Article ID: 1003 - 6326(1999)03 - 0611 - 06

Calculation of Al-Zn diagram from central atoms model①

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Abstract: A slightly modified central atoms model was proposed. The probabilities of various clusters with the central atoms and their nearest neighboring shells can be calculated neglecting the assumption of the parameter of energy in the central atoms model in proportion to the number of other atoms i (referred with the central atom). A parameter P_α is proposed in this model, which equals to reciprocal of activity coefficient of α component, therefore, the new model can be understood easily. By this model, the Al-Zn phase diagram and its thermodynamic properties were calculated, the results coincide with the experimental data.

Key words: central atoms model; diagram calculation; Al-Zn **Documment code:** A

1 INTRODUCTION

In order to calculate phase diagrams and analyze thermodynamic properties of alloys, various models, such as the ideal solution model, the regular solution model[1], the quasi-chemical model[2], the central atoms(CA) model have been proposed. In the ideal and regular solution models, the atoms of each components are assumed in random states, while in the quasi-chemical model, only atoms pairs are considered in the evaluation of the positional entropy. On the other hand, "the central atoms model" developed almost simultaneously by Lupis *et al*[3] and by Hicte *et al*[4], has several advantages over the models above mentioned. Firstly, instead of assuming the cluster contents only atom pairs in the quasi-chemical model, the central atoms model is based on a larger cluster of all atoms in the nearest neighboring shell, therefore, the accuracy of evaluating the positional entropy and the cohesive energy of the whole system is improved[5~7]. Secondly, the most probable atomic configuration (cluster) of the system in CA model was determined under the condition that the free energy of the system should be a minimum, while the atoms in the regular solution model are assumed in random states. Therefore, the central atoms model has gained a wide application in phase diagrams calculation[7~10]. Moreover, the idea of this type cluster in the central atoms model has been used to calculate the composition dependence of bulk alloy properties[11] and the electronic structures of alloys[12,13]. However, on the whole, application of the central atoms model is more limited than that of the regular solution model or quasi-chemical model on the calculation of alloy diagram and thermodynamic properties, because the equations in the CA model are much more and much complicated and there is much difference between the parameters in the CA model and those of the models usually used. In this paper, we slightly modified the central atoms model, simplified the equations in this model and made them much similar to the equations which we usually used. At last, the Al-Zn diagram is calculated by the modified central atoms model.

2 DERIVATION OF MODIFIED CENTRAL MODEL

In order to reduce the difficulty of deriva-

① Received Jan.4, 1999; accepted Mar.22, 1999

tion of the equation in the central atoms model, we only cope with binary substitution solutions. Most notations of this model similar to that in the CA model generalized by Foo and Lupis[5].

It can be assumed that the alloy is A-B system, the atom percent of each components are x_A and x_B, respectively. If the central atom α (A or B) has i ($i = 0, 1, 2, \cdots, I$, I is the coordination number and equals to 12) atoms of B in its nearest neighboring shell, then the atom can be said in the Ψ_i^α state and its energy, volume, atomic partition function are U_i^α, V_i^α, q_i^α, respectively, the probability of finding this atomic state is P_i^α.

At constant pressure, temperature and the number of moles, the partition function may be written as

$$Q = \sum gq\exp[-(E + PV)/KT] = \sum b \quad (1)$$

$$E + PV = N_A P_i^A (U_i^A + PV_i^A) + N_B P_i^B (U_i^B + PV_i^B) \quad (2)$$

where N_A, N_B are the number of A and B atoms, respectively, g and q, the degeneracy of the level $E + PV$ and the total contribution from all degrees of internal freedom, they are equal to

$$q = \prod_i (q_i^A)^{N_A P_i^A} \cdot \prod_i (q_i^B)^{N_B P_i^B} \quad (3)$$

$$g = \frac{(N_A + N_B)!}{N_A! N_B!} \prod_i \left[\frac{(N_A \alpha_i^{*A})!}{(N_A \alpha_i^A)!}\right]^{C_i^A} \cdot \prod_i \left[\frac{(N_B \alpha_i^{*B})!}{(N_B \alpha_i^{*B})!}\right]^{C_i^B} \quad (4)$$

