

CALORIMETRIC STUDY OF LIQUID GADOLINIUM-BASED ALLOYS

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Abstract

The enthalpies of mixing of liquid Gd–Si (1770±5 K) and Al–Gd (1760±5 K) alloys have been measured by high-temperature isoperibolic calorimetry. The calorimetric study of the gadolinium-based liquid alloys demonstrates the great negative enthalpies of mixing, which is associated with the contribution of GdSi and GdAl₂ intermetallides into the liquid-state thermodynamics. The comparison of obtained results with literature data has been performed.

Keywords: aluminium–gadolinium, calorimetry, gadolinium–silicon, liquid alloys, mixing enthalpy

Introduction

High cross-sections capture of thermal neutrons and magnetocaloric effect are characteristics of the gadolinium and the gadolinium-based alloys, which make them an attractive for modern engineering [1, 2].

The Gd–Si phase equilibrium was experimentally examined by Gokhale and Eremenko [3, 4]. Gadolinium silicides enthalpies of formation ($\Delta_f H$) measured by calorimetry [5–7] show good agreement (Fig. 1a), hence less precise electromotive force data of [8] are overstated by absolute values. Liquid Gd–Si alloys have been studied using calorimetry for $0 \leq x_{\text{Gd}} \leq 0.06$ [9].

The numerous experimental studies of Al–Gd phase equilibrium were reviewed in [10]. The Al–Gd state diagram was assessed recently by Calphad method [11, 12] using $\Delta_{\text{form}} H$ of gadolinium aluminides [13, 14] shown in Fig. 1b. However, the calculations were performed in absence of available experimental data on the liquid phase thermodynamics.

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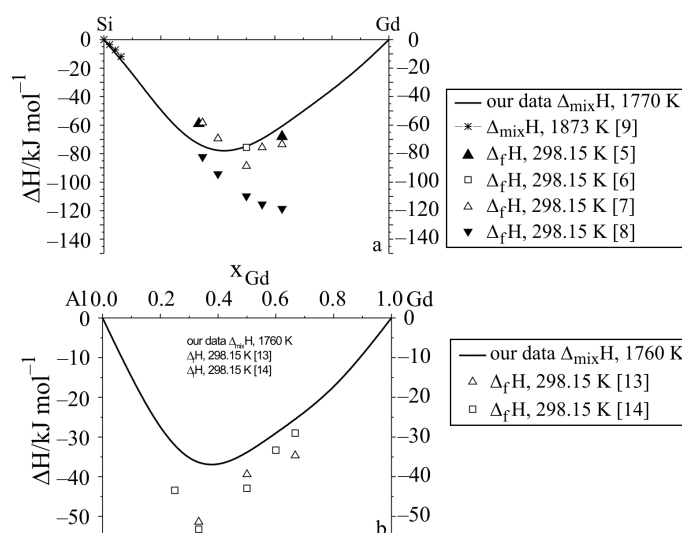


Fig. 1 The enthalpies of mixing ($\Delta_{\text{mix}}H$) and intermetallics formation ($\Delta_f H$) vs. gadolinium mole fraction (x_{Gd}). a – Gd–Si, b – Al–Gd system

The present contribution is devoted to study of liquid Gd–Si and Al–Gd alloys by high-temperature isoperibolic calorimetry at 1770 ± 5 and 1760 ± 5 K, respectively, which is necessary for precise assessment of the state diagrams of both systems.

Experimental procedures

The reagents silicon (purity, 99.99 mass%), gadolinium (purity, 99.85 mass%) and aluminium (purity, 99.99 mass%) were supplied by Alfa. Tungsten (purity, 99.96 mass%) of same origin has been used as a reference.

The calorimeter construction, experimental performance and data treatment have been described in [15, 16]. The mixing experiments were carried out under argon at atmospheric pressure. The liquid Gd–Si alloys were studied in two concentration ranges with gadolinium mole fraction (x_{Gd}) from 0 to 0.25 and x_{Gd} from 0.75 to 1. The Al–Gd system was examined in the range of x_{Gd} from 0 to 0.2 and from 0.6 to 1. The masses of the samples entering into a melt were from 0.013 to 0.07 g for Si, from 0.03 to 0.3 g for Gd, from 0.013 to 0.1 for Al, and from 0.26 to 0.35 g for W.

