High-temperature Calorimetry of Liquid Gd–Si and Y–Si Alloys

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Molten Gd–Si and Y–Si alloys were examined calorimetrically at 1760 and 1770 K, respectively. The partial enthalpies of mixing of gadolinium ($\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Gd}}$), yttrium ($\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Y}}$) and silicon ($\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Si}}$) were measured. The integral enthalpy of mixing ($\Delta_{\mathrm{mix}}H$) was calculated by Darken's method. The available thermodynamic data of liquid (Gd,Y)–Si alloys were compared. The partial enthalpies of mixing of Gd and Y, and appropriate integral enthalpies of mixing, were described by polynomial dependencies versus mole fraction of Gd or Y.

Key words: (Gd,Y)–Si; Liquid Alloys; Calorimetry; Mixing Enthalpy.

1. Introduction

Strong interactions between free and local electrons near the temperature of metal-insulator transitions affect significantly the specific heat and magnetic properties. In some cases the transition leads to a colossal magnetocaloric effect (CMCE) [1]. This effect makes possible the commercial adaption of CMCE materials, in particular for magnetic refrigeration [2, 3].

Gadolinium and its alloys with semiconducting silicon or germanium are used as CMCE materials. Gd_5Si_4 is one of the promising materials for magnetic refrigeration. However, for useful commercial application Curie temperature tuning from 340 K to near-room temperature is required. A study of $(Gd_{1-x}Y_x)_5Si_4$ alloys [4] shows that the Curie temperature can be optimized for magnetic refrigeration, using in particular substitution of Gd by Y. Such an effect of Y addition was also found for films of α-Gd_xSi_{1-x} spin-glasses [5].

In the present article we analyse the thermodynamic literature data and report results of our calorimetric examination of liquid Gd–Si and Y–Si alloys.

The phase diagram of Gd–Si has been studied by differential thermal analysis and X-ray powder diffraction [6, 7], but no thermodynamic optimization was performed. The phase diagram of Y–Si was published in [8] and later based on available thermodynamic data in [9]. However, the liquidus curves in [8] and [9] differ in the region of yttrium silicides formation.

Both phase diagrams are characterized by refractory silicides, which make the examination of the liquid phase too complicated at $0.30 < x_{\mathrm{Gd}} < 0.70$ and $0.35 < x_{\mathrm{Y}} < 0.75$.

Thermodynamic literature data on liquid silicides are scanty and partly contradictory. Calorimetric standard enthalpies of formation [$\Delta_{\mathrm{f}}H^0(298.15)$] of gadolinium silicides [10 – 12] agree (Fig. 1). Hence the $\Delta_{\mathrm{f}}H^0(298.15)$ measured by the electromotive force (EMF) method [13] are more negative. Several standard enthalpies of formation of yttrium silicides were measured by calorimetry [14, 15], EMF [16] and one was calculated by the Miedema method [17]. The data of [16] are more negative than the data of [14, 15, 17] (see Fig. 3).

The thermodynamics of the liquid phase of the systems was examined by calorimetry only. A set of enthalpies of mixing of Gd–Si melts was measured for $0 \le x_{\mathrm{Gd}} \le 0.06$ [18]. Enthalpies of mixing of the Y–Si alloys were reported in [19 – 22] (see Figs. 2 and 3) and compared in [9]. As one can see in Fig. 2, the $\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Y}}$ determined in [19, 20] do not agree with the ones in [21, 22].

2. Experimental

The Alfa reagents gadolinium (purity 99.995 mass%), tungsten (purity 99.96 mass%), yttrium distillate (purity 99.97 mass%) and silicon (purity 99.9999 mass%) were used in the experiments.

Table 1. Results of the calorimetric study of the Gd–Si system. Run 1: $m_0 = 1.1787$ g[a]; $a = 7.28025$; $b = 0.30510$[b].

