STATISTICAL MECHANICS MODEL OF LIQUID BINARY ALLOY AND ITS PARAMETERS①

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ABSTRACT From the view of chemical short range order and incomplete random mixing existing in liquid binary alloy, absorbing the rational part of past statistical mechanics, a statistical mechanics model of liquid binary alloy has been proposed. From the model, the expressions of component activity were derived. Some parameters have been investigated, and their calculation formulae were obtained. According to the formulae of calculating coordination number, the coordination numbers of Cu-Zr, Fe-B, Ni-B, Co-P, Fe-P systems were calculated, and the results agreed well with those in literature and in experiments.

Key words statistical mechanics model liquid binary alloy coordination number

1 INTRODUCTION

The past statistical mechanics models have provided possibility for thermodynamical calculation of some liquid alloy solutions. However, it can not yet be used for some liquid alloy solutions in which chemical short-range order and incomplete random mixing exist. In most of these models, the chemical short-range order was neglected, complete random distribution was adopted. But most binary or more component alloy solutions are dealt with regular solution model[1-3], the past statistical mechanics models are required to be improved and developed further. Thus, a statistical mechanics model based on chemical short-range order and incomplete random mixing existing in liquid binary alloy has been developed. Simultaneously, this paper gives the expressions of component activity a_i of liquid binary alloy and the expressions of the parameters, such as co-ordination number, probability of pairwise forming chemical bond i-j.

2 STATISTICAL MECHANICS MODEL OF LIQUID BINARY ALLOY

A statistical mechanics model based on chemical short-range order and incomplete random mixing existing in liquid binary alloy is described as follows:

(1) Pairwise interactive energies in solution is symbolized as $\varepsilon_{ij}(i, j = A, B)$, which is varied with compound A_XB_Y forming or not in the solution. When two atoms are combined into chemical bond, the devotion to the interaction energies is symbolized as $\Delta\varepsilon_{ij}(i, j = A, B)$. The probability of forming chemical bond is symbolized as P_{ij}, and the pairwise interactive energies in pure substance is symbolized as $\varepsilon^0_{ii}(i = A, B)$.

(2) Inner and translational degrees of freedom of atom in pure substance are independent, and equal to that in pure substance, therefore only the near pairwise interactive energies are considered.

(3) Because of difference between two atoms and between pairwise interactive energies, when A and B are mixed into solution, the mixing is incomplete random and obeys some rules; and there is chemical short-range order in the system.

(4) The co-ordination number of A is not equal to that of B. The co-ordination numbers of A, B and pure substance $i(i = A, B)$ are sym-

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bolized as Z_A, Z_B and $Z_i^0(i = A, B)$.

(5) Because of existing pair interaction, the solution system can be regarded as a system composed of dependent particles, and its Hamiltonian is

$$H = \sum_i \varepsilon_i + E \tag{1}$$

where ε_i is the energy level of the atom i (associated with inner and translational degrees of freedom), E is the sum of pairwise interactive energies in the solution, named as configurational energy.

The canonical partition function of the liquid binary alloy is as follows:

$$Z_{AB} = \sum_j \frac{(N_{AA} + N_{BB} + N_{AB})!}{N_{AA}!N_{BB}!N_{AB}!} \cdot Q_A^{N_A}(T) Q_B^{N_B}(T) \cdot \exp(-E_{ABj}/kT) \tag{2}$$

where $Q_i(T) = \sum_j \exp(-\varepsilon_{ij}/kT)$ is partition function associated with inner and translational degrees of freedom of atom $i(i = A, B)$, $N_{ij}(i, j = A, B)$ is pair number in the solution.

3 ACTIVITY EXPRESSIONS

3.1 Component activity and canonical partition function

Statistical mechanics shows that macroscopic quantity is assembly average of microscopic quantity, hence it is also an ensemble average. According to above, formula of Helmholtz free energy can be given as follows:

$$F = -kT\ln Z \tag{3}$$

where Z is canonical partition function of the system. And the relation of chemical potential and canonical partition function is

$$\mu_i = -RT\left(\frac{\partial \ln Z}{\partial N_i}\right)_{T, V} \tag{4}$$

Comparing with thermodynamical relation formula of chemical potential and activity, $\mu_i = \mu_i^0 + RT\ln a_i$, relation formula of component activity and canonical partition function is obtained:

$$\ln a_i = \left(\frac{\partial \ln Z(T, V, N_i)}{\partial N_i}\right)_{T, V} - \left(\frac{\partial \ln Z(T, V, N_i, N_j)}{\partial N_i}\right)_{T, V, N_j} \tag{5}$$

3.2 Activity expressions

According to existent pattern of compound in the solution, liquid binary alloy solutions could be divided into two styles: non-compound system and compound system.

