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A Back Look on the Binary Phase Diagrams of Metals from the Mass Action Law and the Coexistence Theory of Metallic Melts

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Abstract: According to the mass action law and the coexistence theory of metallic melts, the mass action concentrations of Cu-Mg, Bi-Tl and Ni-Al melts involving compound formation have been calculated. The calculated results show that, except the ultimate case of pure element, when two elements are present in the melts, all structural units (atoms and molecules) without exception will be present in the melts, i.e., their concentrations may change from great to smali, but they will not vanish into nothing, and only under such conditions, the calculated results both agree with practice and obey the law of mass action. In view of that over considerable wide composition range, the activities of both elements of the three solid binary alloys mentioned above have been measured, this seems in contradiction with the present relevant phase diagrams, in which the structural units are determined by composition range, so the latter needs further investigation and consideration.

Key words: activity; phase diagram; the mass action law; the coexistence theory

In reference [1] the widespread applicability of the mass action law has been demonstrated by the coexistence (atoms and molecules) theory of metallic melts, the coexistence (ions and molecules) theory of slag melts and the model of inseparate cations and anions of molten salts, mattes as well as binary basic oxide solid solutions in combination with a lot of measured activities of corresponding melts. During calculation all compounds used as structural units in the relevant models were determined by the related phase diagrams, in the meantime, the structures and thermodynamic properties of binary metallic melts were satisfactorily classified according to the phase diagrams, finally it was shown that the thermodynamic properties of binary metallurgical melts are consistent with their phase diagrams, hence phase diagrams have played important role in the development of theories of metallurgical melts. However, at the same time, in the process of calculation, it was found that only under conditions of considering all structural units in the melts, the calculated results could both agree with practice and obey the mass action law. This seems to be different with the present relevant phase diagrams, in which the structural units are determined by composition range. For lack of enough knowledge of phase diagrams on my part, little attention was paid to study this problem. But now it appears that if this problem could not be made clear, it would become a great obstacle to the development of theories of metallurgical melts. Hence in this paper, three binary metallic melts involving compound formation (Cu-Mg, Bi-Tl and Ni-Al) are taken as examples, accompanied by measured activities at solid and liquid state, to analyze this problem with the mass action law in combination with the coexistence theory of metallic melts, so as to clearly clarify it.

1 Regularity Observed from Metallic Melts

1.1 Cu-Mg melts

It is seen from phase diagram **figure 1** [2], that there are compounds Cu_2Mg and $CuMg_2$ formed in these melts, both of which have congruent melting points, so the structural units of these melts are Cu, Mg, Cu_2Mg and $CuMg_2$.

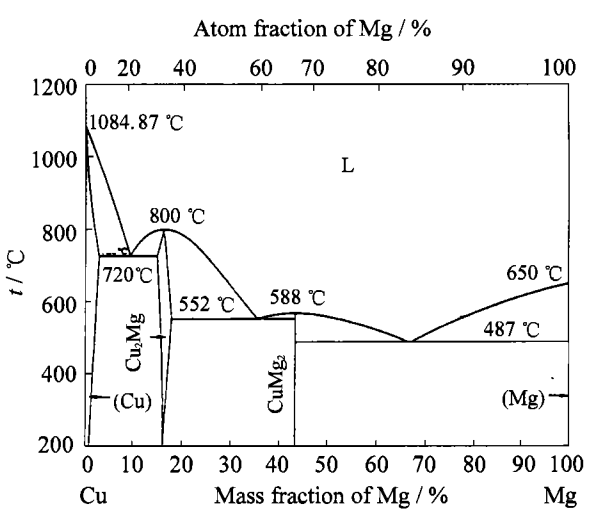

Figure 1 Phase diagram of Cu-Mg system.

