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Structure and electrophysical properties of liquid $Pb_{83}Mg_{17}$ and $Pb_{83}Li_{17}$ eutectics

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Abstract

Short range order structure of $Pb_{83}Mg_{17}$ and $Pb_{83}Li_{17}$ liquid alloys has been studied by means of X-ray diffraction method. The structure factors and pair correlation functions are analyzed. Experimental structure data were used to calculate the partial structure characteristics by means of Reverse Monte Carlo method. It is shown also that Li_4Pb significantly affects the structure of $Pb_{83}Li_{17}$ eutectic melt. For $Pb_{83}Mg_{17}$ eutectic melt the electrical resistivity and thermo-e.m.f. were measured in the temperature range of 550–1300 K. Their analysis confirms the diffraction data concluding the heterocoordinated atomic distribution Pb and Mg atoms.

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1. Introduction

Physical properties of the Pb–Mg and Pb–Li liquid alloys have come under the scrutiny of science over the past decade in connection with their possible use in future nuclear reactors [1–3]. Considerable study is being given to the Pb–Mg and Pb–Li eutectics in the frame of a reassessment of physics and engineering fundamentals of nuclear reactors, especially to design and implementation of 'new-generation inherently-safe' nuclear reactors [4]. The proper choice of a liquid metal as the coolant flowing in direct contact with both the reactor core and the heat exchangers is of fundamental importance.

Certainly that most promising at present time for use as coolant is Pb–Bi eutectic melt. But one component (Bi) can be transformed in Po resulting the formation of solid–liquid mixture with poor content of Bi. On that reason the studying of another eutectic alloy with similar characteristics is need. $Pb_{83}Mg_{17}$ and $Pb_{83}Li_{17}$ are one of them.

Following different fundamental criteria have emerged for the choice of a reliable coolant: small neutron absorption cross section over the energy range and small neutron activation cross section over the energy range from fast to thermal neutrons; low neutron scattering cross section; large heat capacity and heat conductivity; high boiling temperature and low melting temperature; low vapour pressure; inexpensive, easily obtainable; chemical compatibility with all structural materials comprising primary coolant loop, the high temperature stability of these characteristics during long period in order to prevent the formation of 'thrombus' on the reactor walls and overheated local regions, non-toxic, environmentally benign. Appearance of these potential sources of danger is associated with temperature dependencies of structure and physical properties.

Therefore the structure, electric conductivity and thermo-e.m.f. have been studied for $Pb_{83}Mg_{17}$ and $Pb_{83}Li_{17}$ eutectic melts.

2. Experimental

The samples were prepared in the vacuum furnace under Ar gas pressure ~1 MPa to prevent the oxidation and evaporation of the constituents. The purity of the initial metals was 99.999% for Pb, 99.9% for Mg and Li. The structure

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investigations were performed at temperatures 550 K and 820 K (for $Pb_{83}Mg_{17}$) and 508 K, 573 K, 593 K, 653 K, and 673 K (for $Pb_{83}Li_{17}$). It is known from numerous structure studies that simple metals dose not significantly change the structure with heating whereas the molten alloys contrary show the higher sensitivity of atomic distribution to temperature. On that reason we have studied the structure of molten alloys at few temperatures and the structure of constituents at 5 K above the melting point.

X-ray diffraction studies were carried out using a high-temperature diffractometer in Breg–Brentano focusing geometry. Cu K_α radiation monochromatized by means of LiF single crystal, were used. Scattered intensities as functions of scattering angles were recorded and corrected for absorption, anomalous dispersion and incoherent scattering [5]. The structure factors (SF) were obtained. Pair correlation functions (PCF) were calculated from SF [6]. From these functions the main structure parameters – first and second peak positions k_1, k_2, r_1, r_2, number of neighbors Z and first peak height a(k_1) were determined.

The measurements of electrical conductivity and thermo-e.m.f. have been carried out by a contact method in accordance with the 4-point scheme as described elsewhere [7]. The samples were contained in the measuring cells manufactured of BN six graphite electrodes, two for the current and four for the potential measurements, dividing the cell in several sections were inserted into the wall of the container along its vertical axe. The deviation of composition after synthesis was less then 0.02 wt% and was checked by means of weighting the samples before and after the experiment and X-ray microanalysis. The uncertainty of temperature determination increased from about ±1 K at 550 K to ±3 K at 1300 K.

By carefully calibrating each measuring cell and collecting a large data set, we were able to reduce the uncertainty in conductivity to a level no higher than 2%, and in the thermo-e.m.f. – 5% which allowed us to obtain reliable experimental data.

