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FEATURES OF STRUCTURE FORMATION OF MULTI-COMPONENT ALLOYS, $Sn_{55,18}Zn_{44,50}Si_{0,23}Al_{0,09}$, OBTAINED UNDER STRONGLY NON-EQUILIBRIUM CRYSTALLIZATION CONDITIONS

A solidification mechanism is proposed and a mathematical model of crystallization of foil under nonequilibrium conditions is considered. The microstructure in the transverse layer, phase analysis, and component distribution in the initial state and during heat treatment of the rapidly solidified $Sn_{55,18}Zn_{44,50}Si_{0,23}Al_{0,09}$ alloy are studied. The effect of ultra-high cooling rates (up to 10^6 K/s) on the structure and mechanical properties is shown.

Keywords: foil; structure; Sn-Zn-Si-Al; crystallization, cooling rate; supercooling; cluster; microhardness.

Enormous practical interest in alloys obtained in the high crystallization rate mode remains to this day due to the formation of a unique structure and properties unattainable under equilibrium conditions. Due to the fact that ultra-fast quenching allows increasing the strength of alloys, one can expect to obtain by this method such alloys with a homogeneous and dispersed structure, with a narrow melting range, which is important for reducing the negative temperature effect on the elements of microcircuits during soldering. Dispersity and uniformity of phase distribution are especially important in the production of solder paste powders with fine and ultrafine grain, ensuring the overall miniaturization of products in the micron ranges of integrated circuits.

Due to the fact that multicomponent alloys based on the binary tin-zinc system are widely used in industry, small additions of alloying components can lead to improved technological and operational properties. In this regard, the aim of this work was to analyze the kinetics of crystallization with a proposal for a solidification mechanism and a description of a mathematical model of foil crystallization, as well as microstructural studies under natural and forced conditions.

In this work, we investigated rapidly solidified $Sn_{55,18}Zn_{44,50}Si_{0,23}Al_{0,09}$ (wt.%) alloys from components with a purity of no more than 99.99%. The fabrication was carried out by fusing the components in quartz ampoules. The foils were obtained by ultrafast quenching from the liquid phase by solidifying a drop of melt (~ 0.2 g) on the inner polished surface of a copper rotating cylinder. The thickness of the studied foils was 40-90 μm. The cooling rate of the melt, as shown by the calculation of [1], was not less than 10^6 K/s.

The chemical composition and surface structure were studied using a LEO1455VP scanning electron microscope. X-ray spectral microanalysis of the alloy was performed using a Rontec detector. X-ray structural analysis was performed on a Rigaku Ultima IV diffractometer. Microhardness Hμ was studied using the Vickers method on a PMT-3 hardness tester. The relative measurement error of H_μ was no more than 5%.

Let us consider the processes occurring during ultrafast crystallization of thin layers of molten metal. The process of cooling the melt can be divided into two stages. The first stage of cooling the liquid solution begins with the removal of heat through the "melt – *Cu*- substrate" boundary. This process is accompanied by strong supercooling of the molten metal [2].

An analytical solution to the one-dimensional problem of heat conduction under conditions of cooling of thin foil can be obtained under the assumption that the heat characteristics "molten metal – *Cu*-substrate – contact area" do not depend on temperature. Also, there will be no heat flow through the outer surface of the thin foil, but through the contact surface of the molten metal with the *Cu*-substrate, the heat flow is directly proportional to the temperature difference in the contact zone "foil – *Cu*-substrate". We will also assume that the temperature is constant in areas remote from the contact surface of the thin foil and the *Cu*-substrate.

A foil of $Sn_{55,18}Zn_{44,50}Si_{0,23}Al_{0,09}$ alloy of thickness d, heated to temperature T_{10}, is brought into contact with a copper substrate having temperature T_{20}. In this case, the temperature of the investigated foil $T_1(x, t)$ and the copper substrate $T_2(x, t)$ at an arbitrary point x (the x axis is perpendicular to the contact plane, the outer surface of the foil $x = 0$, the contact surface $x = d$) and at an arbitrary time t are determined by the following relationship:

$$T_1(s,\tau) = T_{20} + \frac{(T_{10} - T_{20})n}{\pi} \int_0^{\infty} \frac{\left\{\sin\left[(1-s)\xi\right] + \sin\left[(1+s)\xi\right]\right\} e^{-\xi^2\tau}}{\xi\left[\left(g\xi\sin\xi - \cos\xi\right)^2 + n^2\sin^2\xi\right]} d\xi, \ \ 0 < s < 1, \qquad (1)$$

