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Surface Tension and Density of Indium-Tin Alloys

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***Abstract* – The article presents the results of experimental studies on concentration and temperature dependence of surface tension (ST) and density of indium-tin alloys. The characteristic feature of these experiments is that we studied surface tension and density by two independent methods that improved reliability of data and allowed us to solve some problems. In particular, experimental data on ST received by both methods proved that SF concentration dependence has a shallow minimum, which exceeds the limits of experimental uncertainty, in the area of average compositions. With an increase in temperature, the extremum depth decreases and when temperature is higher 773 K the minimum almost vanishes. It proves that isotherms σ of ideal solutions can be characterized by these minimums if pure components (indium and tin in this case) have similar values of physic-chemical properties. The experiments showed that within temperature ranges from the melting point to 773 K the surface tension and density of pure metals (indium and tin) and binary-based alloys are linearly dependent on temperature. Experimental data on density received by two methods (aerometric and a big drop method) evidence that alloys density values coincide with additive values within experimental uncertainty. Curves show concentration dependence of molar volumes. They have slight positive deviations from the additive straight line.**

Keywords – surface tension; density; alloys; temperature dependence; concentration dependence; molar volumes; adsorption; surface layer composition.

I. INTRODUCTION

Studying physical-chemical properties of metals and alloys is topical nowadays. Precision methods, surface tension and density meters (STM) [1] have been developed. Reliable data have been received on temperature and concentration dependencies of ST and density of pure metals and most of binary bases. Herewith, there are discussions concerning origin of extremum points on isothermal curves of ST [2]. Starting with the 30th years of the last century many researchers tried to relate extremum points on isothermal curves σ with peculiarities of alloys composition (eutecticum, presence of chemical mixture or clusters). However, precise measurements of highly pure metals proved that peculiarities discovered earlier are due to incorrect measurements [3]. However, there are discussions on the character of surface tension isotherm curves of some binary alloys. The results received by different authors differ not only qualitatively but also quantitively. On the concentration dependence curve σ of binary alloys indium-tin, thallium-lead and sodium–potassium-bismuth, mercuric – indium, gallium-plumbum [4] there are extremums (minimum, maximum, flex point etc). The nature of these extremums has not been comprehensively studied yet. That necessitates the study of these properties. In particular, isotherms σ of binary alloys indium-tin have minimum on isotherms of ST [5]. Efforts to connect these peculiarities with constitutional diagrams were not successful. Thus, we have studied temperature dependence of density and surface tension of indium-tin alloys by two independent methods.

II. METHODS AND MATERIALS

Measurements have been conducted from the melting point to (773 K by the method of a maximal pressure in a drop (MMPD) and to 1023 K by the "big drop" method) by two independent methods: by the method of a "big" drop (MBD) and method of maximal pressure in a drop (MMPD). It should be noted that these methods are the most precise. Their main advantages are technical simplicity and theoretical validity.

Experiments on determining σ of liquid metal alloys by sessile drop method were conducted on the experimental apparatus consisting of the exhaust cart, casing, heater, and a photo system.

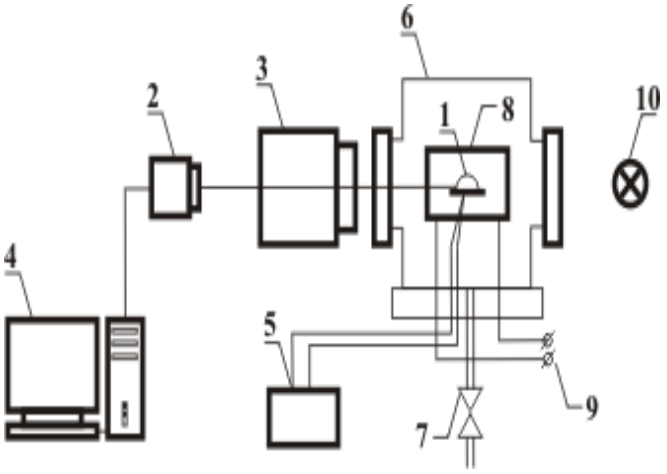

Fig. 1. Experimental apparatus scheme: 1 – a metal drop, 2 – a digital camera, 3 – cathetometer, 4 – PC, 5 – digital voltmeter with a thermocouple, 6 – apparatus casing, 7 – vacuum duct faucet, 8 – heater, 9 – transformer outlets, 10 – light

The casing is a vertical cylinder of stainless steel 12X18N9T. The lower base of the casing is rigidly fixed to the

bedplate and the rest is lifted with counterbalance. To reduce overheating of the vacuum furnace, there are gaps in this apparatus, instead of two compressions of greater diameter as in apparatuses with a vertical casing with two collets.

