ATLANTIS PRESS

Advances in Engineering Research, volume 177

International Symposium on Engineering and Earth Sciences (ISEES 2018)

Surface Properties of Lead and Zinc Alloys

Kutuev R.A.
Department of physics and mathematics researches
Complex Research Institute of the RAS named Kh.I. Ibragimov
Chechen State University
Grozny, Russia
kra-07@mail.ru

***Abstract*—This paper presents results of experimental studies on temperature dependence of surface tension, lead alloy density, bismuth lead wetting angles for ferritic martensitic and high-nickel steels, surface tension polytherms, zinc-aluminum-molybdenum-magnesium system (Serbian bronze) density and wettability of Serbian bronze surface with copper, aluminum, steel.**

Keywords— surface tension, density, polytherms, wettability, wetting angle.

I. Introduction

Studies on surface properties of metal alloys are more and more relevant due to the need for optimization of such important technologies as tinning and soldering, casting, metallization, production of new alloys and composite materials, development of liquid metal coolants for high-energy installations. Among these alloys, one can mention lead-bismuth and zinc alloys. For example, bismuth lead and lead-bismuth eutectics are used for producing coolants. Zinc alloys (Zn-0.56 wt.% Al-0.6 wt.% Mo-0.25 wt.% Mg –Serbian bronze) have a whole combination of properties. They can be used as metal-anodes of electric batteries, new hybrid materials: foams, metal-matrix composites, thin foils, bimetals [1]. Alloys of the near-eutectic composition Zn-0.2 wt.% Al are used as an anti-corrosion coating for steel plates [2, 3].

Wetting of solid alloys with liquid zinc and its alloys is important for producing powdered hard alloys using production wastes.

The data on the temperature dependence of surface tension and density of lead alloys (Pb-Bi, Pb-Ca, Pb-Ni, Pb-Na) are of great importance for development of heavy coolants of high-energy units.

Surface properties of the lead-bismuth system have been thoroughly studied; however, wetting of new reactor steels with bismuth lead has not been studied yet. Polytherms of density and surface tension of the alloy Zn-0.56 wt.% Al-0.6 wt.% Mo-0.25 wt.% Mg have never been studied as well.

II. Methods and Materials

Temperature dependence of wetting angles and surface tension for Pb-10.6 wt.% Bi, Zn-0.56 wt.% Al-0.6 wt.% Mo-0.25 wt.% Mg, Pb-Ca, Pb-Ni, Pb-Na melts were studied in a high-temperature unit using the sessile drop method at a PN measuring error of 1%, and wetting angle of less than 2%.

X-ray phase analysis, atomic force and electron microscopy were used to solve the task. A melt drop was formed in a graphite cup (made from MG fine-grained graphite). To eliminate oxide films, the alloy was fed into the graphite cup through a capillary.

Samples of Pb-Ca, Pb-Bi alloys were produced by the Institute of Low-Temperature Physics and Technology n.a. B.I. Verkin of the NAS of Ukraine (Kharkiv).

The alloys of bismuth lead and Zn-0,56 wt.% Al-0.6 wt.% Mo-0.25 wt.% Mg were produced by the Electrozink plant (Vladikavkaz). The structure of the alloy was monitored using an ARL-ADXP-2353 X-ray fluorescence spectrograph. Other alloys were produced using metals of high purity by the author.

The profile of the liquid drop was photographed using a digital camera with a matrix of 14.1 megapixels. The time interval between shots was 5 minutes.

To determine geometric parameters of the drop, automated software was used [4]. The droplet contour was processed in CorelDraw when measuring the wetting angle, and by numerical integration of the Young–Laplace equation when measuring the surface tension.

Along with the sessile drop method used to determine the wetting angle, a new approach for measuring the wetting angle by geometrical parameters of the drop photo was used. The approach was implemented using the ImageJ application freely distributed by the Swiss Federal Institute of Technology (network address: bigwww.epfl.ch / demo / dropanalysis).

When studying the angles of bismuth lead wetting of reactor steels, we used steel covers for fuel assemblies and fuel rods of reactors (fast neutrons) from which supports 15 × 15 mm in dimension and 0.4-0.5 mm in thickness were produced. Their surfaces were previously polished and washed with alcohol and distilled water.

