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Calorimetric investigation of liquid Al–Ga–Gd alloys

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Abstract

Partial for gadolinium and integral enthalpies of mixing were determined for liquid Al–Ga–Gd alloys using a high-temperature isoperibolic calorimeter at 1760 ± 5 K. The experiments were performed along five sections with constant concentration ratios of Al and Ga in a range of $0.0 \le x_{Gd} \le 0.6$. The resulted integral enthalpies of mixing were fitted by polynomial concentration dependences. The deviation between experimental and predicted by geometric model values of integral enthalpy of mixing was found to be 5.25%, so ternary interaction is negligibly small at the experimental temperature. It has been determined that ternary alloys thermodynamics is preferentially defined by influence of congruently melting binary $GaAl_2$ and $GdGa_2$ intermetallides.
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1. Introduction

Multicomponent aluminium–gadolinium-based alloys are capable to transform into amorphous state at quenching. These alloys have been intensively studied due to their hard magnetic properties and potential applications for magnetic and magneto-optic recording [1,2]. As it is known, the inter-component interaction in liquid is one of the factors, which are responsible for alloys ability to glass-forming [3–5]. Thermodynamic properties of liquid alloys are one of the measures of this interaction therefore represent necessary information for improvement of the amorphous alloys production technology [6]. It is a fact that gallium constituent additions to multicomponent alloys are frequently used for production of metallic glass with high corrosion resistance [7]. Besides, the ternary Al–Ga–Gd system is considered as prospective parent system for engineering of semiconducting magnetic alloys.

The Al–Ga–Gd phase equilibrium experimental investigation is still in progress, only a part of isothermal section

at 723 K is available [8]. Lack of information on thermodynamics of the ternary alloys makes the system off ordinary routes for assessment of the phase diagram. Therefore, the present work is focused on calorimetric measurements of the liquid Al–Ga–Gd alloys necessary for creation of database for the subsequent assessment.

2. Experimental

The enthalpies of mixing were studied using high-temperature isoperibolic calorimeter, which construction and general principles of work have been reported previously in [9]. Measurements and data treatment routine was described in details in [10].

The measurements were performed under pure argon at atmospheric pressure. The experimental heats of mixing were measured by dropping of the pure solid components stated at 298 K into a liquid bath (1760 ± 5 K). Gadolinium rods (Alfa, 99.95%), gallium granules (Alfa, 99.9999%), aluminium wire (Alfa, 99.995%) and tungsten wire (Alfa, 99.96%) were used for the experiments.

The initial component in the crucible was aluminium (0.2–0.5 g). Dropping of the aluminium samples into the molten aluminium performed the first calorimeter calibra-

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tion. After that gallium was added into the melt for initial binary Al_xGa_{1-x} alloy formation. Then gadolinium samples were dropped into the liquid bath. The temperature–time curve was recorded during the component dissolution. The tungsten was used for the finally calorimeter calibration. The absence of interaction between tungsten and liquid alloy was controlled by mass analysis after alloy quenching and ingots cutting. The mass loss was not more than 2–3%. The masses of dropped samples varied in the range of 0.06–0.13, 0.02–0.08, 0.02–0.41 and 0.20–0.42 g for gallium, aluminium, gadolinium and tungsten, respectively. The measurements were performed at 1760 ± 5 K along five sections with constant $x_{Al}:x_{Ga}$ ratios of 0.15:0.85, 0.3:0.7, 0.5:0.5, 0.6:0.4 and 0.85:0.15 for $0.0 \leq x_{Gd} \leq 0.55$–0.62.

3. Results and discussion

Partial enthalpy of mixing was calculated by following expression:

$$\Delta_{mix} \bar{H}_{Gd} = -\Delta_{mix} H_{298}^T + \frac{K}{n_{Gd}} \int_0^{\tau_\infty} \Delta T \, dt \qquad (1)$$

where $\Delta_{mix} H_{298}^T$ is the molar enthalpy of gadolinium heating from 298 K up to experimental temperature, K the thermal coefficient of calorimeter, n_{Gd} the quantity of dropped Gd sample (mol), t and t_∞ the current time and the time of temperature relaxation, respectively, and ΔT the difference between temperature of the melt at the moment t and equilibrium temperature of the melt after relaxation.