where C_i^α is the combination factor,

$$C_i^\alpha = \frac{I!}{(I-i)!\,i!} = C_I^i \quad (5)$$

$\alpha_i^{*\alpha}$ and α_i^α are the probability of the cluster (i atoms of B, $I - i$ atoms of A in the neighboring shell) around the central atom α when alloys are in total random state, or in non-random state respectively, and have

$$\alpha_i^\alpha = \alpha_i^{*\alpha} \cdot f_i^\alpha \quad (6)$$

$$\alpha_i^{*\alpha} = x_A^{I-i} \cdot x_B^i \quad (7)$$

$$P_i^\alpha = C_I^i x_A^{I-i} x_B^i f_i^\alpha \quad (8)$$

In Eqns.6 and 8, f_i^α is a correction factor, in order to get the probability P_i^α, the following mass balance equations are needed

$$\begin{cases} \Psi_A = N_A \sum i_A P_i^A + N_B \sum i_A P_{iA}^B - IN_A = 0 \\ \Psi_B = N_A \sum i_B P_i^A + N_B \sum i_B P_{iB}^B - IN_B = 0 \end{cases} \quad (9)$$

where $i_A = I - i_B = I - i$, $i_B = i$. With the Lagrange multipliers, the most probability can be sought by the rule of the minimum energy (in this condition, the Q is maximum).

$$\frac{\partial(\ln b + \Lambda_A \Psi_A + \Lambda_B \Psi_B)}{\partial P_i^\alpha} = 0 \quad (10)$$

Solving Eqn.10 yields the most probably distribution of atoms

$$P_i^\alpha = C_I^i x_A^{I-i} x_B^i \exp[i_A \Lambda_A + i_B \Lambda_B - \varphi_i^\alpha] / P_\alpha = S_i^\alpha / P_\alpha \quad (11A)$$

$$\varphi_i^\alpha = \frac{U_i^\alpha + PV_i^\alpha}{KT} - \ln q_i^\alpha \quad (11B)$$

$$P_\alpha = \sum_i S_i^\alpha \quad (11C)$$

According to Ref.5, the Gibbs free energy of mixing can be gotten from

$$G^M = RT(x_A \ln x_A + x_B \ln x_B) - RT(x_A \ln P_A + x_B \ln P_B) - (x_A \mu_A^0 + x_B \mu_B^0) + RTI(x_A \Lambda_A + x_B \Lambda_B) \quad (12)$$

where μ_α^0 is the chemical potential of the α component when it is pure. It is clear that, when alloy is in total random state, the G^M can be expressed as

$$G^M = RT(x_A \ln x_A + x_B \ln x_B) \quad (13)$$

and

$$P_i^\alpha = C_I^i x_A^{I-x} x_B^i / P_\alpha = C_I^i x_A^{I-x} x_B^i / \sum C_I^i x_A^{I-x} x_B^i = C_I^i x_A^{I-x} x_B^i \quad (14)$$

$$P_i^\alpha = \sum C_I^i x_A^{I-x} x_B^i = 1 \quad (15)$$

therefore

$$G^M = RT(x_A \ln x_A + x_B \ln x_B) - (x_A \mu_A^0 + x_B \mu_B^0) + IRT(x_A \Lambda_A + x_B \Lambda_B) = RT(x_A \ln x_A + x_B \ln x_B) \quad (16)$$

$$\begin{cases} x_A \mu_A^0 + x_B \mu_B^0 = IRT(x_A \Lambda_A + x_B \Lambda_B) \\ \mu_A^0 = IRT\Lambda_A, \quad \mu_B^0 = IRT\Lambda_B \end{cases} \quad (17)$$

If consider that the term in Eqn.11 equals to zero, then

$$\frac{i_A \mu_A^0}{IRT} + \frac{i_B \mu_B^0}{IRT} = \varphi_i^\alpha \quad (18)$$

