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Application of annexation principle to the study of thermodynamic properties of Ag-Bi-In metallic melts

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Abstract: Based on the measured activities, the phase diagrams and the annexation principle, the calculating models of mass action concentrations for Ag-Bi and Ag-Bi-In melts have been formulated. The calculated results agree with practice and obey the mass action law, showing that the models formulated can reflect the structural characteristics of both melts. Meanwhile, it confirms that annexation principle is applicable to the Ag-Bi-In metallic melts. The melts involving eutectic which give rise to phase separation, and in which activities exhibit positive deviation from Raoult's law is the basic cause of melts transforming from homogeneous to heterogeneous ones.

Key words: the mass action law; annexation principle; two phase melts; activity, mass action; concentration

1 Introduction

In reference [1-3] two kinds of calculating model of binary metallic melts have been introduced, *i.e.*, single phase model: it is used for metallic melts, which obey both the mass action law, and the Raoult's law, and their activity exhibits negative deviation from Raoultian behavior;

$$\begin{cases} xA_{(l)} + yB_{(l)} = A_xB_{y(l)} \\ K_i = N_i/N_1^xN_2^y \\ N_i = K_iN_1^xN_2^y \end{cases} \quad (1)$$

$$N_1 + N_2 + \Sigma K_iN_1^xN_2^y - 1 = 0 \quad (2)$$

$$aN_1 - bN_2 + \Sigma K_i(xa - yb)N_1^xN_2^y = 0 \quad (3)$$

$$1 - (a+1)N_1 - (1-b)N_2 = \Sigma K_i(xa - yb + 1)N_1^xN_2^y \quad (4)$$

and two phase model: it is used for metallic melts, which obey mass action law , but not the Raoult's law, their activity exhibits positive(or negative) deviation from Raoultian behavior.

$$\begin{cases} N_1 + x\Sigma K_iN_1^xN_2^y/b = 1 \\ N_2 + y\Sigma K_iN_1^xN_2^y/a = 1 \end{cases} \quad (5)$$

$$K_i = ab(2 - N_1 - N_2)/(xa + yb)N_1^xN_2^y \quad (6)$$

Where the compositions of components 1 and 2 of the melts are respectively $a = \Sigma x_1$, $b = \Sigma x_2$; the mass action concentrations of every structural unit are respectively N_1, N_2, $N_i = K_iN_1^xN_2^y$.

When a ternary metallic melts are composed of two kinds of melts (one homogeneous, and the other heterogeneous), since only one kind of model could formulated for them (single phase or two phase), hence there would be annexation of one kind of melts by the other during formation of a ternary metallic melts.

The goal of this paper is just to introduce the application of annexation principle to the study of thermodynamic properties of Ag-Bi-In melts. As these melts consist of three binary melts, so the discussion begins with the binary metallic melts.

2 Ag-Bi melts

According to the phase diagram [4], this binary system is a eutectic, the activities of which exhibit unsymmetrical positive deviation from Raoult's law [5,6], hence these melts are two phase in structure. After examination with a lot of variants, it is found that the one with metastable compound Ag_3Bi_2 gives the best agreement with practice. Putting the composition of the melts as $a=\Sigma x_1$, $b=\Sigma x_2$; the mass action concentration of every structural unit after normalization as $N_1=N_{Ag}$, $N_2=N_{Bi}$, $N_3=N_{Ag_3Bi_2}$, the calculating model of mass action concentrations for these melts are:

$$3Ag_{(l)} + 2Bi_{(l)} = Ag_3Bi_{2(l)} \quad (7)$$

$$\begin{cases} N_1 + 3KN_1^3N_2^2/b = 1 \\ N_2 + 2KN_1^3N_2^2/a = 1 \end{cases} \quad (8)$$

$$K = ab(2 - N_1 - N_2)/(3a + 2b)N_1^3N_2^2 \quad (9)$$

Using measured activities from references [5,6] and equation (9), the Gibbs free energy of Ag_3Bi_2 was evaluated as $\Delta G^{\ominus}_{980-1073K} = -5\,137.447 - 3.31T(J\cdot mol^{-1})$. Substituting it into equation (8) gives the comparison of calculated mass action concentrations with measured activities as shown in **figure 1**. It is seen in the figure

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1 that the calculated values agree with the measured ones, and they obey the mass action law, showing that the aforementioned model reflects the structural characteristics of these melts.