Experimental gadolinium partial enthalpies of mixing were presented via gadolinium α function ($\alpha_{Gd} = \Delta_{mix} \bar{H}_{Gd}/(1 - x_{Gd})^2$). The gadolinium α function was smoothed using least-squares regression (l.s.r.) for polynomial equation of form:

$$\alpha_{Gd} = \sum_{i=0}^k Q_i x_{Gd}^i \qquad (2)$$

where Q_i are the polynomial coefficients, x_{Gd} the gadolinium mole fraction and k the polynomial degree determined by the Fisher's exact test [11]. Integral enthalpy of mixing was calculated in accordance with Darken's equation [12]:

$$\Delta_{mix} H = (1 - x_{Gd}) \left[\int_0^{x_{Gd}} \alpha_{Gd} \, dx_{Gd} + \Delta_{mix} H^0 \right] \qquad (3)$$

where $\Delta_{mix} H^0$ is the integral enthalpy of mixing in binary Al–Ga alloy [13].

After substitution of Eq. (2) in Eq. (3) and integration, Eq. (3) should be as follows:

$$\Delta_{mix} H = (1 - x_{Gd})(\Delta_{mix} H^0 + Q_0 x_{Gd} + \frac{1}{2} Q_1 x_{Gd}^2 + \cdots$$
$$+ \frac{1}{k+1} Q_j x_{Gd}^{k+1}) \qquad (4)$$

The deviations of integral enthalpies of mixing were determined as proposed in [10] using the formula:

$$\sigma(\Delta_{mix} H) = (1 - x_{Gd})$$
$$\times \sqrt{D(\Delta_{mix} H^0) + x_{Gd} \int_0^{x_{Gd}} D(\alpha_{Gd}) \, dx_{Gd}} \qquad (5)$$

where $D(\Delta_{mix} H^0)$ and $D(\alpha_{Gd})$ are the dispersions of the functions. The deviations in initial Al–Ga system were assumed as a 10%. This approach is acceptable because the enthalpies of mixing in the Al–Ga system are negligibly small by absolute value in comparison with that in Al–Ga–Gd system. The confidence intervals of the enthalpies of mixing were calculated using the Student's coefficient for 95% probability, which is equal to 2 [11].

The interpolation method discussed in [10] was used for presentation of ternary alloys thermodynamics. Corresponding to the method, the simulation of integral enthalpies of mixing in ternary system is performed by one of geometric models. The difference between experimental data for sections and calculated via the model is treated by l.s.r. using formula:

$$\Delta \Delta_{mix} H = x_{Al} x_{Gd} (1 - x_{Al} - x_{Gd}) \sum_{i,j} Q'_{i,j} x_{Al}^i x_{Gd}^j \qquad (6)$$

Experimental $\Delta_{mix} H$ in the ternary system is represented as a sum of two terms, namely $\Delta_{mix} H$ value predicted by the geometric model and $\Delta \Delta_{mix} H$.

Among the boundaries the insignificant positive $\Delta_{mix} H$ values are observed in Al–Ga system [13], whereas Al–Gd [14] and Ga–Gd [15] are characterised by great negative $\Delta_{mix} H$. In the case, when the thermodynamics of one of the boundaries differs significantly from thermodynamics of two others, it is logically to use non-symmetric models [16].

The divergence between model and experimental data were estimated by the formula:

$$\chi = \left\langle \left| \frac{\Delta_{mix} H_{exp} - \Delta_{mix} H_{cal}}{\Delta_{mix} H_{exp}} \right| \right\rangle \times 100\% \qquad (7)$$

where $\Delta_{mix} H_{exp}$ and $\Delta_{mix} H_{cal}$ are the experimental and the calculated by geometric model $\Delta_{mix} H$ values, respectively. Using of the Toop model [17] with Al–Ga basis system leads to 5.30% deviation between the experimental and predicted values. However, the Bonnier model [18] gives some less deviation of 5.25%, so the model was used in the present study. Integral enthalpies of mixing for the Al–Gd and Ga–Gd boundaries were taken from [14,15], respectively. Optimised data set of [13] for Al–Ga system was used for the calculation and following equation was derived:

$$\Delta_{mix} H_{Al-Ga} = x_{Al}(1 - x_{Al})$$
$$\times (2.382 - 0.128 x_{Al} + 1.36 x_{Al}^2) \qquad (8)$$

Experimentally determined gadolinium partial enthalpies of mixing along sections with constant $x_{Al}:x_{Ga}$ ratios are plotted in Fig. 1(a)–(e). Q_j coefficients of Eqs. (2) and (4), which approximate the $\Delta_{mix}\bar{H}_{Gd}$ and $\Delta_{mix}H$ for studied sec-

tions are listed in Table 1. Calculated $\Delta_{mix}\bar{H}_{Gd}$ and $\Delta_{mix}H$ values with confidence intervals are represented in Table 2.

