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DENSITY AND SURFACE TENSION OF $Sn_{1-x}Bi_x$ MELTS

The surface tension and the density of the $Sn_{1-x}Bi_x$ system with Bi concentrations of 5, 10, and 15 at% have been studied using the lying drop method in a temperature interval of 470–800 K and under a vacuum of 10 Pa. The DROP program is used to obtain experimental values of the studied physical quantities. The addition of bismuth to tin was found to decrease the surface energy of the $Sn_{1-x}Bi_x$ melts. It is also shown that there are linear temperature dependences for the surface tension coefficient and the density of the studied system.

K e y w o r d s: surface tension, density, eutectic melts.

1. Introduction

The interest in the study of the surface properties of metal alloys has considerably grown within a few last decades, which is a result of stricter requirements to those parameters and properties of metal alloys that are responsible for their practical application. This is valid not only for solid but also for liquid surfaces of alloys. The challenging character of such studies follows from the fact that the information about the processes occurring at the interfaces is necessary for both the development of the existing theories in condensed matter physics and the establishment of the physicochemical basis for new technological processes aimed at the creation of modern structural materials, thin-film elements of modern electronics, and other functional systems.

On the other hand, the interest in the study of the surface properties of alloys characterized by the eutectic or near-eutectic concentration is motivated by the necessity of a more detailed information about the relationship between the structures of eutectics in the liquid and solid states, including the amorphous and crystalline ones. This is also confirmed by the fact that near-eutectic alloys, when under other favorable conditions, can be amorphized the best through their ultra-rapid cooling from the liquid state. From the practical point of view, those alloys are of interest for the creation of new ecological solders, functional elements of robotic systems, liquid-metal coolants for nuclear power facilities, matrix materials of liquid magnetic composites, and so forth.

Currently, there exist unique devices and techniques that have been developed to study the surface properties of solids. Unfortunately, most of them cannot always be used to research the properties of materials in the liquid state as well. Therefore, when studying the surface properties of melts, scientists often have to return to traditional methods of their determination such as the measurement of the surface tension coefficient (STC). Then the data obtained are used to determine other properties of the melt, such as the surface layer composition, the adsorption of components, the surface layer thickness, the activities of the melt components in the surface layer, and others.

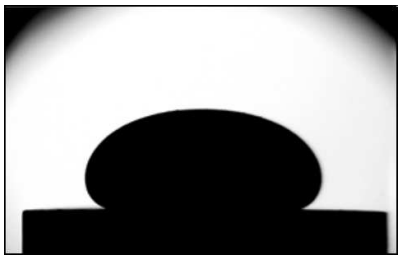

Fig. 1. Digital photo of a melt drop

The measurements of the STC and, especially, its temperature and concentration dependences formed a basis for the methods that are used to determine the thermodynamic properties of the melt surface and for the determination of relationships between the surface structure and the surface properties [1–3]. An analysis of the results obtained while studying the surface tension of metal melts, even the liquid melts of pure metals, by various authors reveals a substantial discrepancy among the experimental STC values and all the more so among their temperature dependences. This is a result of the application of different research methods in those researches and the influence of several other factors, such as the presence of uncontrolled admixtures, the evaporation of the researched substance, the presence of oxides, the influence of the substrate, and so on. It is worth mentioning the levitation method [4–6], a relatively new and interesting technique to measure the surface tension and other structure-sensitive properties. Its main advantages include the lack of contact between the specimen and the substrate, the capability to correct the specimen sphericity, and some others.

Hence, there is a necessity in a further accumulation of experimental data for metal melts both to solve a number of applied problems and to formulate a modern theory of surface phenomena in liquids. A special place is occupied by eutectic alloys based on low-melting-temperature metals. Their melting temperatures at eutectic concentrations are rather low and can be even lower than room temperature. The eutectic systems of this type include the Sn–Bi system with a eutectic concentration of 58 at% Sn and a melting temperature of 412 K. The alloys of this system were studied in the liquid state. The result of those studies concerning the structure and physical properties of the Sn–Bi system were published in works [7–11].