Component (A)	Added amount m_i/g	S_i a. u.	x_A	$\Delta_{\text{mix}}\bar{H}_A$ kJ mol^{-1}
Si	0.0305	0.01095		
	0.0246	0.00969		
	0.0431	0.01938		
	0.0360	0.01388		
	0.0470	0.01972		
	0.0698	0.02771		
	0.0734	0.03426		
	0.0464	0.01886		
Gd	0.0278	−0.00333	0.0016	−208.13
	0.0298	−0.00326	0.0049	−195.49
	0.0370	−0.00444	0.0087	−208.69
	0.0392	−0.00407	0.0130	−188.87
	0.0449	−0.00701	0.0177	−253.45
	0.0437	−0.00489	0.0226	−199.32
	0.0531	−0.00562	0.0279	−192.14
	0.0522	−0.00607	0.0336	−205.30
	0.0694	−0.00754	0.0401	−196.28
	0.0710	−0.01142	0.0475	−261.43
	0.0813	−0.01230	0.0554	−250.10
	0.0835	−0.01259	0.0638	−250.05
	0.0964	−0.01543	0.0728	−262.33
	0.1014	−0.01780	0.0825	−282.65
	0.1091	−0.01697	0.0926	−258.32
	0.1105	−0.01670	0.1029	−253.57
	0.1142	−0.01855	0.1132	−268.79
	0.1203	−0.01907	0.1237	−264.69
	0.1268	−0.01893	0.1345	−253.84
	0.1313	−0.02151	0.1455	−273.46
	0.1311	−0.02078	0.1564	−267.62
	0.1457	−0.02143	0.1676	−253.80
	0.1438	−0.01910	0.1790	−236.13
	0.1644	−0.02671	0.1908	−276.35
	0.1611	−0.02061	0.2029	−231.69
	0.1688	−0.02733	0.2148	−278.10
	0.1683	−0.02329	0.2266	−247.80
	0.1822	−0.02817	0.2385	−270.99
	0.1795	−0.01972	0.2504	−211.42
	0.2003	−0.02515	0.2625	−233.99
	0.1823	−0.04522	0.2743	−404.03
	0.4155	−0.09247	0.2920	−373.31
W	0.2665	0.00707		
	0.2717	0.00624		
	0.2510	0.00643		
	0.2747	0.00643		
	0.2652	0.00646		
	0.2602	0.00564		
	0.2450	0.00542		

[a] m_0 is the starting mass of the initial component in the crucible. [b] a and b are l. s. r. coefficients of (2).

The calorimetric experiments were carried out in argon (99.997 vol.%) at atmospheric pressure, using a self-constructed high-temperature isoperibolic calorimeter [23]. The measurements on Gd–Si and Y–Si were performed at 1760 and 1770 K, respectively.

Table 1 (continued). Run 2: $m_0 = 5.5661$ g[a]; $a = 4.09006$; $b = 0.18190$[b].

Component (A)	Added amount m_i/g	S_i a. u.	x_A	$\Delta_{\text{mix}}\bar{H}_A$ kJ mol^{-1}
Gd	0.3897	0.03200		
	0.2880	0.02044		
	0.1549	0.01356		
	0.1789	0.01193		
	0.1690	0.01103		
	0.1506	0.01080		
	0.2118	0.01536		
	0.1536	0.01299		
Si	0.0130	−0.01006	0.0050	−205.94
	0.0175	−0.01265	0.0165	−198.19
	0.0190	−0.01467	0.0299	−205.75
	0.0193	−0.01361	0.0436	−195.68
	0.0198	−0.01379	0.0572	−194.36
	0.0205	−0.01150	0.0708	−173.79
	0.0226	−0.01426	0.0849	−184.56
	0.0234	−0.01406	0.0995	−180.03
	0.0237	−0.01298	0.1140	−171.94
	0.0277	−0.01606	0.1293	−176.95
	0.0263	−0.01095	0.1448	−152.01
	0.0308	−0.01418	0.1606	−158.80
	0.0377	−0.02039	0.1788	−171.27
	0.0440	−0.02037	0.1995	−159.42
W	0.2371	0.00748		
	0.2611	0.00615		
	0.2765	0.00734		
	0.2714	0.00842		

Table 2. Results of the calorimetric study of the Y–Si system. $m_0 = 1.8279$ g[a]; $a = 6.8507$; $b = -0.01972$[b].

