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Thermodynamic properties of Li-Pb system

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ABSTRACT

The integral mixing enthalpy of liquid Li-Pb alloys was measured with the use of the calorimetric technique. The experimental studies involved measurements at different temperatures: 817, 923, 1021 and 1023 K in the entire concentration range. The thermodynamic optimization was performed basing on the obtained results and the available literature data. The description of the excess Gibbs energy of temperature and composition was proposed with the use of a new model, which connects the polynomial and associated modelling. The obtained molar mixing enthalpy changes, excess Gibbs energy, and the molar excess entropy values are negative in the entire concentration range. Moreover, the existence of Li_4Pb and LiPb associates in the liquid solutions was found, according to the analysis of the partial concentration structure factors ($Scc(0)$) and short range order (SRO) parameters.

1. Introduction

Nowadays, a nuclear fusion is the most promising perspective for an almost endless source of energy for the future, however, it is also the most challenging process for scientists. The lithium lead system (the eutectic $Li_{17}Pb_{83}$) is a candidate for the liquid blanket in fusion reactors [1–4], so the full knowledge of thermodynamic properties and structures of this binary system is crucial.

The first studies on the Li-Pb system were initiated in 1927, when Czochralski and Rassow [5] determined the eutectic reaction for 83.7 at.% of Pb in 504 K, with the use of optical microscopy. Next, Grube and Klaiber [6] published a complete phase diagram for this system. They [6] used the thermal and resistance analysis to confirm the existence of five eutectic reactions, three peritectic reactions and six intermetallic phases (Li_4Pb, Li_7Pb_2, Li_3Pb Li_5Pb_2, αLiPb and βLiPb). Then, Rollier and Arreghini [7] defined the structure of $Li_{10}Pb_3$ phase, which corresponds to Li_7Pb_2 phase. Zalkin et al. [8–11] measured the structure of $Li_{22}Pb_5$, Li_7Pb_2, Li_3Pb Li_8Pb_3, αLiPb and βLiPb phases by X-ray diffraction analysis. Basing on the available data, Hansen and Anderko [12] constructed the phase diagram of Li-Pb system, which contains six intermetallic phases determined by [6,7]. In that elaboration, they [12] rejected the phases proposed by Zalkin et al. [8–11]. Later, Smith and Moser [13] developed the phase diagram, which has nine intermetallic phases. In 1992, Hubberstry et al. [14] calculated, on the basis of they own measurements, the phase diagram of this system, which was also published by Okamoto [15]. Finally, Zhuo et al. [16] optimized the phase diagram of Li-Pb system by means of CALPHAD method.

The integral mixing enthalpy of the liquid Li-Pb system was measured only by Predel and Oehme [17] in 1979. The formation enthalpy of Li_7Pb_2, Li_3Pb and LiPb phases was determined by Kalyanaraman et al. [18] by the high-temperature calorimeter. The heat capacity of liquid Li-Pb alloys was defined experimentally by Sommer [19], Saar and Ruppersberg [20], Ruppersberg and Saar [21] and by molecular dynamics calculations [2].

The activity of Li in Li-Pb alloys was studied with the use of electromotive force measurements (EMF) by many scientists [22–26] in the entire concentration range of Li at various temperatures. Neubert [27] measured the vapour pressure of Li in liquid and solid alloys in the temperature range from 700 to 900 K and at $0.05 \le X_{Li} \le 0.95$ concentration of Li, by Knudsen effusion mass spectroscopy (KEMS). Veleckis [28] determined the activity of Li in two-phase fields ($\beta + Li_7Pb_2$, $Li_7Pb_2 + Li_3Pb_3$ and Li_8Pb_3), using the hydrogen titration method. On the other hand, Wang et al. [29] measured the thermodynamic properties of Li-Pb system at room temperature, with the use of coulometric titration method in organic solvent-based electrolytes.

