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MICROSTRUCTURE OF RAPIDLY SOLIDIFIED ALLOY Al-1.5 WT.% Pb

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Abstract

Ultra-rapid quenching from the melt makes it possible to obtain a significant refinement of the structural components of alloys, a significant increase in the mutual solubility of components during the formation of solid solutions, and the release of metastable phases. When using the ultrafast quenching method, the cooling rate of the liquid reaches 105 K/s and higher. Aluminum alloys doped with bismuth and lead can be used to generate hydrogen by their interaction with water. During ultra-fast quenching from the melt, a microcrystalline structure is formed containing dispersed precipitates of the second component. Foils of the Al-1.5 wt. % Pb alloy are obtained from a melt droplet weighing approximately 0.3 g, injected onto the inner polished surface of a rapidly rotating copper cylinder, where it spreads and solidifies into a foil. The estimated cooling rate of the melt reached 106 K/s. A cellular structure is formed in the Al-1.5 wt. % Pb foil layer adjacent to the free surface. Dispersed lead particles are located at the cell boundaries and in the cell volume. The shape of the lead particles is close to spherical, which is due to the minimum value of the surface energy of the alloy. Isothermal annealing of rapidly solidified foils of the alloy under study at 295 °C did not have a significant effect on the average diameter of lead particle cross-sections, while annealing at 400 °C caused their monotonous growth. With an increase in the annealing temperature above 400 °C, a stronger growth of lead particles located at the grain boundaries is observed than in the volume of their cells. In rapidly solidified foils of the alloy under study, a (111) texture is formed. This is explained by the fact that in the direction of heat removal, predominantly those grains grow whose {111} planes coincide with the interphase boundary and are parallel to the crystallizer surface.

Keywords: ultra-rapid quenching from melt, rapidly solidified foils of monotectic alloy Al-1.5 wt.% Pb, cellular structure, dispersed lead particles.

МИКРОСТРУКТУРА БЫСТРОЗАТВЕРДЕВШЕГО СПЛАВА Al-1.5 МАСС. % Pb

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Реферат

Сверхбыстрая закалка из расплава позволяет получить существенное измельчение структурных составляющих сплавов, значительное увеличение взаимной растворимости компонентов при образовании твердых растворов, выделение метастабильных фаз. При использовании метода сверхбыстрой закалки скорость охлаждения жидкости достигает 105 К/с и выше. Сплавы алюминия, легированные висмутом и свинцом, могут использоваться для генерирования водорода при их взаимодействии с водой. При сверхбыстрой закалке из расплава происходит формирование микрокристаллической структуры, содержащей дисперсные выделения второго компонента. Фольги сплава Al-1,5 масс. % Pb получены из капли расплава массой примерно 0.3 г, инжектируемой на внутреннюю полированную поверхность быстро вращающегося медного цилиндра, где она растекается и затвердевает в виде фольги. Расчетная скорость охлаждения расплава достигала 106 К/с. В слое фольги Al-1,5 масс. % Pb, примыкающей к свободной поверхности, формируется ячеистая структура. На границах ячеек и в объеме ячеек располагались дисперсные частицы свинца. Форма частиц свинца близка к шарообразной, что обусловлено минимальным значением поверхностной энергии сплава. Изотермический отжиг быстрозатвердевших фольг исследуемого сплава при 295 °C не оказал существенного влияния на средний диаметр сечений частиц свинца, а отжиг при 400 °C вызывает их монотонный рост. С увеличением температуры отжига выше 400 °C наблюдается более сильный рост частиц свинца, находящихся на границах зерен, чем в объеме их ячеек. В быстрозатвердевших фольгах исследуемого сплава образуется текстура (111). Это объясняется тем, что в направлении теплоотвода растут преимущественно те зерна, у которых плоскости {111} совпадают с межфазной границей и параллельны поверхности кристаллизатора.

Ключевые слова: сверхбыстрая закалка из расплава, быстрозатвердевшие фольги монотектического сплава Al-1.5 масс.% Pb, ячеистая структура, дисперсные частицы свинца.

Introduction

Technological processes in metallurgy make it possible to give metals and alloys the required mechanical properties and structure, and to change their physical and chemical properties to achieve the necessary performance characteristics of modern structures and products.

In recent decades, innovative approaches to the development and production of new materials have been actively developing. One of these new scientific directions is the production of metals and alloys from the liquid phase by the method of ultrafast quenching from melt, at which the liquid cooling rate reaches 105 K/s and higher. The term "ultra-fast melt quenching" refers to a process operation involving the rapid cooling of the melt.