3.2.1 Activity expressions of non-compound system

Because of no compound existing in the solution, the devotion of chemical bond formed by two atoms is unnecessary to be considered, the configurational energy of the system is

$$E_{AB} = N_{AB}\varepsilon_{AB} + N_{AA}\varepsilon_{AA} + N_{BB}\varepsilon_{BB} \tag{6}$$

For system composed of pure substance A, its configurational energy is

$$E_A = N_A Z_A^0 \varepsilon_{AA}^0 \tag{7}$$

Define $\{X_{ij}\} = \{N_{ij}\}/\sum_{i,j}\{N_{ij}\}$, where $\{X_{ij}\}$ is called pair fraction; substitute Eqns. (2), (6) and (7) into Eqn. 5 and according to the principle of lowest energy, activity expression of component A is obtained as:

$$\begin{aligned}\ln a_A = {} & \left(\frac{\partial\{N_{AB}\}}{\partial N_A}\right)_{T, V, N_B}\ln\{X_{AB}\} + \left(\frac{\partial\{N_{AA}\}}{\partial N_A}\right)_{T, V, N_B}\ln\{X_{AA}\} + \\ & \left(\frac{\partial\{N_{BB}\}}{\partial N_A}\right)_{T, V, N_B}\ln\{X_{BB}\} + \frac{\{N_{AB}\}}{kT}\left(\frac{\partial \varepsilon_{AB}}{\partial N_A}\right)_{T, V, N_B} + \\ & \frac{\{N_{AA}\}}{kT}\left(\frac{\partial \varepsilon_{AA}}{\partial N_A}\right)_{T, V, N_B} + \frac{\{N_{BB}\}}{kT}\left(\frac{\partial \varepsilon_{BB}}{\partial N_A}\right)_{T, V, N_B} - \frac{Z_A^0\varepsilon_{AA}^0}{2kT}\end{aligned} \tag{8}$$

According to the same deduction, activity expression of component B is also given by

$$\begin{aligned}\ln a_B = {} & \left(\frac{\partial\{N_{AB}\}}{\partial N_B}\right)_{T, V, N_A}\ln\{X_{AB}\} + \left(\frac{\partial\{N_{AA}\}}{\partial N_B}\right)_{T, V, N_A}\ln\{X_{AA}\} + \\ & \left(\frac{\partial\{N_{BB}\}}{\partial N_B}\right)_{T, V, N_A}\ln\{X_{BB}\} +\end{aligned}$$

$$\frac{\{N_{AB}\}}{kT}\left(\frac{\partial \varepsilon_{AB}}{\partial N_B}\right)_{T,\ V,\ N_A} + \frac{\{N_{AA}\}}{kT}\left(\frac{\partial \varepsilon_{AA}}{\partial N_B}\right)_{T,\ V,\ N_A} + \frac{\{N_{BB}\}}{kT}\left(\frac{\partial \varepsilon_{BB}}{\partial N_B}\right)_{T,\ V,\ N_A} - \frac{Z_B^0 \varepsilon_{BB}^0}{2kT} \quad (9)$$

Neglecting the relation of pairwise interactive energy and component concentration, activity expressions of component A, B become as follows:

$$\ln a_A = \left(\frac{\partial\{N_{AB}\}}{\partial N_A}\right)_{T,\ V,\ N_B}\ln\{X_{AB}\} + \left(\frac{\partial\{N_{AA}\}}{\partial N_A}\right)_{T,\ V,\ N_B}\ln\{X_{AA}\} + \left(\frac{\partial\{N_{BB}\}}{\partial N_A}\right)_{T,\ V,\ N_B}\ln\{X_{BB}\} - \frac{Z_A^0 \varepsilon_{AA}^0}{2kT} \quad (10)$$

$$\ln a_B = \left(\frac{\partial\{N_{AB}\}}{\partial N_B}\right)_{T,\ V,\ N_A}\ln\{X_{AB}\} + \left(\frac{\partial\{N_{AA}\}}{\partial N_B}\right)_{T,\ V,\ N_A}\ln\{X_{AA}\} + \left(\frac{\partial\{N_{BB}\}}{\partial N_B}\right)_{T,\ V,\ N_A}\ln\{X_{BB}\} - \frac{Z_B^0 \varepsilon_{BB}^0}{2kT} \quad (11)$$

3. 2. 2 Particle number of compound system

Let $[N_{A-B}]$, $[N_A]$ and $[N_B]$ be particle number of compound A_XB_Y, component A and component B in the solution respectively; Q_A, Q_B and Q_{A-B} represent partition function associated with inner and translational degrees of freedom of particles A, B and A_XB_Y. When compound A_XB_Y exists in the solution, chemical equilibrium established among component A_XB_Y, compnent A and component B is as follows:

$$xA(l) + yB(l) = A_xB_y(l)$$

According to the calculation formula of equilibrium constant in statistical mechanics[4], particle number of compound A_XB_Y, component A and component B are related with

$$\frac{[N_{A-B}]}{[N_A]^X[N_B]^Y} = \frac{Q_{A-B}}{Q_A^X Q_B^Y}\exp(-\triangle E_0/kT) \quad (12)$$

where $\triangle E^0$ is the difference of dissociative energy of reactant and product in ground state, it is also the remaining sum of ground state of reactant molecula and product molecula.

The following relation exists among component particle number:

$$[N_A] = N_A - X[N_{A-B}] \quad (13)$$

$$[N_B] = N_B - Y[N_{A-B}] \quad (14)$$

$$\frac{[N_{A-B}]}{(N_A - X[N_{A-B}])^X(N_B - Y[N_{A-B}])^Y} = \frac{Q_{A-B}}{Q_A{}^X Q_B{}^Y}\exp(-\triangle E^0/kT) \quad (15)$$

In Eqn. (15), at given temperature, partition function Q_{A-B}, Q_A, Q_B and $\triangle E^0$ are independent of particle number, they are constant.