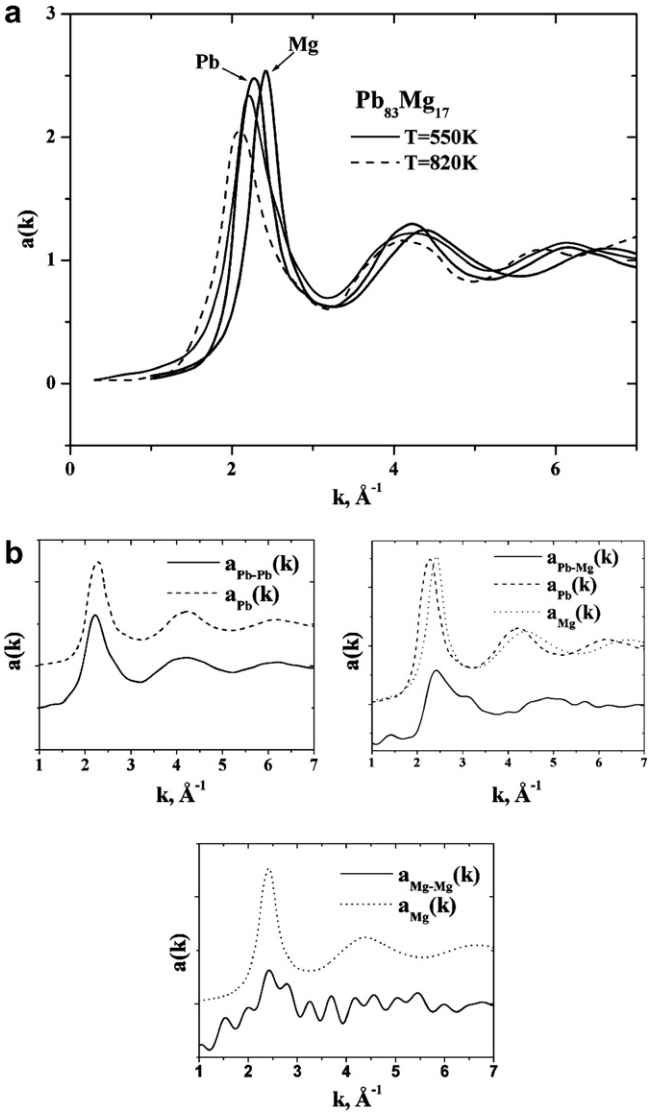

Fig. 1. The total (a) and partial (b) structure factors for liquid eutectic alloy $Pb_{83}Mg_{17}$.

3. Results and discussion

Fig. 1(a) shows that the variation of a(k) as a function of k determined for the molten Pb–Mg eutectic alloy ($T = 550$ K and 820 K) is similar to that measured for liquid Pb ($T = 600$ K) more than to that measured for liquid Mg. ($T = 925$ K). At higher temperature the discrepancy between these SF for $Pb_{83}Mg_{17}$ and Pb becomes larger. Particularly, SF for the $Pb_{83}Mg_{17}$ melt is more shifted to small k-values. Besides its width Δk becomes larger and a principal peak height $a(k_1)$ decreases. (Table 1). These changes in structure parameters estimated from SFs are also revealed in the pair correlation functions. The most probable interatomic distance r_1 significantly increases with heating. At $T = 820$ K the parameter r_1 even prevails over the corresponding value for the liquid Pb ($T = 600$ K). Similar tendency is also observed for the second interatomic distance r_2. Number of neighbors Z for $Pb_{83}Mg_{17}$ is less than for both components. In other words, the structure in liquid $Pb_{83}Mg_{17}$ is of less density of atomic arrangement than one in liquid Pb and Mg. Such kind of structure is suggested to be caused by formation of chemically bonded structural units, where the chemical bonding is covalent partly. Maximal fraction of such kind structural units should be in liquid Mg_2Pb stoichiometric alloy. One can suppose that eutectic melt is inhomogeneous and consists of the Pb-matrix where the Mg_2Pb-associates are randomly distributed.