Added substance (A)	Added amount m_i/g	S_i a. u.	x_A	$\Delta_{\text{mix}}\bar{H}_A$ kJ mol^{-1}
Si	0.0924	0.04430		
	0.0498	0.02201		
	0.1162	0.05351		
	0.0541	0.02540		
	0.0873	0.03956		
	0.1037	0.04927		
	0.0789	0.03663		
	0.0956	0.04430		
Y	0.0974	−0.02304	0.0061	−205.94
	0.1043	−0.02077	0.0185	−183.28
	0.1432	−0.03545	0.0333	−212.48
	0.1488	−0.03133	0.0502	−190.07
	0.2638	−0.05041	0.0731	−178.24
	0.2341	−0.05122	0.0993	−194.86
	0.3020	−0.06593	0.1259	−194.45
	0.2523	−0.05316	0.1518	−189.78
	0.3275	−0.07383	0.1773	−198.51
	0.4733	−0.10531	0.2101	−196.57
	0.4691	−0.08790	0.2455	−175.32
W	0.5497	0.01782		
	0.4852	0.01608		
	0.6324	0.01993		
	0.5941	0.02003		

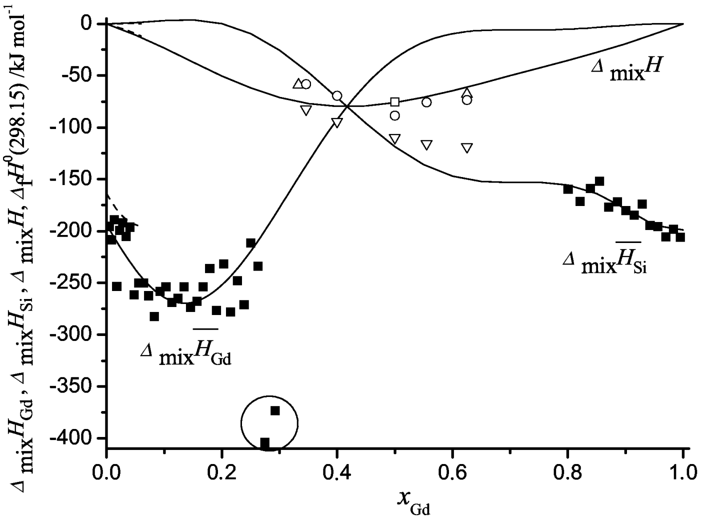

Fig. 1. Enthalpies of mixing ($\Delta_{\mathrm{mix}}\overline{H}_{\mathrm{Gd}}$, $\Delta_{\mathrm{mix}}\overline{H}_{\mathrm{Si}}$, $\Delta_{\mathrm{mix}}H$) and enthalpies of silicides formation [$\Delta_{\mathrm{f}}H^0(298.15)$] vs. x_{Gd} in the Gd–Si system. Enthalpies of mixing: solid squares are experimental data points of the runs 1 and 2 measured at 1760 K; curves are polynomial fitting of the experimental data. Dashed line refers to data of [18] at 1873 K. Data in circle correspond to transition into a heterogeneous state omitted from the extrapolation. $\Delta_{\mathrm{f}}H^0(298.15)$: open up triangles are data of [10]; open square is a datum of [11]; open circles are data of [12]; open down triangles are data of [13].

For details of the measurement technique see [24]. The enthalpies of mixing were calculated from heat-exchange curves, which were registered at dropping of pure samples, stored at 298 K, into the liquid bath.

Two runs were recorded for the examination of the Gd–Si system. In the first experiment the initial component in the bath was Si, and weighted samples of Gd were dropped into the melt up to the mole fraction $x_{\mathrm{Gd}} = 0.3$. In the second experiment Si and Gd were reversed and Si was added up to $x_{\mathrm{Si}} = 0.2$. A single experiment was performed for examination of the Y–Si system, using silicon as the initial component. In the final part of the mixing experiments, samples of W, which was used as a reference material, were dropped into the melt for the calorimeter calibration. The absence of interaction between tungsten and the melt was confirmed by mass analysis after cooling and cutting of the alloys. The heat-exchange coefficient of the calorimeter was calculated by the formula

