*Journal of University of Science and Technology Beijing*
*1994, Vol 1, No 1 ~ 2 : 22 ~ 30*

# Calculating Models of Mass Action Concentrations of Binary Metallic Melts Involving Eutectic

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**ABSTRACT** Based on the appearance of minima of the free energy of mixing and maxima (or minima) of excess free energy, the formation of metastable compounds and eutectics during rapid solidification of metallic melts as well as the presence of miscibility gaps in the phase diagrams of a lot of binary alloys, calculating models of mass action concentrations for Cd－Bi, Ge－Al; Bi－Sn, Cd－Sn, Ag－Cu, Al－Ga; Si－Ag, Pb－Sn and Al－Sn binary metallic melts have been deduced. Good agreement between the calculated and measured values shows that the calculating models reflect the structural characteristics of given metallic melts.

**KEY WORDS** activity, metastable phase, eutectic, mass action concentration

For metallic melts involving compound formation in the corresponding phase diagrams, the coexistence theory of metallic melts structure involving compound formation had been proposed , it had been used in many conditions[1 ~ 3], and showed its exellent applicability. But for metallic melts involving eutectic in the corresponding phase diagrams, for example Cd－Bi, Bi－Sn, Si－Ag, Pb－Sn etc., there isn't any model by means of which, the mass action concentrations of concerned systems can be calculated. In the present paper, an attempt is made to resolve the problem mentioned above.

## 1 Calculating Models

Looking at the thermodynamic characteristics of Cd－Bi, Ge－Al, Cd－Sn, Bi－Sn, Ag－Cu and Al－Ga systems in the Tab.1[4] , it is shown that the free energies of mixing $\Delta G$ exhibit minima, and the excess free energies $\Delta G^{xs}$ exhibit maxima (or minima), in addition, the absolute majority of minima of $\Delta G$ and maxima (or minima) of $\Delta G^{xs}$ is located at $x_i = 0.5$, thus it indicates the possibility of AB－form compound formation, because thermodynamic data are the direct reflection

Received 1994－05－10

of structural characteristics of metallic melts[1] . It is worthwhile to mention that the excess free energies $\Delta G^{xs}$ of Cd－Bi and Ge－Al melts are negative, while that of other metallic melts are positive, this is a question left for further clarification.

**Table 1 The free energy of mixing ΔG and excess free energy $\Delta G^{xs}$ of several metallic melts (J/mol)**

| $x_i$ | Cd－Bi | | Ge－Al | | Cd－Sn | | Bi－Sn | | Ag－Cu | | Al－Ga | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\Delta G$ | $\Delta G^{xs}$ | $\Delta G$ | $\Delta G^{xs}$ | $\Delta G$ | $\Delta G^{xs}$ | $\Delta G$ | $\Delta G^{xs}$ | $\Delta G$ | $\Delta G^{xs}$ | $\Delta G$ | $\Delta G^{xs}$ |
| 0.1 | −2 119 | −25 | −4 823 | −1 578 | −1 788 | 301 | −1 495 | 130 | −2 470 | 1 300 | −2 654 | 113 |
| 0.2 | −3 312 | −96 | −7 804 | −2 809 | −2 663 | 557 | −2 286 | 214 | −3 540 | 2 280 | −4 057 | 201 |
| 0.3 | −4 116 | −188 | −9 734 | −3 710 | −3 182 | 745 | −2 788 | 264 | −4 150 | 2 950 | −4 936 | 264 |
| 0.4 | −4 613 | −285 | −10 957 | −4 241 | −3 462 | 867 | −3 077 | 281 | −4 500 | 3 330 | −5 426 | 301 |
| 0.5 | −4 815 | −360 | −11 325 | −4 409 | −3 538 | 921 | −3 186 | 276 | −4 640 | 3 420 | −5 585 | 314 |
| 0.6 | −4 710 | −381 | −10 911 | −4 191 | −3 429 | 900 | −3 111 | 247 | −4 540 | 3 290 | −5 426 | 301 |
| 0.7 | −4 249 | −318 | −9 688 | −3 576 | −3 333 | 804 | −2 847 | 205 | −4 220 | 2 880 | −4 936 | 264 |
| 0.8 | −3 412 | −197 | −7 616 | −2 621 | −2 587 | 632 | −2 353 | 142 | −3 610 | 2 210 | −4 057 | 201 |
| 0.9 | −2 139 | −46 | −4 626 | −1 382 | −1 725 | 364 | −1 549 | 75 | −2 540 | 1 240 | −2 654 | 113 |

