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Enthalpy of formation of the α-phase AlMnSi

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Abstract

In order to optimise the phase equilibria of higher order alloys containing aluminium, manganese, silicon and iron, it is necessary to use thermodynamic data. In this paper, the heat of dissolution at infinite dilution of manganese in aluminium is determined, and the enthalpy of formation at 298 K of a ternary alloy α-AlMnSi is calculated from calorimetric measurements. These values have been measured with a Tian–Calvet calorimeter (Setaram), by dissolution in an aluminium bath at 1073 K.

Keywords: Enthalpy of formation; AlMnSi alloy; Solution calorimetry; Dissolution calorimetry; Aluminium bath

1. Introduction

Al-based alloys are important for new technologies using light alloys. The knowledge of the phase diagram is of prime importance, but the determination of the equilibria is long and complicated. With a view to minimising the number of experiments, it is preferable to calculate the diagram. First, it is necessary to determine the thermodynamic functions of the ternary phases. We present here the enthalpy of formation of a ternary alloy containing aluminium, manganese and silicon. The main difficulty is due to the oxidation of aluminium and of manganese especially at high temperatures.

2. Experimental procedure

2.1. Source and analysis of the alloy

The AlMnSi alloy had been supplied by SINTEF society, and the composition has been determined by microprobe. A metallographic examination has shown that the alloy was monophase.

The composition in weight percent: Al=60.0%, Mn=29.5%, Si=10.5%.

This corresponds to the following atomic composition: Al=70.9 at.%, Mn=17.1 at.%, Si=11.9 at.%.

2.2. Solution calorimetry

A high-temperature ($T \leq 1273$ K) Setaram microcalorimeter of the Tian–Calvet type was used. The experimental procedure is described in detail in [1].

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Aluminium baths (quality≥6 N) were placed in alumina crucibles previously heated to 1273 K, and these were placed inside silica tubes. Each aluminium bath weighed ca. 3 g. The samples were lowered from an air-lock, thermoregulated at ±3 K, at room temperature (T_0=298 K) down to the liquid aluminium bath maintained at 1073 K. It was not possible to operate at 976 K as in previous work for the determination of the enthalpy of formation of AlCuFe alloys [1] because the rate of dissolution of the AlMnSi alloys at this temperature was too low. Therefore, the experiment was performed at a temperature which was higher by 100 K. The disadvantage of this temperature was the ease of oxidation of the aluminium bath, but the temperature of 1073 K was a good compromise. The samples were guided down to the aluminium bath by stainless steel tubes. These had the advantage of not degassing and of absorbing residual traces of oxygen. After degassing in a vacuum of ca. 10^{-3} mbar, the experiments were performed under flowing purified U argon (99.995 vol.% of purity). The sample mass used for each experiment was typically ca. 15 mg. The microcalorimeter was calibrated with NIST α-Al_2O_3, confirmed by measuring the enthalpy of change pure Al, between 298 and 1073 K. The measured values were in accordance with those reported in [2].

Pieces of manganese of purity≥4 N (99.99%), of about 20 mg, are always covered with a thin film of oxide. To remove these oxides, it is necessary to clean manganese with a ‘nital solution’, which has a composition in vol% of C_2H_5OH 95%, HNO_3 5%. Pieces of manganese are immersed for a few minutes in a recipient (crystalliser) containing the nital solution, a small emission of gas is observed and the colour of the piece turns progressively from brown to bright metal. Then, the pieces are taken out of the crystalliser, and rinsed with absolute ethanol, the surface of the piece is observed with a binocular, if there are no traces of oxide, and the piece is transferred into a desiccant type dryer without humidity and in an atmosphere of nitrogen until the pieces are weighed just before being introduced into the thermoregulated air-lock.

