[Article ID] 1003- 6326(2001)06- 0927- 04

Effect of peritectics on thermodynamic properties of homogeneous binary metallic melts①

ZHANG Jian(张 鉴)
(School of Metallurgical Engineering, University of Science and Technology Beijing, Beijing 100083, P. R. China)

[Abstract] After formulation of the calculating models of mass action concentrations for metallic melts Cu-Al, Ni-Al and Cu-Sn, it is found that in spite of their lower stability than that of compounds with congruent melting point, peritectics are popular structural units in metallic melts, neglecting their presence will make it impossible to study the thermodynamic properties of metallic melts with results which both obey the law of mass action and agree well with practice.

[Key words] metallic melts; peritectic; activity; mass action concentration
[CLC number] TF01; O642.541; O645.11 [Document code] A

1 INTRODUCTION

In Refs.[1~5], clear illustrations of the thermodynamic properties of metallurgical melts have been made. In Ref.[6], the presence of peritectic in binary metallic melts has been demonstrated in detail. However, due to customary misunderstanding of the phase diagrams: considering that if a substance is absent above certain temperature in the solid state, it must disappear in the liquid state. Hence the viewpoint about the presence of peritectic in metallic melts was not so easily accepted. For this reason, it is necessary that the presence of peritectic in metallic melts should be further elucidated with a number of convincing examples. Here, it should be upheld and emphasized that the practice is the sole criterion of truth, but not any indeterminate viewpoint can be taken as a measuring ruler to judge a thing. At the meantime, the law of mass action should be taken as theoretical criterion to determinate the validity of a thermodynamic model.

2 Cu-Al MELTS

In regard to the phase diagrams, there isn't any identical opinion about this binary system yet. In Ref.[7] Cu_9Al_4, Cu_3Al_2, CuAl and $CuAl_2$ are indicated to form in this binary system; while in Ref.[8] Cu_9Al_4, Cu_3Al_2, Cu_4Al_3, CuAl and $CuAl_2$ are given. In a recent literature [9] the presence of compound Cu_3Al with high melting temperature is reported. After comparison of different calculating models of mass action concentrations in consideration of the above mentioned opinions, it is found that only in case of taking Cu_3Al, Cu_3Al_2 and CuAl into account, the calculating model can give good agreement between theory and practice. Hence the structural units of these melts are Cu, Al atoms as well as Cu_3Al, Cu_3Al_2 and CuAl compounds. Assuming the composition of the melts as $a = \Sigma x(\mathrm{Cu})$, $b = \Sigma x(\mathrm{Al})$; the mass action concentration of every structural unit after normalization as $N_1 = N_{\mathrm{Cu}}$, $N_2 = N_{\mathrm{Al}}$, $N_3 = N_{\mathrm{Cu_3Al}}$, $N_4 = N_{\mathrm{Cu_3Al_2}}$, $N_5 = N_{\mathrm{CuAl}}$, Σx is the sum of all equilibrium mole fractions, then the chemical equilibria are obtained:

$$3\mathrm{Cu(l)} + \mathrm{Al(l)} = \mathrm{Cu_3Al(l)}$$

$$K_1 = \frac{N_3}{N_1^3 N_2} \tag{1}$$

$$3\mathrm{Cu(l)} + 2\mathrm{Al(l)} = \mathrm{Cu_3Al_2(l)}$$

$$K_2 = \frac{N_4}{N_1^3 N_2^2} \tag{2}$$

$$\mathrm{Cu(l)} + \mathrm{Al(l)} = \mathrm{CuAl(l)}$$

$$K_3 = \frac{N_5}{N_1 N_2} \tag{3}$$

After making mass balance it gives:

$$N_1 + N_2 + K_1 N_1^3 N_2 + K_2 N_1^3 N_2^2 + K_3 N_1 N_2 = 1 \tag{4}$$

$$aN_1 - bN_2 + (3a - b)K_1 N_1^3 N_2 + (3a - 2b)K_2 N_1^3 N_2^2 + (a - b)K_3 N_1 N_2 = 0 \tag{5}$$

$$1 - (a + 1) - (1 - b)N_2 = K_1(3a - b + 1)N_1^3 N_2 + K_2(3a - 2b + 1)N_1^3 N_2^2 + K_3(a - b + 1)N_1 N_2 \tag{6}$$