The thermodynamic characteristics of Si－Ag, Pb－Sn and Al－Sn binary melts was also listed in [4], which indicated that the free energies of mixing $\Delta G$ exhibit minima as well, only they are not located at $x_i = 0.5$, but at $x_i = 0.4$; the excess free energies $\Delta G^{xs}$ exhibit maxima too, only they are not located at $x_i = 0.5$, but at $x_i = 0.6$. Hence, siminarly according to the consistency of thermodynamic data with the structure of metallic melts, this indicates the possibility of $B_2A_3$ form compound formation.

There are some facts as follows for the possibility of compound (or short range order chemical cluster) formation in the above mentioned metallic melts.

(1) Using splat quenching, rapid solidification, ultrafast cooling ($10^{12}$ K/s) etc. a lot of metastable crystalline phases (compounds or short－range order chemical clusters) have been detected: in Cd－Bi melts a new simple hexagonal $\gamma$ phase (40 at % ~ 75at%)[5]; in Bi－Sn melts of Bi－50at%Sn, a $\beta$ phase of tetragonal structure (bct)[6] ; in Cu－Co melts, a Cu50Co50 crystalline phase[7]; in Cd－Sn alloys, a AlCu－type fcc structure (10 at%~25 at%Sn) and a hexagonal $\omega$ phase (55at%~85at%Sn)[8]; in Ag－Si melts, a cph structure (75at%~95at%Ag) and an orthorhombic phase ($Ag_2Si$ ~ 70 at%Ag)[9] .

(2) The existence of an intermediate phase ($Cr_2Sn_3$) has been reported by amalgamation of Cr and Sn[10]. Formation of $Ga_3In_2$ compound was detected in the metastable phases of Ga－In alloys[11] .

(3) In the metastable phases of Fe−C alloy there are a lot of compounds FeC, $Fe_2C$, $Fe_3C$, $Fe_3C_2$, $Fe_4C$, $Fe_5C_2$, $Fe_6C$, $Fe_7C_3$ etc. have been reported[12] .

From the facts of different sources mentioned above, it is shown that, in spite of experimental difficulties, the chemical compositions of some quenched metastable phases have not determined yet, however, doutlessly by means of different quenching techniques, metastable compounds of definite or unknown compositions have been obtained in the eutectic alloys. This shows that in the eutectic alloys there are great possibilities in the existence of one kind of compound stable in the liquid state, but unstable in the solid state. This kind of compound(or short range order chemical cluster) can be detected only by suitable(for concerned alloy) quenching technique.

There are some facts as follows for the possibility to retain eutectic in these metalllic melts.

(1) The X−ray study of the structure of molten Cd−Ga alloys indicated a quasieutectic structure within the liquid insolubility range. In Fe−C melts, short range ordering in liquid Fe was reported as bcc $\delta$F−based L$\delta$, fcc $\gamma$Fe−based L$\gamma$, and cph$\varepsilon$Fe−based L$\varepsilon$[12] . By undercooling Bi−48.6 at% Sn melts, obtained stable Bi , Sn phases and a metastable phase. By the molecular beam epitaxy technique at liquid He temperatures have been detected $\alpha$−Al, $\beta$−Ge, hexagonal and orthorhombic phase for the Al−40 and 50 Ge alloy films.

(2) Eutectic alloys Cu−Pb, Cr−Sn, Bi−Ga, Bi−Zn, Ga−In, etc. are characterized by partial immiscibility in the liquid state and extensive immiscibility in the solid state.

All these mentioned above indicate that the eutectic structures in the solid state have the great possibility to be retained to different degree in the liquid state of metallic alloys.

Based on the facts given above, the following assumptions can be drawn for the structure of binary metallic melts involving eutectic.

