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Thermodynamic properties and mixing thermodynamic parameters of Ba-Al, Mg-Al, Sr-Al and Cu-Al metallic melts①

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Abstract: Application of equations of mixing thermodynamic parameters formulated on the basis of the coexistence theory of metallic melts in Ba-Al, Mg-Al, Sr-Al and Cu-Al melts leads to fruitful results that not only the evaluated mass action concentrations agree well with the measured activities, but also the calculated mixing thermodynamic parameters are quite coincident with the experimental values. Moreover, the calculated mass action concentrations strictly obey the mass action law. The evaluated mixing thermodynamic parameters have very fine regularity: the mixing free energy is composed of standard free formation energies of all compounds and chemical potentials of all structural units at equilibrium; the mixing enthalpy consists of standard formation enthalpies of all compounds; the mixing entropy is composed of standard entropies of all compounds and configuration entropies of all structural units at equilibrium. As the equations of mixing thermodynamic parameters formulated are widely applicable to metallic melts involving compound formation, they can be used as the second practical criterion to determine whether thermodynamic models of metallic melts are correctly formulated.

Key words: mass action law; mixing thermodynamic parameters; coexistence theory; activity; mass action concentration

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1 INTRODUCTION

Based on the coexistence theory of metallic melts involving compound formation, the following theoretical calculating equations of mixing thermodynamic parameters have been systematically formulated by giving up some empirical parameters in the association solution model and they were successfully applied to the study on thermodynamic properties and mixing thermodynamic parameters of Fe-Al, Mn-Al and Ni-Al melts.

Mixing free energy:

$$\Delta G^{m} = \sum x \left[\sum_{i=3} N_i \Delta G_i^{\ominus} + RT \sum_{j=1} N_j \ln N_j \right] \quad (1)$$

Excess free energy:

$$\Delta G^{xs} = \Delta G^{m} - RT(a\ln a + b\ln b) \quad (2)$$

Mixing enthalpy:

$$\Delta H^{m} = \sum x \sum_{i=3} N_i \Delta H_i^{\ominus} \quad (3)$$

Mixing entropy:

$$\Delta S^{m} = \sum x \left[\sum_{i=3} N_i \Delta S_i^{\ominus} - R \sum_{j=1} N_j \ln N_j \right] \quad (4)$$

Excess entropy:

$$\Delta S^{xs} = \Delta S^{m} - R(a\ln a + b\ln b) \quad (5)$$

where i represents the number of compounds, leaving 2 positions for two components, it starts from 3; while j is the number of structural unit. Considering that the reliability of calculating equations of mixing thermodynamic parameters of metallic melts should be verified in many ways, thermodynamic properties and mixing thermodynamic parameters of Ba-Al, Mg-Al, Sr-Al and Cu-Al melts were studied.

2 COEXISTENCE THEORY OF METALLIC METALS INVOLVING COMPOUND FORMATION

The coexistence theory of metallic melts involving compound formation has been explained and proved in detail[1]. Its main points are as follows:

1) Metallic melts involving compound formation consist of atoms and molecules.

2) There are dynamic equilibrium reactions between atoms and molecules, such as:

$$xA + yB = A_xB_y$$

3) Chemical reactions in metallic melts obey the mass action law.

The common viewpoint of the coexistence theory of metallic melts with associated solution model[2, 3] is that both assume there are atoms and chemical short range orders or compounds in metallic melts. The differences between them are: 1) assuming only a small number of associate to treat the alloy melts is common with associated solution models; while determination of the structural units of metallic melts according to the phase diagrams and physical parameters is the

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starting point of the coexistence theory of metallic melts. 2) The activity coefficient is still used in associated solution models; while in the coexistence theory of metallic melts, using the mass action concentrations conforming with the law of mass action naturally gives calculated results a good agreement with experimental values, so the activity coefficient is not needed.