Results and discussion

The results of calorimetric study are listed in Table 1. The integral enthalpies of mixing for the Gd–Si and the Al–Gd systems were fitted by the least squares method to polynomials of the form (in kJ mol^{-1}):

Table 1 Partial and integral enthalpies of mixing in Gd–Si and Al–Gd systems (in kJ mol^{-1})

x_{Gd}	Gd–Si system at 1760 5 K			Al–Gd system at 1770 5 K		
	$\Delta_{\text{mix}} \bar{H}_{\text{Gd}} \pm 2\sigma$	$\Delta_{\text{mix}} \bar{H}_{\text{Si}} \pm 2\sigma$	$\Delta_{\text{mix}} H \pm 2\sigma$	$\Delta_{\text{mix}} \bar{H}_{\text{Gd}} \pm 2\sigma$	$\Delta_{\text{mix}} \bar{H}_{\text{Al}} \pm 2\sigma$	$\Delta_{\text{mix}} H \pm 2\sigma$
0.0	-194.3±8.7	0	0	-170.5±9.9	0	0
0.1	-264.0±7.0	3.2	-23.6±0.8	-144.1±5.9	-0.8	-15.1±0.8
0.2	-252.0±5.5	0.04	-50.4±1.4	-118.1±7.80	-5.8	-28.3±1.6
0.3	-177.3*	-25.5*	-71.1*	-68.5*	-22.6*	-36.3*
0.4	-92.2*	-71.4*	-79.7*	-27.6*	-44.3*	-37.6*
0.5	-33.8*	-118.5*	-76.1*	-10.4*	-57.8*	-34.1*
0.6	-9.6*	-147.0*	-64.6*	-8.3	-60.1±1.8	-29.0±1.1
0.7	-6.0*	-153.1*	-50.1*	-7.5	-61.9±1.8	-23.8±0.9
0.8	-5.3	-155.5±7.1	-35.3±1.5	-3.3	-74.9±1.9	-17.6±0.7
0.9	-1.5	-178.3±4.5	-19.2±0.8	-0.2	-92.1±2.6	-9.4±0.5
1.0	0	-198.9±10.4	0	0	-91.5±6.4	0

* Extrapolated data for overcooled liquid alloys.

$$\Delta_{\text{mix}}H = x_{\text{Gd}}(1-x_{\text{Gd}}) \left(\begin{array}{l} -194.3 - 650x_{\text{Gd}} - 890x_{\text{Gd}}^2 + \\ + 7500x_{\text{Gd}}^3 - 10050x_{\text{Gd}}^4 + 4100x_{\text{Gd}}^5 \end{array} \right) \quad (1)$$

(Gd–Si, 1770 K)

$$\Delta_{\text{mix}}H = x_{\text{Al}}(1-x_{\text{Al}}) \left(\begin{array}{l} -91.5 - 143x_{\text{Al}} - 86x_{\text{Al}}^2 + 3600x_{\text{Al}}^3 - \\ - 12200x_{\text{Al}}^4 + 14500x_{\text{Al}}^5 - 5750x_{\text{Al}}^6 \end{array} \right) \quad (2)$$

(Al–Gd, 1760 K)

These equations allow to extrapolate $\Delta_{\text{mix}}H$ into all concentration range including area of overcooled liquid alloys. The dissolution of the gadolinium samples in the liquid silicon or aluminium and of Al or Si samples in liquid Gd was accompanied with significant exothermic effects.

The greatest negative $\Delta_{\text{mix}}H$ values were determined for Gd–Si system. As it can be seen from Fig. 1a, good agreement of our data with results of [9] for diluted gadolinium solutions is observed. The values of Δ_fH and $\Delta_{\text{mix}}H$ are closely related. It can testify that the major contribution to the alloys thermodynamics is paid by interaction between atoms of different sort, which can result in chemical short-range order formation in liquid phase. The most refractory intermetallide in the system is GdSi, which congruently melts at 2103 K. Therefore, it is logically to conclude that GdSi binary clusters can pay the major influence onto alloys thermodynamics. Since the GdSi has equiatomic composition, so its influence leads to close to symmetric type of $\Delta_{\text{mix}}H$ curve (Fig. 1a).

