MICROSTRUCTURE AND MECHANICAL PROPERTIES
OF Bi_{27}In_{38}Sn_{35} FOIL PRODUCED BY RAPID SOLIDIFICATION

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Investigations into the microstructure of Bi_{27}In_{38}Sn_{35} alloy have shown that an increase in the melt cooling rate from 10^2 to 10^5 K/s leads to a change in the solidification mechanism. At a melt cooling rate of 10^2 K/s, we observe consecutive solidification of the dendrites of the Sn_{4}In phase, and then that of BiIn and BiIn_{2} phases in the interdendritic space. Bi_{27}In_{38}Sn_{35} foil produced by rapid solidification consists of BiIn, BiIn_{2}, and Sn_{4}In phases forming a lace-like structure. The foil’s chemical composition determined by X-ray spectral analysis was constant in thickness. Alloy foil phase grains have a microcrystalline structure and texture. The aging of rapidly solidified foil at room temperature causes size enlargement in phase and grain precipitations, which determines the change in its physical properties. Foil aging causes an increase in microhardness and affects tensile deformation: there is consolidation of rapidly solidified alloy at the initial stage of deformation and a reduction in its plasticity.

Keywords: bismuth, indium, stannum (tin), lead-free solder, grain, texture, phase, microhardness, specific surface.

Introduction. Active investigations into the structure of low-melting-point solders conducted in different countries [1–5] are due to the desire to replace components that are hazardous for human health and the environment (lead, mercury, etc.) with safer ones (for example, bismuth, indium, silver, etc.) with improved process characteristics. However, the replacement components are significantly more expensive than lead, which leads to a rise in the cost of lead-free solders. To achieve its reduction, it is expedient to use resource- and energy-saving technologies which include rapid solidification. We know [6–8] that at ultrahigh cooling rates, a structure is formed that differs from the structure of alloys produced by traditional technologies. Due to this, the goal of this investigation is to identify the parameters of the structure and the physical properties of Bi_{27}In_{38}Sn_{35} alloy manufactured by rapid solidification.

Experimental Procedure. The initial Bi_{27}In_{38}Sn_{35} alloy (the numbers indicate the atomic concentration of components) is made by alloying the components in a quartz vessel. Samples for investigations were obtained at two melt cooling rates. Bulk samples 3 × 6 × 15 mm in size solidified during melt cooling in the air in a graphite mould. To obtain foil, a piece of alloy with a mass of ≈ 0.15 g was melted and injected onto the inner polished surface of a revolving copper cylinder. The melt spread out over the surface and crystallized in the form of a foil sheet with a length of up to 15 cm and a width of up to 12 mm. Foil of thickness 40–70 μm was used for the investigation. In manufacturing bulk samples, the melt cooling rate was approximately 10^2 K/s, and for the foil, it was at least 10^5 K/s [6]. The foil microstructure was investigated using a LEO 1455 VP scanning electron microscope additionally equipped with attachments for electron probe microanalysis and phase-shift analysis. The foil microstructure and composition were considered for the foil side A fitting closely to the crystallizer, for the opposite side B, and also in the foil cross section C. The microstructure parameters were identified by the random linear intercept method [9] with an error of 10%. Microhardness was measured using a PMT-3 instrument with an error of 5%. Tensile tests were conducted on a Testometric M350-10CT test unit at room temperature.

Results and Discussion. Backscattered electron images of the Bi_{27}In_{38}Sn_{35} alloy microstructure obtained using a scanning electron microscope (SEM) are given in Fig. 1. The microstructure of a bulk sample obtained at a melt cooling rate of 10^2 K/s is shown in Fig. 1a and b. The microstructure of rapidly solidified foil synthesized at a melt cooling rate of 10^5 K/s is shown in Fig. 1c and d. White, gray, and dark particles are observed in both the bulk samples and the foil. However, the dimensions of the particles and their position in the bulk samples and the foil differ. The development of primary large dendrites formed by dark particles is observed in the microstructure of the bulk samples. The length of the dendrite

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branches can reach 1 mm, and their width is 20–30 μm. The interdendritic spaces are filled by gray and white particles. As the melt cooling rate rises there is a reduction in the size of the phase particles by an order of magnitude, viz. from tens to a few μm. The distribution of the particles in the foil has a chaotic pattern, which indicates a change in the mechanism of solidification.

To identify the foil phase composition, investigations were carried out into the elemental composition of several particles of different color using electron probe microanalysis. Figure 2 and Table 1 show the microstructure of one of the fragments and the results of investigations into the elemental composition of individual particles of the bulk samples. It has been established that the bulk samples solidify with the formation of three phases. The concentrations of bismuth and indium in the light fragments of Bi27In38Sn35 alloy coincide and are close to 50% (tin concentration is about 2 at.%), which indicates the development of the ε-phase (BiIn). In the gray regions, the concentration of bismuth reaches 34 at.%, that of indium is 64 at.%, and the concentration of tin is 2–4 at.%, which is indicative of the formation of the BiIn2 phase. In the dark regions, tin has the highest concentration (59 at.%); the concentrations of indium and bismuth are equal to 30–35 and

Fig. 1. Bi27In38Sn35 alloy microstructure: a) and b) bulk samples; c) and d) rapidly solidified foil.