2.1 Ba-Al melts

According to the phase diagram[4], there are three compounds BaAl, $BaAl_2$ and $BaAl_4$ formed in this binary system, in which $BaAl_4$ has congruent melting point, and the rest are all peritectics. Hence, in accordance with the coexistence theory of metallic melts[2], the structural units of these melts are Ba, Al atoms as well as BaAl, $BaAl_2$ and $BaAl_4$ compounds. Assuming that the composition of the melts is $a=\sum x(\mathrm{Al})$, $b=\sum x(\mathrm{Ba})$, the mass action concentration of every structural unit after normalization is $N_1=N(\mathrm{Ba})$, $N_2=N(\mathrm{Al})$, $N_3=N(\mathrm{BaAl})$, $N_4=N(\mathrm{BaAl_2})$, $N_5=N(\mathrm{BaAl_4})$, and $\sum x$ is the sum of all equilibrium mole fractions, in the light of mass action law, chemical equilibria are as follows:

$$\mathrm{Ba(l)+Al(l)=BaAl(l)}$$

$$K_1=\frac{N_3}{N_1N_2},\quad N_3=K_1N_1N_2 \tag{6}$$

$$\mathrm{Ba(l)+2Al(l)=BaAl_2(l)}$$

$$K_2=\frac{N_4}{N_1N_2^2},\quad N_4=K_2N_1N_2^2 \tag{7}$$

$$\mathrm{Ba(l)+4Al(l)=BaAl_4(l)}$$

$$K_3=\frac{N_5}{N_1N_2^4},\quad N_5=K_3N_1N_2^4 \tag{8}$$

Making mass balance, it gives

$$N_1+N_2+K_1N_1N_2+K_2N_1N_2^2+K_3N_1N_2^4=1 \tag{9}$$

$$aN_1-bN_2+(a-b)K_1N_1N_2+(a-2b)K_2N_1N_2^2+(a-4b)K_3N_1N_2^4=0 \tag{10}$$

$$1-(a+1)N_1-(1-b)N_2=K_1(a-b+1)N_1N_2+K_2(a-2b+1)N_1N_2^2+K_3(a-4b+1)N_1N_2^4 \tag{11}$$

Eqns. (9), (10) and (11) are the calculating model of mass action concentrations for these melts, in which Eqns. (9) and (10) are used for evaluation of mass action concentrations, while Eqn. (11) for regression of equilibrium constants under condition that the measured activities ($N_1=a(\mathrm{Ba})$, $N_2=a(\mathrm{Al})$) are known.

According to Eqns. (1)-(5) the concrete calculating equations of mixing thermodynamic parameters of these melts are

Mixing free energy:

$$\Delta G^{\mathrm{m}}=\sum x[N_3\Delta G^{\ominus}(\mathrm{BaAl})+N_4\Delta G^{\ominus}(\mathrm{BaAl_2})+N_5\Delta G^{\ominus}(\mathrm{BaAl_4})+RT(N_1\ln N_1+N_2\ln N_2+N_3\ln N_3+N_4\ln N_4+N_5\ln N_5)] \tag{12}$$

Excess free energy:

$$\Delta G^{\mathrm{xs}}=\Delta G^{\mathrm{m}}-RT(a\ln a+b\ln b) \tag{13}$$

Mixing enthalpy:

$$\Delta H^{\mathrm{m}}=\sum x[N_3\Delta H^{\ominus}(\mathrm{BaAl})+N_4\Delta H^{\ominus}(\mathrm{BaAl_2})+N_5\Delta H^{\ominus}(\mathrm{BaAl_4})] \tag{14}$$

Standard entropy:

$$\Delta S_i^{\ominus}=\frac{\Delta H_i^{\ominus}-\Delta G_i^{\ominus}}{T} \tag{15}$$

Mixing entropy:

$$\Delta S^{\mathrm{m}}=\sum x[N_3\Delta S^{\ominus}(\mathrm{BaAl})+N_4\Delta S^{\ominus}(\mathrm{BaAl_2})+N_5\Delta S^{\ominus}(\mathrm{BaAl_4})-R(N_1\ln N_1+N_2\ln N_2+N_3\ln N_3+N_4\ln N_4+N_5\ln N_5)] \tag{16}$$

Excess entropy:

$$\Delta S^{\mathrm{xs}}=\Delta S^{\mathrm{m}}-R(a\ln a+b\ln b) \tag{17}$$

By the use of the measured activities a_{Ba} and a_{Al} as well as mixing thermodynamic parameters of Ba-Al melts at 1 373 K from Ref. [5] and substituting them into Eqns. (9)-(17), the K, $\Delta G^{\ominus}$, $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ of formation of Ba-Al melts are obtained, as listed in Table 1.

