

Enthalpies of formation for the Al–Y and Al–Y–Ni intermetallic compounds

V.S. Timofeev, A.A. Turchanin, A.A. Zubkov^{1*}, I.A. Tomilin

Moscow State Institute of Steel and Alloys, Leninsky Pr., 4, 117936 Moscow, Russia

Abstract

A method of liquid-metal solution calorimetry has been applied for thermochemical research of intermetallic compounds in the Al–Y and Al–Y–Ni systems. Heats of dissolution for the following intermetallics: Al₃Y; Al₂Y; Al₂Y₃ and Al₄YNi in liquid Al were measured with the help of a high-temperature isoperibol Calvet-type calorimeter. Using these values, standard molar enthalpies of formation for the listed compounds were calculated: $\Delta_{f,298}H_m^\circ(\text{Al}_3\text{Y}) = -185.6 \pm 7.2 \text{ kJ mol}^{-1}$; $\Delta_{f,298}H_m^\circ(\text{Al}_2\text{Y}) = -160.4 \pm 7.5 \text{ kJ mol}^{-1}$; $\Delta_{f,298}H_m^\circ(\text{Al}_2\text{Y}_3) = -234.4 \pm 19.5 \text{ kJ mol}^{-1}$; $\Delta_{f,298}H_m^\circ(\text{Al}_4\text{Y–Ni}) = -361.5 \pm 12.0 \text{ kJ mol}^{-1}$. Comparisons have been made with some available experimental data and theoretical values calculated from the Miedema model with the help of parameters recommended in different papers.

Keywords: Enthalpy of formation; Heat of dissolution; Solution calorimetry; Yttrium intermetallic compounds

1. Introduction

In the last 15–20 years, use of Al–Y based alloys has been extended rapidly mainly due to large neutron-capture cross section and the high tensile strength along with low density of these materials. Recently, there have been reports pertaining to studies on amorphous alloys in the Al–Y [1] and Al–Y–Ni systems [2] with tensile strength comparable to that of Fe–Si–B or Co–Si–B amorphous alloys, combined with good bend ductility and corrosion resistance.

Even though both experimental [3,4] and theoretical [5] research aimed at thermodynamic investigation of the aluminium–yttrium system have been carried out in the recent years, there is still a considerable contradiction and scarcity of reliable thermodynamic data for most intermetallic compounds in this system.

*Corresponding author. Tel.: 81-22 217-5164; fax: 81-22 217-5164; e-mail: zubkov@ibis.iamp.tohoku.ac.jp.

¹Present address: Institute for Advanced Materials Processing, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980, Japan.

2. Experimental

Both, for the preparation of intermetallic compounds and solute–solvent experiments, the following materials were used: aluminium A995, 99.995 metallic purity, yttrium YTM, 99.5% metallic purity with the following main impurities: < 0.5%Cu, 0.04% Al, 0.18% Si, 0.009% Fe and nickel N-1, 99.99% metallic purity. Four intermetallic phases, namely Al₃Y, Al₂Y, Al₂Y₃ and Al₄YNi were prepared. The Al₃Y compound was synthesised by smelting stoichiometric mixtures of the pure metals in an electric resistance furnace in an alumina crucible under a protection atmosphere of purified argon. In order to obtain a homogeneous phase in the course of this alloying, the melt was kept for 30 min at 1673 K which is ≈ 10 K above the liquidus temperature for this composition, and then for more than 30 min at temperature 690 K which is ≈ 10 K below the temperature of peritectoid reaction results in formation of this intermetallic compound. Thereafter, the alloy was cooled with the furnace. The Al₂Y, Al₂Y₃ and Al₄YNi compounds

were synthesised by arc melting on a water-cooled hearth under an atmosphere of purified argon. In order to obtain homogeneous phases, each of the arc-melted ingots was turned over and re-melted three-to-four times. The prepared alloys were checked by X-ray powder diffraction examination which indicated a single-phase composition of all the samples.

Heats of dissolution for the compounds and pure constituent metals in liquid aluminium were measured with a Calvet-type two-unit high-temperature calorimeter designed and built at our laboratory. Construction of this apparatus and details of the experimental technique have been described earlier (see Ref. [6]).

