

Contact Melting in Layered Film Systems of the Eutectic Type

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Abstract—The existing concepts of the mechanism of eutectic melting have been developed on the basis of the study of melting in the Sn–Bi film system. This paper reports on the experimental results indicating the possibility of visualizing an increase in the solubility of components in the Sn–Bi system with increasing temperature and the existence of a critical thickness of the film of one of the components below which no eutectic melting occurs.

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1. INTRODUCTION

The eutectic melting is characteristic of not only highly dispersed structures formed as a result of the crystallization of molten eutectics, but it has also been observed upon heating contacting crystals of two materials forming the eutectic system. Such a melting of contacting crystalline materials at a lower temperature than the melting temperature of each component is referred to as contact melting.

There is a great amount of information on studying eutectic alloys. In view of increasing demands for new materials in nanotechnology, microelectronics, and nanoelectronics, layered film systems that are based on components forming phase diagrams of the eutectic type have been widely used and, correspondingly, such systems, including their melting, have been actively studied in recent years [1–4].

However, the existing concepts of mechanisms of contact melting [5], including those of the most developed diffusion mechanism, contain ambiguities and contradictions. In particular, the main argument against the diffusion mechanism is the absence of conclusive observations of an increase in the solubility in contacting crystals of components as the eutectic temperature is approached. It is generally believed that the contact melting effect is not related to a particular weight ratio of contacting crystals, even though the complete transition to a liquid state at a constant temperature occurs only at the eutectic ratio of their weights.

Thus, it is expedient to continue the studies of the contact melting in two-layer film systems prepared by successive vacuum condensation of corresponding components evaporated from independent sources; in such systems, the contact between contacting samples of different components is known to be provided at the

atomic level. Such a method allows the formation of eutectic materials with given ratio of the thicknesses of the contacting layers. This method, in combination with films of variable compositions obtained by simultaneous condensation of the components, can be used to determine the behavior of the eutectic temperature as the concentration is changed.

To study the effect of the concentration (the ratio of the contacting layer thicknesses) on the eutectic temperature, we chose well-studied tin–lead and tin–bismuth systems. In the tin–lead system [6], the eutectic is formed at 38.1 wt % lead; the eutectic has the melting temperature 183°C. In the tin–bismuth system [6], there are two limited solid solutions forming the eutectic with the melting temperature 139°C at the content of 57 wt % bismuth. The maximum solubility of bismuth in solid tin is 20 wt % at the eutectic temperature and the maximum solubility of tin in solid bismuth sharply decreases with decreasing temperature to 2.4 wt %.

2. SAMPLES, EXPERIMENTAL TECHNIQUE, AND RESULTS

The film systems were prepared by evaporation and subsequent condensation of corresponding metals this a 99.99% purity from extended boat-shape tantalum evaporators in vacuum 10^{-7} – 10^{-8} mbar produced using a system of oil-free evacuation. As substrates, we used 0.3-cm-thick polished stainless-steel plates 16 cm in length and 6 cm in width, on which a 5- to 10-nm-thick carbon film was deposited by evaporation from an arc immediately before the condensation of the metal films. The geometry of mutual arrangement of the evaporators and substrate was chosen in such a way that, in combination with the mobile screens placed between them, the required proportion of the components and alternation of sequence of their

