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MEASUREMENT OF THERMODYNAMIC PROPERTIES OF LIQUID Al-Mg ALLOYS①

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ABSTRACT The activities of Mg element in liquid Al-Mg alloys were determined by electromotive force method in a cell made of BN crucible. The activities of Mg and Al as well as other thermodynamic properties were calculated from the measured EMF data. The results indicate that the Mg-concentration in the alloys at 1 073 K shows a negative deviation from Rault's Law in the whole range of concentration. When X_{Mg} is $\leqslant 0.55$, the deviation is small; when X_{Mg} is > 0.7, the deviation becomes large. When X_{Mg} is < 0.126, the Mg concentration curve follows Henry's Law, the Henry's constant is 0.86. The behavior of Al is characterized by ideal solution in the range of $0 \leqslant X_{Mg} < 0.8$, which shows a positive deviation from Rault's Law in the range of $0.58 < X_{Mg} < 0.8$ and a negative deviation when X_{Mg} is > 0.8.

Key words Al-Mg alloys activity thermodynamic properties boron nitride

1 INTRODUCTION

The thermodynamic properties are useful for the production, application and theoretical study of alloys. Al-Mg alloys have found wide uses as an important structural material. As a result, the study of thermodynamic properties of the Al-Mg alloys becomes an important topic. In literature there is much work on the thermodynamic properties of the Al-Mg alloys[1-6], but the results obtained by various authors show great differences or even principal divergences. The reason is that different experimental methods and apparatuses were used.

Generally, there are two methods, i. e. vapor pressure method and electromotive force method, are used for measuring the activities of components in alloys. Лукоценко *et al*[4] measured the activities of Mg in the Al-Mg alloys by using vapor pressure method and electromotive force method. They pointed out that the data determined by means of the electromotive force method are more precise and reliable, because Mg is a surface active substance, and it tends to segregate at the interface between the carrier gas and the melt; as a result, the activity values of Mg measured by them are higher. Belton *et al*[5,]], Wu *et al*[7] and Ito *et al*[8] hence made some corrections to their activity data measured by the vapor pressure method. In this paper we adopt the electromotive force method, in which the liquid Mg is used as a reference electrode in the measurements, and we calculate the activity values of Mg and Al in the Al-Mg alloys, and other thermodynamic properties of the Al-Mg alloys from the obtained EMF values.

2 EXPERIMENTAL

2.1 Preparation of raw materials

The Al-Mg alloys were prepared by using pure aluminium(Al> 99.99%) and pure magnesium(Mg> 99.9%). The procedures were as follows: firstly, pure aluminium was melted in a corundum crucible in an argon atmoshpere, then the required amount of magnesium was added to it. The mixture was then stirred with a corundum rod, and argon gas was blown into the melt

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for 20 min to remove the dross and gas. The prepared alloys after cooling were cut into small pieces for use. The solid chlorides for flux making were dehydrated in a hydrogen chloride gas.

2.2 Cell configuration

The cell configuration is shown schematically in Fig. 1. The reference electrode was made of 15 g of molten magnesium, and the working electrode was made of 25 g of Al-Mg alloys in which the Al/Mg ratios were variable. The counter electrode was made of a W wire.