2. Method and materials

The integral mixing enthalpy of the liquid Li-Pb system was measured with the use of pure, metallic lead (purity 99.999 mass. %) and lithium (purity 99.9 mass. %) and the Setaram MHTC 96 Line Evo calorimeter. The specifications of the pure metals used in all experiments are listed in Table 1 (Appendix 1). The experimental procedure adopted in all experiments was previously described in [30,31]. All the calorimetric measurements were carried out with the protective argon atmosphere. For the calorimetric study, tungsten crucibles with protective alumina tube were used. Initially, the calorimeter was calibrated with

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pieces of lead or lithium. In the case of the calibration by pieces of lithium, the prepared samples were closed inside the glove box with high purity argon atmosphere in a calorimetric antechamber. Then, this antechamber was removed from the glove box and connected with the calorimeter. The apparatus was evacuated with a vacuum pump several times and flushed with high purity argon before running of each experiment and before the pieces of the Pb or Li were dropped into the calorimeter. The voltage signal from the thermopile was registered in a digital form by the computer with the use of the commercial Calisto software.

The experimental studies of Li-Pb alloys involved measurements at four different temperatures: 817, 923, 1021 and 1023 K.

3. Results and discussion

For the determination of the integral mixing enthalpies ($\Delta_{mix}H$) of the Li-Pb liquid solutions, the following equations were applied:

$$H_{DISS-X} = (\Delta H_{Signal}\cdot K) - \left(H_X^{T_D\to T_M}\cdot n_X\right), \tag{1}$$

$$K = \frac{H_X^{T_D\to T_M}\cdot n_X}{\Delta H_{Calibration}} \tag{2}$$

$$\Delta_{mix}H = \frac{\sum H_{DISS-X}}{n_{Li} + n_{Pb}} \tag{3}$$

where ΔH_{Signal} is the heat effect of each dropped metal (Pb or Li) which equalled the added drop enthalpy; K is the calibration constant; T_D is the dropping temperature (room temperature); T_M is the calorimeter temperature of the respective measurement in Kelvin; $H_X^{T_D\to T}{}_M$ is the enthalpy of the pure metals (Pb or Li), which was obtained from Pandat 2013 (Pan_SGTE database based on the original SGTE v4.4 database); n_x (n_{Pb}, n_{Li}) are the numbers of moles of lead and lithium, respectively; $H_{DISS\text{-}X}$ is the enthalpy of dissolution of pure lead or lithium; $\Delta H_{Calibration}$ is the heat effect of dropped metal, which was used for calibration.

The values of the integral mixing enthalpy of Li—Pb liquid alloys obtained in this study, together with the other information concerning the calorimetric experiment are presented in Tables 2–3 (Appendix 1) and in Fig. 1.

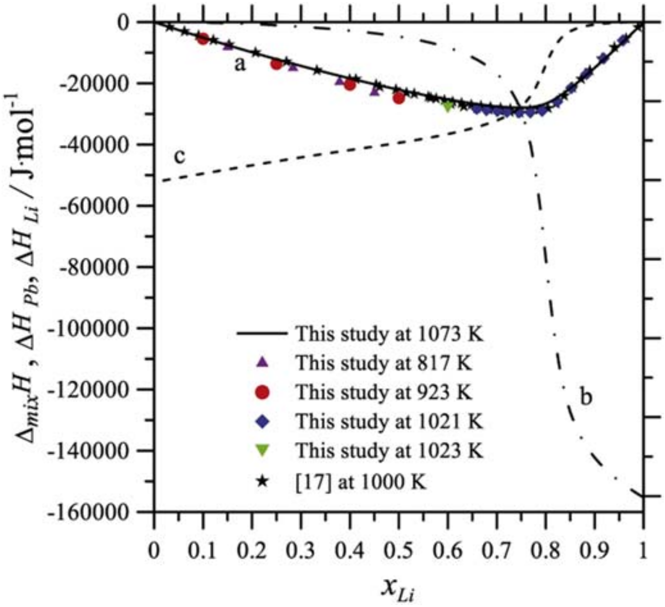

Fig. 1. The molar $\Delta_{mix}H$ (a) and partial enthalpy {ΔH_{Pb} (b), ΔH_{Li} (c)} of Li-Pb solutions. This study together with the literature data [17].

