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Examination of enthalpies of mixing in liquid gallium–yttrium alloys by high-temperature calorimetry

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Abstract

Liquid gallium–yttrium alloys were studied by high-temperature calorimetry at 1750 K. Two calorimetric experiments were performed and the yttrium partial enthalpy of mixing ($\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Y}}$) was measured up to the yttrium mole fraction of 0.6. The integral enthalpy of mixing ($\Delta_{\mathrm{mix}}H$) was calculated by Darken's method. The concentration dependencies of the $\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Y}}$ and $\Delta_{\mathrm{mix}}H$ were represented via polynomial series. The experimental results were compared with literature data on $\Delta_{\mathrm{mix}}H$, standard enthalpies of formation of yttrium gallides and yttrium partial enthalpy of mixing at infinite dilution. The agreement of the values obtained and those in the literature is satisfactory.
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Keywords: Gallium–yttrium; Enthalpy of mixing; Thermodynamics; Calorimetry; Liquid alloys

1. Introduction

Yttrium containing intermetallic compounds can be used as hard magnetic materials [1]. Addition of gallium usually changes intermetallics' crystal lattice parameters and magnetic exchange interactions. This allows increasing Curie temperature and has effect on the magnetocrystalline anisotropy, which can lead to a spin reorientation [2]. The knowledge of the thermodynamic properties and phase equilibria in wide range of concentration and temperature is necessary for the engineering of new yttrium containing magnetic alloys.

Summarising literature data on phase equilibria and thermodynamics, one can conclude that the gallium–yttrium system has been only scantily examined. The phase diagram includes YGa_2, YGa and Y_5Ga_3 gallides [3–5]. The YGa_2 and YGa melt congruently at 1623 and 1658 K, respectively, while Y_5Ga_3 melts incongruently at 1568 K. The phase diagram was constructed based on differential thermal

analysis data. Until now, no thermodynamic assessment has been performed due to lack of experimental thermodynamic data.

The standard enthalpies of formation ($\Delta_{\mathrm{f}}H^0_{298.15}$) of the yttrium gallides were studied by electromotive force (e.m.f.) method [6], by high-temperature solution [7,8] and direct synthesis calorimetry [9], and also were estimated using Miedema's model [10]. Significant heat evolution at the formation of yttrium gallides indicates their high thermodynamic stability.

Thermodynamic properties of liquid Ga–Y alloys were measured at 1125 K up to the yttrium mole fraction (x_{Y}) of 0.1 [8]. Based on the data of [8], one can conclude that the melts are characterised by considerable negative deviations from ideal solutions as exhibited in large exothermal heats of mixing. The yttrium partial enthalpy of mixing at infinite dilution ($\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Y}}^{\infty}$) was measured in [6–8] and calculated from Miedema's model in [10]. Indeed, thermodynamic properties of the Ga–Y melts are virtually unknown for $x_{\mathrm{Y}} > 0.1$.

Continuing examination of the Ga–Y thermodynamics, in the presented paper, we report results of mixing calorimetry measurements in liquid Ga–Y alloys for $0 < x_{\mathrm{Y}} < 0.6$ at 1750 K.

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2. Experimental

2.1. Materials

The gallium rods (Alfa-Aesar, 99.9999%), yttrium distillate rods (Dahuachem, 99.97%) and reference material, i.e. tungsten wire (Alfa-Aesar, 99.96%), were used for the calorimetric experiments. High-purity argon (99.997 vol.%) was utilized for filling of the calorimeter's internal volume to prevent the alloys chemical reactions with air constituents.

2.2. Apparatus

The calorimeter, whose principal schematic was described in [11], was employed for the determination of the enthalpies of mixing. An alumina calorimetric crucible was fitted by stuffing with Aldrich yttrium trioxide to prevent chemical reaction of the melts with crucible material. Gallium was the initial component in the crucible. As gallium melts at $T = 302.91$ K, so the calorimetric cell was evacuated and filled with argon at 298 K. The temperature of the calorimetric bath was 1750 K. The samples in the revolving container were stored at $T = 298$ K. Two independent runs of the calorimetric measurements were performed and their results were treated jointly.

Dropping of gallium samples into the molten gallium produced a first calorimeter calibration, and then weighted samples of Y were dropped. After the mixing experiment, the W samples were added into the melt for the final calorimeter calibration. The absence of interaction between tungsten and the melt was controlled by mass analysis after the ingots were cooled and cut.