Evaluation by the use of Eqns. (9)-(11) gives the comparison of calculated mass action concentrations with the measured activities as shown in Fig. 1. Calculated mixing thermodynamic parameters by the use of Eqns. (12)-(17) are compared with experimental values as shown in Fig. 2. It can be seen from both figures that not only the calculated mass action concentrations agree well with the measured activities, but also the evaluated mixing thermodynamic parameters conform with experimental values. Meanwhile, the calculating process as well as the obtained mass action concentrations strictly obey the mass action law. Thus it testifies that the model formulated couldauthentically embody the structural reality and mixing thermodynamic characteristics of this metallic melt.

Table 1 K, $\Delta G^{\ominus}$, $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ of formation of Ba-Al melts at 1 373 K

Compound	K	$\Delta G^{\ominus}$/(J·mol^{-1})	$\Delta H^{\ominus}$/(J·mol^{-1})	$\Delta S^{\ominus}$/(J·mol^{-1}·K^{-1})
BaAl	29.375 21	−38 606.842	−71 684.25	−24.091 3
$BaAl_2$	96.750 98	−52 221.306	−122 726.1	−51.351
$BaAl_4$	282.094 2	−64 443.601	−116 501.1	−37.915
$F(R)$	554.522 9	(0.994 93)	1 568.996	(0.998 20)

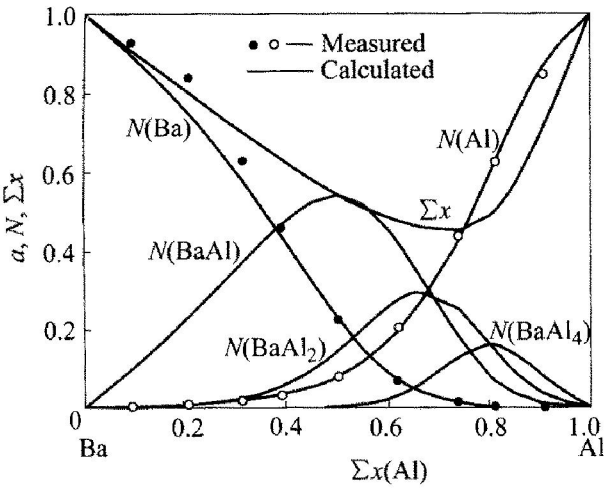

Fig. 1 Comparison of calculated mass action concentrations(N) with measured activities(a) for Ba-Al melts at 1 373 K

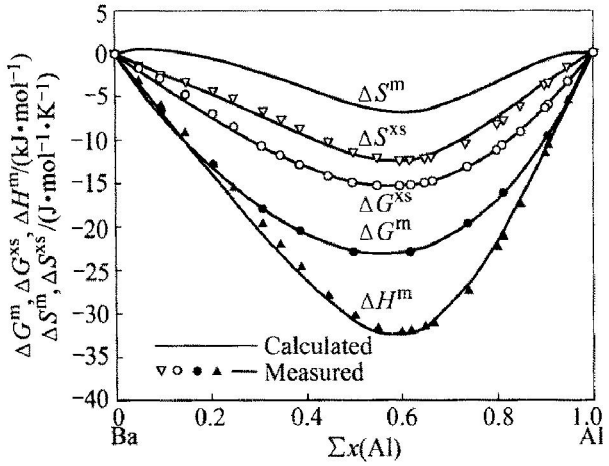

Fig. 2 Comparison of calculated mixing thermodynamic parameters with measured values for Ba-Al melts at 1 373 K

