

## Rules for maximum solid solubility of transition metals in Ti, Zr and Hf solvents<sup>①</sup>

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**Abstract:** Based on the principle of energy change of alloy formation, the rules for the maximum solid solubility ( $C_{\max}$ ) of various transition metals in the metals Ti, Zr and Hf were studied. It is deduced that the  $C_{\max}$  of transition metals in the metals Ti, Zr and Hf can be described as a semi-empirical equation using three atomic parameters, i. e., electronegativity difference, atomic diameter and electron concentration. From the equation analysis by using experimental data, it shows that atomic size parameter and electronegativity difference are the main factors that affect the  $C_{\max}$  of the transition metals in the metals Ti, Zr and Hf while electron concentration parameter has the smallest effect on  $C_{\max}$ .

**Key words:** maximum solid solubility; prediction method; transition metals; electronegativity difference; atomic size factor; electron concentration

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### 1 INTRODUCTION

The maximum solid solubility ( $C_{\max}$ ) of a solute metal in a solvent metal restricts the adjustable range of components in an alloy. It is very important for studying new alloys or new heat treatment methods. Vanadium-based solid solution alloys are very attractive hydrogen storage materials. This triggered scientists to investigate solid solution alloys for hydrogen storage. Ti subgroup based alloys adjacent to V-based ones in Periodic Table are associated with solid solution hydrogen storage materials and this will be instructive for developing new solid solution hydrogen storage alloys through studying the theory of  $C_{\max}$ . Thus it is valuable to investigate the theory of  $C_{\max}$  of Ti subgroup based alloys in order to enrich the predictive theory of solid solution alloys.

There are some good reviews in literatures about the micro theory of solid solubility of alloys, which can be summarized as statistical, elastic and electronic theories that emphasize respectively the effects of electronegativity, atomic size and electron concentration on solid solubility of alloys<sup>[1, 2]</sup>. However, these theories are addressed themselves to the explanation of experimental rules and they cannot be used to predict the solid solubility of other metals in the solvent. For this reason, scientists suggested some predictive methods with two parameters (such as atomic size and electronegativity<sup>[3, 4]</sup>, electronegativity and electron concentration<sup>[5]</sup>, bond parameters functions and

size parameters<sup>[6-8]</sup>) after improving the work of Hume-Rothery. All the predictive methods mentioned above have the same two steps. They define at first a concentration criterion by which a solute in the solvent can be determined as soluble or insoluble. Then they determine the boundary line to divide these solute elements into as soluble or insoluble and to look for the mathematical rules between the atomic parameters for the 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 of dividing soluble or insoluble; 2) it needs to use different fit equations according to different structural parameters for different alloy systems; 3) all methods cannot calculate the value of solid solubility. A mathematical model was once proposed to calculate  $C_{\max}$  by electronegativity, atomic diameter and electron concentration according to the energy change of alloy formation, which is successful to analyze and predict the  $C_{\max}$  of transition metals in Ti and Pd elements<sup>[9, 10]</sup>. Yet, the model has not been applied in other alloys and some more theoretical analysis is necessary to be done. In this paper, it is our aim to make out the model rational and to study the  $C_{\max}$  of transition metals in Ti, Zr, Hf elements in detail.

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## 2 METHODS AND RESULTS

### 2.1 Model of $C_{\max}$ and establishment of coefficient in equation

A mathematical model was once proposed by the authors to calculate  $C_{\max}$  as follows<sup>[9, 10]</sup>:

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

where  $\Delta X = X_0 - X$  is the electronegativity difference between solute and solvent element (subscript 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. The coefficient in Eqn. (1) can be obtained from the data in Table 1 by a computer.

