

Eutectic Na–Tl and Pb–Mg alloys as liquid-metal coolants for fast nuclear reactors

P. N. Alekseev, A. L. Shimkevich & I. Yu. Shimkevich
NRC Kurchatov Institute, Russia

Abstract

The liquid-metal microstructure is a correct subdivision of Delaunay simplexes (triangular pyramids with atoms in their vertexes). Its dense part consists of almost regular tetrahedrons connected by faces in ramified clusters. Any metal additive (as a second component of alloy) can be outside of these tetrahedral clusters or into them as a constituent of dense liquid part. These structural states of liquid alloy convert to each other at its eutectic composition. Such the polymorphic conversion of the liquid-metal alloy is approved by molecular-dynamics simulating the Pb–K alloy and can be applied to any eutectic, for example, $\text{Na}_{0.93}\text{Tl}_{0.07}$ with the melting point of 64°C. At the sodium side of this point, a homogeneous solution of thallium is formed in liquid sodium which becomes the colloidal one with clusters, $(\text{Na}_6\text{Tl})_n$, when it is passing the eutectic point. Such the modified sodium coolant enriched by the isotope, ^{205}Tl , can appear attractive for inhibiting the chemical activity of this coolant maintained by oxygen-free technology. An alternative liquid-metal coolant for fast nuclear reactors is eutectic, $\text{Pb}_{0.83}\text{Mg}_{0.17}$, with the melting point of 248°C. This liquid alloy as a modified lead coolant maintained by the same oxygen-free technology can appear attractive for inhibiting the high corrosion activity of molten lead.

Keywords: liquid-metal eutectics, density fluctuations and tetrahedral clusters, sodium or lead solvent, thallium or magnum additive.

1 Introduction

In liquid alkali metals, A, a non-ideal solution of heavy metals, M, takes place in the whole range of A–M alloy composition [1, 2]. For lead in liquid sodium, the strongest non-ideal effects are observed at 0.2 and 0.5 of its mole fraction [2–4] due to the existence of $(\text{Na}_4\text{Pb})_n$ and $(\text{NaPb})_m$ clusters in the alloy. The first



cluster is set conditions for the compound of $\text{Na}_{15}\text{Pb}_4$ in this system and its managing the microstructure of liquid alloy in the sodium side of phase diagram. This effect is disclosed by a sharp change of the alloy entropy [3, 5] and the increase of its electric resistance [1, 6].

In that case, the cluster model is the most realistic one for considering the Na–Pb alloy in the sodium side of its phase diagram. The molecular-dynamic (MD) simulation [7] of its microstructure and atomic dynamics at the low mole fraction of lead has proved the accuracy of this model. The lead additive in sodium is accepted for inhibiting chemical activity of alkali metal and for automatic shut-down of sodium fires outdoors by forming $(\text{Na}_{15}\text{Pb}_4)_n$ clusters in the liquid alloy [8–10]. Their content is monotonously increased at growing lead concentration of 0.1 upto 10% in liquid sodium without polymorphic changing the liquid alloy microstructure [7, 11]. Just therefore Shimkevich and Shimkevich [7] have shown that the binary systems, Na– M_{IV} , of fourth-group elements, M_{IV} , of the Periodic Table in sodium have no eutectic at such the content of the second component.

It is reasonable searching another alloy of sodium with an additive element from the adjacent groups of the Periodic Table. This alloy is to have the eutectic in the range of 1–10%, for example, the simple eutectic, $\text{Na}_{0.93}\text{Tl}_{0.07}$, with melting point of 64°C. Enriched by the isotope, ^{205}Tl , this alloy as a modified sodium coolant can appear attractive for inhibiting the chemical activity of liquid sodium. The alternative eutectic of $\text{Pb}_{0.83}\text{Mg}_{0.17}$ with the melting point of 248°C and the same oxygen-free technology can be attractive for inhibiting the high corrosion activity of molten lead and can be used as a modified lead coolant in the fast nuclear reactors.

In this paper, a concept is considered for composition correcting the physical and chemical properties of the sodium and lead coolants.

2 Polymorphic converting the liquid metal structure

For studying the effect of alloy additives in liquid metal on its microstructure, a three-component molecular-dynamic (MD) model is built by Kolokol *et al.* [11] and approved by liquid Pb–K alloy.

