Fusion Engineering and Design 89 (2014) 2946–2952

Contents lists available at ScienceDirect

Fusion Engineering and Design

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

Thermodynamic properties of Li, Pb and $Li_{17}Pb_{83}$ with molecular dynamics simulations

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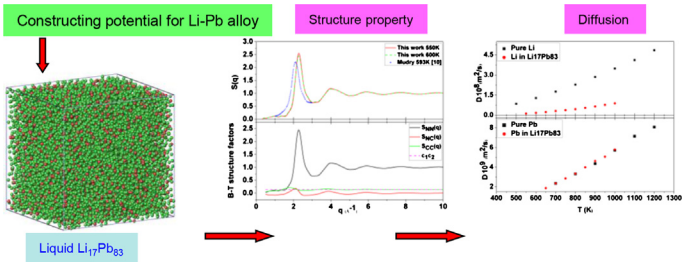
GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 30 November 2013
Accepted 16 September 2014
Available online 13 November 2014

Keywords:
$Li_{17}Pb_{83}$
Structure property
Thermodynamic properties
Diffusion
EAM
Molecular dynamics

ABSTRACT

In this work, new EAM potentials for Li, Pb and Li–Pb alloy have been constructed. Based on these potentials, the structural, thermodynamic and diffusion properties of Li, Pb and $Li_{17}Pb_{83}$ have been studied with molecular dynamics simulations. The calculated radial distribution functions and static structure factors agree well with previous reported data. The partial radial distribution functions indicate that liquid $Li_{17}Pb_{83}$ shows a hetero-coordination tendency and the partial Bhatia–Thornton structure factor $S_{CC}(q)$ suggests the concentration fluctuation in $Li_{17}Pb_{83}$ is not large. As comparing to the self-diffusion coefficients, the component diffusion coefficients are much smaller for Li atoms, and almost the same for Pb atoms. Density, enthalpy, capacity, melting point, latent heat of fusion and surface tension are also in reasonable agreement with the literature data within the experimental error.

1. Introduction

In recent years, many efforts have been continuously done to research and develop the materials used in fusion reactor [1–3]. $Li_{17}Pb_{83}$ is one of the promising candidates for the liquid blanket [4,5]; then the knowledge of physical properties is of primary importance. The database for Li and Pb is very complete, but the same cannot be said for $Li_{17}Pb_{83}$. Brandt [6], Schulz [7], Atanov [8] and Tiwari et al. [9] studied the physical properties of $Li_{17}Pb_{83}$, including the specific heat, latent heat of fusion, thermal expansion and thermal conductivity. Mudry et al. [10] investigated the short range order of liquid $Li_{17}Pb_{83}$ by means of X-ray diffraction. However, the existing data are scattered and the investigations were carried out in a relatively narrow temperature range, and there is a general lack of data on structure and diffusion. In order to acquire more valuable information about $Li_{17}Pb_{83}$, it is imperative to undertake a systematic research on this material. Using molecular dynamics simulations, Canales et al. [11] investigated the structural and dynamical properties of liquid Li at 470 K and

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http://dx.doi.org/10.1016/j.fusengdes.2014.09.016
0920-3796/

843 K. Cui et al. studied the melting point, radial distribution function (RDF) and structural stability of Li [12]. Recently, Fraile et al. [13] has calculated the radial distribution functions, free energies and entropies of melting of Li and Pb, as well as the capacities of Li, Pb and $Li_{17}Pb_{83}$ [14,15]. In this paper, we have constructed embedded-atom method (EAM) potentials for Li, Pb and Li–Pb alloy, and studied their structural, thermodynamic and diffusion properties. This work has enriched the physical property database of Li, Pb and Li–Pb alloys and established a solid base for further research.

2. Potential and methodology

2.1. EAM potential

The potential functions for Li, Pb and Li–Pb alloy are constructed within the framework of the modified analytic embedded-atom method (MAEAM) proposed by our group [16], which is based on the original EAM model [17]. For the MAEAM potentials, the total energy of the simulation system is expressed as

$$E_{tot} = \sum_i E_i \tag{1}$$

$$E_i = \frac{1}{2}\sum_{j\neq i}\varphi(r_{ij}) + F(\rho_i) + M(P_i) \tag{2}$$

where $\varphi(r_{ij})$, $F(\rho_i)$ and $M(P_i)$ represent the two-body interaction, embedding energy and the modified term, respectively. They are taken as

$$\varphi(r_{ij}) = v_0\left[1 + v_1\ln\left(\frac{r_{ij}}{r_1}\right) + v_2\left(\frac{r_{ij}}{r_1}\right)\right]\left[\left(\frac{r_1}{r_{ij}}\right)^{u_1} + v_3\left(\frac{r_1}{r_{ij}}\right)^{u2}\right] \times\left(1-\frac{r_{ij}}{r_c}\right)^2 \tag{3}$$

$$F(\rho_i) = -F_0\left[1 - n\ln\left(\frac{\rho_i}{\rho_e}\right)\right]\left(\frac{\rho_i}{\rho_e}\right)^n \tag{4}$$

