt, Pd) are less than 50%, which is in agreement with D-G method. Thus the rules of variable C_{max} of most transition metals (not all solute) in vanadium can be judged according to D-G method. It mainly ascribes to the reason that all the d-group elements have the common metallic structures and have d-electrons, when one substitutes a d-group solute element into the d-group solvent there is no major distortion of the electronic bands and no large change in the total energy of the system[7, 8].

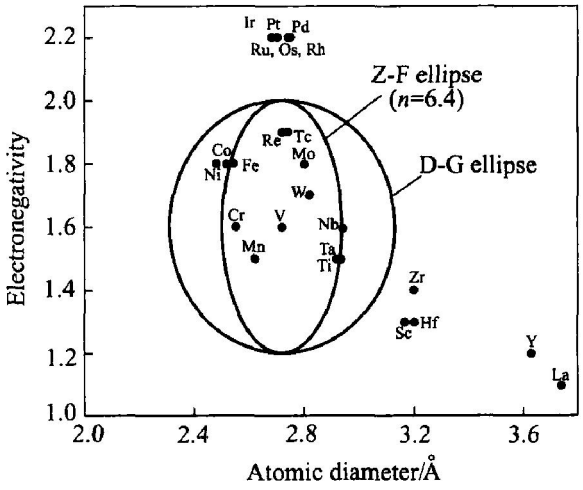

Fig. 2 D-G ellipse and Z-F ellipse about solvent vanadium ($C_{max_0} = 50\%$)

Z-F ellipse equation of V binary alloys when $n = 6.4$ is expressed as Eqn. (8) and shown in Fig. 2. It is clear that C_{max} of (Co, Ni) are in D-G ellipse, but outside Z-F ellipse. Function Z_f theory is in agreement with the experiment that C_{max} of all elements in Z-F ellipse are larger than 50% while it is smaller than 50% for the element outside the ellipse.

Function Z_f can also be applied to explain M-C theorem that Miedema-Chelikowsky estimated the value of solid solubility by a dimensional chart with parameters $n^{1/3}$ and Φ^* which is relative with elec-

tronegativity. Function Z_f can also be applied to explain the rule of electron concentration[12].

4 CONCLUSIONS

1) The maximum solid solubility of transition metals in vanadium can be represented as function Z_f of electronegativity difference, atomic size parameter and electron concentration as follows: $\ln C_{max} = Z_f = a_0 + a_1(\Delta X)^2 + a_2\delta^2 + a_3 n^{2/3}$.

2) The factor of atomic size parameter has the largest effect on the C_{max} of the V binary alloy, followed by the factor of electronegativity difference; the electrons concentration has the smallest effect among the three bond parameters.

3) Function Z_f can be applied to determine the main atomic factor effect on C_{max} and predict C_{max} of transition metals in vanadium solvent. Function Z_f can also be applied to explain D-G theorem.

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