Fig. 2. Microstructure of a portion of a bulk Bi27In38Sn35 alloy sample.
10–12 at.% respectively. Dark particles belong to the \( \gamma \)-phase (Sn\(_4\)In), which is a phase with variable solubility. The excess of indium leads to the formation of a great number of vacancies and ensures a Bi solubility of up to 10 at.%. The cited results show that in bulk samples, solidification occurs consecutively. Despite the closeness of melting temperatures of the obtained phases, equal to 119, 110, and 89°C for Sn\(_4\)In, In\(_2\)Bi, and InBi respectively [10], the most refractory Sn\(_4\)In in phase is the first to solidify, forming large primary dendrites. The In\(_2\)Bi and InBi phases are pronounced in the interdendrite space.

Figure 3 shows the results of investigating the elemental composition of the foil particles. The distribution of the elements along the scanning line demonstrates the elements’ concentrations in different regions that are identical to those for the bulk samples. Analysis shows that a rise in the melt cooling rate does not lead to the development of new phases. However, uniform distribution of the phase particles is observed in the microstructure of the rapidly solidified foil. The intercept method was used to identify the volume fractions of the above-said regions. The volume fraction of the light regions is equal to \( V_1 = 0.41 \), that of the gray ones is \( V_2 = 0.04 \), and the volume fraction of the dark regions is \( V_3 = 0.55 \). The average chord of the random secant lines \( d \) falling on the phase cross section does not exceed 2.2 \( \mu \)m. The specific surface of the boundaries separating the light, gray, and dark regions reaches the value \( S = 1 \, \mu \text{m}^{-1} \).

**TABLE 1. Elemental Composition of Particles Making up a Bulk Sample**

| Spectrum No. | Concentration of components, at.% |
|-------------|----------------------------------|
|             | Bi  | Sn  | In    |
| 8           | 49.8| 1.3 | 48.9  |
| 9           | 33.0| 2.5 | 64.5  |
| 10          | 9.3 | 59.0| 31.7  |

**TABLE 2. Chemical Composition of Bi\(_{27}\)In\(_{38}\)Sn\(_{35}\) Alloy Foil**

| Foil surface | Components, at.% |
|--------------|------------------|
|              | Bi  | Sn  | In    |
| A            | 26.8| 34.9| 38.3  |
| B            | 27.4| 34.7| 37.9  |
| C            | 27.2| 34.7| 38.1  |
| Average value| 27.1| 34.8| 38.1  |
The chemical composition of the foil determined by electron probe microanalysis in the layers adjacent to the surfaces A and B and in the layer C is shown in Table 2. The difference between the concentrations of each of the components in the layers is insignificant, i.e., in the movement of the melt–solid interface boundary from the surface A to the surface B, the redistribution of the components is insignificant, which is due to the substantial overcooling of the liquid phase at its high cooling rate.

### Table 3. Pole Density of the Diffraction Lines of the $\varepsilon$- and $\gamma$-Phases

| Diffraction line of the $\varepsilon$-phase | Pole density | Diffraction line of the $\gamma$-phase | Pole density |
|-------------------------------------------|--------------|----------------------------------------|--------------|
| 111                                       | 0.3          | 1010                                   | 0.0          |
| 200                                       | 0.0          | 1120                                   | 0.1          |
| 002                                       | 0.2          | 0002                                   | 6.6          |
| 102                                       | 2.0          | 1110                                   | 0.0          |
| 211                                       | 1.6          | 2002                                   | 0.0          |
| 112                                       | 0.3          | 2012                                   | 0.2          |
| 220                                       | 0.2          | 2011                                   | 0.1          |
| 202                                       | 1.6          | –                                      | –            |
| 212                                       | 2.8          | –                                      | –            |

Fig. 4. Grain structure of the Bi$_{27}$In$_{38}$Sn$_{35}$ alloy foil phases and the grain color diagram: a and c) $\varepsilon$-phases (BiIn); b and d) $\gamma$-phases (Sn$_{4}$In).
Figure 3 shows the images of the grain structure of the ε-phase (BiIn) and γ-phase (Sn₄In) of the Bi₂₇In₃₈Sn₃₅ alloy foil, and also of the color diagram of the ε-phase and γ-phase grains. The phase sections are made up of one or several grain sections. For the ε-phase, the average length of the chord of the random secants on the grain sections is \( d = 0.7 \mu m \), the specific surface of the grains' large-angle boundaries is \( S_b = 0.22 \mu m^{-1} \), and the linear density of the linear grain boundaries (edges) is \( L = 0.17 \mu m^{-2} \). These data are indicative of the formation of a microcrystalline structure in the ε-phase. A microcrystalline structure also develops in the γ-phase. The dispersivity of the phases and the microcrystallinity of the grain structure are positive factors in the use of rapidly solidified foil as solders [11].