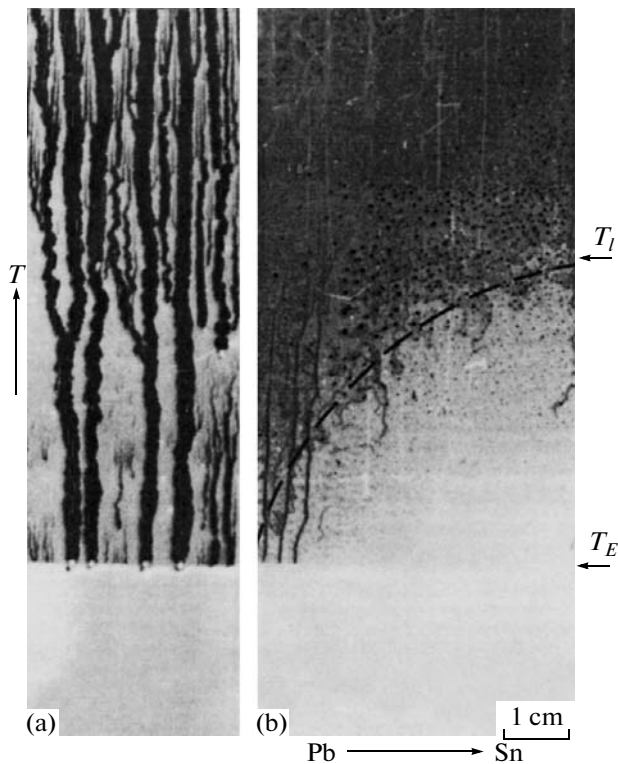


Fig. 1. Photograph of two-layer lead–tin films of (a) constant (eutectic) and (b) variable (hypereutectic) compositions on the substrate with a temperature gradient.

deposition can be provided in different points of the substrate.

The geometry used with some variations allowed us to obtain on the substrate films of components with the thickness variable over the substrate width during successive condensation and also films of variable composition by simultaneous condensation of the components. In this case, the equal thickness lines upon the successive condensation and equal concentration lines upon the simultaneous condensation are parallel to the substrate length. The film thickness was controlled during the condensation using quartz sensors.

We prepared and studied the two-layer lead–tin films, in which the thickness (several tens of micrometers) ratio corresponds to the eutectic composition over the entire substrate, and the film systems, in which the thickness ratio is changed over the substrate width and answer the regions of hypereutectic compositions (more than 62 wt % tin) [7]. After cessation of the condensation, we create the temperature gradient in the range 30–350°C along the substrate by heating of one its edge and cooling of the other edge. In this case, on the sample of two-layer lead–tin films with the thickness ratio corresponding to the eutectic composition, after a constant temperature distribution

controlled by welded chromel–alumel thermocouples is established along the substrate length, a clear boundary perpendicular to the substrate length is observed over whole its width (Fig. 1a); above and below the boundary, the films sharply differ in light scattering. The boundary corresponds to a temperature of 183°C that coincides with the eutectic temperature of lead–tin alloys [6].

Microscopically, we observed the individual spherical particles at temperatures above the boundary, and continuous polycrystalline film was observed below the boundary. This circumstance demonstrates that, above the boundary, the two-layer films were melted with formation of the liquid eutectic. It is seen that, till the steady-state temperature distribution is stated, the droplets of the formed melt are carried away by the melting boundary (Fig. 1a), since the melt does not wet the carbon sublayer but wets the intrinsic crystalline film.

The samples of the two-layer films of the hypereutectic composition (Fig. 1b) have, along with the boundary corresponding to the eutectic temperature, whose position is independent of the composition, one more less pronounced boundary, whose position is changed as the composition of the film system is changed along the substrate width. It separates the region of existence of the liquid phase at high temperatures from the two-phase region consisting of the liquid phase and tin-based crystalline phase. The calculations of the concentration and temperature show that the boundary corresponds to the liquidus line of the lead–tin phase diagram in the hypereutectic region. It is seen as well that the motion of the liquid phase droplets along the substrate in the temperature gradient field occurs only in the single-phase region of existence of the liquid phase, i.e., above the liquidus temperature T_l . It is due to the fact that in the transition through T_l at the lower temperatures, along with the liquid phase, there exist as well particles of the crystalline phase which are stoppers limiting the motion of droplets of the liquid phase along the substrate.

The results presented show that the observation of the contact melting in the two-layer films with both constant and variable ratio of the thicknesses of the contacting layers (Fig. 1) on the substrate with the temperature gradient allows us not only to determine the eutectic temperature T_E , but also to show that it is independent of the thickness ratio (the composition) of the contacting alloys according to the phase diagram for thick (several micrometers) films.