$\Delta_{\text{mix}}H$ for Al–Gd alloys are twice less than for Gd–Si. The run of $\Delta_{\text{mix}}H$ concentration dependence is similar with Δ_fH changing with intermetallide composition. The shift of the extreme point of $\Delta_{\text{mix}}H$ to area enriched by the aluminium (Fig. 1b) can be explained by the influence of congruently melting aluminide GdAl₂ ($T_m=1798$ K). In contrast to the Gd–Si system, the $\Delta_{\text{mix}}H$ in the Al–Gd alloys are less negative than Δ_fH . It can testify, that at temperature of our study, the influence of the intermetallides on liquid alloys thermodynamics in the Al–Gd is less, than for the Gd–Si system.

The lowering of the exothermal effects of mixing in binary Gd-based systems with IIIA and IVA elements determined in present study agrees well with decreasing of difference in electronegativity for the elements pairs in the sequence: Ge–Gd [17]→Gd–Si→Gd–Ga [16]→Al–Gd.

Conclusions

The studied gadolinium-based liquid alloys, due to contribution of intermetallides (GdSi and GdAl₂) into thermodynamics of liquid, demonstrate the great negative enthalpies of mixing. The integral enthalpies of mixing measured by calorimetry are in well agreement with literature data on $\Delta_{\text{mix}}H$ and Δ_fH .

References

- 1 B. Predel, in (Ed. O. Madelung): Phase equilibrium, crystallographic and thermodynamic data of binary alloys, Subvolume A and F, XXVI, Landolt-Börnstein, Berlin 1996, p. 380.
- 2 F. Hellman, M. Q. Tran, A. E. Gebala, E. M. Wilcox and R. C. Dynes, *Phys. Rev. Lett.*, 77 (1996) 4652.
- 3 A. B. Gokhale and G. J. Abbaschian, *Bull. Alloy Phase Diagr.*, 9 (1988) 574.
- 4 V. N. Eremenko, K. A. Meleshevich, Yu. I. Buyanov and P. S. Martsenuk, *Ukr. Khim. Zh.*, 57 (1991) 1047.
- 5 S. V. Meschel and O. J. Kleppa, *J. Alloys Comp.*, 217 (1995) 235.
- 6 S. V. Meschel and O. J. Kleppa, *J. Alloys Comp.*, 224 (1995) 343.
- 7 N. I. Usenko, M. I. Ivanov, V. V. Berezutski and R. J. Polotska, *J. Alloys Comp.*, 266 (1998) 186.
- 8 G. M. Lukashenko, R. J. Polotskaya and V. R. Sidorko, *J. Alloys Comp.*, 179 (1992) 295.
- 9 G. I. Batalin, V. S. Sudavtsova and N. V. Stroganova, *Ukr. Khim. Zh.*, 51 (1985) 775.
- 10 A. Saccone, A. M. Cardinale, S. Delfino and R. Ferro, *Z. Metallkd.*, 91 (2000) 17.
- 11 J. Grobner, D. Koverkov and R. Schmid-Fetzer, *Z. Metallkd.*, 98 (2001) 22.
- 12 R. E. Hackenberg, M. C. Gao, L. Kaufman and G. J. Shiflet, *Acta Materialia*, 50 (2002) 2245.
- 13 F. Sommer and M. Keita, *J. Less-Common Met.*, 136 (1987) 95.
- 14 C. Colinet, A. Pasturel and K. H. J. Buschow, *Physica B*, 150 (1988) 397.
- 15 D. S. Kanibolotsky, O. A. Bieloborodova, N. V. Kotova and V. V. Lisnyak, *J. Therm. Anal. Cal.*, 71 (2003) 583.
- 16 D. S. Kanibolotsky, N. V. Kotova, O. A. Bieloborodova and V. V. Lisnyak, *Z. Naturforsch. A.*, 58 (2003) 473.
- 17 I. V. Nikolaenko, Ph.D Thesis, Enthalpies of formation of Ge binary alloys with rare earth metals, Kiev 1981, p. 21 (in Russian).