

Inner Size Effect in the Polycrystalline Metal Films of Fusible Metals

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We have studied the morphology changes of the continuous polycrystalline films made of fusible metals during their heating and annealing on the substrate affected by a temperature gradient. It was found that melting of the polycrystalline metal films with grain sizes distributed in a wide interval occurred only in a certain temperature range, and this range is expanded with decreasing average characteristic grain size. We also have estimated the average energy of intergranular borders in the tin and lead films.

Keywords: Boundary energy, Polycrystalline films, Inner size effect, Melting of polycrystalline films.

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1. INTRODUCTION

Recently, nanomaterials have attracted great attention in various fields of science and technology. As it was established in long-term studies, behavior of nano-objects can significantly differ from the behavior of bulk samples. Thus, for example, because of the increase in the contribution of surface atoms (the relative number of which increases with decreasing size), an isolated nanoparticle can have the melting temperature, lattice parameters and other properties, which differ from similar properties of bulk objects. Since structural and phase transformations occurring in the matter have not only a general scientific, but also a great practical importance, then the phase size effect [1, 2] is of special interest for scientific investigations and practical applications of nano-objects. The mentioned effect consists in the following: in small size samples one can observe the change in the phase transition temperatures as well as the existence of equilibrium phases, which, in the case of bulk samples, either do not occur at all under the specified conditions or are metastable ones (for example, [3-9]).

Thus, the influence of the characteristic size on the temperatures of the melting/crystallization phase transitions was theoretically and experimentally studied by many researchers [2, 10-15]. For the first time, decrease in the melting temperature for thin films was discovered by the electron-diffraction method in the work [10], in which it was reported about the decrease in the melting temperature of lead, tin and indium films of thickness of 5 nm by 41, 30 and 23 K, respectively. In the sequel, development of the electron diffraction technique, electron microscopy and nanocalorimetry, the use of which allowed to obtain reliable quantitative results on melting of fine particles, has conditioned the appearance of a cycle of works. The size dependences of the melting temperature for a number of metals [11-13], alloys [13, 14] and multi-layer systems [15] have been obtained by different techniques.

In whole, the performed investigations have confirmed a general tendency, according to which the decrease in the melting temperature, which can reach 500 K, is observed with decreasing size for free particles with the characteristic size less than 10 nm.

Decrease in the melting temperature with decreasing characteristic size for isolated nanoparticles is usually associated with the increase in small objects of the fraction of surface atoms, which is inversely proportional to the characteristic particle size. Since surface energy of the liquid phase is lower than of the solid one, starting from a certain size, existence of the liquid phase below the equilibrium melting temperature is found to be energetically favorable even despite the increase in the surface area, which occurs at the crystal-liquid transition. The problem of melting of nanoparticles was quantitatively solved for the first time in the work [16], the author of which has proposed to use the triple point model based on the assumption of equality of chemical potentials for small liquid and solid particles of the same mass being in equilibrium with its own vapor and obtained the following expression:

$$\frac{T_s - T_R}{T_s} = \frac{3}{\lambda R} \left(\sigma_s - \sigma_l \left(\frac{\rho_l}{\rho_s} \right)^{\frac{1}{3}} \right),$$

where T_s is the melting temperature of a bulk sample; T_R is the melting temperature of the sample of radius R ; σ_s , σ_l are the surface energy of the solid and liquid phases, respectively; λ is the melting heat; ρ_s , ρ_l are the density of the crystalline and liquid phases, respectively.

Within the framework of another approach based on the account of the influence of surface heterophase fluctuations [16] and known as the surface melting concept, decrease in the melting temperature of the object with small characteristic size is determined by the expression

$$\frac{T_s - T_r}{T_s} = K \frac{V_s}{\lambda} \left(\frac{\sigma_{sl}}{R_l - t_0} + \frac{\sigma_l}{R_l} \left(1 - \frac{\rho_l}{\rho_s} \right) \right),$$

where K is the form factor; σ_{sl} is the interfacial energy of the crystal-melt interface; V_s is the molar volume and $R_l = (R_s - t_0)$ is the molten particle radius.

Both thermodynamic models allow to conclude the decrease in the melting temperature of the matter during the transition from the bulk to nanometer samples and satisfactorily describe the experimental results. However,

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the absence of reliable experimental data, which confirms the existence of a skin-layer, and also the presence in models, which use the surface melting concept, of the hard measurable parameters allows to give preference to the triple point model for the description of the nanoparticle melting processes.

The above considered results are related to isolated nanoparticles. Difference between the surface energies of the solid and liquid phases, which is usually equal to about 10 % of the value of σ_s , is the main driving force leading to the decrease in their melting temperature.