3. Results

3.1. Theory

The enthalpy of formation of the ternary phase was obtained indirectly by measuring the heats of dissolution of the pure components Al, Mn, Si and those of the $Al_xMn_ySi_z$ ($x+y+z=1$) phase in the aluminium bath at 1073 K. The enthalpy of formation of 1 mol of $Al_xMn_ySi_z$ at 298 K is obtained following relationship from [3]:

$$\begin{aligned}\Delta_f H_m(\mathrm{Al}_x\mathrm{Mn}_y\mathrm{Si}_z) &= x\Delta_{\mathrm{sol}}H_m(\mathrm{Al}) + y\Delta_{\mathrm{sol}}H_m(\mathrm{Mn}) \\ &\quad + z\Delta_{\mathrm{sol}}H_m(\mathrm{Si}) - \Delta_{\mathrm{sol}}H_m(\mathrm{Al}_x\mathrm{Mn}_y\mathrm{Si}_z) \quad (1)\end{aligned}$$

In this formula, $\Delta_{\mathrm{sol}}H_m(\mathrm{Al})$, $\Delta_{\mathrm{sol}}H_m(\mathrm{Mn})$ and $\Delta_{\mathrm{sol}}H_m(\mathrm{Si})$ are the enthalpies of solution of pure Al, pure Mn and pure Si in the aluminium bath according to the reactions

$$x\langle \mathrm{Al}\rangle_{T_0} + \mathrm{Al}_{(l,T)} \rightarrow (\mathrm{Al})_T; \qquad \frac{\Delta Q}{x_{\mathrm{Al}}} = \Delta_{\mathrm{sol}}H_m(\mathrm{Al}) \quad (2)$$

$$y\langle \mathrm{Mn}\rangle_{T_0} + \mathrm{Al}_{(l,T)} \rightarrow (\mathrm{Mn})_T; \quad \frac{\Delta Q}{y_{\mathrm{Mn}}} = \Delta_{\mathrm{sol}}H_m(\mathrm{Mn}) \quad (3)$$

$$z\langle \mathrm{Si}\rangle_{T_0} + \mathrm{Al}_{(l,T)} \rightarrow (\mathrm{Si})_T; \qquad \frac{\Delta Q}{z_{\mathrm{Si}}} = \Delta_{\mathrm{sol}}H_m(\mathrm{Si}) \quad (4)$$

$\Delta_{\mathrm{sol}}H_m(\mathrm{Al}_x\mathrm{Mn}_y\mathrm{Si}_z)$ is the enthalpy of solution of $Al_xMn_ySi_z$:

$$n\langle \mathrm{Al}_x\mathrm{Mn}_y\mathrm{Si}_z\rangle_{T_0} + \mathrm{Al}_{(l,T)} \rightarrow (\mathrm{Mn,Si})_T; \quad \frac{\Delta Q}{n_{\mathrm{Al}_x\mathrm{Mn}_y\mathrm{Si}_z}} = \Delta_{\mathrm{sol}}H_m(\mathrm{Al}_x\mathrm{Mn}_y\mathrm{Si}_z) \quad (5)$$

In Eqs. (1)–(5), x, y, and z are the number of moles of Al, Mn and Si, respectively; n is the number of moles of $Al_xMn_ySi_z$; $\langle \mathrm{Al}\rangle$, $\langle \mathrm{Mn}\rangle$, $\langle \mathrm{Si}\rangle$ and $\langle \mathrm{Al}_x\mathrm{Mn}_y\mathrm{Si}_z\rangle$ refer to the elements Al, Mn, Si and to the ternary phase in the solid state at 298 K; $(\mathrm{Al})_{l,\,T}$ refers to the liquid aluminium bath at temperature T; $(\mathrm{Mn})_T$and $(\mathrm{Si})_T$refer to the elements Mn and Si in a solution of liquid aluminium at temperature T; and ΔQ is the heat of effect for each experiment.

The heat of solution for Si and Mn is given by the following formula:

$$\Delta_{\mathrm{sol}}H_m = \int C_p \, dT + \Delta_{\mathrm{diss}}h^{\infty}$$

In fact, we did not measure $\Delta_{\mathrm{diss}}h^{\infty}$ for Mn and Si because the never is an infinite dilution. We have to

Table 1
Comparative results for Mn dissolved in an aluminium bath at 1073 K

	This work	SGTE	Pasturel et al. [5]	Kek et al. [6]	Esin et al. [8]
$\Delta_{\mathrm{diss}}h_{\mathrm{m(Mn)}}$ (J/mol) referred to β-Mn	−59648 at 1073 K	−59524 at 1073 K	−81170 at 1007 K	−69645 at 1123 K	−63900 at 1626 K
$\Delta_{\mathrm{sol}}H_{\mathrm{m}}$ (J/mol) (298–1073 K)	−31907	−31783	−53429	−41900	−36159

check if a correction is necessary or not. We must draw the curve $\Delta_{\mathrm{diss}}h=f(x_i)$. From [4] we consider that this is linear for Si; for this element, a correction is not necessary. For Mn unfortunately, in the experimental conditions, only the first drop of Mn in the aluminium bath was acceptable. For the other drops, we observed the start of oxidation. Under these conditions, we had to use the infinite dilution value of manganese in an aluminium bath at 1073 K calculated from thermodynamic data; we shall see in Section 3.1.1 that the calculated value is acceptable. Therefore, the values of the enthalpies of the solution defined above and given in Table 1 can be used without correction to calculate the enthalpies of formation.