The structural composition of the support surface before and after melt wetting was studied using a PHENOM G2 Pure scanning electron microscope which helps produce images with magnification of up to 15.000 times (20 nm in size) and a SOLVER NEXT atomic force microscope.

III. Results

The influence of small additions of alkaline earth and alkali elements on the lead tension surface has not been studied yet [5]. We tried to study PN-polytherms of lead-calcium melts.

The density values in the Pb-Ca system are described by the linear dependence (Figure 1).

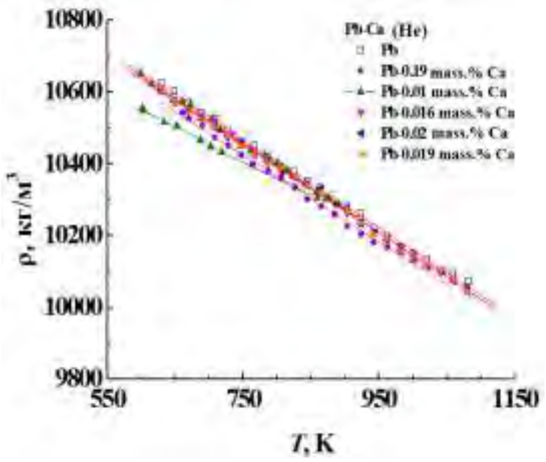

Fig. 1. Polytherms of lead-calcium melt density.

Fig. 2 presents the results of measurements of the surface tension (PN) of the Pb–Ca system. The PN temperature coefficient for pure lead is $d\sigma/dT < 0$. Fig. 2 shows that small calcium additives change the PN temperature coefficient: $d\sigma/dT > 0$. Different courses of PN polymers can be explained using the Popel and Pavlov equations.

Thus, our data identified the temperature posing action in the Pb – Ca system [6].

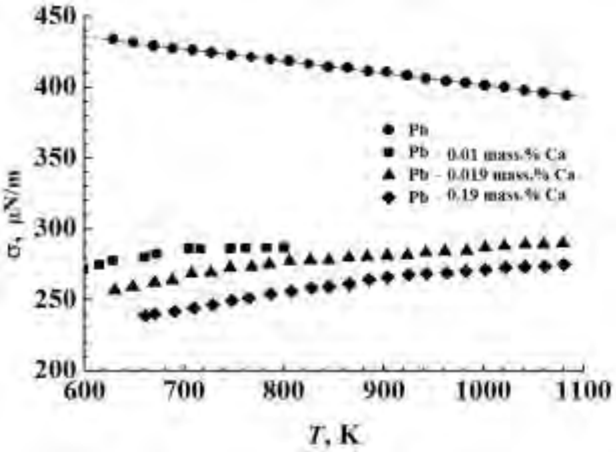

Fig. 2. Polytherms PN in Pb-Ca.

Surface properties of liquid alloys of the Pb-Ni system have not been studied yet. Poor solubility of solid nickel in lead (solubility limit of 0.68 wt% Ni at 600 K) is used to form composite solders [7].

Measurements results for the PN temperature dependence are presented in Fig. 3 as PN polytherms. Fig. 3 – temperature dependence of the liquid melt Pb–Ni. Nonlinearity of the Pb-Ni polytherm systems can be explained using the Gibbs adsorption equation:

$$d\sigma + s^{\omega} dT + \sum_i \Gamma_i d\mu_i = 0$$

s^{ω} – the excessive specific entropy (surface unit formation entropy), Γ_i, μ_i – adsorption and chemical potential of the *i*-th component.

For pure metal, the polytherm σ is described by the straight line with a negative temperature coefficient. With a rising temperature, PN falls. In this case, $s^{\omega} = - d\sigma/dT$. Since $s^{\omega}>0$ at $d\sigma/dT<0$, surface formation is accompanied by an increase in entropy.

For the lead-nickel alloy, we can see that with an increase in the surface layer temperature, concentrations of components with higher nickel surface tension increase. As a result, σ of the whole system should increase. However, with an increasing temperature, σ should decrease. Non-linearity of polytherms σ in these alloys explains adjustments of these two mutually exclusive factors.