Kolokol and Shimkevich [12] have offered an exact topological criterion for MD identifying the tetrahedral clusters of the dense part of liquid metals in the structural analysis of their atomic configurations. Now, one can strictly plot the dense part of MD model for any liquid metal. This part shown in fig. 1 consists of the almost perfect tetrahedrons connected in pairs by faces.

One can see that these ramified tetrahedral clusters are interlinked in atomic percolation configuration by only tetrahedron vertexes and edges. Then, the “free” faces of tetrahedral clusters form a surface fractal. An effective tool for identifying such the superstructure of liquid metals can be the small-angle scattering of neutrons. Kovalev *et al.* [13] have verified such the two-structural model of liquid Pb–K alloy at least for two compositions that are shown in fig. 2 by red vertical dotted lines.



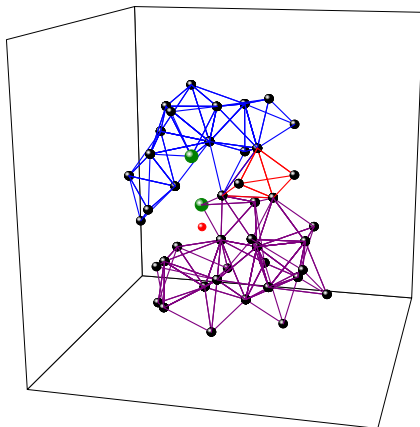


Figure 1: Typical tetrahedral clusters (differently coloured) of the dense part of MD model for liquid $Pb_{0.91}K_{0.09}$ with the vertex and edge connectivity between these clusters: black points are lead atoms, green points are its anions, and the red one is the cation of potassium.

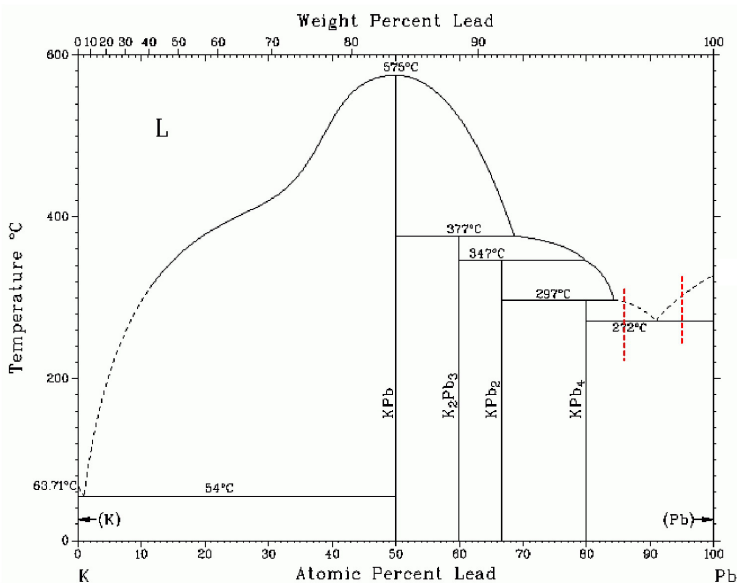


Figure 2: The phase diagram of Pb–K system presented by Meijer *et al.* [14]; the red vertical lines on the liquidus denote two compositions for structural analysis of the system MD models.

Structural factors of $\text{Pb}_{0.95}\text{K}_{0.05}$ and $\text{Pb}_{0.86}\text{K}_{0.14}$ at 660 K have been calculated after the MD models of these alloys reached the thermodynamic equilibrium. Blagoveshchenskii *et al.* [15] have compared the simulation results with the experimental data of neutron scattering on these alloys (see figs 3 and 4).

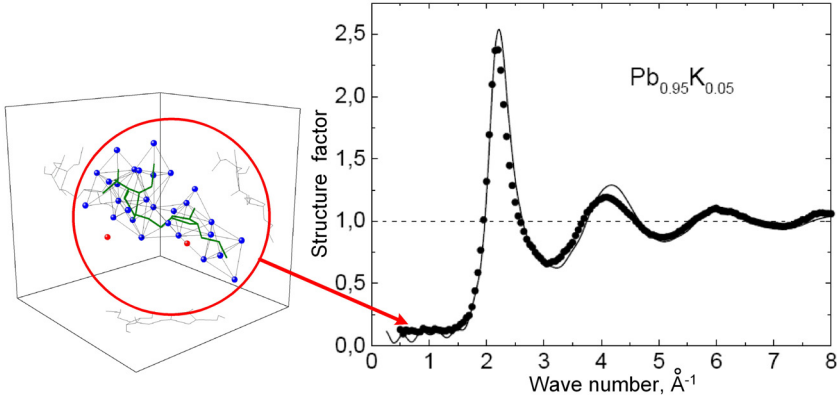


Figure 3: Typical tetrahedral cluster (left) of the dense part of liquid $\text{Pb}_{0.95}\text{K}_{0.05}$ alloy at 660 K and its structural factor (right) as a three-component MD model (full line) and experimental data (points).