The results of STC measurements for tin, bismuth, and Sn–Bi melts with concentrations of 20, 40, 60, and 80 at% Bi at various temperatures testify to some specific features in their surface properties [10]. In particular, the concentration dependence of the STC shows a negative deviation from the additivity, whereas the concentration dependence of the density demonstrates a positive deviation from the linear dependence. From the analysis of the literature data, it also follows that, despite the structural similarity of liquid tin and bismuth and their low mixing enthalpy, the corresponding concentration dependences of the structural parameters and other physical characteristics are not such as they should be in the case of the statistical distribution of different atoms. Therefore, it was of interest to determine how the addition of a small number of bismuth atoms affects the surface properties of tin. It was the aim of this work. For our research, alloys belonging to the Sn–Bi system with concentrations of 5, 10, and 15 at% Bi were chosen.

2. Experimental Technique

The surface tension and the density of melts were measured on an installation the main elements of which included a vacuum chamber, a molybdenum furnace, a holder for a test specimen, and a lamp to create a shadow image of the drop. A test specimen was arranged on a cylindrical graphite substrate. A light filter was installed behind the output window of a vacuum chamber, which was used to get the photos of the melt drop. The role of the filter was to eliminate the parasitic light reflection of the rays from the molybdenum furnace by the drop. Behind the light filter, a lens with a Canon Power Shot SX130 IS photocamera was rigidly mounted on a special stand. The photocamera was used to get the photos of the melt drop at the maximum optical magnification.

The obtained digital photo was transformed into the tif format with an image size of 669×502 pixels suitable for its processing with the help of the DROP program [12, 13]. The drop image was represented by a brightness distribution function. The latter, after a special transformation, was converted into a set of numbers, the matrix A_{ij}. The problem of finding the radius and height of a molten metal drop was to determine the geometric dimensions of the digital image described by the matrix A_{ij}. Then the melt density ρ was calculated according to the formula

$$\rho = m/V, \tag{1}$$

where m is the specimen mass measured before the experiment, and V is the drop volume determined by the DROP program. Afterward, on the basis of the data obtained for the drop density, the surface tension coefficient was calculated.

A crucial factor of the whole registration system was the component of video camera errors, i.e. the error of image digitization by the matrix photodetector. According to work [13], its maximum absolute value equals $\Delta = 0.5$ pixels.

3. Results and Their Discussion

From the viewpoint of their structural and physical properties, the components of the Sn–Bi system are similar in both the solid and liquid states. The both elements belong to semimetals, and their structures have a lower density of atomic packing than typical metals. In the course of melting, some compaction of the structure takes place, but the structure still remains micro-inhomogeneous in a certain temperature interval. Therefore, it is of interest how such features manifest themselves in the surface tension and density, and how they change, if bismuth is added to tin.

The results of ST measurements for liquid Sn and Bi (see Fig. 2) demonstrate an almost linear decrease in this parameter with the temperature growth. At higher temperatures, however, the ST of bismuth begins to decrease more rapidly than that of tin, i.e. the temperature coefficient of the ST for Bi is larger than for Sn. An assumption can be made that the degree of structural micro-inhomogeneity is a crucial characteristic not only for the melt volume, but also for the surface layers, and that this parameter changes differently for tin and bismuth as the temperature varies. For both elements, their ST dependences on the atomic volume value are well described by almost exponential functions, and the lower ST value for bismuth corresponds to the larger value of its atomic volume. From whence, it follows that bismuth must be a surface-active element with respect to tin.

The temperature dependences of the ST for the $Sn_{1-x}Bi_x$ system with Bi concentrations of 5, 10, and 15 at% are presented in Fig. 3. One can see that the addition of Bi to pure Sn leads to a decrease of the ST for the tin melt. In particular, the addition of 5 at% of bismuth decreases the surface tension coefficient more strongly than the further concentration growth. One