3.1.1. Dissolution of manganese in liquid aluminium

The experimental conditions were as follows: temperature of the aluminium bath: T=1073 K; heat content of Mn between 298.15 and 1073 K: ΔH=27 741 J/mol from [2]; heat capacity of Mn at 307 K: C_p=26.33 J/K mol from [2].

Run 1: amount of aluminium: m_{Al}=3075.73 mg, n_{Al}=0.11399403 mol; amount of manganese: m=18.87 mg, $n_{\mathrm{Mn}}=3.4348\times10^{-4}$ mol; molar fraction of manganese: $x_{\mathrm{Mn}}=3.00407\times10^{-3}$; constant of the calorimeter deduced from three drops of Al: k=0.5016; temperature of the air-lock: T_0=307.35 K; area measured: S=−22.0653 (arbitrary units).

Run 2: amount of aluminium: m_{Al}=3126.10 mg, n_{Al}=0.11586087 mol; amount of manganese: m=10.94 mg, $n_{\mathrm{Mn}}=1.99133\times10^{-4}$ mol; molar fraction of manganese: $x_{\mathrm{Mn}}=1.722\times10^{-3}$; constant of the calorimeter deduced from three drops of Al: k=−0.720016; temperature of the air-lock: T_0=300.65 K; area measured: S=8.82095 (arbitrary units).

The results are as follows:

$$\varepsilon\langle\mathrm{Mn}\rangle_{298}+n(\mathrm{Al})_{1073}\rightarrow(\mathrm{Mn})_{\mathrm{Al},1073}$$

Run 1:

$$\Delta_{\mathrm{sol}}H_{\mathrm{m}}=-31\,981\pm350\,\mathrm{J/mol}$$

Run 2:

$$\Delta_{\mathrm{sol}}H_{\mathrm{m}}=-31\,833\pm350\,\mathrm{J/mol}$$

The average value is

$$\Delta_{\mathrm{sol}}H_{\mathrm{m}}=-31\,907\pm350\,\mathrm{J/mol}$$

The experimental curve, heat flow versus time of Run 1, is presented in Fig. 1. The heat flow measured is expressed in μV (the knowledge of the constant of calibration is necessary to convert μV into mW); the first part of the peak corresponds to an endothermic effect due to the variation of temperature of manganese from 298 to 1073 K. The second part is exothermic and corresponds to the enthalpy of the mixing of manganese in the solid state with liquid aluminium. The molar partial enthalpy of dissolution of manganese in aluminium at 1073 K is

$$\Delta_{\mathrm{diss}}h_{\mathrm{m}}(\mathrm{Mn})=-59\,648\pm650\,\mathrm{J/mol}$$

This result must be compared with former works. Pasturel et al. [5] measured at 1007 K the enthalpy of dissolution of β-Mn in Al liquid at infinite dilution to be

$$\Delta_{\mathrm{diss}}h_{\mathrm{m}}(\mathrm{Mn})=-81\,170\,\mathrm{J/mol}$$

Kek et al. [6] measured the enthalpy of dissolution of Mn in Al (liquid) from room temperature to 1123 K. The value is obtained by extrapolation to x_{Al}=1 from eight measurements, from x_{Mn}=0.024–1.90 at.%; the value obtained is the average of the eight measurements:

$$\Delta_{\mathrm{sol}}H_{\mathrm{m}}=-40\,000\pm600\,\mathrm{J/mol}$$

The partial heat of mixing at infinite dilution at 1123 K is

$$\Delta_{\mathrm{diss}}h_{\mathrm{m}}(\mathrm{Mn})=-83\,800\,\mathrm{J}\pm600\,\mathrm{J/mol}$$