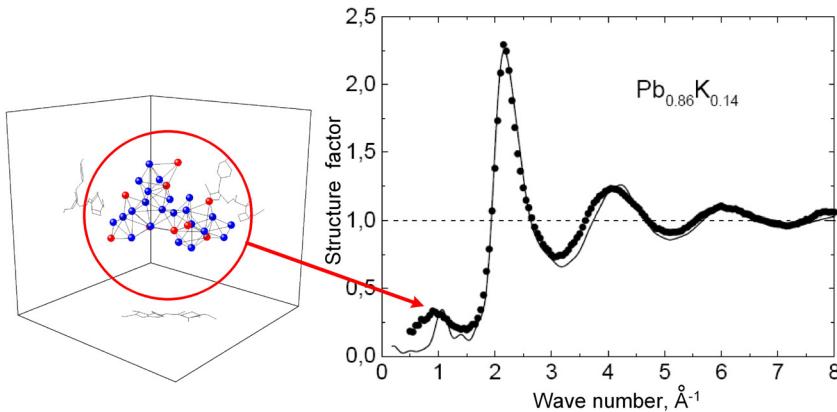


Figure 4: Typical tetrahedral cluster (left) of the dense part of liquid $\text{Pb}_{0.86}\text{K}_{0.14}$ alloy at 660 K and its structural factor (right) as a three-component MD model (full line) and experimental data (points).

Fig. 3 shows that potassium particles (red points) don't form the dense liquid part which only consists of lead tetrahedrons at the mole fraction of potassium less than eutectic point (0.09). The potassium cations are situated on the "free" faces of the lead tetrahedrons and this state of liquid alloy is interpreted as an introduction solution. Shimkevich [10] has considered this solution in detail as well as the addition one at a mole fraction of potassium more than eutectic point.

In this case, we get a forepeak found by Blagoveshchenskii *et al.* [15] in neutron scattering and MD simulation (see fig. 4).

The figures 3 and 4 show how the microstructure of liquid lead is changed (as a polymorphic conversion found by Kolokol *et al.* [11]) when the mole fraction of potassium passes the eutectic point (0.09).

Indeed, a structural state of additive particle in the liquid matrix has a dual character due to density fluctuations of liquid alloy [16, 17]. At low mole fraction, additive atoms settle outside the dense part of liquid alloy, i.e. they form the introduction solution. In increasing the mole fraction, these atoms embed in the tetrahedral clusters of liquid dense part as their inherent constituents, so that the alloy becomes a micro-heterogeneous (two-phase) solution for the additive component and the single-phase one for the basic component, i.e. it forms the addition solution [8, 10]. It is set conditions for a parameterization of the energy functional of condensed matter.

So, one can see in fig 5 that a correlation radius of fluctuations of liquid density, R_1 , and the one of its composition fluctuations, R_2 , have a different behaviour at growing the additive mole fraction, x . Shimkevich [10] has shown that R_2 is decreased sharply at some point denoting a decay of the composition fluctuations into molecular clusters in contrast to the long-wave fluctuations of the alloy density. A subsequent growth of R_2 should be interpreted as a region of clusters existence in the liquid alloy and then, it is their allocation from the addition solution when R_2 increases sharply. The observed clustering into this solution can be considered as an analogue of the first-order phase transition in micro regions of liquid which has continuous character with the eutectic break of liquidus line and appears as a change of the additive form in alloy.

