Journal of University of Science and Technology Beijing
1995, Vol 2, No 2: 92 ~ 96

CALCULATING MODEL OF MASS ACTION CONCENTRATIONS FOR Cd－Sb ALLOY MELT

CHENG GUOGUANG ZHANG JIAN
Department of Metallurgy, USTB, Beijing 100083, PRC
(Received 1994－04－14)

ABSTRACT According to the Cd－Sb alloy phase diagram, resistivity, heat capacity, partial molar entropy and viscosity, the structural units of this alloy melt have been determined as Cd and Sb atoms as well as Cd_3Sb_2, Cd_4Sb_3 and CdSb compounds. Based on these structural units and the coexistence theory of metallic melt structure involing compound formation, a calculating model of mass action concentrations has been deduced. The calculated mass action concentrations N_{Cd} are in good agreement with measured activities a_{Cd}. The Gibbs standard free energy of formatioin for above three compunds have been obtained too.

KEY WORDS Cd－Sb alloy, mass action concentration, compound, activity

IN recent years much progress has been made in the development of techniques for computerassisted thermodynamic analysises in binary and multicomponent melt systems. The main trends are connected with determination of the mutual relations among thermodynamic properties, physical properties, structure and the type of phase diagrams. Most common phase diagrams of systems with negative deviations exhibit the existence of intermetallic or intermediated phases in the solid state. In liquid state, such systems display the presence of "associates" which influences various properties and many associated solution models have been reported [1 ~ 3] . Zhang Jian suggests the coexistence theory of metallic melts involving compound formation, based on the atomicity and molecularity of metallic melt [4]. This theory has been applid to a variety of melt systems successfully [5 ~ 7] . For Cd－Sb alloy melt, phase diagram, resistivity, heat capacity, partial molar entropy and viscosity have been interpreted as in the liquid alloy system forming intermetallic compounds. Therefore, the aim of this paper is to deduce the model of mass action concentrations for Cd－Sb alloy melt according to Zhang's theory to connect the relation between thermodynamic properties and liquid structure.

1 CALCULATING MODEL OF MASS ACTION CONCENTRATIONS

In order to deduce the model of mass action concentrations for Cd－Sb alloy melt, the

structural units of this melt must be determined firstly.

Hansen suggested that two compounds exist in the Cd−Sb system: stable CdSb (M. P. 459 ℃) and metastable Cd_3Sb_2(M. P. 420 ℃) [8]. Ugai, Dolgova and Zyubina[8] reported the existence of a third metastable compound Cd_4Sb_3. Geffken, Komarek and Miller concluded that the characteristic S- shaped partical molar entropy are due to the existence of Cd_4Sb_3 -clusters in the liquid alloys from the quasichemical theory, and suggested that there was the second order phase transition associated with the formation of Cd_4Sb_3 molecules in Cd−Sb melt [10]. Miller, Paces and Klomarek have measured the resistivity of liquid Cd−Sb alloy [11]. Fig. 1 shows the measured results that the resistivity curves is characterized by two maxima corresponding in composition to CdSb and Cd_3Sb_2. Fisher and Phillips investigated the influence of temperature and composition on the viscosity of liquid Cd−Sb alloys [12]. They found that there was a maximum in viscosity composition curve which occurs at the composition CdSb. The heat capacities of liquid Cd−Sb alloys were determined by Schick and Komarek [13]. At lower temperatures the C_p exhibits a plateau between 50at% and 58at%Cd and a maximum at 57at% Cd(Cd_4Sb_3).

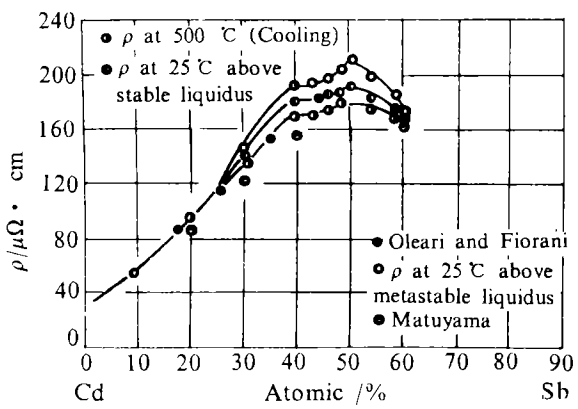

Fig. 1 Resistivity vs compositon for Cd−Sb melts [11]

In accordance with the above facts, the structural units of Cd−Sb alloy melt are Cd and Sb atoms as well as Cd_3Sb_2 , Cd_4Sb_3 and CdSb compounds.