2.2 Mg-Al melt

According to the phase diagram[6], there are three compounds Mg_2Al, $Mg_{17}Al_{12}$ and $MgAl_2$ formed in Mg-Al binary system, in which $Mg_{17}Al_{12}$ has congruent melting point, and the rest are all peritectics. Hence, in accordance with the coexistence theory of metallic melts[1], the structural units of these melts are Mg, Al atoms as well as Mg_2Al, $Mg_{17}Al_{12}$ and $MgAl_2$ compounds. Here, we assume that the composition of the melts is $a = \sum x(\mathrm{Al})$, $b = \sum x(\mathrm{Mg})$; the mass action concentration of every structural unit after normalization is $N_1 = N(\mathrm{Mg})$, $N_2 = N(\mathrm{Al})$, $N_3 = N(\mathrm{Mg_2Al})$, $N_4 = N(\mathrm{Mg_{17}Al_{12}})$, $N_5 = N(\mathrm{MgAl_2})$; and $\sum x$ is the sum of all equilibrium mole fractions.

Using measured activities and mixing thermodynamic parameters of Mg-Al melts at 1 073 K from Ref.[7], K, $\Delta G^{\ominus}$, $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ of formation of Mg-Al melts are evaluated, as listed in Table 2.

The calculated mass action concentrations of Mg-Al melts at 1 073 K are compared with measured activities, as shown in Fig. 3. Meanwhile, comparison of evaluated mixing thermodynamic parameters with experimental values is shown in Fig. 4. Similarly, It can be seen from both figures that the agreement between calculated mass action concentrations and measured activities is quite well, and the conformability of evaluated mixing thermodynamic parameters with experimental values is also very well. Furthermore, thermodynamic properties of these melts strictly obey the mass action law. Thereby, it testifies that the model formulated can exactly reflect the structural reality and mixing thermodynamic characteristics of Mg-Al melt.

2.3 Sr-Al melt

According to Ref.[4], there are three com-

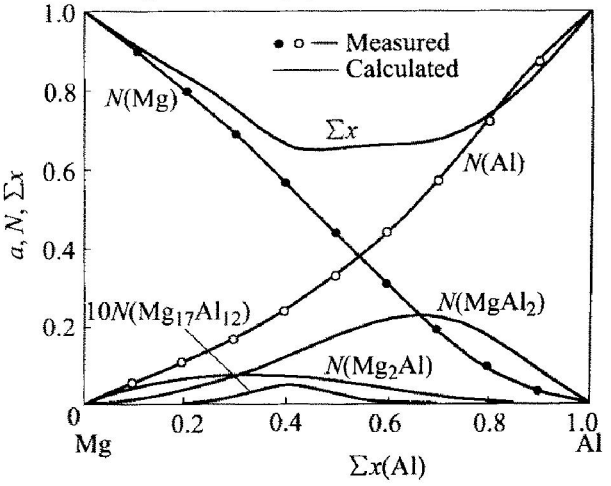

Fig. 3 Comparison of calculated mass action concentrations(N) with measured activities(a) for Mg-Al melts at 1 073 K

Table 2 K, $\Delta G^{\ominus}$, $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ of formation of Mg-Al melts at 1 073 K

Compound	K	$\Delta G^{\ominus}$/(J·mol^{-1})	$\Delta H^{\ominus}$/(J·mol^{-1})	$\Delta S^{\ominus}$/(J·mol^{-1}·K^{-1})
Mg_2Al	0.944 744 4	507.362	− 25 262.99	− 24.017 1
$Mg_{17}Al_{12}$	$2.197\,788\times10^{9}$	− 192 004.87	− 179 267.9	11.870 4
$MgAl_2$	3.667 28	− 11 598.905	− 18 098.21	− 6.057 1
$F(R)$	4 992.637	(0.999 43)	3 529.391	(0.999 20)