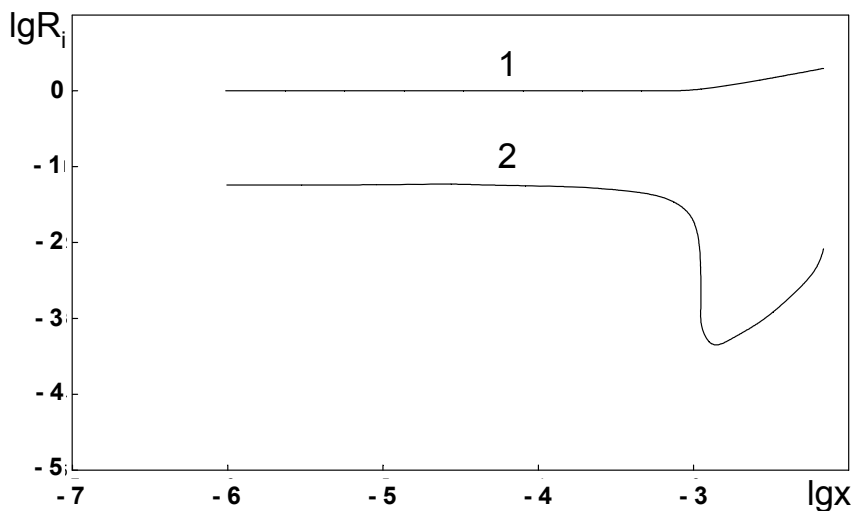


Figure 5: Logarithm of correlation radius, R_i , for fluctuations of the solution density (1) and the one for its composition fluctuations (2) as a function of the mole fraction, x , of the additive component.

3 Composition modifying the liquid metal coolants

Thus, the binary system, $\text{Na}_{1-x}\text{M}_x$, has a eutectic at its sodium side if M, for example, thallium first forms the homogeneous intermetallic solution in liquid sodium at growing x and then, makes polymorphic transition in the addition (colloidal) one.

Grube and Schmidt [18] have presented the phase diagram of Na–Tl system (see fig. 6) which has the simple eutectic at $x \sim 0.07$ with the melting point of $\sim 64^\circ\text{C}$. As a heavy metal, thallium belongs to main III subgroup in VI period of the Periodic Table. The web site [19] shows that in nature, this element consists of two stable isotopes: ^{205}Tl (70.5%) and ^{203}Tl (29.5%).

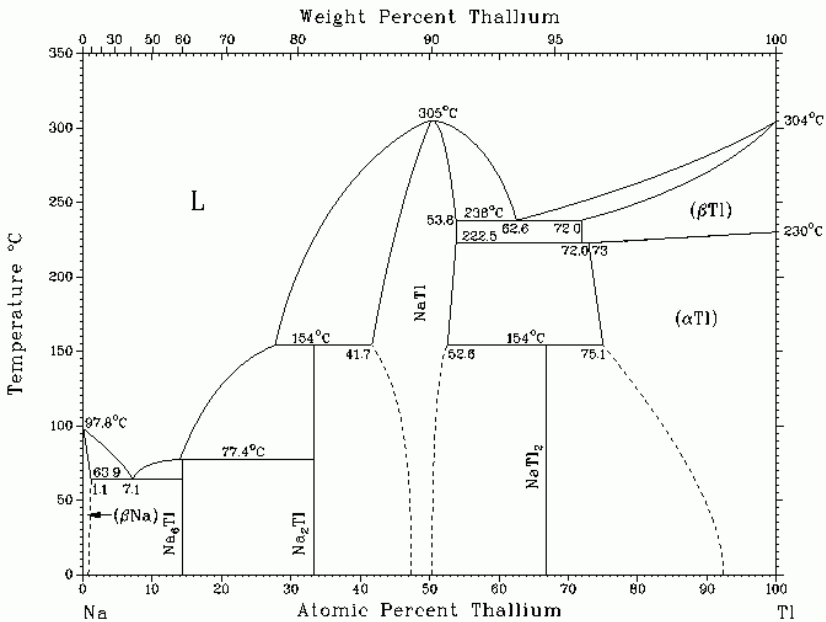


Figure 6: The phase diagram of the binary system, Na–Tl.

It is known from Data [20] that the first has a low neutron-capture cross-section (~ 0.5 barn) as opposed to the second one (~ 130 barn), i.e. the eutectic, $\text{Na}_{0.93}\text{Tl}_{0.07}$, (as a modified sodium coolant) enriched by ^{205}Tl is attractive for inhibiting the chemical activity of sodium due to a low level of such the activity of thallium. On the other hand, its high boiling point (1473°C) excludes thallium volatility from the sodium coolant.