Let $a=\Sigma n_{Cd}$, $b=\Sigma n_{Sb}$, $N_1=N_{Cd}$, $N_2=N_{Sb}$, $N_3=N_{Cd_3Sb_2}$, $N_4=N_{Cd_4Sb_3}$, $N_5=N_{CdSb}$, and according to chemical balances :

$$3Cd(l)+2Sb(l)=Cd_3Sb_2(l) \qquad N_3=K_1N_1^3N_2^2 \tag{1}$$

$$4Cd(l)+3Sb(l)=Cd_4Sb_3(l) \qquad N_4=K_2N_1^4N_2^3 \tag{2}$$

$$Cd(l)+Sb(l)=CdSb(l) \qquad N_5=K_3N_1N_2 \tag{3}$$

The mass balances equations are as follows :

$$N_1+N_2+N_3+N_4+N_5=1 \tag{4}$$

$$a=\Sigma n(N_1+3N_3+4N_4+N_5) \tag{5}$$

$$b=\Sigma n(N_2+2N_3+3N_4+N_5) \tag{6}$$

from Eqs. (5) and (6)

$$aN_2 - bN_1 + (2a-3b)N_3 + (3a-4b)N_4 + (a-b)N_5 = 0 \quad (7)$$

from Eqs. (4) and (7)

$$1-(1-b)N_1-(1+a)N_2 = (2a-3b+1)N_3 + (3a-4b+1)N_4 + (a-b+1)N_5 \quad (8)$$

The combination of the Eqs (1) ~ (8) is the calculating model of mass action concentrations for Cd−Sb alloy melt.

2 RESULTS AND DISCUSSION

It is of great importance to determine the Gibbs free energies of the three compounds to solve the above model. The equilibrium constants of the compounds at 420 ℃ and 500 ℃ can be regressed out from Eq. (8), respectively. Then the $\Delta G^\circ \sim T$ functional relations are expressed as follows :

$$\Delta G^\circ_{Cd_3Sb_2} = -18\,465.33 + 3.063T \quad \text{J/mol}$$

$$\Delta G^\circ_{Cd_4Sb_3} = -10\,504.0 + 2.605T \quad \text{J/mol}$$

$$\Delta G^\circ_{CdSb} = -13\,649.78 + 2.817T \quad \text{J/mol}$$

Furthmore, the changes of mass action concentrations with compositions can be calculated. As shown in Fig. 2 the N_{Cd} , N_{Sb} with compositions present negative deviation because of the formation of Cd_3Sb_2, Cd_4Sb_3 and CdSb compounds in liquid melt. When $\Sigma n_{Cd}=0.5$ and 0.6, the N_{CdSb} and $N_{Cd_4Sb_3}$ have a maxium respectively. The valueof $N_{Cd_4Sb_3}$ is very little and could not be described out in Fig. 2. The comparisons of calculated N_{Cd} with the measure activities a_{Cd} at 420 ℃ and 500 ℃ are listed in Table 1 , and described in Fig. 1 respectively. It is obvious that the calculated values are in good agreement with expermental results. So the above model is reasonable and the thermodynamic properties of metallic melt are closely connected with its liquid structure.