However, we should note that grains in a polycrystalline film, in contrast to the isolated nanoparticles, have grain boundaries which separate them with the adjacent grains. The excess energy [18, 19], which in the case of fine-grained polycrystalline films can make a significant contribution to the total energy of the system, is associated with the presence of a grain boundary. Grain boundaries disappear during melting of a grain with characteristic size R and located in a polycrystalline thin film. This is accompanied by the decrease in the total energy of the given region of the melting film and can lead to its isolation from neighbors being in the solid state. As a result, formation of liquid particles in a polycrystalline film can be found energetically favorable not only at temperatures lower than the equilibrium melting temperature, but also lower than the phase transition temperature for an isolated nanoparticle with the same size R .

Earlier [19], in the study of melting of polycrystalline Pb and Bi films of the thickness of 200-2000 nm on the substrate with the temperature gradient one observed a blurring of the boundary between the liquid and crystalline states of the investigated film. This blurring is conditioned by the fact that melting of the studied polycrystalline films occurs in a certain temperature range, whose existence is conditioned by the presence of the energy of grain boundaries [19].

Because of this fact, it is reasonable to perform the investigation of melting of polycrystalline metal films with different characteristic grain sizes, for which contribution of the energy of grain boundaries will be substantially different.

2. EXPERIMENTAL

Continuous polycrystalline Pb, Bi, Sn and In films of the thickness of 200-2000 nm deposited on the amorphous carbon substrate were selected as the objects of study. Amorphous carbon is poorly wetted by melts of the chosen metals [2, 5, 9, 20, 21], whereby interaction of a metal film with the substrate material substantially decreases, and the studied films, to a certain degree, can be considered as the free ones.

The experiments were performed in vacuum of 10^{-6} - 10^{-7} mm Hg as follows. The carbon film-substrate, on which the film of the studied metal of the desired thickness was sputtered from molybdenum or tantalum evaporator, was condensed by the arc evaporation method on the rectangular glass or alumina ceramic substrate holder. Film thickness was controlled during the film deposition using quartz resonator.

Condensation of Bi, Sn and In films was carried out on room temperature substrates. Substrate temperature during condensation of different Pb samples was varied

in the range of 150-400 K. Since microstructure of the films directly depends on the temperature, at which its condensation is performed [2, 22], this gave the possibility to obtain a number of polycrystalline films with different average grain size.

After completion of condensation, one end of the substrate holder was heated up to the temperature, which exceeds the melting temperature of the investigated metal, and another end, due to the forced cooling, was maintained at room temperature. As a result, the temperature gradient was established along the substrate and its value of which was determined based on the data of chromel-alumel thermocouples attached to the back side of the substrate holder. Thus, a set of the film states corresponding to heating to different temperatures was realized on the substrate in one experiment and under the same conditions. The obtained samples were cooled in vacuum to room temperature, extracted from the vacuum plant, and then studied in the scanning electron microscope Jeol JSM-840.

3. RESULTS AND DISCUSSION

As a result of the carried out electron-microscopic investigations, it was established that the morphological structure of the film, as expected [2, 19, 20, 23], significantly depends on the temperature, to which the given region of the substrate was heated up.

As seen from the electron-microscopic images (Fig. 1), the film condensed on the substrate region, which after deposition of the sample was heated to the temperature higher than the equilibrium melting temperature of the investigated metal, was divided into separate particles of spherical shape. Such behavior is a clear evidence of short-term stay of this region of the film in the liquid state. The film remained continuous polycrystalline one in the low-temperature region of the substrate. At that, as a result of the condensation and diffusion processes, which, as known, are more intensive in thin vacuum condensates compared with bulk samples [24], through pores are formed, and their size is determined by the conditions of thermal treatment of the sample, i.e. by the temperature and annealing time [23].

Between the specified regions there is the transition zone, in which the labyrinthine structure with expressively round (fritted) shapes is observed on the electron microscopic images, and separate particles of spherical shape are observed in the ruptures of a continuous film. According to the assumption stated in [19], this region of the substrate corresponds to a partial melting of the polycrystalline film.

The quantitative study of the obtained images was performed using a specially developed software, which allows to determine the degree of filling of the film by the substrate with the temperature step in the range of 0.005-0.01 K depending on the temperature hysteresis and microscopic magnification (Fig. 2).