Using the methods described for the first time in [8], we prepared as well the ~10 μm-thick Sn–Bi films enriched in tin of variable compositions and in variable

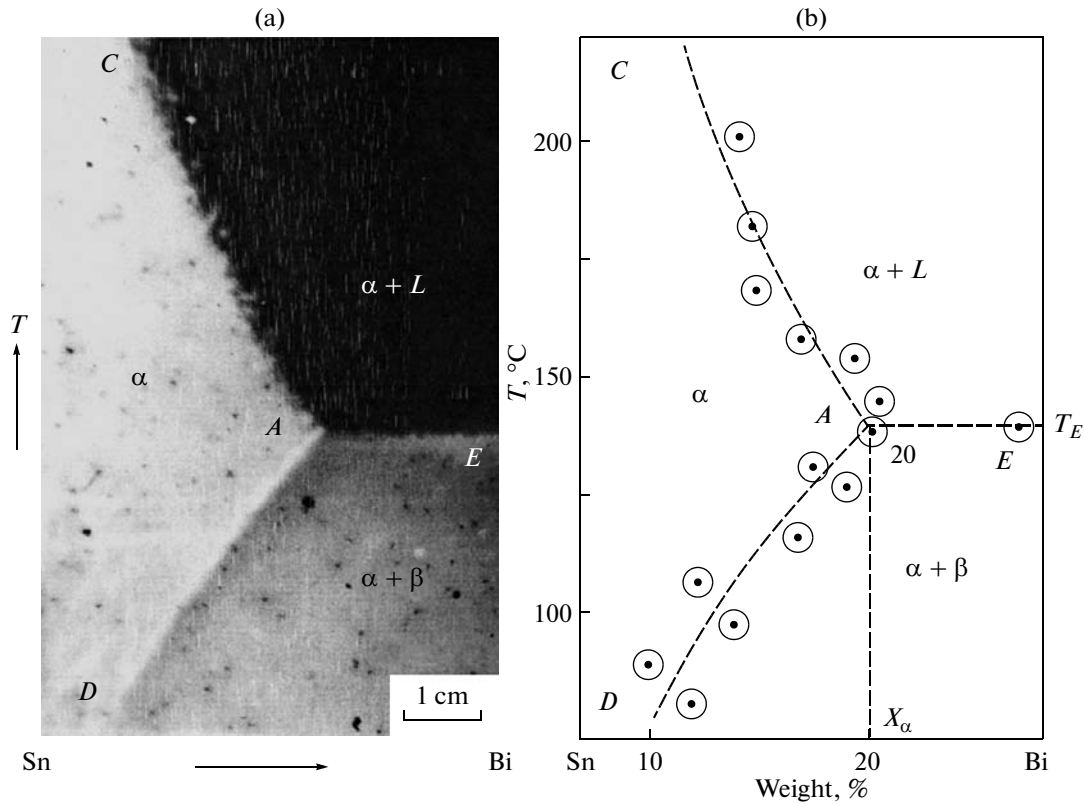


Fig. 2. (a) Photograph of the substrate with a film of a variable composition and a variable state of a fragment of the Sn–Bi system enriched in tin and (b) the corresponding fragment of the phase diagram.

states by simultaneous condensation of the components (Fig. 2a). Owing to the geometry used, the film concentration is continuously changed along the substrate width, and temperature is continuously varied along the film length. Figure 2a clearly shows three boundaries AE , AC , and AD . According to the microscopic and X-ray diffraction studies, the noted boundaries correspond to lines AE , AC , and AD of the known Sn–Bi phase diagram (Fig. 2b) [6]. It is seen that the AE boundary corresponds to the eutectic temperature T_E ; AD and AC limit the region of existence of the tin-based α solid solution; in this case, the AD boundary corresponds to the temperature dependence of the bismuth solubility in tin which has the maximum value X_α in point A at the eutectic temperature T_E . Above line AE and to the right of AC , there exists a two-phase area consisting of the crystals of the α solid solution and liquid phase; below AE and to the right of AD , there is a two-phase area corresponding to a mixture of the tin-based α and bismuth-based β solid solutions. We clearly see in this case that the bismuth solubility in tin increases with temperature and reaches its maximum value $\sim 20\%$ at the eutectic temperature against 7% at 50°C (curve DA). It is seen that it is exactly the concentration (X_α , point A) at which the contact (eutec-

tic) melting is pronounced, and, according to the phase diagram, the eutectic temperature is unchanged as the bismuth concentration increases further.

It follows from the results presented for the Sn–Bi system (Fig. 2) that if a thick film of one of the components is brought into contact with a thin film with variable thickness of the other component, the contact melting is observed only when the film thickness of the latter component exceeds certain value. Similar situation must be as a thick film of the latter component is brought into contact with a thin film with variable thickness of the former component, i.e., the critical thickness of the contact melting must exist.