$$T_2(s,\tau) = T_{20} + \frac{2(T_{10} - T_{20})}{\pi} \times$$

$$\times \int_0^{\infty} \frac{\left\{n\left(\cos\xi - g\xi\sin\xi\right)\cos\left[m\xi(s-1)\right] - n^2\sin\xi\sin\left[m\xi(s-1)\right]\right\}\sin\xi\, e^{-\xi^2\tau}}{\xi\left[\left(g\xi\sin\xi - \cos\xi\right)^2 + n^2\sin^2\xi\right]} d\xi, \qquad (2)$$

$$1 < s < \infty,$$

where index 1 refers to the rapidly solidified foil; index 2 – to the *Cu*-substrate;
$s = x/d$ и $\tau = ta_1/d^2$ – dimensionless distance and time respectively;
$m = \sqrt{a_1/a_2}$, $n = \sqrt{a_2/a_1}\,\lambda_1/\lambda_2$, – dimensionless parameters characterizing the heat transfer process;
h – heat transfer coefficient at the alloy-substrate interface, depending on the substrate material, alloy composition and ultra-rapid solidification method;
a и λ – coefficients of thermal diffusivity and thermal conductivity;
ξ – variable of integration.

Let's change the problem statement. Let the cooling surface (in this case, the *Cu*-substrate) have a constant temperature, then the solution will have the form of the sum of an infinite series:

$$T_1(s,\tau) = T_{20} + 2(T_{10} - T_{20}) \sum_{n=1}^{\infty} \frac{\sin\mu_n}{\mu_n + \sin\mu_n\cos\mu_n} \cos\left(\mu_n s\right) e^{-\mu_n^2\tau}, \qquad (3)$$

where μ_n — successive solutions of the equation $\mathrm{ctg}\,\mu_n = g\mu_n$.

It should be noted that the homogeneity of cooling is expressed by the Bio number, which determines whether cooling can be considered homogeneous (at small Bio numbers), or whether the condition (at $h \to \infty$) of good thermal contact between the melt and the substrate.

The cooling rate of the melt in this case during ultrafast crystallization with uniform cooling is estimated as the following ratio:

$$u = \langle \dot{T}_1 \rangle = \frac{h\Delta T}{c_1 \rho d} = \frac{a_1 h \Delta T}{\lambda_1 d}. \tag{4}$$

For the alloy under study $Sn_{55,18}Zn_{44,50}Si_{0,23}Al_{0,09}$ $h = (1 \div 2) \cdot 10^5$ W/(m^2·K) [2]. Other thermophysical characteristics were taken from reference materials.

Ultra-high cooling rates u lead to an increase in the degree of supercooling of the alloy ΔT_{sup}, necessary for the start of the crystallization process. Then, according to the study of data [3] for the components of a multicomponent alloy, the dependence of ΔT_{sup} on $lg\ u$ in the range of 10^2–10^6 K/s can be approximated by a power function of the form:

$$\Delta T_{пер.} = (1,09 \pm 0,14)\left(\lg u[\text{К/с}]\right)^{3,09 \pm 0,09}. \tag{5}$$

According to calculations, the amount of supercooling of the system is about 100 °C.