In order to check this model the partial structure factors (PSF) have been calculated by means of Reverse Monte Carlo (RMC) method. In Fig. 1(b) $a_{Pb–Pb}(k)$, $a_{Pb–Mg}(k)$ and $a_{Mg–Mg}(k)$ are shown. It can be seen that $a_{Pb–Pb}(k)$ is close to $a_{Pb}(k)$. Another partial SF $a_{Pb–Mg}(k)$ is significantly different from SF for the components. Its right hand side reveals the shoulder which is not pronounced in SF for liquid Pb and Mg. The existence of shoulder is the evidence

Table 1
The main structure parameters for Pb83Mg17 and Pb83Li17 liquid eutectics

	T, K	k_1, Å^{-1}	k_2, Å^{-1}	$a(k_1)$	Δk	r_1	r_2	r_2/r_1	Z
Pb83Mg17	550	2.21	4.23	2.34	0.72	3.29	6.17	1.87	8.1
	820	2.09	4.10	2.04	0.77	3.39	6.72	1.98	9.8
Pb83Li17	508	2.06	3.83	2.30	0.53	3.57	6.77	1.89	8.6
	573	2.08	3.91	1.77	0.60	3.52	6.67	1.89	8.2
	593	2.10	3.91	2.21	0.56	3.55	6.72	1.89	9.9
	653	2.01	3.75	1.66	0.70	3.60	6.81	1.89	8.5
	673	2.02	3.88	1.65	0.72	3.56	6.89	1.93	8.4
	Pb	2.27	4.23	2.48	0.56	3.33	6.40	1.92	10.9
	Li	2.5	4.64	2.69	0.53	3.15	6.00	1.90	9.5
	Mg	2.42	4.39	2.53	0.49	3.21	6.00	1.87	10.9

of covalent bonding between Pb and Mg atoms, which can lead to formation of stable chemical ordering in structure.

The $a_{Mg-Mg}(k)$ partial SF also differs from SF for the liquid Mg. Principal peak is low and accompanied by oscillations. Second maximum is not resoluted. Therefore the Mg-atoms are distributed in Pb-matrix in another way than in case of pure liquid Mg. Taking into account the features of PSFs one can conclude that self-associated Mg–Mg atomic groups do not exist in the liquid $Pb_{83}Mg_{17}$ eutectic alloy, whereas the Pb–Pb atomic distribution with main parameter as in liquid Pb is more probable. On the other hand, Mg-atoms have as neighbors only the Pb-atoms, forming in such way the chemical ordering. Since the width of principal peak in a_{Pb-Mg}(k) is significantly larger, the size of structural units $L = \frac{2\pi^3\hbar^2}{2.5^2\Delta k}$, where the chemical ordering is a characteristic of atomic distribution, is small. Besides, these results are confirmed also by viscosity measurements. The viscosity as a function of composition shows a maximum at 33.3 at.%Pb corresponding to the Mg_2Pb chemical compound [8].

Additions of Mg into Pb reduce the melting temperature and the electric conductivity (T). As is seen from Fig. 2, at 800 K the electrical conductivity decreases from 10^4 Ohm^{-1} cm^{-1} for pure Pb to 7.2×10^3 Ohm^{-1} cm^{-1} ($Pb_{83}Mg_{17}$). In the same concentration range the thermo-e.m.f. is practically not sensible to Mg additions and decreases monotonically from $-(2–3)$ VK^{-1} to -9 VK^{-1} with an increase in temperature (Fig. 3).

From the obtained results it may be deduced that Pb alloying with Mg (up to 20 at.% of Mg) does not affect considerably the energy structure of an electron spectrum. These facts are in accordance with conclusions drawn from diffraction data.

The total structure factors for $Pb_{83}Li_{17}$ eutectic melt at different temperatures ($T = 508$ K, 573 K, 593 K, 653 K, 673 K) are shown in Fig. 4(a). Principal peak positions at all temperatures are shifted to small k-values in respect to those for Li ($T = 523$ K) and Pb. This shift corresponds to an increase of the most probable interatomic distance r_1 to larger values than for the components. Such behavior is not commonly observed in case of random distribution or like kind atom microgroups formation. With heating k_1 parameter shifts to larger k-values at $T = 573$ K and 593 K, and than its behavior changes by shifting to smaller k-values.

Analysis of PSF for this molten alloy (Fig. 4(b)) indicates the significant difference in principal positions of $a_{Pb-Pb}(k)$ and $a_{Pb}(k)$. Another PSF $a_{Pb-Li}(k)$ shows the principal peak of a large width positioned between ones for Li and Pb. The Li–Li correlations are weak, that is indicated by small peaks in $a_{Li-Li}(k)$ function.

