

Thermodynamic investigation on $Al_{1-x}Mn_x$ melts by Knudsen cell mass spectrometry

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Abstract

The thermodynamic activities of the components in $Al_{1-x}Mn_x$ alloys have been measured from 1250 to 1550 K by Knudsen cell mass spectrometry, using the “ion–current ratio method”. Owing to the high pressure of Mn, the measurements are limited to the range $0 < x_{Mn} < 0.5$ and a reference based on the measurements of pure metals is introduced. The excess Gibbs free energies are deduced and the minimum value of the excess molar Gibbs free energy is $-(8500 \pm 350) \text{ J mol}^{-1}$ at $x=0.45$. Combined with calorimetric quantities, these data allow calculation of the entropies of formation which are found to be very small. The thermodynamic behaviour corresponds to rather large negative interactions between the aluminium and manganese atoms and a moderate chemical short-range order in agreement with the conclusions of the structural study of the literature.

1. Introduction

The first experimental thermodynamic investigations by Russian scientists [1, 2] on $Al_{1-x}Mn_x$ liquid alloys have been reviewed by Desai [3], who pointed out the lack of consistency between the partial values of the given thermodynamic quantities as regards the Gibbs–Duhem equation. Moreover, owing to the peculiarities of the system, in part due to the manganese, the experimental difficulties are numerous especially concerning the achievement of equilibrium [4]. The recent thermodynamic assessment of McAlister and Murray [5], emphasizes the existence of numerous metastable equilibria in the Al-rich side of the diagram and in particular, the quasicrystalline phase discovered in a melt-spun sample containing 14 at.% Mn.

According to the original investigation by the electromotive force (EMF) method of Batalin *et al.* [1], the excess Gibbs free energy of mixing liquid alloys presents a minimum shifted towards Mn-rich solutions at $x=0.80$. Moreover, the above-mentioned assessment [5] evidenced discrepancies between the experimental thermodynamic data in the liquid and the values necessary to obtain a correct coherency with the phase diagram. The selected thermodynamic behaviour corresponds to a subregular solution with a minimum at $x=0.45$. The results deduced from the very recent assessment proposed by Jansson [6], not very different

from [7], are in agreement with the aluminium activity values of Batalin [1], but yield quite different values as far as manganese activity values are concerned although these latter have been directly measured by EMF [1]. Then a new investigation of the activities of the Al–Mn melts is of particular interest.

In the present work, mass spectrometric measurements of partial vapour pressures of Al and Mn in equilibrium with Al–Mn melts in a Knudsen cell are carried out in the temperature range 1250 to 1550 K and composition range 0.06 to 0.48 at.% manganese. The same technique has been used recently to investigate the thermodynamic stabilities of the solid phase at lower temperature (1175 K) and in the composition range 0.42 to 0.62 at.% manganese [8].

2. Experimental details

The mass spectrometer system has been described in more detail in a previous paper [9]. Binary alloys were provided by mixing together weighed amounts of pure Al and Mn directly in the Knudsen cell. The alloys were vapourized from an electron bombardment heated Knudsen cell with 0.5 mm diameter and an orifice to sample ratio of about 1/100. Experiments were made using a graphite outer crucible and a boron nitride inner crucible.

The ions formed in the ionization source were mass analysed by a single focusing mass spectrometer (Varian

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Mat CH5 Bremen). We used a 14.5 V electron beam to produce Al^+ and Mn^+ , which were identified by their masses. The temperature of the cell was measured by a 10% RhPt/Pt thermocouple located at the bottom, the calibration being performed by the mass spectrometric observation of the melting temperature of silver and copper. Measurements were done step-by-step on heating the alloys. After the last measurement the cell was cooled and weighed to check the loss of the sample mass by evaporation. Owing to the high pressure of Mn, we calculated a 1%–3% correction drift in the molar composition of the sample depending on the experiment.

