Physical properties of some Sn-Cu melts at high temperatures

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Abstract. Several physical properties (density, viscosity, ultrasound velocity, electroresistivity and magnetic susceptibility) of pure tin, copper, silver and their alloys with near eutectic compositions are investigated in the wide temperature range up to 1600 °C. In cases of copper and silver the temperature dependences of properties are found to be smooth. As for liquid tin, three temperature ranges with abnormal behaviour of properties were discovered: \( t_1 \) near 400 °C (anomalies in density and electroresistivity); \( t_2 \) = 1000-1050 °C (anomalies in viscosity and electroresistivity); \( t_3 \) approx. 1400 °C (anomalies in density, electroresistivity and magnetic susceptibility). The decrease in heating rate from 4 to 1 °C/min shifts \( t_2 \) down to 800 °C, and the purification of samples from 99.9 to 99.999% provides the incoincidence of viscosity heating and cooling curves for all the temperatures below 800 °C. The introduction of copper into liquid tin (99.9% purity) shifts the temperature of anomaly \( t_2 \) from 1000-1050 °C to 790 °C. We connect this abnormal behaviour of physical properties at \( t_{in} \) with \( \beta-\gamma \) structural transformation. Hence, by warring regimes of melts heat treatment before solidification it becomes possible to obtain samples with different properties in solid state.

1. Introduction

Nowadays Sn-Cu alloys are of permanent interest because they are considered to be the first candidates for lead-free solders. However, their properties in liquid state, especially at high overheatings above liquidus, are practically unknown. The influence of impurities content on their physical properties is investigated in several works only [1,2]. That is why the aim of this work was to study some physical properties (density, viscosity, ultrasound velocity, electroresistivity and magnetic susceptibility) of pure tin, copper, silver and their alloys with near eutectic compositions in the wide temperature range up to 1600 °C

2. Experimental

The samples for investigations were prepared from tin of different purity (99.9 – 99.999%) and copper (99.999%) by melting in vacuum for 1 hour at 750 °C. The chemical composition was checked afterwards using atom adsorption spectrometer Spectrum Flame Modula S. Oxygen content before and after experiments was determined also.

Density was measured by gamma-penetration method, kinematic viscosity – by damping oscillation method, ultrasound velocity – by impulse-phase method, electroresistivity – by contactless method in rotating magnetic field, magnetic susceptibility – by Faraday’s method. All the experiments were performed in helium atmosphere in BeO crucibles during heating end subsequent cooling with isothermal expositions at each temperature.

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3. Results and Discussion

The results obtained for pure metals are shown at figures 1-3. The temperature curves are found to be smooth in cases of copper and silver. It means that no sharp structural changes take place in these melts during heating and the following cooling.

As for liquid tin, three temperature ranges with abnormal behavior of properties were discovered: $t_1$ near 400$^0$C (anomalies in density and electroresistivity); $t_2 = 1000-1050^0$C (anomalies in viscosity and electroresistivity); $t_3$ approx. 1400$^0$C (anomalies in density, electroresistivity and magnetic susceptibility).

For example, kinematic viscosity of tin (99.9%) demonstrates a little jump down in the range 1000-1050$^0$C and starting from this temperatures the cooling curve does not coincide with the heating one up to 650$^0$C (see hysteresis loop in figure 3). The decrease in heating rate from 4 to 1$^0$C/min shifts $t_{an}$ down to 800$^0$C, and the purification of samples from 99.9 to 99.999% provides the incoincidence of heating and cooling curves for all the temperatures below 800$^0$C.

In the previous work of Brazhkin et al [3] the influence of external pressure on structure and properties of liquid tin was investigated. Basing on experimental data, the hypothesis of structural transformation from $\beta$-Sn to $\gamma$-Sn was generated. The position of this transition depends on pressure. The extrapolation of the results to normal pressure gives the transition temperature $t_{tr} \approx 800^0$C. We performed the calculations of P-T diagram for tin in the frames of Patashinski model [4,5] and confirmed the existence of $\beta$-$\gamma$ transformation in liquid tin.

