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Comparison of Some Methods on Prediction of Activity Interaction Coefficient

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Abstract: Based on Miedema's semiempirical formation enthalpy model for binary alloys, free volume theory and a general solution model, a new model for prediction of activity interaction coefficient ε_i^j is proposed. The calculated results are better in agreement with the experimental values than the two previous models. The related theories and models are discussed according to the degree of agreement with experimental values.
Key words: Miedema's semiempirical formation enthalpy model; activity interaction coefficient; free volume theory; similarity coefficient

Nomenclature

x — mole fraction
γ — activity coefficient
V — mole volume
R — gas constant
T — thermodynamical temperature
T_i — melting temperature of element i, K
ε — activity interaction coefficient
φ — electroneutrality
n_{ws} — electronic density
G^E — partial excess Gibbs free energy
H_{mix} — enthalpy of mixing
$\Delta_{mix}H^E$ — mixing excess enthalpy
$\Delta_{mix}S^E$ — mixing excess entropy
$\Delta\varphi$ — difference of φ_A and φ_B
$\Delta(n_{ws})$ — difference of $(n_{ws})_A$ and $(n_{ws})_B$
$\Delta_{mix}G^E$ — mixing excess Gibbs free energy

Activity coefficient is related to the mixing excess Gibbs free energy, in a binary system A—B:

$$\Delta_{mix}G^E = RT(x_A \ln\gamma_A + x_B \ln\gamma_B) \quad (1)$$

$\Delta_{mix}G^E$ is defined as:

$$\Delta_{mix}G^E = \Delta_{mix}H^E - T\Delta_{mix}S^E \quad (2)$$

From Eqs. (1) and (2), if the calculation equations of $\Delta_{mix}H^E$ and $\Delta_{mix}S^E$ are known, then the prediction of activity coefficient can be done.

Recently, Miedema's semiempirical formation enthalpy model for binary system has been successfully used in prediction of activity coefficients[1]. $\Delta_{mix}S^E$ is obtained by combining first approximation to regular solution with free volume theory[2]. Then, $\Delta_{mix}G^E$ for a binary system is obtained.

When consideration of ternary or multi-component system is taken, geometrical model is often used. According to the different weight factor, geometrical models are classified into symmetrical model and asymmetrical model. The symmetrical model seems too simple and the asymmetrical model is not reasonable because of the interference of human being. Kuo-Chih Chou proposed a new model called a general solution model[3], in which three similarity coefficients are introduced for ternary system. This model is takes advantages of former geometrical models.

1 Derivation of New Equation

According to the thermodynamic relationships and definition of activity interaction coefficient[4], formula of ε_i^j is obtained as follows:

$$\varepsilon_i^j = (a + b + c) / RT \quad (3)$$

where,

$$a = \frac{f_{ki}}{V_i^{2/3}V_k^{2/3}}\{-[1+u_i(\varphi_i-\varphi_k)]V_i^{2/3} - V_i^{2/3}(\varphi_i-\varphi_k)(1-\xi_{ki})[u_i+u_k+u_iu_k(\varphi_i-\varphi_k)] -$$
$$\frac{V_i^{2/3}}{V_k^{2/3}}[1+u_i(\varphi_i-\varphi_k)](1-\xi_{ki})[V_i^{2/3}[1+u_i(\varphi_i-\varphi_k)] + V_k^{2/3}[1+u_k(\varphi_k-\varphi_i)] - 2V_k^{2/3}]\} \cdot \left[1-\frac{T}{14}\left(\frac{1}{T_i}+\frac{1}{T_k}\right)\right]$$

$$b = \frac{f_{jk}}{V_j^{2/3}V_k^{2/3}}\{-[1+u_j(\varphi_j-\varphi_k)]V_j^{2/3}-V_i^{2/3}(\varphi_i-\varphi_k)\cdot\xi_{ik}\cdot[u_i+u_k+u_ju_k(\varphi_j-\varphi_k)]-$$
$$\frac{V_j^{2/3}}{V_k^{2/3}}[1+u_j(\varphi_j-\varphi_k)]\cdot\xi_{jk}\cdot[V_j^{2/3}[1+u_j(\varphi_i-\varphi_k)]+V_k^{2/3}[1+u_k(\varphi_k-\varphi_j)]-2V_k^{2/3}]\}\cdot\left[1-\frac{T}{14}\left(\frac{1}{T_j}+\frac{1}{T_k}\right)\right]$$