(1) Within metallic melts, eutectic structure is still retained to different degree, so the metallic melts are practically composed of two solutions.

(2) There are intermetallic compounds(or short range order chemical clusters) formation within metallic melts, which plays role of reducing the mass action concentrations of metallic melts and can dissolve in both metallic solutions.

(3) Chemical reactions between the two metallic solutions obey the mass action law.

According to the assumptions given above, taking Cd−Bi and Ag−Si alloys as examples, the calculating models of mass action concentrations for these metallic melts can be deduced respectively as:

As the thermodynamic characteristics of 6 binary alloys in Tab.1 indicate the formation of AB−form compounds within the metallic melts, hence for Cd−Bi melts, it can be assumed that they consist of Cd, Bi atoms and CdBi intermetallic compound (short range order chemical cluster), and form two solutions Cd+CdBi and Bi+CdBi.

Putting $b=\sum n_{Cd}$, $a=\sum n_{Bi}$, $x=n_{Cd}$, $y=n_{Bi}$, $z=n_{CdBi}$, $N_1=N_{Cd}$, $N_2=N_{Bi}$, $N_3=N_{CdBi}$, then give chemical equilibrium:

$$Cd(l) + Bi(l) = CdBi(l) \qquad K = N_3/N_1N_2 \tag{1}$$

and mass balance:

$$b=x+z, \quad a=y+z \tag{2}$$

$$N_1=x/b, \; N_2=y/a, \; N_3=KN_1N_2 \tag{3}$$

Substituting Eqs.(3) into Eq.(2) then

$$N_1 + KN_1N_2/b = 1, \qquad N_2 + KN_1N_2/a = 1 \tag{4}$$

from Eqs.(4)

$$\left.\begin{aligned} &N_1+N_2+KN_1N_2(1/a+1/b)=2 \\ &K=ab(2-N_1-N_2)/(a+b)N_1N_2 \end{aligned}\right] \tag{5}$$

Equation (5) is used for calculation of equilibrium constant $K$ at give measured activities ($N_1=a_1$, $N_2=a_2$).

Furthermore from Eqs.(4)

$$N_1+KN_1N_2/b=N_2+KN_1N_2/a \tag{6}$$

and from Eqs.(2)

$$y=a-b+x, \qquad N_2=y/a=1-b(1-N_1)/a \tag{7}$$

Substitution of Eqs.(7) into Eq.(6) gives

$$\left.\begin{aligned} &bKN_1^2+[(a-b)K+ab]N_1-ab=0 \\ &N_1=\{-[(a-b)K+ab]+[(a-b)K+ab]^2+4ab^2K]^{1/2}\}/2bK \end{aligned}\right] \tag{8}$$

Eqations (3), (5), (7) and (8) are the calculating models of mass action concentrations for this kind of metallic melts. If the calculating model is consistent with practice, then the calculated mass action concentrations should be agree or nearly so with measured activities.

As the thermodynamic characteristics of three binary alloys indicates the formation of $B_2A_3$ form compounds (or short range order chemical clusters) hence for Ag−Si melts, it can be assumed that they consiste of Ag, Si atoms and $Si_2Ag_3$ intermetallic compounds (or short range order chemical clusters), and form two solutions $Si+Si_2Ag_3$ and $Ag+Si_2Ag_3$.

Assuming $b=\sum n_{Si}$, $a=\sum n_{Ag}$, $x=n_{Si}$, $y=n_{Ag}$, $z=n_{Si_2Ag_3}$, $N_1=N_{Si}$, $N_2=N_{Ag}$, $N_3=N_{Si_2Ag_3}$, then give chemical eqilibrium:

$$2Si(l) + 3Ag(l) = Si_2Ag_3(l) \qquad K = N_3/N_1^2N_2^3 \tag{9}$$

mass balance:

$$b=x+2z,\quad a=y+3z \tag{10}$$

$$N_1 = x/b,\quad N_2 = y/a,\quad N_3 = KN_1^2\ N_2^3 \tag{11}$$

Substituting Eqs.(11) into Eq.(10) gives

$$N_1 + 2KN_1^2\ N_2^3\ /b = 1,\quad N_2 + 3KN_1^2\ N_2^3\ /a = 1 \tag{12}$$

from Eqs.(12)

$$\left.\begin{aligned} N_1 + N_2 + KN_1^2\ N_2^3\ (3/a+2/b) &= 2 \\ K = ab(2-N_1-N_2)/(2a+3b)N_1^2\ N_2^3 & \end{aligned}\right] \tag{13}$$

Equation (13) is used for calculation of equilibrium constant at given measu－red acticities($N_1=a_1$, $N_2=a_2$).

