STRUCTURE, PHASE TRANSFORMATIONS, AND DIFFUSION

Supercooling upon Crystallization in Layered Al/Bi/Al Film System

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Abstract—The possibilities of determination of supercooling upon crystallization of binary alloys whose components in the solid state are virtually insoluble in each other and exhibit a wide immiscibility range in the liquid state are analyzed using layered film systems that are produced by sequential condensation of the components upon their evaporation from independent sources. This work presents the results of investigation of the melting–crystallization temperature hysteresis and the magnitude of supercooling upon crystallization of a bismuth-based phase contacting with solid aluminum in the case of a layered Al/Bi/Al system film. The processes occurring therein are discussed.

INTRODUCTION

In order to understand the phenomenon of nucleation upon liquid–crystal phase transitions and to clarify its effect on the microstructure and properties of stable and metastable phases formed upon solidification, it is important to study the magnitude of supercooling upon crystallization. To reach the ultimate supercoolings, methods using very high cooling rates leading to the suppression of heterogeneous nucleation as well as methods based on controlling nucleation process via the elimination of potential nucleation centers are employed.

The method of division of the melt into small drops and examination of their crystallization proposed by Turnbull [1] was widely used to estimate the supercooling. The efficient way to increase the attainable supercoolings is the containerless performance of the process of crystallization of melts in a medium of high purity. Such conditions are ensured by using freely falling droplets in special vacuum towers [2] and levitation methods (retention of the melt in a suspended state using different noncontact effects, e.g., electromagnetic or acoustic), including zero-gravity conditions in space.

The use of island vacuum condensates deposited on different substrates is very promising for the determination of supercoolings upon crystallization [3, 4]. Due to variations of the melting temperature with the size of small particles, the condensed-phase islands formed at the substrate in the initial period are liquid at temperatures below the melting temperature T_s of macroscopic samples. As the size of the islands increases in the condensation process, they are retained in the supercooling state to a temperature T_g corresponding to the supercooling upon crystallization at a given substrate. It is natural that, in this case, the temperature T_g and the supercooling $\Delta T = T_s - T_g$ depend on the substrate material and condensation conditions. As a measure of the effect of the substrate material on the magnitude of supercooling, the angle of wetting of the substrate with liquid islands is usually used. In such a way, supercoolings of a number of metals, both low-melting and refractory [3–5], and of some binary systems [6] were studied at different substrates. The investigations performed made it possible, for the first time, to obtain the dependence of supercooling on the wetting angle, which indicates that, as the wetting angle approaches 180°, the ultimate supercooling apparently becomes close to $0.4T_s$. A feature common to these investigations is that the formation and thermal stability of the liquid phase upon condensation, i.e., the magnitude of supercooling, are very sensitive to the conditions of preparation of island condensates (pressure and composition of residual gases, condensation rate, etc.). For this reason, to obtain unambiguous results, the experiments were carried out in an ultrahigh vacuum produced with an oil-free pump at high condensation rates. Under these conditions the only solid "impurity" determining the magnitude of supercooling is the substrate; the wetting angle between the substrate and liquid islands, as was noted above, serves as a measure of its influence. It seems, however, that a more adequate generalized characteristic determining the supercooling of island condensates on a substrate is the corresponding "island condensate–substrate" phase diagram. Apparently, this is especially justified since, frequently, the condensed material interacts with the substrate. With such an approach, the vacuum condensates can prove to be convenient to investigate the supercooling upon crystallization of binary alloys whose components are virtually insoluble in the solid state and exhibit a miscibility gap in the liquid state. Note also that a considerable body of data about supercoolings of pure metals investigated using vacuum condensates on different neutral amor-

phous substrates and employing other methods have been accumulated. At the same time, there are only poor data about supercoolings upon crystallization of eutectics in contact with one of the solid components, in spite of the importance of this information. In recent years the melting and crystallization in binary systems in which the second, lower-melting-point component is embedded in the matrix of a more refractory component have been intensively studied using samples obtained by mechanical milling of mixtures of powders of the corresponding components with subsequent pressing or by quenching from the single-phase liquid state from high temperatures [7, 8]. During the preparation of samples by mechanical milling, insoluble solid refractory impurities can fall into a mixture of high-purity initial powders of the components [7, 8].

It is obvious that the influence of these factors is minimized upon the preparation of vacuum condensates. Indeed, we can use the more refractory component as a substrate and investigate the formation and stability of the liquid phase of the second, more easily fusible component by applying a temperature gradient. In this way, detailed information about the supercooling of the alloy rich in easily fusible component in contact with the second solid (refractory) component may be obtained.

