

## Thermodynamics and phase equilibria in the Al–Mn system

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### Abstract

The Al–Mn system has been investigated by Knudsen cell-mass spectrometry in the temperature range 1100–1275 K and composition range 42–62 at.% manganese. Thermodynamic activities were obtained by direct comparison with the elements. The variation of manganese activity with composition at 1175 K was found to be in accordance with the published phase diagram. The free energies of phase formation at 1175 K were calculated as: for  $\text{Al}_{0.57}\text{Mn}_{0.43}$  ( $\gamma_2$ ),  $-3790 \text{ cal (g-atom)}^{-1}$ ; for  $\text{Al}_{0.50}\text{Mn}_{0.50}$  ( $\gamma$ ),  $-3860 \text{ cal (g-atom)}^{-1}$ ; for  $\text{Al}_{0.45}\text{Mn}_{0.55}$  ( $\epsilon$ ),  $-3890 \text{ cal (g-atom)}^{-1}$ .

### 1. Introduction

The research described here is part of a broad study of compounds of first-row transition metals with p-block elements. Among the goals of this program are the acquisition of reliable thermodynamic data for those systems in which such data are lacking, the documentation of stability trends and the development of an understanding of these trends in terms of atomic properties and concepts of chemical bonding. The current focus is on an isoelectronic series of 1:1 compounds with 10 valence electrons, namely TiS, VP, CrSi, and “MnAl”. The first three of these substances are stoichiometric compounds with narrow ranges of homogeneity, whereas it can be seen from the phase diagram of the Al–Mn system [1] shown in Fig. 1 that “MnAl” does not form at a unique stoichiometry but rather as a solid solution in the  $\gamma$  and  $\gamma_2$  single-phase regions. It has been shown that the  $\gamma$  to  $\gamma_2$  transition is sufficiently rapid that the  $\gamma$ -phase cannot be retained by quenching, even by splat-cooling techniques, and the transition was accordingly studied by high temperature X-ray diffraction [2]. A rather large number of Mn–Al compounds not shown on the equilibrium diagram have also been reported [1]. In the present study, high-temperature vaporization experiments with a mass spectrometer were undertaken to study the Mn–Al system near the 1:1 composition in order to measure the thermodynamic stabilities of the phases, to obtain information about the location of phase boundaries, and to compare the stability of Al–Mn alloys having compositions near 1:1 with true compounds which have the same number of valence electrons.

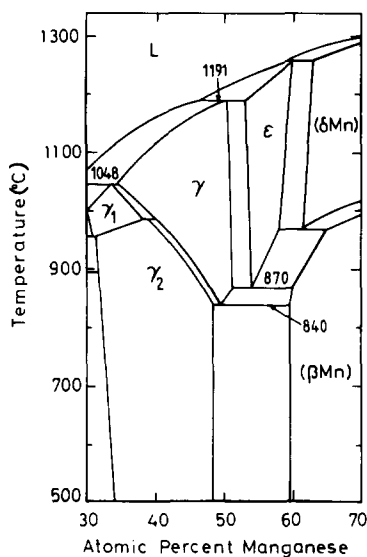


Fig. 1. Al-Mn phase diagram, 30–70 at.% Mn [1].

## 2. Experimental details

Mn–Al samples of composition between 40 and 60 at.% Mn were prepared by arc-melting appropriately weighed mixtures of elemental manganese and aluminium on a water-cooled copper hearth under flowing high-purity argon. The samples were found to shatter on cooling from the melt, making estimates of weight loss during the arc-melting procedure difficult. The as-cast samples were crushed in a tool steel mortar and routinely examined by X-ray powder diffraction to identify the crystalline phases present. Portions of the samples were then loaded into a Knudsen cell mass spectrometer for high-temperature vaporization experiments.