Eqns.(4), (5) and (6) are the calculating model of mass action concentrations for Cu-Al melts, in which Eqns.(4) and (5) are used for calculating the mass action concentrations, while Eqn.(6) for regressing equilibrium constants in case of known measured activities ($a(\mathrm{Cu}) = N_1$, $a(\mathrm{Al}) = N_2$). Substituting the measured activities $a(\mathrm{Cu})$ and $a(\mathrm{Al})$ at two temperatures 1 373 K and 1 073 K from Refs.[7, 9] into Eqn.(6) gives the corresponding relationships

① [Received date] 2000- 12- 21; [Accepted date] 2001- 03- 19

of equilibrium constants and Gibbs free energies $\Delta G^{\ominus}$ with temperature as

$$\lg K_{Cu_3Al} = \frac{989.3946}{T} + 1.735 \quad (r = 1.00)$$

$$\Delta G^{\ominus} = -17208.398 - 33.234T \quad (T = 1073 \sim 1373\ K) \tag{7}$$

$$\lg K_{Cu_3Al_2} = \frac{2905.9044}{T} + 1.2675T \quad (r = 1.00)$$

$$\Delta G^{\ominus} = -55661.46 - 24.278T \quad (T = 1073 \sim 1373\ K) \tag{8}$$

$$\lg K_{CuAl} = \frac{-246.524}{T} + 1.534T \quad (r = 1.00)$$

$$\Delta G^{\ominus} = 4722.07 - 29.38T \quad (T = (1073 \sim 1373\ K) \tag{9}$$

Substituting the preceding thermodynamic parameters into Eqns. (4) and (5), it gives the comparison of calculated mass action concentrations with respect to measured activities respectively at 1073 K and 1373 K as shown in Fig. 1. It can be seen that the agreement between calculated and measured values is quite good, showing that the structural units determined and the calculating model deduced can reflect the structural reality of the melts indeed. However, it should be pointed out that except Cu_3Al having congruent melting temperature, Cu_3Al_2 and CuAl are all peritectics. According to the viewpoint in the past, there radically would be no possibility for the presence of the latter two compounds in the Cu-Al melts. But practice shows that only on condition of their presence, it is possible to reach the consistency of theory with practice. Hence, it is necessary to revise the antiquated ideas which do not conform to practice.

3 Ni-Al MELTS

According to the phase diagram[10], there are 5 compounds formed in these binary metallic melts, except NiAl having congruent melting point, the rest are all peritectics. Hence the structural units of these melts are Ni, Al atoms as well as Ni_3Al, Ni_5Al_3, NiAl, Ni_2Al_3 and $NiAl_3$ compounds. Putting the composition of the melts as $b = \sum x(\mathrm{Ni})$, $a = \sum x(\mathrm{Al})$; the mass action concentration of every structural unit after normalization as $N_1 = N_{Ni}$, $N_2 = N_{Al}$, $N_3 = N_{Ni_3Al}$, $N_4 = N_{Ni_5Al_3}$, $N_5 = N_{NiAl}$, $N_6 = N_{Ni_2Al_3}$, $N_7 = N_{NiAl_3}$, $\sum x$ is the sum of all equilibrium mole fractions, then it gives chemical equilibria:

$$3Ni(l) + Al(l) = Ni_3Al(l)$$

$$K_1 = \frac{N_3}{N_1^3 N_2},\quad N_3 = K_1 N_1^3 N_2 \tag{10}$$

$$5Ni(l) + 3Al(l) = Ni_5Al_3(l)$$

$$K_2 = \frac{N_4}{N_1^5 N_2^3},\quad N_4 = K_2 N_1^5 N_2^3 \tag{11}$$

$$Ni(l) + Al(l) = NiAl(l)$$

$$K_3 = \frac{N_5}{N_1 N_2},\quad N_5 = K_3 N_1 N_2 \tag{12}$$

$$2Ni(l) + 3Al(l) = Ni_2Al_3(l)$$

$$K_4 = \frac{N_6}{N_1^2 N_2^3},\quad N_6 = K_4 N_1^2 N_2^3 \tag{13}$$

$$Ni(l) + 3Al(l) = NiAl_3(l)$$

$$K_5 = \frac{N_7}{N_1 N_2^3},\quad N_7 = K_5 N_1 N_2^3 \tag{14}$$

After making mass balance it gives:

$$N_1 + N_2 + K_1 N_1^3 N_2 + K_2 N_1^5 N_2^3 + K_3 N_1 N_2 + K_4 N_1^2 N_2^3 + K_5 N_1 N_2^3 - 1 = 0 \tag{15}$$

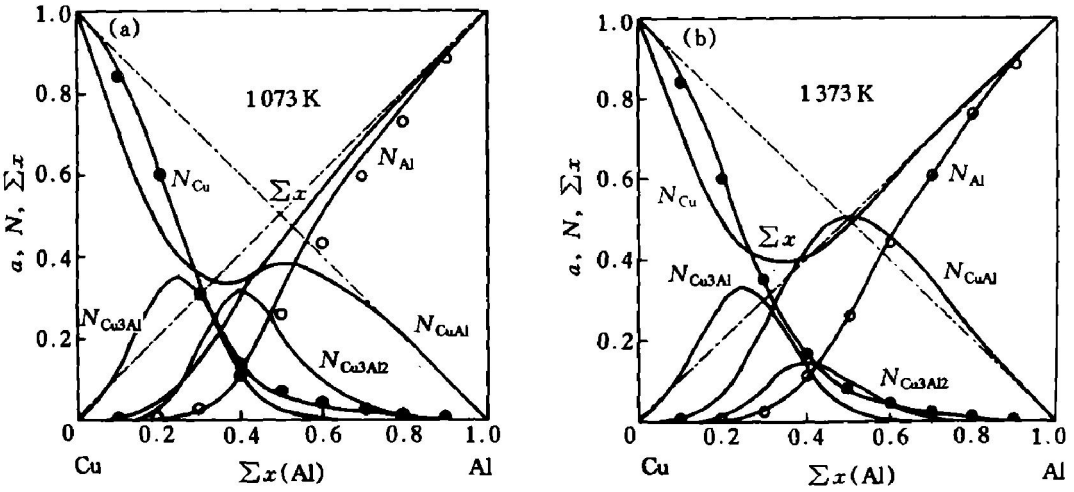

Fig. 1 Comparison of calculated mass concentrations N (" —") with measured activities a(" ●", " ○") of Cu-Al melts
(a) —1073 K; (b) —1373 K

$$aN_1 - bN_2 + (3a - b)K_1N_1^3N_2 + (5a - 3b)K_2N_1^5N_2^3 + (a - b)K_3N_1N_2 + (2a - 3b)K_4N_1^2N_2^3 + (a - 3b)K_5N_1N_2^3 = 0 \quad (16)$$

$$1 - (a + 1)N_1 - (1 - b)N_2 = K_1(3a - b + 1)N_1^3N_2 + K_2(5a - 3b + 1)N_1^5N_2^3 + K_3(a - b + 1)N_1N_2 + K_4(2a - 3b + 1) \cdot N_1^2N_2^3 + K_5(a - 3b + 1)N_1N_2^3 \quad (17)$$

Eqns. (15), (16) and (17) are the calculating model of mass action concentrations for these melts. Using the measured activities a(Ni) and a(Al) of Ni-Al melts at 1873 K from Ref. [10] and inserting them into Eqn. (17) gives $K_{Ni_3Al} = 607.62$ ($\Delta G^{\ominus} = -99867.21$ 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), ($F = 10787.8$, $R = 0.99986$). Substituting these thermodynamic parameters into Eqns. (15) and (16), the calculated mass action concentrations are compared with measured activities as shown in Fig. 2. It is seen that the calculated mass action concentrations agree well with the measured activities, showing that the calculating model can reflect the characteristics of these melts, the majority number of compounds of which being peritectics; otherwise, if stubbornly sticking to the past viewpoint and absolutely negating the presence of four peritectics Ni_3Al, Ni_5Al_3, Ni_2Al_3 and $NiAl_3$, except NiAl, then it would be impossible to obtain results agreeable with practice under condition not running counter to the law of mass action. From this, it once again indicates the great effect of peritectics on the thermodynamic properties of metallic melts.