The distance between first neighbors in the $Pb_{83}Li_{17}$ eutectic melt is larger (3.55 Å) than one in liquid Pb (3.33 Å), while the distance between unlike kind atoms (2.79 Å) (Tables. 1 and 2) is significantly less than in assumption of random atomic distribution (3.3 Å). Such behavior is supposed to be caused by influence of Li_4Pb like atomic groups (associates) diluted in Pb-matrix [11]. Therefore the structure of $Pb_{83}Li_{17}$ eutectic melt is rather inhomogeneous with two kind structural units: Li_4Pb associates and Pb_n clusters. As follows from Table 2 the most probable interatomic

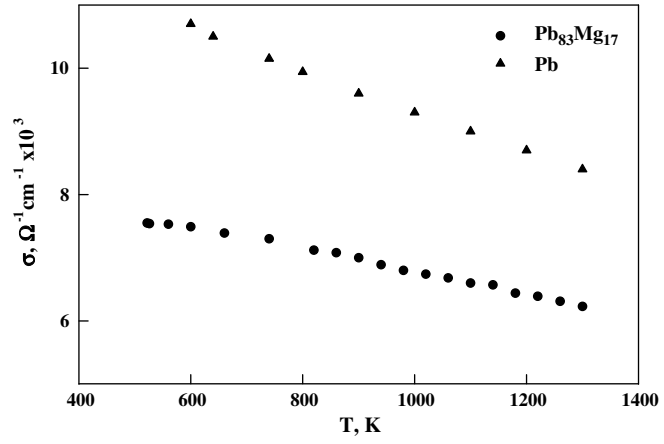

Fig. 2. Temperature dependence of electrical conductivity for liquid eutectic $Pb_{83}Mg_{17}$.

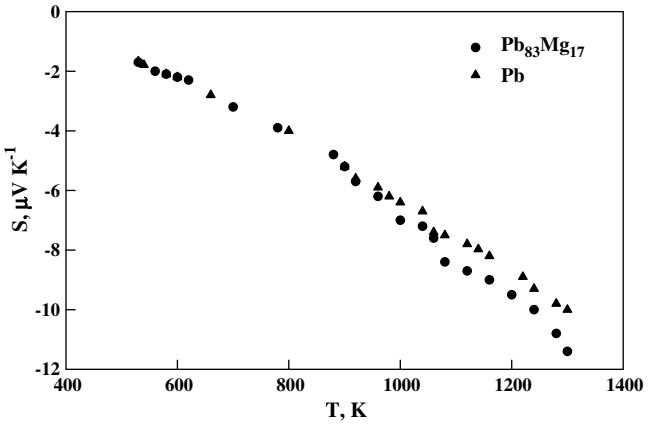

Fig. 3. Temperature dependence of thermo-e.m.f. for liquid eutectic $Pb_{83}Mg_{17}$.

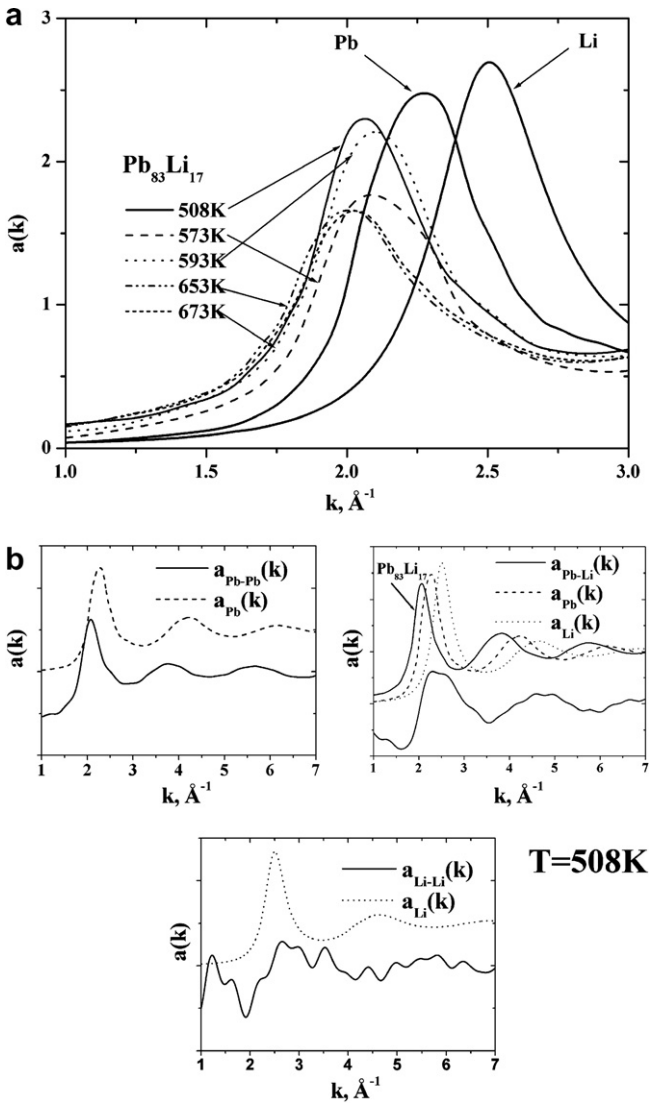

Fig. 4. The total (a) and partial (b) structure factors for liquid eutectic $Pb_{83}Li_{17}$.