The  $C_{\max}$  data in this paper were read from equilibrium phase diagram<sup>[11]</sup>. For an eutectic phase diagram the solid solubility of solute in the solvent at the eutectic temperature was regarded as the  $C_{\max}$  of the alloy system. For a peritectic phase diagram the solid solubility of solute in solvent at the peritectic temperature was not sure to be regarded as the  $C_{\max}$  of the

alloy system, among them only the one that was the maximum solid solubility of solute in the solvent was regarded as the  $C_{\max}$  of the alloy system. For a phase diagram showing complete liquid, solid solubility 100% was regarded as the  $C_{\max}$  of the alloy system (note: the data that are not sure from the phase diagram are not used for determining the coefficient in the equation, which is marked “?” in Table 1). It is difficult to determine the covalence electron of transition metals whose d electrons are between local state and common state. If a model for predicting has to make sure the type of valence electron, it will encounter some troubles. For this reason, (s+ d) out-layer electrons are taken as valence electrons of solute or solvent. The data of Pauling electronegativity that is not affected by atomic valence, Goldschmidt atomic diameter whose coordination number is 12 (in this paper, both atomic diameter of solute and that of Ti, Zr and Hf with body-center structure are converted into Goldschmidt atomic diameter) and covalent electrons of solute and solvent are read from the literature<sup>[1]</sup>.

### 2.2 Results

$C_{\max}$  of transition metals in Ti, Zr and Hf can

**Table 1** Data of electronegativity  $X$ , atomic size  $D$ , electron number s+ d and  $C_{\max}$  for solvent  $\beta$ -Ti,  $\beta$ -Zr,  $\beta$ -Hf<sup>[1, 11]</sup>

Element	$X$	$D/0.1 \text{ nm}$	s+ d	$C(\text{Ti})_{\max}$	$C(\text{Zr})_{\max}$	$C(\text{Hf})_{\max}$
Sc	1.3	3.2	3	100	100	0.000 1?
Ti	1.5	2.93	4	100	100	100
V	1.6	2.72	5	100	16.6	23.6
Cr	1.6	2.55	6	100?	8.45	13
Mn	1.5	2.62	7	30?	10.2	2
Fe	1.8	2.54	8	22	6.74	9
Co	1.8	2.52	9	14.5	3	0.000 1?
Ni	1.8	2.48	10	11	3.5	0.000 1?
Y	1.2	3.63	3	0.5	3.9?	0.000 1?
Zr	1.4	3.2	4	100	100	100
Nb	1.6	2.94	5	100	100	100
Mo	1.8	2.8	6	100	41	43.07
Tc	1.9	2.72	7		30?	0.0301 ?
Ru	2.2	2.68	8	25	12	0.039 5
Rh	2.2	2.68	9	25	10	0.042
Pd	2.2	2.74	10	31	11.5	0.047 4
La	1.1	3.74	3	1	5?	0.000 1?
Hf	1.3	3.17	4	100	100	100
Ta	1.5	2.92	5	100	100	100
W	1.7	2.82	6	100	28	13.46
Re	1.9	2.74	7	50	10?	12
Os	2.2	2.68	8	23	14	0.03?
Ir	2.2	2.7	9	15	5	1
Pt	2.2	2.75	10	10?	8	0.03?

be calculated step-by-step regression analysis program from the data in Table 1 as follows:

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

$$\ln C_{\max} = 6.659 - 0.678 4\Delta X^2 - 55.65 \delta^2 - 0.752 5n^{2/3} \quad (3)$$

$$\ln C_{\max} = 9.588 6 - 5.816 8\Delta X^2 - 39.786 \delta^2 - 1.743 4n^{2/3} \quad (4)$$

The relative coefficients are 95.2%, 96% and 92%, respectively, which are by far greater than the values in relative coefficient check table that are equal to 0.514 ~ 0.413 when experimental data are between 15 to 23 and check value  $\alpha = 0.05$ . Thus it is enough to prove that the above regression equations are creditable. Figs. 1 ~ 3 show the comparative values of  $\ln C_{\max}$  of transition metals in Ti, Zr and Hf (calculated and experimental values). All experimental data (points) lie in two sides of the diagonal of 45° and this indicates that the calculated values of  $\ln C_{\max}$  are in good agreement with the experimental ones.