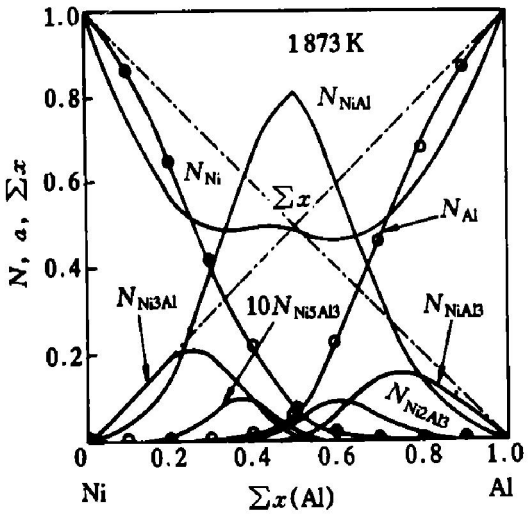

Fig. 2 Comparison of calculated mass action concentrations N ("—") with measured activities a("○", "●") for Ni-Al melts at 1873 K

4 Cu-Sn MELTS

According to the phase diagram[8], there are $Cu_{31}Sn_8$, Cu_3Sn, Cu_6Sn_5, $Cu_{41}Sn_{11}$, $Cu_{20}Sn_6$ compounds etc, formed in these binary metallic melts. In which $Cu_{31}Sn_8$ and $Cu_{41}Sn_{11}$ might as well be written as Cu_4Sn, while $Cu_{20}Sn_6$ might as well be changed to Cu_3Sn, since these complicated compounds are seldom to be found in binary metallic systems. After comparison with different calculating models of mass action concentrations, it is found that the calculating model with four compounds Cu_4Sn, Cu_3Sn, Cu_6Sn_5 and CuSn gives the best agreeable results with practice. Thus the structural units of these melts are determined as Cu, Sn atoms as well as Cu_4Sn, Cu_3Sn, Cu_6Sn_5 and CuSn compounds. Assuming the composition of the melts as $b = \sum x$(Cu), $a = \sum x$(Sn); the mass action concentration of every structural unit after normalization $N_1 = N_{Cu}$, $N_2 = N_{Sn}$, $N_3 = N_{Cu_4Sn}$, $N_4 = N_{Cu_3Sn}$, $N_5 = N_{Cu_6Sn_5}$, $N_6 = N_{CuSn}$, $\sum x$ is the sum of all equilibrium mole fractions, then it gives chemical equilibria:

$$4Cu(l) + Sn(l) = Cu_4Sn(l)$$

$$K_1 = \frac{N_3}{N_1^4N_2}, \quad N_3 = K_1N_1^4N_2 \quad (18)$$

$$3Cu(l) + Sn(l) = Cu_3Sn(l)$$

$$K_2 = \frac{N_4}{N_1^3N_2}, \quad N_4 = K_2N_1^3N_2 \quad (19)$$

$$6Cu(l) + 5Sn(l) = Cu_6Sn_5(l)$$

$$K_3 = \frac{N_4}{N_1^6N_2^5}, \quad N_4 = K_3N_1^6N_2^5 \quad (20)$$

$$Cu(l) + Sn(l) = CuSn(l)$$

$$K_4 = \frac{N_6}{N_1N_2}, \quad N_6 = K_4N_1N_2 \quad (21)$$

After making mass balance it gives:

$$N_1 + N_2 + K_1N_1^4N_2 + K_2N_1^3N_2 + K_3N_1^6N_2^5 + K_4N_1N_2 - 1 = 0 \quad (22)$$

$$aN_1 - bN_2 + (4a - b)K_1N_1^4N_2 + (3a - b)K_2N_1^3N2 + (6a - 5b)K_3N_1^6N_2^5 + (a - b)K_3N_1N_2 = 0 \quad (23)$$

$$1 - (a + 1)N_1 - (1 - b)N_2 = K_1(4a - b + 1)N_1^4N_2 + K_2(3a - b + 1)N_1^3N_2 + K_3(6a - 5b + 1)N_1^6N_2^5 + K_4(a - b + 1)N_1N_2 \quad (24)$$

The above mentioned Eqns. (22), (23) and (24) are the calculating models of mass actions for these melts, in which Eqns. (22) and (23) are used for calculation of mass action concentrations, while Eqn. (24) for regressing equilibrium constants in case of known measured activities ($N_1 = a$(Cu), $N_2 = a$(Sn)). Using the measured activities at 1400 K from Ref. [7], substituting them into Eqn. (24) and regressing, the equilibrium constants and Gibbs free