Table 2
The main partial structure parameter for $Pb_{83}Li_{17}$ liquid eutectic melt

	T, K	k_1, Å^{-1}	Shoulder	r_1, Å
Pb–Pb	508	2.07	–	3.55
	593	2.11	–	3.54
Pb–Li	508	2.3	2.58	2.79
	593	2.38	–	2.77
Li–Li	508	2.65	–	2.40
	593	2.63	–	2.76

distances r_{Pb-Pb} is almost unchangeable within some temperature region above melting temperature (~100 K). Parameter r_{Li-Pb} shows the decrease, whereas the r_{Li-Li} increases. Therefore one can conclude that Pb-matrix persists its structure but chemically ordered associates change it. Some part of Li atoms removes from associates and dilutes in Pb-matrix.

The concentration dependence of the electrical resistivity of Pb–Li, communicated in [9–11], shows a sharp maximum at 20 at.%Pb. The maximum is also observed for this alloy in the concentration dependencies (~20 at.%Pb) of few thermodynamic parameters [12,13].

Taking into account the X-ray diffraction data and results of RMC simulation one can compare the structure of $Pb_{83}Li_{17}$ and $Pb_{83}Mg_{17}$ eutectic melts. First of them consists of Li_4Pb complexes and Pb_n clusters. Taking into account that temperature of Li_4Pb formation (920 K) is higher than one for Mg_2Pb (820 K), it is more probably to suppose that Li_4Pb associates upon reaching of critical size and sticking with walls can transit in solid state resulting the changes of main working characteristics of coolant. In $Pb_{83}Mg_{17}$ melt such tendency is weaker due to the existence of the heterocoordinated structure. Nevertheless, in this alloy the effective clusters can exist too, but their transformation into nuclei of critical size is of less probability.

4. Conclusion

The structure of the liquid $Pb_{83}Mg_{17}$ eutectic melt reveals the short range order with heterocoordinated atomic distribution. This atomic arrangement exists at temperatures near the eutectic melting point and persists at heating. Atomic distribution in the $Pb_{83}Li_{17}$ eutectic melt is significantly affected by the Li_4Pb associates. These chemically ordered structural units are randomly distributed in Pb-matrix.

References

[1] S.J. Zinkle, Summary of physical properties for lithium, Pb–17Li, and (LiF)BeF coolants, ORNL, APEX Study Meeting, Sandia National Lab, 1998.
[2] Mike Cappiello, Lead–alloy, liquid–metal-cooled fast reactor advanced reactor, fuel cycle, and energy products, Workshop for Universities, Gaithersburg, 2004.
[3] S. Banerjee, Int. J. Nucl. Power 18 (2&3) (2004) 45.
[4] B.Yu. Sharkov, N.N. Alexeev, M.M. Basko, M.D. Churazov, D.G. Koshkarev, S.A. Medin, Yu.N. Orlov, V.M. Suslin, Nucl. Fusion 45 (2005) S291.
[5] D.T. Cromer, J.T. Waber, Funct. Acta Cryst. 18 (1965) 104.
[6] Y. Waseda, The Structure of Non-Crystalline Materials, McGraw-Hill, New York, 1980.
[7] Yu. Plevachuk, V. Sklyarchuk, Meas. Sci. Technol. 12 (2001) 23.
[8] E. Gebhardt, M. Becker, S. Schafer, Z. Metallkd. 43 (8) (1952) 292.
[9] K. Hoshino, W.H. Young, J. Phys. F: Metal Phys. 10 (1980) L193.
[10] O. Akinlade, Physica B 175 (1991) 389.
[11] W. Van der Lugt, W. Geertsma, Can. J. Phys. 65 (1987) 326.
[12] H. Ruppersberg, J. Saar, J. Phys. Condens. Matter 1 (1989) 9729.
[13] B.P. Alblas, W. Van Der Lugt, Physica B 114 (1982) 59.