The gaps are for taking pictures of the studied object and its lighting. They are at the top of the casing. They are made of optical quartz. To fasten them there are rubber and fluoropolymer collars in collets. A welded-on wrapper is for cooling installation. Water-cooling does not allow the case to overheat and keeps elastomeric seals safe.

A case bottom is very important. It is rigidly fixed to the bedplate and has several inlets with different functions. Current leads are for the heater power supply, which are under big current load and contact the heater. They are copper bars cooled with water through the internal hole. The bar diameter is 25 mm.

Substrate holder is fixed to three vertically moving stocks flexibly connected with the case bottom by stainless steel sylphons to ensure movement. Substrate can move inside the apparatus by external screws. To prevent condensation of metallic vapors on the gaps there are front and radial shields on the heater.

There is a thermal couple in the case inserted through the case bottom. The bottom, as well as a casing, are cooled by water. A seal of cromel alumel thermocouple is used as a registering device.

The vacuum system has been preliminary exhausted for 40 minutes. Then the casing was filled with helium. ST measurements have been done by a big drop method in a wide range of temperatures with a tolerance about 1 % in vacuum ~0.01 Pa.

Before photographing the drop has been held at a certain temperature for 5-10 minutes in a graphite cup.

The period between taking pictures was 7-8 minutes. The temperature step was 20-30 degrees. The received picture of the drop was processed with CAD software, which allowed determining thermo physical properties of the liquid. The implementation of the software system was based on the numerical integration of Young-Laplace equation [6].

The software complex consists of three blocks:

1. Image-processing unit;
2. Computation block;
3. Final results display unit.

The block-scheme of the software complex is in figure 2.

Density and surface tension of pure tin (OOO-type) and indium (In-000) have been measured by a big drop method, as well as diluted tin-indium alloys at temperature range from the melting point to 1023K. [7].

Binary alloys In-Sn (Sn – {0.01; 0.10; 0.53 at.%} In) were prepared in B. Verkin ILTPE of NASU (Kharkov, Ukraine). The ready alloys were kept in silicone oil before measurement, which prevented them from corrosion.

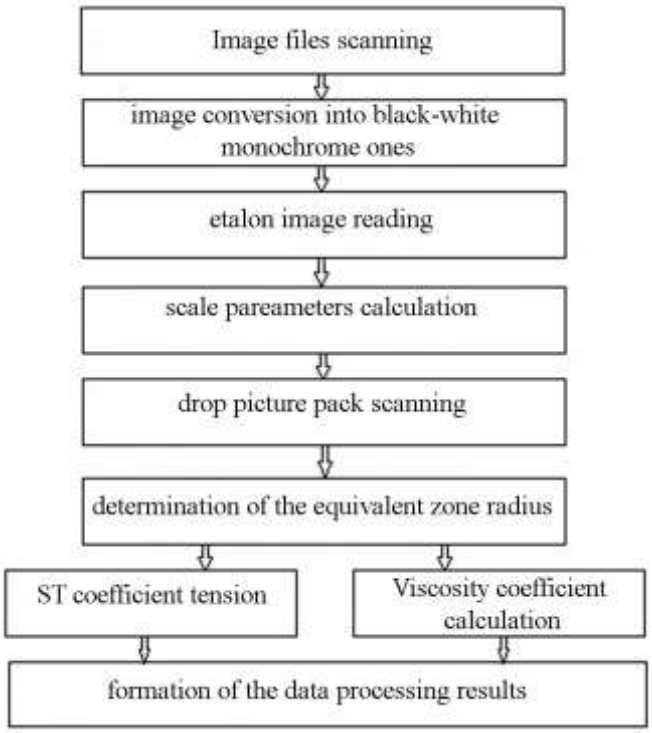

Fig. 2. Software block-scheme

Density and surface tension measuring fault were 1% and < 2% correspondingly.

