ФОРМИРОВАНИЕ СТРУКТУРЫ БЕССВИНЦОВЫХ СПЛАВОВ ОЛОВО – ЦИНК, ПОЛУЧЕННЫХ МЕТОДОМ ВЫСОКОСКОРОСТНОГО ЗАТВЕРДЕВАНИЯ, И ОСОБЕННОСТИ ИХ КРИСТАЛЛИЗАЦИИ

Д. А. ЗЕРНИЦА1, В. Г. ШЕПЕЛЕВИЧ2

1) Мозырский государственный педагогический университет им. И. П. Шамякина, ул. Студенческая, 28, 247760, г. Мозырь, Беларусь
2) Белорусский государственный университет, пр-т Независимости, 4, 220030, г. Минск, Беларусь

Приведены результаты исследования микроструктуры бессвинцовых сплавов олово – цинк, полученных высокоскоростной кристаллизацией при скорости охлаждения не менее 105 К/с. В сплавах олова и цинка с концентрациями 1,2–2,0 мас. % Zn и 1,5 мас. % Sn соответственно при высокоскоростном охлаждении расплав происходит захват легирующего элемента. Образованные твердые растворы являются пересыщеными и при комнатной температуре распадаются по механизму образования и роста зародышей новой фазы. Средний размер выделений цинка и олова после выдержки фольги в течение двух суток не превышает 0,5 мкм. Расплавы составов Sn – 4,4–15,0 мас. % Zn после высокоскоростного охлаждения являются переохлажденными и пересыщенными двумя компонентами и испытывают спинодальный распад (расщепление) с последующим образованием пересыщенных твердых растворов на основе олова и цинка, которые распадаются при комнатной температуре. Средний размер выделений цинка в неравновесной эвтектике не превышает 2 мкм. В быстрозатвердевших фольгах сплавов, содержащих 50–80 мас. % Zn, формируется двухфазная структура из твердых растворов на основе олова и цинка. Средний размер выделений цинка в неравновесной эвтектике не превышает 1 мкм. По мере перемещения фронта кристаллизации происходит укрупнение частиц олова и уменьшение удельной поверхности межфазной границы.

Ключевые слова: быстрозатвердевшие сплавы; олово; цинк; пересыщенный раствор; микроструктура; эвтектика.

STRUCTURE FORMATION AND PECULIARITIES OF CRYSTALLISATION OF LEAD-FREE TIN – ZINC ALLOYS OBTAINED BY RAPID SOLIDIFICATION

D. A. ZERNITSA1, V. G. SHEPELEVICH2

1) Mozyr State Pedagogical University named after I. P. Shamiakin, 28 Studenckaja Street, Mazyr 247760, Belarus
2) Belarusian State University, 4 Niezaliežnasci Avenue, Minsk 220030, Belarus

Corresponding author: D. A. Zernitsa (dzernitsa@mail.ru)

The results of the study of the microstructure of lead-free alloys of the tin – zinc system obtained by rapid solidification at a cooling rate of at least 105 K/s are presented. In tin and zinc alloys with concentrations of 1.2–2.0 wt. % Zn and...
1.5 wt. % Sn, respectively, during rapidly cooling of the melt, the alloying element is captured. The formed solid solutions are supersaturated and at room temperature disintegrate according to the mechanism of formation and growth of nuclei of a new phase. The average size of zinc and tin precipitates after holding the foil for two days does not exceed 0.5 µm. Melts of compositions Sn – 4.4–15.0 wt. % Zn after rapidly cooling are supercooled and supersaturated by two components and experience spinodal decomposition (stratification) followed by the formation of supersaturated solid solutions based on tin and zinc, which disintegrate at room temperature. The average size of zinc precipitates in non-equilibrium eutectic does not exceed 2 µm. In rapid solidified foils of alloys containing 50–80 wt. % Zn, a two-phase structure is formed from solid solutions based on tin and zinc. The average size of tin precipitates does not exceed 1 µm. As the crystallisation front moves away from the contact surface of the foil with the surface of the mold, the tin particles become larger and the specific surface of the interphase boundary decreases.

**Keywords:** rapid solidified alloys; tin; zinc; supersaturated solution; microstructure; eutectic.

**Introduction**

Lead-free tin – zinc alloys are used in various industries. They have found application as protective coatings with a thickness of several tens of micrometers. Numerous solders have been developed based on the alloys of the tin – zinc system (for example, alloys of the tin – zinc brand, in which the concentration of components varies from 10 to 90 %). Tin- and zinc-based alloys are also widely used in foundry, mechanical engineering, etc. [1].