Another possibility also exists; namely, it seems appropriate, when investigating the melting and crystallization in binary systems, to employ layered film systems that are prepared by sequential condensation of pure components by their evaporation from independent sources. In such systems the film of a low-melting component may be sandwiched between the films of a more refractory component. The required total composition of the system may be specified by changing the ratio between the film thicknesses. It is natural that the condensation temperature upon preparation of such a layered system must be chosen so as to prevent the interaction between the component films. The heating and cooling of such a system after condensation make it possible to determine the melting temperature of the eutectic on the side of the more easily fusible component and the magnitude of supercooling upon its crystallization. In this case, the effect of foreign insoluble solid impurities is eliminated almost completely and the effect of soluble gaseous impurities may be eliminated by performing the condensation process in a high vacuum at large deposition rates; the film of refractory component remains the only solid impurity determining the supercooling.

EXPERIMENTAL

As an object of the investigation to realize and check the considerations outlined, we chose the binary Al–Bi system whose components in the solid state are virtually insoluble in each other and form a eutectic-type phase diagram with a marked immiscibility range in the liquid state [9]. The eutectic that forms on the bismuth side is close to pure bismuth in composition and melting temperature.

In accordance with the sought-for aim, various experiments were carried out. To estimate the boundary temperature T_g, i.e., the supercooling corresponding to condensation of Bi onto an Al substrate, the experiments were conducted as follows. First, a temperature gradient in a range from room temperature to ~570 K was realized along a polished plate 3 mm thick with dimensions of 30×150 mm made of stainless steel; then, a thin layer of carbon was applied onto it in a vacuum, after which an Al film of about 1000–2000 Å thick was condensed on it. Immediately after the application of aluminum, a bismuth layer was condensed on it. The thickness of the bismuth films did not exceed 1000 Å. Aluminum and bismuth of 99.99% purity were evaporated from independent sources (tungsten crucibles). Temperature along the substrate was measured with the help of chromel–alumel thermocouples. The temperature T_g was pinpointed from changes in the microstructure of the films above and below it [3]. The experiments were performed using a VUP-5M conventional vacuum setup at a pressure of residual gases $(1–3) \times 10^{-6}$ mmHg.

In the alloys that are rich in bismuth and make contact with solid aluminum, the supercooling upon crystallization was determined by measurements of electrical resistance in the layered Al/Bi/Al film system. The experiments were carried out as follows. Using the thermal evaporation of aluminum, contact (printed circuit) tracks were applied onto a glass plate with dimensions of 32×32 mm. The disposition of the contact tracks made it possible, in one experiment under completely identical conditions and simultaneously, to measure the electrical resistance in three layered film systems. The substrate with the contacts was attached to a copper block (heater); a special mask ensured condensation at three specified areas of the substrate. The experiments were performed employing a vacuum setup with an oil-free pump at a pressure of residual gases 1×10^{-7} mmHg. The system of movable shields, which allowed one to obtain in one experiment three samples of the layered Al/Bi/Al film system with different thicknesses of aluminum and bismuth films controlled with a quartz sensor from the drift of its frequency, was placed between the substrate and evaporators of aluminum and bismuth. The cooling and heating were effected in a range from room temperature to ~570 K, i.e., somewhat above the melting temperature of bismuth. Temperature was measured with a chromel–alumel thermocouple; electrical resistance, with a digital ohmmeter.

The used geometry of the relative positions of evaporators, substrate, and system of movable shields likewise enabled one to obtain single-layer films of the Al–Bi system of the desired thickness through the simultaneous condensation of aluminum and bismuth as well as two-layer Al–Bi films with a given ratio between the

thicknesses and to measure the electrical resistance on such samples upon subsequent heating–cooling cycles without the break of vacuum.

The structure of the films was studied with a DRON-3 X-ray diffractometer using the unfiltered K radiation from a copper anode as well as by optical and electron microscopy.

RESULTS AND DISCUSSION

At the films that are formed upon condensation of bismuth on an aluminum substrate with a temperature gradient, a boundary is observed in the direction of increasing temperature with a change-over of condensation mechanisms: the vapor $\longrightarrow$ liquid mechanism at $T > T_g$ and the vapor $\longrightarrow$ crystal mechanism at $T < T_g$. The boundary is at 453 K, i.e., $\Delta T = 91$ K. Above the boundary temperature, the films exhibit an island structure characteristic of condensation via the liquid phase (Fig. 1). According to electron-microscopic data, the wetting angle between the aluminum substrate and the condensed islands is ~120°. This value of the wetting angle and the above magnitude of supercooling are in agreement with available data about the dependence of supercooling on the wetting angle obtained for a number of metals (including bismuth) at different substrates [3].

