Determination of thermophysical properties of prototypes of tin-lithium alloy by differential scanning calorimetry

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Abstract. This paper presents a description of research works to determine the thermophysical properties of a tin-lithium alloy with a different percentage of lithium and tin atoms in the alloy. The method of differential scanning calorimetry (DSC) was used for the studies, by which the thermophysical properties of the alloy (temperature of phase transition and enthalpy) were determined. The work was carried out at the TiGrA experimental complex. Studies to determine the enthalpy and temperature of phase transition of prototypes of tin-lithium alloy were carried out in the temperature range from 150ºC to 500ºC at a heating rate of 10°C/min. The experiments were carried out with a pristine sample of tin (reference) and prototypes of a tin-lithium alloy, the percentage of lithium in which was 20, 25 and 27 at. %. As a result of the work performed, the melting point of the prototypes was determined, which was 224ºC and 218ºC. The values of the specific heat of fusion (enthalpy) of the investigated alloys were determined, which amounted to 76.5 J/g, 80.7 J/g and 86.3 J/g, respectively.

Keywords: tin-lithium alloy, TiGrA experimental complex, DSC, melting point, enthalpy.

1. Introduction

In the design and construction of future fusion plants, the primary engineering task is the selection of plasma-facing materials (PFM) that operate steadily under high-energy loads. The studies carried out at operating fusion facilities have shown the prospects of using liquid lithium as PFM [1-10]. However, there are a number of problems, associated with the high evaporation rate of lithium in a vacuum at high temperatures. An innovative solution to these problems is the use of tin-lithium eutectics as a plasma-facing material [11-13], which has lower vaporization parameters in a vacuum. Due to the fact that tin-lithium eutectic is a relatively new candidate material, there is a need to study of the properties of this material in detail. One of the primary tasks of studying the properties of a new material is to determine, by calculation and experimental means, the possibility of using liquid tin-lithium eutectic in fusion plants as PFM. However, the available data on the thermophysical parameters of tin-lithium eutectics with different lithium content in the alloy are quite limited and most of these data were obtained theoretically [14].

To confirm the data presented in the scientific literature on the properties of lithium-tin alloys of various compositions, as well as to obtain new data, it was necessary to determine experimentally the thermophysical properties, such as melting point and enthalpy of this material.

2. Experimental part

2.1. Test samples

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To determine the thermophysical properties of the tin-lithium alloy with different lithium and tin content in the alloy, the prototypes were taken, manufactured using the developed experimental device.

The experimental device was a sealed pumped capsule made of 12Cr18Ni10Ti steel, at the bottom of which a molybdenum crucible was installed, designed for mixing lithium and tin. The device was equipped with an external ohmic heater, which allows mixing liquid metals (at temperatures of about 500°C - 550°C) in vacuum conditions, without breaching the capsule tightness.

Preliminarily, using calculation methods, the ratios of the amount of lithium and tin necessary for the manufacture of the tin-lithium alloy with the specified parameters were determined. After the calculations, weighed portions of these metals were loaded into the experimental device, and prototypes were manufactured in accordance with the previously developed technological procedures [15]. In total, three types of prototypes of a tin-lithium alloy with different contents of lithium atoms (20, 25, and 27 at. %) were manufactured. A change in lithium concentration with respect to tin leads to the changes in alloy’s thermo-physical properties and a change in the vaporization parameters. It was assumed, that ratio containing 20, 25 and 27 at.% of lithium, is optimal as for improving alloy’s thermo-physical properties and reducing the pressure of saturated vapors in the liquid phase.

Figure 1. The appearance of test prototypes of a tin-lithium alloy

Figure 1 shows the appearance of one of the manufactured prototypes of a tin-lithium alloy in a molybdenum crucible.