The interpolation method adequately describes the experimental results by the equation:
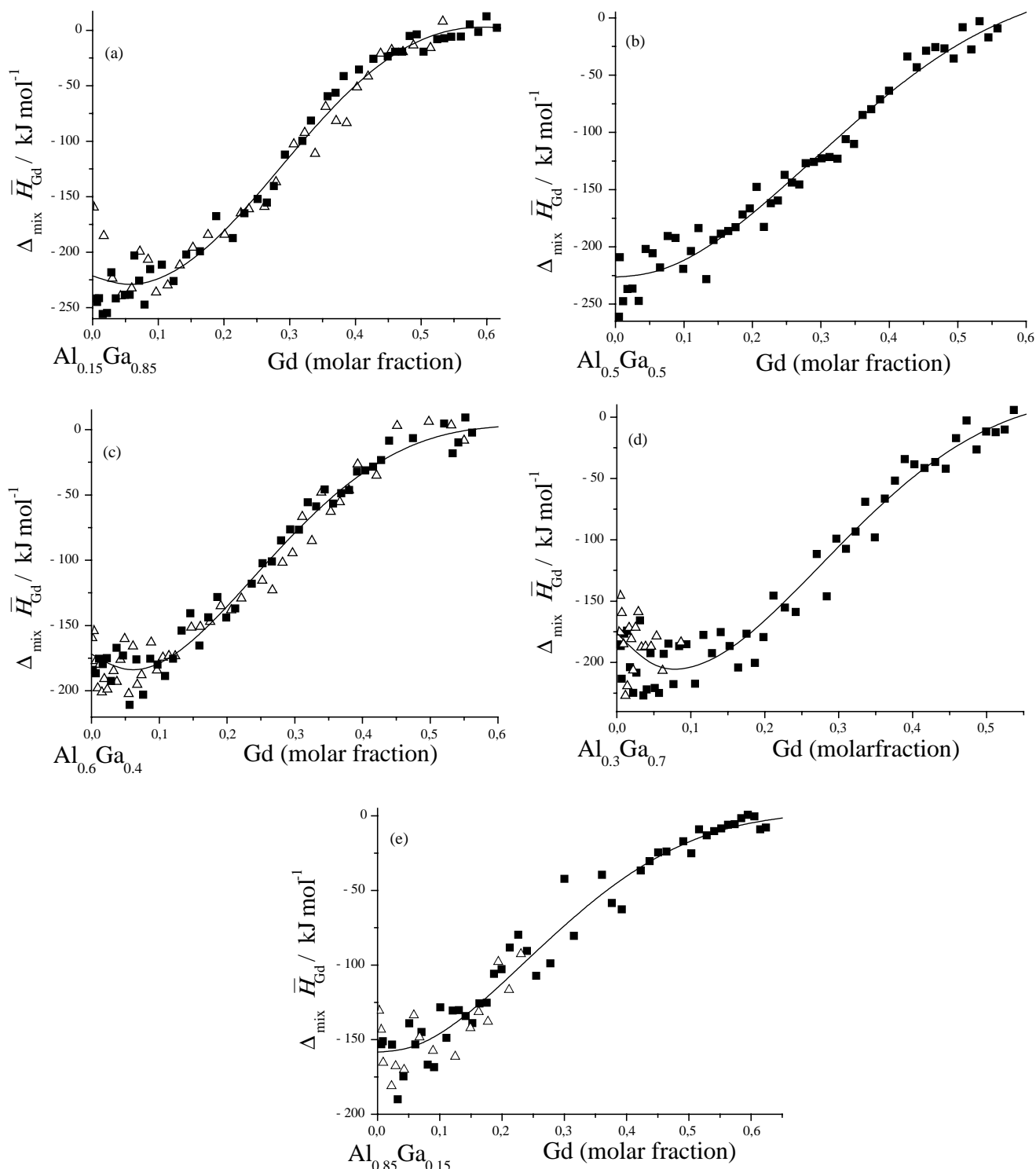

Fig. 1. Partial enthalpies of mixing of aluminium for sections (a–e) of liquid Al–Ga–Gd alloys at 1760 ± 5 K: (■) run 1; (△) run 2; (—) polynomial fitting of the experimental values.