Subbotin *et al.* [8] have shown that this coolant is maintained by oxygen-free technology when its RedOx potential appears less than the one of $\text{Cr}_2\text{O}_3/\text{Cr}$ electrode during operation in the fast nuclear reactor. An alternative liquid-metal coolant for this reactor can be the eutectic, $\text{Pb}_{0.83}\text{Mg}_{0.17}$, represented by Nayeb-

Hashemi and Clark [21] (see fig. 7). This liquid alloy as a modified lead coolant with the same oxygen-free technology can appear attractive for inhibiting the high corrosion activity of molten lead.

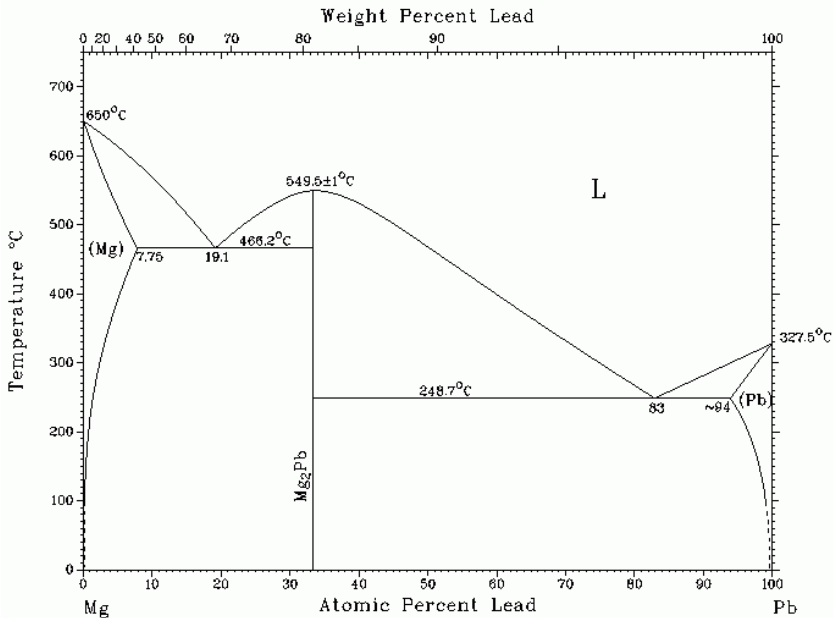


Figure 7: The phase diagram of the binary system, Pb–Mg.

Just Subbotin *et al.* [8] have shown (see fig. 8) that the corrosion rate of steels versus the total solubility of their elements in liquid metals increases at growing the RedOx potential of liquid metals. Therefore the strongest reducer (potassium or magnesium) dissolved in lead can inhibit its corrosion activity in the modified lead coolant maintained by the oxygen-free technology.

4 Discussion of results

A passivity of structural materials in the modified lead coolant, $\text{Pb}_{0.91}\text{K}_{0.09}$, can be qualitative because its RedOx potential at saturation by oxygen is lower than the one in liquid lead reduced by iron. Then, it is possible proceeding to corrosive protection of fuel-rod cladding by chrome-oxide film. The growth of Cr_2O_3 layer does not depend on concentration of oxygen in the modified lead coolant and it will grow slowly because the diffusion coefficient of steel elements in Cr_2O_3 film is limited by 10^{-12} cm²/sec at 500°C.



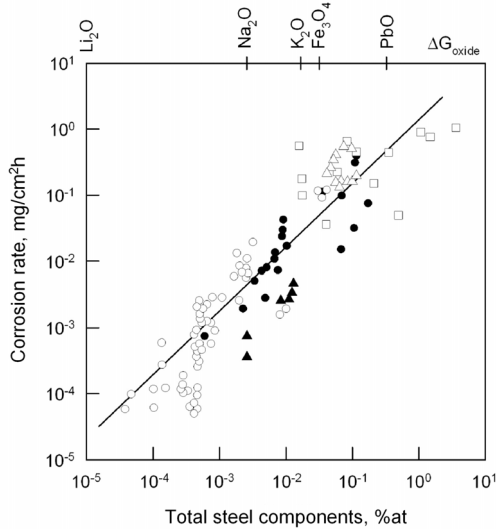
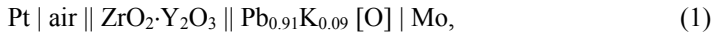


Figure 8: The corrosion rate of stainless steel, SS316, in liquid metals (points) versus the total solubility of its elements in liquid sodium (\circ), Na–K eutectic (\blacktriangle), lithium (\bullet), lead (Δ), and Pb–Bi eutectic (\square); the full line is the linear approximation of data in these coordinates; the top scale is the RedOx potential of these metals.