Lead-sodium melts can be applied as promising coolants for fast-neutron nuclear reactors. However, many thermodynamic properties of the Pb–Na system have not been studied yet. For example, a gradual increase in sodium in lead improves wetting of some steels, but increases fire hazards. To control these processes, surface properties have to be studied. Therefore, it is crucial to obtain reliable data on surface properties for this system.

Fig. 4 and 5 show measurements results. As is seen, an increase in temperatures decreases density and PN. This decrease can be expressed by the linear dependence with a negative temperature coefficient.

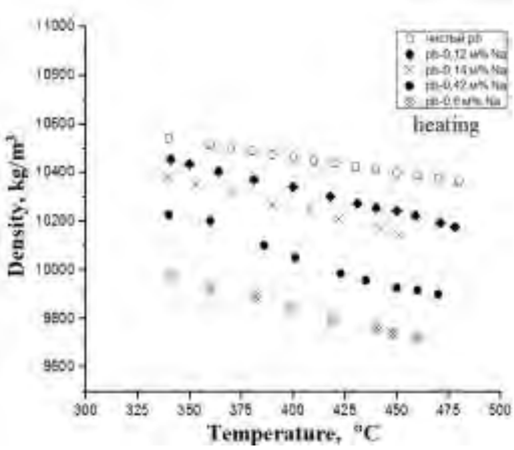

Fig. 4. Polytherms of Pb-Na melt density at different concentration values when heating.

Due to their practical significance, the lead-bismuth system and its eutectic have been studied by a lot of researchers [8–15]. We studied the density and PN of the Pb-Bi eutectic using the sessile drop method and measurement techniques based on modern information technologies. The results of photo measurements are shown in Fig. 6, 7. As is seen, with an increasing temperature, density and PN decrease.

Fig. 6 and 7 show that temperature coefficients $d\rho/dT$ and $d\sigma/dT$ are close to the recommended ones.

The results of bismuth lead measurements (Pb-10.6 wt.% Bi) (Fig. 8, 9) are shown. Bismuth lead can be used as a coolant for atomic reactors.

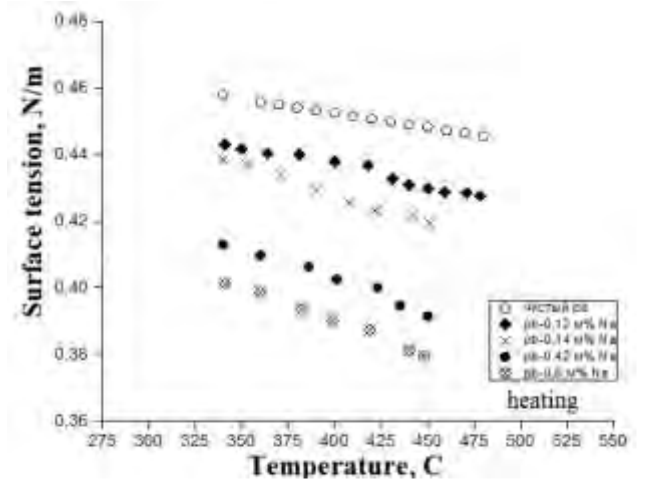

Fig. 5. Politherms of surface tension of Pb-Na melt at different concentration values when heating.

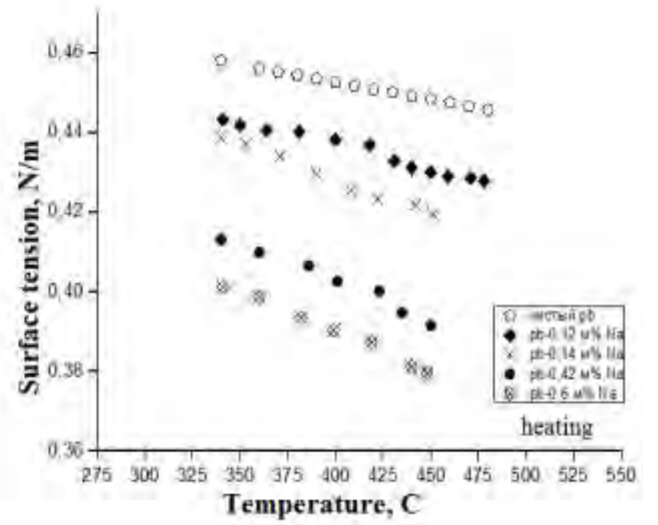

Fig. 6. Density of liquid Pb–Bi alloys: 1 – Pb, 2 – $(Pb\text{-}Bi)_{ЭВТ}$, 3 – Bi. Dotted line – recommended data [8].