Each sample for the dissolution experiments including those of pure yttrium weighed 40 to 70 mg. All the samples were thermostatted at 298 ± 2 K and dropped into one of the two calorimetric cells with liquid aluminium thermostatted at ca. 1023 K. Each cell contained ca. 1.5 mol of pure aluminium. Heat of dissolution of pure nickel has been measured earlier (see Ref. [6]). Calibration of the cells both, before and after each series of dissolutions was achieved by dropping into the aluminium bath 8–10 pieces of annealed aluminium wire of 2 mm diameter and 70 to 100 mg weight thermostatted at room temperature. The reference values [7] were used to calculate the enthalpy increment for pure aluminium. Within a single series of measurements, the calibration was reproducible to $\pm 1.5\%$.

3. Results and discussion

For pure yttrium as well as for the intermetallic compounds, the least squares method revealed no dependence of partial molar heat of dissolution $\Delta_{\text{sol},298}Q_m$ on concentration of the dissolved element in liquid aluminium bath in the concentration range concerned. So the partial molar heats of dissolution at infinite dilution $\Delta_{\text{sol},298}Q_m^\infty$ in all the cases were calculated as average values of $\Delta_{\text{sol},298}Q_m$. The measured values of $\Delta_{\text{sol},298}Q_m^\infty$ for the pure metals and compounds are reported in Table 1. Experimental errors for all the values were calculated with the limits-of-confidence coefficient equaling 0.95. For pure yttrium molar partial enthalpy of dissolution at infinite dilution at the temperature of liquid aluminium $\Delta_{\text{sol},H_m^\infty}$ was calculated with the help of data on

enthalpy increment of this metal between the room temperature and the temperature of liquid aluminium T^* :

$$\Delta_{\text{sol}}H_m^\infty(Y) = \Delta_{\text{sol},298}Q_m^\infty(Y) - \Delta_{298}^{T^*}H_m(Y)$$

Enthalpy increment for pure yttrium $\Delta_{298}^{T^*}H_m(Y)$ was taken from Ref. [7]. This value along with the available literature data is represented in Table 1. The most stable crystalline modification of pure yttrium at the experimental temperatures (α -yttrium) was chosen as the standard state. For this reason it was necessary to recalculate results [10] reported relative to liquid yttrium even though the experimental temperature in [10], namely 1213 K, was lower than the melting point of pure yttrium. The same reference data [15], as in [10], were used for this recalculation to the new standard state. The value of $\Delta_{\text{sol}}H_m^\infty(Y)$ was derived from the result [8] with the help of reference data [7]. As it can be seen from this table, the present value of $\Delta_{\text{sol}}H_m^\infty(Y)$ is in a very good agreement with the results [8,9] and close to the values reported in [10,11].

Standard molar enthalpies of formation of the intermetallic compounds, $\Delta_{f,298}H_m^\circ$ were deduced from the values of $\Delta_{\text{sol},298}Q_m^\infty$ for the compounds and their pure constituent metals according to the following equation:

$$\Delta_{f,298}H_m^\circ(\text{Al}_x\text{Y}_y) = x\Delta_{\text{sol},298}Q_m^\infty(\text{Al}) + y\Delta_{\text{sol},298}Q_m^\infty(\text{Y}) - \Delta_{\text{sol},298}Q_m^\infty(\text{Al}_x\text{Y}_y)$$

In our case, because the dissolution has been carried out in liquid aluminium the value of $\Delta_{\text{sol},298}Q_m^\infty(\text{Al})$ is evidently the enthalpy increment for this metal taken from [7]. To correct temperature differences of the aluminium bath among the various series of experiments, we assumed that the values of $\Delta_{\text{sol},298}Q_m$ for both pure metals and compounds do not change within an interval of ca. 20 K. The calculated values of $\Delta_{f,298}H_m^\circ$ for the four intermetallic compounds with the available literature data are also listed in Table 1.