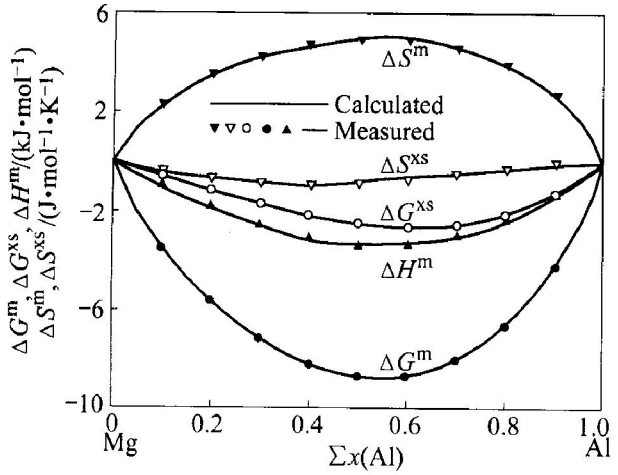

Fig. 4 Comparison of calculated mixing thermodynamic parameters with measured values for Mg-Al melts at 1 073 K

pounds $SrAl_4$, $SrAl_2$ and SrAl formed in Sr-Al binary system, in which $SrAl_4$ has congruent melting point, and the rest are peritectics. While in the light of Ref. [6], the compounds formed are $SrAl_4$, $SrAl_2$ and Sr_8Al_7. After examination with a lot of variants, it is found that only the model considering the presence of four compounds $SrAl_4$, $SrAl_2$, SrAl and Sr_8Al_7 gives the best agreement with experimental data. Hence, in accordance with the coexistence theory of metallic melts[1], the structural units of these melts are Sr, Al atoms as well as $SrAl_4$, $SrAl_2$, SrAl and Sr_8Al_7 compounds. Here, the composition of the melts is assumed as $a = \Sigma x(\mathrm{Al})$, $b = \Sigma x(\mathrm{Sr})$; the mass action concentration of every structural unit after normalization as $N_1 = N(\mathrm{Sr})$, $N_2 = N(\mathrm{Al})$, $N_3 = N(\mathrm{Sr_4Al})$, $N_4 = N(\mathrm{Sr_2Al})$, $N_5 = N(\mathrm{SrAl})$, $N_6 = N(\mathrm{Sr_8Al_7})$; Σx as the sum of all equilibrium mole fractions.

Applying the measured activities and mixing thermodynamic parameters of Sr-Al melts at 1 323 K from Ref. [8], K, $\Delta G^{\ominus}$, $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ of formation of Sr-Al melts are evaluated, as listed in Table 3.

The calculated mass action concentrations of Sr-Al melts at 1 323 K are compared with measured activities as shown in Fig. 5. And the comparison of evaluated mixing thermodynamic parameters with experimental values is shown in Fig. 6. It can be seen in both figures that not only the calculated mass action concentrations agree excellently with measured activities, but also the conformability of evaluated mixing thermodynamic parameters with experimental ones is quite well. In the meantime, the agreements are all obtained under condition of strictly obeying the mass action law. Hence, this testifies that the model deduced can authentically embody the structural reality and mixing thermodynamic characteristics of this melt.

2.4 Cu-Al melt

There isn't any identical opinion about Cu-Al 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. [9], Cu_9Al_4, Cu_3Al_2, Cu_4Al_3, CuAl and $CuAl_2$ are given. Recently in Ref. [10], 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 compounds, it is found that 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 Cu-Al melt are Cu, Al atoms as well as Cu_3Al, Cu_3Al_2 and CuAl compounds. Here the composi-

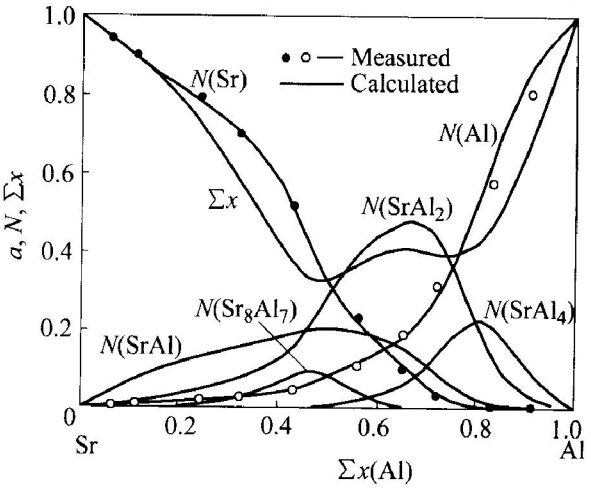

Fig. 5 Comparison of calculated mass action concentrations(N) with measured activities(a) for Sr-Al melts at 1 323 K

