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Calorimetric measurements of the Li–Zn system. Direct reaction method and mixing enthalpy

A. Dębski *, W. Gąsior

Institute of Metallurgy and Materials Science, Polish Academy of Sciences, 25, Reymonta Street, 30-059 Kraków, Poland

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ABSTRACT

The formation enthalpy of the βLi_2Zn_3, βLi_2Zn_5 and $\beta LiZn_4$ intermetallic phases and the integral enthalpy of mixing of liquid Li–Zn alloys were measured with the use of two calorimetric techniques. The direct reaction calorimetric method was used for the determination of the formation enthalpy of the βLi_2Zn_3, βLi_2Zn_5 and $\beta LiZn_4$ intermetallic phases, and the obtained values equal: -16.7 ± 0.5 kJ/mol at., -19.0 ± 0.6 kJ/mol at., and -14.2 ± 0.6 kJ/mol at., respectively. The integral molar enthalpies of mixing for the Li–Zn liquid alloys were determined by means of drop calorimetry in three separate series at 814 K. The obtained experimental values are negative in the entire range of concentrations. The minimum of the integral enthalpy of mixing was observed for 0.3790 mole fraction of lithium and it equals -12.3 kJ/mol Based on the data of this study and those available in the literature, the interaction parameters of the Redlich–Kister equation for the liquid Li–Zn phase were calculated by the least square method.

1. Introduction

Owing to such properties as a high rigidity, a low density and a good machine cutting workability, Li-Zn-based alloys are applied in the aerospace industry as well as the military industry. Due to the scientific difficulties related to lithium's high reactivity with nitrogen, oxygen and moisture, the thermodynamic properties of the Li–Zn system have not as yet been thoroughly discussed in the literature.

The investigations of the Li–Zn alloys were initiated in 1931 by Fraenkel and Hahn [1], who measured the liquidus and solidus lines of the Li–Zn system using the thermal analysis for the concentration range of 60–100 at.% Zn and established that the intermetallic phase Li_2Zn_3 has a wide homogeneity range. In 1933, Grube and Vosskühler [2], and next, in 1934, Baroni [3], applying the thermal and X-ray analyses, discovered the existence of intermetallic phases Li_2Zn_3 and $LiZn_4$, which were both stoichiometric. The authors stated the presence of 3 high temperature phases: βLi_2Zn_3, βLi_2Zn_5 and $\beta LiZn_4$, 2 infinitely dilute solid solutions: βLi and Zn, as well as 5 intermetallic phases existing at room temperature: LiZn, αLi_2Zn_3, $LiZn_2$, αLi_2Zn_5 and $\alpha LiZn_4$. In 1935, Zintl and Schneider [4], and next, in 1976, Schonemann and Schuster [5], confirmed the presence of the above intermetallic phases. Moreover, Zintl and Schneider [4] stated that the $LiZn_2$ phase has a narrow homogeneity range, whereas the $\beta LiZn_4$ phase has a compact hexagonal structure. The $\alpha LiZn_4$ phase, which has an oriented structure, was obtained by Schonemann and Schuster in 1976 [5] as a result of a very slow cooling of the sample. The solubility of Li in Zn at 423 K has been determined by Farrar and King [6].

The activity of Li in liquid alloys has been measured by Hoshino et al. [7] for the concentration range of 70.37–99.26 at.% Zn at 773 K, by Moser et al. [8] in the whole concentration range and at the temperatures of 803–833 K as well as by Gąsior and Moser [9] at the temperatures of 773–850 K in the concentration range of 0.12–0.975 at.% Zn. The results of the activity of Li in liquid alloys obtained by the above mentioned authors remain in good agreement. In 1989, Moser et al. [10], by means of the calorimetric technique, determined the enthalpies of mixing for liquid Li–Zn alloys in the whole concentration range and at the temperatures of 816, 818 and 820 K. In 1991, Pelton [11], and next, in 2008, Liang et al. [12] optimised the Li–Zn system and the elaboration of last mentioned authors is presented in Fig. 1. In 2012, Morachevskii et al. [13] performed a thermodynamic analysis of liquid Al–Li–Zn alloys by presenting the calculated values of the Gibb's free energy as well as the enthalpies of mixing of binary and ternary alloys.

2. Experimental

To determine the formation enthalpy of the intermetallic phases from the Li–Zn system (βLi_2Zn_3, βLi_2Zn_5 and $\beta LiZn_4$) and the integral enthalpy of mixing of liquid Li–Zn alloys, lithium and

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* Corresponding author.
E-mail address: a.debski@imim.pl (A. Dębski).

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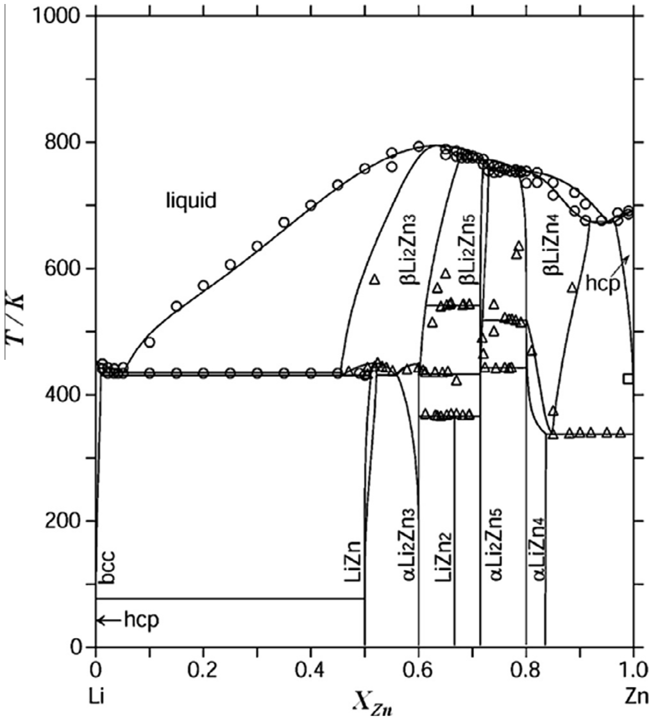