The obtained results of the mixing enthalpy changes of Li are negative in entire concentration range. The experimental change of the integral mixing enthalpy (presented in Fig. 1) reaches the minimum for the Li concentration of 0.75 mol fraction of Li and this value is −29.4 J·mol^{-1}. The calculated molar $\Delta_{mix}H$ has the minimum for the same mole fraction of Li and it equals −27.9 kJ·mol^{-1}, so the difference is only 1.5 kJ·mol^{-1}. The partial mixing enthalpy change of Li for a dilute solution has the value slightly higher than −52 kJ·mol^{-1}. On the other hand, the partial mixing enthalpy change of Pb decreases to the value −155.3 kJ·mol^{-1}. In general obtained results of $\Delta_{mix}H$ are in a good agreement with the literature [17] and calculated data based on new presented below formalism.

Before using this new method, at first, the attempts were undertaken to apply the Redlich-Kister model [32]. However, in case of S-shape of experimental data (as the partial lithium excess Gibbs energy), this model turned out to be improper because the approximation curve was characterized by maxima and minima for high number of parameters (>4, at T = const.) and for lower ones the shape of curve was distinctly different in comparison with that suggested by the experimental values. Additionally, the standard deviation calculated was unacceptable. The associate model [33] was also examined, however, it turned out also to be improper for this system.

Thus, for determination of the excess Gibbs energy of temperature and composition, based on literature data, and those obtained in this study, we proposed another model for liquids, which could be called *qualitative associates model* and was first presented in the Gąsior's PhD thesis [34]. This new description method of molar and partial mixing excess Gibbs energy with the strong negative deviations from the ideal solutions was proposed, as the result of observations that the heat of mixing and the molar excess Gibbs energy of solutions are of the shape similar to the triangle. The conclusion was that description of such (shape of) data set is possible if the equation describing sides of the triangle will be found (proposed) as the function of concentration. One of such equation can be as given below:

$$F = f(T)\cdot f(X) = f(T)\cdot[M\cdot(1-X) + N\cdot X - |M\cdot(1-X) - N\cdot X|] \tag{4}$$

in which: $f(T)$ is the temperature function described as $f(T) = \mathrm{a} + \mathrm{b}\cdot T + \mathrm{c}\cdot T\cdot\ln(T) + \mathrm{d}\cdot T^2$; $f(X)$ is the function of solution composition; $(1-X)$ and X are the concentrations of component 1 and 2, N and M are any integer numbers.

If from the experimental data one conclusion is that the F function is linear-dependent of temperature, c and d parameters are assumed to be equal zero ($c = 0$, $d = 0$). If the experimental data of F function are independent of the temperature or measured only at one temperature the parameters b, c and d are assumed to be equal zero. If the temperature dependence of the mixing enthalpy change is the linear function of temperature only $d = 0$, and if it is a curve-linear function the a, b, c and d parameters are different from zero and in consequence of this, ΔC_p is the linear function of the temperature.

The shape of molar thermodynamic function F as the function of elements concentration is always the same as the shape of composition function $f(X)$. Modifying $f(X)$ function of Eq. (4) the author [34] proposed new F function, which from many functions studied, is the best one after [34] and is described by the following equation:

$$F = f(T)\cdot f(X) = f(T)\cdot\left[F2^m\cdot X_1 + F1^m\cdot X_2 - FFD^m\right] \tag{5}$$

where: $F1 = N^2 + \Delta^2$; $F2 = M^2 + \Delta^2$; $FF = M\cdot X_1 - N\cdot X_2$; $FFD = FF^2 + \Delta^2$; $\Delta = 1\text{–}2\cdot m$; N and M are the stoichiometric factors from the associates formula (1_N2_M or A_NB_M); X_1 ($X_1 = 1 - X_2$) and X are the mole fraction of component 1 and 2; m is the parameter calculated with the use of measurement results of given thermodynamic properties (functions).

The dependence of the $f(X)$ function on the m parameter is shown in Fig. 2.