The mass spectrometer system used in the experiments has been described in more detail in a previous paper [3]. In the current Mn–Al work only a few experimental variations were adopted. The Mn–Al samples were placed into a suitably lined graphite Knudsen cell. The sample was heated to a temperature at which vapor effusing from the cell could just be detected with the mass spectrometer, the temperature was then reduced by *ca.* 100 K, and the sample was allowed to anneal for at least one hour before again raising the temperature to make measurements. Thermodynamic activities of manganese and aluminium in a Mn–Al alloy were determined by monitoring the variation with temperature of manganese and aluminium ion intensity resulting from the respective partial pressures of the elemental gases over the alloy. The temperature program used was a 5–10° “stairstep” with a 3 min delay between measurements. The instrument was calibrated by means of effusion runs on the respective pure elements with identical experimental parameters. The Mn–Al samples and manganese standards were contained

in a fused silica cup inside a tantalum-lined graphite cell. Elemental aluminium was contained in a boron nitride liner. Other liner materials (*e.g.* tungsten and tantalum) were found not to give reproducible results. Reliable aluminium measurements were particularly difficult to make owing to a combination of low ion current signals and difficulty in containing liquid aluminium. Measurements of aluminium activity were thus restricted to three samples having high atom fractions of aluminium.

The residues of the effusion experiments were again examined by X-ray powder diffraction and subjected to a wet chemical analysis. The analysis was performed by dissolving the Mn–Al sample in nitric/sulfuric acid and oxidizing to permanganate using  $\text{KIO}_3$ . The permanganate content was then determined colorimetrically. A vacuum fusion analysis was also performed on one of the residues to determine the extent of oxygen contamination, which was found to be less than 0.1% by weight.

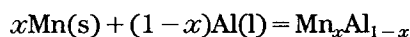
A standard electron impact ionization source was used in the mass spectrometer experiments. The electron energy was set at 12.5 eV for these measurements as this value was found to eliminate interference from organic contaminants in the vacuum system without significantly altering the intensity of the species of interest. A few runs were performed with differing effusion cell orifice areas, but no systematic dependence on orifice area was observed.

### 3. Treatment of data

Thermodynamic activities relative to the pure solid elements were obtained as follows. The partial pressure of a species in a Knudsen cell mass spectrometry experiment is proportional to  $IT$ , where  $I$  is the ion current due to that species, and  $T$  is the temperature of the effusing vapor. Hence the thermodynamic activity of a species in the sample is given by  $a = I/I^0$ , where  $I$  is measured for the elemental vapor above the sample and  $I^0$  is measured above the pure element under the same experimental conditions of temperature, orifice area, and electron energy [3]. Although  $I$  and  $I^0$  are measured in different experiments, the mass spectrometer is sufficiently stable that reproducible results are obtained. In practice, activities at a given temperature were calculated from the slopes and intercepts of  $\log IT$  and  $\log I^0T$  vs.  $1/T$  plots:

$$\text{Log } a_i = (A_i - A_i^0)/T + (B_i - B_i^0)$$

where  $A_i$  and  $A_i^0$  are the slopes and  $B_i$  and  $B_i^0$  are the intercepts of the  $\log IT$  vs.  $1/T$  plots for the sample and pure element, respectively. Free energies of formation:



were calculated by the relation

$$\Delta G_{f, T}^0 = 2.303RT[x \log a_{\text{Mn}} + (1-x) \log a_{\text{Al}}]$$

where  $x$  is the atom fraction of Mn in the solid. Enthalpies of phase formation at 298.15 K were obtained from

$$\Delta H_{f, 298}^0 = \Delta G_{f, T}^0 + T\Delta\Phi'$$

where

$$\Phi' = -(G_T^0 - H_{298}^0)/T = S_T^0 - (H_T^0 - H_{298}^0)/T$$

#### 4. Results

A typical set of  $\log IT$  vs.  $1/T$  curves is presented in Fig. 2 and the experimentally determined activity parameters are listed in Table 1. The variation of activities with composition at 1175 K is given in Fig. 3. A certain amount of caution should be exercised in equating the slope ( $A$ ) parameters to a "second-law" type enthalpy change since the temperature ranges over which data were collected overlap with possible phase transitions in the solid. These parameters were used only to calculate component activities in the temperature range of the measurements. These activities were then used to calculate the free energies of phase formation of the  $\gamma_2$ ,  $\gamma$  and  $\epsilon$  phases at 1175 K. The results are given in Table 2. As there are no heat capacity or entropy data for these solid alloys, these were estimated to be additive of the solid elements (extrapolated data for solid aluminium). The resulting enthalpies of formation at 298.15 K are given in Table 2.