### 3 DISCUSSION

#### 3.1 $C_{\max}$ equation—theoretical basis of proposed mathematical model

Solid solution alloy is composed of positive ions

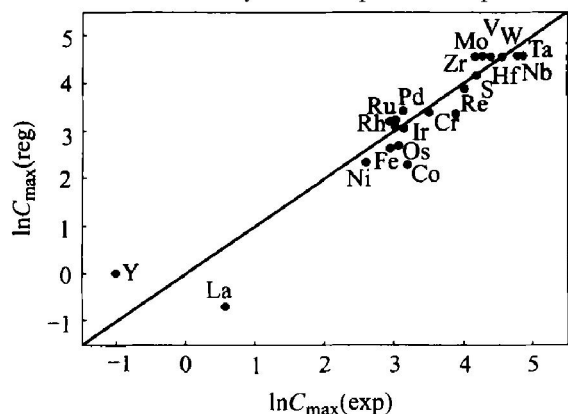


Fig. 1 Comparison between calculated and experimental values of  $\ln C_{\max}$  for solvent Ti

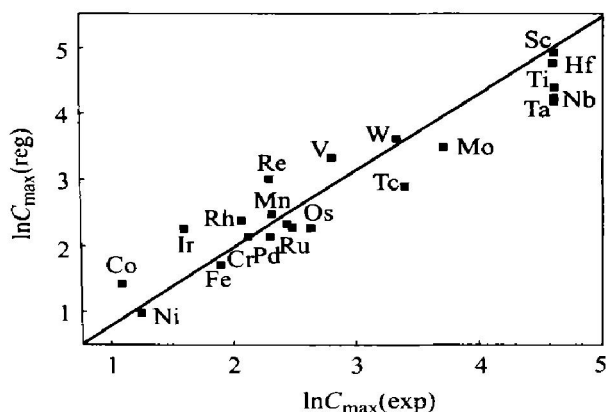


Fig. 2 Comparison between calculated and experimental values of  $\ln C_{\max}$  for solvent Zr

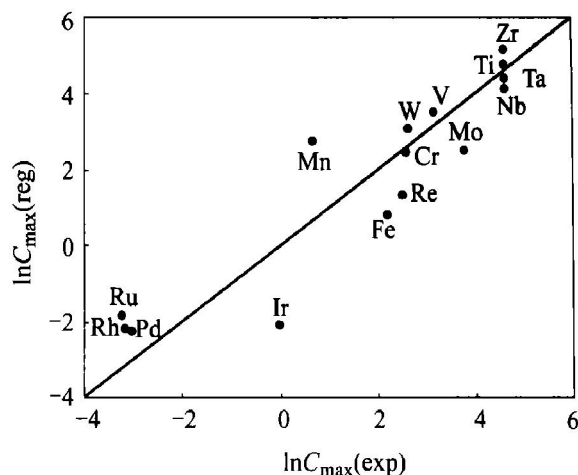


Fig. 3 Comparison between calculated and experimental values of  $\ln C_{\max}$  for solvent Hf

and common electrons of solvent and solute elements. Based on the alloy energetics, the Gibbs free energy change  $\Delta G$  is mainly composed of three items when solute and solvent elements form a solid solution alloy: chemical energy ( $E_c$ ) caused by the difference between the electronegativities, elastic strain energy (or distortion energy) ( $E_d$ ) due to atomic size difference and electronic Fermi energy ( $E_f$ ) caused by elemental out-layer electrons<sup>[1, 2]</sup>.