Taking into account the noted reasoning, we performed the microscopic studies of layered systems of different thickness with the component proportion corresponding to the eutectic composition and different from it. The studies were carried out immediately on preparing the systems on the substrate at room temperature and after heating somewhat above the eutectic temperature and subsequent cooling. We also studied the layered systems consisting of a film of one of the component with a constant thickness and a film of the other component with continuously varying thickness. Such systems were prepared as follows. In one of

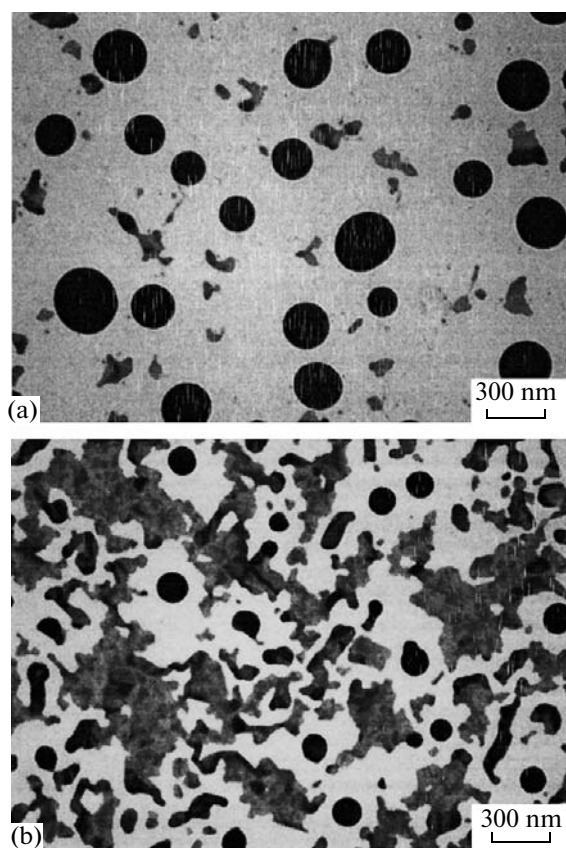


Fig. 3. Electron microscope images of the Sn/Bi film system of (a) approximately eutectic composition and (b) composition significantly different from the eutectic composition after heating.

the experiments, a film of one of the components (tin or bismuth) with a thickness constant over entire substrate length was condensed by evaporation from a linear source on an extended ~ 10 -cm-long substrate covered by a sublayer of thin carbon film deposited from an arc in vacuum immediately before preparation of the layered system. On the film prepared, in the same vacuum, a film of the other component (bismuth or tin) was condensed by evaporation from a point source of the other component; the film thickness was varied along the substrate between the opposite edges in the range ~ 10 – 1 nm. After the preparation was completed, the noted layered systems were heated to a temperature exceeding the eutectic temperature by several kelvins, and after cooling to room temperature, the systems were studied in an electron microscope.

The microscopic studies show that, in all the systems with the eutectic proportion of the components, after their melting and cooling, there are practically only spherical particles independent of the thickness (we studied the systems with the thickness more than 2 nm) (Fig. 3a). This fact demonstrates that, according to the phase diagram, at temperatures somewhat

