Calorimetric measurements of liquid La–Mg, Mg–Yb and Mg–Y alloys

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Abstract

The enthalpies of mixing of liquid La–Mg, Mg–Yb and Mg–Y alloys are determined calorimetrically by two different methods, (1) direct enthalpy measurements by starting from the pure metal and (2) determination of the integral enthalpy from partial enthalpy measurements of the elements in an alloy. The extrapolated maximum of the enthalpy of mixing is about −13 kJ mol^{-1} at about 23.0 at.% La for La–Mg liquid alloys, which corresponds to the composition of the highest melting compound, Mg$_3$La, while for Mg–Yb the value is −4.3 kJ mol^{-1} at about 35 at.% Yb, coinciding with the composition of the only intermetallic compound of this system, Mg$_2$Yb. The enthalpies of mixing of liquid magnesium-rich Mg–Y alloys are found to be exothermic, with a value of −8 kJ mol^{-1} at 20 at.% Y. The results indicate the presence of short-range ordering in these liquid alloys.

Keywords: Calorimetric measurements; Enthalpies of mixing; Liquid alloys

1. Introduction

Rapidly solidified magnesium–rare earth metal alloys offer the possibility of better corrosion behaviour of magnesium-based alloys via improved microstructural and chemical homogeneity along with an enhanced solid solubility limit [1,2]. Thermodynamic properties are important to understand the solidification behaviour of the metastable phases and their transformation behaviour. Secondly, rare earth metals are of interest because they show a tendency of chemical short-range ordering in liquids [3–6]. The enthalpies of mixing of liquid La–Mg, Mg–Yb and Mg–Y alloys were determined calorimetrically and the results are presented in this paper. To our knowledge no thermodynamic data are available for Mg–Y and Mg–Yb liquid alloys, whereas vapour pressure measurements over La–Mg liquid alloys are reported by Afanasyev et al. [7].

2. Experimental details

The alloy samples were prepared in a calorimeter from Mg (purity 99.9 at.%), Y (purity 99.9 at.%), Yb

(purity 99.9 at.%) and La (purity 99.6 at.%). Rare earth samples were prepared and stored in an argon glove-box and transported to the calorimeter in closed glass bottles at the time of measurement. The calorimeter used for measurements has been described previously [8]. The experiments were performed at constant temperature in a closed argon atmosphere of pressure 1 bar, with continuous stirring throughout the measurements. The heat effect was detected by an Ni–NiCr thermopile situated below the reaction crucible. In the present investigation two methods were used to determine the enthalpy of mixing of liquid alloys. In the first method the integral enthalpy of mixing is obtained by dropping solid samples of the second metal at room temperature into the liquid bath material, starting with pure liquid Mg as the initial bath. Correction for the heat content of the second metal was made using data from the literature [9]. The system was calibrated by adding the bath metal, i.e. Mg, before the additions of the second metal. For the investigated Mg–rare earth metal alloys it was not possible to perform measurements over the entire concentration range, because at temperatures above about 1060 K severe losses of magnesium occur during the measurement time owing to the high partial pressure of magnesium. For La–Mg alloys it was observed that

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Table 1
Enthalpy of mixing of liquid La–Mg alloys at various temperatures

Measured			Calculated	
Starting amount n_{Mg} (mol)	Added amount Δn_{La} (mol)	Heat effect ΔQ (J)	Mole fraction La (at.%)	Enthalpy of mixing ΔH (kJ mol^{-1})
Temperature 970 K				
0.2158	0.0031	−180	1.4	−1.2
	0.0040	−205	3.2	−2.7
	0.0037	−186	4.8	−3.9
	0.0032	−157	6.1	−5.0
	0.0044	−201	7.8	−6.3
	0.0049	−192	9.7	−7.5
Temperature 985 K				
0.2219	0.0014	−81	0.6	−0.5
	0.0028	−152	1.8	−1.6
	0.0056	−286	4.2	−3.5
	0.0035	−150	5.6	−4.5
	0.0030	−135	6.8	−5.4
	0.0046	−155	8.6	−6.5
Temperature 1060 K				
0.2563	0.0051	−231	2.0	−1.5
	0.0035	−93	3.3	−2.3
	0.0047	−189	5.0	−3.5
	0.0053	−173	6.8	−3.5
	0.0045	−126	8.3	−4.7
	0.0056	−166	10.1	−5.6
	0.0059	−86	12.0	−7.5

Table 2
Partial enthalpies of mixing of liquid La–Mg alloys at 1031 K (starting amounts (mol): $n_{Mg} = 0.0371$, $n_{La} = 0.0688$)