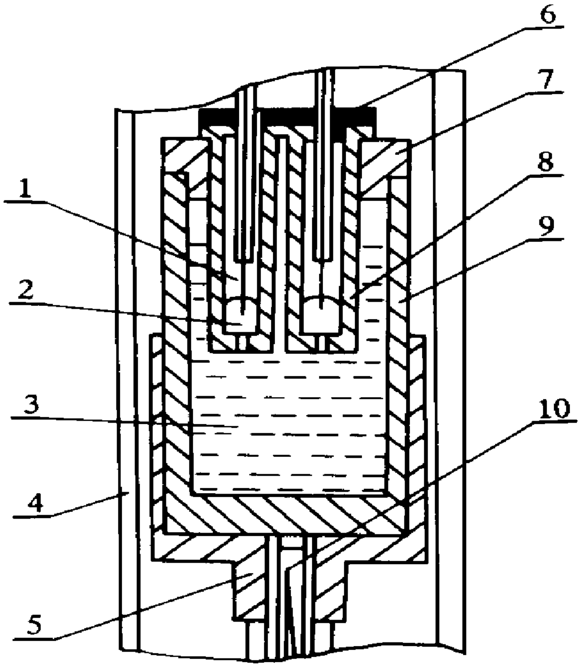

Fig. 1 Schematic of molten-salt cell

1 —Electrode lead wire; 2 —Al-Mg alloy;
3 —Electrolyte; 4 —Alumina pipe;
5 —Support(stainless steel); 6 —BN lid;
7 —Graphite cover; 8 —BN crucible;
9 —Alumina crucible; 10 —Thermocouple

There were two *d* 18 mm × 60 mm BN crucibles for containing the reference electrode and working electrode, separately.

The electrolyte was composed of KCl-LiCl melt in equal mole ratios containing 5% $MgCl_2$. The working temperature was 1 073 K.

The electromotive forces were measured by using a UJ25 type high-resistance potentiometer and an HP3468A type digital voltmeter connected in parallel. The former was used for regular measurements and the later was for monitoring and detecting the instantaneous change of the electromotive force.

The cell configuration is

$Mg(l) \mid KCl\text{-}LiCl\text{-}MgCl_2 \mid Mg\text{-}Al(l)$

The electrode reactions may be written as follows.

At cathode: $Mg^{2+} + 2e^- = [Mg]_{Al}$

At anode: $Mg(l) = Mg^{2+} + 2e^-$

The total cell reaction: $Mg(l) = [Mg]_{Al}$

The activity of Mg was calculated by using Nernst's equation:

$$\Delta G = -2FE$$

$$\Delta G_{Al} = RT \ln a_{Mg}$$

$$E = -[RT/(2F)] \ln a_{Mg} \qquad (1)$$

where E —Electromotive force of the cell; a_{Mg} —Activity of Mg in Al-Mg alloy vs pure liquid magnesium($a_{Mg} = 1$); T —Absolute temperature, K; R —Universal gas constant, $J \cdot mol^{-1} \cdot K^{-1}$; F —Faraday's constant.

3 RESULTS AND DISCUSSION

3.1 Electromotive forces of cells

The electromotive forces of the cells were measured in both the heating and cooling processes. The results agree well with each other, and they vary along the same straight line.

In Table 1 are listed the measured EMF values at 1 073 K in these experiments.

3.2 Determination of activities and activity coefficients

From eq. (1), the activity of Mg can be obtained as

$$a_{Mg} = \exp[-2EF/(RT)] \qquad (2)$$

and the activity coefficients can be calculated as follows:

$$\gamma_{Mg} = a_{Mg}/X_{Mg} \qquad (3)$$

$$\ln \gamma_{Al} = -a_{Mg} \cdot X_{Mg} \cdot X_{Al} - \int_{1}^{X_{Al}} a_{Mg} \mathrm{d}X_{Al} \qquad (4)$$

where $a_{Mg} = \ln \gamma_{Mg}/(1 - X_{Mg})^2$.

Similarly, the activity of aluminium can be calculated by Eq. (5).

$$a_{Al} = \gamma_{Al} \cdot X_{Al} \qquad (5)$$

The calculation of activities and activity coefficients of Mg and Al for liquid Al-Mg alloys at 1 073 K are listed in Table 1.

Table 1 Cell EMF, activities and activity coefficients of Mg and Al for liquid Al-Mg alloys at 1 073 K

X_{Mg}	E/mV	a_{Mg}	γ_{Mg}	a_{Al}	γ_{Al}
0.008	236.36	0.006	0.750	0.992	1.000
0.014	208.35	0.011	0.786	0.986	1.000
0.029	170.43	0.025	0.862	0.972	1.001
0.047	145.37	0.043	0.915	0.952	0.999
0.102	112.28	0.088	0.863	0.895	0.997
0.126	102.40	0.109	0.865	0.871	0.997
0.149	98.73	0.118	0.792	0.853	1.002
0.186	89.53	0.144	0.774	0.821	1.008
0.277	72.32	0.209	0.754	0.730	1.009
0.402	54.71	0.306	0.761	0.605	1.011
0.586	35.48	0.464	0.792	0.403	0.973
0.694	33.72	0.482	0.695	0.366	1.198
0.782	27.2	0.555	0.710	0.240	1.101
0.867	19.06	0.662	0.764	0.095	0.716
0.942	8.39	0.834	0.885	0.008	0.131

