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Wetting and spreading phenomena in liquid bismuth-alkali halide systems

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This investigation is devoted to the study of the features of wetting phenomena in high temperature systems that are promising as environments for processing and disposal of man-made and radioactive wastes. New data on the phase wetting transition in two-phase liquid media have been obtained by analyzing the values of the adhesion of salt melts to liquid metals. The present study is focused on the systems composed of molten alkali halides and liquid bismuth. Their adhesion was calculated using experimental data on the surface tension of metals and salts, as well as the interfacial tension between metals and salts. A regular change in the adhesion work is illustrated depending on the temperature, electrical potential and nature of the contact phases. The transition phenomenon from incomplete wetting to full wetting has been established. It is shown that this transition is facilitated by an increase in temperature, a potential jump in the phase contact plane, and the polarizability of salt phase ions. The potential dependence of the adhesion work near the wetting transition point is described by a power equation with a critical index equal to 1.1.

keywords: wetting transition, adhesion, liquid bismuth, alkali halide melts

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1. Introduction

A liquid metal – ionic salt melt interface has long attracted the attention of scientists and technologists, since the processes that proceed there have a great impact on the number of technological parameters. It is enough to mention the multi-tonnage production of magnesium, calcium, aluminium and alkali metals by electrolysis of molten salts [1]. In recent years, this interest has become even more acute due to increased demands for the technological characteristics of materials, solving environmental problems, and creating new knowledge-intensive industries. Thus, based on the results of studying the behavior of aluminium in oxide-fluoride melts, it has been shown that it is possible to develop an energy-efficient electrochemical method for producing aluminium master alloys with silicon, zirconium, scandium and boron [2], necessary for modern metallurgy. By processing aluminium and its alloys under a layer of molten salts, composites consisting of a metal matrix and graphene were synthesized [3, 4]. As it turned out, the resulting composites demonstrate increased (2.5 times) hardness and elastic limit (2 times) compared to the starting metal. Modern society is increasingly concerned about the uncontrolled spraying of harmful and hazardous waste into the environment. Therefore, technologies for the disposal and processing of industrial waste are becoming more and more in demand. Certain prospects in this direction have, for example, technologies for processing lead waste in molten salt media with the return of new lead-containing materials into technological circulation [5, 6]. Liquid metal-salt systems can be very useful in solving the problems of nuclear energy related to the operation of promising fast neutron reactors. Anhydrous methods of its regeneration with the extraction of actinoids and transuranic elements using thermally and radiation-resistant salt and metal melts are

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being developed for accelerated processing of highly irradiated nuclear fuel [7–9]. These systems demonstrate a very impressive effect of element's separation. Thus, the separation coefficient of uranium and lanthanum in LiCl + KCl melts on bismuth was found to be equal to 400, on lead – to 770 [7], whereas the metal phase was enriched with uranium. An even greater separation coefficient (more than 30.000) was obtained for dysprosium and uranium on gallium in an eutectic melt of lithium and potassium chlorides [8].

The processes listed above and those similar to them are based on the transfer of substances across the liquid metal – molten salt interface. The flows of substances have a significant disturbing effect on the stability of the interface. In particular, interface convection occurs, which manifests itself in the appearance of dissipative structures in the form of sufficiently stable circulation cells, for example [10, 11]. The marked interface convection is caused by the Marangoni effect, which is a response of the system to a local change in interface energy, caused particularly by the uneven distribution of flows over the contact area of the phases. The gradient of interface energy is the driving force that unbalances the system and contributes to its destruction. In order to prevent or rationalize the phenomenon of interface convection, it is necessary to study the fundamental properties of the liquid metal - molten salt interfaces. In particular, information is needed on the influence of physicochemical parameters on the wettability of the metal surface by the molten salt, on the nature and degree of the phase interaction, as well as on the impact of external factors (temperature, electric potential) on the energy of the interface. Such information can be scarcely found in the scientific literature.

The presented work is devoted to the study of adhesion between liquid metal and molten salts as a function of temperature, electrical potential, and composition of the salt phase. Alkali halides being the basic compound of the most widely used electrolytes, and liquid bismuth, being a promising active electrode for pyroelectrochemical technology of spent nuclear fuel processing.