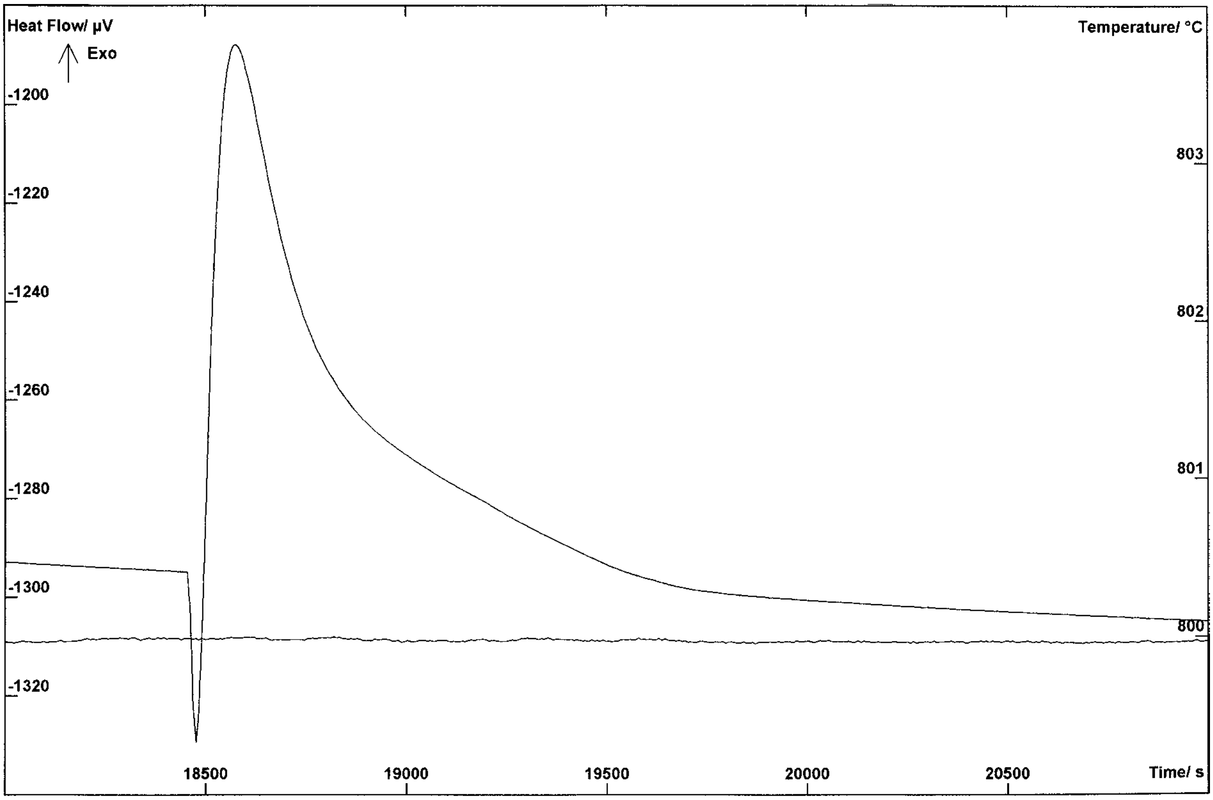

Fig. 1. Variation of heat flow signal for Mn (solid) dropped into Al (liquid).

This value is referred to Mn liquid; the enthalpy of melting of Mn extrapolated at 1123 K is from [7], and we can calculate the value with reference to Mn solid at 1123 K. In this case, we obtain

$$\Delta_{\mathrm{diss}}h_{\mathrm{m}}(\mathrm{Mn}) = -69\,645\ \mathrm{J/mol}$$

Using Kek's values, we calculate the enthalpy of solution for the temperature of our experiment (1073 K).

Esin et al. [8] measured the integral enthalpy of the mixing of Mn and Al at 1626 K. From these results, it is possible to extrapolate the partial enthalpy of mixing of Mn in Al at infinite dilution:

$$\Delta_{\mathrm{diss}}h_{\mathrm{m}}(\mathrm{Mn}) = -63\,900\ \mathrm{J/mol}$$

The different works devoted to this subject have been performed at different temperatures; with a view to comparing these results with the present work, it is necessary to present all the results of dilution of Mn in Al at infinite dilution, and assuming that there is no temperature dependence, then to calculate the heat of solution of Mn in Al liquid from 298 to 1073 K. The results are presented in Table 1.