The activity curves of the components in the Al-Mg alloys are presented in Fig. 2 and Fig. 3. It can be seen from Fig. 2 that the activity of magnesium shows a negative deviation from the ideal solution in the whole range of concentration. The activity of aluminium follows the ideal solution law in the range of $0 \leqslant X_{Mg} \leqslant 0.58$, and it shows a positive deviation from the ideal solution in the range of $0.58 < X_{Mg} < 0.8$ and a negative deviation when X_{Mg} is > 0.8. When X_{Mg} is < 0.126, the behavior of Mg follows Henry's Law, and the Henry's constant is 0.86.

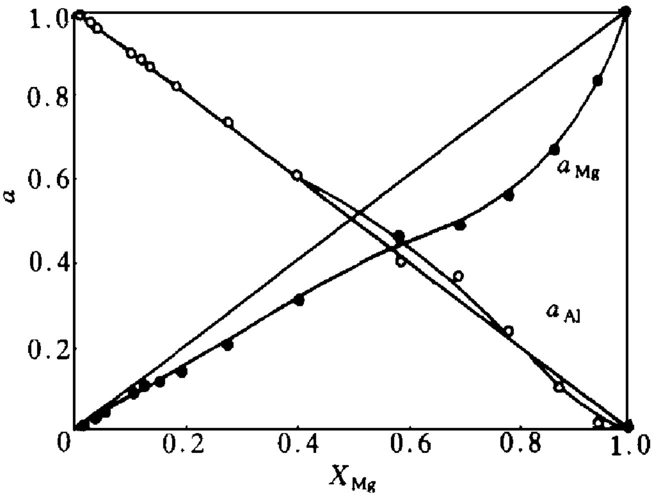

Fig. 2 Activities of Mg and Al vs X_{Mg} in Al-Mg alloys at 1 073 K

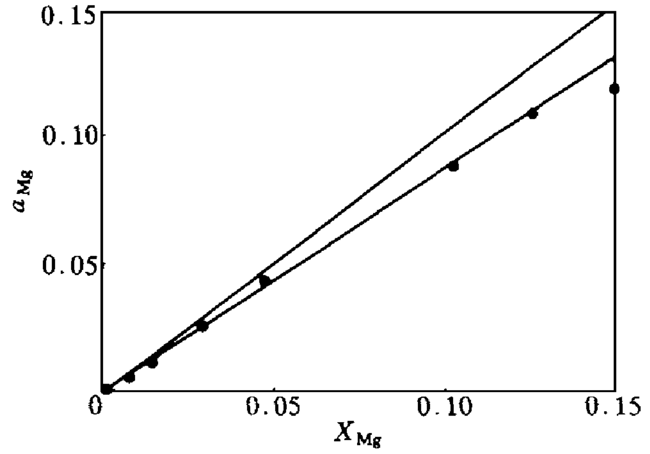

Fig. 3 Activity of Mg vs X_{Mg} in range of $X_{Mg} < 0.15$ at 1 073 K

Еременко *et al*[2] indicated that the activity of Mg shows a negative deviation when X is < 0.55 and a positive deviation when X_{Mg} is > 0.55 from the ideal solution, respectively.

Belton *et al*[5] indicated that the activity of Mg shows a large negative deviation from the ideal solution when X_{Mg} is > 0.5, but the deviation is small up to approaching the ideal solution. There is a wide difference between these results and ours.

Лукошенко *et al*[4] measured the activity of Mg in Al-Mg alloys simultaneously by means of the vapor pressure method and the electromotive force method. The results determined by the vapor pressure method indicated that the activity of Mg shows a positive deviation from the ideal solution in the whole range of concentration, while the results determined by the electromotive force demonstrate that the activity of Mg shows a negative deviation from the ideal solution, the later agrees with those in Ref. [6].