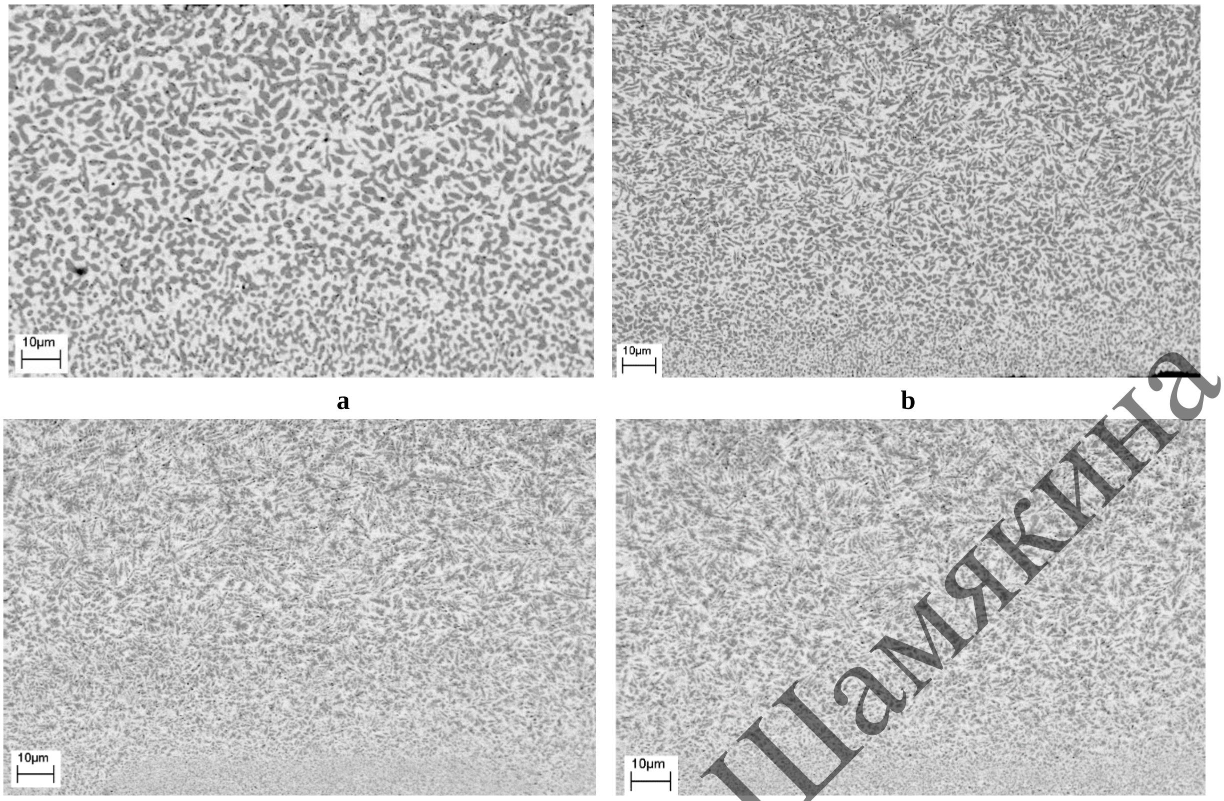
Based on the analysis of diffraction patterns, it was found that the rapidly solidified foil of the $Sn_{55,18}Zn_{44,50}Si_{0,23}Al_{0,09}$ alloy has tin and zinc diffraction lines, therefore, the rapidly solidified alloy consists of solid solutions of tin and zinc. There are also low-intensity reflexes of silicon and aluminum phases.

An image of the microstructure in the cross section of the rapidly solidified foil of the $Sn_{55,18}Zn_{44,50}Si_{0,23}Al_{0,09}$ alloy, obtained one day after production, is shown in Figure 1, a. The photograph shows dark and light areas that correspond to zinc precipitates (dark areas) and tin precipitates (light areas). Silicon and aluminum are uniformly distributed in tin as a solid solution.

The formation of the structure shown in Figure 1, a, is associated with high supercooling of the liquid. Supercooled liquid melt is a supersaturated liquid solution in which clusters are formed at temperatures close to eutectic. The structure of such clusters is close to the structure of crystalline phases. At temperatures exceeding eutectic, clusters are unstable and dissolve due to thermal atomic motion. Cluster stability is in the regions of hypoeutectic temperatures. Under such conditions, clusters grow with the formation of crystallites. Cluster formation is random, which is the reason for the homogeneity of the crystalline phases of the rapidly solidified alloy.

In rapidly solidified foils of the alloys under study, a preferential orientation of the grains of both phases is observed. The maximum values of the pole density are found in the diffraction lines of tin 200 and zinc $10\bar{1}0$, which indicates the formation of the texture (100) of tin and $(10\bar{1}0)$ of zinc. Such a pronounced character of the forming texture is observed during the crystallization of pure components [4].

Rapidly solidified $Sn_{55,18}Zn_{44,50}Si_{0,23}Al_{0,09}$ alloy is in a thermodynamically unstable state [5]. During isothermal annealing, the structure of the rapidly solidified alloy (Fig. 1, b-d) changes and becomes more dispersed. According to the results of X-ray spectral microanalysis, it was established that zinc atoms dissolve in the matrix solution of the tin phase.