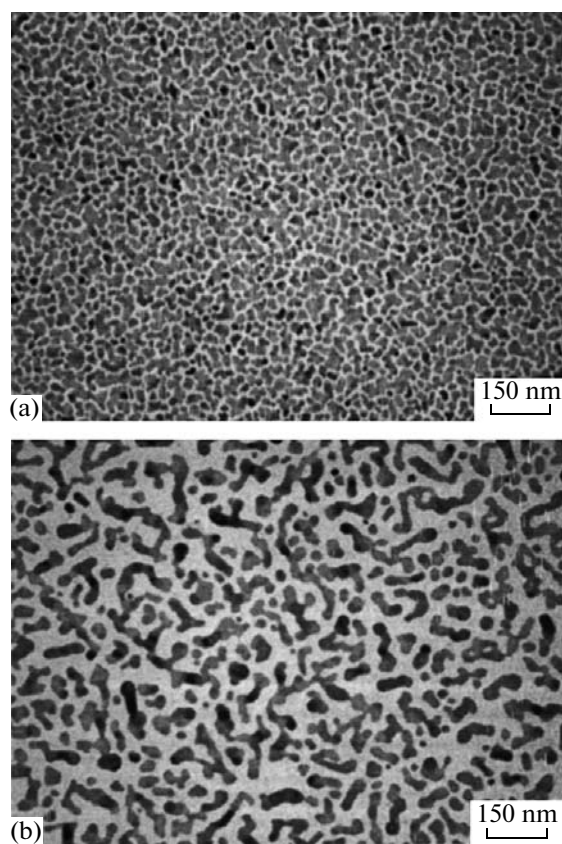


Fig. 4. Electron microscope images of the Sn/Bi film system (a) before heating and (b) after the heating–cooling cycle for thickness ratios of 1.3 nm : 8.4 nm and 1 nm : 7 nm, respectively.

exceeding the eutectic temperature, the systems contain only the liquid phase of the eutectic composition.

If the thickness ratio of the component films in such a system is different than the eutectic ratio, along with the spherical particles, there are the portions of a flattened shape. It is a result of the existence, at a temperature somewhat exceeding the eutectic temperature, of the crystalline phase based on the excess component, along with the liquid (Fig. 3b). In this case, the larger difference of the thickness of one of the components from the eutectic composition, the smaller amount of the liquid phase. As the thickness of this component is very small, the liquid phase is not observed, and the microscopic character of the structure of the layered film system is not principally changed after its heating and cooling (Fig. 4). The photomicrographs show only insignificant difference in the coverage factor, which is due to a difference of the total thickness of the system in Fig. 4 and an enlargement of the structure fragments on heating. This fact demonstrates the existence of a critical thickness of the contact melting.

To estimate the critical thickness, we used the dependences of the coverage factor of the layered systems on the film thickness of one of the components at the film thickness of the other component being constant (Fig. 5). The coverage factor which is the ratio of the area covered by the film material on the substrate to the total area is very sensible to variations of the morphology of the layered system as the liquid phase is formed in it and is assembled into spherical particles on the nonwetted substrate as a result of action of the surface tension force. It is seen from the figures presented that, as both the Sn film thickness on the Bi film of a constant thickness (Fig. 5a) and the Bi film thickness on the Sn film of a constant thickness (Fig. 5b) decrease, the coverage factor, as follows from the electron microscope images (Fig. 3), increases as a result of a decrease in the liquid phase amount and reaches a constant value at the thicknesses ~ 1.5 nm. These data show that the liquid phase is not formed at such small thicknesses of one of the components and there is a critical thickness of the contact melting (the data give its approximate value).

3. DISCUSSION OF THE EXPERIMENTAL RESULTS

The results obtained, as can be seen from what follows, substantially correlate with the diffusion mechanism of the contact melting and nature of the eutectics formed in this case. Along with it, they allow us to expand and make deeper current concepts, including the role of the characteristic size of the contacting samples.

Really, according to the diffusion mechanism, the contact melting can be considered as the process of formation and subsequent melting of solid solutions [9]. In this case, to describe the contact melting from the thermodynamic standpoint, it is worthwhile to analyze, according to [6, 10], the curves of dependence of the free energy on the composition for the solid and liquid phases of a two-component system of the eutectic type at various temperatures.

The typical dependences for a simple eutectic system with different crystal structures of the components at the temperature of existence of only the liquid phase [10] are shown in Fig. 6a and those at the eutectic temperature T_E are shown in Fig. 6b. Figure 6c shows the corresponding phase diagram.

As can be seen from Fig. 6b, at T_E , all three curves of the free energy have one common tangent line. Thus, at this temperature, the liquid with the composition e is in equilibrium with the α solid solution of the composition X_α and β solid solution of the composition X_β . It is natural that this three-phase equilibrium can be only at a well-defined temperature. It is seen