Measurements of electrical resistance in the layered film Al/Bi/Al system in the process of heating to a temperature somewhat above the melting temperature of the bismuth-based eutectic and subsequent cooling showed that the electrical resistance is very sensitive to the processes that occur in the system considered upon both heating and cooling. The feature common to all dependences obtained in the heating–cooling cycle is the presence of temperature hysteresis. Figure 2 displays such dependences for the layered Al/Bi/Al film system with each layer ~1000 Å thick. These dependences are obtained both immediately after stopping condensation of the components and upon subsequent heating–cooling cycles performed at different time intervals. It is seen from Fig. 2 (curve *1*) that in the process of heating immediately after condensation the electrical resistance builds up linearly and gradually with increasing temperature to approximately 440 K; then, the electrical resistance grows more rapidly and, with approaching the melting temperature of the bismuth-based eutectic, drops similarly to the electrical resistance of pure bismuth, and further increases smoothly. Note that upon the first heating, after condensation, separate irregularities manifest themselves against the background of the total increase in the electrical resistance. Upon subsequent heating (cycle *2* in Fig. 2) performed on the same sample after an 8-day-residence of the sample in the setup without vacuum failure, the electrical resistance builds up linearly to about 500 K, then decreases, reaching a minimum value at the melting temperature of the eutectic. Above this temperature the resistance increases and upon cool-
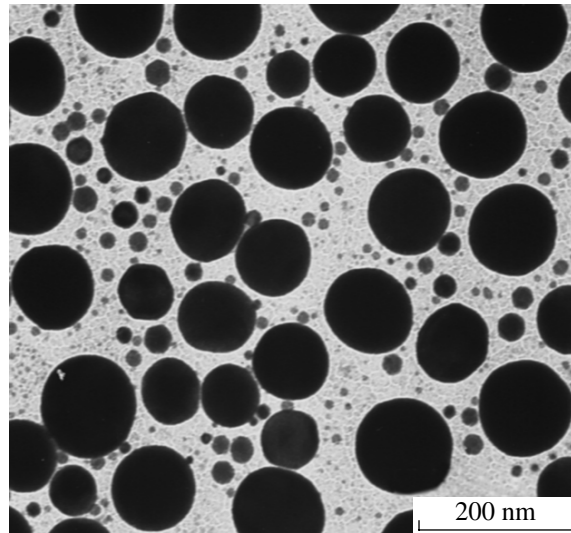

Fig. 1. Electron micrograph of Bi particles on an Al substrate at a temperature above T_g.

ing decreases approximately linearly to 449 K. After attainment of the latter temperature, the resistance builds up in a jumplike way by a factor of about 1.5 and then increases very slowly with lowering temperature in the process of cooling and finally decreases smoothly beginning from approximately 370 K.

With each successive heating–cooling cycle, the qualitative character of changes in the resistance remains unaltered. Upon heating at temperatures below 449 K, the behavior of the resistance qualitatively coincides with its behavior upon cooling in the preceding cycle; then, the resistance decreases gradually and, with approaching the melting temperature of the bismuth-based alloy, drops sharply; upon subsequent cooling it decreases smoothly to 449 K and then undergoes a jumplike rise again. With each subsequent heating–cooling cycle, the temperature dependences of resistance are shifted in an approximated parallel way toward increasing resistance, while the temperature at which a jumplike rise in the resistance occurs in the next cooling cycle remains unaltered. Since the temperature corresponding to a jumplike rise in the resistance upon cooling is the same for all the cycles, the curves in Fig. 2 are specially shifted along the temperature axis for the cycles performed 9 and 10 days (curves *3* and *4*) and 14 (curves *5–7*) and 16 days (curves *8* and *9*) after the sample has been prepared with respect to the value corresponding to the cycle (curve *2*) performed 8 days after the initial heating performed immediately after termination of condensation, in order that one may trace more clearly the behavior of resistance when the heating–cooling cycles follow one after another.