Measured			Calculated		
Added amounts		Heat effect ΔQ (J)	Mole fraction La (at.%)	Partial enthalpies of mixing	
Δn_{Mg} (mol)	Δn_{La} (mol)			$\Delta \bar{H}_{Mg}$ (kJ mol^{-1})	$\Delta \bar{H}_{La}$ (kJ mol^{-1})
0.0035		49	63.9	−15.7	
	0.0013		63.1		
0.0036		51	62.3	−15.9	
	0.0009	26	61.4		−2.1
0.0027		37	60.9	−16.3	
	0.0007	24	60.3		0.4
0.0032		40	59.7	−17.2	
	0.0011	35	59.1		0.3

Calculated average integral enthalpy of mixing: $\Delta H(x_{La} = 61$ at.%) $= -6.6$ kJ mol^{-1}.

the alloy tends to creep out of the molybdenum crucible beyond 1030 K and 12 at.% La. A partial enthalpy measurement method was used for the composition ranges 50.9–61 at.% La and 35–72 at.% Yb with starting alloy compositions of La$_{63}$Mg$_{37}$ and Mg$_{28}$Yb$_{72}$ respectively. The alloys were prepared in the calorimeter by loading closed molybdenum crucibles containing weighed amounts of the components. In each mea-

Table 3
Enthalpy of mixing of liquid La–Mg alloys at 1031 K (starting amounts (mol): $n_{Mg} = 0.0510$, $n_{La} = 0.0740$)

Measured		Calculated		
Added amount Δn_{Mg} (mol)	Heat effect ΔQ (J)	Mole fraction La (at.%)	Integral enthalpy of mixing	
			$\delta \Delta H$ (kJ mol^{-1})	ΔH (kJ mol^{-1})
0.0040	48	57.4	−0.5	−7.1
0.0057	76	54.9	−0.6	−7.7
0.0053	78	52.8	−0.5	−8.2
0.0054	86	50.9	−0.4	−8.6

Table 4
Enthalpy of mixing of liquid Mg–Yb alloys at various temperatures

Measured			Calculated	
Starting amount n_{Mg} (mol)	Added amount Δn_{Yb} (mol)	Heat effect ΔQ (J)	Mole fraction Yb (at.%)	Enthalpy of mixing ΔH (kJ mol^{-1})
Temperature 1013 K				
0.0585	0.0028	12	4.5	−1.2
	0.0026	26	8.4	−2.0
	0.0038	66	13.5	−2.6
Temperature 1018 K				
0.2205	0.0027	1	1.2	−0.4
	0.0032	18	2.6	−0.7
	0.0060	51	5.2	−1.3
	0.0068	51	7.8	−1.9
	0.0061	72	10.1	−2.4
	0.0071	116	12.7	−2.7
0.0466	0.0075	94	13.9	−2.6
	0.0033	51	18.8	−3.3
	0.0046	103	24.8	−3.7
	0.0023	54	27.4	−3.8
	0.0026	66	30.3	−3.9
	0.0050	110	35.2	−4.3
	0.0058	154	40.1	−4.3

surement one of the elements was added continuously to determine the change in the integral enthalpy of mixing at various compositions. At the beginning or end of each measurement run a few alternative additions of small samples of the components were made to determine the partial enthalpy of mixing at approximately the same composition and to get from this the integral enthalpy of mixing of the composition at the beginning or end of the measurement. On the basis of these ΔH and additional measured $\delta \Delta H(x)$ values, the concentration dependence of ΔH is calculated with the partial enthalpy measurement method (see Tables 2, 3 and 5). Calibration was done by adding Mo pieces with known enthalpy content [9] in between the measurements. The reproducibility of the calibration was in the range $\pm 5\%$–7%.

Table 5
Enthalpy of mixing of liquid Mg–Yb alloys at 1016 K (starting amounts (mol): $n_{Mg}=0.0148$, $n_{Yb}=0.0380$)