Let

$$AA = \frac{Q_{A-B}}{Q_A^X Q_B^Y}\exp(-\triangle E^0/kT) \quad (16)$$

hence

$$\frac{[N_{A-B}]}{(N_A - X[N_{A-B}])X(N_A - X[N_{A-B}])Y} = AA \quad (17)$$

In Eqn. (17), N_A, N_B, X, Y and AA are fixed value in a given system, therefore particle number of component A_XB_Y is easily obtained. According to Eqn. (13) and Eqn. (14), particle number of component A, B are also easily obtained.

3. 2. 3 Activity expression of compound system

Considering the effect of compound existing in the solution on particle number, canonical partition function is

$$Z_{AB} = \sum_j \frac{(N_{AA} + N_{BB} + N_{AB})!}{N_{AA}!N_{BB}!N_{AB}!} \cdot Q_A^{N_A}(T)\, Q_B^{N_B}(T)\, Q_{A-B}^{N_{A-B}} \cdot (T)\exp(-E_{ABj}/kT) \quad (18)$$

When compound exists in the solution, the devotion of bond-forming to configurational energy is needed to be considered. Thus, configurational energy is

$$E_{AB} = N_{AB}(\varepsilon_{AB} + P_{AB}\triangle\varepsilon_{AB}) + N_{AA}(\varepsilon_{AA} + P_{AA}\triangle\varepsilon_{AA}) + N_{BB}(\varepsilon_{BB} + P_{BB}\triangle\varepsilon_{BB}) \quad (19)$$

where $P_{ij}(i, j = A, B)$ is the probability of pairwise forming chemical bond i-j.

According to the similar deduction of section 3. 2. 1, activity expressions of component A, B in compound system are

$$
\begin{aligned}
\ln a_A = & \left(\frac{\partial\{N_{AB}\}}{\partial N_A}\right)_{T,\,V,\,N_B}\ln\{X_{AB}\} + \\
& \left(\frac{\partial\{N_{AA}\}}{\partial N_A}\right)_{T,\,V,\,N_B}\ln\{X_{AA}\} + \\
& \left(\frac{\partial\{N_{BB}\}}{\partial N_A}\right)_{T,\,V,\,N_B}\ln\{X_{BB}\} + \\
& \frac{\{N_{AB}\}}{kT}\left[\left(\frac{\partial \varepsilon_{AB}}{\partial N_A}\right)_{T,\,V,\,N_B} + \right. \\
& \left(\frac{\partial P_{AB}}{\partial N_A}\right)_{T,\,V,\,N_B}\triangle\varepsilon_{AB} + \\
& \left.\left(\frac{\partial \triangle\varepsilon_{AB}}{\partial N_A}\right)_{T,\,V,\,N_B}P_{AB}\right] + \\
& \frac{\{N_{AA}\}}{kT}\left[\left(\frac{\partial \varepsilon_{AA}}{\partial N_A}\right)_{T,\,V,\,N_B} + \right. \\
& \left(\frac{\partial P_{AA}}{\partial N_A}\right)_{T,\,V,\,N_B}\triangle\varepsilon_{AA} + \\
& \left.\left(\frac{\partial \triangle\varepsilon_{AA}}{\partial N_A}\right)_{T,\,V,\,N_B}P_{AA}\right] + \\
& \frac{\{N_{BB}\}}{kT}\left[\left(\frac{\partial \varepsilon_{BB}}{\partial N_A}\right)_{T,\,V,\,N_B} + \right. \\
& \left(\frac{\partial P_{BB}}{\partial N_A}\right)_{T,\,V,\,N_B}\triangle\varepsilon_{BB} + \\
& \left.\left(\frac{\partial \triangle\varepsilon_{BB}}{\partial N_A}\right)_{T,\,V,\,N_B}P_{BB}\right] - \\
& \left(\frac{\partial[N_{A-B}]}{\partial N_A}\right)_{T,\,V,\,N_B}\ln Q_{A-B} - \\
& \left(\frac{\partial[N_A]}{\partial N_A}\right)_{T,\,V,\,N_B}\ln Q_A - \\
& \left(\frac{\partial[N_B]}{\partial N_A}\right)_{T,\,V,\,N_B}\ln Q_B - \\
& \ln Q_A - \frac{Z_A^0\varepsilon_{AA}^0}{2kT}
\end{aligned}
\qquad (20)
$$