Let's consider measuring methods of ST by the method of the maximal pressure in the drop (MMPD). The principle of this method is in determining pressure necessary for the drop forcing – through the orifice with a predetermined radius. Maximal pressure method is more precise for measuring ST of fusible metals. It is sufficient to say that dispersion calculated basing on large amounts of measurements (more than 8000) was 0.32 mJ/m^2. It should be noted that exactly dispersion determines the range of experimental data received by the same apparatus.

The resultant error of measurements in MMPD method is influenced by ellipticity value of the orifice internal sections, orifice internal radius measurement accuracy, and measurement accuracy of the meniscus height and vessel diameter of the monometrical cylinder, gap damping with melt, orifice verticality etc [1].

The precision of ST measurement is mostly determined by the quality of the measuring orifice. For sufficient quality, we made more than 100 orifices. To receive trustworthy results orifices of a certain radius are required (for the metal height in the monometrical cylinder to be effective), without internal splits with minimal ellipticity. Such orifice is difficult to produce. We can choose it from a great number of outstretched orifices. After studying the cuts with the microscope, we chose orifices with radii in the range from 2×10^{-4} m to 3×10^{-4} m and ellipticity less 0.5%. While calculating the measurement accuracy of ST orifice ellipticity radius-measuring error was considered. Orifice radius precision is - 10^{-6} m.

The measurements were conducted in vacuum 10^{-6} Pa from the melting point to 773^0 K by maximum pressure in a drop in the combined instrument (fig. 3) where ST is measured by maximal pressure in a drop, by P.P. Pugachevich gravitation method, and density is measured with the improved density hydrometer with the account of capillary forces and heat expansion [8].

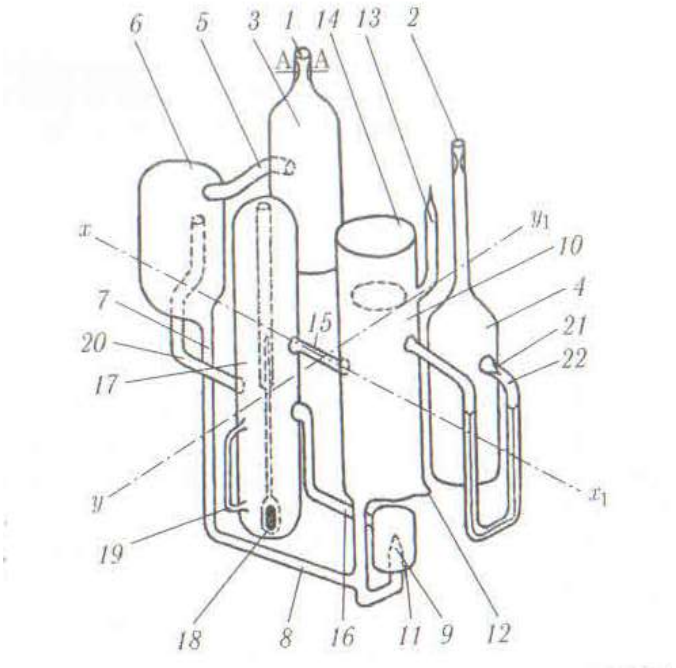

Fig. 3. Combined instrument for codetermination of density and ST of liquid metals and alloys

During the experiments it has been determined that after the heat-vacuum treatment for 4-6 hours, at the second twenty-four hours there is loss of vacuum after multiple increase in temperature from the melting point to 7673 K that could have a negative impact on the measurement accuracy of ST. To solve this problem we conducted a more detailed preliminary heat vacuum treatment of the instrument and metals under study. In particular, metals were placed into crystal cylinders and heat vacuum treated for several hours with the continuous exhaust at temperature 973K.

For some experiments we used an experimental installation consisting of exhaust cart, receiving negative pressure about $5 \cdot 10^{-6}$ Pa in the instrument at continuous cooling with liquid nitrogen traps; thermostatic air-bath with access holes, with operational temperature from room to 823 K.; glass combined instrument; furnace for heat-vacuum treatment of the apparatus with temperature ranges from room to 1000 K; electrical power unit of the experimental apparatus; cathetometer CM-8; cylinder for thermal treatment and metal filtration. The vacuum was measured with the vacuum meters VIT-1A, with sensors LM-2 and LT-2.