Namely, φ_i^α equals to the average value of the chemical potential of i_A pure atoms of A and i_B pure atoms of B divided by RT. From above, it can be derived that: $\Lambda_A = \mu_A^0/IRT$, $\Lambda_B = \mu_B^0/IRT$, and φ_i^α is the ratio of the chemical potential of Ψ_i^α state and RT even in the non-random state. Therefore, after transformation of Eqn.11, it can get

$$\begin{cases} P_i^\alpha = C_I^i x_A^{I-i} x_B^i \exp\left(\dfrac{(I-i)\mu_A^0}{IRT} + \dfrac{i\mu_B^0}{IRT} - \dfrac{\mu_i^\alpha}{RT}\right)/P_\alpha \\ \quad = S_i^\alpha / P_\alpha \\ P_\alpha = \sum C_I^i x_A^{I-i} x_B^i \exp\left(\dfrac{(I-i)\mu_A^0}{IRT} + \dfrac{i\mu_B^0}{IRT} + \dfrac{\mu_i^\alpha}{RT}\right) \end{cases} \quad (19)$$

$$G^M = RT(x_A \ln x_A + x_B \ln x_B) - RT(x_A \ln P_A + x_B \ln P_B) \quad (20)$$

For any thermodynamic model, it has

$$G^M = RT(x_A \ln x_A + x_B \ln x_B) + RT(x_A \ln \gamma_A + x_B \ln \gamma_B) \quad (21)$$

so, $P_A = 1/\gamma_A$, $P_B = 1/\gamma_B$ (22)

where γ_α is the activity coefficient of component α.

Eqns.19 ~ 22 show that, P_α is reciprocal of activity coefficient of component α, it provides the relations of activity coefficient of component α, the probability of Ψ_i^α state, the Gibbs free energy and the chemical potential u_α^i of Ψ_i^α state. If the u_α^i connecting with composition, I, temperature T is known, the thermodynamic properties of the alloy and the alloy phase diagram can be gotten, and vice versa. Considered for any I, if the chemical potential of Ψ_i^α state equals to average chemical potential value of $(I-i)$ atoms of A and i atoms of B when the alloy is at total random state, we can assume

$$\begin{cases} \mu_i^A = \dfrac{(I-i)\mu_A^0}{IRT} + \dfrac{i\mu_B^0}{IRT} - \dfrac{iA_\beta}{IRT} \\ \mu_i^B = \dfrac{(I-i)\mu_A^0}{IRT} + \dfrac{i\mu_B^0}{IRT} - \dfrac{i(I-i)B_\beta}{IRT} \end{cases} \quad (23)$$

where A_β, B_β are the functions of i, T and composition, β denotes liquid, FCC or other phase. When $i = 0$, $\mu_i^A = \mu_A^0$; $i = 12$, $\mu_i^B = \mu_0^B$, then, Eqn.19 can be transformed to

$$\begin{cases} P_i^\alpha = C_I^i x_A^{I-i} x_B^i \exp(J\alpha_\beta/IRT)/P_\alpha \\ \quad = S_i^\alpha / P_\alpha \\ P_\alpha = \sum C_I^i x_A^{I-i} x_B^i \exp(J\alpha_\beta/IRT) \end{cases} \quad (24)$$

As A_β, B_β are the function of T, the entropy is

$$S_\alpha = -\left[\frac{\partial u_\alpha}{\partial T}\right] = -\left[\frac{\partial u_\alpha^0}{\partial T}\right] + R\ln P_\alpha - R\ln x_\alpha + \frac{RT}{P_\alpha}\left[\frac{IRTJP_\alpha \dfrac{\partial u_\beta}{\partial T} - IRJ\alpha_\beta}{(IRT)^2}\right] \quad (25)$$

If $\alpha = A$ then $\alpha_\beta = A_\beta$, $J = i$; if $\alpha = B$, then $\alpha_\beta = B_\beta$, $J = I - i$. When we want to calculate the phase diagram, what we should notice is the functions A_β, B_β are not defined in proportion to i, they may change with T, I, pressure, composition. For multicomponent solution, we can derive the similar equations as the Eqns.19 ~ 24.

