

# Calorimetric Investigation of Liquid Gallium-based Alloys

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In this work, enthalpies of mixing of binary liquid gallium-gadolinium and gallium-silicon alloys have been measured by high-temperature isoperibolic calorimetry at  $1760 \pm 5$  K. Significant negative enthalpies of mixing have been found for Ga–Gd system, while these values are positive for Ga–Si melts.

**Key words:** Calorimetry; Mixing Enthalpy; Liquid Alloys; Gallium Alloys; Ga–Gd; Ga–Si.

## 1. Introduction

The investigation of the thermophysical properties of liquid metallic alloys is relevant for basic materials science and applications. For instance, the addition of gallium to alloys increases their corrosion resistance. In this contribution two gallium containing melts Ga–Gd and Ga–Si, have been studied by means of calorimetry at  $1760 \pm 5$  K.

## 2. Experimental

### 2.1. Materials

The reagents silicon (purity, 99.99% mass), gadolinium (purity, 99.95% mass) and gallium (purity, 99.999% mass) were supplied by Alfa Aesar (Johnson Matthey). Tungsten (purity, 99.96% mass) of same origin has been used as a reference.

### 2.2. Calorimetric Procedure

The heats of mixing have been measured under argon at atmospheric pressure using a high-temperature isoperibolic calorimeter. The apparatus, operating technique, and data treatment have been described in [1].

The calorimetric alundum crucible was lined with  $Y_2O_3$  to prevent interaction with gadolinium. The initial weight of the components was in the range 1.1 to 5.8 g. The masses of the samples entering the melt

were 0.013 up to 0.070 g silicon, 0.028 to 0.288 g gadolinium, 0.028 to 0.158 g gallium, and 0.237 to 0.283 g tungsten. The values of the enthalpies of heating necessary for the calculation of the enthalpy of mixing, were taken from [2]. The absence of an interaction between tungsten and the melt was controlled by mass analysis after quenching. Two experiments were performed for the Ga–Gd system. In the first one the initial component in the crucible was gadolinium, and gallium was added up to a gallium mole fraction of 0.45. The second experiment was carried out with reverse component adding up to  $x_{Gd} = 0.55$ . Only one experiment with the Ga–Si system was performed for concentrations in the range of  $0.0 \leq x_{Ga} \leq 0.65$ .

## 3. Results and Discussion

The results of the calorimetric study are listed in the Table. The integral enthalpies of mixing for the Ga–Gd and Ga–Si systems were fitted by the least squares method [1] to respective polynomials of the form

$$\begin{aligned} \Delta_{\text{mix}}H = & x_{Gd}(1-x_{Gd})(-204.3 - 585x_{Gd} \\ & - 750x_{Gd}^2 + 12600x_{Gd}^3 - 29400x_{Gd}^4 \\ & + 27100x_{Gd}^5 - 9000x_{Gd}^6), \end{aligned} \quad (1)$$

$$\Delta_{\text{mix}}H = 18.4x_{Ga}(1-x_{Ga}), \quad (2)$$

where  $\Delta_{\text{mix}}H$  = integral enthalpy of mixing [kJ/mol],

Table 1. Partial and integral enthalpies of mixing in Ga–Gd and Ga–Si systems (in kJ/mol).

$x_{\text{Ga}}$	Ga–Gd system			Ga–Si system		
	$\Delta_{\text{mix}}\bar{H}_{\text{Ga}}$ $\pm 2\sigma$	$\Delta_{\text{mix}}\bar{H}_{\text{Gd}}$ $\pm 2\sigma$	$\Delta_{\text{mix}}H$ $\pm 2\sigma$	$\Delta_{\text{mix}}\bar{H}_{\text{Ga}}$ $\pm 2\sigma$	$\Delta_{\text{mix}}\bar{H}_{\text{Si}}$ $\pm 2\sigma$	$\Delta_{\text{mix}}H$ $\pm 2\sigma$
0.0	–176±15	0	0	18.4±3.1	0	0
0.1	–162.6±6.7	–0.4	–16.6±1.1	14.9±2.5	0.2	1.7±0.3
0.2	–143.8±4.5	–4.0	–32.0±1.8	11.8±1.9	0.7	2.9±0.5
0.3	–114.9±3.8	–13.6	–44.0±2.2	9.0±1.5	1.6	3.9±0.6
0.4	–97.5±4.4	–22.8	–52.7±3.1	6.6±1.1	2.9	4.4±0.7
0.5	–87.0	–31.4±4.2	–59.2±5.0	4.6±0.8	4.6	4.6±0.8
0.6	–67.6	–56.0±6.4	–62.9±4.9	2.9±0.5	6.6	4.4±0.7
0.7	–36.1	–116±7	–59.9±4.4	1.6*	9.0*	3.9*
0.8	–8.0	–199±10	–46.3±3.6	0.7*	11.8*	2.9*
0.9	1.5	–248±12	–23.4±2.3	0.2*	14.9*	1.7*
1	0	–204±32	0	0	18.4*	0

\* Extrapolated data.

$x_{\text{Gd}}$  and  $x_{\text{Ga}}$  = mole fractions of gadolinium and gallium in the liquid alloys, respectively.

As can be seen from the Table, the great negative enthalpies of mixing are observed for the Ga–Gd system. The extremum is at  $x_{\text{Ga}} = 0.62$ . This fact is well explained by the Ga–Gd phase diagram, containing  $\text{GdGa}_2$ , which melts congruently ( $T_m = 1673$  K) [3]. The strong interaction between Ga and Gd atoms is maintained at the transition into the liquid state. In the Ga–Si system positive enthalpies of mixing were determined, which evidences the domination of the interaction of the same-sort atoms. This is in a good accords with the phase diagram of the simple eutectic type [4], and consequently segregation in the solid phase.

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