In recent decades, increased attention has been paid to the crystallisation of materials under non-equilibrium conditions. The problem of zinc crystallisation was described in the works [2–6]. Methods of obtaining materials under non-equilibrium conditions include laser and plasma treatment, ion implantation, as well as rapid solidification, at which the liquid cooling rate reaches 10⁶ K/s [7; 8]. The structure of materials, as well as properties, can differ significantly compared to materials obtained under equilibrium conditions, which is noted in the works [8; 9], etc.

In this regard, the manufacture of solders based on this system in the form of rapidly solidified foils is of undoubted interest. The quality of the products depends on the chemical composition and structure formed during crystallisation [7]. The solidification of alloys at rapidly cooling rates from the melt in the form of foils makes it possible to create a structure significantly different from the structure of massive alloys manufactured using traditional technologies [10].

Unfortunately, there are very few works devoted to the study of crystallisation of zinc with tin under non-equilibrium conditions, and work is mainly carried out in areas of low concentrations of components, including eutectic compositions, which is reflected in the experiments described in the works [11–14]. Nevertheless, the study of phase formation during high-speed solidification of tin – zinc alloys at concentrations of zinc and tin in wide ranges has scientific and practical significance, which determines the relevance of the work.

**Experimental procedures**

Alloys of the tin – zinc system are obtained by fusing components having a purity of at least 99.99 %. To obtain rapidly solidified foils, a piece of alloy weighing ~0.2 g was melted, and then a drop of melt was injected onto the inner polished surface of a rapidly rotating copper cylinder (rotation speed 25 rpm), spread on the surface of the mold and solidified in the form of a thin foil. Foils with a thickness from 30 to 80 µm were used for the study. The melt cooling rate was 10⁵–10⁶ K/s [15].

The study of the microstructure of rapidly solidified foils was carried out using a LEO-1455VP scanning electron microscope (Carl Zeiss, Germany), which has an attachment for X-ray spectral microanalysis, and a Ultima IV X-ray diffractometer (Rigaku, Japan) with a copper anode. The diffractograms of the studied samples were recorded at speeds of 0.5–2.0 deg/min. The hkl diffraction reflection indices of the studied alloys were determined from the International Centre of Diffraction Data databases (PDF-2, PDF-4).

Measurements of the parameters of the elementary cells of the crystal lattice were carried out in accordance with the positions of the diffraction lines belonging to tin and zinc. The relative error in determining the diffraction lines was no more than 0.01 %:

$$\frac{\Delta d}{d} = \left| \text{ctg} \theta \Delta \theta \right|,$$

where $d$ is the interplane distance, pm.

Microhardness measurements were carried out on the PMT-3 device (JSC «LOMO», Russia) with an error of up to 4 %. In order to study the effect of exposure at room temperature with the establishment of various processes, the rapidly solidified foils were subjected to natural aging. A series of experiments were conducted to measure the parameters of the unit cell over time after receiving the foil (after 15 min).
Results and discussion

When studying the process of structure formation during rapid solidification of tin – zinc alloys, it is advisable to divide them into three groups: 1) tin and zinc alloys with a low concentration of alloying elements; 2) eutectic alloy, and alloys whose compositions are close to eutectic; 3) other alloys in which the concentrations of tin and zinc are comparable [16].

Rapidly solidified foils of double alloys with a small concentration of alloying elements Sn – 1.2–2.0 wt. % Zn and Zn – 1.5 wt. % Sn after manufacture and exposure at room temperature have a two-phase structure (fig. 1). In foils of the Sn – 1.2–2.0 wt. % Zn alloy, dark zinc precipitates are formed, and in foils of the Zn – 1.5 wt. % Sn alloy, light tin precipitates are formed. The average size of the precipitates of the second phase after exposure for 2 days after their manufacture does not exceed 0.5 µm. There is no formation of dendrites and lamellar zinc precipitates in the foils.

The formation of the observed microstructure is due to the fact that when cooling at a high rate of the main phase, the capture of alloying elements occurs. As a result, solid solutions based on tin and zinc are formed. Since the maximum solubility of zinc in tin and tin in zinc in the solid state does not exceed ∼0.36 at. % [16], then solid crystalline solutions are supersaturated and have an increased value of free energy $F$. The room temperature for tin and zinc is high. Therefore, diffusion processes are actively occurring in supersaturated solid solutions [17]. Due to energy and concentration fluctuations, the decomposition of supersaturated solid solutions occurs through the formation and growth of nuclei [18]. The formation of the nuclei of a new phase is heterogeneous and occurs mainly in places (dislocations, grain boundaries, crystalliser surface) with an excess of free energy. The decay of supersaturated solid solutions is confirmed by a change in their crystal lattice parameters (table 1).