Electronegativity presents the relative attractive ability of a monovalent ion to a valence electron<sup>[1]</sup>. So, the energy change for forming an AB bond in an alloy can be expressed as follows:

$$E_c = Z(\Delta X)^2/N \quad (5)$$

where  $Z$  is coordination number and  $N$  is atomic number. As we known, Fermi energy means the energy needed when a system is adding an electron and the volume is unchangeable. Thus the electronic Fermi energy caused by out-layer electrons at zero K can be calculated by

$$E_{f0} = \frac{h^2}{2m} \left( \frac{3\pi}{8} \right)^{2/3} n^{2/3} \quad (6)$$

where  $h$  is Planck constant,  $m$  is electronic mass and  $n$  is electronic concentration. The strain energy caused by the atomic size difference between the two kinds of atoms can be presented as follows:

$$E_d = G\delta^2 \quad (7)$$

where  $G$  is the shear modulus. If we take the effect of temperature into account when calculating energy by the above three items, Eqn. (1) should be added an item  $E(T_c)$  which means the energy change as the temperature rises to  $T_c$ . The effect of temperature on the energy change is not sure and the relation between  $E(T_c)$  and temperature is also not sure. One of the dealing methods is that it can be taken as progressions of  $T_c$ . We take simply the first item that is one power approximate. So, the free energy change when forming solid solution at  $T_c$  can be calculated as follows:

$$\Delta G(T_c) = E_c + E_d + E_f + E(T_c) \quad (8)$$

Replacing  $E_c$ ,  $E_d$  and  $E_f$  by Eqns. (5)–(7), one can easily get:

$$\Delta G(T_c) = \frac{Z(\Delta X)^2}{N} + G\delta^2 + \frac{h}{2m} \left( \frac{3}{8\pi} \right)^{2/3} n^{2/3} + KT_c \quad (9)$$

Presume that the free energy change at  $T_c$  when forming solid solution alloy can be expressed by activity, namely

$$\Delta G(T_c) = RT_c(\gamma C_{\max}) \quad (10)$$

where  $\gamma$  is activity coefficient, the following equation is obtained:

$$RT_c \ln(\gamma C_{\max}) = \frac{Z(\Delta X)^2}{N} + G\delta^2 + \frac{h^2}{2m} \cdot \left( \frac{3}{8\pi} \right)^{2/3} \cdot n^{2/3} + KT_c \quad (11)$$

By transposition, one can get

$$RT_c \ln C_{\max} = -RT_c \ln \gamma + \frac{Z(\Delta X)^2}{N} + G\delta^2 + \frac{h^2}{2m} \cdot \left( \frac{3}{8\pi} \right)^{2/3} \cdot n^{2/3} + KT_c \quad (12)$$

Rewriting Eqn. (12) yields

$$\ln C_{\max} = \frac{1}{RT_c} \left[ -RT_c \ln \gamma + KT_c + \frac{Z(\Delta X)^2}{N} + G\delta^2 + \frac{h^2}{2m} \cdot \left( \frac{3}{8\pi} \right)^{2/3} \cdot n^{2/3} \right] \quad (13)$$

The above relation is the mathematical model of the  $C_{\max}$ . This model is very important to analyze the rule of  $C_{\max}$ , which elucidates the relation between  $C_{\max}$  of some solute elements in a solvent and the associative atomic parameters of solute and solvent. There are seven concerned parameters:  $T_c$ ,  $\gamma$ ,  $Z$ ,  $\Delta X$ ,  $G$ ,  $\delta$  and  $n$ , and among them three parameters ( $\Delta X$ ,  $\delta$ , and  $n$ ) are related to electronegativity, atomic diameter and valence electrons.

The corresponding coefficients in Eqn. (13) can be considered approximately equal when different transition metals dissolve in a definite solvent. So the  $C_{\max}$  equation can be rewritten simply as Eqn. (1) by setting  $(K - R \ln \gamma)/R = a_0$ ,  $Z/NRT_c = a_1$ ,  $G/RT_c = a_2$ ,  $0.5(3/8\pi)^{2/3}(h^2/RT_cm) = a_3$ . It is rational of the above theory that  $C_{\max}$  of 24 transition metals in solvents Ti, Zr, Hf, Pd, V binary alloys can be fitted by Eqn. (1). In the same way, Eqn. (12) can be simply rewritten as

$$T_c \ln C_{\max} = b_0 + b_1 \Delta X^2 + b_2 \delta^2 + b_3 n^{2/3} + b_4 T_c \quad (14)$$

$C_{\max}$  data may have two methods to deal with from the above analysis. One is the calculation of Eqn. (1) by taking  $\ln C_{\max}$  as variable. The other is the calculation of Eqn. (14) by taking  $T \ln C_{\max}$  as variable. The latter is stricted to calculate but is not convenient to use while the former is convenient to use though its conditions are more than the latter. Here, Eqn. (1) is used to deal with the

data of  $C_{\max}$ .