2.2. Experimental technique and research conditions

Study of thermophysical properties of tin-lithium alloys of various composition were carried out on the TiGrA experimental complex [16, 17] under the following conditions: Temperature range of sample heating: from 150 ºC to 300 ºC; Rate of linear heating of the sample: 10 ºC/min; Gas medium composition in the chamber – air. Figure 2 shows a general view of the TiGrA complex.

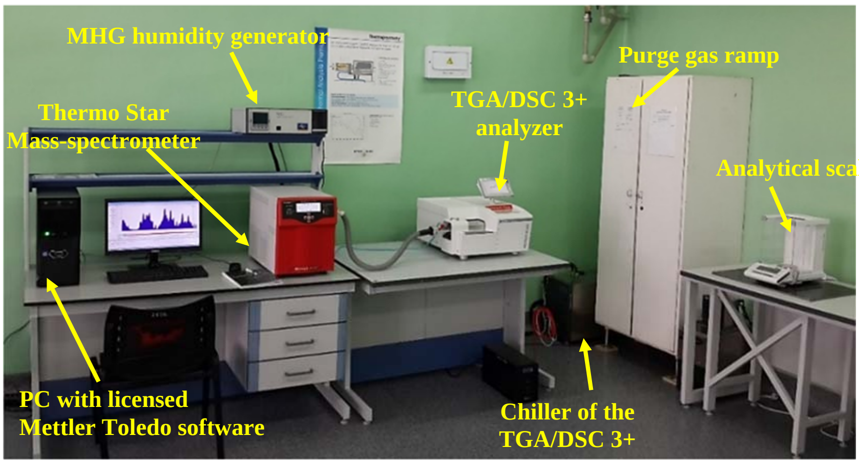


Figure 2. General view of the TiGrA experimental complex

The TIGrA experimental facility is a research complex, created based on a TGA/DSC 3+ (Mettler Toledo) thermogravimetric analyzer with an integrated ThermoStar mass-spectrometric gas analyzer and MHG humidity generator. The complex is also equipped with Mettler Toledo analytical scales, for preliminary weighing of the test samples.

This complex allows you to implement different research methods simultaneously, i.e., using a reaction chamber with one loaded sample; you can apply three analytical methods simultaneously: thermogravimetry, differential scanning calorimetry and mass-spectrometry of the gas phase during heating of the test sample in the temperature range from 22°C to 1600°C. In this case, the programmed heating rate of the test sample can be set in the range from 0.02°C/min to 100°C/min, in increments of not more than 0.01°C/min. Integrated DTA analyzer and ultramicrobalance in the TGA sensor analyzer carried out registration of changes in heat flux and mass of the test sample during the experiment. TGA sensor resolution is about 0.1 micrograms and measuring accuracy of 0.005% over the entire weighing range [18]. Changes in the composition of the gas medium above the test sample were carried out by the ThermoStar quadrupole mass spectrometer. The Quadera (mass spectrometer) licensed software allows qualitative and quantitative analysis of 128 molecular compounds simultaneously, with monitoring of various mass numbers set by the experiment program,, in the range from 1 a.m.u. up to 200 a.m.u. [19]. A combination of a thermogravimetric and calorimetric analyzers allows recording the change in heat flux and mass of the test sample which gives qualitative information about phase transitions in the investigated materials. In addition, this complex simultaneously with TGA and DSC analysis, using an integrated mass-spectrometer allows to receive and record information about the released gaseous products, formed as a result of phase transformations.

In our case, in experiments with prototypes of tin-lithium alloys and pristine tin sample, only the DSC method was used.

2.3. Procedure of conducting experiments on the study of thermophysical properties of tin-lithium alloy

All experiments on the study of samples of tin-lithium alloy of different composition were carried out by differential scanning calorimetry method [20, 21], in accordance with the general scheme of the experiment, shown in Figure 3.