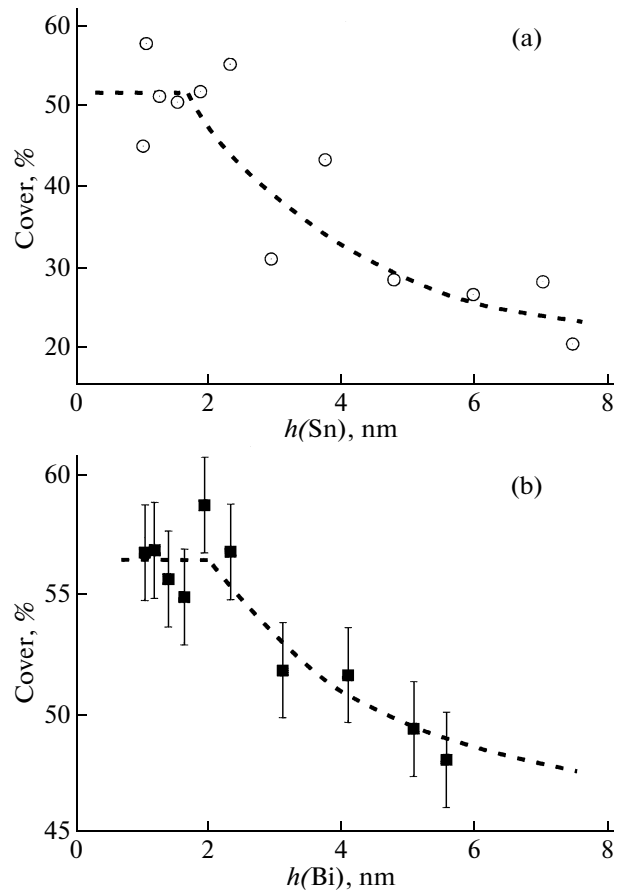


Fig. 5. Dependences of the coverage of the Sn–Bi system on the thickness of one of the components for a fixed thickness of the other component: (a) $h(\text{Bi}) = 7.5$ nm, $h(\text{Sn}) = 1.0$ –7.5 nm and (b) $h(\text{Bi}) = 1$ –6 nm, $h(\text{Sn}) = 20$ nm.

from Fig. 6c that the liquid of the eutectic composition (corresponding to point E) crystallizes and forms a crystal mixture of two solid solutions X_α and X_β , the mass ratio of which is measured by the ratio of the segments $eX_\beta/X_\alpha e$.

In [3, 4], where the general theory of crystallization was developed, it was shown that, in a melt of the eutectic composition, a unified critical nucleus radius determined by the supersaturation in both the components is formed. In this case, the concept of the diffusion dipole being a two-phase object placed in the eutectic melt, in which two nuclei of different compositions are jointed by a common diffusion field, is introduced and properties of the dipole are described. Correspondingly, at the crystallization temperature, the nucleus is formed and simultaneously decomposes into crystals based on components A and B .

It follows from Fig. 6 that, as the components A and B of the system described by the phase diagram of eutectic type are brought into contact, the free energy of the composition at $T < T_E$ is significantly higher