Measured			Calculated				
Added amounts		Heat effect ΔQ (J)	Mole fraction Yb (at.%)	Partial enthalpies of mixing		Integral enthalpy of mixing	
Δn_{Mg} (mol)	Δn_{Yb} (mol)			$\Delta \bar{H}_{Mg}$ (kJ mol⁻¹)	$\Delta \bar{H}_{Yb}$ (kJ mol⁻¹)	$\delta \Delta H$ (kJ mol⁻¹)	ΔH (kJ mol⁻¹)
			71.9				−2.0
0.0074		161	63.2			−0.9	−2.9
0.0064		148	57.1			−0.5	−3.4
0.0111		274	48.9			−0.4	−3.8
0.0102		255	43.2			−0.2	−4.0
0.0103		261	38.7			−0.2	−4.2
0.0104		265	35.0			−0.1	−4.3
0.0012		27	34.8	−6.6			
	0.0006	10	34.8				
0.0014		34	34.7	−5.9			
	0.0004	13	34.6		−1.5		
0.0012		28	34.5	−5.9			−4.3
	0.0005	14	34.5		−2.0		
0.0017		41	34.4	−5.1			
	0.0005	14	34.3		−1.1		

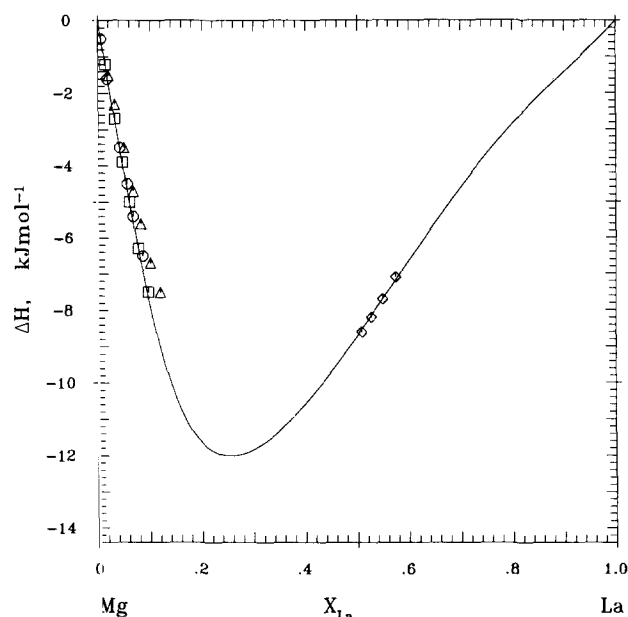
Fig. 1. Enthalpy of mixing of liquid La–Mg alloys at 1031 K calculated using the association model (□ 970 K, ○ 985 K, △ 1060 K, integral enthalpy measurements; ◇ 1031 K, calculated from enthalpy difference measurements on the basis of partial enthalpy measurements).
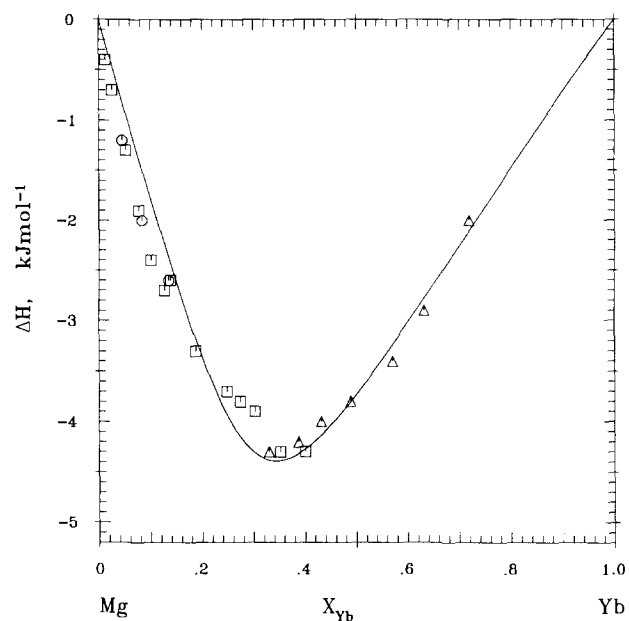

Fig. 2. Enthalpy of mixing of liquid Mg–Yb alloys at 1016 K calculated using the association model (○ 1013 K, □ 1018 K, integral enthalpy measurements; △ 1016 K, calculated from enthalpy difference measurements on the basis of partial enthalpy measurements).

3. Results and discussion

Experimental results for the enthalpies of mixing of liquid Mg–Y, Mg–Yb and La–Mg are given in Tables 1–6 and integral enthalpy values are plotted as a function of concentration in Figs. 1–3 respectively. For Mg–Y alloys the maximum composition attained was 21.8 at.% Y at 1020 K. As is evident from the phase diagram, the liquid alloys of higher yttrium content could be obtained at higher temperature, but with simultaneous enhancement of severe magnesium losses. The enthalpy of mixing of liquid Mg–Yb alloys was determined in the composition range 0.0–72 at.% Yb and of liquid La–Mg alloys in the composition ranges 0–12 and 50.1–61 at.% La.