2. Materials and methods

When two phases are in contact with each other, there is an interface between them with a certain interfacial energy, σ. The thermodynamic work of adhesion is defined as a work required to separate unit area of two adjacent phases from each other. When the two phases are separated, this interface disappears but two new interfaces (metal – gas and salt – gas) are formed. They are characterized by the surface energies of the metal σ_M and the salt σ_S. The work required to separate these phases is work of adhesion and it is described by Dupré as: $W = \sigma_M + \sigma_S - \sigma$. In essence, the adhesion work characterizes the mutual affinity of the coexisting liquid phases: the greater it is, the more likely it is that components move from one phase to another.

To date, there is no direct method for measuring the energy of separation of one liquid phase from another. Therefore, so far the only way to determine the work of adhesion is to calculate it according to the above Dupré equation using experimental values of σ_M, σ_S and σ. The surface tension of liquid bismuth was measured by the large drop method with an uncertainty of 1 mJ/m^2 [12]. The surface tension of molten alkali halides was found by the method of maximum pressure in an argon bubble formed at the end of a capillary immersed in the melt with an uncertainty of 0.1 mJ/m^2 [13]. The values of the interfacial tension of bismuth in alkali chloride, bromide, and iodide melts were found with an uncertainty of 0.2 mJ/m^2 by measuring the pressure difference over the metal-salt interfaces located in the knees of the communicating vessel with different cross-sections [14–20]. The uncertainty in determining the adhesion work is estimated as the sum of the uncertainties of each of the properties and amounts to 1.3 mJ/m^2.

3. Results and Discussion

3.1. Adhesion of the phases

Figure 1 presents the dependences of the adhesion work, *W*, on temperature, *T*, for the two-phase systems studied at a zero charge potential (zcp).

For them, in all cases, a decrease in the adhesive interaction of phases was found when the temperature increased. At first glance, this seems strange, since the mutual solubility of the phase components should increase

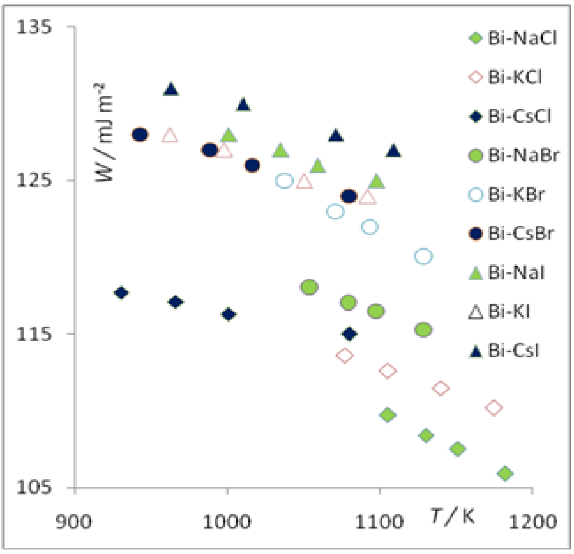

Figure 1 Adhesion work between liquid Bi and molten sodium, potassium and cesium halides vs. the temperature at the zero charge potential (zcp) of metal.

as the temperature increases, which is supposed to be accompanied by an increase in adhesion. On the other hand, however, according to the fundamental concepts of the interparticle interaction, the binding energy of particles is inversely proportional to the distance between them up to the degree from 1 to 8, depending on the nature of the interaction [21]. It is clear that the intensification of the particles thermal motion at the temperature increase should lead to an increase in the distance and, consequently, to a decrease in the energy of interaction between them both in the volumes of the phases and at their interfaces. It is possible that the considerable distance of the experimental temperature from the phase mixing temperature makes the temperature sensitivity of the interparticle interaction energy a decisive factor determining the adhesion of phases in liquid uncharged metal/molten salt systems.