The use of such a cooling rate leads to the formation of one or another metastable state. The value of this rate depends on both the type of alloy and the nature of metastability. High-speed solidification of materials allows obtaining various states: amorphous, quasi-crystalline and microcrystalline. This type of hardening causes a significant grinding of structural components, a significant increase in the mutual solubility of components during the formation of solid solutions, and the release of metastable phases. To achieve the required cooling rates ($10^7 - 10^{10}$ K/s), technological solutions are required that differ significantly from traditional casting methods. The main method for ultra-fast melt quenching is to cool the melt by removing heat through a solid substrate through thermal conduction.

The main condition for ultra-fast cooling in this case is that the thickness of the melt in the direction of heat transfer should be as small as possible. For effective heat removal, good contact of the melt with the coolant, high thermal conductivity of the coolant, and an increase in the heat transfer coefficient at its boundary with the heat-conducting substrate are also important.

According to the type of cooling, there are three methods of ultra-fast melt quenching: single-sided, double-sided and multi-sided cooling. Single-sided cooling methods involve the injection of droplets or a melt jet on a well-dissipated heat removal substrate. The increase in the contact area is achieved by spreading the drop upon impact with the substrate.

The formation of a thin layer of liquid that is in good thermal contact with the heat receiver is based on the use of contact between the thin liquid belt and the moving cooling substrate. In the spinning method, a drop of molten metal hits the polished surface of a fast-rotating copper cylinder and solidifies in the form of foil.

The structure of rapidly solidified foils differs significantly from the structure of massive samples obtained at low and medium cooling rates, and also has features compared to the structure of rapidly solidified metals with a higher melting point. Micro- and nanocrystalline materials obtained by ultra-fast quenching from the melt have characteristics almost equal to those of amorphous metals and have greater thermal stability. This has generated interest in rapidly cooled alloys with a low melting point. Aluminum-based alloys are quite dependent on the rate and history of cooling and are well modified by annealing, cold working, and other methods of external action.

Alloys of the aluminum-lead system, in which monotectic transformation takes place at 659 °C and eutectic transformation at 327 °C, are used in mechanical engineering as antifriction and damped materials [1, 2, 3]. In alloys of the Al-Pb, Al-Bi, Al-In and other systems, stratification into two liquids occurs, one of which is enriched with aluminum, and the other with an alloying element [3]. There have been reports of the use of aluminum alloys doped with bismuth and lead to generate hydrogen when interacting with water [4, 5]. Studies have been carried out on the interaction of aluminum with water at high pressures and temperatures in order to produce hydrogen [6–10]. In recent decades, research has been actively carried out on materials synthesized under highly non-equilibrium conditions, for example, during ultrafast melt quenching, when the cooling rate reaches 10^6 K/s [11–13]. Studies of the influence of external energy influences, in particular, a weak magnetic field, on the physical and mechanical properties of non-magnetic metals are also being actively investigated [14, 15]. In case of ultra-rapid quenching, a microcrystalline structure is formed, containing dispersed precipitates of the second component. It has been established that rapidly solidified alloys of the Al-Bi system interact with water at room temperature and normal atmospheric pressure, forming aluminum oxides and generating hydrogen [15, 16], which can be used immediately after its release. In this regard, the study of the structure and properties of rapidly solidified foils of the monotectic alloy Al-1.5 wt.% Pb, as well as their stability, is relevant and has scientific and practical significance.

Experimental methods

Monotectic alloy Al-1.5 wt. % Pb is made by fusing the components in a quartz ampoule. The purity of the components used is 99.99. The foils are obtained from a drop of melt weighing ≈ 0.3 g, injected onto the inner polished surface of a rapidly rotating copper cylinder, where it spreads and solidifies into a foil [17]. In the study of the structure, fast-hardened foils with a thickness of 40–70 μm were used. The estimated cooling rate of the melt reached 10^6 K/s. The study of the structure of the foils was carried out on a LEO 1455VP scanning electron microscope with a special "HKL CHANNEL 5" attachment. X-ray spectral microanalysis of rapidly solidified alloy foils was carried out using a Rontec detector. X-ray structural studies were performed on the Ultima 1V diffractometer using copper radiation. The pole densities of the diffraction lines of the inverse polar figures were calculated using the Harris method [18]. The parameters of the microstructure (grain size and specific surface energy of grain boundaries) were determined by the method of random secant cross-sections of grains [19]; the measurement error was 5–8 %. The microhardness of the foils was measured using a microhardness tester using a load of 3 g.