![Table 1](image)

<table>
<thead>
<tr>
<th>Crystal lattice parameter, nm</th>
<th>State of the rapidly solidified alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn – 1.2 wt. % Zn 0.5827</td>
<td>Alloy foil cured for 3 h after fabrication</td>
</tr>
<tr>
<td>Sn – 2.0 wt. % Zn 0.5824</td>
<td></td>
</tr>
<tr>
<td>Zn – 1.5 wt. % Sn 0.4952</td>
<td></td>
</tr>
<tr>
<td>0.5828</td>
<td>Alloy foil cured for 50 h after fabrication</td>
</tr>
<tr>
<td>0.5828</td>
<td></td>
</tr>
<tr>
<td>0.4944</td>
<td>Unalloyed tin and zinc foils</td>
</tr>
</tbody>
</table>

The radius of the tin atom is greater than the radius of the zinc atom [19]. Therefore, the parameters of the crystal lattice of a solid solution of tin decrease, and zinc increase with rapid crystallisation. Exposure of foils for 50 h at room temperature leads to an increase in the parameters of the crystal lattice of tin, and to a decrease in the parameter of the crystal lattice of zinc. Thus, rapidly solidified tin and zinc alloys containing a small amount of alloying elements, after manufacture and exposure at room temperature, consist of solid solutions of tin and zinc, and dispersed particles of alloying elements.

Consider the crystallisation of tin – zinc alloys with a concentration of components close to eutectic (the second group of alloys). Image of the microstructure of rapidly hardened foils of hypoeutectic Sn – 4.4 wt. % Zn, eutectic Sn – 8.8 wt. % Zn and hypereutectic Sn – 15 wt. % Zn of alloys after exposure for 3 days is shown.
in fig. 2. On a light background corresponding to a solid solution of tin, dark dispersed zinc particles are observed. They have an equiaxial shape. The distribution of the chords of random secant zinc particles in the cross-sections in the rapidly solidified foils of these alloys are the same [20], which indicates the same nature of the crystallisation process in them. A non-equilibrium eutectic with a globular structure is formed [21].

Zinc particles precipitated near the surface $A$ of the foil in contact with the crystalliser are more dispersed than in the volume adjacent to the opposite surface $B$ of the foil, which is associated with a decrease in supercooling of alloys as they move away from the surface $A$. The average length of the chords $d_{Zn}$ does not exceed 1 µm. The volume fraction of zinc $V_{Zn}$ increases, and the specific surface of $S_{MPG}$ decreases with increasing distance from the surface $A$ of the foil (fig. 3).

**Fig. 2.** Microstructure of rapidly solidified foils of hypoeutectic (Sn – 4.4 wt. % Zn) ($a$), eutectic (Sn – 8.8 wt. % Zn) ($b$) and hypereutectic (Sn – 15 wt. % Zn) ($c$) alloys

**Fig. 3.** Dependence of the volume fraction of zinc $V_{Zn}$ ($1$), the average length of chords $d_{Zn}$ ($2$) and the specific surface of $S_{MPG}$ ($3$) of the Sn – 15 wt. % Zn alloy foil
The supercooling of the melt during rapidly cooling is at least 100 °C. Therefore, supercooled melts have a temperature below the eutectic. In this case, the liquid is not only supercooled, but also supersaturated with both components [22]. The dependence of free energy on the concentration of \( F(c) \) has a \( W \)-shaped form, and its second derivative is \( \frac{d^2F}{dc^2} < 0 \). The supersaturated liquid solution disintegrates by the spinodal mechanism as a result of numerous small fluctuations [23], in which two supersaturated solutions based on tin and zinc are formed. The formation of a supersaturated solid solution based on tin is confirmed by a change in the parameters of the crystal lattice of tin (table 2) depending on the exposure time at room temperature.

\[
\begin{array}{|c|c|c|c|c|c|c|}
\hline
\text{Tin lattice parameters} (a \text{ and } c) \text{ for Sn – 8.8 wt. } \% \text{ Zn depending on holding time} \\
\hline
\text{Holding time, h} & 2 & 3.5 & 5 & 6 & 26 & 29 & 31 \\
\hline
a & 0.5823 & 0.5823 & 0.5824 & 0.5825 & 0.5825 & 0.5826 & 0.5826 \\
c & 0.3178 & 0.3179 & 0.3179 & 0.3180 & 0.3181 & 0.3182 & 0.3182 \\
\hline
\end{array}
\]

Alloys Sn – 60 wt. % Zn and Sn – 80 wt. % Zn belong to the third group. The microstructure of the foil layers adjacent to the surface \( A \) of the specified alloys, kept at room temperature for 3 days, is shown in fig. 4. There are light highlights having an equiaxed shape on a dark background. X-ray spectral microanalysis showed that the dark areas are enriched with zinc, and the light ones are enriched with tin. The average length of the chords of random secant tin particles in the studied alloys is fractions of a micrometer.