#### 5. Discussion

A comparison of the log activity plot at 1175 K in Fig. 3 with the sequence of phases at 900 °C in the phase diagram shown in Fig. 1 shows

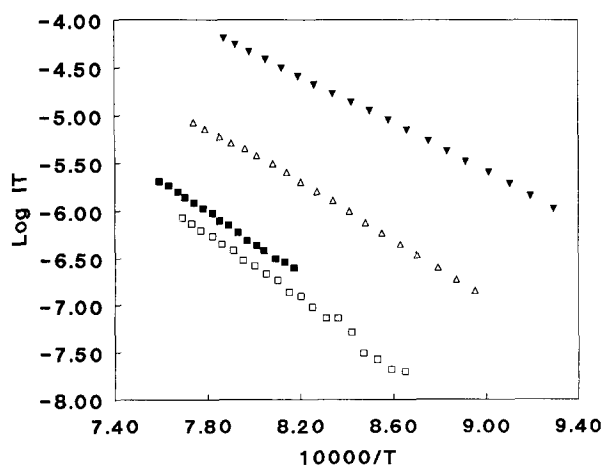


Fig. 2. Typical data from effusion mass spectrometry experiments: □ Al sample; ■ Al standard; △ Mn sample; ▼ Mn standard.

TABLE 1

Activity parameters

Manganese			Aluminum		
$x_{\text{Mn}}$	$A-A^0$	$B-B^0$	$x_{\text{Mn}}$	$A-A^0$	$B-B^0$
0.421	-1097	-0.397	0.430	-1419	0.808
0.430	-2424	0.840	0.470	-1303	0.588
0.435	-883	-0.327	0.435	-1018	0.397
0.488	-1044	-0.049			
0.539	-561	-0.296			
0.551	-1231	0.273			
0.461	-523	-0.495			
0.547	-313	-0.468			
0.609	-1735	0.823			
0.449	-283	-0.789			
0.513	-262	-0.579			
0.495	-484	-0.467			
0.547	-1904	0.945			

$$\text{Log } a = (A-A^0)/T + (B-B^0)$$

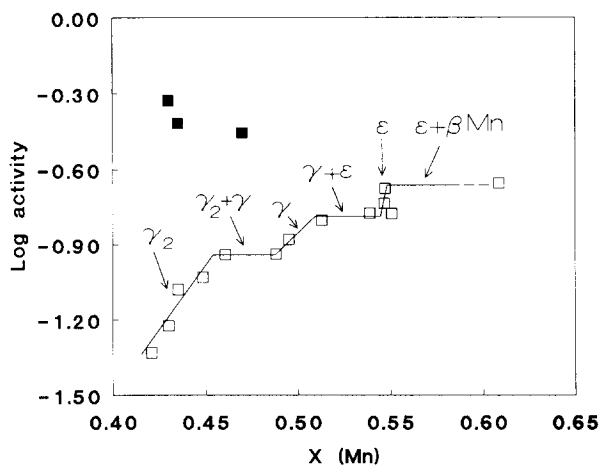
Fig. 3. Log activity vs. composition at 1175 K:  $\square$  Mn;  $\blacksquare$  Al.