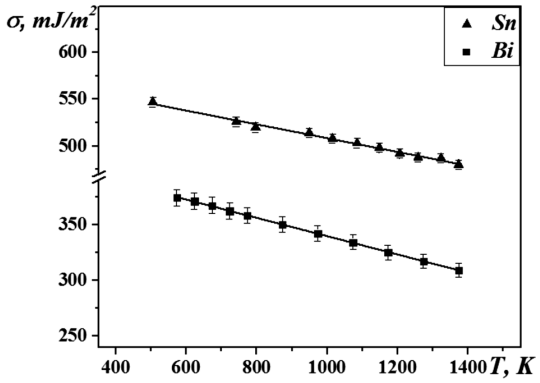

Fig. 2. Surface tension polytherms of Sn and Bi melts

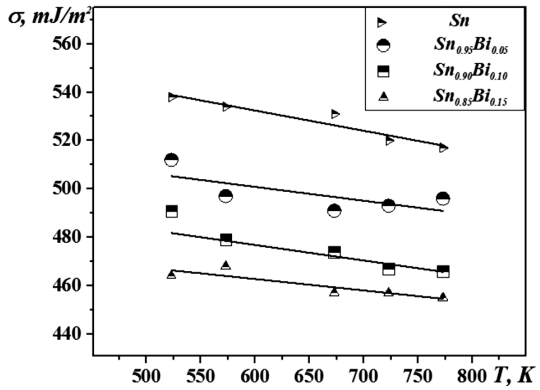

Fig. 3. Surface tension polytherms of $Sn_{1-x}Bi_x$ melts

can also see that a negative deviation from the linear dependence is observed, which is typical of the systems, where the interaction of identical atoms prevails, i.e. for systems with the eutectic or monotectic point.

From the obtained results, it is possible to predict the influence of the component with the lower surface tension on the component with the larger surface tension in binary systems, where the interaction of the atoms belonging to the same kind prevails. From a qualitative graphic analysis (Fig. 4), it follows that, in this case, the indicated regularity has to reveal itself. It can be argued that the larger the difference between the ST values of the binary system components, the more substantial is the reduction of the larger ST value after adding a small amount of the other component.

The results of the $Sn_{1-x}Bi_x$ melt density measurements (Fig. 5) testify to a somewhat different regularity. In particular, the density increases rapidly up

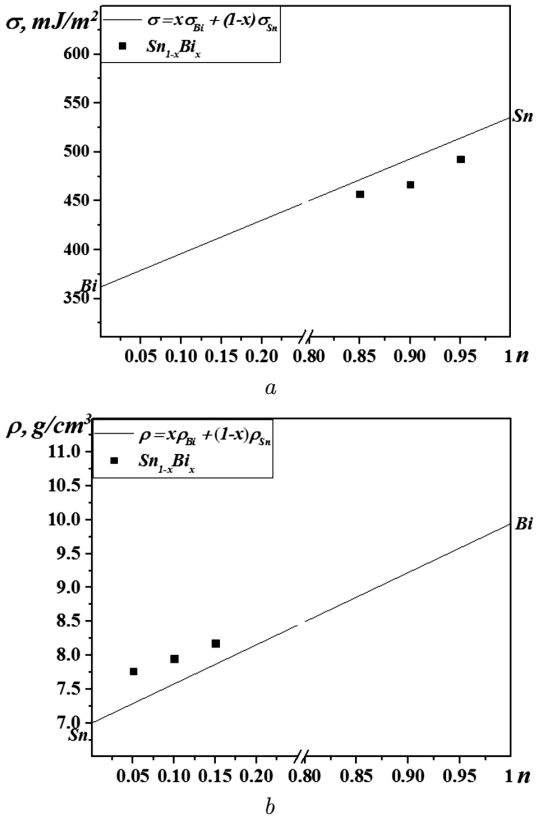

Fig. 4. Qualitative interpretation of the influence of a bismuth admixture on the STC (a) and density (b) of liquid tin

