On composition converting liquid metal alloys

A S Kolokol¹, A L Shimkevich¹ and I Yu Shimkevich ²

¹Russian Research Center “Kurchatov Institute”, 1 Kurchatov Sq., 123182 Moscow, Russia
²Atominform, 2 Dmitrovskoe Shosse, 127 431 Moscow, Russia

E-mail: kolokol@dhtp.kiae.ru

Abstract. For studying the effect of impurity on the structure of basic component in the solvent, three-component molecular-dynamics model for liquid PbK and NaPb is represented. The analysis of atomic configurations is performed by statistical-geometry method. It is shown that with increasing potassium concentration in liquid lead more than 14% at., a microstructure transition is possible. The lead influence to liquid sodium does not make an impact on the NaPb structure up to 20% at. of the lead.

1. Introduction

Microstructure of liquid matrix is known to be a heterogeneous [1,2]. One can pick out in it the dense part which consists of the atoms located in the vertexes of almost regular tetrahedrons (simplexes Delaunay) [1-3]. The simplexes have a common faces and form the clusters. The typical dense part of a liquid matrix for a simple metal is shown on figure 1. The dot is the centers of the sphere which is circumscribed the simplexes. If two simplexes have a common face, they centers are connected by line and form skeleton of a cluster.

Figure 1. The dense part of the liquid lead MD-model at 623 K. The dots are the centers of the spheres which are circumscribed the simplexes. Segments connect simplexes by common faces. Bold segments are the skeletons of the cluster are shown on figure 2.
Typical clusters of the dense part of a liquid matrix are shown on figure 2. Bold line indicates the clusters skeleton. Projection of the skeleton is depicted on the axial planes.

**Figure 2.** Typical clusters of a liquid matrix dense part.

For a long time the problem of structural identification of the dense part of a liquid matrix is discussed. For example, the effectiveness of the tetrahedral index $K_T$ which is determined the deformation of a simplex form from an ideal tetrahedron [1,2]:

$$K_T = \frac{9\sqrt{3}V}{8R^3},$$

where $V$ – volume of a simplex, $R$ – radius of circumscribed sphere.

For regular triangular pyramid (tetrahedron) $K_T = 1$ and as the form of tetrahedron is deformed the $K_T \leq 1$ is droningly tend to zero. One can use some number $K_T \leq 1$ as the criterion of selection simplexes for the dense part of a liquid matrix. It is obviously that such geometrical method will not provide a single-valued result.

For the purpose of providing the unique approach of initialization the liquid matrix dense part we have suggested the topological criterion [3,4]. The essence of the criterion is to determine such edge length of a simplex at which number of clusters in all simplicial dissection of a liquid matrix will be a maximum.

Using the topological criterion one can select the dense part of a liquid matrix in a unique way. The criterion provides the possibility to investigate the microstructure of the simple liquids in detail as well as influence of impurity on microstructure of the basic component in a solution.

2. **Molecular-dynamics model**

The MD–simulation of liquid Pb$_{1-x}$K$_x$ and Na$_{1-x}$Pb$_x$ is carried out by micro-canonical code with cubic periodic boundary conditions. All the impurity atoms are ionized as well as the same number of the basic component atoms. Such three-components model has made a good showing for K–O [5] and is used for Pb$_{1-x}$K$_x$ and Na$_{1-x}$Pb$_x$ in the form of (Pb, Pb', K') and (Na, Na', Pb').

For Na$_{0.98}$Pb$_{0.02}$ are used model of $N = 2041$ particles in the MD-box, including 1959 sodium atoms, 41 sodium cations and the same number of lead anions. For Na$_{0.91}$Pb$_{0.09}$ there are $N = 2198$, including 1802 sodium atoms, 198 its cations and the same number of lead anions. For Na$_{0.80}$Pb$_{0.20}$ are 2500, 1500 and 500 correspondingly. The edge length of MD-box is $L = 44.78$ Å, chosen at condition: $N_{Na} = 2000$, $p_{Na} = 850.48$ kg/m$^3$ at 698 K.

For five melts of Pb$_{1-x}$K$_x$ is performed the model of $N_{Pb} = 2048$ particles in MD–box, including 108, 203, 333, 578 and 683 lead anions at $x = 0.05$, 0.09, 0.14, 0.22 and 0.25 correspondingly. The equal number of potassium cations are added to them according to its atomic portion $x$ in melt Pb$_{1-x}$K$_x$. The edge length of MD-box is $L=46.90$ Å at 660 K.
Taking into account the strong electron-ion correlation in liquid sodium [6], in MD-modeling of Na\textsubscript{1-x}Pb\textsubscript{x} for sodium neutral atoms is used Ashcroft local pseudopotential [7]. At modeling interaction of couples: (Na\textsuperscript+Na\textsuperscript+), (Na\textsuperscript+Pb\textsuperscript+), (Pb\textsuperscript+Pb\textsuperscript+), and (NaPb\textsuperscript+) is used Born–Mayer pair potential was recommended for Na\textsubscript{0.5}Pb\textsubscript{0.5} [8].