$$k_i = \Delta H^T_{298.15} n_i S_i^{-1}, \tag{1}$$

where $\Delta H^T_{298.15}$ is the standard enthalpy of heating from 298.15 K up to the experimental temperature [25], i is the dropped sample number, n_i is the mole quantity of the dropped sample and S_i is the area of the heat-exchange peak. The k_i values were treated by the least squares regression (l. s. r.) for the linear model

$$k = a + b m_{\mathrm{alloy}}, \tag{2}$$

where m_{alloy} is the mass of the alloy. The partial enthalpy of mixing was calculated from the experimental heat-exchange curves by the formula

$$\Delta_{\mathrm{mix}}\overline{H}_{\mathrm{A}} = -\Delta H^T_{298.15} + k_i S_i n_i^{-1}, \tag{3}$$

where A is the component, i.e. Gd, Y or Si. The values of $\Delta_{\mathrm{mix}}\overline{H}_{\mathrm{Gd}}$ were assigned to the middle point of the composition range before and after the sample addition. The experimental partial enthalpy of mixing was smoothed using the l. s. r. for the polynomial equation

$$\Delta_{\mathrm{mix}}\overline{H}_{\mathrm{A}} = (1 - x_{\mathrm{A}})^2 \sum_{j=0}^{l} Q_j x_{\mathrm{A}}^j, \tag{4}$$

where Q_j is the polynomial coefficient and l is the polynomial degree determined by Fisher's exact test. The calculation of the integral enthalpy of mixing was performed by Darken's method:

$$\Delta_{\mathrm{mix}}H = (1 - x_{\mathrm{A}}) \int_0^{x_{\mathrm{A}}} \Delta_{\mathrm{mix}}\overline{H}_{\mathrm{A}} (1 - x_{\mathrm{A}})^{-2} \mathrm{d}x_{\mathrm{A}}. \tag{5}$$

After substitution of (4) in (5) and integration, (5) should be

$$\Delta_{\mathrm{mix}}H = x_{\mathrm{Y}}(1 - x_{\mathrm{Y}}) \sum_{j=0}^{l} (j+1)^{-1} Q_j x_{\mathrm{Y}}^j. \tag{6}$$

The integral enthalpy of mixing determined for the two concentration intervals was extrapolated into the range of overcooled liquid alloys by statistical treatment of the ζ-function ($\zeta = \Delta_{\mathrm{mix}}H(x_{\mathrm{A}} - x_{\mathrm{A}}^2)^{-1}$) via the polynomial model.

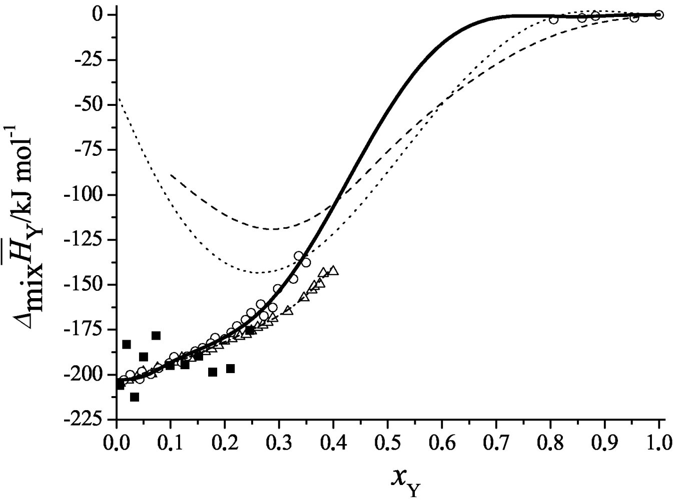

Fig. 2. Comparison of partial enthalpy of mixing of yttrium ($\Delta_{\text{mix}}\overline{H}_{\text{Y}}$) vs. x_{Y} measured at different temperatures in the Y–Si system. Solid squares are data of the present study at 1770 K; open up triangles are data of [19] at 1880 K; open circles are data of [20] at 1870 K. Data fit: dash-dotted line describes data of [19]; solid line describes data of [20]; dotted line describes data of [21] at 2053 K; dashed line describes data of [22] at 1973 K.