Again from Eqs.(12)

$$\left.\begin{aligned} N_1 + 2KN_1^2\ N_2^3\ /b &= N_2 + 3KN_1^2\ N_2^3\ /a \\ ab(N_1-N_2) + KN_1^2\ N_2^3\ (2a-3b) &= 0 \end{aligned}\right] \tag{14}$$

and from Eqs.(10)

$$\left.\begin{aligned} z=(b-x)/2 &= (a-y)/3 \\ 3b(1-N_1) &= 2a(1-N_2) \\ N_2 &= 1-1.5b(1-N_1)/a \end{aligned}\right] \tag{15}$$

Substitution of Eq.(15) into Eq.(14) gives

$$(2a-3b)\ KN_1^2\ [1-1.5b(1-N_1)/a]^3 + ab(N_1-1)(1-1.5b/a) = 0 \tag{16}$$

Eqations (11), (13), (15) and (16) are the calculating models of mass action concentrations for this kind of metallic melts. Similarly, validity of the calculating model should be verified by the degree of agreement between calculated and the measured values.

## 2 Calculated Results and Discussion

According to the measured activities of literatures [6,7] and using equation (5),the calculated equilibrium constants and standard free energies of formation of intermetallic compounds at definite temperatures of this kind of metallic melts are given in Tab. 2. It is shown from the table, that the equilibrium constants for intermetallic compound formation of these metallic melts are considerably constant,this in turn tells us that these chemical reactions rigouously obey the mass action law . In the mean time, two cases can be seen from the table:

(1) In first case, for alloys, whose equilibrium constants are greater than one and the standard free energies of compound formation $\Delta G^\circ$ are negative, for example Cd－Bi and Ge－Al alloys. According to equations (3), (5), (7) and (8), the calculated mass action concentrations of these melts are compared with measured activities in Fig. 1. From this figure, it also shows the fair agreement between the

**Table 2 Equilibrium constants and standard free energy of intermetallic compound formation in several metallic melts at definite temperatures**

| $x_i$ | Equilibrium constants | | | | | |
|---|---|---|---|---|---|---|
| | Cd−Bi | Ge−Al | Cd−Sn | Bi−Sn | Ag−Cu | Al−Ga |
| 0. 1 | 1.075 983 | 4.622 88 | 0.601 201 | 0.780 40 | 0.300 588 | 0.871 598 |
| 0.2 | 1.125 540 | 3.979 25 | 0.614 323 | 0.810 11 | 0.321 628 | 0.871 132 |
| 0.3 | 1.155 009 | 3.556 30 | 0.626 395 | 0.830 13 | 0.341 363 | 0.891 335 |
| 0.4 | 1.170 715 | 3.346 13 | 0.654 304 | 0.839 72 | 0.357 138 | 0.892 910 |
| 0.5 | 1.179 668 | 3.270 05 | 0.635 393 | 0.846 46 | 0.365 412 | 0.892 854 |
| 0.6 | 1.197 510 | 3.338 85 | 0.630 816 | 0.845 46 | 0.358 269 | 0.892 910 |
| 0.7 | 1.229 293 | 3.547 91 | 0.616 724 | 0.844 69 | 0.347 971 | 0.891 335 |
| 0.8 | 1.247 947 | 3.849 10 | 0.594 569 | 0.844 18 | 0.329 796 | 0.880 858 |
| 0.9 | 1.208 157 | 4.164 66 | 0.562 092 | 0.848 28 | 0.315 866 | 0.871 598 |
| $K$ | 1.176 647 | 3.751 153* | 0.615 091 | 0.832 184 | 0.337 559 | 0.8 840 590 |
| $\Delta G°$/J·mol$^{-1}$ | −1 046 | −13 198 | 1 641 | 917 | 12 648 | 1 048.7 |
| $T$/K | 773 | 1 200 | 406 | 600 | 1 400 | 1 023 |

There is still $K=3.84821$ at $x_{Ge}=0.97$ included in $K$ calculation.