The parameters of the components of the metal-salt melt systems also have a significant impact on the processes behavior at the interface. This is confirmed by the graphs illustrated in Figure 2, where the values of the phase adhesion at 1100 K are postponed relative to the polarizability of the salt phase cation. It should be emphasized that the adhesion values indicated in Figure 2 refer to a metal at zero charge potential when there are no Gibbs surpluses of metal ions and electrons at its surface. This circumstance gives reason to believe that the phase interaction is carried out mainly due to the van der Waals attraction of the induced dipoles resulting from the mutual polarization of metal particles with polarizability α_M and salt with polarizability α_S near the surface. In the first approximation, the energy of this attraction can be taken proportional to the product of the specified polarizabilities, then $W = -k\alpha_M\alpha_S$ [22], where k is the proportionality coefficient. The validity of this ratio is confirmed by the graphs in Figure 2. Here, the adhesion work values are plotted relative to the polarizability of the salt, accepted equal to the sum of the polarizabilities of the ions included in its composition [23]. It can be seen that adhesion increases as the polarizabilities of both the cation and the anion in the salt phase increase.

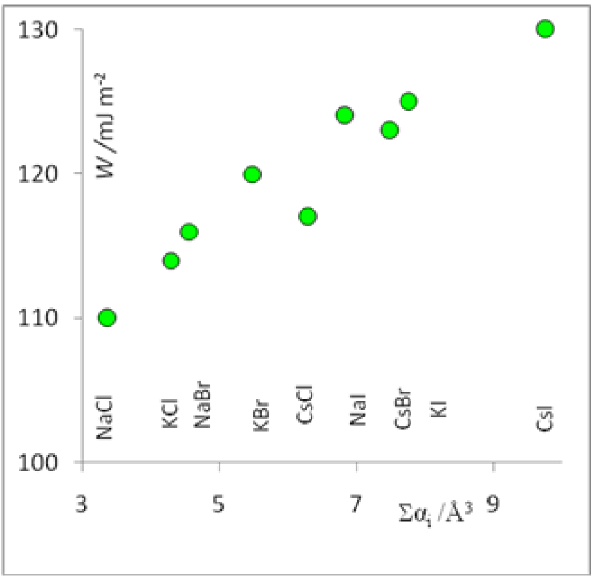

Figure 2 Adhesion work between liquid Bi and molten sodium, potassium and cesium halides vs. the polarizability of salts at 1100 K.

3.2. Partial and complete wetting of the uncharged metal surface

From a theoretical point of view, the problem of wetting a certain surface with a liquid is of interest [22]. In relation to the objects studied in the work, we are talking about the shape of a salt drop on the surface of a liquid metal. The equilibrium of such a system is described by the Young equation:

$$0 = \sigma_M - \sigma - \sigma_S \cdot \cos\theta, \qquad (1)$$

where θ is the wetting angle, the value of which in partial wetting conditions is greater than zero. Full wetting is achieved when $\theta = 0$, and then the balance of surface energy values is determined by the spreading index $S = \sigma_M - \sigma - \sigma_S$. The combination of this expression with the Dupré equation gives $S = W - 2\sigma_S$. Under conditions of complete wetting, $S \geq 0$ and then $W \geq 2\sigma_S$, i.e. the adhesion work should be greater or equal to the cohesion work of the liquid salt.

In fact, it turned out that for the vast majority of the studied systems, the adhesion work is less than the cohesion work, which indicates incomplete wetting of the liquid bismuth surface with the studied molten salts

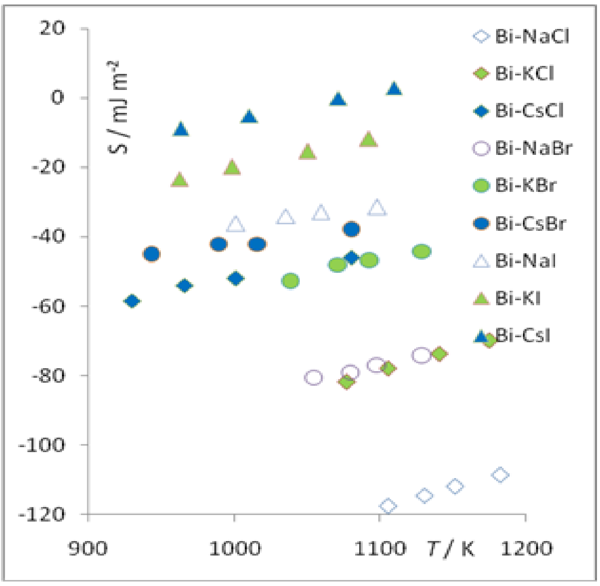

Figure 3 Temperature dependence of the spreading index of molten alkali halides over liquid bismuth.