Table 3 K, $\Delta G^{\ominus}$, $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ of formation of Sr-Al melts at 1 323 K

Compound	K	$\Delta G^{\ominus}$/(J·mol^{-1})	$\Delta H^{\ominus}$/(J·mol^{-1})	$\Delta S^{\ominus}$/(J·mol^{-1}·K^{-1})
$SrAl_4$	485.936	− 68 085.075	− 88 089.41	− 15.120
$SrAl_2$	125.151	− 53 152.235	− 85 346.59	− 24.334
SrAl	7.536 086	− 22 228.234	− 42 598.98	− 15.397
Sr_8Al_7	$2.314\,365 \times 10^{10}$	− 262 650.758	− 272 050.2	− 7.104 6
$F(R)$	831.732 4	(0.998 60)	774.674 6	(0.998 43)

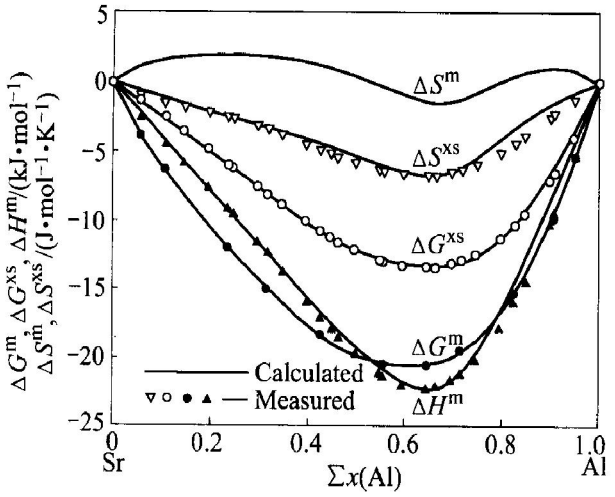

Fig. 6 Comparison of calculated mixing thermodynamic parameters with measured values for Sr-Al melts at 1 323 K

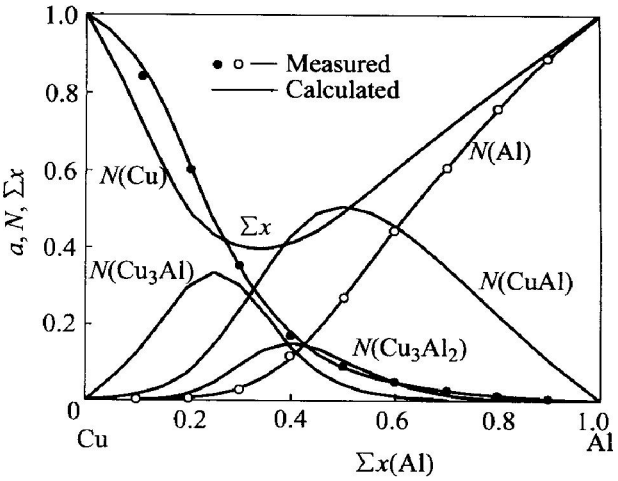

Fig. 7 Comparison of calculated mass action concentrations(N) with measured activities(a) for Cu-Al melts at 1 373 K

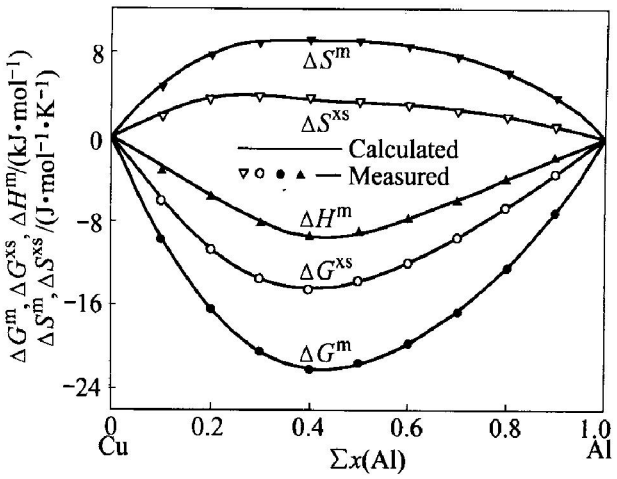

Fig. 8 Comparison of calculated mixing thermodynamic parameters with measured values for Cu-Al melts at 1 373 K

tion of the melts is assumed as $a = \Sigma x$(Al), $b = \Sigma x$(Cu); the mass action concentration of every structural unit after normalization as $N_1 = N$(Cu), $N_2 = N$(Al), $N_3 = N$(Cu$_3$Al), $N_4 = N$(Cu$_3$Al$_2$), $N_5 = N$(CuAl), and Σx as the sum of all equilibrium mole fractions.