Fig. 1. The Li–Zn phase diagram assessed by Liang et al. [12] with the experimental data [2] (circles – thermal analysis, triangles – resistometric study) and [6] (squares – X-ray and metallographic studies).

zinc were used (Table 1). Calorimetric measurements were performed with the use of the Setaram MHTC 96 Line evo calorimeter. All the measurements were carried out with the protective atmosphere of high purity argon.

In the whole calorimetric study, tantalum crucibles with a protective alumina tube were used. At the beginning of the whole series, the calorimeter was calibrated with pieces of Li or Zn. Before each experimental run and before dropping the pieces of the sample of Li or Zn into the calorimeter, the calorimeter was evacuated with a turbo molecular pump several times, and then flushed with high purity argon. The impurity concentration (N_2, H_2O and O_2) was much lower than 1 ppm.

2.1. Direct synthesis method

The direct synthesis method is based on the measurement of the reaction energetic effect of the components (Li, Zn) at a fixed temperature. In the case of the Li–Zn system, the calculation procedure of the formation enthalpy is based on the following deduction: The synthesis of the compound can be described by the following thermochemical reaction:

- for βLi_2Zn_3 ($Li_{41}Zn_{59}$) phase:

$$0.41\mathrm{Li}_{(T_D)} + 0.59\mathrm{Zn}_{(T_M)} = \mathrm{Li}_{0.41}\mathrm{Zn}_{0.59_{(T_M)}} + \Delta H^{ef} \tag{1}$$

- for βLi_2Zn_5 ($Li_{28.57}Zn_{71.43}$) phase:

$$0.2857\mathrm{Li}_{(T_D)} + 0.7143\mathrm{Zn}_{(T_M)} = \mathrm{Li}_{0.2857}\mathrm{Zn}_{0.7143_{(T_M)}} + \Delta H^{ef} \tag{2}$$

- for $\beta LiZn_4$ ($Li_{20}Zn_{80}$) phase:

$$0.20\mathrm{Li}_{(T_D)} + 0.80\mathrm{Zn}_{(T_M)} = \mathrm{Li}_{0.20}\mathrm{Zn}_{0.80_{(T_M)}} + H^{ef} \tag{3}$$

where: T_D designates the temperature of the components before the introduction into the reaction zone (crucible), T_M is the temperature at which the reaction goes on (crucible), and H^{ef} is the reaction heat effect measured by the calorimeter.

In such a case, the formation enthalpy $\Delta_f H$ at temperature T_M is the difference between the determined reaction heat effect and the heat consumed by the components for the heating up to temperature T_M from T_D and, it is expressed according to the following equation:

$$\Delta_f H = H^{ef} - X_{\mathrm{Li}}\Delta H_{\mathrm{Li}} \tag{4}$$

where: X_{Li} is the mole fraction of lithium and ΔH_{Li} is the enthalpy changes of liquid lithium between temperatures T_M and T_D which was obtained from Thermo–Calc [14].

Before the measurements by the direct reaction method, the calorimeter had been heated up to the assumed temperature and after the baseline stabilization, the calibration constant was established by the determination of the heat effects relating to the heating of the zinc pieces from T_D to T_M. After the determination of the calibration constant, the known amount of lithium was added to the crucible, and next the reaction heat effect H^{ef} was measured and used for the formation enthalpy calculation according to Eq. (4).

2.2. Mixing enthalpy measurement

The measured mixing enthalpy is the integrated heat flow at a constant pressure and, in the case of the Li–Zn system, it is given by the following equations:

$$H_{\text{DISS-X}} = (\Delta H_{Signal} \cdot K) - (H_X^{T_D \to T_M} \cdot n_X), \tag{5}$$

$$\Delta H_{mix} = \frac{\sum H_{\text{DISS-X}}}{n_{\mathrm{Li}} + n_{\mathrm{Zn}}} \tag{6}$$

where: ΔH_{Signal} is the heat effect for each drop of metal (Li or Zn) which equalled the added drop enthalpy, K is the calorimeter constant, T_D and T_M are the drop and calorimetric absolute temperatures of the measurement in Kelvin, respectively. The $H_X^{T_D \to T_M}$ is the enthalpy of the pure metals (Li or Zn) which was obtained from Thermo–Calc [14], n_{Li} and n_{Zn} are the numbers of moles of Li and Zn, respectively. The $H_{\text{DISS-X}}$ is the enthalpy of dissolution of pure Li or Zn.

3. Results and discussion

The experimental data of the formation enthalpy of the βLi_2Zn_3, βLi_2Zn_5 and $\beta LiZn_4$ intermetallic phases, together with the average values are presented in Table 2. In this study, liquid lithium and liquid zinc at temperature T were assumed as the reference state.

Table 1
Materials applied in this study.

Chemical name	Source	Final purity [mass.%]	Purification method	Analysis method
Lithium	Alfa Aesar	99.9	None	Certified purity
Zinc	Alfa Aesar	99.999	None	Certified purity
Argon	Air Products	99.9999	None	Certified purity