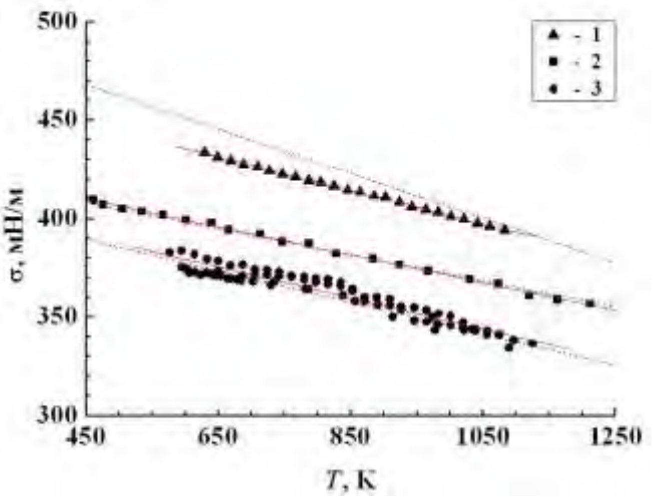

Fig. 7. Liquid Pb–Bi alloy PN: 1 – Pb, 2 – $(Pb\text{-}Bi)_{ЭВТ}$, 3 – Bi [author's data]. Dotted line – recommended data [8].

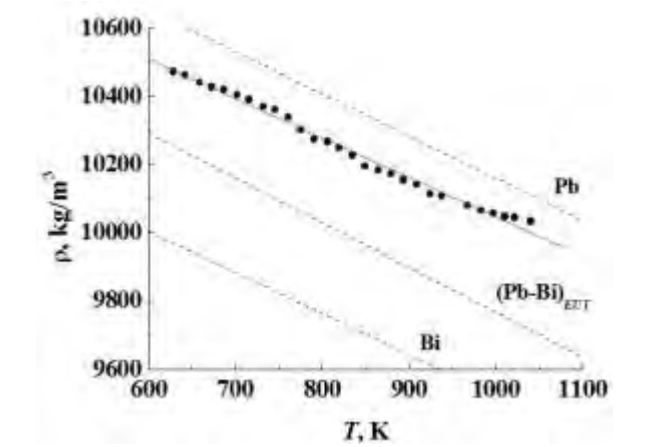

Fig. 8. Temperature dependence of bismuth lead density (the dotted line shows density dependences for Pb, Bi and $(Pb\text{–}Bi)_{ЭВТ}$) [8].

Fig. 8 and 9 show that the values of $d\rho/dT$ and $d\sigma/dT$ are close to the similar values for the eutectic alloy. The density of bismuth lead is lower than the density of pure lead, and the surface tension is close to the value of σ for pure lead.

The research results for the angle of Pb-Bi melt wetting of new high-nickel and ferritic-martensitic reactor steels (EC and EP classes) show that various alloy additives change the wetting angle ỿ(Fig. 10) [16].

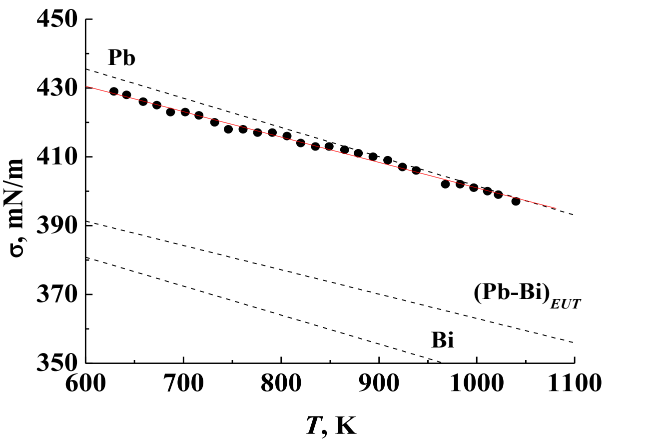

Fig. 9. Temperature dependence for surface bismuth lead tension (the dotted line shows recommended data for Pb, Bi and $(Pb\text{–}Bi)_{ЭВТ}$)[8].