Table 1
Evaluated Q_j coefficients for Eqs. (2) and (4), which approximate the $\Delta_{mix}\bar{H}_{Gd}$ and $\Delta_{mix}H$ for studied sections of the Al–Ga–Gd system

Section x_{Al}:x_{Ga}	Q_0 (kJ mol^{-1})	Q_1 (kJ mol^{-1})	Q_2 (kJ mol^{-1})	Q_3 (kJ mol^{-1})	Q_4 (kJ mol^{-1})
0.15:0.85	−221.36	−707.86	989.13	6908.59	−9137.11
0.3:0.7	−226.38	−522.83	1583.65		
0.5:0.5	−176.18	−1148.75	4232.80	−2788.91	
0.6:0.4	−171.83	−907.09	4275.71	−3748.95	
0.85:0.15	−158.32	−397.92	1816.65	−1318.47	

Table 2
Partial for gadolinium and integral enthalpies of mixing in liquid Al–Ga–Gd alloys

x_{Gd}	x_{Al}:x_{Ga}				
	0.15:0.85	0.3:0.7	0.5:0.5	0.6:0.4	0.85:0.15
$\Delta_{mix}\bar{H}_{Gd}$ (kJ mol^{-1})					
0.0	−221.4 ± 22.0	−226.38 ± 25.1	−176.2 ± 14.0	−171.8 ± 14.4	−158.3 ± 20.5
0.1	−223.8 ± 10.5	−212.9 ± 11.5	−203.7 ± 9.5	−181.1 ± 7.5	−146.8 ± 8.8
0.2	−180.9 ± 7.4	−171.3 ± 7.3	−165.7 ± 8.0	−135.8 ± 5.6	−112.5 ± 7.0
0.3	−113.8 ± 6.0	−117.9 ± 6.1	−105.4 ± 6.4	−78.6 ± 4.5	−73.4 ± 6.5
0.4	−49.7 ± 3.9	−65.6 ± 5.0	−49.3 ± 5.2	−32.6 ± 3.8	−40.0 ± 5.7
0.5	−8.9 ± 3.3	−23.0 ± 3.8	−10.2 ± 4.6	−6.3 ± 3.2	−17.0 ± 3.5
$\Delta_{mix}H$ (kJ mol^{-1})					
0.0	0.305 ± 0.031	0.518 ± 0.052	0.665 ± 0.067	0.671 ± 0.067	0.415 ± 0.042
0.1	−22.4 ± 1.4	−21.8 ± 1.6	−19.2 ± 1.0	−17.7 ± 1.0	−15.2 ± 1.3
0.2	−42.6 ± 2.3	−40.8 ± 2.6	−37.9 ± 1.9	−33.6 ± 1.6	−27.9 ± 2.1
0.3	−55.7 ± 2.9	−53.7 ± 3.2	−50.0 ± 2.6	−42.6 ± 2.1	−35.9 ± 2.7
0.4	−59.0 ± 3.2	−58.8 ± 3.5	−53.6 ± 3.1	−44.0 ± 2.4	−38.7 ± 3.3
0.5	−53.4 ± 3.3	−56.0 ± 3.7	−49.1 ± 3.4	−39.5 ± 2.6	−36.7 ± 3.4

$$\Delta_{mix}H = \frac{x_{Al}}{1-x_{Gd}}\Delta_{mix}H_{Al-Gd}(x_{Gd}) + \frac{1-x_{Gd}-x_{Al}}{1-x_{Gd}}$$
$$\Delta_{mix}H_{Gd-Ga}(x_{Gd}) + (1-x_{Gd})$$
$$\times \Delta_{mix}H_{Al-Ga}\left(\frac{x_{Al}}{1-x_{Gd}}\right) + \Delta\Delta_{mix}H \qquad (9)$$

where integral enthalpies of mixing in boundary binary alloys are represented by following relationships (in kJ mol^{-1}):

$$\Delta_{mix}H_{Al-Gd} = x_{Gd}(1-x_{Gd})\{-91.5 - 143(1-x_{Gd})$$
$$- 86(1-x_{Gd})^2 + 3600(1-x_{Gd})^3$$
$$- 12200(1-x_{Gd})^4 + 14500(1-x_{Gd})^5$$
$$- 5750(1-x_{Gd})^6\} \qquad (10)$$

$$\Delta_{mix}H_{Gd-Ga} = x_{Gd}(1-x_{Gd})(-204.3 - 585x_{Gd} - 750x_{Gd}^2$$
$$+ 12600x_{Gd}^3 - 29400x_{Gd}^4 + 27100x_{Gd}^5$$
$$- 9000x_{Gd}^6) \qquad (11)$$

$$\Delta_{mix}H_{Al-Ga} = \frac{x_{Al}}{1-x_{Gd}}\left(1 - \frac{x_{Al}}{1-x_{Gd}}\right)$$
$$\times \left[2.382 - 0.128\left(\frac{x_{Al}}{1-x_{Gd}}\right)\right.$$
$$\left. + 1.36\left(\frac{x_{Al}}{1-x_{Gd}}\right)^2\right] \qquad (12)$$