TABLE 2

Thermodynamic stability

Phase		$\Delta G_f^0$ , 1175 (cal)	$\Delta H_f^0$ , 298 (cal)
$\text{Al}_{0.57}\text{Mn}_{0.43}$	$\gamma_2$	-3790	-4150
$\text{Al}_{0.50}\text{Mn}_{0.50}$	$\gamma$	-3860	-4180
$\text{Al}_{0.45}\text{Mn}_{0.55}$	$\epsilon$	-3890	-4180

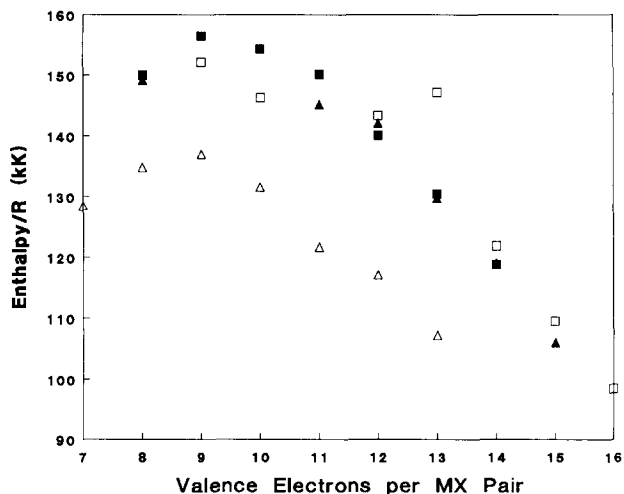


Fig. 4. Enthalpy of atomization to valence state metal atoms *vs.* number of valence electrons per MX pair ( $X \equiv \text{Al, Si, P, S}$ ): ■ MSi; ▲ MP; □ MS; △ MAI.

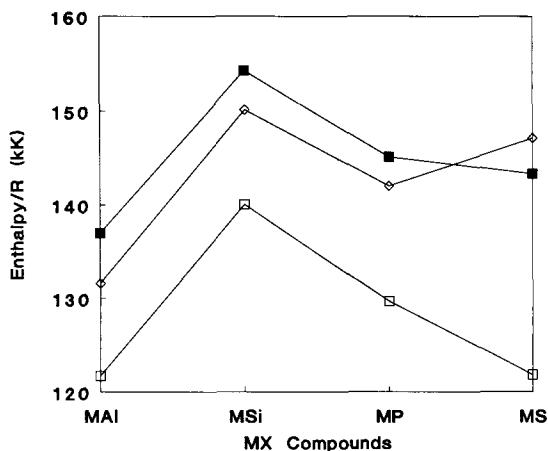


Fig. 5. Enthalpy of atomization to valence state metal atoms: comparison of MnX with CrX and FeX ( $X \equiv \text{Al, Si, P, S}$ ): (—■—) CrX; (—◇—) MnX; (—□—) FeX.

the variation of activity with composition to be consistent with the phase diagram. The enthalpy of phase formation found here for the  $\gamma$ -phase is comparable with the value  $-5150$  cal found by Kubaschewski and Heymer [4] for the  $x_{\text{Mn}} = 0.50$  solid alloy by direct reaction calorimetry at 600 K. A comparison of the stabilities of MAI phases with those of isoelectronic stoichiometric compounds is shown in Fig. 4. The enthalpy of atomization of the respective MAI phases to valence state metal atoms [5] is 10–15 kK (20–30 kcal) lower than for the isoelectronic sulfides, phosphides, and silicides. This result is evidence for a significant difference in the nature of chemical bonding in the aluminide phases compared with the stoichiometric compounds,

a conclusion which is consistent with the differences in physical properties. Enthalpies of atomization of manganese compounds with p-block elements are shown in Fig. 5; available data [5, 6] for corresponding chromium and iron compounds are shown for comparison. MnS departs from the regular trend exhibited by the CrX and FeX compounds, and all of the MAI phases have lower stabilities than would be predicted from a simple extrapolation based on the stoichiometric compounds of each transition metal. On this evidence the bonding in the MAI phases and MnS must be significantly different from the other MX compounds in each series. MnS has been shown to have significant ionic character [7] whereas there is little net electron transfer in the other compounds being compared (ref. 5 and references contained therein).

### Acknowledgment

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