Only diffraction reflections of tin and zinc are observed on the X-ray of the foil of the alloy Sn – 60 wt. % Zn (fig. 5). Diffraction reflections of other phases were not detected.

![Fig. 4. Microstructure of foil layers adjacent to surface A for Sn – 60 wt. % Zn (a) and Sn – 80 wt. % Zn (b)](image)

![Fig. 5. X-ray pattern of Sn – 60 wt. % Zn foil](image)
The distribution of phase precipitation on the cross-section of the alloy foil Sn – 80 wt. % Zn, shown in fig. 6, is inhomogeneous. In the foil layer adjacent to the surface $A$ with a thickness of 15–20 $\mu$m, more dispersed tin precipitates are formed than in the rest of it. The dependence of the average length of the chords of random secant tin particles on the sections $d_{Sn}$ monotonically increases (fig. 7), and the dependence of the specific surface of the interfacial boundaries $S_{MPG}$ monotonically decreases with distance from the surface $A$.

![Fig. 6. Microstructure of the cross section of the Sn – 80 wt. % Zn alloy foil](image)

![Fig. 7. Dependence of the microstructure parameters on the distance to the surface $A$ in the rapidly solidified foil of the Sn – 80 wt. % Zn: the average chord of random secants on the sections of tin $d_{Sn}$ (1) and the specific surface of the interfacial boundaries $S_{MPG}$ (2)](image)

This character of change in $d_{Sn}$ and $S_{MPG}$ is due to the fact that during crystallisation, the layer adjacent to the surface $A$ has a supercooling of more than 100 °C, and releases heat, which reduces the supercooling of more distant layers to several degrees [15], which contributes to the formation of larger precipitates.

During annealing of the fast-hardened foil of the Sn – 80 wt. % Zn alloy, the change in the interplane distances for tin and zinc (table 3) is within the measurement error.
The effect of annealing on the interplane distances \( d (\text{Å}) \) of tin and zinc crystal lattices in the alloy Sn – 50 wt. % Zn

<table>
<thead>
<tr>
<th>Annealing conditions</th>
<th>Diffraction lines Sn</th>
<th>Diffraction lines Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>420</td>
<td>411</td>
</tr>
<tr>
<td>The initial state</td>
<td>1.304 7</td>
<td>1.293 5</td>
</tr>
<tr>
<td>Within 60 min at 50 °C</td>
<td>1.305 3</td>
<td>1.293 7</td>
</tr>
<tr>
<td>Within 120 min at 50 °C</td>
<td>1.305 3</td>
<td>1.293 7</td>
</tr>
<tr>
<td>Within 60 min at 150 °C</td>
<td>1.305 3</td>
<td>1.293 7</td>
</tr>
</tbody>
</table>

The absence of changes in the parameters of the crystal lattices of tin and zinc is explained by the fact that after supercooling of the melt, its temperature is higher than the eutectic temperature. The subsequent solidification of the alloy occurs at a lower cooling rate in the region of higher temperatures than alloys of the first and second groups.

**Conclusions**

Thus, according to the results of the study of the microstructure of lead-free tin – zinc alloys obtained by rapid crystallisation, the following conclusions can be drawn.

1. During the rapid crystallisation of alloys with a small concentration of alloying elements (Sn – 1.2–2.0 wt. % Zn and Zn – 1.5 wt. % Sn) the capture of alloying elements and the subsequent decomposition of supersaturated solid solutions occurs; the average length of the chords of random secants on zinc sections does not exceed 0.5 µm.

2. Rapid crystallisation of alloys whose composition is close to eutectic occurs as a result of spinodal decomposition of supercooled and supersaturated liquid solution, and subsequent decomposition of supersaturated solid solutions; the average length of random secant chords on zinc sections does not exceed 1 µm.

3. In alloys containing 60–80 wt. % Zn, tin precipitates are formed, having an equiaxed shape, the average chord of which does not exceed 1 µm.

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