The contribution of fourth term of Eq. (9), which may be partially attributed to ternary interactions, is presented by the formula (in kJ mol^{-1}):

$$\Delta\Delta_{mix}H = x_{Gd}x_{Al}(1 - x_{Al} - x_{Gd})(69.22 - 258.7x_{Gd}$$
$$- 845.9x_{Al} + 581.6x_{Gd}^2 + 1208x_{Al}^2$$
$$+ 795.0x_{Gd}x_{Al}) \qquad (13)$$

As it can be seen from Table 2, $\Delta_{mix}\bar{H}_{Gd}$ become less negative at x_{Al}:x_{Ga} ratio increasing, i.e. at the ternary alloy composition drift from boundary Ga–Gd to Al–Gd system. As it is shown in Fig. 2(a), the $\Delta_{mix}H$ values calculated from the Bonnier model are in well agreement with experimental data.

The deviations between experimental and calculated values are in a range of −0.5±2 kJ mol^{-1} as shown in Fig. 2(b). An extreme value of $\Delta\Delta_{mix}H$ is −2.53 kJ mol^{-1} for x_{Gd} = 0.66 and x_{Al} = 0.18. As it can bee seen from Fig. 2(b), it is possibly to establish that thermodynamic properties of Al–Ga–Gd ternary liquid alloys are defined by component interaction in the boundaries (mainly in Ga–Gd and Al–Gd systems), while the ternary interaction is negligibly small.

Congruently melting GdGa$_2$ (T_m = 1673 K) and GdAl$_2$ (T_m = 1798 K) compounds are formed in binary Ga–Gd [19] and Al–Gd [20] systems, respectively. Characteristic of the compounds strong inter-component interaction remains at transition of the alloys into the liquid state. It results in significant negative enthalpies of mixing in the boundaries [14,15] with extremes shifted into compositions depleted by
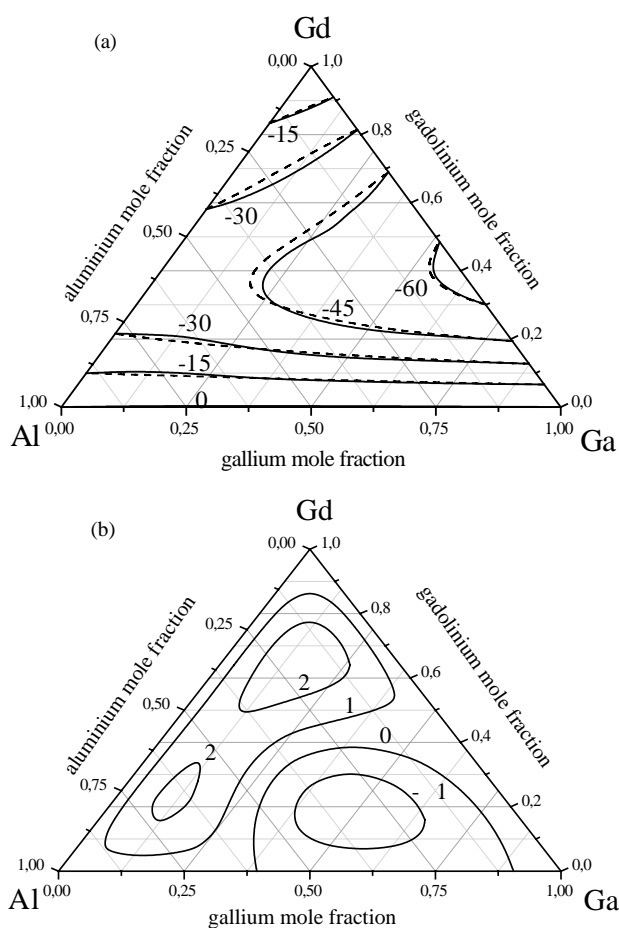
Fig. 2. (a) Projection of isoenthalpy lines on the Gibbs triangle: solid lines are the experimental data; dash lines are the data calculated by Bonier model. (b) The contribution of the term $\Delta\Delta_{mix}H$ in Eq. (9) (in kJ mol^{-1}).