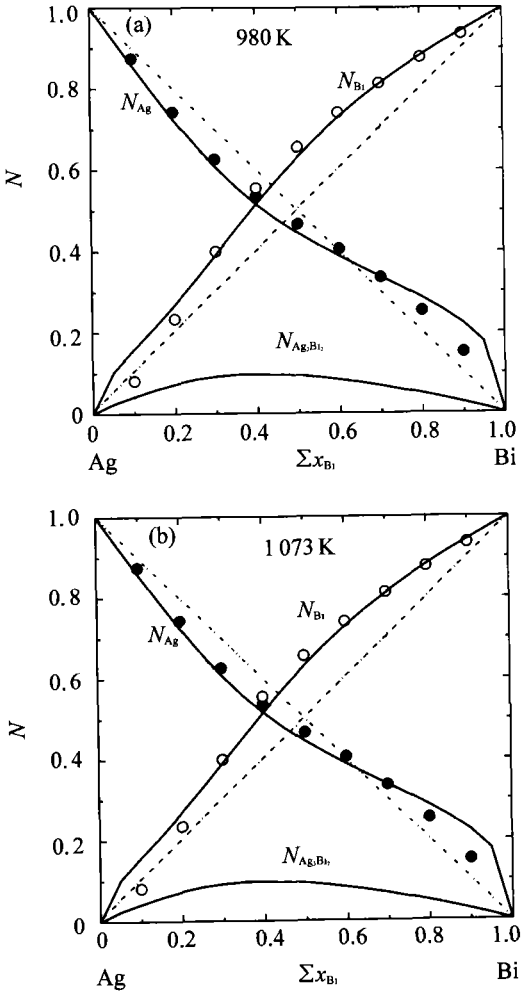

Figure 1 Comparison of calculated mass action concentrations N (—) with measured activities a (•, ○) for Ag-Bi melts.

3 Ag-In melts

As stated in reference [7], the compounds of this binary system are all peritectics, hence the melts are homogeneous. However, as the activities of Ag-Bi melts exhibit unsymmetrical positive deviation relative to Raoult's law, the homogeneous melts, owing to the restriction $\Sigma N_i = 1$, is not able to express the positive deviation of activity. So Ag-In melts had to be annexed by the two phase melts Ag-Bi. It has been determined in reference [8], that in condition of two phase Ag-In melts, consideration of the presence of metastable compounds AgIn and Ag_3In gives the best agreement with practice. Hence the structural units of these melts are Ag, In atoms as well as AgIn and Ag_3In metastable compounds, and they form two solutions Ag+AgIn+Ag_3In and In+ AgIn+Ag_3In. The compound formation reactions and thermodynamic parameters are respectively:

$$\begin{cases} Ag_{(l)} + In_{(l)} = AgIn_{(l)} \\ \Delta G^{\ominus} = -3\,207.585 - 7.466T,\ J\cdot mol^{-1} \end{cases} \quad (10)$$

$$\begin{cases} 3Ag_{(l)} + In_{(l)} = Ag_3In_{(l)} \\ \Delta G^{\ominus} = -26\,487.756 + 9.20T,\ J\cdot mol^{-1} \end{cases} \quad (11)$$

The calculating model of mass action concentrations and the calculated results are illustrated in reference [8], here they are omitted.

4 Bi-In melts

According to the phase diagram [4], there are three compounds BiIn, Bi_5In_3 and $BiIn_2$ formed in this binary system, in which BiIn and $BiIn_2$ are compounds with congruent melting point, while Bi_5In_3 is a peritectic. Hence, these binary melts are typical homogeneous melts. In general, their structural units are Bi and In atoms as well as compounds BiIn, Bi_5In_3 and $BiIn_2$. However, owing to the positive deviation of activities of the binary melts Ag-Bi in ternary melts Ag-Bi-In with respect to th Raoult's law, under the effect of their annexation, during the formation of ternary melts Ag-Bi-In, Bi-In melts would also transform into two phase melts, which were otherwise studied [3]. Here only the corresponding chemical reactions and thermodynamic parameters are given respectively as follows:

$$\begin{cases} Bi_{(l)} + In_{(l)} = BiIn_{(l)} \\ \Delta G^{\ominus} = -6\,972.069 + 1.656T,\ J\cdot mol^{-1}\ (900-1\,200\,K) \end{cases} \quad (12)$$

$$\begin{cases} Bi_{(l)} + 2In_{(l)} = BiIn_{2(l)} \\ \Delta G^{\ominus} = 1\,912.584 + 8.84T,\ J\cdot mol^{-1}\ (900-1\,200\,K) \end{cases} \quad (13)$$

5 Ag-Bi-In melts

From the above mentioned discussion, it is evident that Ag-Bi-In melts are heterogeneous in structure, their structural units are Ag, Bi, In atoms as well as Ag_3Bi_2, AgIn, Ag_3In, BiIn and $BiIn_2$ compounds, and they form three solutions Ag+Ag_3Bi_2+AgIn+Ag_3In, Bi+Ag_3Bi_2+BiIn+$BiIn_2$ and In+AgIn+Ag_3In+BiIn+$BiIn_2$. Assuming the composition of the melts as $a=\Sigma x_{Ag}$, $b=\Sigma x_{Bi}$, $c=\Sigma x_{In}$; the equilibrium mole fraction of every structural unit expressed by the composition of the melts as $x=x_{Ag}$, $y=x_{Bi}$, $z=x_{In}$, $u_1=x_{Ag_3Bi_2}$, $u_2=x_{AgIn}$, $u_3=x_{Ag_3In}$, $u_4=x_{BiIn}$, $u_5=x_{BiIn_2}$; the mass action concentration of every structural unit as $N_1=N_{Ag}$, $N_2=N_{Bi}$, $N_3=N_{In}$, $N_4=N_{Ag_3Bi_2}$, $N_5=N_{AgIn}$, $N_6=N_{Ag_3In}$, $N_7=N_{BiIn}$, $N_8=N_{BiIn_2}$, then it gives chemical equilibria: equations (7), (10), (11), (12), and (13), mass balance:

$$\begin{cases} a = x + 3u_1 + u_2 + 3u_3 \\ b = y + 2u_1 + u_4 + u_5 \\ c = z + u_2 + u_3 + u_4 + 2u_5 \end{cases} \quad (14)$$

$$N_1+(3K_1N_1^3N_2^2+K_2N_1N_3+3K_3N_1^3N_3)/a=1 \quad (15)$$

$$N_2+(2K_1N_1^3N_2^2+K_4N_2N_3+K_5N_2N_3^2)/b=1 \quad (16)$$

$$N_3+(K_2N_1N_3+K_3N_1^3N_3+K_4N_2N_3+2K_5N_2N_3^2)/c=1 \quad (17)$$

Addition of equations (15)+(16)+(17) gives:

$$abc(3-N_1-N_2-N_3)=c(2a+3b)K_1N_1^3N_2^2+b(c+a)K_2N_1N_3+b(3c+a)K_3N_1^3N_3+a(b+c)K_4N_2N_3+a(2b+c)K_5N_2N_3^2 \quad (18)$$

Equations (15),(16),(17) and (18) are the calculating model of mass action concentrations for these melts, in which equatins (15),(16) and (17) are used to calculate the mass action concentrations, while equation (18) for evaluation of equilibrium constants.

Using the aforementioned model, the calculated mass action concentrations N_{In} are compared with the measured activities a_{In} from reference [9] as shown in **figure 2**. It is seen in the figure 2 that the calculated values agree with the measured ones, and they obey the mass action law, this in turn shows that the preceding model can represent the structural characteristics of these melts. Meanwhile, it shows that annexation principle is applicable to the ternary metallic melts Ag-Bi-In. In addition, there are also calculated N_{Ag} and N_{Bi} in figure 2. As there isn't any measured a_{Ag} and a_{Bi} to compare with, so they are given only for reference.

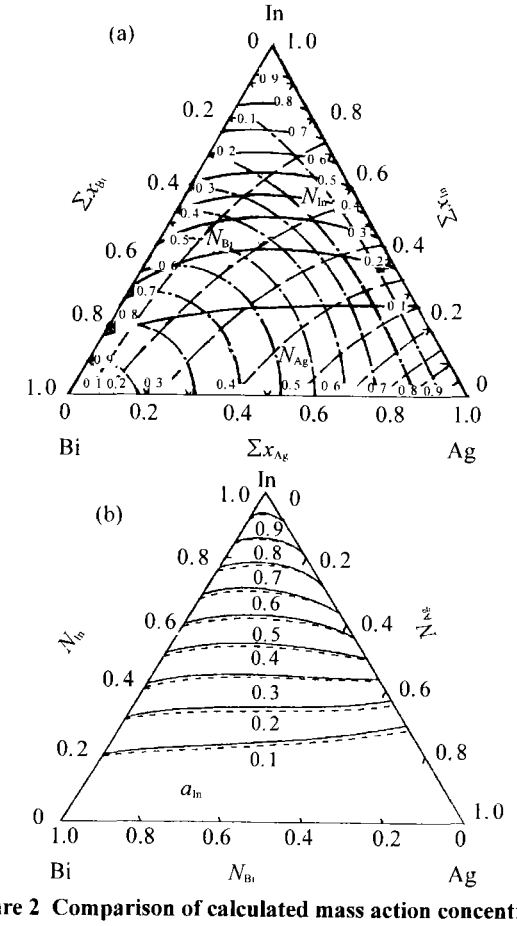

Figure 2 Comparison of calculated mass action concentrations N_{In} (a) with measured activities a_{In} (b) for Agi-Bi-In melts at 1 100 K, a_{In}—1 100 K, ……1 200 K.

From the calculation of thermodynamic properties of these ternary melts, it is clear that the melts involving eutectic which give rise to phase separation, and in which activities exhibit positive deviation from Raoult's law is the basic cause of melts transforming from homogeneous to heterogeneous ones.

6 Conclusions

(1) Based on the phase diagrams and annexation principle, the calculating models of mass action concentrations for Ag-Bi and Ag-Bi-In melts have been formulated. The calculated results agree with practice and obey the mass action law, showing that the models formulated can reflect the structural characteristics of both melts.

(2) The melts involving eutectic which give rise to phase separation, and in which activities exhibit positive deviation from Raoult's law is the basic cause of melts transforming from homogeneous to heterogeneous ones.

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