As it can be seen from this table for the Al_3Y intermetallic compound, the present value of $\Delta_{f,298}H_m^\circ$ agrees – within experimental error limits – with both, the data obtained by combustion calorimetry [12] and EMF measurements [13,14]. For the Al_2Y intermetallic compound our result agrees, within experimental error, with the value measured by direct reaction calorimetry [3]; moreover, it lies close to the

Table 1
Thermodynamic values for the Al–Y and Al–Y–Ni intermetallic compounds and the pure constituent metals in kJ mol^{-1}

Phase	$T^*(\text{K})$	$-\Delta_{\text{sol}}H_m^\infty$	$-\Delta_{\text{sol}}Q_m^\infty$	Number of runs	$-\Delta_{\text{f},298}H_m^\circ$	Reference
Y	1038	159.57 ± 4.86	138.04 ± 4.86	5		This work
Y	1000	158.8	138.5	7		[8]
Y	1000	158.1	138.4			[9]
Y	1213	153.7 ± 6^a		9		[10]
Y	1213	142.0 ± 6		9		[10]
Y	1873	160.2^a				[11]
Y	—	225^a				[16]
Ni	1023	131.8 ± 4.1	109.2 ± 4.1	8		[6]
Al ₃ Y	1016		-143.2 ± 5.2	9	185.6 ± 7.2	This work
Al ₃ Y					188.3	[12]
Al ₃ Y					180.7 ± 3.3^b	[13]
Al ₃ Y					190.0 ± 4.0^b	[14]
Al ₃ Y					278.8	[16]
Al ₂ Y	1029		-86.1 ± 5.4	10	160.4 ± 7.5	This work
Al ₂ Y					151.2 ± 3.8	[3]
Al ₂ Y					242.7	[12]
Al ₂ Y					173.2 ± 3.8^b	[13]
Al ₂ Y					250.8	[16]
AlY					175.7	[12]
AlY					153.1 ± 5.0^b	[13]
AlY					169.6	[16]
Al ₂ Y ₃	1029		116.0 ± 12.5	5	234.4 ± 19.5	This work
Al ₂ Y ₃					200.0 ± 8.0	[4]
Al ₂ Y ₃					439.3 ± 16.7	[13]
Al ₂ Y ₃					362.0	[16]
Al ₄ YNi	1038		-241.8 ± 10.2	7	361.5 ± 12.0	This work

^a Standard state for these values: liquid yttrium. ^b These values are at 800 K.

value derived from EMF measurements [13]. However, there is a strong discrepancy between the values listed here and the result obtained by combustion calorimetry [12]. For the Al₂Y₃ intermetallic compound, our value is in line with the calorimetric result [4], but disagrees with that obtained by EMF measurements [13].

A good agreement of the present results with the values obtained by EMF measurements [13] for the Al₃Y and Al₂Y intermetallic compounds on the one hand, and considerable discrepancy of those for the Al₂Y₃ phase on the other, can be explained by the following. In [13], the integral values have been calculated from the partial ones derived with the help of the results of EMF measurements at different temperatures. This calculation, carried out according to Gibbs–Duhem equation, was started for the intermetallic phase with the lowest yttrium content, i.e. for Al₃Y. Values of $\Delta_{\text{f},298}H_m^\circ$ for the next, and all the other

intermetallic compounds with higher mole fraction of yttrium were derived using the value of $\Delta_{\text{f},298}H_m^\circ$ for the nearest compound with lower yttrium content. In the course of this procedure, the error of $\Delta_{\text{f},298}H_m^\circ$ should increase towards the yttrium-rich phases. Moreover, Kober et al. [13] proposed the existence of an additional intermetallic compound between the Al₂Y and AlY phases. Taking this phase into account in this calculation should also give an additional error in the values of $\Delta_{\text{f},298}H_m^\circ$ for the AlY and all the other phases with a higher mole fraction of yttrium. Hence, the values of $\Delta_{\text{f},298}H_m^\circ$ obtained in [13] for phases with low yttrium content should be relied on rather than those for the compounds rich in yttrium.

Enthalpy of formation for the Al₄YNi (in kJ per gram) turned out to be more negative than those measured for any binary Al–Y intermetallic compounds. Thus, partial substitution of yttrium by nickel results in increasing $\Delta_{\text{f},298}H_m^\circ$ in absolute value.