The heat-exchange coefficient of the calorimeter was calculated by the formula:

$$k_i = \Delta H_{298}^T n_i / S_i, \tag{1}$$

where ΔH_{298}^T is the standard enthalpy of component heating from 298.15 K up to the experimental temperature [12], i is the dropped sample number, n_i is the mole quantity of the dropped sample and S_i is the area of heat-exchange peak on the e.m.f. versus time curve. The k_i values were treated by the least square regression (l.s.r.) using a linear model:

$$k = a + bm_{\text{alloy}}, \tag{2}$$

where m_{alloy} is the current alloy mass in the crucible, a and b are the l.s.r. coefficients. The partial enthalpy of mixing was calculated from the experimental heat-exchange curves by the formula:

$$\Delta_{\text{mix}} \bar{H}_Y = -\Delta H_{298}^T + k S_i / n_i. \tag{3}$$

The values of the $\Delta_{\text{mix}} \bar{H}_Y$ were assigned to the middle point of the composition range before and after sample addition. The experimental partial enthalpy of mixing was expressed by the alpha function:

$$\alpha_Y = \Delta_{\text{mix}} \bar{H}_Y / (1 - x_Y)^2. \tag{4}$$

The alpha function, in turn, was smoothed using l.s.r. for the polynomial equation:

$$\alpha_Y = \sum_{j=0}^{l} Q_j x_Y^j, \tag{5}$$

where Q_i are the polynomial coefficients and l is the polynomial order as defined in Fisher's test of correctness. The concentration dependence of $\Delta_{\text{mix}} \bar{H}_Y$ can be then represented by the equation:

$$\Delta_{\text{mix}} \bar{H}_Y = (1 - x_Y)^2 \sum_{j=0}^{l} Q_j x_Y^j. \tag{6}$$

Calculation of the integral enthalpy of mixing was performed by Darken's method:

$$\Delta_{\text{mix}} H = (1 - x_Y) \int_0^{x_Y} \alpha_Y \, dx_Y. \tag{7}$$

After substitution of Eq. (5) into Eq. (7) and integration, one gets:

$$\Delta_{\text{mix}} H = x_Y (1 - x_Y) \sum_{j=0}^{l} (j+1)^{-1} Q_j x_Y^j. \tag{8}$$

The deviations of the integral enthalpy of mixing were determined as proposed in [13]:

$$\sigma(\Delta_{\text{mix}} H) = (1 - x_Y) \left(x_Y \int_0^{x_Y} D(\alpha_Y) \, dx_Y \right)^{1/2}, \tag{9}$$

where $D(\alpha_Y)$ is the dispersion of the alpha function. The confidence intervals were calculated from deviations of appropriate functions as $t\sigma$, where t is the Student's coefficient for a 0.95 confidence level, which is equal to 2.

3. Results and discussion

The results of our calorimetric measurements are listed in Table 1. The experimental α_Y data scatter for both runs is shown on Fig. 1. The following equations have been derived for the concentration dependence of the enthalpies of mixing (in kJ mol^{-1}):

$$\Delta_{\text{mix}} \bar{H}_Y = (1 - x_Y)^2 (-189.76 - 401.58 x_Y + 1016.67 x_Y^2 \\ - 23666.51 x_Y^3 + 88843.54 x_Y^4 - 81990.83 x_Y^5), \tag{10}$$

$$\Delta_{\text{mix}} H = x_Y (1 - x_Y)(-189.76 - 200.79 x_Y + 338.89 x_Y^2 \\ - 5916.63 x_Y^3 + 17768.71 x_Y^4 - 13665.14 x_Y^5). \tag{11}$$

The downturn of the α_Y-function at $x_Y > 0.57$ (shown in Fig. 1) is an artefact of the fit. So the Eqs. (10) and (11) are valid only at $0 \leq x_Y \leq 0.57$.