$$
\begin{aligned}
\ln a_B = & \left(\frac{\partial\{N_{AB}\}}{\partial N_B}\right)_{T,\,V,\,N_A}\ln\{X_{AB}\} + \\
& \left(\frac{\partial\{N_{AA}\}}{\partial N_B}\right)_{T,\,V,\,N_A}\ln\{X_{AA}\} + \\
& \left(\frac{\partial\{N_{BB}\}}{\partial N_B}\right)_{T,\,V,\,N_A}\ln\{X_{BB}\} + \\
& \frac{\{N_{AB}\}}{kT}\left[\left(\frac{\partial \varepsilon_{AB}}{\partial N_B}\right)_{T,\,V,\,N_A} + \right. \\
& \left(\frac{\partial P_{AB}}{\partial N_B}\right)_{T,\,V,\,N_A}\triangle\varepsilon_{AB} + \\
& \left.\left(\frac{\partial \triangle\varepsilon_{AB}}{\partial N_B}\right)_{T,\,V,\,N_A}P_{AB}\right] + \\
& \frac{\{N_{AA}\}}{kT}\left[\left(\frac{\partial \varepsilon_{AA}}{\partial N_A}\right)_{T,\,V,\,N_A} - \right. \\
& \left(\frac{\partial P_{AA}}{\partial N_B}\right)_{T,\,V,\,N_A}\triangle\varepsilon_{AA} - \\
& \left.\left(\frac{\partial \triangle\varepsilon_{AA}}{\partial N_B}\right)_{T,\,V,\,N_A}P_{AA}\right] + \\
& \frac{\{N_{BB}\}}{kT}\left[\left(\frac{\partial \varepsilon_{BB}}{\partial N_B}\right)_{T,\,V,\,N_A} + \right. \\
& \left(\frac{\partial P_{BB}}{\partial N_B}\right)_{T,\,V,\,N_A}\triangle\varepsilon_{BB} + \\
& \left.\left(\frac{\partial \triangle\varepsilon_{BB}}{\partial N_B}\right)_{T,\,V,\,N_A}P_{BB}\right] - \\
& \left(\frac{\partial[N_{A-B}]}{\partial N_B}\right)_{T,\,V,\,N_A}\ln Q_{A-B} - \\
& \left(\frac{\partial[N_A]}{\partial N_B}\right)_{T,\,V,\,N_A}\ln Q_A - \\
& \left(\frac{\partial[N_B]}{\partial N_B}\right)_{T,\,V,\,N_A}\ln Q_B + \\
& \ln Q_B - \frac{Z_B^0\varepsilon_{BB}^0}{2kT}
\end{aligned}
\qquad (21)
$$

Neglecting the relation of pairwise interactive energy and component concentration, activity expressions of component A, B in the solution are as follows:

$$
\begin{aligned}
\ln a_A = & \left(\frac{\partial\{N_{AB}\}}{\partial N_A}\right)_{T,\,V,\,N_B}\ln\{X_{AB}\} + \\
& \left(\frac{\partial\{N_{AA}\}}{\partial N_A}\right)_{T,\,V,\,N_B}\ln\{X_{AA}\} + \\
& \left(\frac{\partial\{N_{BB}\}}{\partial N_A}\right)_{T,\,V,\,N_B}\ln\{X_{BB}\} + \\
& \frac{\{N_{AB}\}}{kT}\left(\frac{\partial P_{AB}}{\partial N_A}\right)_{T,\,V,\,N_B}\triangle\varepsilon_{AB} + \\
& \frac{\{N_{AA}\}}{kT}\left(\frac{\partial P_{AA}}{\partial N_A}\right)_{T,\,V,\,N_B}\triangle\varepsilon_{AA} + \\
& \frac{\{N_{BB}\}}{kT}\left(\frac{\partial P_{BB}}{\partial N_A}\right)_{T,\,V,\,N_B}\triangle\varepsilon_{BB} - \\
& \left(\frac{\partial[N_A]}{\partial N_A}\right)_{T,\,V,\,N_B}\ln Q_A - \\
& \left(\frac{\partial[N_B]}{\partial N_A}\right)_{T,\,V,\,N_B} ln Q_B + \ln Q_A - \\
& \left(\frac{\partial[N_{A-B}]}{\partial N_A}\right)_{T,\,V,\,N_B}\ln Q_{A-B} - \\
& \frac{Z_A^0\varepsilon_{AA}^0}{2kT}
\end{aligned}
\qquad (22)
$$

$$
\ln a_B = \left(\frac{\partial\{N_{AB}\}}{\partial N_B}\right)_{T,\,V,\,N_A}\ln\{X_{AB}\} +
$$

$$\left(\frac{\partial\{N_{AA}\}}{\partial N_B}\right)_{T,V,N_A}\ln\{X_{AA}\}+\left(\frac{\partial\{N_{BB}\}}{\partial N_B}\right)_{T,V,N_A}\ln\{X_{BB}\}+\frac{\{N_{AB}\}}{kT}\left(\partial\frac{P_{AB}}{\partial N_B}\right)_{T,V,N_A}\triangle\varepsilon_{AB}+\frac{\{N_{AA}\}}{kT}\left(\frac{\partial P_{AA}}{\partial N_B}\right)_{T,V,N_A}\triangle\varepsilon_{AA}+\frac{\{N_{BB}\}}{kT}\left(\frac{\partial P_{BB}}{\partial N_B}\right)_{T,V,N_A}\triangle\varepsilon_{BB}]-\left(\frac{\partial[N_A]}{\partial N_B}\right)_{T,V,N_A}\ln Q_A-\left(\frac{\partial[N_B]}{\partial N_B}\right)_{T,V,N_A}\ln Q_B+\ln Q_B-\left(\frac{\partial[N_{A-B}]}{\partial N_B}\right)_{T,V,N_A}\ln Q_{A-B}-\frac{Z_B^0\varepsilon_{BB}^0}{2kT} \quad (23)$$

4 PAIR NUMBER

4.1 Pair number and Cowley-Warren chemical short range order parameter

Because of the difference between two atoms and between pairwise interactive energies, when different metals A and B are mixed into solution, the mixing is incomplete random, the chemical concentration around each atom is not equal to their average concentration, and there exists chemical short range order in the system. In general, the probability of finding atom A as a nearest neighbour of a given atom A is not equal to that of a given atom B. Similarly, the probability of finding atom B as a nearest neighbour of a given atom A is not equal to that of a given atom B.