3 CALCULATION OF Al-Zn DIAGRAM

The phase diagram of Al-Zn is relatively simple. There exist only three solution phases, i.e., the liquid, FCC and HCP phase, but there are two equilibria in this system, one is eutectic equilibrium, L ←→FCC + HCP, the other is critical point for phase seperation of the FCC phase, FCC ←→FCC1 + FCC2, one eutectoid transformation, FCC2 ←→FCC1 + HCP. Some experimental values of the composition and temperature can be shown in Fig.4. It is not strange that there is some deviation between different works. The phase diagram of Al-Zn and their thermodynamic properties have been calculated by some authors[14~17], but there is no one to calculate them by the central atom model. In this paper, the thermodynamic properties and phase diagram of Al-Zn will be calculated by the slightly modified central atoms model. The lattice stabilities of pure elements Al and Zn are gained from Ref. 17.

Lots of thermodynamic properties used for the Al-Zn diagram are accepted by Ref.17. In order to calculate the Al-Zn diagram, the only thing is to optimize the vulues of A_α, B_β for the liquid, FCC and HCP phase. As Eqn.24 is not easy to calculate, there is no good computer program. All the values of model parameters are

gotten by many times of calculation, and perhaps are not the best ones. The parameters for the liquid, FCC and HCP phases are given in Table 2 and the phase diagram of Al-Zn calculated and some thermodynamic properties by these parameters are shown in Figs.1 ~ 4.

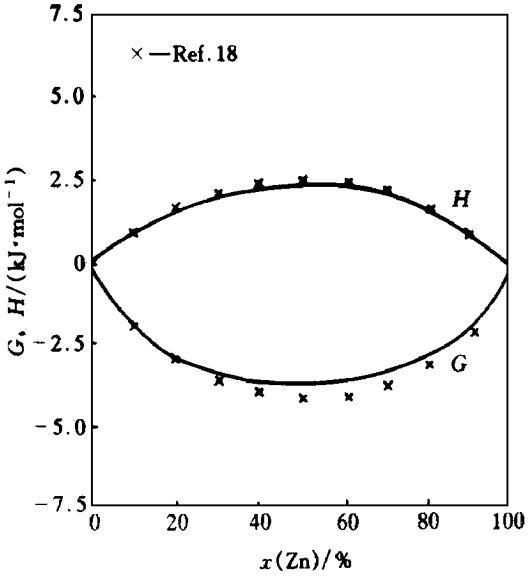

Fig.1 Enthalpy and Gibbs free energies of liquid phase at 1 000 K, referred to Al(L) and Zn(L)[18]

4 DISCUSSION

From Figs.2,3 it is shown that the partial Gibbs energy of liquid at 1 000 K and the energy of FCC phase at 653 K are much similar to the calculated values of Chen and Chang[17], which perhaps result from a lot of experimental thermodynamic data used here according to this reference and the rationality of their model. Although the calculated enthalpy of the liquid at 1 000 K(referred to Al(L) and Zn(L)) has little deviation from the experiment values, the calculated Gibbs free energies is not very agree with the experiment values, seen from Fig.1. This results from that there is not good computer program to optimize the parameters of the CA model.

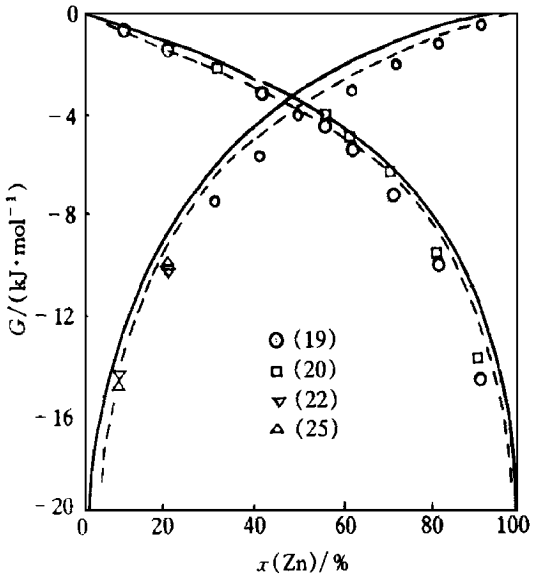

Fig.2 Partial Gibbs energies of liquid phase at 1 000 K referred to Al(L) and Zn(L). (Dashed line according to Ref.17)