For EK-181, EK-450 steel support, wetting thresholds are observed at a temperature of ~ 1000 K. For EP-753A steel supports, in the temperature range of 900-1000 K, a significant decrease in the wetting angle is also observed. This temperature dependence of the wetting angle might be due to destruction of chromium oxide films at temperatures above 900 K.

For EK-173 and EP-753TyuR steel supports, wetting thresholds are not observed. This might be due to higher concentrations of aluminum which, being adsorbed on the steel surface, creates stable protective anti-corrosion film.

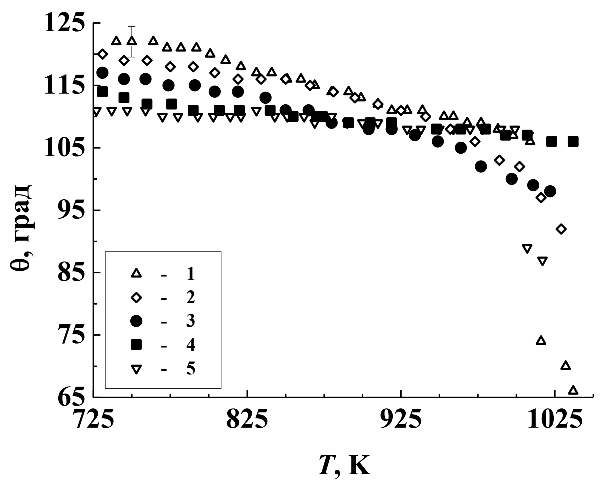

Fig. 10. Politherms of the angle of steel support wetting with bismuth zinc: EK-181 (1), EP-753A (2), EK-173 (3), EP-753TYR (4) and EK-450 (5).

Intensification of anticorrosive properties of steels containing aluminum was found in earlier experiments with pure Pb, Bi [17] and purified eutectic Pb-Bi. At high temperatures (when the need for oxygen increases), the droplet substance “pulls” oxygen out of the support where Fe_3O_4 is the weakest link.

Figure 11 shows the results of experimental determination of density and PN of the Zn-0.56 wt.% Al – 0.6 wt.% Mo – 0.25 wt.% Mg alloy by a large droplet method in a graphite cup in helium at temperatures varying from the melting point to ~ 950 K. For comparison, Fig. 11 shows literature data on the density and PN of pure aluminum and zinc. The density of the alloys decreases with temperature in the heating mode.

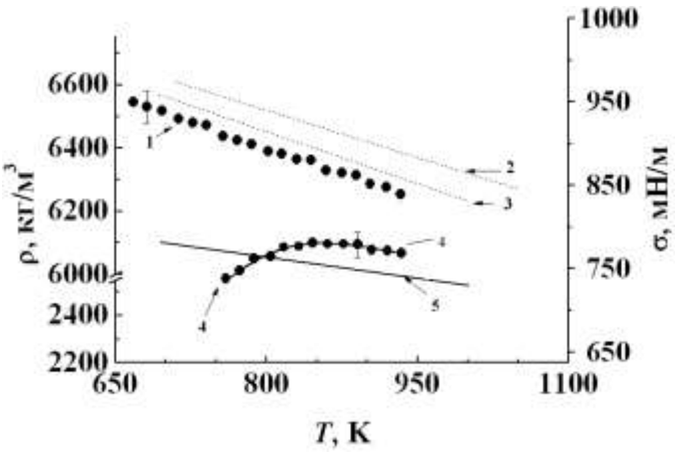

Fig. 11. Polytherms with density of: 1 – of Zn-0.56 mass% Al-0,6mass % Mo-0,25mass %Mg 2, 3 – pure zinc [8]. Pytherms of tension surface of: 4 – Zn-0,56mass% Al-0,6mass % Mo-0,25mass%Mg and 5 – pure zinc [8].