3. Results and Discussion

The primary experimental data are listed in Tables 1 and 2. The concentration dependences of $\Delta_{\text{mix}}\overline{H}_{\text{Gd}}$, $\Delta_{\text{mix}}\overline{H}_{\text{Si}}$, and $\Delta_{\text{mix}}H$ in the Gd–Si system are shown in Figure 1. Evidently $\Delta_{\text{mix}}\overline{H}_{\text{Gd}}$ decreases sharply from -234 to -404 kJ mol^{-1} at $x_{\text{Gd}} = 0.27$. This effect is caused by the transition into a heterogeneous state, where the weighted Gd is dissolved in the melt with simultaneous crystallization of β-GdSi$_2$ [7]. Significant heat-evolution accompanies the crystallization, and so $\Delta_{\text{mix}}\overline{H}_{\text{Gd}}$ decreases sharply. Therefore, the $\Delta_{\text{mix}}\overline{H}_{\text{Gd}}$ data at $x_{\text{Gd}} > 0.27$ were omitted from the subsequent calculations.

It has been found that $\Delta_{\text{mix}}\overline{H}_{\text{Gd}}$ and $\Delta_{\text{mix}}H$ in the Gd–Si system can be expressed for the whole composition range as

$$\begin{aligned}\Delta_{\text{mix}}\overline{H}_{\text{Gd}} = {} & (1-x_{\text{Gd}})^2(-194.33-1301.42x_{\text{Gd}} \\ & -2668.02x_{\text{Gd}}^2+30029.28x_{\text{Gd}}^3 \\ & -50276x_{\text{Gd}}^4+24499.92x_{\text{Gd}}^5),\end{aligned} \tag{7}$$

$$\begin{aligned}\Delta_{\text{mix}}H = {} & x_{\text{Gd}}(1-x_{\text{Gd}})(-194.33-650.71x_{\text{Gd}} \\ & -889.34x_{\text{Gd}}^2+7507.32x_{\text{Gd}}^3 \\ & -10055.2x_{\text{Gd}}^4+4083.32x_{\text{Gd}}^5).\end{aligned} \tag{8}$$

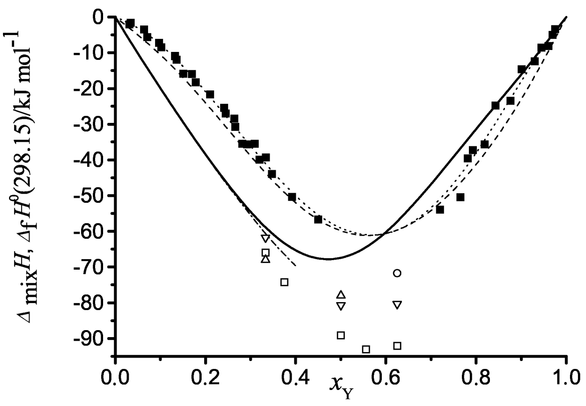

Fig. 3. Comparison of thermodynamic functions ($\Delta_{\text{mix}}H$) and $\Delta_{\text{f}}H^0$(298.15) vs. x_{Y} in the Y–Si system. $\Delta_{\text{mix}}H$: solid squares are data of [21] at 2053 K; dotted line corresponds to the polynomial dependence describing data of [21] at 2053 K; dashed line corresponds to the polynomial dependence describing data of [22] at 1973 K; solid line corresponds to the polynomial dependence describing data of [20] at 1870 K; dash-dotted line corresponds to the polynomial dependence describing data of [19] at 1880 K. $\Delta_{\text{f}}H^0$(298.15): open down triangles are data of [14]; open circle is datum of [15]; open squares are data of [16]; open up triangles are data of [17].

The Gd–Si melts are characterized by significant negative enthalpies of mixing. The extreme of $\Delta_{\text{mix}}H$ is found to be -79.86 kJ mol^{-1} at $x_{\text{Gd}} = 0.417$. The present data agree well with those of [18] for diluted gadolinium solutions. The values of $\Delta_{\text{f}}H^0$(298.15) and $\Delta_{\text{mix}}H$ are closely related, excluded the EMF data of [13]. Consequently, interaction of Gd and Si atomic pairs paid the major contribution to the thermodynamics of the liquid, and clusters isostoichiometric to the gadolinium silicides can be formed in the liquid phase.