Assuming the composition of the melts as $b=\Sigma x_{Cu}$, $a=\Sigma x_{Mg}$; the mass action concentration of each structural unit after normalization as $N_1=N_{Cu}$, $N_2=N_{Mg}$, $N_3=N_{Cu_2Mg}$, $N_4=N_{CuMg_2}$; Σx = sum of all equilibrium mole fractions, then it gives

(1) chemical equilibria:

$$2Cu_{(l)}+Mg_{(l)}=Cu_2Mg_{(l)},$$

$$K_1=N_3/N_1^2N_2,\ N_3=K_1N_1^2N_2 \quad (1)$$

$$Cu_{(l)}+2Mg_{(l)}=CuMg_{2(l)},$$

$$K_2=N_4/N_1N_2^2,\ N_4=K_2N_1N_2^2 \quad (2)$$

(2) after making mass balance it gives:

$$N_1+N_2+K_1N_1^2N_2+K_2N_1N_2^2-1=0 \quad (3)$$

$$aN_1-bN_2+(2a-b)K_1N_1^2N_2+(a-2b)K_2N_1N_2^2=0 \quad (4)$$

$$1-(a+1)N_1-(1-b)N_2=K_1(2a-b+1)N_1^2N_2+K_2(a-2b+1)N_1N_2^2 \quad (5)$$

Equations (3), (4) and (5) are the calculating model of mass action concentrations for these melts.

After treating the measured a_{Cu} and a_{Mg} at 1100 K from reference [3], it has been obtained that $K_{Cu_2Mg}=28.43(\Delta G^{\ominus}=-30631.18$ J/mol), $K_{CuMg_2}=9.723$ ($\Delta G^{\ominus}=-20813.02$ J/mol), ($F=616.074$, $R=0.99317$). The comparison of calculated and measured values is shown in **figure 2**. It is seen that the calculated mass action

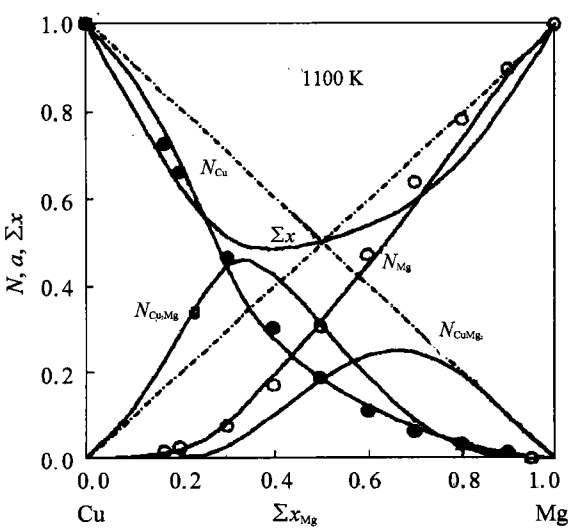

Figure 2 Comparison of calculated mass action concentrations (—) with measured activities (○, ●) for Cu-Mg melts at 1100 K.

concentrations are in good agreement with the corresponding measured activities, both showing that the model deduced can reflect the structural reality of these melts and that the mass action law and the coexistence theory of metallic melts are valid. At the same time, it can be seen that except the ultimate case of pure element, all structural units N_{Cu} (i.e., a_{Cu}), N_{Mg}(i.e., a_{Mg}), N_{Cu_2Mg} and N_{CuMg_2} although may change from great to small, but from beginning to end retain certain values, and will not vanish into nothing. It is worthwhile to point out that only under such conditions, it is possible to obtain the calculated results which both have good agreement with practice and obey the mass action law. This is obviously contradictory with relevant phase diagram, in which, the structural units are determined according to composition range, hence it is necessary to be investigated further.

1.2 Bi-Tl melts

According to the phase diagram (see **figure 3**) [2], there are Bi_2Tl, BiTl, $BiTl_3$ and $BiTl_7$ formed in these melts, but after examination with different variants, it was found that only one which considers the existence of comounds BiTl and $BiTl_3$ has good agreement with practice, hence the structural units of these melts are Bi, Tl, BiTl and $BiTl_3$.