The procedure of thermal vacuum treatment of the apparatus is described in details in [1]. That is why we will only mention that maximal measurement errors of the ST with P. P. Pugachevich gravitational method are 0.8%, density is 0.2%. Herewith, the dispersion responsible for the experimental data range equals 0.32 mJ/m^2. We used VHF-000 tin and indium-00.

Both methods have advantages and disadvantages.

The advantages of a big drop method are measuring simplicity, small amount of the studied metal; static character,

possibility to conduct experiments in different mediums (in gas and vacuum).

Electivity of couples bowl – base layer;

The drawbacks of this method are:

Drop surface renewal difficulties;

Difficulties in alloy composition homogenization;

Drop setting difficulties;

These drawbacks can be eliminated by the following actions:

to conduct detailed preliminary thermal-vacuum treatment of the measured cell and the drop itself;

to provide precisely circular form of the bowl brim to form a liquid drop;

to take into account error dependence on the drop size when taking a picture of its sizes.

To the **advantages** of the maximal pressure in a drop or gas bubble are:

High measurement precision;

Possibility to measure ST of the renewed surface;

Possibility of measuring again many times;

Possibility to intermix alloy many times;

Short term of the experiment;

Possibility to achieve thermodynamic equilibrium of liquid with vapor before measurements;

Possibility of codetermination of ST and density.

The drawbacks of the MMPD method are:

Temperature range limitation;

Longer period for preliminary apparatus and alloy thermal-vacuum treatment;

Thus, these methods partially complement each other, which allow receiving data that are more reliable.

III. Results

Using the methods described above we measured density and ST of pure metals indium and tin, as well as binary alloys indium-tin. Figures 4 and 5 show temperature dependencies of ST and density of pure indium and tin. As figure 4 shows in all temperature ranges ST values of indium and tin received MMPD are significantly higher than the data of the big drop method. Granted that MBD as a rule gives high experimental data on ST. We can assume that it is the impact of the gas faze which is in MBD measurements, but it is contradicted by the

fact that values of ST temperature coefficients received by different methods nearly coincide. It is known that additives as a rule influence on the ST temperature coefficient. However, it should be noted that the received deviations in ST values do not exceed bias error of the experiment. Indeed, the bias error in both methods is 2.8% that is greater than differences (2.6%) received by different methods. The detailed experimental data review on ST temperature dependence on pure indium of different authors is in [9]. The experimental data we received with MMDP within error limits of the experiment coincide with the results recommended in this article.

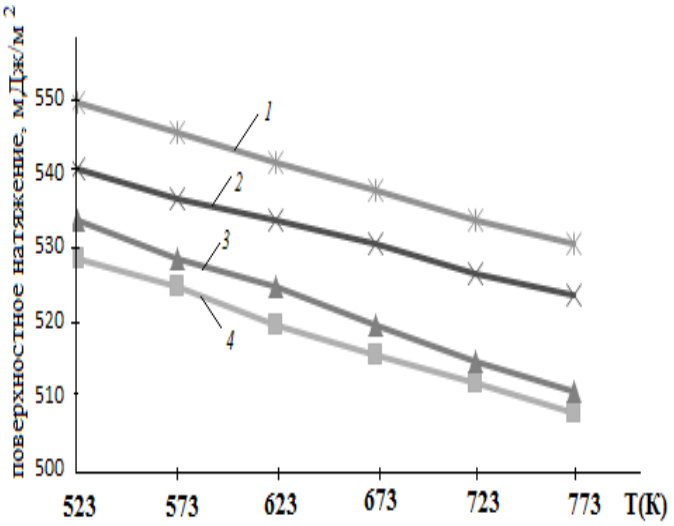

Fig. 4. Surface tension of indium and tin: 1.2-In, Sn (MMDP); 3,4-In,Sn (MBD)

Experimental data on tin density received by different methods coincide within the total measurement error. Pure indium density data received by different methods at low temperatures coincide within the measurement accuracy. However, with temperature increase difference in data received by different methods increases significantly at temperature 773 K and achieves 0.74%, that exceeds total measurement value by both methods.

Using these data on density, we have determined volume values of indium-tin liquid melts. As figure 6 shows isotherms of molar volumes are characterized by insignificant positive deviations from additive straight line that evidences about the tendency for layering. Thus, indium-tin alloy formation is accompanied by volume increase. With temperature increase, molar volume values approach additive values.