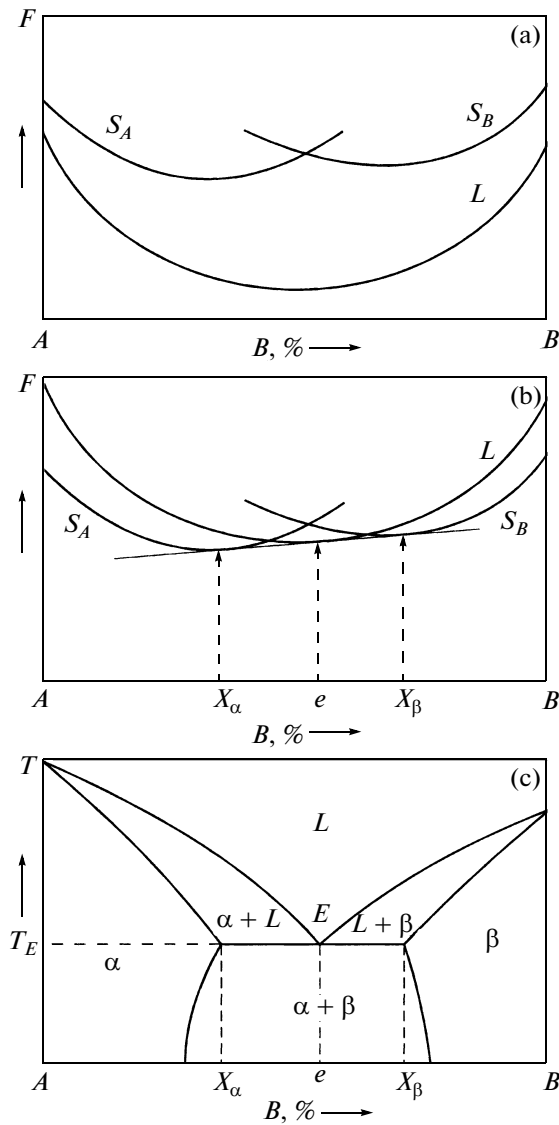


Fig. 6. Curves of the free energy for the system with a limited solubility of the components in the solid state (a) at the temperature of existence of only the liquid phase (L), (b) at the eutectic temperature, and (c) the corresponding phase diagram of the eutectic type (S_A and S_B are the solid solutions based on the components A and B , respectively) [10].

than the free energy of the solid solutions formed in this system. Thus, in the system, the processes decreasing the free energy must spontaneously occur according to the Le Chatelier principle. As temperature increases, the formation of the solid solutions favors such processes owing to the mutual diffusion of the components.

According to the Raoult's law, the formation of the solid solutions is a necessary condition of appearance of a liquid phase at temperatures which are significantly lower than the melting temperatures of the pure components, since, according to this law, the melting

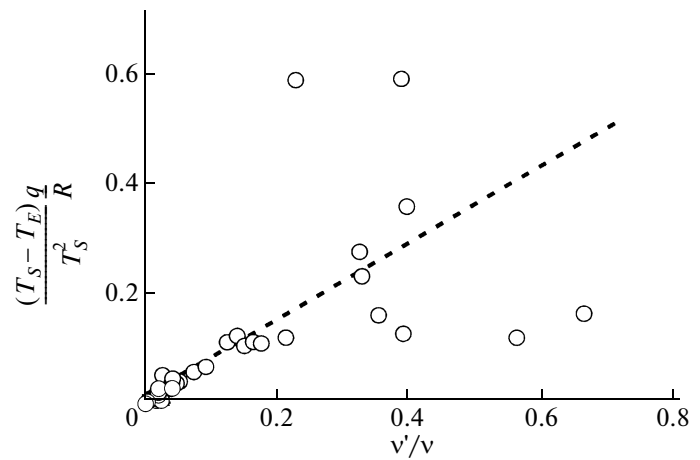


Fig. 7. Dependence of the relative decrease in the melting temperature of the eutectic in comparison with the melting temperature of the solvent on the molar concentration for the simplest eutectic systems.

point of the solution decreases compared to the melting temperature of the pure solvent.

In this case, the melting temperature decrease is dependent only on the number of moles of the dissolved material and independent of the chemical nature of the material, namely,

$$T - T' = \frac{v' RT^2}{v q}. \quad (1)$$

Here, T and T' are the melting temperatures of the pure solvent and solution, respectively; v' and v are the numbers of molecules of the dissolved material and solvent, respectively, in the solution unit volume; q is the solvent melting heat, and R is the universal gas constant.

The data presented in Fig. 7 on the decrease in the melting temperature of the eutectic compared to the solvent melting temperature for the simplest eutectic systems [6] is a clear confirmation of the foregoing (naturally, at low concentrations). Here, we do not discuss deviations from the linearity for some systems; for the problem considered in this work, the general law is important.

According to the concepts of formation of the diffusion dipoles upon the eutectic crystallization developed in [3, 4], the initial stage of the contact melting can likely be explained using the diffusion mechanism as follows.

As the temperature increases, in the contact zone, the diffusion dipoles, namely, two-phase objects, in which the solution nuclei based on the A and B components are joined by a common diffusion field, are formed. At T_E , when the solution concentrations become equal to the limiting values X_α and X_β , and their mass ratio becomes equal to the $eX_\beta/X_\alpha e$, and the

total amount is sufficient to form the viable nuclei of the liquid phase, the liquid of the eutectic composition is formed in the contact zone, i.e., the process opposite to that occurred during the crystallization of the eutectic and described in [3, 4].