Recently, an attempt has been made to optimise thermodynamic description of the Al–Y system [5]. Values of experimental thermochemical data for the Al–Y phase diagram were used for this optimisation procedure. For the Al–Y intermetallic compounds values of $\Delta_{f,298}H_m^\circ$ were taken from [12]. In the course of this procedure, a contradiction between experimental values of $\Delta_{f,298}H_m^\circ$ [11,12] and experimental data in the phase diagram was revealed, namely "...according to the reported enthalpy of formation of the melt at ≈ 12.5 mol% Y [11] and that of the solid phases Al_3Y and Al_2Y [12], the compound Al_3Y has more positive enthalpy at 1253 K than the mixture of the melt with Al_2Y at the same overall composition." This means that the compound Al_3Y should be stable up to higher temperatures than the temperature of formation of this phase, namely 1253 K [5]. Hence, at least one of the experimental data is incorrect. To solve this contradiction, Ran et al. [5] used the Miedema theory [16] to decide which of these experimental values for the intermetallic compounds are more reliable. The values of $\Delta_{f,298}H_m^\circ$, calculated from the Miedema model [16] and used in [5] for the optimisation procedure, are reported in Table 1. As it can be seen from this table, the calculated value for Al_3Y is essentially more negative than that reported in [12], while those for the Al_2Y and AlY are very close with the experimental data [12]. So the values calculated from the Miedema model [16] were accepted in [5] for the optimisation procedure as reliable ones for thermodynamic description of the Al–Y system. Thus, considerably more negative values of $\Delta_{f,298}H_m^\circ$ than the present experimental results were recommended in [5] for the Al–Y intermetallic compounds.

It was, however, pointed out in later publications, e.g. in [17], that enthalpies of formation for the rare-earth metal compounds calculated after the Miedema model are often more negative than the experimental values, and in a number of papers [17–20] there are reports of parameters of this model adjusted with the help of new experimental data. Thus, Miedema and co-workers reduced the parameter R for Sc, Y, the rare-earth metals and Th by a factor of 0.7, according to the latest available data on enthalpies of formation of compounds of these elements and their enthalpies of dissolution in liquid metals [18]. More recently, parameters of this model have been corrected for the rare-earth metals according to the measured partial

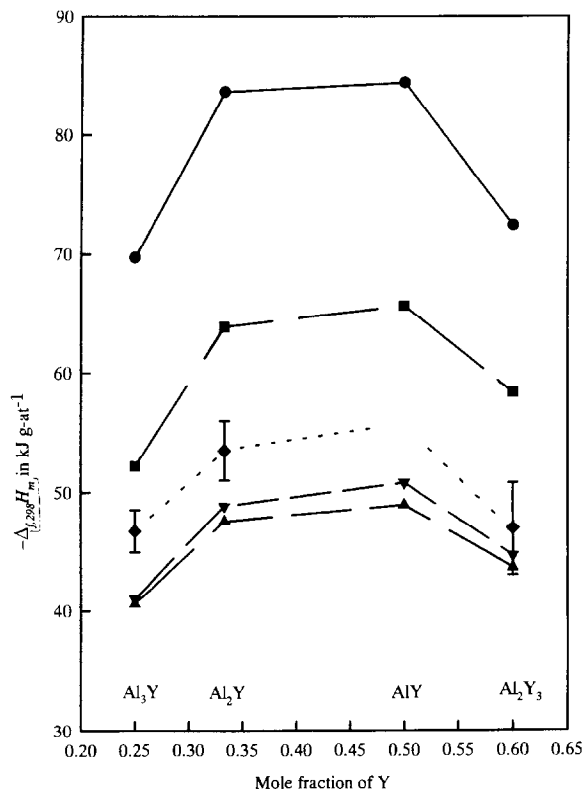


Fig. 1. Experimental and theoretical values of enthalpies of formation for the Al–Y intermetallic compounds calculated from the Miedema model: (●) – experimental values; theoretical values calculated with the help of parameters of the Miedema model recommended in (●) – [16], (▲) – [17], (■) – [18], and (▼) – [19,20].

enthalpies of dissolution at infinite dilution of these elements in liquid aluminium [17] and tin [19,20]. However, as pure yttrium was not under investigation in [17] and the parameters offered in this paper were only recommended for the trivalent rare-earth metals, parameters [19,20] should be relied on rather than those reported in [17] when Y and its compounds are considered. The theoretical values of standard enthalpies of formation for the Al–Y intermetallic compounds, calculated according to the Miedema model with the help of parameters recommended in [16–20], are given in Fig. 1, in comparison with the present experimental results. As it can be seen from this figure, all the theoretical values represent correctly the main features of the dependence $\Delta_{f,298}H_m^\circ$ vs. mole fraction of Y. Our data being close to the values calculated with the help of parameters [19,20] fall into the interval

between these theoretical values and those calculated according to [18]. This increases our confidence in the significance of the reported experimental results.