Suppose (i/j) to represent the probabilities of finding atom i as a nearest neighbour of a given atom j $(i, j = A, B)$; and (i, j) to represent the probabilities of atoms i, j becoming nearest neighbour $(i, j = A, B)$, obviously,

$$(B/A)+(A/A)=1 \quad (24)$$

$$(A/B)+(B/B)=1 \quad (25)$$

The probabilities (A, A), (A, B), (B, B) and (B, A) are related to the conditional probabilities (A/B), (A/A), (B/B) and (B/A) through the relations:

$$(A, B)=X_A(B/A) \quad (26)$$

$$(A, A)=X_A(A/A) \quad (27)$$

$$(B, B)=X_B(B/B) \quad (28)$$

$$(B, A)=X_B(A/B) \quad (29)$$

where $X_i(i=A, B)$ are the molar fraction of atom i.

The total nearest neighbour pair number is then:

$$N_{\text{total}}=(Z_AN_A+Z_BN_B)/2 \quad (30)$$

where $Z_i(i=A, B)$ are the co-ordination number of atom i in the solution, $N_i(i=A, B)$ are the number of atom i.

According to the definition of Cowley-Warren chemical short range order parameter α_1 for the first co-ordination shell[5-7], conditional probabilities (A/B), (B/A) are related to α_1 as follows:

$$(A/B)=X_A(1-\alpha_1) \quad (31)$$

$$(B/A)=X_B(1-\alpha_1) \quad (32)$$

Thus, above-mentioned relations are readily reduces to the relations of nearest neighbour pair number and Cowley-Warren chemical short range order parameter, namely

$$\{N_{AB}\}=(A, B)N_{\text{total}}+(B, A)N_{\text{total}}=(Z_AN_A+Z_BN_B)X_AX_B\cdot(1-\alpha_1) \quad (33)$$

$$\{N_{AA}\}=(A, A)N_{\text{total}}=(Z_AN_A+Z_BN_B)X_A\cdot(X_A+X_B\alpha_1)/2 \quad (34)$$

$$\{N_{BB}\}=(B, B)N_{\text{total}}=(Z_AN_A+Z_BN_B)X_B\cdot(X_B+X_A\alpha_1)/2 \quad (35)$$

4.2 Cowley-Warren chemical short range order parameter

When the solution is considered to be an open system, its grand partition function is

$$\Xi=\sum_j\omega\, Q_A^{N_A}(T)\,Q_B^{N_B}(T)\cdot\exp[(\mu_AN_A+\mu_BN_B-E_j)/kT] \quad (36)$$

where $\mu_i(i=A, B)$ denote the chemical potentials of component i, $Q_i(T)(i=A, B)$ are partition functions associated with inner and translational degrees of freedom of atom i, E_j are the configurational energy when the system is in level j.

The solution system can be considered to be composed of lots of small domains, and each domain is also an open system, assuming that the solution system is divided into two domains, domain 1 and domain 2. This enables us to write down the grand partition function as the product of the grand partition of the two domains:

$$\Xi = \Xi_1 * \Xi_2 \qquad (37)$$

where

$$\Xi_1 = \sum_j \omega_1 \zeta_A^{N_{1A}} \zeta_B^{N_{1B}} \cdot \exp[-(E_j + \overline{E}_{12})/kT] \qquad (38)$$

$$\Xi_2 = \sum_j \omega_2 \zeta_A^{N_{2A}} \zeta_B^{N_{2B}} \cdot \exp[-(E_j + \overline{E}_{12})/kT] \qquad (39)$$

$$\zeta_A = Q_A(T)\exp(\mu_A/kT) \qquad (40)$$

$$\zeta_B = Q_B(T)\exp(\mu_B/kT) \qquad (41)$$

$$N_{1A} + N_{2A} = N_A \qquad (42)$$

$$N_{1A} + N_{2B} = N_B \qquad (43)$$

$N_{ij}(j = A, B, i = 1, 2)$ are the particle number of atoms j in domain j. $E_{ij}(i = 1, 2)$ are the configurational energy of domain 1, 2 in level j. $\overline{E}_{12}$ is the average value of the interaction between atoms of domain 1 and domain 2. Estimation of $\exp(-\overline{E}_{12}/kT)$ of equations (38) and (39) is quite difficult, $\overline{E}_{12}$ is related to concentration, coordination number, atomic volume and so on. Instead of making a rigorous approach, we resort to a simple approximation for $\overline{E}_{12}$ which is gained by Fowler and Guggenheim[8]:

$$\exp(-\overline{E}_{12}/kT) \approx \Phi_A^{f_A} \Phi_B^{f_B} \qquad (44)$$

where f_A are the numbers of atoms in domain 2 which are the nearest neighbours of atom A in domain 1, f_B is similar to f_A; Φ_A, Φ_B are constant.