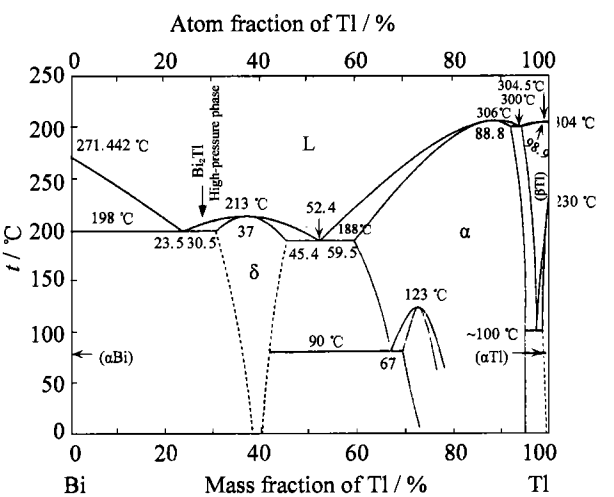

Figure 3 Phase diagram of Bi-Tl system.

Putting the composition of the melts as $b=\Sigma x_{Bi}$, $a=\Sigma x_{Tl}$; the mass action concentration of each structural unit after normalization as $N_1=N_{Bi}$, $N_2=N_{Tl}$, $N_3=N_{BiTl}$, $N_4=N_{BiTl_3}$; Σx = sum of all equilibrium mole fractions, then it gives

(1) chemical equilibria:

$$Bi_{(l)}+Tl_{(l)}=BiTl_{(l)},$$

$$K_1=N_3/N_1N_2,\ N_3=K_1N_1N_2 \quad (6)$$

$$Bi_{(l)}+3Tl_{(l)}=BiTl_{3(l)},$$

$$K_2=N_4/N_1N_2^3,\ N_4=K_2N_1N_2^3 \quad (7)$$

(2) after making mass balance it gives:

$$N_1+N_2+K_1N_1N_2+K_2N_1N_2^3-1=0 \quad (8)$$

$$aN_1-bN_2+(a-b)K_1N_1N_2+(a-3b)K_2N_1N_2^3=0 \quad (9)$$

$$1-(a+1)N_1-(1-b)N_2=K_1(a-b+1)N_1N_2+$$

$K_2(a-3b+1)N_1N_2^3$ (10)

The above mentioned three equations (8), (9) and (10) are the calculating model of mass action concentrations for these melts.

After regression with the measured activities at 750 K of Bi-Tl melts from reference [3], it has been obtained that $K_{BiTl}=7.74964$ ($\Delta G^{\ominus}=-12775.38$ J/mol), $K_{BiTl_3}=33.96964$ ($\Delta G^{\ominus}=-21995.59$ J/mol), ($F=491.01$, $R=0.99096$). The calculated mass action concentrations are compared with the measured activities as shown in **figure 4**. Similarly it is seen that the calculated mass action concentrations agree with the measured activities, showing that not only the model can reflect the structural reality of the melts, but also that the mass action law and the coexistence theory of metallic melts are all correct. In the meantime, it also can be seen that although N_{Bi} (i.e., a_{Bi}), N_{Tl} (i.e., a_{Tl}), N_{BiTl} and N_{BiTl_3} may change their values from high to low, but except the ultimate case of pure element, from start to finish, they retain certain values, and will not vanish into nothing. And only under such conditions, it is possible to obtain the calculated results that both agree with practice and obey the mass action law. This is also not identical with the corresponding phase diagram, in which the structural units are determined according to the composition range, hence it is worthwhile to study further.

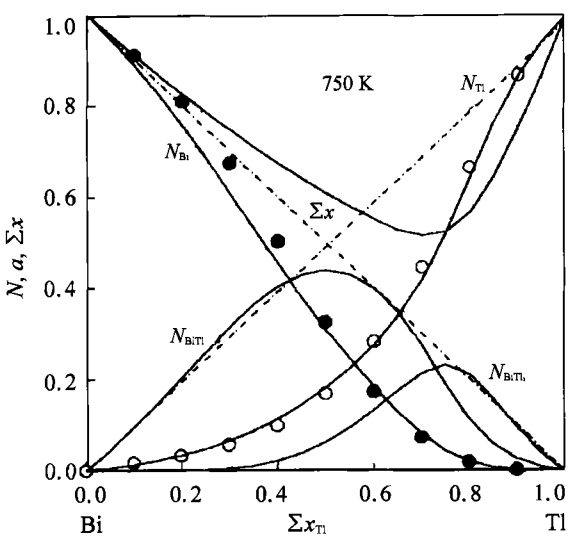

Figure 4 Comparison of calculated mass action concentrations (—) with measured activities (○, ●) for Bi-Tl at 750 K.