3. Treatment of data

By means of the intensity ratio method proposed by Belton and Fruehan [10], the excess Gibbs free energy of mixing the liquid phase can be determined. This method consists of measuring the ratio of the ionic intensities of the isotopes $I(^{27}Al)$ and $I(^{55}Mn)$ at the same temperature for different molar fractions of the alloys. Practically, the measurements are performed over a certain temperature range and a mean value is then selected. At this value, the knowledge of the ratio I_{Mn}/I_{Al} in the whole range of composition leads to the excess chemical potential referred to pure liquid components according to:

$$\ln \gamma_{Al} = - \int_{x_{Mn}=0}^{x_{Mn}=x} x_{Mn} d \ln \left\{ \frac{I_{Mn}}{I_{Al}} \frac{x_{Al}}{x_{Mn}} \right\} \quad (1)$$

where γ_{Al} and γ_{Mn} are the activity coefficients of Al and Mn. With this method the pressure calibration of the mass spectrometer is not necessary.

In the present work, due to the high pressure of Mn and the high temperature values of the liquidus in the Mn-rich side, we limited our investigations to the range $0 < x_{Mn} < 0.5$ and then introduce a calibration coefficient measured for pure elements.

We have already applied the classical Belton's method to different metallic and silicate melts [11] or mixed oxides [12].

4. Results

In this work, the measurements were carried out in the temperature range 1250 to 1550 K and the experimental values of the activities are given at 1520 K. Figure 1 presents the logarithm of the ratio of the ionic intensities $\ln\{I_{Mn}/I_{Al}\}$ plotted *vs.* the reciprocal temperature $1/T$ for 16 different molar fractions ranging from 0.06 to 0.48 x . As an example, the break observed

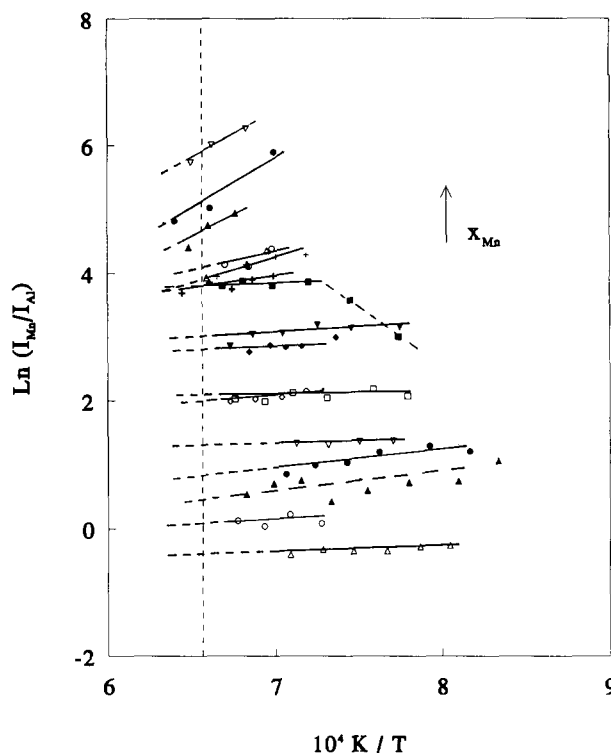


Fig. 1. Logarithm of the ratio of the ionic intensities I_{Mn}/I_{Al} plotted against the reciprocal temperature for different mole fractions of x . $x=0.060, 0.08, 0.095, 0.135, 0.16, 0.18, 0.23, 0.27, 0.295, 0.335, 0.355, 0.385, 0.39, 0.435, 0.46, 0.48$.

on one of the lines corresponds to the temperature of the liquidus at the related molar fraction. The variation of the function $\ln\{I_{Mn} \cdot (1-x)/I_{Al} \cdot x\} = f(x)$ at 1520 K is shown on Fig. 2. The experimental points are fitted with a linear function $y = A + Bx$ valid in the composition range 0 to 0.5 x , with $A = 2.1$ and $B = 6.2$. The integration, following eqn. (1), leads to the values of γ_{Al} and a_{Al} .