energies $\Delta G^{\ominus}$ are obtained respectively as K_{Cu_4Sn} = 39.332 11 ($\Delta G^{\ominus}$ = - 42 765.47 J/mol), K_{Cu_3Sn} = 7.878 154 ($\Delta G^{\ominus}$ = - 24 038.93 J/mol), $K_{Cu_6Sn_5}$ = 13 124.29 ($\Delta G^{\ominus}$ = - 110 432.2 J/mol), K_{CuSn} = 1.932 505 ($\Delta G^{\ominus}$ = - 7 672.74 J/mol), (F = 736.865 1, R = 0.997 297). Substituting these equilibrium constants into Eqns. (22) and (23), the calculated mass action concentrations are compared with measured activities as shown in Fig. 3. Good agreement between calculated and measured values testifies that the calculating model formulated can reflect the structural characteristics of these melts. And similarly, if according to the past viewpoint about phase diagrams, negating the presence of peritectics Cu_4Sn, Cu_6Sn_5, CuSn etc, in the melts, it is also impossible to obtain good agreement between calculated and measured values on condition not running counter to the law of mass action. This example once again demonstrates that peritectics are important structural units of the majority of homogeneous metallic melts, admission or negation of their presence is the key problem whether the thermodynamic properties of metallic melts can be successfully investigated. Of course, the expressions Cu_4Sn and CuSn must be proved practically further.

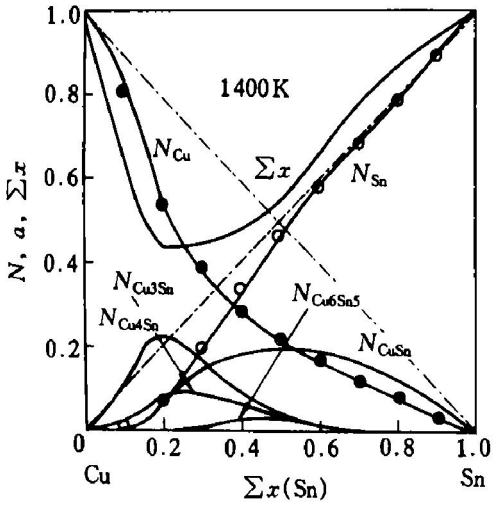

Fig. 3 Comparison of calculated mass action concentrations N ("—") with measured activities a("○","●") for Cu-Sn melts at 1 400 K

5 CONCLUSIONS

1) Peritectics are important structural units of the majority of homogeneous metallic melts, neglecting their presence will make it impossible to study the thermodynamic properties of metallic melts with results which do not run counter to the law of mass action, but agree well with practice.

2) The sole practical criterion of the validity of the calculating model of thermodynamic properties is scientific experiment (in this case, the measured activities), the sole theoretical criterion of the validity of the thermodynamic model is the law of mass action.

[REFERENCES]

[1] ZHANG Jian. Coexistence theory of metallic melts structure involving compound formation and its applications [J]. Special Steel, (in Chinese), 1994, 15(6): 43-53.

[2] ZHNG Jian. Classification of thermodynamic properties of binary metallic melts according to their phase diagrams [J]. Acta Metallurgica Sinica, 1998, 34(1): 75- 85.

[3] ZHANG Jian. Consistency (or similarity) of thermodynamic properties of metallurgical melts with their phase diagrams [J]. Acta Metallurgica Sinica, 1998, 34(7): 742- 752.

[4] ZHANG Jian, WANG Ping. The widespread applicability of the mass action law to metallurgical melts and organic solutions involving compound formation [J]. Special Issue for Physical Chemistry of metallurgical Processes, 2000, 18: 80- 85.

[5] ZHANG Jian. Calculating models of mass action concentrations for metallic melts involving monotectic [J]. Journal of University of Science and Technology Beijing, 2001, 8(4): 432.

[6] ZHANG Jian. Calculating models of mass action concentrations for binary metallic melts involving peritectics [J]. The Chinese Journal of Nonferrous Metals, (in Chinese), 1997, 7(4): 30- 34.

[7] Hultgren R, Desai P D, Hawkins D T, et al. Selected Values of the Thermodynamic Properties of Binary Alloys [M]. Ohi: American Society for Metals, Metals Park, 1973. 152- 154; 798- 799.

[8] Hansen M. Constitutions of Binary Alloys [M]. New York, Toronto, London, McGraw-Hill Book Company. Inc. 1958. 88; 633- 635.

[9] Stolz U K, Arpshofen I, Sommer F, et al. Determination of the enthalpy of mixing of liquid alloys using a high-temperature mixing calorimeter [J]. Jounal of Phase Equilibria, 1993, 14(4): 473- 478.

[10] Desai P D. Thermodynamic properties of selected binary aluminium alloy systems [J]. J Phys Chem Ref Data, 1987, 16(1): 110- 121.

(Edited by LONG Huai-zhong)