INTRODUCTION

Lead contained in solders influences human health and the environment negatively. All the industrial countries are doing their best to decrease that influence, and thus, global industry is extremely interested in introduction of lead-free solders into electronics and electro- and radio-technology. Since 2006, according to a decision of the EC Coordination Council, all the EC consumer electronics should be produced with lead-free solders.

To date, tin-based binary and ternary alloys with copper, bismuth, silver, and zinc additions (Sn–Zn, Sn–Cu, Sn–Bi–Zn, Sn–Bi–Ag, Sn–Bi–Cu, and Sn–Ag–Cu) are the main alternative to the conventional Pb–Sn solders. The chemical composition of those solders is, as a rule, already specified and patented, and thus, further improvement of their properties may only come about by modernization of production technology and soldering modes.

It is well-known fact that the properties of cast alloys are predominantly governed by its melt state before crystallization; liquid alloys with near-eutectic compositions may reside in nonequilibrium or metastable states for a long time. For this reason the investigation of physical and chemical properties of the melts may discover processes taking place and may make it possible to vary the structure of these objects by means of external impacts.

Recently, the tin–bismuth system has attracted attention as a potential lead-free solder for microelectronics. It is also of interest as a model system to study the dimension-dependent properties in two-phase nanoparticles.

Additional interest in this system occurred after publication of the data on the existence of a metastable phase in the supercooled melt [1, 2]. However, various opinions concerning the nature of this phase are stated in literature. In the equilibrium phase diagram of tin–bismuth system, only the simple eutectics of tin and bismuth is present [3]. At room temperature, tin has a tetragonal structure (the space group I4l, the lattice parameters \(a = 0.5831\) nm, \(c = 0.3182\) nm) known as white tin and bismuth is characterized by rhombohedral structure (the space group R3m, the lattice parameters \(a = 0.4547\) nm, \(c = 1.186\) nm). These metals keep their structures until melting [4]; although in several works, it is claimed that at the temperature of \(\sim 173^\circ\)C \(\beta\)-tin converts into \(\gamma\)-tin with the lattice change from tetragonal to orthorhombic [5]. The metastable phase existence was first discovered in rapidly quenched tin–bismuth alloys [6]. In [7], the metastable phase diagram for white tin and for one of the bismuth modifications occurring at high pressure (Bi(II)) is calculated. Using the drop supercooling technique, the authors of [8, 9] discovered, in 10–50 nm drops, the origin of the metastable supersaturated phase with the white tin structure and determined the melting temperature of this phase. To find the melting temperature as a function of the particle sizes, diffusion analysis was applied. Publication [1] reports that the bismuth phase typical for high pressures originates in the supercooled Sn–Bi alloys. In [2], the process of the tin–bismuth alloy particle solidification under high pressure is investigated. The results obtained show the increase in the metastable phase content with pressure increase. There is some data on the formation of an amorphous (fluidlike) phase at room temperatures in very small volumes (<7 nm) in the process of Bi–Sn alloy production by the metal vapor deposition method [10]. In [11], the tin-enriched metastable phase was discovered in the samples obtained by rapid quenching the supercooled melt. The authors suppose...
that this phase occurs in the case when the liquidus in bismuth-rich alloys is below the tin melting temperature.

In [12], the phase composition in Sn–Bi alloys is investigated using DTA/DSC, electron microscopy, and X-ray analysis. The eutectic temperature is experimentally found to be equal to 138.6°C; at this temperature tin dissolves about 10% (mass) of bismuth. In crystal state, an increased bismuth content is discovered, by means of Auger spectroscopy, at the grain boundaries [13].

In [14], the influence of supercooling on phase composition and phase morphology in the eutectic alloy Sn–57% Bi (mass) is investigated. The overcooling increase from 10°C to 19°C is shown to cause creation, besides the eutectic, of primary dendrites, β–Sn. Further increase of overcooling up to 29°C causes the β–Sn dendrite sizes decrease, as well as a decrease in all the structure constituents of the alloy. For the creation of critical nuclei in the hypoeutectic alloys, overcooling of 20–30°C is needed, whereas in the hypereutectic ones, it is by only 5°C; then, bismuth is a more powerful nucleation center than tin [15]. A similar result is obtained in [16]: supercooling of the Sn–Bi alloys by 11°C causes the primary and eutectic phase precipitations to become finer.