Table 1
Results of the calorimetric study of the Ga–Y system

Added substance	Added amount (m_i) (g)	S_i (arb. units)	x_Y	$\Delta_{mix}\bar{H}_Y$ (kJ mol^{-1})	Added amount (m_i) (g)	S_i (arb. units)	x_Y	$\Delta_{mix}\bar{H}_Y$ (kJ mol^{-1})
Ga	0.0685	0.00450			0.0624	0.00544		
	0.0926	0.00496			0.0805	0.00542		
	0.0734	0.00468			0.0861	0.00660		
	0.0982	0.00511			0.0879	0.00695		
	0.0854	0.00556			0.0882	0.00551		
	0.0887	0.00519			0.0892	0.00674		
	0.1162	0.00648			0.0898	0.00635		
					0.1103	0.00767		
Y	0.0112	−0.00161	0.0029	−197.64	0.0202	−0.00386	0.0052	−207.66
	0.0158	−0.00167	0.0098	−161.69	0.0221	−0.00362	0.0159	−186.71
	0.0164	−0.00209	0.0179	−182.11	0.0240	−0.00363	0.0273	−177.00
	0.0179	−0.00271	0.0264	−204.58	0.0244	−0.00463	0.0390	−206.33
	0.0191	−0.00255	0.0354	−187.65	0.0261	−0.00493	0.0509	−205.59
	0.0225	−0.00289	0.0453	−182.78	0.0266	−0.00453	0.0630	−191.27
	0.0226	−0.00257	0.0558	−168.85	0.0274	−0.00480	0.0751	−195.00
	0.0226	−0.00281	0.0661	−178.72	0.0326	−0.00606	0.0882	−202.88
	0.0245	−0.00344	0.0766	−193.67	0.0364	−0.00669	0.1028	−201.19
	0.0260	−0.00365	0.0876	−193.52	0.0399	−0.00675	0.1184	−190.01
	0.0272	−0.00340	0.0989	−179.00	0.0402	−0.00673	0.1343	−188.55
	0.0278	−0.00363	0.1103	−184.08	0.0381	−0.00670	0.1492	−194.86
	0.0301	−0.00461	0.1220	−205.01	0.0391	−0.00605	0.1634	−178.85
	0.0299	−0.00437	0.1338	−198.32	0.0396	−0.00750	0.1774	−204.83
	0.0323	−0.00428	0.1457	−185.45	0.0400	−0.00702	0.1911	−194.12
	0.0333	−0.00478	0.1579	−195.55	0.0405	−0.00755	0.2045	−202.24
	0.0370	−0.00498	0.1707	−187.04	0.0415	−0.00727	0.2177	−193.69
	0.0436	−0.00644	0.1847	−199.00	0.0433	−0.00707	0.2309	−184.66
	0.0447	−0.00580	0.1997	−182.15	0.0458	−0.00794	0.2443	−192.01
	0.0451	−0.00628	0.2143	−190.71	0.0465	−0.00772	0.2577	−186.33
	0.0468	−0.00702	0.2287	−200.39	0.0492	−0.00677	0.2711	−164.99
	0.0479	−0.00583	0.2430	−174.10	0.0524	−0.00661	0.2848	−156.29
	0.0483	−0.00659	0.2570	−187.40	0.0618	−0.00913	0.2996	−172.21
	0.0523	−0.00769	0.2711	−196.87	0.0622	−0.00807	0.3149	−158.71
	0.0515	−0.00591	0.2851	−167.07	0.0632	−0.00758	0.3298	−151.23
	0.0636	−0.00648	0.3000	−155.06				
	0.0623	−0.00761	0.3156	−173.28				
	0.0694	−0.00648	0.3312	−146.85				
	0.0659	−0.00500	0.3465	−130.79				
	0.0712	−0.00567	0.3613	−133.99				
	0.0694	−0.00411	0.3758	−115.41				
	0.0768	−0.00287	0.3902	−95.63				
	0.0743	−0.00231	0.4044	−89.91				
	0.0819	−0.00263	0.4184	−90.73				
	0.0772	−0.00079	0.4320	−71.18				
	0.0897	0.00028	0.4456	−59.31				
	0.0922	0.00087	0.4597	−53.75				
	0.0995	0.00137	0.4738	−49.97				
	0.0954	0.00354	0.4874	−29.58				
	0.1054	0.00565	0.5007	−15.33				
	0.1096	0.00674	0.5142	−8.69				
	0.1246	0.00602	0.5280	−20.35				
	0.1220	0.00852	0.5418	−2.06				
	0.1321	0.00724	0.5552	−15.24				
	0.1461	0.00848	0.5690	−12.78				
	0.1572	0.01045	0.5831	−5.99				
	0.1507	0.01118	0.5965	0.12				
W	0.2753	0.00596			0.2358	0.00562		
	0.2746	0.00720			0.2343	0.00701		
	0.3005	0.00791			0.4082	0.01116		
	0.3018	0.00752			0.3527	0.00915		
	0.3066	0.00661						

