Journal of Nuclear Materials 477 (2016) 95–101

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Thermodynamic optimization of the Li–Pb system aided by first-principles calculations

Chenyang Zhou, Cuiping Guo, Changrong Li, Zhenmin Du*

Department of Material Science and Engineering, University of Science and Technology Beijing, Beijing 100083, PR China

HIGHLIGHTS

- The enthalpies of formation of Li–Pb compounds at 0 K were obtained using first-principles calculations.
- The Li–Pb system was optimized using an associated solution model in liquid phase due to short-range-order in liquid.
- A reliable thermodynamic assessment of the Li–Pb system was obtained and can be used to build the nuclear materials database.

ARTICLE INFO

Article history:
Received 29 November 2015
Received in revised form
20 April 2016
Accepted 27 April 2016
Available online 7 May 2016

Keywords:
Li–Pb system
First-principles calculations
CALPHAD method
Thermodynamic optimization

ABSTRACT

The Li–Pb system was optimized using CALPHAD (CALculation of PHAse Diagram) method. The enthalpies of formation of eight intermetallic compounds Li_4Pb ($Li_{22}Pb_5$), Li_7Pb_2, $Li_{10}Pb_3$, Li_3Pb, Li_8Pb_3, Li_5Pb_2, αLiPb and βLiPb at 0 K were calculated from first-principles calculations with DFT + GGA approximations. The liquid phase was treated as ($Li,Li_{0.8}Pb_{0.2},Pb$) using an associated solution model because a short-range-order phenomenon was proven to exist in liquid. The solution phases fcc and bcc were described as (Li,Pb) with a simple substitutional model. The intermetallic compounds Li_4Pb, Li_3Pb and Li_5Pb_2 were treated as stoichiometric compounds. With certain solubility ranges, the intermetallic compounds Li_7Pb_2, αLiPb and βLiPb were modeled as $Li_7(Li,Pb)_2$, (Li,Pb)(Li,Pb) and (Li,Pb)(Li,Pb) using the two-sublattice model. A set of self-consistent thermodynamic parameters in the Li–Pb system was obtained in the present work.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Nuclear fusion is considered to be a great way to solve the currently looming energy crisis. In recent years, the materials adopted in nuclear fusion reactor [1–4] have received more and more concern. Based on the many unique properties such as low activation, good tritium breeding potential, high head load capability etc. [5], the Pb–17Li eutectic liquid alloy is foreseen as one of the promising candidates for the liquid blanket in fusion reactor. Lately, the Pb–17Li eutectic liquid alloy has been used in some blanket concepts such as the EU-HCLL (He-cooled lead lithium) and the US-HCLL (Dual-cooled lead lithium) in ITER (International Thermonuclear Experimental Reactor) [6]. Furthermore, a blanket concept of the Pb–17Li eutectic liquid alloy has been used as wet wall in the KOYO-Fast ignition fusion reactor [7]. The further research and design of the Li–Pb liquid alloys require the information about the related phase equilibria and thermodynamic properties, which require the reasonable optimization of the Li–Pb binary system.

The CALPHAD method and first-principles calculations with DFT + GGA approximations can enhance the efficiency and reliability of the thermodynamic models. On the basis of the experimental data of phase equilibria and thermochemical properties and combined with the predicted values of first-principles calculations, the Li–Pb system is assessed thermodynamically in this work by means of the CALPHAD method.

2. Literature review

2.1. Phase diagram data

A eutectic reaction, liquid → fcc + βLiPb at 83.7 at.% Pb and 504 K was determined by Czochralski and Rassow [8] using optical microscopic technique and thermal measurement, which was the

---

* Corresponding author.
E-mail address: zmdu2@hotmail.com (Z. Du).

http://dx.doi.org/10.1016/j.jnucmat.2016.04.061
0022-3115/© 2016 Elsevier B.V. All rights reserved.

first experimental data in the Li–Pb system. Later, the Li–Pb phase diagram was completely measured for the first time using thermal and resistometric analyses by Grube and Klaiber [9], who confirmed five eutectic and three peritectic type reactions and presented six intermetallic compounds Li_4Pb, Li_7Pb_2, Li_3Pb, Li_5Pb_2, αLiPb and βLiPb. Rollier and Arreghini [10] determined the structure of the compound $Li_{10}Pb_3$, which is corresponding to Li_7Pb_2 described in Ref. [9] in the Li–Pb system. Pogodin and Schpilineshkii [11] used the same method as Ref. [9] to measure the same eutectic reaction as Ref. [8] with close eutectic point (83.6 at.% Pb and 509 K). The crystal structures of six intermetallic compounds $Li_{22}Pb_5$, Li_7Pb_2, Li_3Pb, Li_8Pb_3, αLiPb and βLiPb, were investigated by Zalkin et al. [12–15]. Based on the above investigated results [8–11], the earlier phase diagram of the Li–Pb system was reviewed by Hansen and Anderko [16], and three solution phases liquid, fcc and bcc, and six intermediate phases Li_4Pb, $Li_{10}Pb_3$, Li_3Pb, Li_5Pb_2, αLiPb and βLiPb were confirmed. And the experimental results from Refs. [12–15] were mentioned but not accepted in Ref. [16].