The asymmetric dependences on concentration of enthalpy values for La–Mg, Mg–Yb and Mg–Y indicate the presence of chemical short-range order in these

Table 6
Enthalpy of mixing of liquid Mg–Y alloys at various temperatures

Measured			Calculated	
Starting amount n_{Mg} (mol)	Added amount Δn_Y (mol)	Heat effect ΔQ (J)	Mole fraction Y (at.%)	Enthalpy of mixing ΔH (kJ mol^{-1})
Temperature 955 K				
0.2409	0.0036	−123	1.5	−0.9
	0.0039	−115	3.0	−1.9
	0.0052	−141	5.0	−3.0
	0.0052	−118	6.9	−4.0
	0.0063	−112	9.1	−5.0
	0.0057	−43	11.0	−5.7
	0.0073	−36	13.4	−6.2
Temperature 975 K				
0.1423	0.0013	−65	0.9	−0.7
	0.0015	−48	1.9	−1.4
	0.0012	−48	2.7	−1.9
	0.0016	−64	3.7	−2.7
	0.0020	−20	5.0	−3.2
	0.0019	−54	6.2	−3.8
	0.0019	−48	7.4	−4.5
	0.0019	−44	8.5	−5.1
	0.0019	−31	9.6	−5.6
0.1808	0.0007	−37	0.4	−0.3
	0.0012	−45	1.1	−0.8
	0.0010	−60	1.6	−1.3
	0.0016	−85	2.5	−2.0
	0.0014	−38	3.2	−2.4
	0.0015	−34	3.9	−2.8
	0.0018	−42	4.8	−3.3
	0.0012	−29	5.4	−3.6
	0.0018	−40	6.3	−4.0
	0.0017	−58	7.1	−4.6
	0.0013	−18	7.7	−4.8
	0.0015	−19	8.4	−5.1
	0.0017	−14	9.2	−5.4
	0.0017	−26	10.0	−5.7
	0.0019	−28	10.8	−6.1
Temperature 984 K				
0.2519	0.0072	−189	2.8	−1.6
	0.0077	−192	5.6	−3.1
	0.0097	−178	8.9	−4.8
	0.0080	−77	11.5	−5.7
	0.0072	−19	13.7	−6.4
	0.0069	−23	15.6	−7.1
	0.0036	−60	16.6	−7.2
Temperature 1020 K				
0.2365	0.0050	−141	2.1	−1.2
	0.0066	−184	4.7	−2.8
	0.0125	−216	9.3	−5.0
	0.0097	−46	12.5	−6.2
	0.0100	−3	15.7	−7.1
	0.0108	66	18.8	−7.8
	0.0042	25	19.9	−8.1
	0.0073	94	21.9	−8.3
Temperature 1057 K				
0.1381	0.0033	−115	2.3	−1.6
	0.0041	−75	5.0	−3.0
	0.0041	−60	7.6	−4.2

(continued)

Table 6
Enthalpy of mixing of liquid Mg–Y alloys at various temperatures

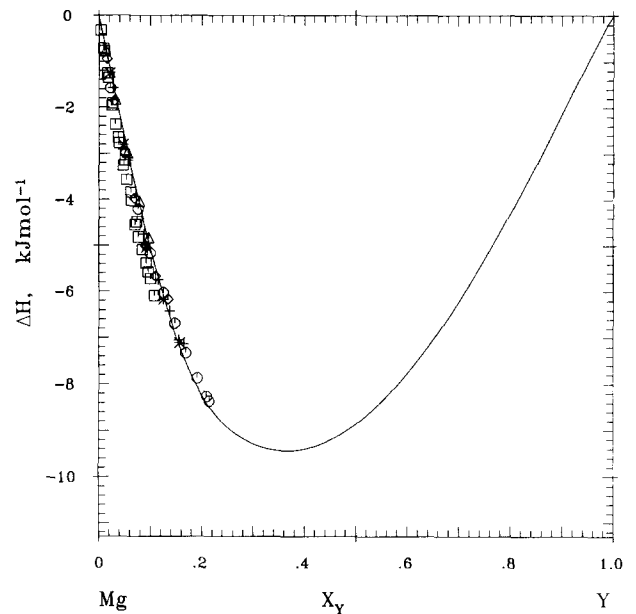| Measured			Calculated	
Starting amount n_{Mg} (mol)	Added amount Δn_Y (mol)	Heat effect ΔQ (J)	Mole fraction Y (at.%)	Enthalpy of mixing ΔH (kJ mol^{-1})
	0.0040	−31	10.0	−5.2
	0.0044	−12	12.5	−6.0
	0.0040	2	14.7	−6.7
	0.0043	7	16.9	−7.3
	0.0046	28	19.1	−7.9
	0.0042	37	21.0	−8.3
	0.0011	11	21.5	−8.4
Temperature 1074 K				
0.1418	0.0018	−46	1.3	−0.8
	0.0030	−59	3.3	−1.8
	0.0034	−62	5.5	−3.0
	0.0039	−41	7.9	−4.0
	0.0033	−25	9.8	−4.9