The calculated results are: at 655 K, L(88.5 %Zn(mole fraction)) ↔FCC(65.5 %Zn(mole fraction)) + HCP(97.5 %Zn(mole fraction)); at 550 K, FCC2(59.5 %Zn(mole fraction)) ↔FCC1(22.5 %Zn(mole fraction)) + HCP(98.5 %Zn(mole fraction)); at 625 K, FCC(36.5 %Zn) ↔FCC2(59.5 %Zn(mole fraction)) + FCC1(22.5 %Zn(mole fraction)). Compared the calculated Al-Zn phase diagram with the experimental data from Fig.4, it is clear that, the liquid solution line and FCC solid line are in good agreement with the experimental data, but the miscibility gap for the FCC phase

Table 2 Values of model parameters for liquid, FCC and HCP phases

Phases	Parameters of Al	Parameters of Zn
Liquid	$A_L = 18.37 - 7668.5x - 2190.3x^2 + 4x^2(T - 400)$	$B_L = -8586 + 5720x + 2862.5x^2 + 3.2(1-x)^2(T - 400)$
HCP	$A_{HCP} = 18.12 - 16397x - 1284.6x^2 + 0.5x^2(T - 400)$	$B_{HCP} = 14987 + 14085x + 1052x^2 + 0.5(1-x)^2(T - 400)$
FCC	$A_{FCC} = 109 - 14695x - 11874x^2 + [225 - \left(\frac{x - 0.6}{0.1}\right)^2] \cdot (T/100 - 6)$	$B_{FCC} = -987.7 + 138.3x + 3516\ln x + [-545 + 12.1x + (\log\lvert x - 0.25\rvert)(x - 0.9)](T/1000 - 10)$

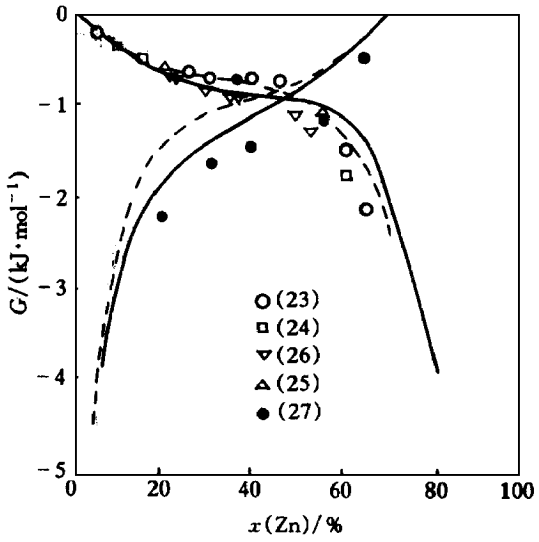

Fig.3 Partial Gibbs energies of FCC phase at 654 K, referred to Al(FCC) and Zn(HCP) (Dashed line according to Ref.17)

and eutectoid equilibrium are not in good accordance with the experiment data. The calculated miscibility gap for Al-rich portion is too high in composition. However, in lots of alloys system, there always exist some relative serious disagreements of the miscibility gap experimental data of different investigators. Considered most of the thermodynamic properties and most part of phase diagram, such as FCC/L, FCC/HCP, HCP/L phase boundary accordance with experimental data, the calculated miscibility gap may be accepted. Therefore, the modified central atoms model can be used to calculated Al-Zn phase diagram and the parameters in Table 2 are rational.

But there are still some things had to be noted here. First, For liquid phase, the coordination number does not equal to solid phase and it varies slightly with temperature changes. So, the physical meanings is not very proper, the equations of CA model are nothing but equations when we use them to calculate the thermodynamic properties of the liquid phase. We use them only in order to keep the unity of the model. Of course, the results show that it hardly have difference when I changes.