As can be seen from Fig. 2, our $\Delta_{\text{mix}}\overline{H}_{\text{Y}}$ data in the Y–Si system agree well with those of [19, 20] and are more negative than in [21, 22]. Therefore, the data of [21, 22] can be considered as overstated. Considering the data of [19, 20], we have chosen those of [20]

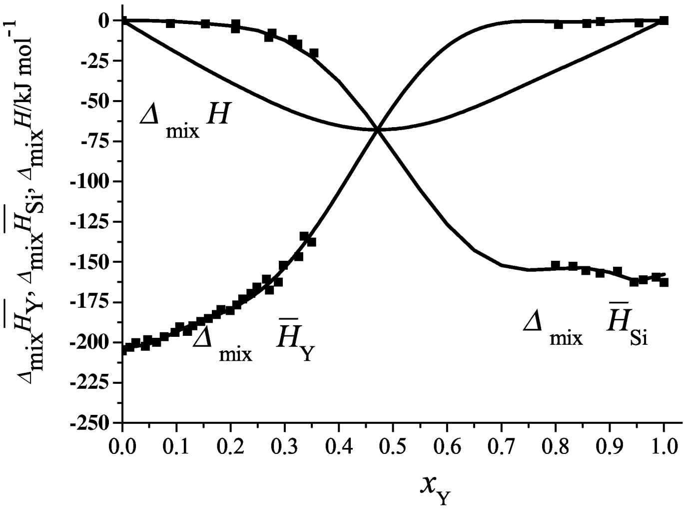

Fig. 4. Enthalpies of mixing ($\Delta_{\text{mix}}\overline{H}_{\text{Y}}$, $\Delta_{\text{mix}}\overline{H}_{\text{Si}}$ and $\Delta_{\text{mix}}H$) vs. x_{Y} in the Y–Si system. Solid squares are experimental data points [20]; curves are polynomial fitting of data [20].

as the most relevant ones. These data are the latest ones reported by Yesin's working-group. Moreover, the enthalpies of mixing were measured in [20] for two concentration ranges ($0 < x_{\text{Y}} < 0.35$ and $0.8 < x_{\text{Y}} < 1$), in contrast to [19]. Therefore, the initial data of [20] were used for the optimization of the enthalpies of mixing, and the corresponding equations were

$$\Delta_{\text{mix}}\overline{H}_{\text{Y}} = (1-x_{\text{Y}})^2(-202.94 - 518.82x_{\text{Y}} + 3901.47x_{\text{Y}}^2 - 31491.16x_{\text{Y}}^3 + 98369.95x_{\text{Y}}^4 - 118183.2x_{\text{Y}}^5 + 48300.98x_{\text{Y}}^6), \tag{9}$$

$$\Delta_{\text{mix}}H = x_{\text{Y}}(1-x_{\text{Y}})(-202.94 - 259.41x_{\text{Y}} + 1300.49x_{\text{Y}}^2 - 7872.79x_{\text{Y}}^3 + 19673.99x_{\text{Y}}^4 - 19697.2x_{\text{Y}}^5 + 6900.14x_{\text{Y}}^6). \tag{10}$$

The extreme of $\Delta_{\text{mix}}H$ is found to be -67.83 kJ mol^{-1} at $x_{\text{Y}} = 0.471$ (see Figs. 3 and 4). The extremes of $\Delta_{\text{mix}}H$ in the liquid Y–Si alloys and of $\Delta_{\text{f}}H$ of yttrium silicides are at the same concentration, which testifies the significant effect of the intermetallides on the thermodynamics of liquid Y–Si alloys. Contrary to the thermodynamic behaviour of the Gd–Si system, the standard enthalpies of formation of yttrium silicides are found to be more negative than the $\Delta_{\text{mix}}H$. This evidences that the inter-component interaction is weakening at the transition into the liquid state.

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