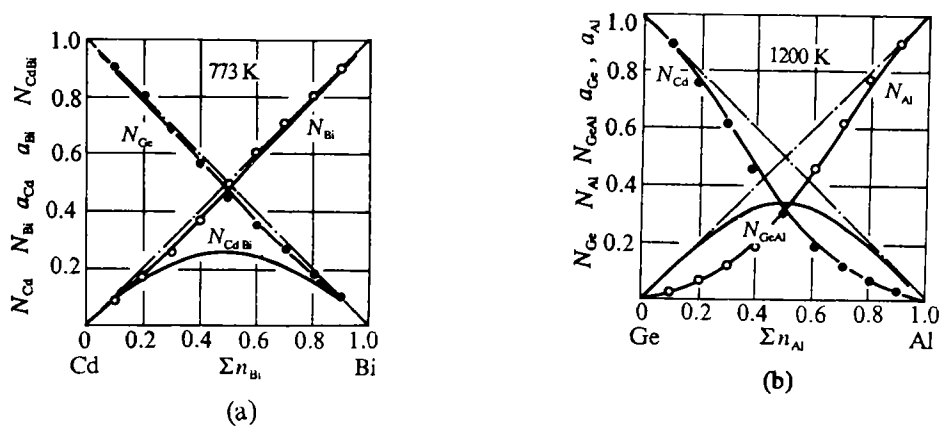


**Fig. 1 Comparison of calculated mass action concentrations with measured activities for (a) Cd−Bi; (b) Ge−Al melts**

calculated and measured values, this in turn shows the correctness and feasibility of the calculating model; on the other hand, it is seen that the activities of these two binary alloys exhibit negative deviation from Roultian behavior, this is evidently caused by the equilibrium constants being greater than one and the negative values of

standard free energy of formation $\Delta G$ . This clearly shows, in spite of that in the majority of cases, the activities of binary metallic melts involving eutectic exhibit positive deviation, but in the minority of cases, they could also exhibit negative deviation from Roultian behavior.

(2) In the second case, for alloys, whose equilibrium constants are less than 1 and the standard free energies of formation have positive values, for example Cd－Sn, Bi－Sn, Ag－Au and Ag－Ga alloys. The calculated mass action concentrations are compared with the measured activities of these metallic melts in Fig. 2. Good agreement between the calculated and measured values similarly demonstrates that the preceding calculating model is correct.

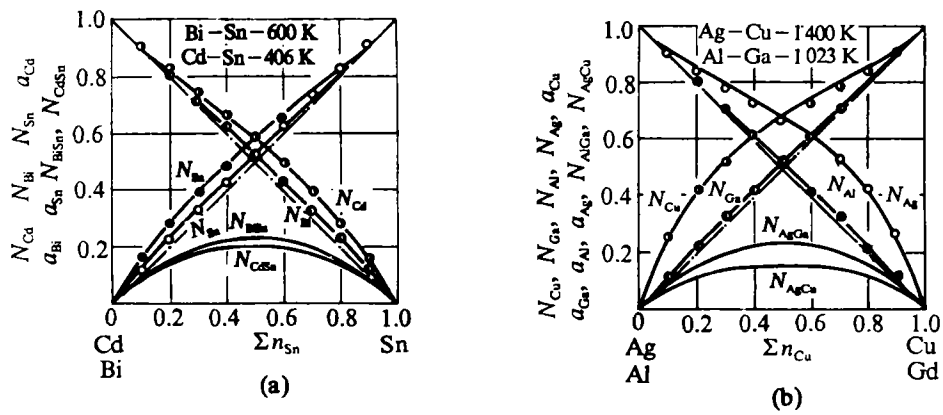


**Fig.2 Comparison of calculated mass action concentrations with measured activities for (a) Cd－Sn and Bi－Sn; (b) Ag－Cu and Al－Ga melts**

The foregoing paragraph is about the comparison of calculated mass action concentrations with the measured activities of those metallic melts which exhibit symmetrical positive or negative deviation from Roultian behavior. According to equations (13), (15), (17) and (18), the calculated mass action concentrations are compared with the measured activities of metallic melts which exhibit asymmetrical positive deviation relative to Roultian behavior in Fig. 3. Their equilibrium constants and standard free energies of formation are given in Tab. 3.