If we introduce the basic relation connecting the vapour pressure and the ionic intensity measured, $P_i S = I_i T$, we can write $\ln\{I_{Mn}/I_{Al}\} = \ln\{a_{Mn}/a_{Al}\} + \ln\{I_{Mn}^\circ/I_{Al}^\circ\}$ where the last term represents the ratio of the ionic intensities of the pure elements, *i.e.* a constant term, independent of x . We can calculate a_{Mn} from the upper relation, a_{Al} being obtained from the precedent integration of Belton's relation. Afterwards, we performed measurements on pure Al and pure Mn, and determine the value of 5.3 for $\ln(I_{Mn}^\circ/I_{Al}^\circ)$ at 1300 K, *i.e.* the highest temperature where the Knudsen conditions are still valid towards the pressure of pure manganese. Taking into account the variation of the vapour pressure ratio between 1300 and 1520 K given in the literature [13], we finally selected a value of 4.9 for $\ln(I_{Mn}^\circ/I_{Al}^\circ)$ at 1520 K. Table 1 gives the experimental values of the activities of aluminium and manganese obtained following the above-mentioned method in the concentration range $0 < x < 0.5$; the manganese activity, a_{Mn} , calculated from the aluminium activity by

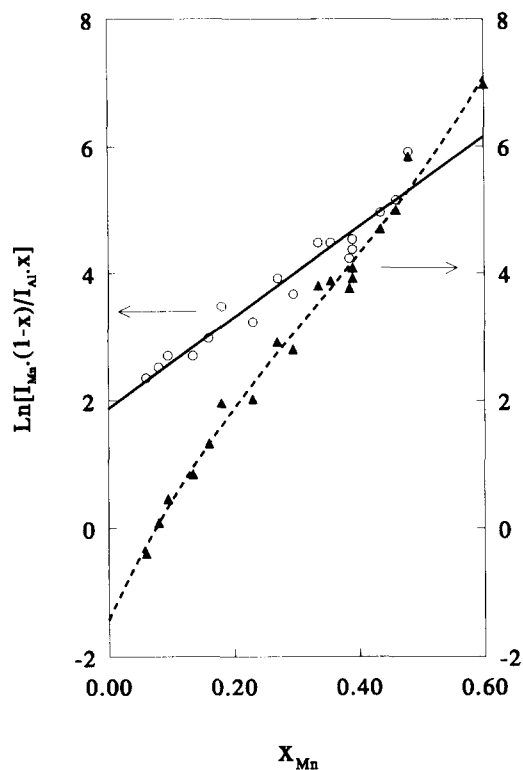


Fig. 2. Logarithm of the ratio $\ln[I_{Mn}(1-x)/I_{Al}x]$, —, and the ratio $\ln[I_{Mn}/I_{Al}]$, ---, against the mole fraction x at $T=1520$ K.

TABLE 1. Experimental values of the activities a_i of aluminium and manganese and calculated a_{Mn} from the Gibbs–Duhem relation at $T=1520$ K

x	a_{Al}	a_{Mn}	$a_{Mn}(GD)$
0	1	0	0
0.1	0.872	0.011	0.010
0.2	0.706	0.037	0.036
0.3	0.529	0.088	0.085
0.4	0.365	0.176	0.169
0.5	0.230	0.310	0.298
0.6	0.150 ^a		0.424
0.7	0.080 ^a		0.594
0.8	0.040 ^a		0.748
0.9	0.015 ^a		0.885
1	0		1

^aExtrapolated values.

the Gibbs–Duhem relation is reported in the same table and it can be seen that the difference does not exceed 5%. The corresponding results are shown on Fig. 3 as well as the experimental data of Batalin [1].

In order to compare our results with earlier literature data, the values of the ratio of the ionic intensities were extrapolated at 1570 K. The corresponding excess chemical potential of aluminium and manganese, μ_i^E , the excess Gibbs free energy, G_m^E , and the Gibbs free energy of mixing $\Delta_{mix}G_m$, derived from the classical relations are listed in Table 2. The excess Gibbs free