Then, Smith and Moser [17] reviewed the phase diagram of the Li–Pb system on the basis of the investigation of the crystal structures from Zalkin et al. [12–15], with nine stable phases included, liquid, fcc, bcc, $Li_{22}Pb_5$, Li_7Pb_2, Li_3Pb, Li_8Pb_3, αLiPb and βLiPb.

Hubberstry et al. [18] re-determined the Li–Pb phase diagram at the Pb-rich region and reported the eutectic reaction, liquid → fcc + βLiPb at 84.3 at.% Pb and 508 K using lots of experimental data of resistance–temperature measurements. Furthermore, the phase diagram of the Li–Pb system was reviewed by Okamato [19], and following phases liquid, fcc, bcc, Li_4Pb, $Li_{10}Pb_3$, Li_3Pb, Li_5Pb_2, αLiPb and βLiPb were presented.

The crystallographic data for the intermetallic compounds [10,12–15] and the pure elements [20–22] in the Li–Pb system are presented in Table 1. Rollier and Arreghini [10] observed the existence of $Li_{10}Pb_3$ ($Li/Pb = 3.33$). However, Zalkin and Ramsey [12] did not find its diffraction patterns when the Li/Pb atom ratio was between 3.0 and 3.5, only confirmed the existence of two compounds Li_3Pb ($Li/Pb = 3.0$) and Li_7Pb_2 ($Li/Pb = 3.5$), and then supposed the compound $Li_{10}Pb_3$ to be a mixture of the stable compounds Li_3Pb and Li_7Pb_2. Since it was very difficult to distinguish the two compounds, the first-principles calculations were used to predict their stability at 0 K and supplied the necessary reference for present modeling.

2.2. Thermodynamic data

Predel and Oehme [23] measured the enthalpies of mixing of liquid at 1000 K using high-temperature calorimetric method. All available activity data of lithium [24–30] in liquid were determined by EMF (electromotive force) and vapor pressure. The heats of formation of some intermetallic compounds [31,32] were measured using drop calorimetric method. The enthalpies of formation and the uncertainties of the compounds [31,32] are summarized in Table 2. In addition, Jauch et al. [33] investigated the heat capacities of the compound αLiPb at 300, 340, 400 and 450 K.

All the original experiment work about the thermodynamic properties [23–32] in the Li–Pb binary system is reviewed in Table 3.

2.3. Short-range-order phenomenon

Li–Pb liquid alloys with the compositions of 0, 17, 34, 48, 61, 80 and 100 at.% Li were measured to investigate the short-range-order using neutron diffraction patterns by Ruppersberg and Egger [34]. The concentration correlation function $S_{CC}(k)$, related to the short-range-order coefficients, was calculated using neutron diffraction results. The calculated $S_{CC}(k)$ showed that the unlike nearest neighbors had a reduction of the distance compared with pure components, which was the typical feature of the short-range-order phenomenon. Furthermore, Ruppersberg and Reiter [35] determined short-range-order phenomenon at five different temperatures between the liquidus temperature T_L and ($T_L + 230$) in the same way. And the results for the Li–Pb liquid alloys confirmed that short-range-order existed at the composition of $Li_{0.8}Pb_{0.2}$ in liquid.

Table 2
The enthalpies of formation of the compounds in the Li–Pb system according to the first-principles calculations at 0 K along with the literature data.

Phase	ΔH_f(kJ/mole of atom^{-1})	Temperature(K)	Reference
Li_4Pb	−34.06 ± 2.04	298	[31]
	−26.81	0	Calculation
Li_7Pb_2	−35.14 ± 2.11	298	[31]
	−33.48 ± 0.50	298	[32]
	−31.03	0	Calculation
$Li_{10}Pb_3$	−22.00	0	Calculation
Li_3Pb	−34.56 ± 2.07	298	[31]
	−37.02 ± 0.75	298	[32]
	−31.61	0	Calculation
Li_8Pb_3	−22.28	0	Calculation
Li_5Pb_2	−33.34 ± 2.00	298	[31]
	−31.00	0	Calculation
αLiPb	−30.30 ± 1.82	298	[31]
	−24.25 ± 0.55	298	[32]
	−26.44	0	Calculation
βLiPb	−1.08	0	Calculation

Table 1
Cell types, space groups and cell constants of the intermetallic compounds and the pure elements Li and Pb from literature.

Phase	Cell type	Space group	Cell constants				Reference
			a(Å)	b(Å)	c(Å)	α(deg)	
Li	Cubic	Im3m	3.508				[20]
$Li_{22}Pb_5$	Cubic	F23	20.08				[15]
Li_4Pb	Cubic (Subcell)		3.34				[15]
Li_7Pb_2	Hexagonal	P321	4.751		8.589		[12]
$Li_{10}Pb_3$	Cubic	$P\bar{4}3m$	10.08				[10]
Li_3Pb	Cubic	Fm3m	6.687				[12]
Li_8Pb_3	Monoclinic	C2/m	8.24	4.757	11.03	β 104.5	[13]
αLiPb	Rhombohedral	R3m	3.542			α 89.5	[14]
βLiPb	Cubic	Pm3m	3.563				[14]
Pb	Cubic	Fm3m	4.95				[21,22]

Download English Version:

https://daneshyari.com/en/article/7964226

Download Persian Version:

https://daneshyari.com/article/7964226

Daneshyari.com