For controlling the corrosion activities of $\text{Pb}_{0.91}\text{K}_{0.09}$ melt, its Redox potential is monitored by the galvanic cell,



with the solid electrolyte from the oxide solution, $(\text{ZrO}_2)_{0.9}(\text{Y}_2\text{O}_3)_{0.1}$.

Subbotin *et al.* [8] have represented the experimental data of the RedOx potential of $\text{Pb}_{0.91}\text{K}_{0.09}$ alloy saturated by oxygen (see fig. 9) that are slightly above the line for forming potassium oxide (K_2O) at its activity equal to 1.

At the same time, the thermodynamic activity of potassium in such the solution should be less than 10^{-2} according to the known literature data, i.e. the experimental points in fig. 9 should be appreciably below the line “ K_2O ” at precipitating potassium oxide from the liquid metal alloy. Hence, the obtained RedOx potential of the eutectic $\text{Pb}_{0.91}\text{K}_{0.09}$ alloy saturated by oxygen is defined by the superposition of lead and potassium oxides.

Obviously in the eutectic $\text{Pb}_{0.83}\text{Mg}_{0.17}$ alloy saturated by oxygen, the RedOx potential will be less than the one of $\text{K}_2\text{O}/\text{K}$ and $\text{Cr}_2\text{O}_3/\text{Cr}$ electrodes as seen in fig. 9. Then, this modified lead coolant will be maintained by the oxygen-free technology which provides the low corrosion activity of any liquid-metal coolant (see fig. 8).

Thus, understanding the physical and chemical processes proceeding in the liquid metals allows to consider an opportunity for composition correcting the



properties of liquid-metal coolants for fast nuclear reactors on given attributes by additives strengthening these attributes.

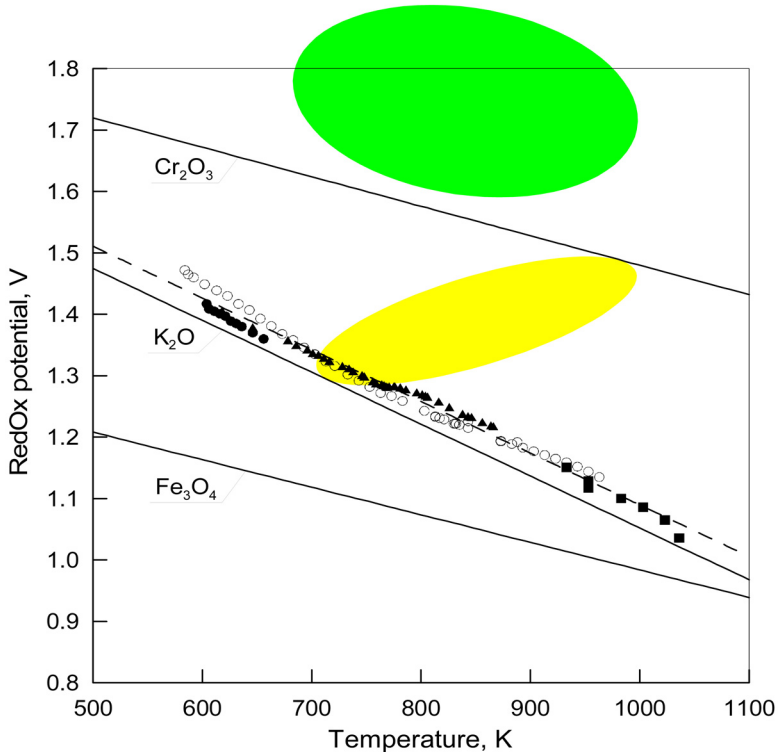


Figure 9: Experimental RedOx potential of $Pb_{0.91}K_{0.09}$ eutectic (points) measured by the galvanic cell (1) versus temperature and obtained in four runs; their LSM approximation (---) is compared with RedOx potentials of Cr_2O_3/Cr , K_2O/K , and Fe_3O_4/Fe electrodes; the yellow area is the RedOx range for maintaining the passive state of steels; the green area is maintained by the oxygen-free technology in the range of operation temperatures.

5 Conclusions

Theoretical studying the microstructure of liquid-metal alloy shows that the fluctuation-induced clustering of the additive component at the polymorphic transition of its introduction solution to the addition one in the liquid metal is defined by a nearest eutectic point of this metal in the phase diagram. It is possible at the high solubility of the additive component in this liquid metal.