As seen from Fig. 2, dependences of the filling factor on the temperature can be divided into several regions corresponding to those, which can be separated on the electron microscopic images (Fig. 1) and differing by the behavior of the filling factor. Dependence of the filling factor on the temperature is almost absent in the temperature range of $T > T_s$. This area corresponds to the

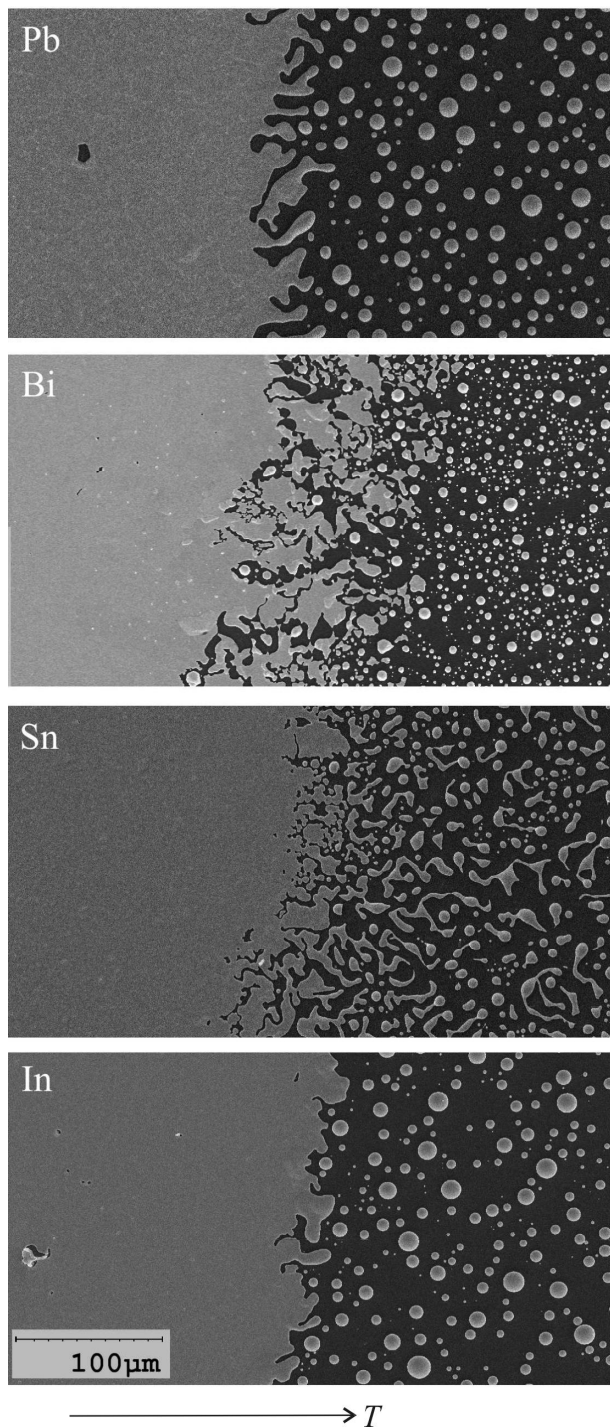


Fig. 1 – SEM images of the lead, tin and indium films in the crystalline (on the left) and molten (on the right) states

completely molten film region, in which individual particles of spherical shape are observed on the electron microscopic images. A rapid increase in the filling factor occurring under the law, which is close to the linear one, is observed on the images near the melting temperature when moving towards lower temperatures. This zone is the transition zone between the completely molten and continuous film. Structure of the transition zone for the studied films is well seen in Fig. 1. Then with decreasing temperature, the region of diffusion porosity is located on the image. Here, the film remains continuous poly-

crystalline film during heating, at that, one can observe individual pores in it, whose size decreases exponentially with decreasing temperature, and filling factor of the substrate by the film increases tending to 1 [23].