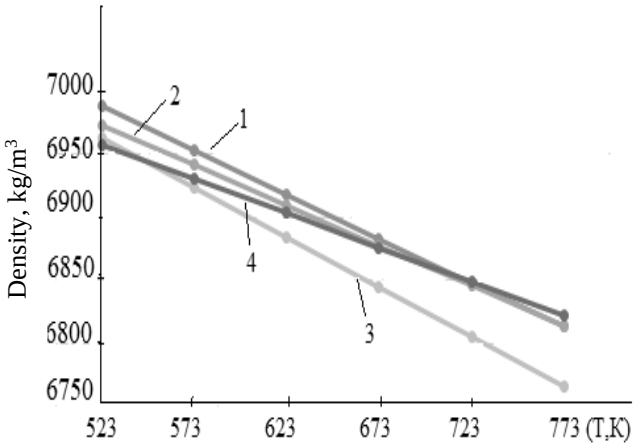

Fig. 5. Density polytherms of pure tin and indium: 1,2- ρ_{Sn} MMPD and MBD, correspondingly; 3,4-ρ_{In} MMPD and MBD correspondingly

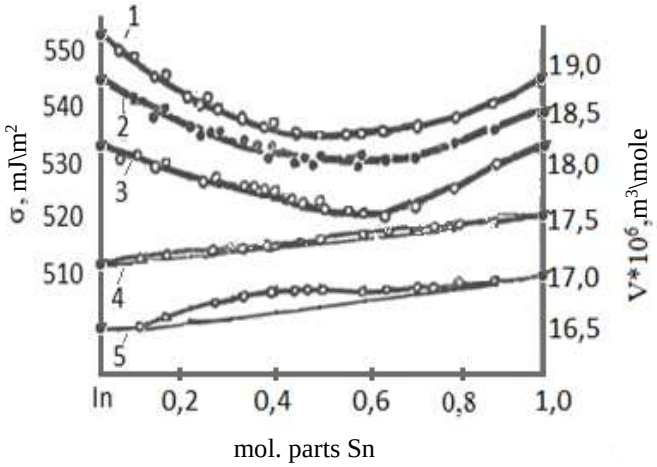

Fig. 6. Surface tension isotherms: 1-at 523 K; 2- at 623 K; 3-at 723 K and molar volumes in the system indium-tin: 4-773K; 5-523K

Figure 6 shows concentration dependencies of ST in this system at 523K, 623K and 773 K. An interesting peculiarity of these isotherms is minimal in the range of intermediate alloys. Both tin on indium and indium on tin are surface active. These graphs show the experimental data on ST received by MMPD method. These results are a little bit higher than the data received by MBD. However, despite the results received by both MMPD and a big drop method show that ST isotherm of the system have reclined minimum in the range of equimolar composition. It has been conditioned by that both indium on tin and tin on indium are surface active that is they decrease the surface tension. Herewith, surface activity of tin above the indium is greater than that of indium above tin.

IV. CONCLUSION

Thus, the article presents experimental data on ST and density of pure metals indium and tin, as well as melts of binary alloysindium-tin. It has been shown that temperature dependence of density and surface tension of pure metals and studied indium-tin melts is linear.

Results of density measurement by two methods at temperatures lower 773 K coincide in the dimension error limit. At higher temperatures difference in indium density values received by different methods exceed the dimension error limit. Isotherms of molar volumes of the studied binary base have positive deviations from additive straight lines, that evidences the tendency for layering. With temperature increase molar volumes, values approach additive values.

Results of measuring ST by two independent methods show that ST isotherms of the studied binary base are characterized by minimum in the area of equimolar composition. With temperature increase, the minimum flattens. These data coincide with the experimental data received by other authors [10].

Appearance of minimum on isotherms σ of some binary alloys (indium-tin, thallium-plumbum and sodium-potassium), is not conditioned by the peculiarities of alloys composition. The state diagrams of these systems prove it. Common for these systems is that pure components have close values of physic-chemical properties (density, surface tension, atomic size etc). The work [1] proves that similar extremums can appear on isotherms of ideal solutions if they are characterized by proximity of concentration depth profile. These conditions can be accomplished only in those systems where pure components are characterized by close values of physic-chemical properties. Pure components of the studied binary base meet these conditions.

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