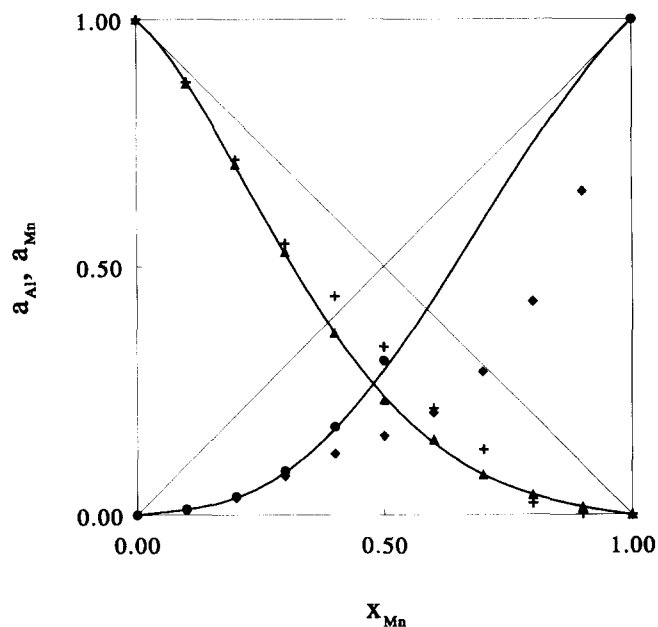


Fig. 3. Variation of the activities a_{Mn} and a_{Al} of the components against the mole fraction x at 1520 K: ●, ▲, a_{Mn} and a_{Al} in this work; ◆, +, ref. 1.

TABLE 2. Excess chemical potential μ_i^E of aluminium and manganese, excess Gibbs free energies G_m^E and free energies of mixing $\Delta_{mix}G_m$ at $T=1570$ K

x	$-\mu_{Al}^E$ (J mol ⁻¹)	$-\mu_{Mn}^E$ (J mol ⁻¹)	$-G_m^E$ (J mol ⁻¹)	$-\Delta_{mix}G_m$ (J mol ⁻¹)
0	0	35680	0	0
0.1	412	29625	3334	7580
0.2	1630	22510	5807	12635
0.3	3655	16486	7505	15480
0.4	6490	11222	8380	17165
0.5	10136	6734	8435 ± 300	17480
0.6	12803	4529	7840	16625
0.7	17255	2155	6680	14655
0.8	21010	874	4900	11430
0.9	24760	212	2665	6910
1	28720	0	0	0

energies can be represented by the following polynomial expression:

$$G_m^E = x(1-x)[A + B(2x-1)]$$

with $A = -33705$ and $B = -4840$. Figure 4 presents the variation of the excess Gibbs free energy *vs.* the molar fraction at 1570 K obtained in this work as well as the different results of the literature.

5. Discussion

The comparison of both experimental results on Fig. 3 clearly shows a large discrepancy for $x > 0.3$ between our and Batalin's results, especially for a_{Mn} which were

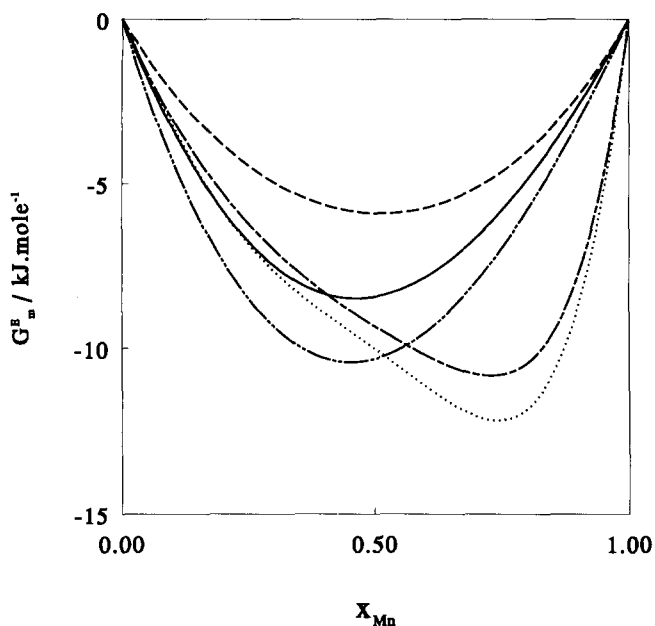


Fig. 4. Variation of the excess molar Gibbs free energy against the mole fraction x at 1570 K: —, our results; ·····, ref. 1; ---, ref. 3; - · - ·, ref. 5; - - - -, ref. 6.

directly measured by EMF; in the case of a_{Al} deduced from the Gibbs-Duhem relation, the difference is smaller but the whole data lead to very negative values of G_m^E with a minimum at $x=0.8$ as seen on Fig. 4. In their critical assessments based on the coherency between the phase diagram and the thermodynamic properties, McAlister and Murray [5] and Jansson [6] discard the Batalin's values and propose less negative values, the minimum of which is shifted towards $x=0.5$.