The starting masses of the initial component in the crucible are 0.8927 and 0.8217 g, the coefficients of Eq. (2) are $a = 11.2216$, $b = −0.40263$ and $a = 8.87748$, $b = −0.20646$ for runs 1 and 2, respectively.
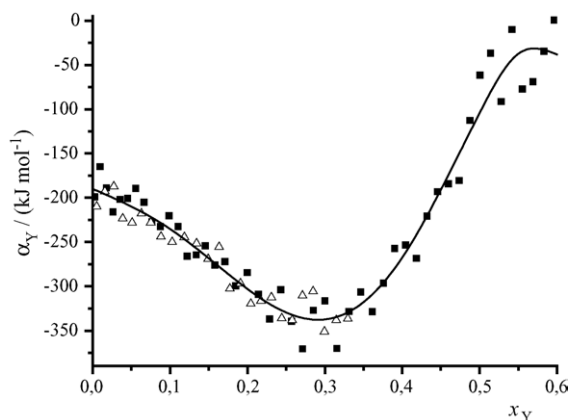
Fig. 1. Plot of yttrium alpha-function vs. mole fraction of yttrium; (■) data of run 1; (△) data of run 2; (—) smoothed data of runs 1 and 2.
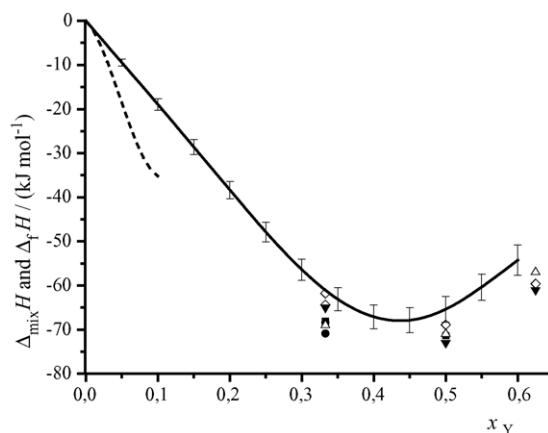

Fig. 2. Plot of integral enthalpy of mixing in the liquid Ga–Y alloys vs. mole fraction of yttrium: (—) our data at 1750 K; (– – –) smoothed data of [8] at 1125 K. Enthalpies of formation of yttrium gallides: (●) e.m.f. data of [6]; (△) calorimetric data of [7]; (◇) calorimetric data of [8]; (■) calorimetric data of [9]; (▼) data calculated by Miedema's method [10].

The enthalpies of mixing calculated by Eqs. (10) and (11) with respective deviation intervals are listed in Table 2. The α_Y-function at $x_Y < 0.28$ can be described by a linear dependence, consequently the $\Delta_{mix}\bar{H}_Y$ and $\Delta_{mix}H$ functions become:

$$\Delta_{mix}\bar{H}_Y = (1 - x_Y)^2(-181.63 - 589.73x_Y), \qquad (12)$$

$$\Delta_{mix}H = x_Y(1 - x_Y)(-181.63 - 294.86x_Y). \qquad (13)$$

The linear alpha function dependence lead to more precise determination of the $\Delta_{mix}\bar{H}_Y^\infty$ and enable to decrease deviation intervals of the enthalpies of mixing at low yttrium percentage (Table 2).

The $\Delta_{mix}\bar{H}_Y^\infty$ is found equal to $-181.6 \pm 7.9\,\text{kJ mol}^{-1}$. The value is in a good agreement with ones of $-184.4 \pm 5.3\,\text{kJ mol}^{-1}$ measured at 1099 K [8] and of $-180.25\,\text{kJ mol}^{-1}$ estimated in [10]. Besides, the $\Delta_{mix}\bar{H}_Y^\infty$ value is in a satisfactory agreement with data of [6] measured at 650–854 K ($-175.0 \pm 1.8\,\text{kJ mol}^{-1}$) and of [7] measured at 1176 K ($-174.4\,\text{kJ mol}^{-1}$). However, the $\Delta_{mix}\bar{H}_Y^\infty$ value

of $-167.0 \pm 1.8\,\text{kJ mol}^{-1}$ determined at 854–1150 K in [6] should be considered as understated by absolute value.