Our results are in a perfect agreement with the selected data of Scientific Group Thermodata Europe (SGTE, Domaine Universitaire de Grenoble, 1001 Av Centrale, BP66 38402 Saint Martin d'Heres Cedex) for the molar partial enthalpy of dissolution of manganese in aluminium at 1073 K; the difference between these two values is of 124 J (0.2%), which is very low and we may consider that our value is acceptable. Our values are close to the values of Esin et al. [8], but the difference with Kek et al. [6] is greater and with Pasturel et al. [5] there is a huge difference. As we can see from the Table 1, the results are very scattered. This is due to the considerable difficulties of this kind of experimental measurement with two elements particularly sensitive to oxidation at this temperature; furthermore, it takes a rather long

Table 2
Heat of solution at 1073 K

	$\Delta_{sol}H_m$ (J/mol)	Error (J/mol)	$x_i\Delta_{sol}H_m$ (J/mol)	x_i error (J/mol)
Al	33281	242	23596	172
Mn	−31907	350	−5469	60
Si	58434	650	6954	78
$Al_{0.709}Mn_{0.171}Si_{0.119}$	39228	430	39228	430

time (more than 1 h) between the moment when the manganese is dropped into the aluminium bath and the time when the heat-flow has the same value as before the drop.

3.1.2. Dissolution of Si in the aluminium bath

$$\varepsilon\langle \mathrm{Si}\rangle_{298} + n(\mathrm{Al})_{1073} \rightarrow (\mathrm{Si})_{\mathrm{Al},1073}$$

$$\Delta_{sol}H_m = 58\,434 \pm 650\,\mathrm{J/mol}$$

This value is the same as used for the determination of the enthalpies of formation of AlFeSi ternary alloy [8].

3.1.3. Variation of enthalpy of aluminium between 298 and 1073 K

Our value is calculated from an average of measurements [4]:

$$\Delta H = -33\,039 \pm 240\,\mathrm{J/mol}$$

and is very close to the value of [2] (ΔH=33 281 J/mol).

3.1.4. Dissolution of the alloy AlMnSi in liquid aluminium

The experimental conditions are as follows: composition of the alloy: Al=60.0 wt.%, Mn=29.5 wt.%, Si=10.5 wt.%; Al=70.9 at.%, Mn=17.1 at.%, Si=11.9 at.%; temperature of the aluminium bath: T=1072.95 K; amount of aluminium in the bath: 3219.30 mg or n_{Al}=0.11931657 mol; amount of alloy: m=6.77 mg or $n_{AlMnSi}=2.11221\times10^{-4}$ mol; constant of the calorimeter deduced from three drops of Al: k=0.4745; temperature of the air-lock: T_0=304.15 K; heat capacity of the alloy at 304 K: C_p=25.13 J/K mol calculated from Koop–Neuman law using for the elements C_p values of [2]; area measured: S=17.47 (arbitrary units).

The results are as follows:

$$\varepsilon\langle \mathrm{Al}_{0.709}\mathrm{Mn}_{0.171}\mathrm{Si}_{0.119}\rangle_{298} + n(\mathrm{Al})_{1073} \rightarrow (\mathrm{Mn},\mathrm{Si})_{\mathrm{Al},1073}$$

$$\Delta_{sol}H_m = 39\,228 \pm 430\,\mathrm{J/mol}$$

Using the value of [2] for Al in Eq. (2) and our measured values for Eqs. (3)–(5) (see Table 2), we calculated the enthalpy of formation at 298 K of the ternary alloy using Eq. (1):

$$\Delta_f H_{m,298} = -14\,134 \pm 740\,\mathrm{J/mol}$$

4. Conclusion

We have measured the enthalpy of dissolution of Mn in an aluminium bath at 1073 K. This value is different from those proposed earlier but is consistent with thermodynamic data of the enthalpy of formation in the liquid state of Al–Mn alloys, given by the selected values of the data base SS-Sol proposed by SGTE.

Combining this result with the enthalpy of dissolution of Si and a monophase ternary alloy AlMnSi in an aluminium bath, it has been possible to calculate its enthalpy of formation at 298 K.

This is a first contribution to the elaboration of a set of data necessary for the optimisation of the ternary phase diagram Al–Fe–Si. The main difficulty in these experiments has been to avoid oxidation of the aluminium bath and of manganese.

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