Цыплакова *et al*[3] used Al-10% Mg as reference electrode, whose stability was affected by the variation of the activity of Mg with temperature and the change of the electrode composition.

In the above literatures, the errors are caused by the pollution of the electrodes from the alumina cells and the evaporation of magnesium.

3.3 Determination of thermodynamic properties

The thermodynamic properties of the solutions are determined by the following equations

For the partial molar free energies:

$$\Delta G_{Mg}/\text{J}\cdot\text{mol}^{-1} = 2FE \qquad (6)$$

$$\Delta G_{Al}/\text{J}\cdot\text{mol}^{-1} = RT\ln a_{Al} \qquad (7)$$

For the partial molar entropies:

$$\Delta S_{Mg}/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = 2F(\partial E/\partial T) \qquad (8)$$

$$\Delta S_{Al}/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = 2\partial\Delta G_{Al}/\partial T = -R\ln a_{Al} - RT\partial\ln a_{Al}/\partial T \qquad (9)$$

For the partial molar enthalpies:

$$\Delta H_i/\text{J}\cdot\text{mol}^{-1} = \Delta G_i + T\Delta S_i \qquad (10)$$

For the mixing free energy:

$$\Delta G/\text{J}\cdot\text{mol}^{-1} = X_{Mg}\cdot\Delta G_M + X_{Al}\cdot\Delta G_{Al} \qquad (11)$$

For the mixing entropy:

$$\Delta S/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = X_{Mg}\cdot\Delta S_{Mg} + X_{Al}\cdot\Delta S_{Al} \qquad (12)$$

For the mixing enthalpy:

$$\Delta H/\text{J}\cdot\text{mol}^{-1} = X_{Mg}\cdot\Delta H_{Mg} + X_{Al}\cdot\Delta H_{Al} \qquad (13)$$

For the excess partial molar free energy:

$$\Delta G_i^{xs} = RT\ln\gamma_i \qquad (14)$$

For the excess free energy:

$$\Delta G^{xs} = X_{Mg}\Delta G_{Mg}^{xs} + X_{Al}\Delta G_{Al}^{xs} \qquad (15)$$

For the excess partial molar entropy:

$$\Delta S_i^{xs} = -\partial(\Delta G_i^{xs})/\partial T \qquad (16)$$

Substituting Eqn. (14) into Eqn. (16) yields

$$\Delta S_{Mg}^{xs} = -R\ln\gamma_{Mg} - RT\partial\ln\gamma_{Mg}/\partial T \qquad (17)$$

$$\Delta S_{Al}^{xs} = -R\ln\gamma_{Al} - RT\partial\ln\gamma_{Al}/\partial T \qquad (18)$$

Thus, the excess entropy will be

$$\Delta S^{xs} = X_{Mg}\Delta S_{Mg}^{xs} + X_{Al}\Delta S_{Al}^{xs} \qquad (19)$$

The various thermodynamic property curves at 1 073 K are presented in Figs. 4~ 10.

The mixing free energy is zero in the whole range of concentration, which means that Al and Mg can be completely mixed at this temperature (1 073 K). At $X_{Mg} \approx 0.7$, the mixing free energy reaches its minimum value, $\Delta G_{\min} = -7.33$ kJ/mol. This value is a little higher than those in Ref. [6] (6.7 kJ/mol) and Ref. [2] (5.75 kJ/mol), but a little smaller than that in Ref. [3] (8.57 kJ/mol).

The mixing free energy $\Delta\overline{G}$ is negative in the whole range of concentration and the