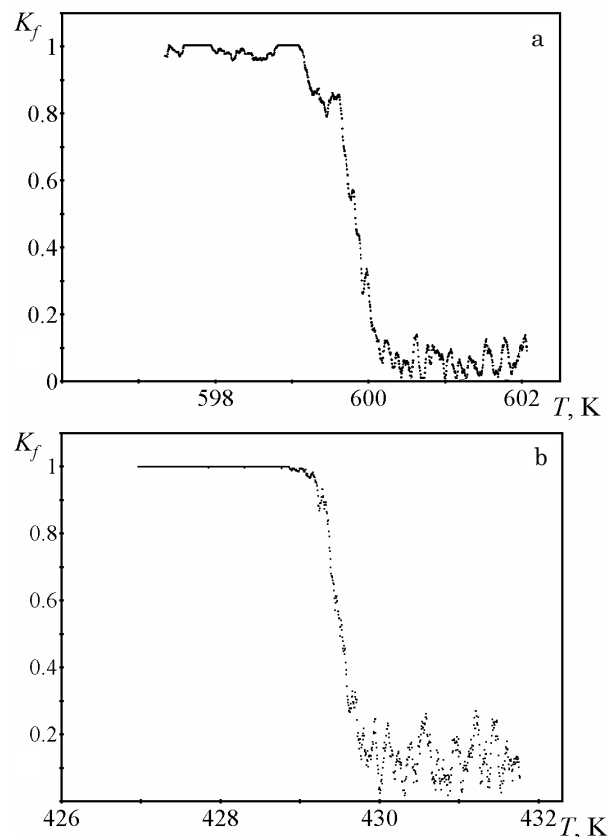


Fig. 2 – Dependence of the filling factor on the temperature in the lead (a) and indium (b) films

Transition zone is clearly manifested on sufficiently thick films (at films thickness of about 1000 nm). With decreasing film thickness, transition zone becomes poorly visible on the background of porosity, which is conditioned by the diffusion processes actively occurring in the films of smaller thickness [19, 24, 23]. Width of the transition zone for the studied films is equal to 0.6, 2.5, 0.3, 0.7 K for lead, bismuth, tin and indium, respectively.

As an explanation of transition zone formation, in which partial melting of the film occurs, the authors of [19] have made the assumption that prolonged melting of a polycrystalline film is associated with the fact that sizes of its constituent grains are distributed in a wide range of values. Obviously, since contribution of the energy of grain boundaries to the total energy of a grain and, consequently, its melting temperature are determined by its size and orientation with respect to neighbors, each grain will begin to melt at its own temperature, which will be different for different grains. As a result, film melting will occur in a certain temperature range determined, for the specified material, by the distribution of grains in sizes.

Since energy of grain boundaries is the main driving force, which is responsible for the broadening of the melting range of single-component polycrystalline films, then the data about the existence interval of the transition band gives the possibility to evaluate this value.

To this end, using the triple point model and obvious geometric relations, we can obtain the expression, which allows to estimate the energy of grain boundaries [19]:

$$\sigma_{12} = \frac{2\Delta T \lambda h S}{T_s h l} = \frac{2\Delta T \lambda S}{T_s l},$$

where h is the film thickness; S is the average cross-sectional area of the crystallite by the plane parallel to the film surface; l is the average length of its boundary; $\Delta T = (T_s - T_R)$ is the change in the melting temperature of the film.

In order to determine the energy of grain boundaries, besides the value of the melting interval, it is necessary to perform an independent determination of the average cross sectional area of a grain and average value of its perimeter, i.e. the length of the grain boundary surrounding a grain in the substrate plane.

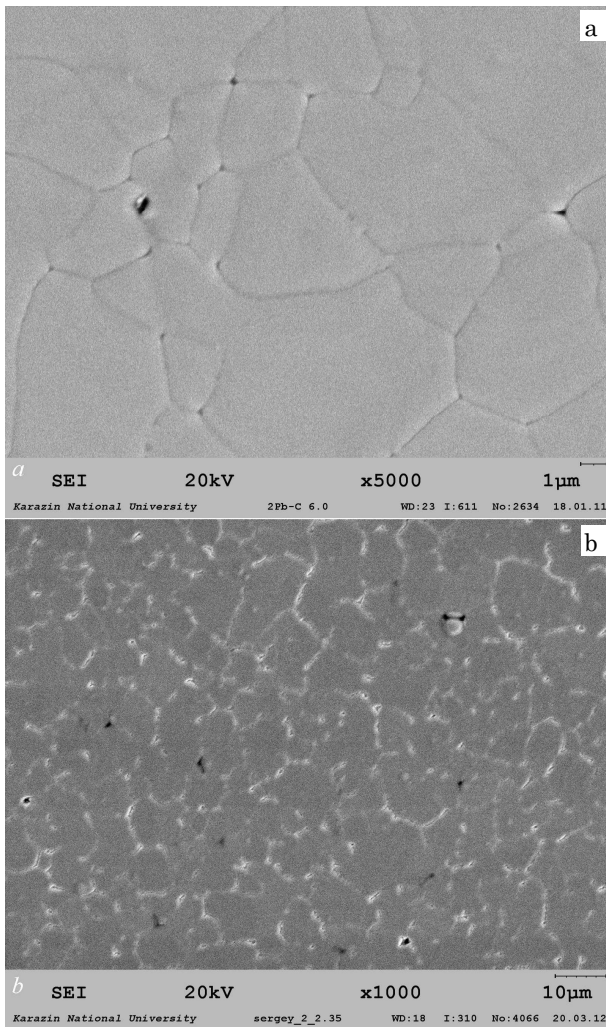


Fig. 3 – SEM images of the lead (a) and tin (b) films

Processes of thermal etching of polycrystalline films occur more actively in areas of structural defects, which are usually grain boundaries. Due to this fact, visualization of grain boundaries is found to be possible during heating and annealing of the films that was observed in the lead and tin films (Fig. 3). The average grain size in the film condensation on room-temperature substrates was approximately equal to 5 and 7 μm for the lead and

tin films, respectively. The value of the average length of a grain boundary for these films is 10-20 μm .