### 3.2 Comparison among $C_{\max}$ equations of transition metals in Ti, Zr and Hf elements

It can be seen from Eqns. (2)–(4) that the expression form of  $C_{\max}$  and the signs of corresponding coefficient are the same. The coefficient change regularly with the increase of periodic numbers, i. e.,  $a_0$  and  $a_3$  increase,  $a_2$  decreases while  $a_1$  decreases first and then increases.

When investigating  $C_{\max}$  of transition metals in Ti element, it is pointed out that the atomic size parameter has the greatest effect on the  $C_{\max}$ , next on electronegativity difference; and the electron concentration has the smallest effect on  $C_{\max}$ . The statistical value  $F_i$  of Eqns. (2)–(4) are 8.15, 45.87 and 4.10 for Zr solvent, 4.95, 0.81 and 0.38 for Hf solvent, respectively. According to the regression theory, the bigger the statistical value, the greater the effect of the parameter. As a result, the effects of three atomic parameters on  $C_{\max}$  of transition metals in Zr element have the same order with those in Ti element. However, changes are found that the effect of electronegativity difference is greater than that of atomic size parameter on  $C_{\max}$  of transition metals in Hf solvent. The main reason is the special change rule of atomic diameters of Ti, Zr and Hf elements (2.92, 3.2 and 3.17, respectively). That is to say, the atomic diameters increase first and then decrease while the electronegativity decreases (1.5, 1.4 and 1.3, respectively) with the increase of periodic numbers.

### 3.3 Comparison between $C_{\max}$ equation and traditional solid solution theory

The  $C_{\max}$  equation and the traditional solid solution theory are different. The latter is used to deal with the relation between solid solution of a definite binary alloy system and temperature, which is used to deduce the solid solubility at unknown temperatures.  $C_{\max}$  equation is about the relation between  $C_{\max}$  of different solutes in the same solvent and their structural parameters, which elucidates the effects of the atomic parameters ( $X$ ,  $\delta$  and  $n$ ) on the maximum solid solubility.  $C_{\max}$  of unknown solutes in known solvent can be calculated by this relation. The traditional solid solution theory is deduced on the basis of quasi-chemical method that mainly considered the energy change by statistical theory.  $C_{\max}$  equation considers synthetically the energy change not only according to statistical theory but also elastic theory and electronic theory. From this point of view,  $C_{\max}$  equation is a theory for prediction that develops the traditional one.

### 3.4 $Z_f$ function

Simply, the right part of Eqn. (1) is defined as  $Z_f$  function, that is

$$Z_f = a_0 + a_1 \Delta X^2 + a_2 \delta^2 + a_3 n^{2/3} = \ln C_{\max} \quad (15)$$

The similar relation is got when calculating the hydride formation enthalpy of different type of hydrogen-storage materials<sup>[12-15]</sup>:

$$\Delta H = RZ_f \quad (16)$$

where  $R$  is gas constant and  $\Delta H$  is hydride formation enthalpy. The critical step to calculate hydride formation enthalpy or  $C_{\max}$  of transition metals in a solvent is determining the coefficients of  $Z_f$  function. That is to say, this function reflects the structural parameter change of solvent and solute elements and it combines the structural change with energy change. Thus it is very practical to calculate energy change such as  $\Delta H$ ,  $\Delta G$  and the characteristic parameters such as  $p$  (pressure) and  $C_{\max}$  just by using  $Z_f$  function.

## 4 CONCLUSIONS

1) The maximum solid solubility of transition metals in Ti, Zr, Hf can be expressed by a mathematical model, i. e.,  $C_{\max}$  equation that concerns with the three atomic parameters: electronegativity, atomic diameter and electron concentration. The calculated values are in good agreement with the experimental ones.