Therefore,

$$\Xi = \sum_j \omega_1 \zeta_A^{N_{1A}} \zeta_B^{N_{1B}} \Phi_A^{f_A} \Phi_B^{f_B} \exp(-E_{ij}/kT) \qquad (45)$$

When there is only one atom in domain 1, no pair(AA, AB or BB) is existing in the system, the configurational energy E_1 is zero. The nearest neighbours of atom A, B in domain 2 are equal to their coordination number, thus grand partition Ξ of the system composed of domain 1 can be written as

$$\Xi_1^{(1)} = \zeta_A \Phi_A^{Z_A} + \zeta_B \Phi_B^{Z_B} \qquad (46)$$

When there are two atoms in domain 1, pair (AA, AB or BB) is existing in the system, the configurational energy E is not equal to zero, and the devotion of pair which becomes a part of compound A_xB_y to interaction energy must also be considered, therefore its grand partition can be obtained as

$$\Xi_1^{(2)} = \zeta_A^2 \Phi_A^{2(Z_A-1)} Q_{AA} + \zeta_B^2 \Phi_B^{2(Z_B-1)} Q_{BB} + \zeta_A \Phi_A^{Z_A-1} \zeta_B^{Z_B-1} Q_{AB} \qquad (47)$$

and

$$Q_{ij} = \exp[-(\varepsilon_{ij} + P_{ij}\triangle\varepsilon_{ij})/kT] \quad (i, j = A, B) \qquad (48)$$

where $\varepsilon_{ij}(i, j = A, B)$ are the interaction energy between $i.j$, $\triangle\varepsilon_{ij}(i, j = A, B)$ are the devotion of pair forming chemical bond to interaction energy. By employing Eqn.(47), we can immediately express the probabilities of two atom i, $j(i, j = A, B)$ becoming the nearest neighbour.

$$(A, A) = \zeta_A^2 \Phi_A^{2(Z_A-1)} Q_{AA}/\Xi_1^{(2)} \qquad (49)$$

$$(B, B) = \zeta_B^2 \Phi_B^{2(Z_B-1)} Q_{BB}/\Xi_1^{(2)} \qquad (50)$$

$$(B, A) = (A, B) = \zeta_A \Phi_A^{Z_A-1} \zeta_B \Phi_B^{Z_B-1} Q_{AB}/\Xi_1^{(2)} \qquad (51)$$

Therefore,

$$\frac{(A, A)*(B, B)}{(A, B)^2} = Q_{AA} * Q_{BB}/Q_{AB}^2 \qquad (52)$$

By setting

$$\eta^2 = Q_{AA} * Q_{BB}/Q_{AB}^2 \qquad (53)$$

Equation (50) provides

$$(A, A)*(B, B)/(A, B)^2 = \eta^2 \qquad (54)$$

Equations (36) ~ (39) and(54) provide

$$(A, B) = \frac{2X_AX_B}{(\beta + 1)} \qquad (55)$$

where

$$\beta = \sqrt{1 + 4X_AX_B(\eta^2 - 1)} \qquad (56)$$

Equations (36), (41) and (56) further yield

$$\alpha_1 = (\beta - 1)/(\beta + 1) \qquad (57)$$

4.3 Nearest neighbour pair number

By making use of the relations of nearest neighbour pair number to chemical short range parameter to the relations of chemical short range parameter and interaction energy between atoms, we readily obtain the relation of nearest neighbour pair number and interaction energy as follows.

$$\{N_{AB}\} = 2(Z_A N_A + Z_B N_B) X_A / (\beta + 1) \quad (58)$$

$$\{N_{AA}\} = (Z_A N_A + Z_B N_B) X_A \cdot (\beta - 1 + 2X_A)/2(\beta + 1) \quad (59)$$

$$\{N_{BB}\} = (Z_A N_A + Z_B N_B) X_B \cdot (\beta + 1 - 2X_A)/2(\beta + 1) \quad (60)$$

From the above equations, we can know that if the interaction energy between atoms $\varepsilon_{ij}(i, j = A, B)$, devotion of forming chemical bond to interaction energy $\Delta\varepsilon_{ij}(i, j = A, B)$ and the probabilities of forming chemical bond are given, neighbour pair number can be obtained.

5 PROBABILITIES OF FORMING CHEMICAL BOND

Assuming that if $(X-1)A$, $(Y-1)B$ are the nearest neighbour of pair AB, compound A_xB_y is formed, thus the probabilities of pairwise(i, j) becoming a part of compound A_xB_y are

$$P_{AB} = [(B/B)^Y - (B/A)^Y] \cdot [(A/A)^X - (A/B)^X] / [(A/A) - (A/B)]^2 \quad (61)$$

$$P_{AA} = (X-1)(Y+1) \cdot (A/A)^{X-2}(B/A)^Y \quad (62)$$

$$P_{BB} = (X+1)(Y-1) \cdot (A/B)^X (B/B)^{Y-2} \quad (63)$$

When X or Y equals to one, the chemical bond AA or BB does not exist in solution, in this instance, P_{AA} or P_{BB} is zero, the above equations (62) and (63) are also correct.