(Figure 3). Only for the Bi / CsI interface, the transition of temperature from partial to full wetting (1075 K) was recorded, the physical meaning of which is the transformation of a lenticular salt drop to the film. Previously, such a film composed of a heavier liquid on the surface of a light liquid was observed in experiments with methanol solutions and cyclohexane [24]. The analysis of the results obtained by us for high-temperature liquid metal-salt systems leads to the conclusion that the wetting phase transition temperature, T_W, is smaller when the size (polarizability) of the salt phase ion is larger.

3.3. Potential-induced wetting transition

All above arguments are related to metal at a zcp, when there are no excess charges of any sign on its surface. The displacement of the potential relative to the zcp in one direction or another, as experiments show, has a noticeable effect on the surface energy. As an example, Figure 4 shows the dependence of the adhesion work on the electric potential (relative to the lead reference electrode) for liquid bismuth in a sodium chloride melt, taking into account the values of interfacial tension at a fixed potential [25]. Similar dependences were also found for all other systems studied. As can be seen, as the potential is removed from the zcp, the adhesion of the phases increases.

The increment of the adhesion work to that found at the zero charge potential, ΔW, in the first approximation can be taken as proportional to the energy of the electrostatic interaction of charges of the opposite sign in the phase contact zone, U. The Coulomb part of the interaction of particles at the electrode surface can be represented by the equation $U = q^2/D \cdot a$, where q is the charge density per unit area of each plate of the double electric layer, D is the dielectric constant, and a is the distance between the plates of the double layer. At potentials more positive than the zcp, the charge carriers on the metal and salt parts of the double electric layer in the studied systems are potential-induced cations Bi^{n+} on the metal and single – charge anions of the salt phase. The Coulomb interaction energy of this pair is $u = \frac{n^2 \cdot e^2}{D \cdot a}$, where e is the electron charge. The number of such pairs per unit surface is determined by the Gibbs excess of bismuth ions, $\Gamma_{\mathrm{Bi}^{n+}}$, therefore $U = \frac{n^2 \cdot e^2 \cdot \Gamma_{\mathrm{Bi}^{n+}}}{D \cdot a}$. In the anode potential range, $\Gamma_{\mathrm{Bi}^{n+}} > 0$ and increases as the potential exceeds the zcp, whereby the energy of the Coulomb interaction in the double layer increases, which leads to a monotonic increase in the electrode adhesion. In the cathode potential range, the charge carriers in the interphase zone are potential-induced electrons on the metal and cations of the salt phase. The potential shift in the cathode direction relative to the zcp is accompanied by an increase in the Gibbs excess of electrons, Γ_e, which also contributes to an increase in the affinity of the contacting phases. The proposed scheme, as it turned out, correctly conveys the dependence of phase adhesion on experimentally obtained potential values.

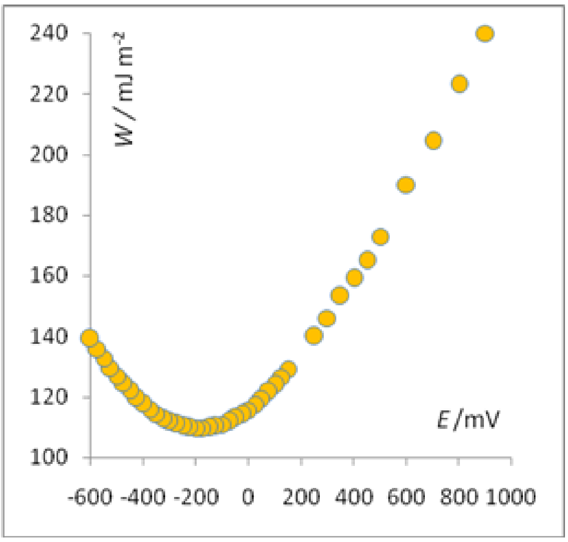

Figure 4 Dependence of the adhesion between liquid bismuth and molten sodium chloride on the electric potential (relative to the lead reference electrode) at 1105 K.