2) The  $C_{\max}$  equation can be deduced from the free energy change when an alloy is to be formed.

3) The maximum solid solution equation is very useful to solve two kinds of problems about  $C_{\max}$ : one is to calculate the  $C_{\max}$  of transition metals in Ti, Zr and Hf by the atomic parameters of the corresponding solvent and solutes; the other is to estimate the relative contributions of the three atomic parameters to  $C_{\max}$ .

4) Function  $Z_f$  reflects the structural parameter change of solvents and solute elements when an alloy forms. It can be used to connect the structural parameter change with energy change.

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## REFERENCES

- [1] XIAO Jī mei. Energetics of Alloys [M]. Shanghai: Shanghai Science and Technology Press, 1985. 256. (in Chinese)
- [2] FENG Duan. Metal Physics [M]. Beijing: Science Press, 1987. 155. (in Chinese)
- [3] Gschneidner K A Jr. L S Larry Darken's contributions to the theory of alloy formation and where we are today [A]. Bennett L H. Theory of Alloy Phase Formation [C]. New York: A Publication of the Metallurgical Society of AIME, 1980. 1 - 39.
- [4] Darken L S, Gurry R W. Physical Chemistry of Metals [M]. New York: McGraw-Hill Co, Inc, 1953. 74 - 92.
- [5] Phillips J C. From Wigner-Seitz to Miedema to...? [A]. Bennett L H. Theory of Alloy Phase Formation [C]. A Publication of the Metallurgical Society of AIME, 1980. 332 - 335.
- [6] LIAO Shur zhi, ZHANG Bang-wei, OUYANG Yī-fang. A further study for the theory of solid solubilities on the binary transition metals based alloys [J]. Rare Metal Materials & Engineering, 1994, 23(5): 19 - 28. (in Chinese)
- [7] LI D, LIU Y Y, WAN X J. On the thermal stability of Ti alloys [J]. Acta Metall Sinica, 1984, 20(6): 375 - 384.
- [8] LI D, LIU Y Y, WAN X J. The Electron Concentration rule for the formation of  $Ti_3X$  phase [J]. Metal Sci Tech, 1985, 1(1): 33 - 40.
- [9] ZHOU Zī-qiang, ZHANG Jīr-long, PING Xīr-yi, et al. Advance in Energy Sources Materials, Intelligent Materials and Gradient Materials [M]. Beijing: Publishing Company of Metallurgy, 1998. 37 - 40. (in Chinese)
- [10] FANG S S, LIN G W, ZHANG J L, et al. The maximum solid solubility of the transition metals in palladium [J]. International Journal of Hydrogen Energy, 2002, 27: 329 - 332.
- [11] Massalski T B. Binary Alloy Phase Diagrams [M]. Ohio: ASM, Metals Park, 1996.
- [12] ZHOU Zī-qiang, FENG Feng, ZHANG Jīr-long, et al. A calculation model and prediction for the enthalpy of formation of  $TiFe_xM_y$  hydrides [J]. Materials Science Progress, 1991, 5: 117 - 123. (in Chinese)
- [13] ZHOU Zī-qiang, ZHANG Jīr-long, GE Jīn-sheng, et al. Effect of 3d transition metal additive on the hydrogen storage properties of  $Mm_{1-x}Ml_xNi_{5-y}M_y$  alloys [A]. Ohta T, Homma T. New Energy Systems and Conversions [C]. Universal Academy Press, Inc, 1993. 79 - 82.
- [14] FENG Feng, ZHOU Zī-qiang. Two mathematical models for hydrogen storage materials [J]. Functional Materials, 1995, (S126): 476 - 478. (in Chinese)
- [15] FANG Shou-shi, ZHOU Zī-qiang, Zhang Jīr-long, et al. Two mathematical models for the hydrogen storage properties of  $AB_2$  type alloys [J]. J Alloys & Compounds, 1999, 293 - 295: 10 - 13.

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