$$c = \frac{f_{ij}[1+u_i(1-\xi_{ij})(\varphi_i-\varphi_j)]\cdot[1+u_j\xi_{ij}(\varphi_j-\varphi_i)]}{V_i^{2/3}\xi_{ij}[1+u_i(1-\xi_{ij})(\varphi_i-\varphi_j)]+V_j^{2/3}[1+u_j\xi_{ij}(\varphi_i-\varphi_j)]}\cdot\left[1-\frac{T}{14}\left(\frac{1}{T_i}+\frac{1}{T_j}\right)\right]$$

Where, ξ_{AB}(A, B = i, j) is the similarity coefficients.

$$f_{AB} = \frac{2pV_A^{2/3}V_B^{2/3}\left[\frac{q}{p}(\Delta n_{ws}^{1/3})^2-(\Delta\varphi)^2-a\cdot\frac{r}{p}\right]}{(n_{ws}^{1/3})_A^{-1}+(n_{ws}^{1/3})_B^{-1}} \quad (4)$$

Where p, q, r, u, and a are all empirical constants, their values are given in the reference [5].

2 Calculation and Comparison

Some values for activity interaction coefficients in Ni- and Co-base liquid alloys are obtained by use of new equation for ε_i^j and compared with the experimental values[6] and with the values by use of two previous models in which the general solution model is not used[2]. Fig. 1 ~ Fig. 4 illustrate the comparison, where "Cal I" means the results when Toop model is used and mixing excess entropy is neglected; "Cal II" means the results when Toop model is used and mixing excess entropy is considered; "Cal III" means the results of this article.

In Fig 1, three kinds of calculated values agree with the experimental results in sign. "Cal II" varies in the same tendency as "Cal I", and "Cal II" approaches the experimental values more closely than "Cal I", which means that considering mixing excess entropy has slight improvement, but not apparently.

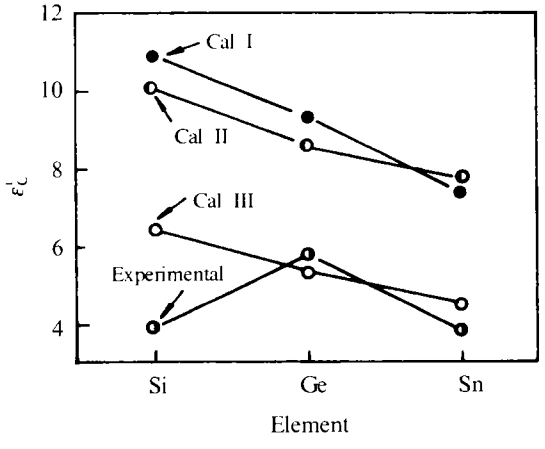

Fig. 1 Comparison of some calculated values of ε_C^i in Ni-based alloys at 1879K

"Cal III" approaches the experimental values most closely and both distribute in one quantity order, which implies the certain accuracy of the application of similarity coefficient in calculation.

In Fig 2, some values of ε_N^i are listed. "Cal I" and "Cal III" accord with the experimental values in sign and changing tendency, and "Cal III" approaches the