As it turned out, at a small charge density on the metal, the adhesion work does not reach those values that ensure complete wetting of the surface. The picture changes when the anode polarizations of the metal become large. The observation of the Bi/NaCl interface in the capillary showed that the hemispherical shape of the meniscus persists with electrical polarization up to 0.85 V. Above this value, a wedge of metal begins to rise between the salt and the capillary wall, the height of which increases as the anode potential grows. The effect is reversible with respect to the potential: when the voltage decreases, the shape of the meniscus returns to hemispherical, and the interfacial tension coincides within 0.2 mJ/m^2 with the value observed before the potential causing the meniscus distortion. Calculations demonstrated that at a potential of 0.85 V, the adhesion work reached a critical value, W_C, becoming equal to the cohesion work of the salt phase. Thus, this potential can be considered as the critical wetting transition potential, E_C, for a given system at a given temperature.

Having determined the critical values of the adhesion work and potential, it is not difficult to find the nature of the change in the adhesion work near the critical potential. Figure 5 shows the differential dependence between the critical and current adhesion works, $W_C - W$, relative to the difference between the critical and current potentials, $E_C - E$, in logarithmic coordinates. As can be seen, the mentioned dependence is well described by a linear

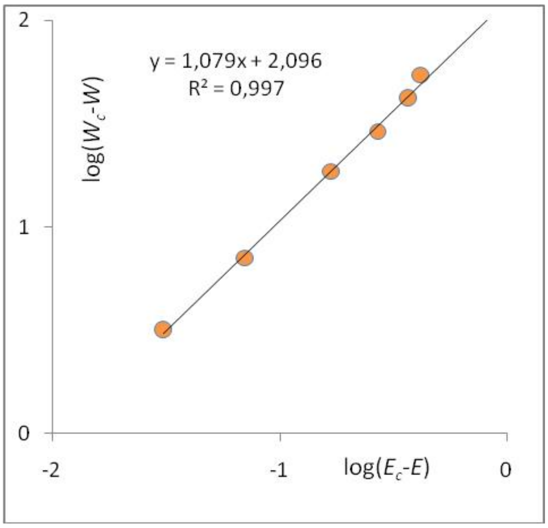

Figure 5 Logarithmic correlation between the adhesion work and the potential near the critical potential of the wetting transition at 1105 K.

equation with a slope equal to 1.1. It can be interpreted as a critical index of the wetting phase transition, which has not been previously discussed in the scientific literature. Additional studies of other similar objects are required to verify the universality of the obtained dependence.

4. Conclusions

The results of the study of the interfacial boundary of liquid bismuth with molten sodium, potassium, and cesium halides revealed the following patterns:

– The adhesion work at the metal zero charge potential decreases linearly with increasing temperature, which may be due to the intensification of the thermal motion of particles against the background of low mutual solubility of the components.

– Adhesion increases with increasing polarizability of the salt ions, which corresponds to the van der Waals type of interaction between salt phase ions and the surface of an uncharged metal.

– In the majority of the studied systems, a partial wettability of the metal surface was observed when the adhesion work was less than the cohesion one of the salt phases.

– A transition from partial to complete wettability of liquid bismuth was detected in cesium iodide at 1075 K.

– The wetting phase transition potential of the Bi/NaCl system is fixed (0.87 V), in the vicinity of which the change in the adhesion work from the potential is described by a power equation with a critical index equal to 1.1.

Supplementary materials

No supplementary materials are available.

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Author contributions

Victor Stepanov:

Conceptualization; Data curation; FormalAnalysis; Investigation; Methodology; Project administration; Supervision; Resources; Software; Validation; Writing – original draft, Review & Editing.

Conflict of interest

The authors declare no conflict of interest.

Additional information

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