The values of energy of grain boundaries determined in such way are equal to 230 mJ/m² and 140 mJ/m² for the lead and tin films, respectively.

To study the influence of the average characteristic grain size on the temperature region of the transition band existence, we performed a series of experiments, in which distribution of grains, which are the constituents of the polycrystalline film, in sizes was artificially changed. To this end, Pb/C samples were deposited on glass or alumina ceramic substrates maintained at different temperatures during condensation. The obtained dependence of the temperature region of the transition band existence on the average characteristic size and inverse average characteristic grain size is shown in Fig. 4.

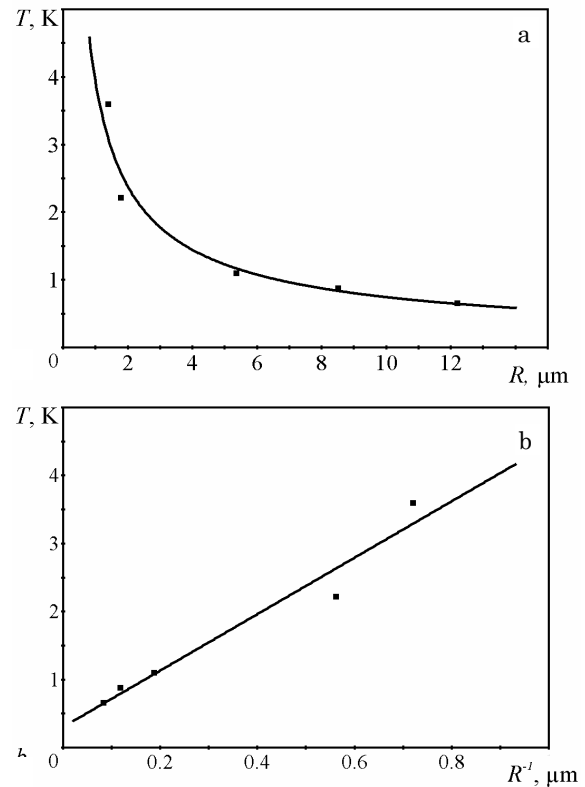


Fig. 4 – Dependence of the width of the temperature melting range of the polycrystalline lead film on the characteristic grain size in “ $T - R$ ” (a) and “ $T - R^{-1}$ ” (b) coordinates

As seen from Fig. 4b, the obtained results are well approximated by a straight line in “ $T - R^{-1}$ ” coordinates. As a result of the performed investigations it is established that width of the transition band increases with decreasing characteristic grain size. That is increase is well described by the hyperbolic dependence following from the triple point model.

Size dependence of the intercrystalline energy was not discovered in the studied range of grain sizes. The average energy of grain boundaries in a polycrystalline film, obtained by averaging of the values corresponding to different grain sizes, is equal to 230 mJ/m². According to the data of the theoretical works (for example, [25]), the value of the grain boundary energy for metals with the face-centered cubic (fcc) structure is approximately equal to one third of the surface energy for a metal in the

solid state at the temperature of $0.8 T_s$. Surface energy of the crystalline lead at the temperature of $0.8 T_s$ is in the range of 530-580 mJ/m², and of tin – ≈ 630 mJ/m² [26, 27]. The obtained values of the grain boundary energy, which are equal to 230 mJ/m² and 140 mJ/m² for lead and tin, respectively, are about 40 % and 20 % of the surface energy of metals in the solid state that does not contradict the known experimental and theoretical data (for example, [16, 25]).

4. CONCLUSIONS

Investigation of the melting of polycrystalline lead, bismuth, tin, and indium films on the amorphous carbon

substrate has been performed using the original differential technique of study the phase transformations on the substrate with temperature gradient.

It is established that melting of polycrystalline single-component films, the crystallite sizes of which are distributed in a wide range of values, occurs in a certain temperature range.

It is shown that width of the temperature melting range of polycrystalline films increases with decreasing average crystallite size.

The average energy of grain boundaries in polycrystalline lead and tin films has been estimated by the triple point model based on the data about the crystallite sizes and temperature width of the melting range.

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