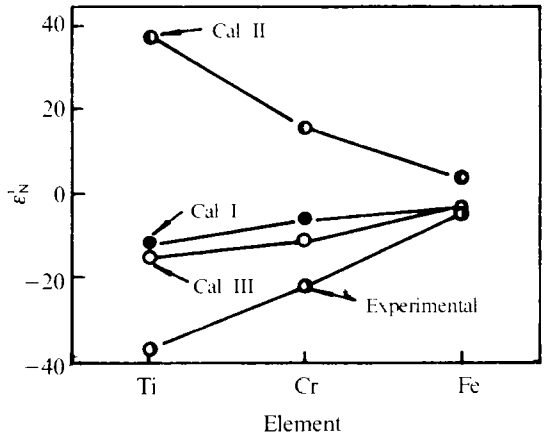

Fig. 2 Comparison of some calculated values of ε_N^i in Ni-based alloys at 1879

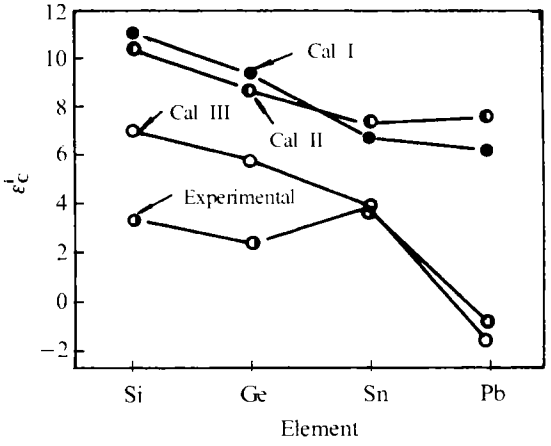

Fig. 3 Comparison of some calculated values of ε_C^i in Co-based alloys at 1879

experimental values more closely than "Cal I". But "Cal II" deviates from the experimental values apparently, not only in sign but in changing tendency. This phenomenon may result from the consideration of mixing excess entropy. According to free volume

theory[7], it is only applicable to those system in which the ratio of component's atom radiuses is approximate to 1. In the gas-contained system, this can not be met.

In Fig 3, three kinds of calculated values accord

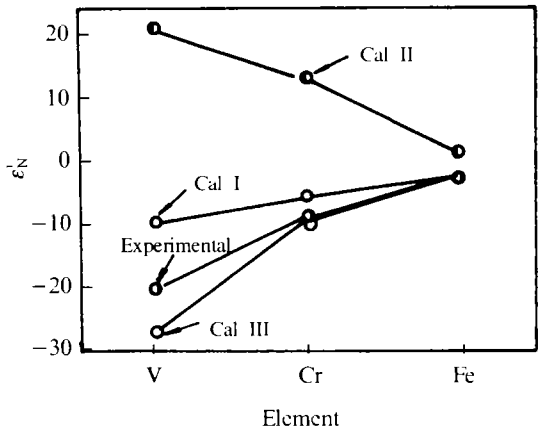

Fig.4 Comparison of some calculated values of ε_N^V in Co-based alloys at 1879

with the experimental values in changing tendency. "Cal I" and "Cal II" is slightly different, and "Cal III" has the best agreement with the experimental values, both in sign and quantity order.

In Fig 4, "Cal II" deviates from the experimental values apparently, and the other two kinds of calculation agree well with the experimental values.

4 Discussion

It seems from the calculation and comparison in this article that the application of Miedema's model for formation heat and similarity coefficient has certain accuracy in prediction of activity interaction coefficient, and consideration of mixing excess entropy has different effects in different cases, so it is necessary to evaluate those related theories and models in the calculation.

(1) Miedema's model for formation heat

Miedema's model for formation enthalpy is valid for the whole concentration range, which makes it possible to calculate activity coefficient between elements through mathematical derivation and thermodynamic theories. But some parameters of some common elements such as O, S are lacked, this limits the model's application and should be resolved urgently.

(2) Free volume theory

This theory is successfully used in estimation of the melt's excess entropy, but it also has its limitation. It is valid and accurate only to those system with ratio of component's atom radiuses within 1～1.26. When used to system containing gas elements whose atom radiuses are very little, more effective and accurate formula should be suggested.

(3) Geometrical model

Because of the complexion of interaction among elements in actual melts, the way of classifying systems into special geometrical kinds seems inflexible and too simple, and then not accurate. This may be just cause and unavoidable result of the suggestion of so many geometrical models.

(4) Similarity coefficient and a general solution model

This model describes the thermodynamic properties of melts in a relatively reasonable way by application of similarity coefficient, which has a breakthrough in research on multi-component melts.

5 Conclusions

A new equation of activity interaction coefficient is proposed on basis of Miedema's model for formation heat, free volume theory and a general solution model. Some calculated values are compared with the experimental values and some former calculated values in references. The results implied that application of similarity coefficient in prediction of activity interaction coefficient is effective and valid.

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