In [17], the dependence of electrical resistivity, crystallization kinetics, and structure on overheating of the Sn–40% Bi (mass) melt was studied. The melt structure is shown to vary (this variation is reflected in the anomalous resistivity behavior) at its overheating above a particular temperature and under a particular exposure at the maximal temperature. The higher the overheating, the less exposure time is needed. Yet, the higher the exposure time, the higher the supercooling and, the crystallization rate.

The influence of the Sn–Bi melt overheating, its isothermal exposures, and its cooling rate on the solid metal structure is studied in [18]. The authors reveal the zones of metastable crystallization that may occur under the particular conditions of the melt heat treatment.

In [19], the authors stated that if the melt was overheated above the temperature of structural transformation then the degree of its overcooling increases, its structure grains become finer, and its morphology changes (equiaxial crystals occur) for both the eutectic and primary phases. In the eutectic melt, overheating causes, later on, decrease of the eutectic phase percentage.

The microstructure and phase composition of rapidly quenched Sn–Bi ribbons are studied in [20, 21]. Precipitation of a separate bismuth phase is shown to take place at a bismuth concentration above 3.47% (mass). With the Bi content up to 13.27% (mass), the bismuth phase is needle-shaped. The initial bismuth needle thickness grows in time. Nonuniformity of the ribbons over the cross section is observed.

In the liquid state, EMF of binary Sn–Bi alloys is studied within the whole concentration range and of ternary Sn–Bi–Ag alloys (at the ratio of $x_{\beta}$/$x_{\text{Bi}} = 1/3, 1/1, and 3/1) within the temperature range of 430–630°C [22]. The tin activity for the binary alloys is shown to differ slightly from the Raoult law within the whole concentration range, whereas for the ternary alloys, the dependence is very complicated.

The study of electrical resistance of Sn–Bi melts performed by the DC four-probe method [23] shows the presence of inflection on the resistance curve observed during both heating and cooling. The inflection temperature depends on the melt composition. For example, for the Sn–20% Bi (mass) melt, it equals 725°C and monotonically increases up to 880°C for the Sn–80% Bi (mass) melt. This fact, in the authors’ opinion, is an evidence of the liquid-liquid structural transition in the melt, and tin seems to cause this transition. However, comparison of the heating and the cooling curves for the eutectic Sn$_{39}$Bi$_{61}$ alloy lets the authors assert that this transition is irreversible [24].

Thus, to date, it has been shown experimentally that crystallization of the Sn–Bi melts may proceed by either the equilibrium or the metastable mechanism. The degree of supercooling, the morphology, and the sizes of the originated phases depend significantly on the heat treatment of the melts before crystallization. Nonetheless, there is no unified opinion on the nature and the temperatures of the structural transformations in Sn–Bi melts. Thus, the present work is aimed at detailed experimental investigation of physical properties (density, electrical resistivity, magnetic susceptibility) of tin–bismuth alloys with near-eutectic compositions.

**EXPERIMENT**

In the present study, temperature dependencies of density (by the gamma-penetrating method method [25]) electrical resistivity (by the contact-less method in rotating magnetic field [25]) and magnetic susceptibility (by the Faraday’s method [26]) of Sn–Bi alloys are investigated. All the measurements were made in a helium atmosphere up to the temperatures of 1000–1100°C with the step of 10–20°C and isothermal exposition for 5–20 min at each temperature. The temperature dependencies were measured in the heating and subsequent cooling mode. Three compositions containing 37, 42, and 47% tin (mass), respectively are investigated. The Bi–42% Sn (mass) composition is eutectic one. The chemical composition of the samples is studied by means of the Spectroflame Modula S analyzer by the atomic emission method with inductively coupled plasmas. All the samples are also tested for the oxygen content before and after the experiments.