Fig. 3. Enthalpy of mixing of liquid Mg–Y alloys at 1000 K calculated using the association model (◇ 955 K, □ 975 K, + 984 K, * 1020 K, ○ 1057 K, △ 1074 K, experimental results).

liquids which can be described by the formation of associates with a definite stoichiometry [10]. The expressions for the enthalpy and entropy of mixing for binary liquid alloys with the formation of a single type of associates are

$$\Delta H = \frac{n_{A_1} n_{B_1}}{n} C^{reg}_{A_1, B_1} + \frac{n_{A_1} n_{A_i B_j}}{n} C^{reg}_{A_1, A_i B_j}$$

$$+ \frac{n_{B_1} n_{A_i B_j}}{n} C^{reg}_{B_1, A_i B_j} + n_{A_i B_j} \Delta H^0_{A_i B_j} \quad (1)$$

and

Table 7
Association model parameters

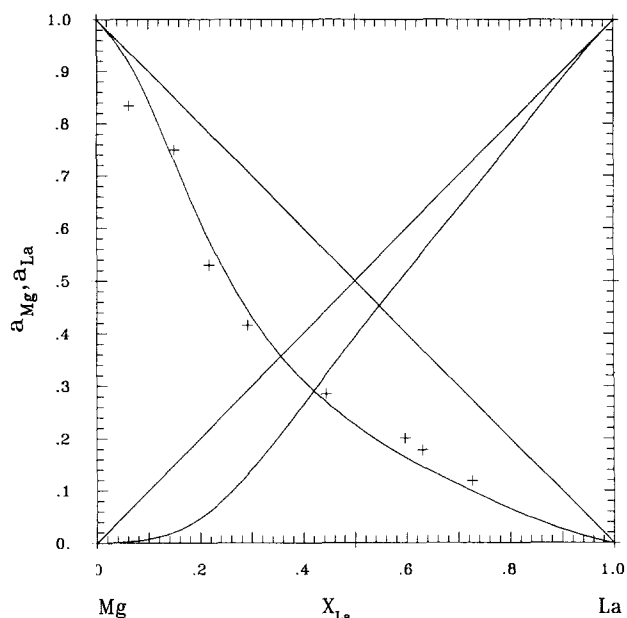| System	Data used to fit model parameters	Associate A_iB_j	$\Delta H^0_{A_iB_j}$ (kJ mol^{-1})	$\Delta S^0_{A_iB_j}$ (J K^{-1} mol^{-1})	$C^{reg}_{A_i,\,B_1}$ (kJ mol^{-1})	$C^{reg}_{A_i,\,A_iB_j}$ (kJ mol^{-1})	$C^{reg}_{B_1,\,A_iB_j}$ (kJ mol^{-1})
La–Mg	ΔH, $\Delta \bar{H}_i$: Tables 1–3 a_{Mg} at $T = 1083$ and 1133 K	LaMg$_3$	−68.0	−51.4	−15.3	−21.1	−24.0
Mg–Yb	ΔH, $\Delta \bar{H}_i$: Tables 4 and 5	Mg$_2$Yb	−20.5	0	−6.4	0	0
Mg–Y	ΔH: Table 6	Mg$_2$Y	−19.0	0	−15.0	−37.0	−35