We do not claim to be the first to discover these anomalies in physical properties of liquid tin (see, for example, rather old russian publication [6,7]), however we showed that the transformation in short-range order of $\beta$-$\gamma$ type takes place in liquid tin at near 800$^0$C and impurities influence greatly on position and amplitude of this transition. It is naturally to think that the samples prepared by rapid solidification of high-temperature melt state will have physical properties different from those for samples obtained from low-temperature melt state. Unfortunately, the mentioned temperature of structural transformation in liquid tin is rather high for practical use, but in can be shifted down by introducing small amounts of the second component into the melt. To check the idea, some Sn-Cu alloys with near eutectic compositions (0.5, 0.7 and 1.0 wt.% Cu) were investigated.

For Sn-0.5 wt.% Cu melt the abnormal behavior of viscosity (jump down) was found at $t_{an} = 790^0$C. At subsequent cooling the hysteresis of heating and cooling curves appears above 700$^0$C. This phenomenon takes place at each overheating the melt above 800$^0$C. When the highest temperature in the scan does not exceed 700$^0$C, the heating and cooling curves are smooth and no hysteresis was fixed.
From magnetic measurements it comes that at the same temperature $t_m = 790^\circ$ C the melt transforms from paramagnetic to diamagnetic state, and it remains diamagnetic during cooling up to crystallization (figure 2).

Hence, viscosity and magnetic susceptibility studies showed that introduction of 0.5 wt.% Cu into liquid tin (99.9 % purity) shifts the temperature of structural $\beta-\gamma$ transformation from 1000-1050$^\circ$ C to 790$^\circ$ C. However, this temperature is still rather high to practical use in lead-free solders production.

The increase of copper content give the following: for Sn-0.7 wt.% Cu melt the temperature of anomaly shifts down for 20$^\circ$; for Sn-1.0 wt. % Cu melt it increases for 20$^\circ$ and becomes equal $t_m = 810^\circ$ C (figure 4). From practical point of view, Sn-0.7 wt.% Cu alloy, corresponding to eutectic composition, seems to be the main attractive one for heat treatment.

The introduction of the third component (3.8 wt.% Ag) into Sn-0.7 wt.% Cu melt leads to smooth behavior of viscosity heating and cooling curves if the highest temperature of the melt does not exceed 900$^\circ$ C. May be the anomaly, i.e. structural transformation, location in somewhere higher.

4. Conclusions

Several physical properties (density, viscosity, ultrasound velocity, electroresistivity and magnetic susceptibility) of pure tin, copper, silver and their alloys with near eutectic compositions were investigated in the wide temperature range up to 1600$^\circ$ C.

In cases of copper and silver the temperature dependences of properties are found to be smooth.

As for liquid tin, three temperature ranges with abnormal behavior of properties were discovered: $t_1$ near 400$^\circ$ C (anomalies in density and electroresistivity); $t_2 = 1000-1050^\circ$ C (anomalies in viscosity and electroresistivity); $t_3$ approx. 1400$^\circ$ C (anomalies in density, electroresistivity and magnetic susceptibility). The decrease in heating rate from 4 to 1$^\circ$C/min shifts $t_2$ down to 800$^\circ$ C, and the purification of samples from 99.9 to 99.999% provides the incoincidence of viscosity heating and cooling curves for all the temperatures below 800$^\circ$ C. The introduction of copper into liquid tin (99.9 % purity) shifts the temperature of anomaly from 1000-1050$^\circ$ C to near 790$^\circ$ C. We connect this abnormal behavior of physical properties at $t_m$ with $\beta-\gamma$ structural transformation.

Hence, by warring impurities content and regimes of melts heat treatment before solidification it becomes possible to obtain samples with different properties in solid state.

Acknowledgments

The work is financially supported by RFBR (grants NN 06-03-90568, 07-02-96045 and 07-03-96116).
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