The PN temperature dependence is characterized by the weak dome on the polytherm. The nature of this extremum has not been identified yet. This might be due to formation and destruction of oxide films on the alloy surface. Let us present experimental data on the temperature dependence of the angle of wetting of aluminum, copper, and 12X18H9T steel with zinc and Serbian bronze.

Polytherms of wetting angles were studied by the sessile drop method using modern information technology. Hard alloy supports were pressed from WC + Co powder at a pressure of 107 Pa, with a diameter of 10 mm and a height of 3-5 mm using a SirioP400 hydraulic press.

The polyterm of zinc wetting angles is a straight line. The angles of wetting of the WC + Co alloy with Serbian bronze are lower than zinc wetting angles. In addition, dependence θ (t) is nonlinear in the range from the melting point to 600°C. It is followed by a falling branch. This nonlinear dependence is related to the nonlinear PN temperature dependence. The results of measurements of Serbian bronze wetting angles are shown in Fig. 12. As is seen, if the temperature value is lower than 813K the melt does not wet copper: θ>90°. Then, at T>813K, the wetting angle decreseas sharply to θ → 10–15°. When Serbian bronze is spreading over the copper substrate, intermetallic compounds are formed. They can be identified when studying the morphology of the spreading area using a scanning electron microscopy.

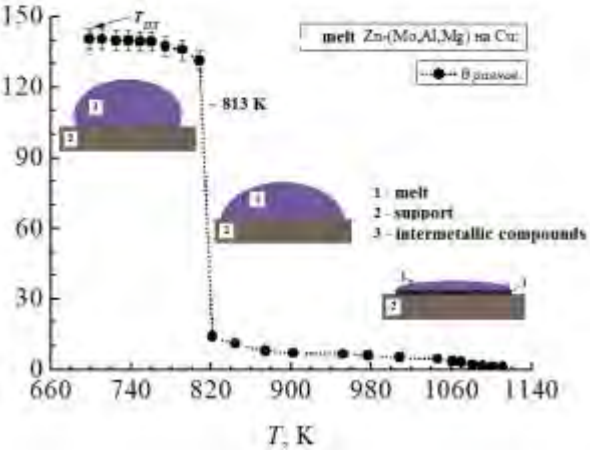

Fig. 12. Temperature dependence of the contact angle of Zn-0.56 mass% Al-0.6 mass% Mo-0.25 mass% Mg wetting of copper.

Fig. 13 shows the temperature dependence of the contact Zn-0.56 wt.% Al-0.6 mol. Mo-0.25 wt.% Mg melt wetting angle for the 12Kh18N9T stainless steel surface. Fig. 15, 16 show the drop after spreading (top view) and morphology structures in zone 3. Fig. 18 shows that angle θ at temperatures varying from the melting point of Serbian bronze to 1050 K changes slightly: it decreases by 15 degrees (from 141 ° to 124 °) for 350 degrees Kelvin, i.e. there is no significant interaction between the melt and the support. However, immediately after the temperature of 1050K, there is a sharp drop in the wetting angle (up to 80 °) and the melt spreads over the support. This change is due to destruction of oxide formations, both on the support surface and melt drop.

At higher temperatures, the wetting angle decreases, the melt covers the support. It has been revealed that spherical microphases are formed under the film of Serbian bronze. Since thermodynamic affinity of aluminum to iron is higher than to zinc, interaction of the Zn-0.56 wt.% Al-0.6 wt.% Mo-0.25 wt.% Mg melt and iron forms Fe_2Al_5 and $FeAl_3$ compounds which break the solder film.