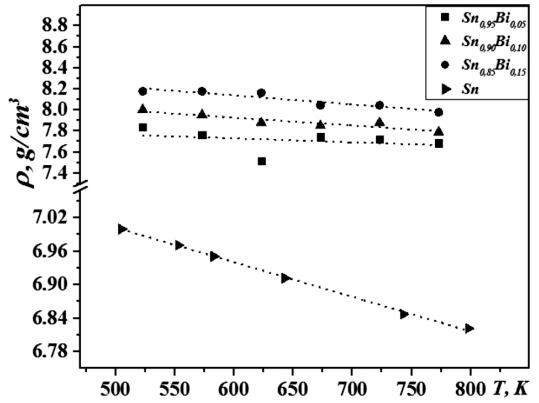

Fig. 5. Temperature dependences of the densities of $Sn_{1-x}Bi_x$ melts for various bismuth concentrations

to a Bi concentration of about 5 at%, but does it a little bit more slowly, if the bismuth content increases further. One can also see that the temperature coefficient of the melt density becomes lower

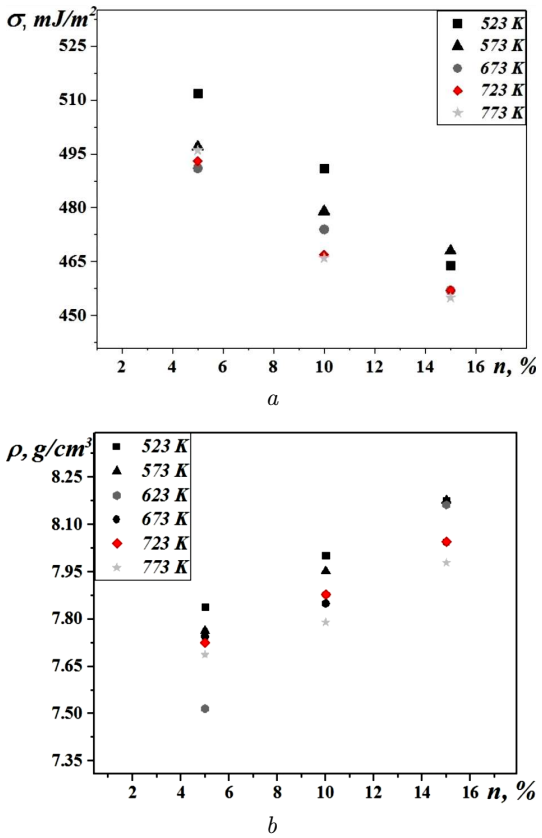

Fig. 6. Concentration dependences of the STC (a) and density (b) for tin-enriched melts of the Sn–Bi system

for larger bismuth concentrations, which may testify that the formation of an atomic solution from the tin and bismuth atoms is accompanied by a reduction of the free volume fraction in the melt, which remains almost constant within a wide temperature interval (and even decreases a little up to a temperature of about 650 K).

The concentration dependences make the influence of bismuth on the surface tension coefficient and density of tin more obvious (Fig. 6). One can see that the concentration dependence of the density in this concentration interval is characterized by a positive deviation from the linear behavior (Fig. 4, b). Thus, in the case concerned, a substantial increase of this quantity is also observed. It may occur because, if the concentration of admixture Bi atoms is low, the latter occupy vacancies in the liquid-tin structure and form an atomic solution, which ultimately results in the density growth.

Hence, there exists a correlation between the influence of bismuth on the tin surface tension and the tin density, which is based on the change of the free volume fraction in the short-range structure. It can be argued that such specific feature of the structure formation and, as a result, the formation of physical properties manifests itself, if the other component is added to a concentration of about 5 at%. We may also assume that since the number of structural vacancies is limited, their occupation level will not increase with the further growth of the bismuth atom concentration, and the structure will become microinhomogeneous. In other words, together with the structural units that are the solution of atoms of different kinds, clusters consisting of identical atoms will also be formed. As a result, the surface properties and the density of the system will change. This conclusion is confirmed by the experimental results obtained for the thermodynamic parameters of the Bi–Sn melts [9]. In particular, they demonstrate that the mixing enthalpy of the melts belonging to the Bi–Sn system reveals insignificant positive deviations from the linearity within the whole concentration interval.