The alloy phases are characterized by anisotropy of physical properties. Due to this, an important factor that determines the physical properties of polycrystalline rapidly solidified foil is the presence of texture in it. Table 3 shows the pole densities of the diffraction lines of the foil γ- and ε-phases one day after it was manufactured. The diffraction line 0002 is characterized by the highest value of the pole density in the γ-phase, which indicates the formation of texture (0001). This orientation accounts for 94% of the volume of the grains oriented by the plane (0001) parallel to the foil surface. The formation of texture in rapidly solidified foil was observed in Al, Sn, and Pb alloys [12–14]. The formation of texture in alloys during rapid solidification is explained by the theory of irreversible processes. According to the principle of the maximum dissipation work rate [15], the transition of the melt to an equilibrium state occurs in such a way that the rate of reducing the alloy enthalpy in the process of crystallization is a maximum. Therefore, there is growth predominantly in grains whose close-packed planes are perpendicular to the direction of the heat flux. In the γ-phase, such a plane is the basal plane (0001). In the ε-phase, a complex texture is observed. The highest values of the pole densities (from 1.6 to 2.8) belong to the diffraction lines 102, 211, 202, and 212. There is a formation of a weakly pronounced texture (102) + (211) + (202) + (212), which is due to the insignificant difference in the stacking density of respective crystallographic planes in the ε-phase.

Figure 4 shows the microhardness of Bi₂₇In₃₈Sn₃₅ alloy rapidly solidified foil as a function of curing time at \( T_r \). During the time of aging for 100 h, the microhardness increased almost twofold and became equal to the microhardness of bulk alloy. In the process of measuring the foil microhardness, there is a plastic deformation of its volume located under the diamond pyramidion. Since the room temperature \( T_r \) for the alloy is high (\( T_r \approx 0.8T_m \)), the grain boundaries are weakened zones [16]. Therefore, plastic deformation is due to slip with the grain and grain boundary sliding [17].
rapid solidification, the grain boundaries contain a great number of various defects. The large area of imperfect grain boundaries in rapidly solidified foil leads to low foil microhardness, viz. twofold, compared to bulk samples. However, due to diffusion, there is improvement in the structure of the grain boundaries, which results in a reduction of the contribution of grain boundary sliding to the level of deformation, which in turn is manifested in a rise of the microhardness value of a bulk sample (Fig. 5).

The aging of Bi$_{27}$In$_{38}$Sn$_{35}$ alloy rapidly solidified foil also affects other mechanical properties. Figure 6 shows the foil tensile curve three hours after its manufacture. At low deformations, there is a surge in the intensity of tension maximum value $σ_{\text{max}} = 20$ MPa is achieved at the relative elongation $ε \approx 4\%$, then $σ$ decreases monotonically and foil destruction occurs due to the development of micro- and macropores, with the relative elongation during the foil destruction $δ$ making 25%. The increase in the time of aging at room temperature from 3 to 2300 h results in the increase of $σ_{\text{max}}$ from 20 to 40 MPa and the decrease in the relative elongation $δ$ from 25 to 10%. The observed changes in mechanical properties during stretching are also due to the occurrence of diffusion processes resulting in the improvement of the grain boundary structure and a reduction in the contribution of grain boundary sliding to the total level of deformation.

**Conclusions.** Bi$_{27}$In$_{38}$Sn$_{35}$ alloy foil obtained by rapid solidification is made up of the BiIn, BiIn$_2$, and Sn$_4$In phases forming a lace-like structure. The alloy foil phase grains have a microcrystalline structure. The $γ$-phase has a sharp texture (0001) in rapidly solidified foils. Curing rapidly solidified foil at room temperature causes the enlargement of phase and grain precipitations and determines a change in its mechanical properties.

**NOTATION**

- $A$, foil surface contacting the crystallizer;
- $B$, foil surface opposite to surface $A$;
- $C$, surface in the central portion of the foil cross section;
- $L$, density of linear elements in grain boundaries (edges), $\mu$m$^{-2}$;
- $S$, specific surface of phases and grains, $\mu$m$^{-1}$;
- $T_r$, room temperature, °C;
- $T_{\text{mt}}$, alloy melting temperature, K;
- $V$, phase volume fraction, rel. unit;
- $δ$, foil relative (percentage) elongation at failure, %;
- $ε$, relative tensile deformation of the foil as it is stretched, %;
- $σ_{\text{max}}$, maximum intensity of tension in the foil as it is stretched, MPa.

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