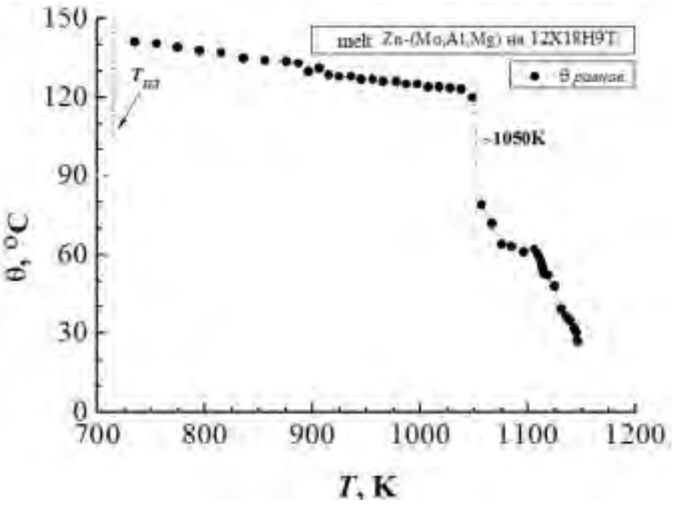

Fig.13. Temperature dependence of the contact angle of 12X18H9T steel wetting with melt of Zn-0.56 mass.% Al-0.6 mass.% Mo-0.25 mass.% Mg.

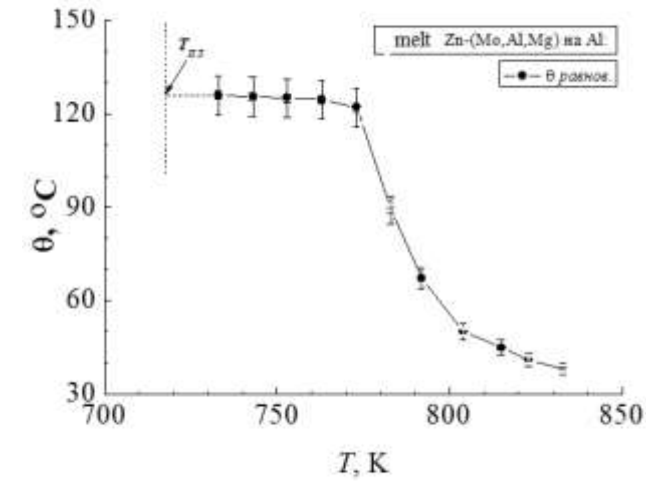

Fig. 14. Temperature dependence of the contact angle of Zn-0.56 mass% Al-0.6 mass% Mo-0.25 mass% Mg of aluminum.

Fig. 14 shows the polytherm of the Serbian bronze wetting angle for aluminum. As is seen, when the droplet is heated to a temperature of 770 K there is no wetting, and at temperatures above 780 K Serbian bronze wets aluminum.

Unlike copper and 12X18H9T steel, when the detected wetting threshold is clearly pronounced, aluminum wetting occurs in the temperature range of 770-850K. After Serbian bronze has been spread over the aluminum surface, lamellar phases are formed on the aluminum support.

IV. Conclusion

The article studies polytherms of density and surface tension of lead combined with 10,59 wt.%, bismuth (bismuth lead) and polyterms of angles of bismuth lead wetting of new reactor steels (EK-173, EK-181, EK-450, EP-753A and EP-753TyuR) in a wide range of temperatures (up to 1050 K). It was shown that both density and surface tension decrease linearly with a temperature. It was identified that at temperatures below 900-1000 K, the supports are not wetted with bismuth lead. Supports containing aluminum additives are not wetted with bismuth lead even at temperatures above 1000 K.

The article presents the results of experimental studies on wetting of copper, 12X18H9T steel and aluminum surfaces with Zn-0.56 wt.% Al-0.5 wt.% Mo-0.25 wt.% Mg and morphology of phases formed by spreading. On copper and stainless steel wetting angle polymers, sharp wetting thresholds were found at temperatures of 813K and 1050K respectively. For the aluminum support, transition from non-wetting to wetting occurs at temperatures varying from 770L to 850K. Wetting thresholds are due to destruction of oxides on the support surface and Serbian bronze drop. In the "melt - copper" system, crystalline formations (of about 2 microns) were found. In the "melt – steel 12X18H9T" system, granular formations of spherical shape were found; in the "melt - aluminum" system, lamellar structures were found.

References

[1] V.V. Lozenko, V.G. Shepelevich, "Structure and mechanical properties of rapidly solidified foils of Zn-Al alloys", The physics of metals and metallography, vol.107, No.4, pp. 70-374, 2009.

[2] Srinivasan, S. Selective surface oxidation and segregation upon short term annealing of model alloys and industrial steel grades. Dissertation … Doktor der Naturwissenschaften, Fakultat fur Physik und Astronomie der Ruhr-Universitat Bochum, 136 p, 2007.