4. Conclusions

A method of liquid-aluminium solution calorimetry was used to determine standard formation enthalpies for the following intermetallic compounds: Al_3Y ; Al_2Y ; Al_2Y_3 and Al_4YNi . The lowest value of $\Delta_{f,298}H_m^\circ$ (in kJ per g-atom) for the binary phases corresponds to the Al_2Y compound. Partial substitution of Y by Ni results in increasing $\Delta_{f,298}H_m^\circ$ in absolute value. The reported experimental results are in good agreement with the values obtained recently by direct synthesis calorimetry [3,4] and for the Al_3Y intermetallics with those determined by EMF measurements [13,14]. Theoretical values of $\Delta_{f,298}H_m^\circ$ for the Al–Y intermetallics calculated from the Miedema model represent correctly the main features of the dependence $\Delta_{f,298}H_m^\circ$ vs. mole fraction of Y. The best agreement between the reported experimental results and the theoretical values is observed for the ones calculated with the help of parameters adjusted according to enthalpies of dissolution for some rare-earth metals in liquid tin [19,20].

References

- [1] A. Inoue, K. Ohtera and T. Masumoto, *Jpn. J. Appl. Phys.*, 27 (1988) L736.
- [2] A. Inoue, K. Ohtera, A.-P. Tsai and T. Masumoto, *Jpn. J. Appl. Phys.*, 27 (1988) L280.
- [3] W.-G. Jung, O.J. Kleppa and L. Topor, *J. Alloys Comp.*, 176 (1991) 309.
- [4] S.V. Meschel and O.J. Kleppa, *J. Alloys Comp.*, 191 (1993) 111.
- [5] Q. Ran, H.L. Lukas, G. Effenberg and G. Petzow, *J. Less-Common Met.*, 146 (1989) 213.
- [6] A.A. Zubkov, A.A. Turchanin and I.A. Tomilin, *Zavodskaya Laboratoria*, 61 (1995) 544.
- [7] I.V. Gurvich, V.S. Iorish, D.V. Chehovskoi and V.S. Yungman, *IVTANTERMO-A Thermodynamic Database and Software System for the Personal Computer, User's Guide*, Boca Ration CRC Press Inc., 1993.
- [8] C. Colinet and A. Pasturel, *Phys. Stat. Sol.(a)*, 80 (1983) K75.
- [9] C. Colinet and A. Pasturel, *Calorim. An. Therm.*, 14 (1983) 233.
- [10] J.-J. Lee and F. Sommer, *Z. Metallkde*, 76 (1985) 750.
- [11] G.M. Ryss, Yu.O. Esin, A.I. Stroganov and P.V. Geld, *Zh. Fiz. Khim.*, 50 (1976) 985.
- [12] R.L. Snider, *Yttrium-Aluminium Alloy Studies*, Ph.D. Thesis, Iowa State University of Science and Technology, Ames, Iowa, USA, 1960, p. 46.
- [13] V.I. Kober, I.F. Nichkov, S.P. Raspopin and V.N. Nauman, *Izv. Vyssh. Ucheb. Zaved., Tzvetn. Metall.*, 5 (1979) 40.
- [14] L.F. Yamshikov, V.I. Kober, V.A. Lebedev, I.F. Nichkov and S.P. Raspopin, *Zhurn. Fiz. Khim.*, 49 (1975) 2933.
- [15] R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, K.K. Kelley and Wagman, *Selected Values of the Thermodynamic Properties of the Elements*, ASM, Metals Park, Ohio, 1973.
- [16] A.R. Miedema, *J. Less-Common Met.*, 46 (1976) 67.
- [17] A. Pasturel, C. Chatillon-Colinet, A. Percheron-Guegan and J.C. Achard, *J. Less-Common Met.*, 90 (1983) 21.
- [18] A.R. Miedema, F.R. de Boer and Boom, *CALPHAD*, 1 (1977) 341.
- [19] C. Colinet, A. Pasturel, A. Percheron-Guegan and J.C. Achard, *J. Less-Common Met.*, 102 (1984) 167.
- [20] C. Colinet, A. Pasturel, A. Percheron-Guegan and J.C. Achard, *J. less-Common Met.*, 102 (1984) 239.