The enthalpy of mixing measured in [8] at 1125 K can be treated by the following equations:

$$\Delta_{mix}\bar{H}_Y = (1 - x_Y)^2(-183.80 - 12114.46x_Y + 117562.62x_Y^2), \qquad (14)$$

$$\Delta_{mix}H = x_Y(1 - x_Y)(-183.80 - 6057.23x_Y + 39187.54x_Y^2). \qquad (15)$$

The heat capacity change at alloy formation ($\Delta_{mix}C_p$) can be estimated combining Eqs. (13) and (15) under the assumption of linear temperature dependence of the integral enthalpy

Table 2
The enthalpies of mixing in the liquid Ga–Y alloys at 1750 K (in kJ mol^{-1})

x_Y	Results of data smoothing by a fifth order polynomial, Eqs. (10) and (11)			Results of data smoothing by a linear dependence, Eqs. (12) and (13)		
	$\Delta_{mix}\bar{H}_Y \pm 2\sigma$	$\Delta_{mix}\bar{H}_{Ga}$	$\Delta_{mix}H \pm 2\sigma$	$\Delta_{mix}\bar{H}_Y \pm 2\sigma$	$\Delta_{mix}\bar{H}_{Ga}$	$\Delta_{mix}H \pm 2\sigma$
0.00	-189.76 ± 21.03	0.0	0.0	-181.63 ± 7.93	0.00	0.00
0.05	-189.28 ± 8.75	-0.02	-9.48 ± 0.78	-190.53 ± 5.33	0.21	-9.33 ± 0.33
0.10	-190.64 ± 7.59	0.11	-18.97 ± 1.3	-194.89 ± 3.67	0.54	-19.00 ± 0.57
0.15	-193.81 ± 6.07	0.56	-28.59 ± 1.68	-195.14 ± 3.19	0.56	-28.80 ± 0.75
0.20	-193.81 ± 5.68	0.53	-38.34 ± 1.99	-191.73 ± 3.62	-0.19	-38.50 ± 0.93
0.25	-185.30 ± 4.79	-2.02	-47.84 ± 2.23	-185.10 ± 4.28	-2.14	-47.88 ± 1.16
0.30	-165.29 ± 4.35	-9.72	-56.39 ± 2.41			
0.35	-134.31 ± 4.50	-24.74	-63.09 ± 2.59			
0.40	-96.33 ± 4.11	-47.61	-67.10 ± 2.73			
0.45	-57.79 ± 3.5	-76.10	-67.86 ± 2.82			
0.50	-26.05 ± 3.44	-104.70	-65.38 ± 2.91			
0.55	-7.56 ± 2.89	-124.88	-60.35 ± 2.94			
0.60	-6.11 ± 5.09	-126.44	-54.24 ± 3.46			

of mixing. Consequently, the $\Delta_{\mathrm{mix}}C_p$ can be expressed by the following equation at average temperature of 1437 K (in $\mathrm{J\,mol^{-1}\,K^{-1}}$):

$$\Delta_{\mathrm{mix}}C_p = x_{\mathrm{Y}}(1 - x_{\mathrm{Y}})(3.47 + 9219.79 x_{\mathrm{Y}}$$
$$-62700.06 x_{\mathrm{Y}}^2). \tag{16}$$

Fig. 2 demonstrates the comparison of the $\Delta_{\mathrm{mix}}H$ values measured in the present study and ones obtained at 1125 K [8] together with the $\Delta_{\mathrm{f}}H^0_{298.15}$ of yttrium gallides [6–10]. It should be noted that the $\Delta_{\mathrm{mix}}H$ values measured in the present study are close to the $\Delta_{\mathrm{f}}H^0_{298.15}$ of the gallides but are somewhat less negative than aforementioned. This observation confirms the remaining of a short-range ordering of chemical compound type at the melting of the gallides. The short-range ordering leads to significantly negative $\Delta_{\mathrm{mix}}H$ values, which are close to the $\Delta_{\mathrm{f}}H^0_{298.15}$ (Fig. 2). On the other hand our $\Delta_{\mathrm{mix}}H$ data are less negative than the ones reported in [8] for lower temperature. This $\Delta_{\mathrm{mix}}H$ temperature dependence can be explained by the partial destruction of the short-range ordering at heating.

4. Conclusions

In this work, $\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Y}}$ was measured in the liquid Ga–Y alloys by mixing calorimetry at 1750 K for $0.0 < x_{\mathrm{Y}} < 0.6$ and the $\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Ga}}$ and $\Delta_{\mathrm{mix}}H$ values were calculated. The data obtained were compared with those found in literature, and the heat capacity change at alloy formation was estimated.

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