Gd. So, in the ternary system extreme interaction is observed for section connecting points of GdGa$_2$ and GdAl$_2$ stoichiometry. The Al–Ga phase diagram is of simple eutectic type [21] and is characterised by a low reciprocal solubility of components. As a result insignificant positive enthalpies of mixing are observed in the liquid state for the Al–Ga system and consequently effect of component interaction in the Al–Ga alloys on ternary system thermodynamics is minor.

4. Conclusions

It has been established that the liquid Al–Ga–Gd alloys are formed with significant calorification up to −60 kJ mol^{-1}. The concentration dependencies of partial for gadolinium

and integral enthalpies of mixing testify that thermodynamic properties of Al–Ga–Gd alloys are predominantly determined by component interaction in boundary Al–Gd and Ga–Gd systems. It should be mentioned that strong interaction of Gd with Al and Ga is observed for the intermetallics GdGa$_2$ and GdAl$_2$ and remains at transition into the liquid state. The interaction can leads to possible formation of iso-stoichiometric clusters in the melt and to significant negative enthalpy of mixing in the ternary Al–Ga–Gd system with the function extreme shifted to alloys compositions depleted by the gadolinium.

References

[1] W. Suski, in: K.A. Gschneidner Jr., L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths, vol. 22, Elsevier, Amsterdam, 1996, pp. 143–294.
[2] H.S. Li, J.M.D. Coey, in: K.H.J. Buschow (Ed.), Handbook of Magnetic Materials, vol. 6, Elsevier, Amsterdam, 1991, pp. 1–83.
[3] D.S. Kanibolotsky, V.V. Lisnyak, J. Non-Cryst. Sol. 333 (2004) 194.
[4] A.A. Turchanin, M.A. Turchanin, P.G. Agraval, Mater. Sci. Forum 360–362 (2001) 481.
[5] B. Predel, Key Eng. Mater. 40/41 (1990) 17.
[6] A.A. Turchanin, I.A. Tomilin, M.A. Turchanin, I.V. Belokonenko, P.G. Agraval, J. Non-Cryst. Sol. 250–252 (1999) 585.
[7] A. Inoue, Mater. Sci. Found. 6 (1999) 36.
[8] M.V. Speka, N.I. Zakharenko, V.Ya. Markiv, N.M. Belyavina, in: T. Ya Velikanova (Ed.), Phase Diagrams in Materials Science, MSIWP and Natl. Acad. Sci. Ukraine, Kiev, 2001, pp. 175–176. www.msiwp.com/scienceforum/conferences/pdms/abstracts-presented.html.
[9] D.S. Kanibolotsky, O.A. Bieloborodova, N.V. Kotova, V.V. Lisnyak, J. Therm. Anal. 71 (2003) 583.
[10] D.S. Kanibolotsky, O.A. Bieloborodova, N.V. Kotova, V.V. Lisnyak, Thermochim. Acta 408 (2003) 1.
[11] G.A. Korn, T.M. Korn, Mathematical Handbook for Scientists and Engineers, McGraw-Hill, NY, 1968, p. 832.
[12] C. Wagner, Thermodynamics of Alloys, Addison-Wesley, Cambridge, 1952, p. 174.
[13] B. Predel, U. Stein, J. Less-Common Met. 17 (1969) 377.
[14] D.S. Kanibolotsky, N.V. Golovataya, V.V. Lisnyak, J. Therm. Anal. 76 (2004) 323.
[15] D.S. Kanibolotsky, N.V. Golovata, O.A. Bieloborodova, V.V. Lisnyak, Z. Naturforsch. 58A (2003) 473.
[16] Z. Qiao, X. Xing, M. Peng, A. Mikula, J. Phase Equilibr. 17 (1996) 502.
[17] G.W. Toop, Trans. AIME 233 (1965) 850–855.
[18] E. Bonnier, R. Caboz, Comput. Rend. Acad. Sci. (Paris) 250 (1960) 527.
[19] A. Palenzona, S. Ciratici, Bull. Alloy Phase Diagrams 11 (1990) 57.
[20] A. Saccone, A.M. Cardinale, S. Delfino, R.Z. Ferro, Z. Metallkd. 91 (2000) 17.
[21] J.L. Murrey, Bull. Alloy Phase Diagrams 4 (1983) 45.