Results and discussion

To study the structure and properties, rapidly solidified foils were used, the length and width of which reached 10 and 1 cm, respectively. Micron-sized cavities were observed on the mirror surface (A) of the foil in contact with the crystallizer. Due to the decrease in heat transfer in this area of the foil, the cooling rate of the melt decreased, which led to the appearance of lead particle precipitation on the surface of the cavities. The opposite surface of the rapidly solidified foil (B) had a bumpy structure. A cellular structure was observed on it (Figure 1); the size of the cell cross-sections varied in the interval from 2 to 8 μm. Dispersed lead particles were located at the cell boundaries and in the cell volume.
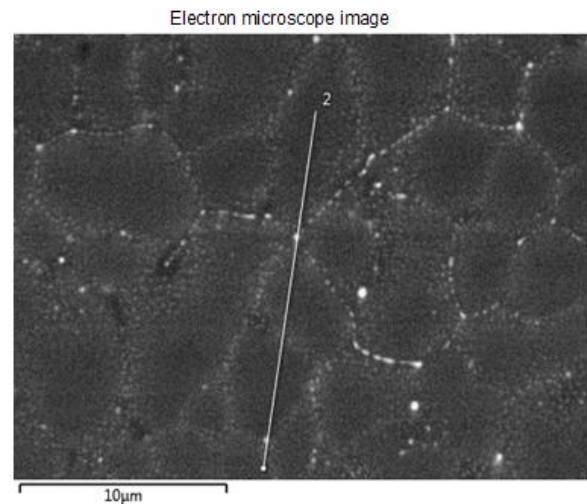

Figure 1 – Cellular structure of surface B of rapidly solidified Al-1.5 wt.% Pb alloy foil

The cross-sectional image of the rapidly solidified Al-1.5 wt.% Pb alloy foil is shown in Figure 2. Layers *a* and *b* are adjacent to the foil surfaces A and B, respectively, and layer *c* is located in the middle part of the foil. Layer *a* has more dispersed lead particles than layers *b* and *c*. As the crystallization front moves from surface A to B, enlargement of lead particles is observed, which is associated with a decrease in supercooling of the liquid phase. The shape of lead particles is close to spherical, which is due to the minimum value of the surface energy of the alloy [20].
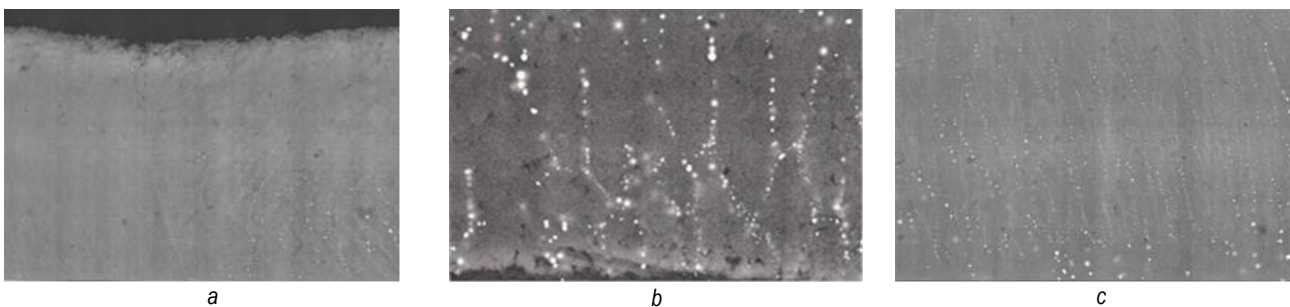

| *a* | *b* | *c* |

Figure 2 – Cross-sectional microstructure of Al-1.5 wt.% Pb alloy foil. (*a*, *b* are the foil layers adjacent to its surfaces A and B, respectively, *c* is the middle part of the foil)

Distributions of cross-section diameters of lead particles of the Al-1.5 wt.% Pb alloy by size groups in layers *a*, *b* and *c* are characterized by the presence of a maximum. The average size of lead precipitates in the foil increases as the crystallization front moves. The structure of foils and massive samples was compared. In massive samples obtained at cooling rates of 10^{-2} and 10^{2} K/s, the average size of lead particles is 15 and 1.2 μm, respectively, and in layers *a*, *b*, and *c* of rapidly solidified foils, 0.11, 0.13, and 0.15 μm, respectively.

Isothermal annealing of quickly solidified foils of the alloy under study was performed for eight hours at temperatures below and above the melting point of lead. Annealing at 295 °C did not have a significant effect on the average diameter of lead particle cross-sections, while annealing at 400 °C caused their monotonous growth.