[3] T. Radu, A. Ciocan, F. Potecasu, L. Balint, "Obtaining and characterizing Zn-Al-Bi coatings on steel band", Proceedings of the International Conference METAL-2012, pp. 1-623, Brno, Czech Republic, 2012.

[4] L. B. Director, A. Z. Kashezhev, I. L. Maikov, A. G. Mozgovoy, M. Kh. Ponezhev, V. A. Sozaev, "Computing complex for determining thermophysical properties of liquids", Abstracts of the Interdepartmental Seminar "Technology of alkaline liquid metal coolants", pp. 46-47, Obninsk, October 28-30, 2009.

[5] A.Z. Kashezhev, R.A. Kutuev, M.Kh. Ponezhev, V.A. Sozaev, "The Effect of Alkali and Alkaline-Earth Elements on the Surface Tension of Lead, Tin, and Indium", Melt, No 5, pp. 66-77, 2013.

[6] A.Z. Kashezhev, R.A. Kutuev, M.Kh. Ponezhev, V.A. Sozaev, A.I. Khasanov, "Polyterms of density and surface tension of lead-based alloys", News of the Russian Academy of Sciences. Physical series, vol. 76, No. 6, pp. 881-883, 2012.

[7] M.M. Gubzhokov, Kh.I. Ibragimov, V.Z. Kanchukoev, M.Kh. Ponezhev, V.A. Sozaev, A.B. Sozaeva, A.I. Khasanov, "Influence of small impurities on the surface tension of lead , "Melts, No. 3, pp. 76-79, 2006.

[8] Handbook on lead-bismuth eutectic alloy and lead properties, materials compatibility, thermal-hydraulics and technologies. Nuclear science, ISBN 978-92-64-99002-9. OECD/NEA Nuclear Science Committee. Nuclear energy agency. Organization for economic co-operation and development. NEA no. 6195, OECD 2007.

[9] Yu. Plevachuk, V. Sklyarchuk, S. Eckert, G. Gerbeth, "Some physical data of the near eutectic Liquid lead-bismuth", Journal of Nuclear Materials, vol. 373, pp. 335-342, 2008.

[10] O.E. Awe, Y.A. Odusote, O. Akinlade, L.A. Hussain, "Energetics of mixing in Bi-Pb and Sb-Sn liquid alloys", Phisica, vol. 403, pp. 2732-2739, 2008.

[11] V.P. Sobolev, "Thermophysical properties of lead and lead-bismuth eutectic", Journal of Nuclear Materials, vol. 362, pp. 235-247, 2007.

[12] V.P. Sobolev, "Thermodinamic properties and equation of state of liquid lead and lead-bismuth eutectic", Journal of Nuclear Materials, vol. 376, pp. 358-362, 2008.

[13] B.B. Alchagirov, A.M. Chochaeva, A.G. Mozgovoy, M.N. Arnoldov, V.B. Bekulov, H.B. Khokonov, "Surface tension of liquid near-eutectic

alloys of the lead-bismuth system", TVT, vol. 41, No. 6, pp. 852-859, 2003.

[14] B.B. Alchagirov, T.M. Shamparov, A.G. Mozgovoy "Experimental study on the density of a dilute lead-bismuth eutectic", TVT, vol. 41, No. 12, pp. 247-253, 2003.

[15] G. Benamati, A. Gessi, "Corrosion behavior of steels and refractory metals in flowing lead – bismuth eutectic at low oxygen activity", Journal of materials science, vol. 40, pp. 2465-2470, 2005.

[16] D.A. Kambolov, A.Z. Kashezhev, R.A. Kutuev, M.Kh. Ponezhev, V.A. Sozaev, A.Kh. Shermetov. "Wetting of high-nickel and ferritic-martensitic steels with bismuth lead", News of the Russian Academy of Sciences. Physical series, vol.76, No 13, pp. 59-61, 2012.

[17] A.Z. Kashezhev, M.Kh. Ponezhev, A.G. Mozgovoy, V.A. Sozaev, A.I. Khasanov, "Experimental study on the wetting of reactor steels by molten lead and bismuth", Thermal Physics of High Temperatures, vol. 48, No. 5, pp. 1-4, 2010.