$$M(P_i) = -\frac{\alpha P_i P_e}{(P_i+P_e)^2} \tag{5}$$

where ρ_i and P_i denote the electronic density and modification parameter for atom i contributed by the surrounding atoms and they can be expressed by

$$\rho_i = \sum_{j\neq i} f_e\left(\frac{r_1}{r_{ij}}\right)^{\beta}\left(\frac{r_{ce}-r_{ij}}{r_{ce}-r_1}\right)^2 \tag{6}$$

$$P_i = \sum_{j\neq i} g_e\left(\frac{r_1}{r_{ij}}\right)^{\lambda}\left(\frac{r_{ce}-r_{ij}}{r_{ce}-r_1}\right)^2 \tag{7}$$

r_c and r_{ce} represent the cut-off distances for the two-body interaction and the electronic density, respectively. And

$$r_c = r_4 + \zeta(r_5 - r_4) \tag{8}$$

$$r_{ce} = r_5 + 0.5(r_6 - r_5) \tag{9}$$

The alloy potential is taken as

$$\varphi^{ab}(r_{ij}) = \frac{1}{2}\mu\left[\varphi^a\left(r_{ij}\frac{r^a}{r^c}\right) + \varphi^b\left(r_{ij}\frac{r^b}{r^c}\right)\right] \tag{10}$$

$$r^c = \frac{1}{2}(r_1^a + r_1^b) \tag{11}$$

where $\varphi^a(r_{ij}(r^a/r^c))$ and $\varphi^b(r_{ij}(r^b/r^c))$ are the two-body interactions for element a and b. In these expressions, r_{ij} is the distance between atom i and atom j, and r_i (i = 1, 4, 5, 6; r_1^a and r_1^b for element a and b) denotes the ith nearest-neighbor distance. v_i (i = 0, 1, 2, 3), u_1, u_2, F_0, n, ρ_e, P_e, f_e, g_e, α, β, λ and ζ are the parameters determined by fitting the elastic constant, lattice constant and cohesive energy. μ, r^a and r^b are determined by fitting the formation enthalpies of Li–Pb alloys. Their values are listed in Table 1. Fig. 1 shows the calculated formation enthalpies together with the experiment results [18,19], and our results match well with the experiment results.

Table 1
Potential parameters for Li, Pb and Li–Pb alloy.

Parameters	Li	Pb	Li–Pb alloy
v_0 (eV)	0.542	9.175	
v_1	6.578	1.673	
v_2	−2.796	−1.142	
v_3	−0.610	−0.818	
u_1	−2	2	
u_2	2	4	
F_0 (eV)	0.912	1.602	
n	0.249	0.747	
ρ_e	14.369	8.125	
f_e	1.223	0.641	
β	2.88	5.54	
α (eV)	5.556×10^{-5}	9.791×10^{-3}	
P_e	4.243×10^{-7}	6.138×10^{-3}	
g_e	4.807×10^{-8}	4.85×10^{-4}	
λ	11.85	5.61	
ζ	0.25	0.1	
μ			2.7
r^a (Å)			4.3
r^b (Å)			3.6

2.2. Methodology

2.2.1. Structure characterization

Static structure factor is the Fourier transform of RDF. Here RDF and static structure factor are used to characterize the structure of liquid metals and alloys. The Bhatia–Thornton formalism [20] is a convenient way to investigate the topological and chemical ordering in binary mixtures, which includes the autocorrelation of number density $S_{NN}(q)$, concentration density $S_{CC}(q)$, and the cross-correlations $S_{NC}(q)$ between the number and concentration density. The three parts are defined as [20]

$$S_{NN}(q) = c_1^2 S_{11}(q) + c_2^2 S_{22}(q) + 2c_1c_2S_{12}(q) \tag{12}$$

$$S_{CC}(q) = c_1c_2\{1 + c_1c_2[S_{11}(q) + S_{22}(q) - 2S_{12}(q)]\} \tag{13}$$

$$S_{NC}(q) = c_1c_2[c_1(S_{11}(q) - S_{12}(q)) - c_2(S_{22}(q) - S_{12}(q))] \tag{14}$$

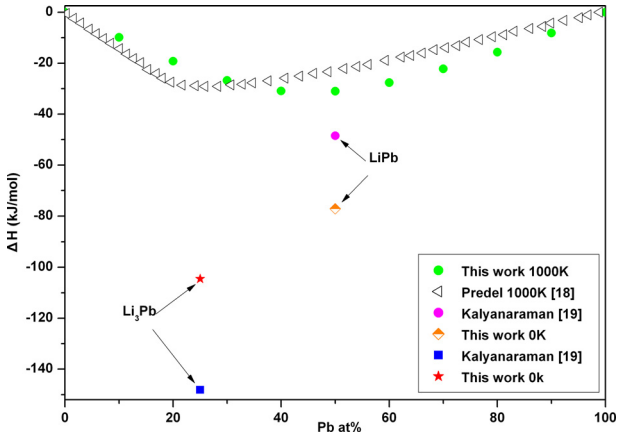

Fig. 1. Formation enthalpies for Li–Pb alloys. The mixing enthalpies for liquid Li–Pb alloys at 1000 K in whole composition range and the formation enthalpies for two intermediate phases, Li_3Pb and LiPb, at 0 K.