During high-speed solidification, due to significant supercooling of the melt, lead atoms are "captured" by aluminum precipitates. According to the data of work [21], devoted to the study of the effect of supercooling on the decomposition of a supersaturated aluminum-lead solution, it was found that when the melt is supercooled by more than 20 °C, lead nanoclusters are formed in it. During high-speed cooling of the melt [12], supercooling in the layer adjacent to the crystallizer surface reaches 200 °C, which promotes the formation of dispersed lead deposits. When the crystallization front moves from surface A to surface B, due to the release of heat during crystallization, the value of supercooling of the liquid phase decreases, which causes an increase in lead deposits and the formation of a cellular structure.

When the alloy is cooled below the eutectic temperature, the remaining lead-rich liquid undergoes a eutectic transformation, which produces lead and aluminum precipitates. The aluminum precipitates are adjacent to the previously solidified aluminum. Lead deposits are located at the grain boundaries of the main component; they are larger compared to previously formed lead particles and localized at the cell boundaries and inside them. This difference is 2–4 times.

Rapidly solidified foils of the monotectic Al-1.5 wt.% Pb alloy have a microcrystalline structure. Figure 3 shows images of the grain structure on the A side of the foil.
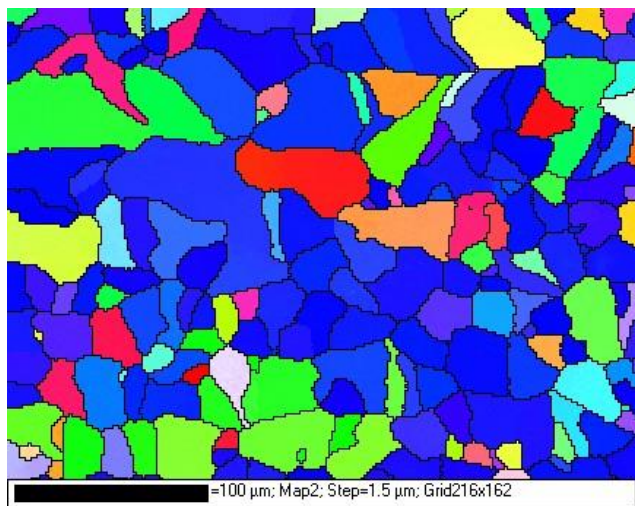
Figure 3 – Grain structure of rapidly solidified Al-1.5 wt.% Pb alloy foil on surface A.

The random intercept method was used to determine the distribution of chords on grain cross-sections by size groups and presented as histograms in Figure 4. The maximum proportion of chords falls on the size group from 20 to 40 μm. The parameters of the grain structure were determined. The average values of the chord lengths on grain cross-sections on surfaces A and B are 31 and 30 μm, respectively. The average value of the grain size is 52 and 50 μm, respectively. The specific surface area of the grain boundaries is 120 $μm^{-1}$.
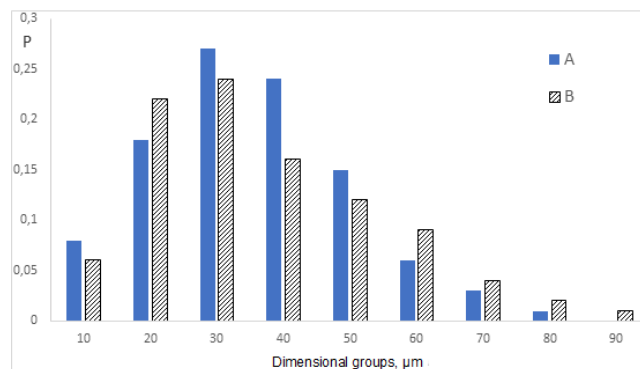
Figure 4 – Histogram of the distribution of chords of random secants on the sections of grains of rapidly solidified foils of the Al-1.5 wt.% Pb alloy in the initial state on the surface A (a) B (b)

In rapidly solidified foils of the alloy under study, a preferred grain orientation is formed. Figure 5 shows the pole figures of the {111} planes of aluminum on the surface of foil A. Gnomostereographic projections of the {111} planes of aluminum are located predominantly in the center of the projection circle or at a small distance from it, which indicates the formation of the {111} texture. A weaker similar texture is formed in the foil layer adjacent to the free surface, i. e. the texture of the rapidly solidified foil {111} is retained as the crystallization front moves.
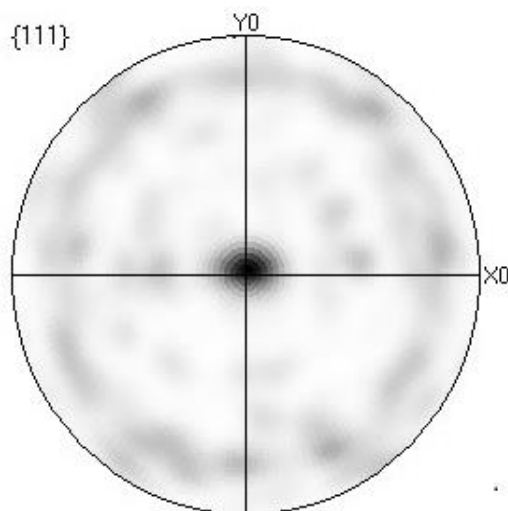
Figure 5 – Pole figure of the gnostereometric projections of the {111} planes of the aluminum foil of the Al-1.5 wt.% Pb alloy on the surface A