Just this concept allows realizing the effective designing method for correcting the properties of liquid-metal coolants for fast nuclear reactors by additives on the given attributes of designed coolants.

Acknowledgements

The authors thank their colleagues for helping with this work and for useful discussion of mainstream in developing a new approach to additive modifying sodium and lead coolants of fast nuclear reactors as well as are pleased to the Russian Foundation for Basic Research in supporting this work (grant #12-08-12025-ofi).

References

- [1] Van der Lugt, W., Zintl ions as structural units in liquid alloys. *Physica Scripta*, **39**, 372, 1991.
- [2] Reijers, H.T.J. & van der Lugt, W., Molecular-dynamics study of liquid NaPb, KPb, RbPb, and CsPb alloys. *Phys. Rev. B*, **42**, 3395, 1990.
- [3] Hoshino, K. & Young, W.H., On the entropy of mixing of the liquid Na–Pb alloy. *J. Phys. F: Met. Phys.*, **11**, L7, 1981.
- [4] Matsunaga, S., Ishiguro, T. & Tamaki, S., Thermodynamic properties of liquid Na–Pb alloys. *J. Phys. F: Met. Phys.*, **13**, 587, 1983.
- [5] Senda, Y., Shimojo, F. & Hoshino, K., The origin of the first sharp diffraction peak in liquid Na–Pb alloys: *ab initio* molecular-dynamics simulations. *J. Phys.: Condens. Matter*, **11**, 2199, 1999.
- [6] Thakur, A., Negi, N.S. & Ahluwalia, P.K., Electrical resistivity of NaPb compound-forming liquid alloy using *ab initio* pseudo potentials. *Pramana–Journal of Physics*, **65**, 349, 2005.
- [7] Shimkevich, I.Yu. & Shimkevich, A.L., MD Simulated Microstructure of Liquid Sodium Alloyed with Lead. *Materials Sciences and Applications*, **5**, 556, 2014.
- [8] Subbotin, V.I. *et al.*, Liquid-metal coolants for nuclear power. *Atomic energy*, **92**, 31, 2002.
- [9] Shimkevich, A.L. & Shimkevich, I.Yu., Molecular dynamics simulation of the clustering of minor lead additives in liquid sodium. *Journal of Metallurgy*, **2011**, Article ID 890321, 2011.
- [10] Shimkevich, A.L., *The composition principles for designing nuclear-reactor materials*, edited by N.N. Ponomarev-Stepnoi, IzdAt: Moscow, 2008 (Russ).
- [11] Kolokol, A.S., Shimkevich, A.L. & Shimkevich, I.Yu., On composition converting liquid metal alloys. *J. Phys.: Conference Series*, **98**, 042021, 2008.
- [12] Kolokol, A.S. & Shimkevich, A.L., Topological structure of liquid metals. *Atomic energy*, **98**, 197, 2005.
- [13] Kovalev, Yu. S. *et al.*, The microstructure of Pb–K liquid alloy from small-angle neutron scattering experiments. *Journal of Non-Crystalline Solids*, **353**, 3532, 2007.
- [14] Meijer, J.A., Geertsma, W. & van der Lugt, W., Electrical resistivities of liquid alkali-lead and alkali-indium alloys. *J. Phys. F, Met. Phys.*, **15**, 899, 1985.



- [15] Blagoveshchenskii, N.M. *et al.*, Microscopic Structure of Liquid Lead–Potassium Alloys: Neutron–Diffraction and Molecular Dynamics Investigation. *Physica B: Condens. Matter*, **364**, 255, 2005.
- [16] Bernal, J.D., The Structure of Liquids. *Proc. R. Soc.*, **280A**, 299, 1964.
- [17] Kolokol, A.S. & Shimkevich, A.L., Topological structure of density fluctuations in condensed matter. *J. Non-Crystal. Solids*, **356**, 220, 2010.
- [18] Grube, G. & Schmidt, A., The Na–Tl phase diagram. *Z. Elektrochem.*, **42**, 201, 1936.
- [19] Wikipedia: <http://en.wikipedia.org/wiki/Thallium>.
- [20] *Tables of physical constants*, Handbook edited by I.K. Kikoin, AtomIzdat: Moscow, 1976.
- [21] Nayeb-Hashemi, A.A. & Clark, J.B., The Mg–Pb system. *Bulletin of Alloy Phase Diagrams*, **6(1)**, 56, 1985.