4. Conclusions

The addition of bismuth to tin decreases the total surface tension coefficient and increases the density. A negative deviation of the surface tension coefficient from the linear dependence and a positive deviation of the density from the linear dependence were observed. Such a behavior testifies to a considerable reduction of the ST and a substantial growth of the density, when a small amount of Bi atoms is added. We assume that the indicated regularities can also manifest themselves in other binary systems with a substantial difference between the surface tension coefficients and the densities of the pure components. The observed concentration dependences of those parameters in the tin-enriched melts of the Sn–Bi system are a result of the process of solution formation, when bismuth atoms become distributed over the "vacancies" in the short-range structure of liquid tin.

1. S. Ono, S. Kondo. *Molecular Theory of Surface Tension in Liquids* (Springer, 1960).
2. V.I. Nizhenko, L.I. Floka. *Surface Tension of Liquid Metals and Alloys* (Metallurgy, 1981) (in Russian).
3. A.I. Rusanov. *Phase Equilibria and Surface Phenomena* (Khimiya, Leningrad, 1967) (in Russian).
4. Won-Kyu Rhim, K. Ohsaka, P.-F. Paradis, R.E. Spjut. Noncontact technique for measuring surface tension and viscosity of molten materials using high temperature electrostatic levitation. *Rev. Sci. Instrum.* **70**, 2796 (1999).
5. Y. Tian, R. Holt, R. Apfel. A new method for measuring liquid surface tension with acoustic levitation. *Rev. Sci. Instrum.* **66**, 3349 (1995).
6. H. Fujii, T. Matsumoto, K. Nogi, N. Hata, T. Nakano. M. Kohno. Surface tension of molten silicon measured by the electromagnetic levitation method under microgravity. *Metall. Mater. Trans.* **31**, 1585 (2000).
7. S. I. Popel, Yu. I. Maslennikov. Structure of eutectic Bi–Sn, Bi–In, and Ga–Sn alloys studied by electron diffraction. *Zh. Fiz. Khim.* **51**, 816 (1977) (in Russian).
8. I. I. Shtablavyji, S. I. Mudry, U. I. Liudkevych. The transformation of the structure at heating and mechanism of thermal expansion of Sn–Bi eutectic alloy. *Phys. Chem. Solid State* **18**, 198 (2017).
9. N. A. Asryan, A. Mikula. Thermodynamic properties of Bi–Sn melts. *Inorg. Mater.* **40**, 386 (2004).
10. Z. Moser, W. Gasior, J. Pstrus. Surface tension measurements of the Bi-Sn and Sn–Bi-Ag liquid alloys. *J. Electron. Mater.* **30**, 1104 (2001).
11. J. Li, Zh. Yuan, Zh. Qiao, J. Fan, Y. Xu, J. Ke. Measurement and calculation of surface tension of molten Sn–Bi alloy. *J. Colloid Interf. Sci.* **297**, 3349 (1995).
12. L.I. Muravskyi, R.S. Bachevskyi, T.I. Voronyak. Experience of using optical-digital systems to measure the capillary characteristics of materials. *Fiz. Khim. Mekh. Mater.* **5**, 81 (1997) (in Ukrainian).
13. O.V. Lychak, V.B. Kmet', V.M. Pidzharyi. Application of polarizing contrast to determine the size of the contour of a lying drop of melt. *Fiz. Khim. Mekh. Mater.* **5**, 88 (1997) (in Ukrainian).
14. P.V. Novitskii, I.A. Zograf. *Evaluation of Errors of Measurement Results* (Energoatomizdat, 1991) (in Russian).

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ГУСТИНА ТА ПОВЕРХНЕВИЙ НАТЯГ РОЗПЛАВІВ $Sn_{1-x}Bi_x$

Р е з ю м е

Методом лежачої краплі досліджено поверхневий натяг та густину системи $Sn_{1-x}Bi_x$ із вмістом 5, 10 та 15 ат.% Bi в температурному інтервалі 470–800 K у вакуумі 10 Па. Для отримання експериментальних значень досліджуваних фізичних характеристик використовувалась програма DROP. Виявлено, що додавання вісмуту до олова приводить до зменшення поверхневої енергії розплавів системи $Sn_{1-x}Bi_x$. Також показано, що існують лінійні температурні залежності для коефіцієнта поверхневого натягу та густини.