In the MD-model of liquid Pb\textsubscript{1-x}K\textsubscript{x} is used Larsson potential [9] for (PbPb) and (PbPb\textsuperscript-) interactions. Taking into account electrons and ions correlation in liquid lead [10], the interactions of couples: (Pb\textsuperscript+Pb\textsuperscript-), (Pb\textsuperscript+K\textsuperscript+), (K\textsuperscript+K\textsuperscript+), and (PbK\textsuperscript-) are described by Born–Mayer–Huggins pair potential without dispersion terms [11].

Structural functions were calculated after the systems have reached the thermodynamic equilibrium. Comparison with the experimental neutron scattering results [12,13] for Pb\textsubscript{0.75}K\textsubscript{0.25} at \(T = 660\) K shows an overall good agreement (see figure 3.). Figure 3 shows that using suggested three - components MD-model one can get the forepeak that is observed by neutron experiment. The forepeak obtained with the three-components MD-model for Na\textsubscript{0.80}Pb\textsubscript{0.20} is also in a good agreement with experimental dates [14].

![Figure 3. Structural factor obtained with three - components MD-model for liquid Pb\textsubscript{0.75}K\textsubscript{0.25}, \(T = 660\) K. (full line). The dots are the experimental results from [12,13].](image_url)

3. Statistical-geometry analysis

In order to study the effect of impurity on the structure of basic component in the solvent the dense part of a liquid matrix was constructed for each of all investigated systems using topological criterion. At first the dense part of Pb-K was constructed of only Delaunay simplexes which are formed of lead atoms. Then the tetrahedral index \(K_T(1)\) was calculated for each simplex in the dense part. After that distribution of these simplexes depending on \(K_T\) was constructed.

Figure 4 shows distribution of dense part simplexes depending on they form, i.e. tetrahedral index (1), for pure liquid lead (—) and melt Pb\textsubscript{1-x}K\textsubscript{x} where \(x = 0.09\) (••••), 0.14 (••), 0.22 (——) and 0.25 (——) at temperature 660 K. It is visible that the dense parts of liquid lead and Pb\textsubscript{0.91}K\textsubscript{0.09} melt consist of almost regular tetrahedron. The distribution reaches its maximum value at \(K_T = 0.93\), which corresponds to the regular rectangular tetrahedron (a quarter of octahedron). The melts of Pb\textsubscript{0.78}K\textsubscript{0.22} and Pb\textsubscript{0.75}K\textsubscript{0.25} show strong distortion of simplexes of liquid lead dense part. This fact justifies that potassium create a new microstructure in a liquid lead and must be included in the dense part.
Figure 4. Distribution of dense part simplexes depending on they form: (—) – pure lead, (*****) – Pb_{0.9}K_{0.09}, (…) – Pb_{0.86}K_{0.14}, (-----) – Pb_{0.78}K_{0.22}, (—*) – Pb_{0.75}K_{0.25} at a temperature 660K.

Thus, the potassium ≤9% at. does not influence on the lead microstructure. Therefore, potassium is not equipped in forming of the dense part of the melt and it will consist of lead Delaunay simplexes. Potassium atoms are to be positioned outside the clusters of dense part. Geometric analysis displayed that potassium atoms are situated on the faces of the dense part tetrahedrons. This fact can be interpreted as an introduction solution, in view of clusters form a structural lattice of the melt.

With increasing potassium concentration more than 14% at., a microstructure transition is possible. And the forms of simplexes in the dense part essentially improve (see figure 5) if potassium is included in it.

Figure 5. Distribution of dense part simplexes depending on they form in Pb_{0.75}K_{0.25}

Similar analysis of lead influence on the structure of liquid sodium is shown that lead does not make an impact on the NaPb. The system is homogeneous in a wide range lead distribution up to 20% at. in a liquid sodium. And structural transformation does not appear.

Figure 6. shows distribution of dense part simplexes depending on they form, i.e. tetrahedral, for pure liquid sodium (—) and melt Na_{1-x}Pb_x, where x = 0.02 (…) , 0.9 (-----) and 0.20 (—) at temperature 698 K. It is found that lead impurity to sodium improve its dense part. The portion of simplexes which have $K_T>0.9$ is increased. Furthermore, the plot is not strongly changed if the dense part consists of only sodium simplexes.
4. Conclusions
The dense part of a liquid lead are remained in eutectic Pb$_{0.91}$K$_{0.09}$ and consists of almost regular tetrahedrons. From the analysis of cations position in the dense part of eutectic Pb$_{0.91}$K$_{0.09}$, it follows that they are on the faces of tetrahedral clusters. This fact can be interpreted as the introduction of potassium in liquid lead. The melts of Pb$_{0.78}$K$_{0.22}$ and Pb$_{0.75}$K$_{0.25}$ show strong distortion of simplexes of liquid lead dense part on tetrahedral index. This fact justifies a structural transition of lead-potassium alloy microstructure. The lead influence to liquid sodium does not make an impact on the NaPb structure up to 20% at. of the lead. Deformation of the dense part simplexes to a more regular form just takes place.

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