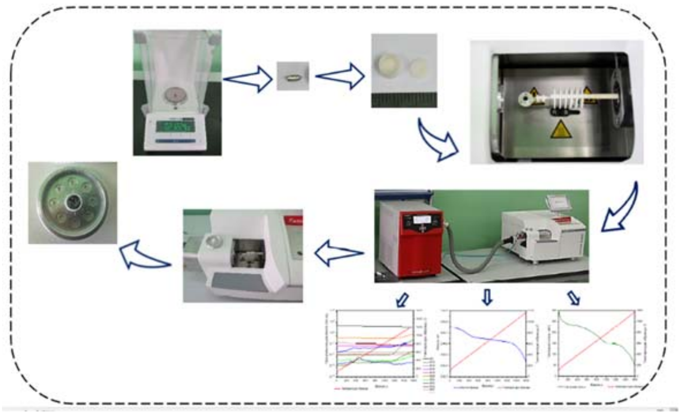


Figure 3. General scheme of experiments with tin-lithium alloy samples at the TiGrA experimental complex

The procedure for conducting experiments corresponded to the scheme presented in Figure 4 and consisted as follows:

1) test sample preparation. Preparation consists in cutting micro-samples from a pristine tin and manufactured tin-lithium alloys, the mass of the samples varied within 35 mg ± 4 mg, one of the micro-samples with a ceramic crucible made of Al_2O_3 is shown in Figure 4;
2) control measurements of the mass of the test sample;

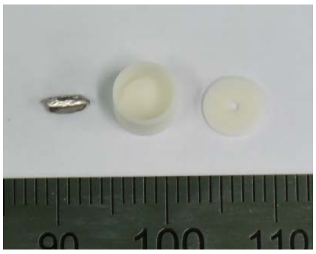


Figure 4. A general view of the test sample and the crucible for sample loading

3) the crucible with the sample is mounted on the platinum base of the TGA SDTA ceramic sensor, installed in the TGA-DSC 3+ analytical tool (Figure 5);

Figure 5. Photo of uploaded and installed sample

4) creating a dynamic heating mode using the StarE software;
5) sample measurement process – registration of the change in the mass of the sample, the heat flux incoming the sample and the change in temperature of the sample during linear heating;
6) processing and analysis of the results.

3. Results of the experiments on studying of thermophysical properties of tin-lithium alloy

Verification of the method of determining thermophysical properties of test samples by the DSC method was carried out, initially, on a pristine tin sample. As a result, the heat flux curve (Figure 6) recorded in experiments with a pristine tin sample was obtained. The values of melting temperatures and enthalpy of a pristine tin sample, obtained as a result of heat flux curve processing were recorded in Table 1.