1.3 Ni-Al melts

From the phase diagram of system Ni-Al in **figure 5** [2], it is seen that there are five compounds (Ni_3Al, Ni_5Al_3, NiAl, Ni_2Al_3 and $NiAl_3$) formed in these melts, in which only NiAl has congruent melting point, other compounds are all peritectics. Hence the structural units of these melts are Ni, Al, Ni_3Al, Ni_5Al_3, NiAl, Ni_2Al_3 and $NiAl_3$.

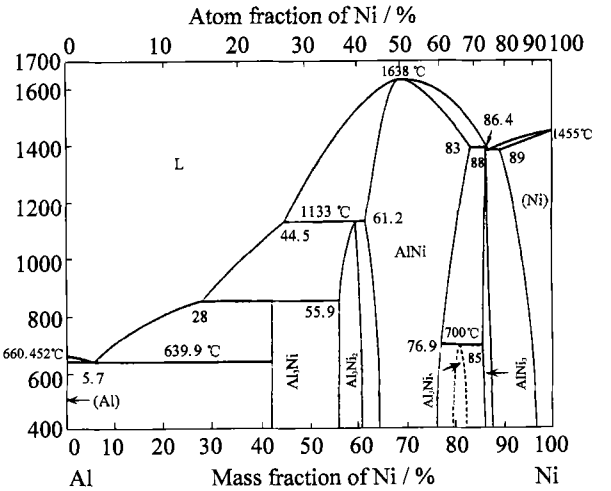

Figure 5 Phase diagram of Ni-Al system.

Assuming the composition of the melts as $b=\Sigma x_{Ni}$, $a=\Sigma x_{Al}$; the mass action concentration of every structural unit after normalization as $N_1=N_{Ni}$, $N_2=N_{Al}$, $N_3=N_{Ni_3Al}$, $N_4=K_{Ni_5Al_3}$, $N_5=N_{NiAl}$, $N_6=N_{Ni_2Al_3}$, $N_7=N_{NiAl_3}$; $\Sigma x=$ sum of all equilibrium mole fractions, then it gives

(1) chemical equilibria:

$3Ni_{(l)}+Al_{(l)}=Ni_3Al_{(l)}$,

$K_1=N_3/N_1^3N_2$, $N_3=K_1NN_2$ (11)

$5Ni_{(l)}+3Al_{(l)}=Ni_5Al_{3(l)}$,

$K_2=N_4/N_1^5N_2^3$, $N_4=K_2N_1^5N_2^3$ (12)

$Ni_{(l)}+Al_{(l)}=NiAl_{(l)}$,

$K_3=N_5/N_1N_2$, $N_5=K_3N_1N_2$ (13)

$2Ni_{(l)}+3Al_{(l)}=Ni_2Al_{3(l)}$,

$K_4=N_6/N_1^2N_2^3$, $N_6=K_4N_1^2N_2^3$ (14)

$Ni_{(l)}+3Al_{(l)}=NiAl_{3(l)}$,

$K_5=N_7/N_1N_2^3$, $N_7=K_5N_1N_2^3$ (15)

(2) after making mass balance it gives:

$$N_1+N_2+K_1N_1^3N_2+K_2N_1^5N_2^3+K_3N_1N_2+K_4N_1^2N_2^3+K_5N_1N_2^3-1=0 \quad (16)$$

$$aN_1-bN_2+(3a-b)K_1N_1^3N_2+(5a-3b)K_2N_1^5N_2^3+(a-b)K_3N_1N_2+(2a-3b)K_4N_1^2N_2^3+(a-3b)K_5N_1N_2^3=0 \quad (17)$$

$$1-(a+1)N_1-(1-b)N_2=K_1(3a-b+1)N_1^3N_2+K_2(5a-3b+1)N_1^5N_2^3+K_3(a-b+1)N_1N_2+K_4(2a-3b+1)N_1^2N_2^3+K_5(a-3b+1)N_1N_2^3 \quad (18)$$