**Table 3 $K$ and $\Delta G$ °values of Si－Ag, Pb－Sn and Al－Sn melts**

| Binary alloy | Si－Ag | Pb－Sn | Al－Sn |
|---|---|---|---|
| $T$/K | 1 700 | 1 050 | 973 |
| $K$ | 0.918 04 | 0.633 281 | 0.409 72 |
| $\Delta G$ °/J · mol$^{-1}$ | 1 182 | 3 990 | 7 222 |

From Fig.3 it is seen that the calculated values are in good agreement with the measured ones, this in turn confirms the validity of the calculating model of mass action concentrations for this kind of metallic melts.

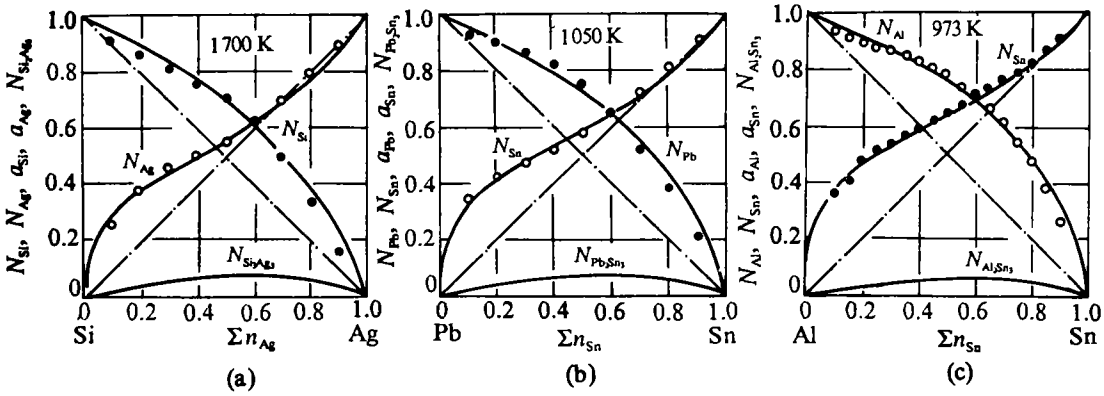


**Fig. 3 Comparison of calculated mass action concentrations with measured activities for (a) Si－Ag; (b) Pb－Sn; (c) Al－Sn melts**

## 3 Conclusions

(1) Based on the appearance of minima of the free energy of mixing and maxima (or minima) of excess free energy, the formation of metastable compounds eutectic during rapid solidification of metallic melts and the presence of immiscibilities in the phase diagrms of a lot of binary alloys, calculating models ofmass action concentrations for binary metallic melts have been deduced.

(2) The activities of metallic melts involving eutectic exhibit either positive or negative deviations from Roultian behavior; their deviations have either symmetrical or asymmetrical form.

(3) The main reason for appearance of positive deviation from Roultian behavior is the retention of eutectic structures to different degree in the metallic melts, their concentrations depend only on the amount of species within the solution and don ′t depend on that of the solution separated from it.

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# 含共晶体二元金属熔体作用浓度的计算模型

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**摘 要** 根据混合自由能有最小值，过剩自由能有最大值(或最小值)，激冷条件下产生化合物状亚稳相及共晶，分层等现象，针对 Cd－Bi, Ge－Al, Bi－Sn, Cd－Sn, Ag－Cu, Al－Ga; Si－Ag, Pb－Sn 和 Al－Sn 金属熔体推导了作用浓度的计算模型．计算结果与实测值符合较好，从而证明所提出的计算模型符合本类熔体的结构特点．

**关键词** 活度，亚稳相，共晶，作用浓度

**中图分类号** O642. 541, O645.11, TF01