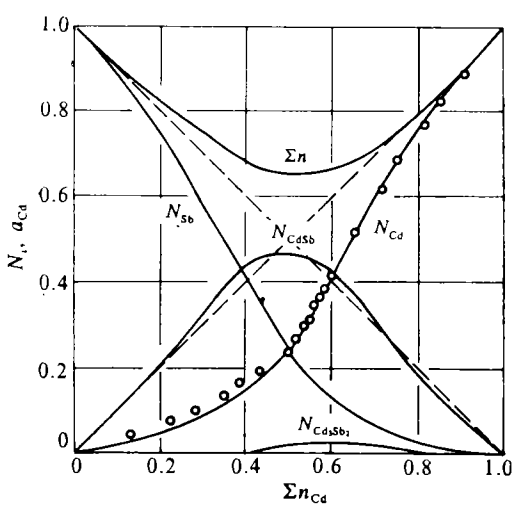

Fig. 2 The changes of mass action concentrations with Σn_{Cd} for Cd−Sb melt at 500 ℃

Table 1 The calculated N_{Cd} with measured a_{Cd} for Cd−Sb melt at 420 ℃

Σn_{Cd}	N_{Cd}	a_{Cd}[10]
0.90	0.892 134 6	0.892 8
0.85	0.830 702 8	0.839 0
0.805	0.769 854 1	0.783 6
0.752	0.690 264 7	0.699 8
0.713	0.625 721 0	0.639 3
0.652	0.515 207 6	0.539 2
0.602	0.419 546 0	0.425 4
0.587	0.391 015 5	0.391 3
0.582	0.381 605 1	0.379 5
0.567	0.353 805 9	0.354 6
0.555	0.332 163 2	0.320 2
0.542	0.309 464 4	0.304 9
0.522	0.276 362 1	0.268 9
0.502	0.245 778 7	0.247 7

3 CONCLUSIONS

(1) According to the Cd−Sb alloy phase diagram, resistivity, heat capacity, partial molar entropy and viscosity, the structure units of this alloy melt have been determined as Cd and Sb atoms as well as Cd_3Sb_2, Cd_4Sb_3, and CdSb compounds.

(2) The calculating model of mass action concentrations has been deduced, and the calculated N_{Cd} are in good agreement with measured activities a_{Cd}.

(3) The Gibbs standard free energies of formation for above three compounds are obtained.

REFERENCES

1 Prigogine I, Defay R. Chemical and Thermodynamics. London : Longmans Green. 1954. 409
2 Schmid R, Austin Chang Y. CALPHAD, 1985, 9(4) : 363
3 Wasai K, Mukai K. J Japan Inst Metals, 1981, 45(6) : 593
4 Zhang J. J Uni of Sci and Tech. Beijing (in Chinese), 1990, 12(3) : 201
5 Zhang J, Cheng G G. J Uni of Sci and Tech Beijing (in Chinese), 1991, 11(6) : 514
6 Cheng G G and Zhang J. Engineering Chemistry and Metallurgy, 1992, 13(1) : 10
7 Zhang J. J Iron and Steel Research, 1991, 3(2) : 7
8 Hansen M , Anderko K. Constitution of Binary Alloys. New York: McGraw−Hill, 1958
9 Ugai Ya A , Dolgova Yu Ya, Zyubina T A. Dokl Akad Naud SSSR, 1961, 138(4) : 856
10 Geffken R, Komarek K L, Miller E. Trans TMS−AIME, 1967, 239(8) : 1152
11 Miller E, Paces J , Komarek K L. Trans TMS−AIME, 1964, 230(12) : 1557
12 Fisher H J, Phillips A. J Metals, 1954(12) : 1060

13 Schick G. Komarek K L. Z Metallkde, 1974, 65(2) : 112

Cd－Sb 合金熔体作用浓度计算模型

成国光　张 鉴
北京科技大学冶金系、北京 100083

摘要 根据 Cd－Sn 合金相图、电阻率、热容量、偏摩尔熵和粘度，确定该合金熔体的结构单元为 Cd 原子，Sb 原子以及 Cd_3Sb_2, Cd_4Sb_3 和 CdSb 化合物．基于以上结构单元，并依据含化合物金属熔体的共存理论，推导了 Cd－Sb 合金熔体的作用浓度计算模型．理论计算的 N_{Cd} 与实测的 Cd 的活度值 a_{Cd} 完全一致．同时也计算出了以上3种化合物的标准自由能．

关键词 Cd－Sb 合金，作用浓度，化合物，活度