Equations (16), (17) and (18) are the calculating model of these melts. After treating the measured activities a_{Ni} and a_{Al} of Ni-Al melts at 1873 K from reference [4], the following thermodynamic parameters

have been obtained: $K_{Ni_3Al}=607.62$ ($\Delta G^{\ominus}=-99\,867.21$ J/mol), $K_{Ni_5Al_3}=5606723$ ($\Delta G^{\ominus}=-242120.63$ J/mol), $K_{NiAl}=199.2221$ ($\Delta G^{\ominus}=-82492.38$ J/mol), $K_{Ni_2Al_3}=44206.13$ ($\Delta G^{\ominus}=-166664.05$ J/mol), $K_{NiAl_3}=409.32$ ($\Delta G^{\ominus}=-93711.9$ J/mol), ($F=10787.8$, $R=0.99986$). The comparison of the calculated mass action concentrations with the measured activities is shown in **figure 6**. It can be seen that the calculated mass action concentrations are in good agreement with the measured activities, showing that not only the model deduced can reflect the structural characteristics of these melts with four peritectics and one compound with congruent melting point, but also that the mass action law and the coexistence theory of metallic melts are all valid. At the same time, it is seen that although N_{Ni} (i.e., a_{Ni}), N_{Al} (i.e., a_{Al}), N_{Ni_3Al}, $N_{Ni_5Al_3}$, N_{NiAl}, $N_{Ni_2Al_3}$ and N_{NiAl_3} may change from great to small, but except the ultimate case of pure element, from beginning to end they retain certain values, and will not vanish into nothing. And only under such conditions, it is possible to obtain the calculated results which both agree with practice, and obey the mass action law. This is contradictory with the corresponding phase diagram, in which the structural units are determined according to the composition range. Hence it is necessary to be studied further.

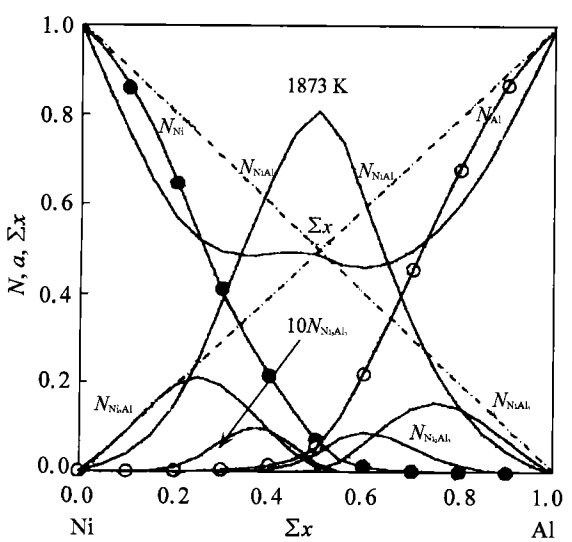

Figure 6 Comparison of calculated mass action concentrations (—) with measured activities (○, ●) for Ni-Al at 1873

Why in the above mentioned three examples, except the ultimate case of pure element, all structural units in the melts will not vanish into nothing in the process of the composition variation of the melts? The basic reason is, except the ultimate case of pure element, from beginning to end, the activities of both components can be measured to a sensible extent (a_{Cu} and a_{Mg}, a_{Bi} and a_{Tl} and as well as a_{Ni} and a_{Al}), hence there should occur chemical reactions (1) and (2), (6) and (7) as well as (11) to (15) to form N_{Cu_2Mg} and N_{CuMg_2}, N_{NiAl} and $N_{Bi_2Tl_3}$ as well as N_{Ni_3Al}, $N_{Ni_5Al_3}$, N_{NiAl}, $N_{Ni_2Al_3}$ and N_{NiAl_3}, thus keep all structural units to certain values, not vanish into nothing. If the structural units were determined according to the composition range and considering that every compound form a new phase, then the calculated results not only would violate the mass action law, but also would be impossible to match with practice, hence it would be unrealizable. Furthermore, considering that the intermetallic compounds don't form phase boundary in metallic melts and one can not remove them from the bulk of metallic melts, hence it is reasonable to regard metallic melts involving compound formation as homogeneous solution, but not heterogeneous solution. This is just the reason why equations (3), (8) and (16) are expressed by $\Sigma N_i - 1 = 0$.