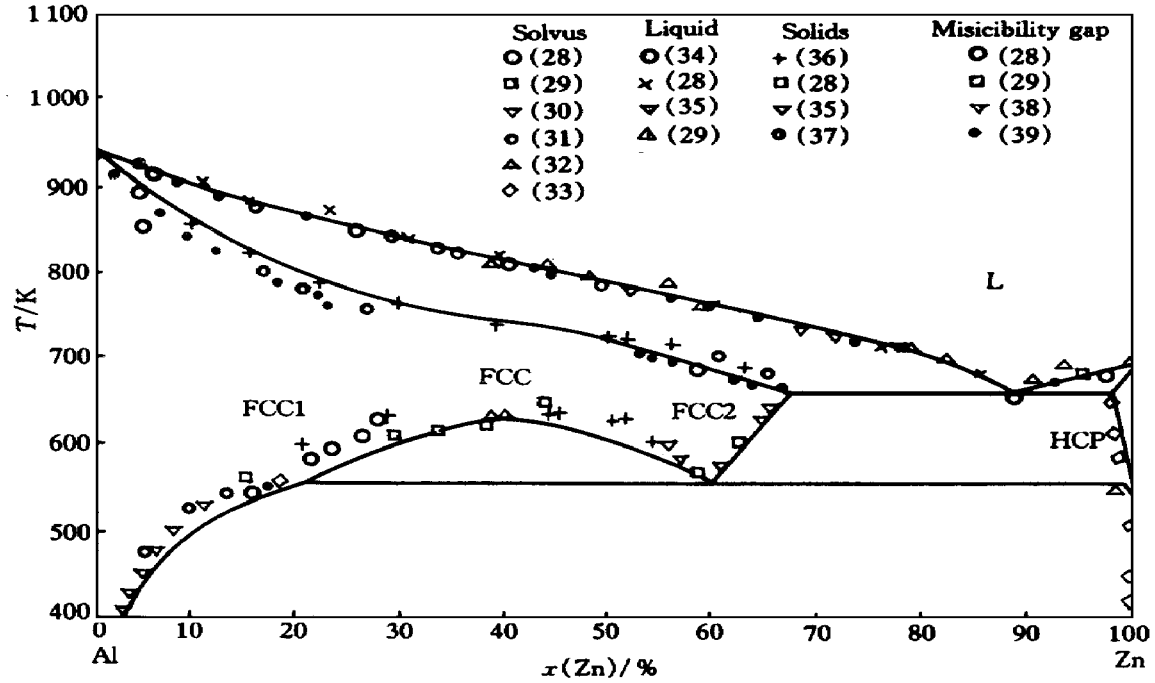

Fig.4 Comparison of calculated diagram with experimental data

Secondly, in Ref.5, the (φ_1^a - φ_0^a) was derivated on base of (φ_1^a - φ_a^0). It's clear that it is not always the case in the actual alloys. In the modified CA model, it stresses the deviation of u_i^a and the average values of chemical potential of (I - i) atoms A and i atoms B. If the deviation equals to zero for any i value and any kind of the central atom, the total interaction in the cluster equals to the mechanical plus of interaction of the central atom with atoms in its nearest neigbouring shell, the solution is at random state. This is just as the situation of ideal solution. If the deviation above mentioned is not zero, the solution will at non-random state, but this deviation need not be proportional to i or (I - i), it can be acquired from A_β and B_β in Eqn.24. From Table 2 and Eqn.23, it can be seen that, except temperature, μ_i^a are also the functions of i and composition, if we can descript by i only, μ_i^a must be the composition functions of i.

Thirdly, Although the parameters of P_a is very easy to understand just as the reciprocal of the activity coefficient of a, it is more difficult to calculate thermodynamic properties by this model than by other ordinary models. Moreover, in this model, the obtaining of experimental activity data is rather crucial.

5 SUMMARY

The slightly modified central atoms model has been constructed, in this model, the probability of finding the Ψ_i^a state can be gained from the deviation of the chemical potential μ_i^a of the Ψ_i^a state and the average chemical potential of I - i atoms pure A and i atoms pure of B. Equations in this model need not on base of in proportion to (φ_1^a - φ_a^0). The P_a is the reciprocal of the activity coefficient of component, therefore, the parameter of P_a is easy to understand and connected with parameters of ordinary thermodynamic properties. The phase diagram of Al-Zn are calculated, most of calculated results concide with experimental data, reflecting that it is possible to calculate phase diagram of binary alloys by this modified central atoms model.

ACKNOWLEDGEMENT

The authors thank Professor Xie Youqing and Professor Jin Zhanpeng, Department of Materials Science and Engineering, Central South University of Technology for helpful discussion and support during this work.

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(Edited by Huang Jinsong)