6 THEORETIC FORMULAE FOR CALCULATING COORDINATION NUMBER

According to the relations of conditional probabilities, concentration and interaction energies in binary system, theoretic formulae of calculating coordination number can be obtained. Generally, atoms in liquid binary alloy are close to each other as shown in figure 1. Obviously, EF is at right angles with AB, EG is at right angles with CD. Relying on theorem about triangle, triangle ABF, ABE, GDC and EDC are right triangles.

In right triangles ABF and ABE,

$$AB^2 + (R_A - H_{A2})^2 = R_A^2 \quad (64)$$

$$AB^2 + (R_A + H_{A2})^2 = (\mathrm{MIN}(R_A, R_B) + R_A)^2 \quad (65)$$

Equations (64) and (65) provide

$$H_{A2} = [(\mathrm{MIN}(R_A, R_B))^2 + 2R_A \mathrm{MIN}(R_A, R_B)]/4R_A \quad (66)$$

$$H_{A1} = \mathrm{MIN}(R_A, R_B) - H_{A2} = [-(\mathrm{MIN}(R_A, R_B))^2 + 2R_A \mathrm{MIN}(R_A, R_B)]/4R_A \quad (67)$$

Similarly,

$$H_{B2} = [(\mathrm{MIN}(R_A, R_B))^2 + 2R_A \mathrm{MIN}(R_A, R_B)]/2(R_A + R_B) \quad (68)$$

$$H_{B1} = [2R_B \mathrm{MIN}(R_A, R_B) - (\mathrm{MIN}(R_A, R_A))^2]/2(R_A + R_B) \quad (69)$$

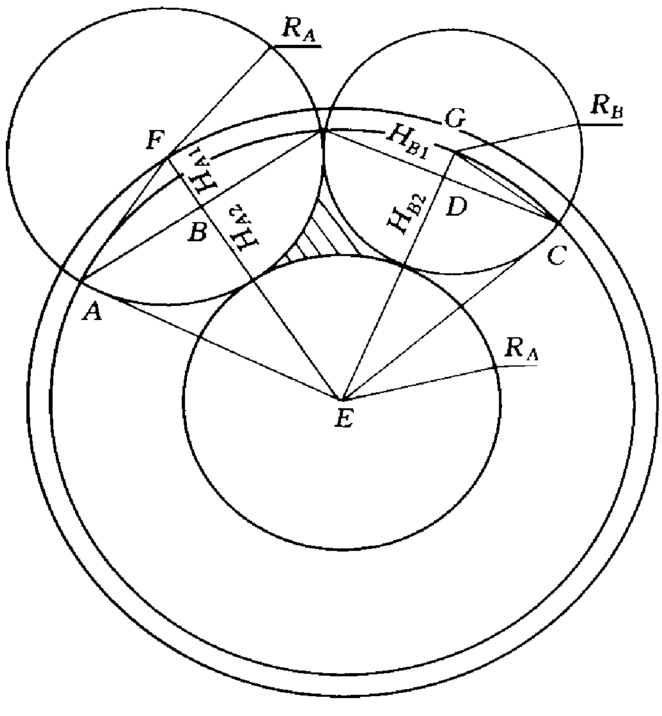

Fig. 1 Sketch of atom distribution

From equations (66), (67), (68) and (69), H_{A2}, H_{A1}, H_{B2}, H_{B1} can be calculated. According to the volume formula, volume of single coordination atom A or B in the globe whose radius is $R_A + \mathrm{MIN}(R_A, R_B)$ and whose center is E can easily be obtained,

$$V_{AA} = \frac{\pi}{3}[H_{A1}^2(R_A +$$

$$\mathrm{MIN}(R_A, R_B)) - H_{A1}] + H_{A2}^2(3R_A - H_{B2})] \qquad (70)$$

$$V_{AB} = \frac{\pi}{3}[H_{B1}^2(R_A + \mathrm{MIN}(R_A, R_B)) - H_{B1}] + H_{B2}^2(3R_B - H_{B2})] \qquad (71)$$

V_{AA}, V_{AB} denote volume of the single coordination atom A and B. Simultaneously, coordination numbers Z_{AA}, Z_{AB} are related to conditional probabilities (B/A), (A/A) and coordination numbers Z_A through

$$Z_{AB} = (B/A)Z_A \qquad (72)$$

$$Z_{AA} = (A/A)Z_A \qquad (73)$$

where Z_A denotes coordination numbers of atom A, Z_{AB} and Z_{AA} denote number of atom B and A around atom A. Thus the volume occupied by the coordination atoms A and B can be expressed as

$$\begin{aligned} V_{co\text{-}A} &= Z_{AA}V_{AA} + Z_{AB}V_{AB} \\ &= \frac{\pi}{3}Z_A\{(A/A)[H_{A1}^2(R_A + \mathrm{MIN}(R_A, R_B) - H_{A1}) + H_{A2}^2(3R_A - H_{A2})] + \\ &\quad (B/A)[H_{B1}^2(3(R_A + \mathrm{MIN}(R_A, R_B) - H_{B1}) + H_{B2}^2(3R_B - H_{B2})]\} \end{aligned} \qquad (74)$$