According to the phase diagram (Fig. 6c), the final phase state of the contact system at a temperature T somewhat below T_E , after the system comes into the equilibrium state, is determined by the concentration of the components. In this case, the complete transition to a liquid state occurs only at the eutectic concentration. According to the phase diagram, if the content of one of the components is beyond the eutectic content, the excess amount remains as a solid phase based on the component. On the other hand, if the mass ratio of the components in the contact system is such that the concentration of one of them is lower than the corresponding limit of the solubility, the liquid phase appeared in the initial moment in the contact zone disappears eventually as the holding time increases owing to existence of the critical thickness of the contact melting, and the system is only the solid solution based on the other component.

The reasoning presented is clearly demonstrated by the data obtained for the films of variable composition in the layered film systems. For example, it is sufficient to indicate one more a clearly observed increase in the bismuth solubility in tin with temperature and the attainment of the limiting value at the eutectic temperature, as well as the critical characteristic size (in the our case, thickness) of one of the components of the onset of the contact melting. In this case, it should be noted that there are specific features of the contact melting in the films of the variable composition obtained by simultaneous condensation and in layered systems prepared by successive condensation of the components.

During simultaneous condensation, at room temperature of the substrate, of the components forming an eutectic system, a polycrystalline film is usually formed on the substrate; the film is a mixture of crystals based on evaporated components with thinnest solution interlayers at crystallite boundaries. As the temperature increases, at grain boundaries of this film system, the solid solutions continue to be formed as a result of the mutual diffusion. First, the solutions are formed in near-boundary layers which have the thickness 0.5–0.8 nm, according to the available data [12]. In the case of a vacancy mechanism, the activation energy in near-boundary layers at the intergrain boundaries can be only 0.3 fraction of the activation energy of the bulk diffusion [12]; in nanodisperse film systems, the activation energy can be still lesser. Because of this, as the eutectic temperature is approached, the saturation solutions are very quickly

formed in near-boundary layers of the contact zone of individual crystals. Clearly, in such polycrystalline films, the melting starts at the intergrain boundaries practically simultaneously over entire film thickness. According to the phase diagram, at a temperature somewhat above the eutectic temperature, there is only the liquid phase if the film has the eutectic composition; at the concentrations from X_α to X_β , there exist the liquid phase and solid phase based on the excess component as compared to the eutectic composition. If the concentration is lower than X_α (or higher than X_β), the corresponding component is sufficient only to form the solid solution, and the contact melting does not occur.

In the layered film system, in which the contact between the components is realized along the interface of the layers, if the thickness of one of the components is larger than the critical thickness, the contact melting at the eutectic temperature is first observed exactly in the contact zone.

According to the current concepts of the kinetics of a melting–crystallization transition, the viable nuclei of the liquid phase, during the contact melting, have sizes of the order of several fractions of a nanometer or several nanometers, i.e., of the order of the critical thickness of contact melting and the near-boundary layer thickness near the grain boundary [10] or the layer interface (contact). The foregoing can likely explain as well that, as noted in [5, 13], significant changes in the factors which play an important part in diffusion processes (the degree of dispersion in the polycrystalline samples, the absence of the grain boundaries in the case of contacting the single crystals, amount and character of defects, heating rate to T_E , and duration of the isothermal holding at a temperature somewhat below T_E) do not influence at all the contact-melting temperature and appearance of the liquid phase at its initial stage.

In summary, it should be noted that, if the thin (<~100 nm) films of one of the components are placed between thick (>100 nm) films of the other component, the contact melting temperature, as shown in [14], decreases with the thin film thickness. Taking into account the results presented in this work, we may assume that the limiting value of the temperature to which it can decrease is determined by the critical thickness of contact melting.

4. CONCLUSIONS

The method used in this work allows the visualization of the eutectic temperature for the films of variable compositions and variable states prepared by both the simultaneous and successive condensation of the components.

Using the Sn–Bi films of variable compositions and variable states prepared by the simultaneous condensation of the components as an example, we show the possibility to visualize the increase in the component solubility, as the temperature increases, to its maximum value observed at the eutectic temperature.

We revealed that, in the layered film system, there exists a critical thickness, namely, the contact melting does not occur, i.e., a liquid layer of the eutectic composition is not formed if the film thickness of one of the components is smaller than certain (critical) thickness.

The results obtained and their analysis count in favor of the diffusion mechanism of the contact melting.

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