The formation of aluminum texture (111) in rapidly hardened foils is confirmed by the calculation of the inverse pole densities of aluminum diffraction lines presented in Table 1. Pole densities were calculated using the Harris method. Texture formation (111) has been observed previously in fast-hardened foils of other aluminum alloys with other elements [22, 23].

Table 1 – Pole densities of diffraction lines of rapidly solidified foils of Al-1.5 wt.% Pb alloy

Diffration reflections	Annealing temperature, °C				
	20 °C	180 °C	350 °C	470 °C	600 °C
200	0,2	0,2	0,3	0,2	0,2
220	0,5	0,4	0,4	0,4	0,4
311	0,3	0,4	0,3	0,3	0,3
222	4,7	4,7	4,6	4,7	4,7
331	0,2	0,2	0,2	0,2	0,2
429	0,1	0,1	0,2	0,2	0,2

The rationale for the formation of the (111) texture in aluminum is given in [24, 25], which presents the results of calculating the energy barrier during the movement of the crystal-liquid interphase boundary for various crystallographic planes. It has been established that its value takes a minimum value for the interphase boundary coinciding with the {111} planes. Therefore, in the direction of heat removal, predominantly those grains grow whose {111} planes coincide with the interphase boundary, i. e. are parallel to the crystallizer surface, thereby forming the (111) texture.

A study was conducted on the effect of annealing on the texture of the foils of the alloy under study. It was found that in the annealing temperature range from 20 to 600 °C, the pole densities of diffraction reflections change by no more than 0.1, i. e. the texture of rapidly solidified foils is preserved, which may be due to the presence of liquid dispersed lead deposits at the grain boundaries.

Rapidly solidified foils of the investigated Al-1.5 wt.% Pb alloy are in an unstable state. Thus, holding rapid solidified foils at room temperature for 2 hours leads to an increase in microhardness by 20 %, which is explained by the decomposition of the supersaturated solid solution based on aluminum, causing the release of strengthening dispersed lead particles.

A subsequent increase in the exposure of foils at room temperature does not change their microhardness. However, with an increase in the annealing temperature above 400 °C, there is a stronger growth of lead particles located at the grain boundaries than in their cell volume (Figure 6). Most likely, this is due to the fact that the diffusion processes that cause the movement of lead atoms in the area of grain boundaries proceed more intensively than in their volume at the same annealing temperature.
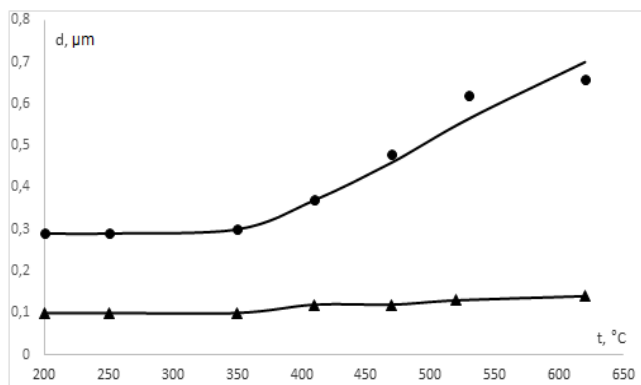

Figure 6 – Dependence of the average diameter of lead particles of the Al-1.5 wt.% Pb alloy located at grain boundaries (1) and in the bulk of cells (2) on the annealing temperature

Conclusions
Thus, a cellular structure is formed in the Al-1.5 wt. % Pb foil layer adjacent to the free surface. The size of the cell sections varied in the range from 2 to 8 µm. The diameter of the lead particle cross-sections increases monotonically with the movement of the crystallization front from 0.1 to 0.3 µm. The average grain size in the foils is 51 µm, and the specific surface area of the grain boundaries is 120 µm^{-1}. In rapidly solidified foils of the alloy, a (111) texture is formed. Annealing the foils above 400°C causes a decrease in the density of lead particles and an increase in the diameter of their cross-sections. The texture of the foils of the 1.5 mass. % Pb alloy is retained upon annealing up to 600 °C.

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