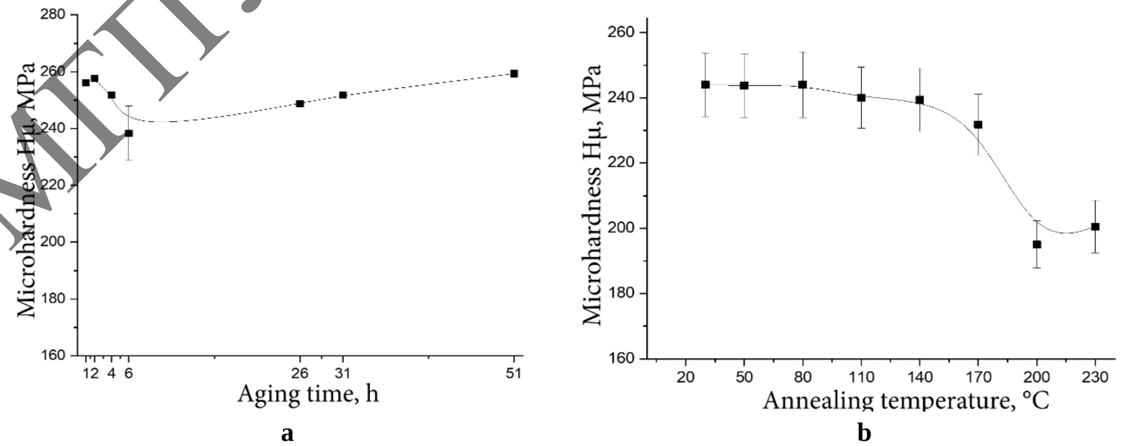


a b

c d

Figure 1 – Image of the microstructure of the cross section of rapidly solidified foil of the $Sn_{55,18}Zn_{44,50}Si_{0,23}Al_{0,09}$ alloy: a – in the initial (freshly quenched) state; b – after annealing for 30 min/150 °C; c – after annealing for 90 min/150 °C; d – after annealing for 170 min/150 °C

When analyzing the microhardness during natural aging of the rapidly solidified $Sn_{55,18}Zn_{44,50}Si_{0,23}Al_{0,09}$ alloy (Figure 2, a), an initial rise in the graph is noted during the first 2 hours of holding, and subsequent stabilization of the H_μ parameter. Some growth in the graph during subsequent holding time intervals is explained by the measurement error. At the first stage of holding, the growth of microhardness is due to the formation of a large number of tin (zinc) clusters due to zinc (tin) supersaturation, as well as the reinforcing effect of alloying elements. Then, the clusters of areas enriched with tin (zinc) turn into tin (zinc) precipitations.



a b

Figure 2 – Graph of change in microhardness of rapidly solidified foil of $Sn_{55,18}Zn_{44,50}Si_{0,23}Al_{0,09}$ alloy: a – during natural aging; b – during isochronous annealing

Isochronous annealing (Figure 2, b) leads to a sharp decrease in microhardness at temperatures starting from 170 °C. Zinc dissolves in the matrix phase, with a decrease in its volume, while the proportion of the softening phase of tin increases, which leads to a decrease in microhardness during heat treatment.

Thus, ultra-high cooling rates *u* lead to an increase in the degree of alloy supercooling ΔT_{sup}, necessary for the onset of the crystallization process. The supercooling value of the studied alloy is about 100 °C. The rapidly solidified $Sn_{55,18}Zn_{44,50}Si_{0,23}Al_{0,09}$ alloy has a dispersed structure consisting, after production and holding at room temperature, of solid solutions of tin and zinc, and dispersed particles of alloying elements. The grinding of phase precipitates is due to the high degree of liquid supercooling. It was revealed that during isothermal annealing at 150 °C, the average size of zinc precipitates decreases by 3 times, and the volume fraction of Zn zinc decreases.

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КОМПЬЮТЕРНОЕ МОДЕЛИРОВАНИЕ СТРУКТУРЫ И ИНФРАКРАСНЫХ СПЕКТРОВ БИОЛОГИЧЕСКИ АКТИВНЫХ МОЛЕКУЛ КЛАССА ФИТОГОРМОНАЛЬНЫХ СТЕРОИДОВ

Для установления спектро-структурных корреляций практически важных биологически активных стероидных фитогормонов – молекул (22S,23S)-24-эпикастастерона и (22S,23S)-28-гомокастастерона – проведен сравнительный анализ экспериментальных ИК спектров и теоретических спектральных кривых поглощения этих близких по химическому строению