Figure 4 allows comparison between the set of published excess Gibbs free energies; our results confirm the position of the minimum at $x=0.45$ but the value of G_m^E amounts to -8500 J mol^{-1} compared with -5907 [6] and $-10\,300 \text{ J mol}^{-1}$ [5].

Then, according to our study, the Al-Mn solutions exhibit a rather large negative deviation from ideality, and the excess Gibbs free energy of mixing displays a slight dissymmetry, giving a minimum G_m^E of $(-8500 \pm 350) \text{ J mol}^{-1}$ at $x=0.45$. This indicates an ordering effect in the liquid due to attractive interactions between aluminium and manganese.

The calculation of excess entropies and the entropies of mixing based on our results and the enthalpies of mixing from Esin *et al.* [2], leads to the values listed in Table 3 and shown on Fig. 5. The entropy of mixing is rather small and a significant feature of the curve is a minimum close to zero around $x=0.3$. The existence of preferred interactions between the atoms no longer distributed at random corresponds to a decrease of the configurational entropy.

TABLE 3. Excess entropies, S_m^E and entropies of mixing $\Delta_{\text{mix}}S_m$ at $T=1570 \text{ K}$

x	$-S_m^E$ ($\text{J mol}^{-1} \text{ K}^{-1}$)	$\Delta_{\text{mix}}S_m$ ($\text{J mol}^{-1} \text{ K}^{-1}$)	$-\Delta_{\text{mix}}H_m^a$ (J mol^{-1})
0	0	0	0
0.1	1.95	0.75	6390
0.2	3.88	0.3	11900
0.3	5.03	0.05	15415
0.4	5.43	0.15	16910
0.5	5.36	0.4	16848
0.6	4.86	0.75	15470
0.7	4.15	0.95	13170
0.8	3.28	0.90	10050
0.9	1.93	0.75	5690
1	0	0	0

^aSee ref. 2.

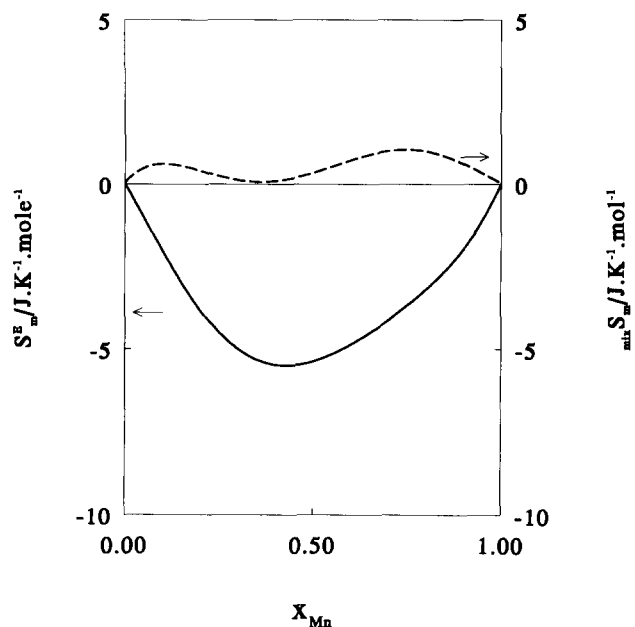


Fig. 5. Variation of the molar entropy (---) and excess of molar entropy of mixing (—) against the mole fraction x .

Since the discovery of quasi-crystalline phases in these alloys, the structure of the liquid has been extensively studied through the determination of the partial pair correlation functions by neutron diffraction [14]. The concluding remarks deduced from our thermodynamic study are in general agreement with the conclusions of the structural study.

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