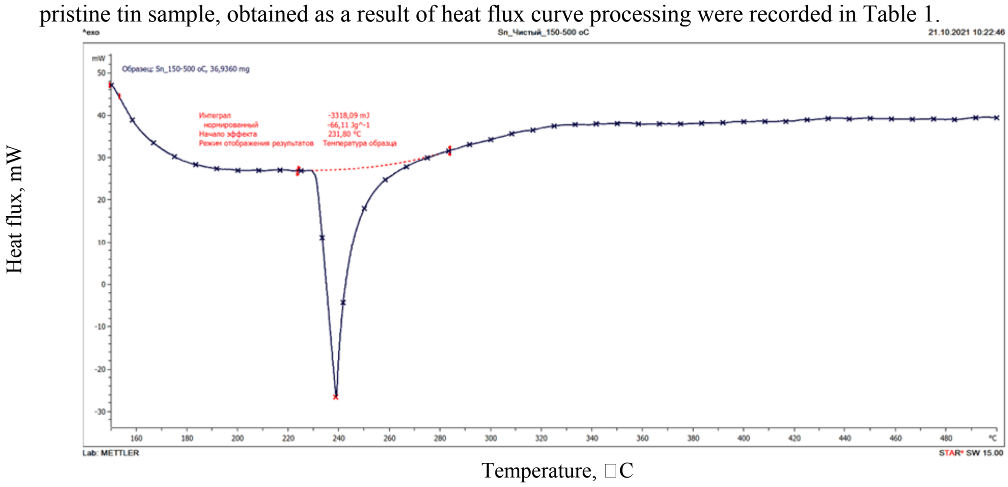
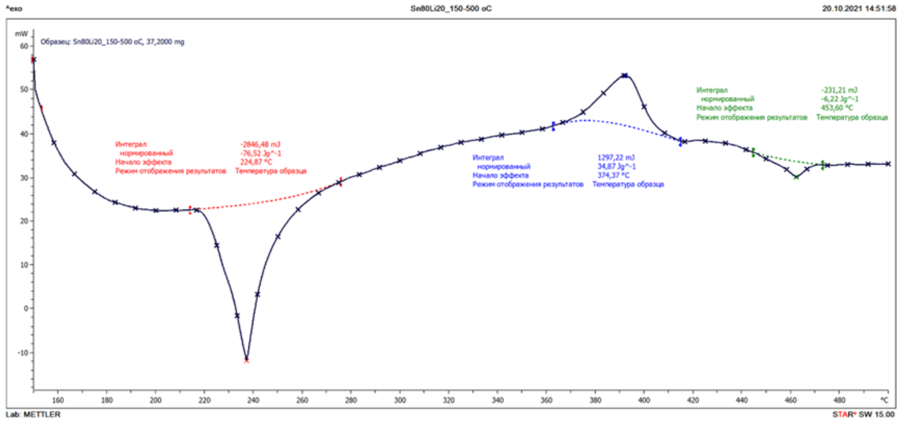


Figure 6. Dependence of the heat flux on the sample temperature during linear heating of a pristine tin sample

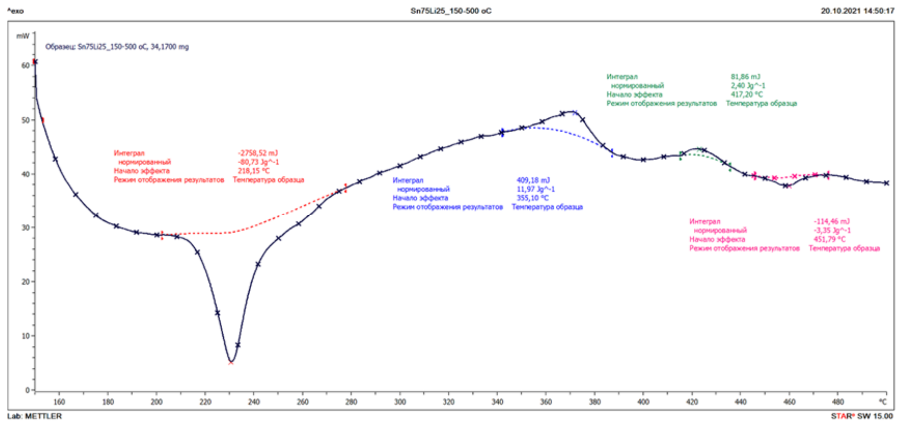
Heat flux, mW



Temperature, °C

Figure 7. Dependence of the heat flux on the sample temperature during linear heating of a Sn_{80}-Li_{20} sample