The volume occupied by the coordination atoms A and B can also be expressed as

$$V'_{co-A} = 4\pi/3\{[R_A + \mathrm{MIN}(R_A, R_B)]^3 - R_A^3\} \qquad (75)$$

Combine Eqn. 74 and Eqn. 75, co-ordination numbers Z_A of atom A are obtained as:

$$\begin{aligned} Z_A = {} & 4\{[\bar{R}_A + \mathrm{MIN}(\bar{R}_A, \bar{R}_B)]^3 - \bar{R}_A{}^3\}/\{(A/A)[H_{A1}^2(3(R_A + \mathrm{MIN}(R_A, R_B)) - H_{A1}) + \\ & H_{A2}^2(3R_A - H_{A2})] + (B/A)[H_{B1}^2(3(R_A + \mathrm{MIN}(R_A, R_B)) - H_{B1}) + H_{B2}^2(3R_B - H_{B2})]\} \end{aligned} \qquad (76)$$

Similarly,

$$\begin{aligned} Z_B = {} & 4\{[\bar{R}_B + \mathrm{MIN}(\bar{R}_A, \bar{R}_B)]^3 - \bar{R}_B{}^3\}/\{(A/B)[H_{A1}^2(3(R_B + \mathrm{MIN}(R_A, R_B)) - H_{A1}) + \\ & H_{A2}^2(3R_A - H_{A2})] + (B/B)[H_{B1}^2(3(R_B + \mathrm{MIN}(R_A, R_B)) - H_{B1}) + H_{B2}^2(3R_B - H_{B2})]\} \end{aligned} \qquad (77)$$

In the above formulae, the atom radius is denoted with different symbol, because the interstitial volume is a part of the volume measured by its radius from equation (74), but it is not a part of that from equation (75); although using the same radius, the error will be very great in equation (74). Therefore we use density radius calculated from mass density instead, the density radius is as follows:

$$R = [3M/4\rho\pi N^\circ]^{1/3} \qquad (78)$$

where M is molar weight, ρ is density.

7 NUMERICAL VALUES OF CO-ORDINATION NUMBER

In general, the interaction energy between atoms increases with bond energy. Because of datum shortage of interaction energy, bond energy was substituted for interaction energy, calculated results are shown in Table 1.

Table 1 Coordination number

Alloys ($A-B$)	Z_A (calculated)	Z_A (ref.)	relative error/ %	references
$Fe_{0.83}B_{0.17}$	12.52	13.2	5.15	[9]
$Ni_{0.64}B_{0.34}$	12.6	13.0	3.00	[9]
$B_{0.36}Ni_{0.64}$	9.93	9.0	10.33	[9]
$Cu_{0.60}Zr_{0.40}$	11.4	10.3	7.18	[10]
$Co_{0.80}P_{0.20}$	11.61	12.3	5.61	[11]
$Co_{0.75}P_{0.25}$	11.69	13.0	10.76	[11]
$Fe_{75.7}P_{24.3}$	11.76	12.78	7.98	[12]
$Fe_{0.75}P_{0.25}$	11.7	13.0	9.46	[13]
$P_{0.25}Fe_{0.75}$	10.15	11.9	14.71	[13]
$Fe_{0.82}P_{0.18}$	11.64	12.54	7.12	experiment
$P_{0.18}Fe_{0.82}$	10.15	11.90	14.71	experiment

8 CONCLUSIONS

(1) From the view of chemical short range and incomplete random mixing existing in liquid binary alloy solution, absorbing the rational part of past statistical mechanics model, a new model

of liquid binary alloy solution has been proposed in this paper. According to the model, expressions of component activity of liquid binary alloy solution are obtained.

(2) According to the model, the formulae of calculating probabilities of forming chemical bond *i-j*, nearest neighbour pair number, Cowley-Warren chemical short range order etc. are obtained.

(3) According to the relation of co-ordination number and condition probabilities, using geometrical relation of atoms distribution, formulae of co-ordination number in liquid binary alloy are obtained.

(4) According to the formulae and reference data, numerical values of co-ordination number are obtained. The results agree well with the reference data and experiment data within the range of error, the key problem about coordination number is solved.

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however, the diamond prepared using No. 2 catalyst not only has higher single yield, but also has larger proportion of coarse particles. Based on the above analyses, the authors think that, the solid phase transformation theory is probably not the sole mechanism responsible for the growth of the diamond; it only makes the graphite nucleates preferably and grows continuously with the progress of the synthesis and the grains will be coarse and perfect because of the relatively long growth time. The nucleation and growth of the diamond can also be completed by the dissolution and precipitation of the graphite in the catalyst. This process will not begin until the catalyst has melted, therefore it is relatively lagging. Furthermore, the diamond may grow using the impurity particles of high melting points in the catalyst as nuclei, thus the resultant diamond is fine-grained and imperfect and has mixed colors under the conditions of identical growth conditions and synthesis time.

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