With the help of measured activities and mixing thermodynamic parameters of Cu-Al melts at 1 373 K from Ref. [7], K, $\Delta G^{\ominus}$, $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ of formation of Cu-Al melt are evaluated, as listed in Table 4.

The calculated mass action concentrations of Cu-Al melts at 1 373 K are compared with measured activities as shown in Fig. 7. Meanwhile, comparison of evaluated mixing thermodynamic parameters with experimental values is shown in Fig. 8. It can be seen from both figures that not only the agreement between calculated mass action concentrations and measured activities is quite good, but also the evaluated mixing thermodynamic parameters conform exactly with experimental values. At the same time, the agreements are wholly accomplished under condition of strictly obeying the mass action law. Hence, this confirms that the model formulated can authentically represent the structural reality and mixing thermodynamic characteristics of this melt.

It is clear from the above-mentioned four examples that the evaluated mixing thermodynamic parameters have quite high regularity: the mixing free energy ΔG^m is composed of standard free formation energies of all compounds and chemical potentials of all structural units at equilibrium; the mixing enthalpy ΔH^m consists of standard formation enthalpies of all compounds; the mixing entropy ΔS^m is composed of standard entropies of all compounds and configuration entropies of all structural units at equilibrium. Hence, in case of the coexistence theory of metallic melts, there is no

Table 4 K, $\Delta G^{\ominus}$, $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ of formation of Sr-Al melts at 1 373 K

Compound	K	$\Delta G^{\ominus}$/(J·mol^{-1})	$\Delta H^{\ominus}$/(J·mol^{-1})	$\Delta S^{\ominus}$/(J·mol^{-1}·K^{-1})
Cu$_3$Al	245.104 1	− 62 841.45	− 29 542.02	24.253
Cu$_3$Al$_2$	2 420.561	− 88 999.156	− 68 060.61	15.250 2
CuAl	22.609 7	− 35 618.819	− 21 022.79	10.630 8
F(R)	10 913.83	(0.999 74)	2 143.474	(0.998 68)

necessity to use empirical parameters.

Finally, there is an important question to be cleared up, that is, why so many peritectics are taken as structural units in Ba-Al, Mg-Al and Sr-Al melts during evaluation of their thermodynamic properties and mixing thermodynamic parameters? The answers could be found in Ref. [11, 12], where the conclusions are "many peritectics yet exist in metallic melts" and "in spite of their lower stability than 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". In addition, in Ref. [13, 14], there are also detailed illustrations about the structure of Ba-Al, Mg-Al and Sr-Al melts.

3 CONCLUSIONS

1) Application of equations of mixing thermodynamic parameters formulated on the basis of the coexistence theory of metallic melts in Ba-Al, Mg-Al, Sr-Al and Cu-Al melts leads to fruitful results that not only evaluated mass action concentrations agree well with measured activities, but also calculated mixing thermodynamic parameters are quite coincident with the experimental values. Moreover, the calculated mass action concentrations strictly obey the mass action law.

2) The mixing free energy is composed of standard free formation energies of all compounds and chemical potentials of all structural units at equilibrium; the mixing enthalpy consists of standard formation enthalpies of all compounds; the mixing entropy is composed of standard entropies of all compounds and configuration entropies of all structural units at equilibrium. Hence, in case of the coexistence theory of metallic melts, there is no necessity to use empirical parameters.

3) As the equations of mixing thermodynamic parameters formulated are widely applicable to metallic melts involving compound formation, they can be used as the second practical criterion to determine whether thermodynamic models of metallic melts are correctly formulated.

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