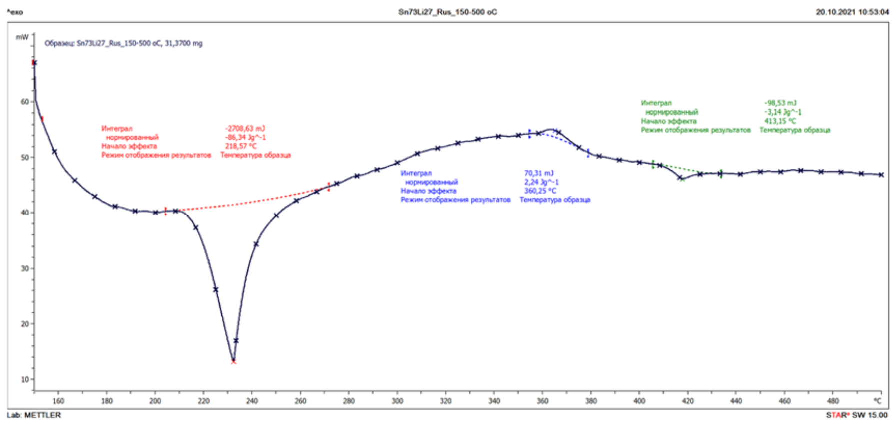
Heat flux, mW



Temperature, °C

Figure 8. Dependence of the heat flux on the sample temperature during linear heating of a Sn_{75}-Li_{25} sample

Heat flux, mW



Temperature, °C

Figure 9. Dependence of the heat flux on the sample temperature during linear heating of a Sn_{73}-Li_{27} sample

A series of DSC experiments with tin-lithium alloys were also performed, similar to the previous (with a pristine tin sample) one. Figure 7-9 shows the time dependences of the change in the heat flux on the test samples during the DSC experiments with tin-lithium alloys of various compositions. Based on the experimental data obtained, using the thermogram handler, equipped into the licensed Mettler Toledo software, the thermophysical properties of test samples with different lithium content in the tin-lithium alloys, such as the melting point and enthalpy were determined (Table 1).

Table 1. Samples parameters obtained as a result of experiments

Sample	Mass, mg	Melting point, ºC	Enthalpy, J/g
Sn	36.94	231.80	66.11
Sn_{80}-Li_{20}	37.20	224.87	76.52
Sn_{75}- Li_{25}	34.17	218.15	80.73
Sn_{73}-Li_{27}	31.37	218.57	86.34

4. An analysis of obtained results

Analysis of the experimental data obtained showed that the melting temperature of a pristine tin sample was about 231.8 °C and the specific heat of fusion (enthalpy) was 66.11 J/g, which almost coincided with the tabular data [22]. This fact indicates the reliability of the differential scanning calorimetry method for determining phase transitions in metals, as well as determining the specific heat of fusion (enthalpy) during experiments at the TiGrA experimental complex. Experiments with prototypes of tin-lithium alloys showed an increase in enthalpy values in the alloy by almost 15 - 19%, which was about 77 - 87 J/g, respectively. The revealed effect is associated with the value of the specific heat of lithium melting, which is much higher than that of tin and this effect is apparently is explained by an increase in the concentration of lithium atoms in the alloy. Besides, a shift in the melting temperature of the alloys in comparison with the melting temperature of tin was noticed. The shift occurred from a temperature of 231°C to the region from 224°C to 218°C, which, according to the Li-Sn phase diagram [23] corresponds to the presence of the physical mixing phase Li + Sn (alloy). As can be seen from the thermograms, it indicates an almost complete absence of eutectic phases ($LiSn_2$, LiSn, and Li_2Sn_5) in the alloys, which melting point is about 320°C and higher. The effects identified during the investigations, can be evaluated as one of a positive property of this candidate material in terms of applicability and relevance of the tin-lithium alloys as PFM, for the fabrication of in-chamber devices in future fusion plants.

Conclusion

Ultimately, the technique was fulfilled and experiments were carried out with one pristine tin sample and three prototypes of the tin-lithium alloy. The lithium content in the test samples of the tin-lithium alloyss corresponded to 20, 25 and 27 at. %. The main result of the conducted research was obtaining new experimental data on the thermophysical properties of a tin-lithium alloy with a different ratio of lithium and tin. This alloy is supposed to be used as a PFM in future fusion plants. Thus, as a result of the conducted research, the verification of the method of manufacturing a tin-lithium alloy with a given ratio of tin and lithium was confirmed.

Further, using the developed methods, investigation the process of interaction of tin-lithium alloys with hydrogen isotopes under conditions of high thermal and radiation loads is planned.

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