2 Abnormal Phenomena Observed from Binary Solid Alloys

The measured activities of three binary solid alloys Cu-Mg, Bi-Tl and Ni-Al [3, 4] are given in **table 1**. According to Cu-Mg phase diagram, at the end of minor Mg content, only $Cu+Cu_2Mg$ and $Cu_2Mg+CuMg_2$ structural units are present in alloys, but the activities of Cu and Mg were measured in Cu-Mg solid alloys. Similarly, over wide range of Bi-Tl and Ni-Al alloys, according to the corresponding phase diagrams, there shouldn't be one or two elements between certain composition range, but the activities of two elements were also measured. Since it is so, the measurement of the activities of two elements confirms that both of them are really present in the corresponding solid alloys, because it is impossible to measure the activity of one element when it is absent in the alloy; these are not unique, but considerably popular phenomena of binary alloy phase diagrams, hence are authentic facts that phase diagrams do not correspond to reality. In spite of that binary solid alloys being heterogeneous are different from the metallic melts which are homogeneous solution, but as long as over considerable composition range of solid alloys, there are measured activities of both components, why they don't combine to form various compounds of the phase diagrams? If this was really true, these compounds would be water without a source or a tree without roots. Owing to the fact that matter of less than 3%–5% content is difficulty to detect by X-rays, whereas activity can be measured with much higher accuracy and less content. Hence the above mentioned contradictory between activity research and phase diagrams may stem from not enough performance (resolving power, accuracy etc.) of X-ray apparatus which required from scientific research for a long time. Therefore this problem should be investigated

Table 1 Measured activitives for solid Cu-Mg, Bi-Tl and Ni-Al alloys

Cu-Mg (750 K)			Bi-Tl (423 K)			Ni-Al (1273 K)		
Σx_{Mg}	a_{Cu}	a_{Mg}	Σx_{Tl}	a_{Bi}	a_{Tl}	Σx_{Al}	a_{Ni}	a_{Al}
0.041	0.959	0.004	0.338	1.000	0.042	0.625	2.70×10^{-5}	4.46×10^{-1}
0.328	0.959	0.004	0.400	0.808	0.059	0.597	4.16×10^{-4}	7.75×10^{-2}
0.333	0.650	0.009	0.470	0.397	0.154	0.571	4.16×10^{-4}	7.75×10^{-2}
0.357	0.089	0.391	0.648	0.397	0.154	0.550	4.71×10^{-4}	7.04×10^{-2}
—	—	—	0.700	0.154	0.238	0.500	3.01×10^{-3}	1.25×10^{-2}
—	—	—	0.800	0.020	0.467	0.450	0.147	1.97×10^{-4}
—	—	—	0.900	9.000×10^{-4}	0.802	0.400	0.320	6.80×10^{-5}
—	—	—	0.950	6.000×10^{-5}	0.988	0.369	0.432	4.30×10^{-5}
—	—	—	0.970	6.000×10^{-5}	0.988	0.272	0.432	4.30×10^{-5}
—	—	—	0.984	5.000×10^{-5}	0.994	0.258	0.596	1.80×10^{-5}
—	—	—	0.988	5.000×10^{-5}	0.994	0.136	0.596	1.80×10^{-5}
—	—	—	1.000	0.000	1.000	0.100	0.754	3.10×10^{-6}
—	—	—	—	—	—	0.050	0.910	3.10×10^{-7}
—	—	—	—	—	—	0.000	1.000	0.000

and discussed further.

3 Conclusions

(1) Phase diagrams play important role in the determination of structural units of metallurgical melts, in the classification of thermodynamic properties of binary metallic melts as well as the verification of the consistency of thermodynamic properties of metallurgical melts with their phase diagrams.

(2) The mass action concentrations of all structural units of binary metallic melts involving compound formation may change with the composition from great to small, but except the ultimate case of pure element, from beginning to end they retain certain values, don't vanish into nothing, and only under such condition, it is possible to obtain the calculated results which both agree with practice and obey the mass action law, hence the expression $\Sigma N_i - 1 = 0$ is valid.

(3) The determination of structural units according to the composition range in phase diagrams is not identical with the activity measurement of binary solid alloys, in which the activities of both components can be measured, hence this problem should be investigated and discussed further.

Acknowledgment

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