Fig. 4. Activity of magnesium of liquid La–Mg alloys at 1133 K calculated using the association model (+, experimental results of Afanasyev et al. [7]).
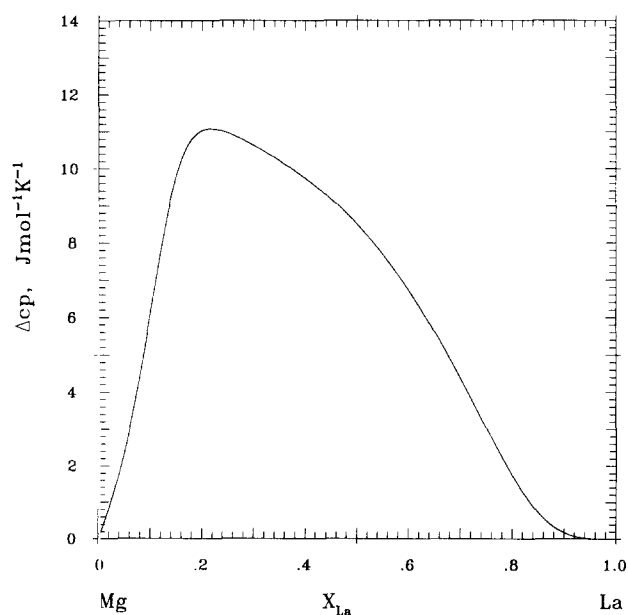

Fig. 5. Excess specific heat of liquid La–Mg alloys at 1031 K calculated using the association model.

$$\Delta S = -R(n_{A_1} \ln x_{A_1} + n_{B_1} \ln x_{B_1}$$
$$+ n_{A_iB_j} \ln x_{A_iB_j}) + n_{A_iB_j} \Delta S^0_{A_iB_j} \qquad (2)$$

In these equations n_{A_1} and n_{B_1} moles of free A and B atoms are in equilibrium with $n_{A_iB_j}$ moles of associates with the composition A_iB_j $(i, j = 1 \ldots n)$ and x_{A_1}, x_{B_1} and $x_{A_iB_j}$ are the mole fractions of the respective species in 1 mol of binary alloy. $C^{reg}_{k,l}$ represents an interaction parameter between the assumed species k and l. The equilibrium value for $n_{A_iB_j}$ is determined by the mass action law with an association constant defined as

$$K_{A_iB_j} = \exp\left(-\frac{\Delta H^0_{A_iB_j} - T\Delta S^0_{A_iB_j}}{RT} \right) \qquad (3)$$

$\Delta H^0_{A_iB_j}$ and $\Delta S^0_{A_iB_j}$ are the enthalpy and entropy of formation of associates.

It is necessary to define the stoichiometry of the associates to calculate the thermodynamic functions of the alloy system using the above expressions. In the La–Mg, Mg–Yb and Mg–Y systems, LaMg$_3$, Mg$_2$Yb and Mg$_2$Y stoichiometries were assumed for the associates respectively. The selected stoichiometries of the associates correspond to the stoichiometry of intermetallic compounds in these systems. The model parameters are determined by fitting the available experimental data (e.g. ΔH, $\Delta \bar{H}^\circ$ and activity a) by the method of least squares. In the paper of Afanasyev et al. [7] only the partial vapour pressure of magnesium obtained from a transpiration method is given for liquid La–Mg alloys and not the vapour pressure of pure magnesium. The activity is taken from a small-scale diagram. The parameters and the data used for the calculation of the La–Mg, Mg–Yb and Mg–Y alloys are given in Table 7. The calculated thermodynamic properties shown in Figs. 1–4 describe the experimental results with good accuracy. The parameter $C^{reg}_{Mg,\,Mg_2Y}$ exhibits a large value in comparison with $\Delta H^0_{Mg_2Y}$ (see Table 7), which suggests an Mg$_3$Y stoichiometry of the associates. Calculations assuming the existence of Mg$_3$Y associates result in a similar description to that presented in Fig. 3. From the obtained ΔH data of liquid Mg–Y alloys it cannot be deduced clearly whether a description with an Mg$_2$Y or Mg$_3$Y associate stoichiometry or both types of association reactions occurring simultaneously is more

appropriate for a safe extrapolation to temperatures below and above the measurement temperatures of the given experimental data. Attempts to measure the activity of magnesium using the isopiestic vapour pressure method were, until now, not successful. The excess specific heat calculated for liquid La–Mg alloys using the expression given in Ref. [10] shows remarkable values (see Fig. 5).

4. Summary

Differential enthalpy measurement with respect to two components at the same composition can be a useful technique to determine the integral enthalpy of mixing at that composition. This method is particularly useful for systems such as La–Mg and Mg–Yb where it is difficult to continue the measurements starting with the pure component as the bath material. However, as is apparent from the results given in Tables 2 and 5, the enthalpy of mixing determined by this method has a larger error, owing to the small weight and energy change involved in the process. The association model is appropriate to describe the dependences on con-

centration and temperature of thermodynamic functions of liquid alloys with compound-forming tendency.

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