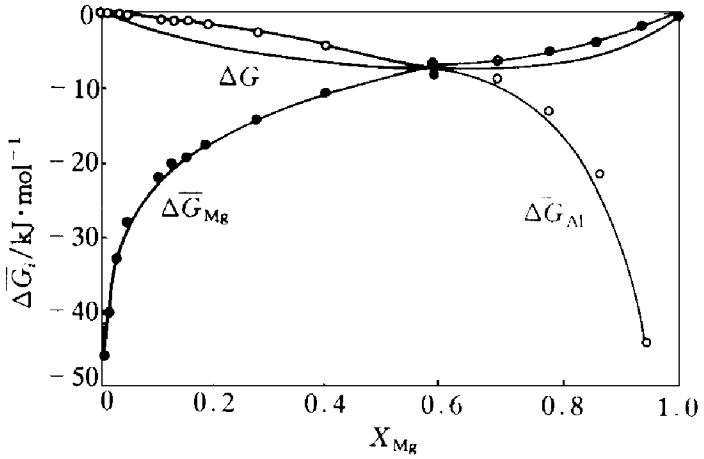

Fig. 4 Variation of partial molar free energy vs X_{Mg} at 1 073 K

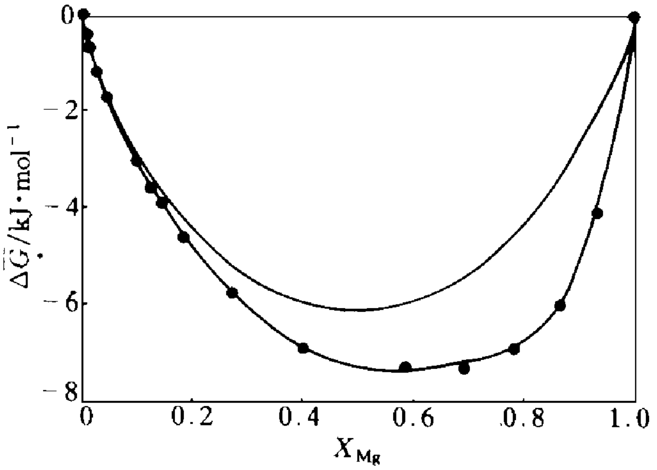

Fig. 5 Variation of mixing free energy vs X_{Mg} at 1 073 K

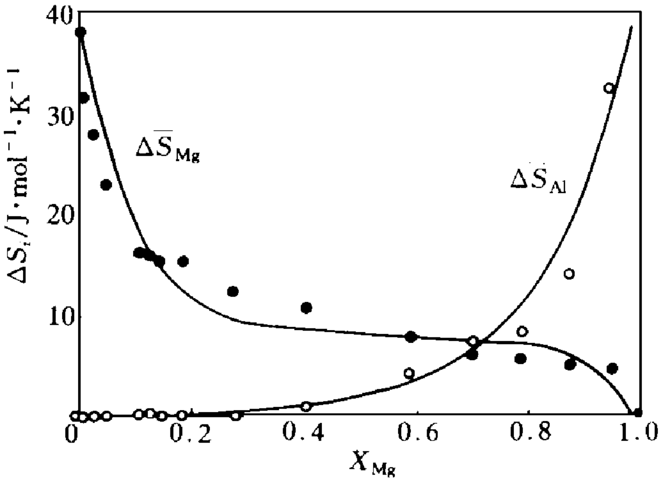

Fig. 6 Variation of partial molar entropy vs X_{Mg} at 1 073 K

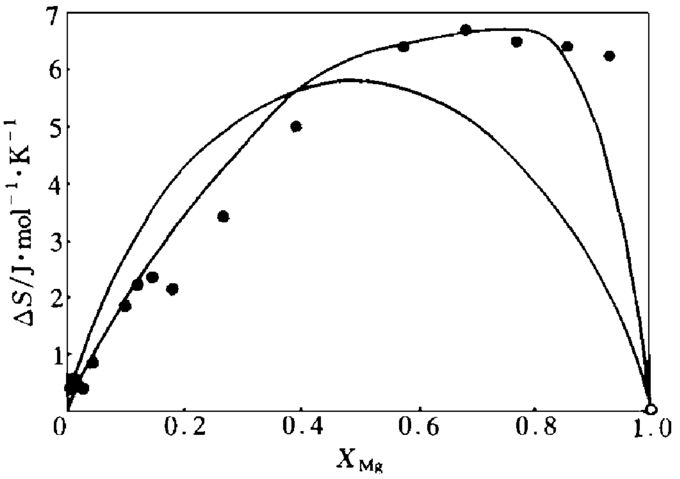

Fig. 7 Variation of mixing entropy vs X_{Mg} at 1 073 K

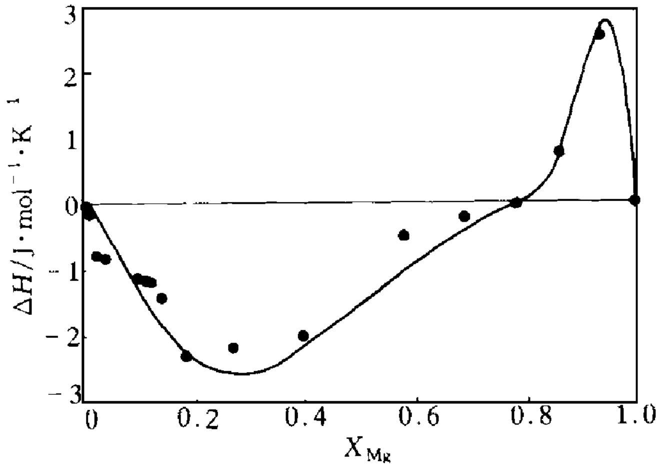

Fig. 8 Variation of mixing enthalpy vs X_{Mg} at 1 073 K

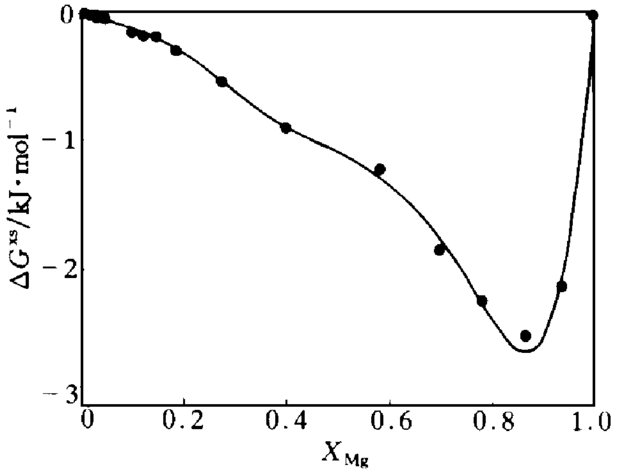

Fig. 9 Variation of excess free energy vs X_{Mg} at 1 073 K

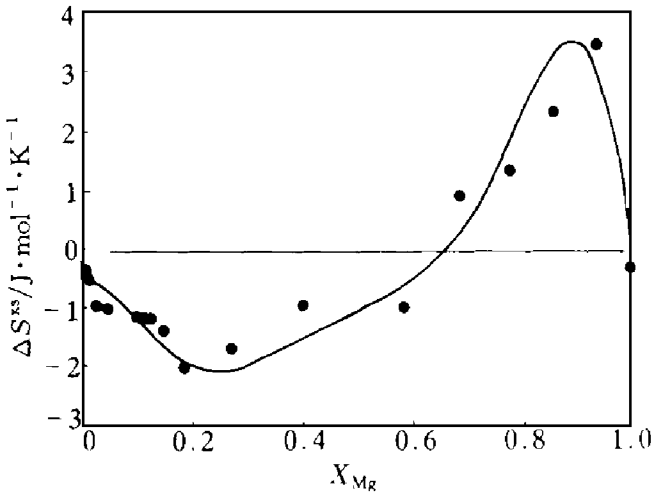

Fig. 10 Variation of excess entropy vs X_{Mg} at 1 073 K

$\Delta G_{min} = -7.33$ kJ/mol. The mixing entropy is positive and $\Delta S_{max} = 6.6$ J/mol·K. The mixing enthapy is negative when X_{Mg} is < 0.78 and $\Delta H_{min} = -2.3$ kJ/mol; it is positive when X_{Mg} is > 0.78 and $\Delta H_{max} = 2.5$ kJ/mol. The excess free energy is negative in the whole range of concentration, and $\Delta G^{xs}_{min} = -2.48$ kJ/mol. The excess entropy is negative when X_{Mg} is < 0.5 and $\Delta S^{xs}_{min} = -1.5$ J/mol·K; it is postitive when X_{Mg} is > 0.5 and $\Delta S^{xs}_{max} = 4.3$ J/mol·K.

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