How the resistance varies with the number of heating–cooling cycles is clearly traced in the dependence of the relative increment of the resistance, i.e.,
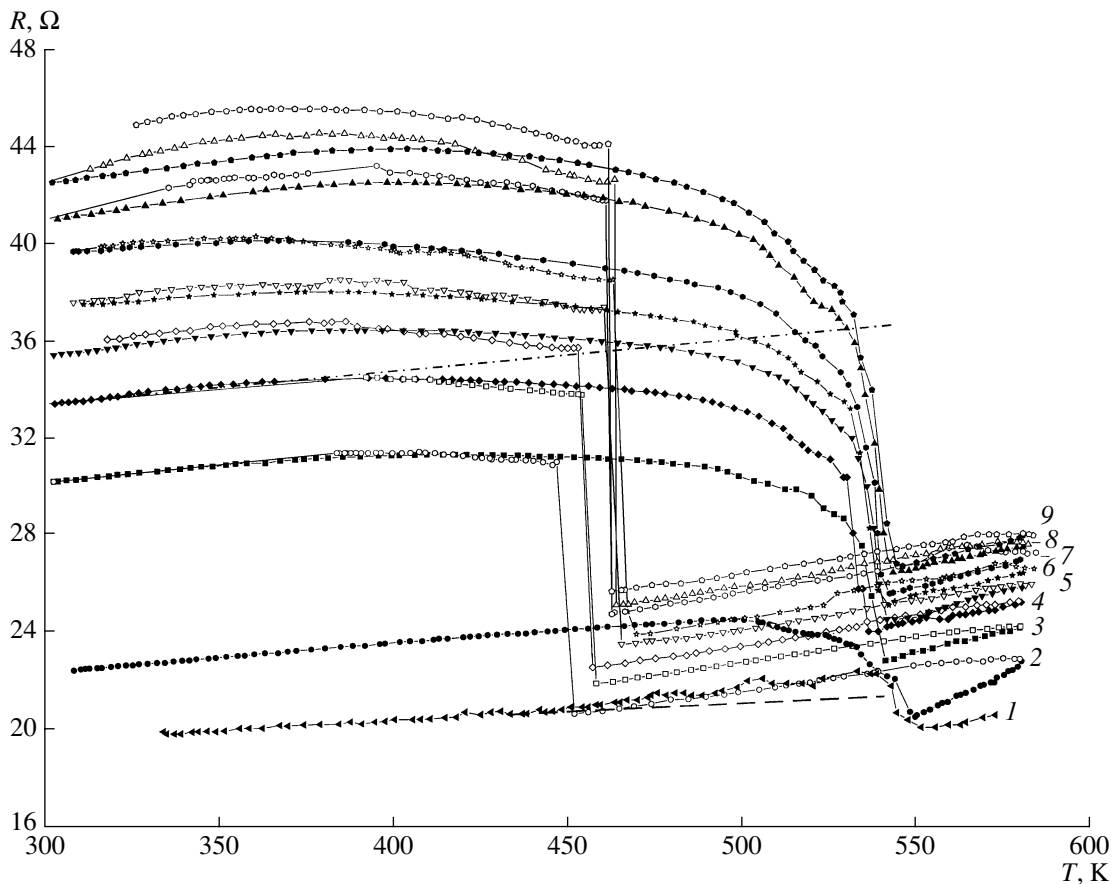
Fig. 2. Dependence of the electrical resistance of the layered Al/Bi/Al film system (thickness of the Al and Bi films is 1000 Å each) on the heating temperature (*1*) immediately after termination of condensation and in the process of subsequent heating–cooling cycles performed after (*2*) 8, (*3*) 9, (*4*) 10, (*5*, *6*, *7*), 14 and (*8*, *9*) 16 days. In each cycle, solid and empty symbols correspond to heating and cooling, respectively.
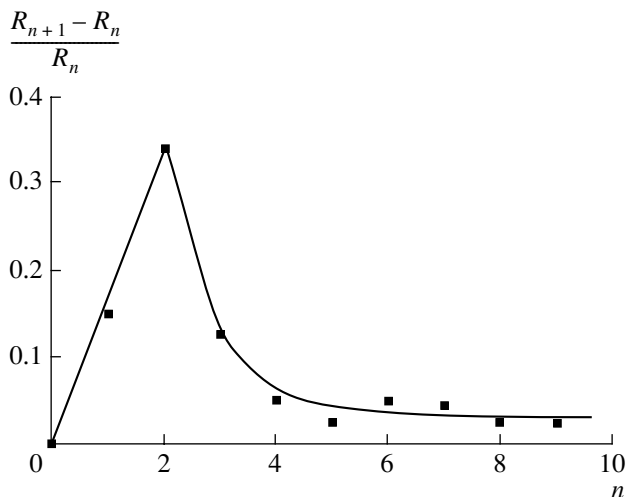

Fig. 3. Dependence of the relative increment in the resistance $\dfrac{R_{n+1} - R_n}{R_n}$ on the number of cycles for the layered Al/Bi/Al system film (thickness of the Al and Bi films is 1000 Å each).

$\dfrac{R_{n+1} - R_n}{R_n}$ (*n* is the order number of cycle), on the number of cycles performed at 370 K (Fig. 3). It is seen from Fig. 3 that the most significant change in the resistance, namely, an increase to ~35%, occurs during the first two heating–cooling cycles; then, a sharp drop in the increment of the resistance is observed after, approximately, the fifth cycle (it reduces to a few percent and continues further slowly lowering).

Note that while the resistance increment near 370 K decreases with increasing number of cycles, the ratio of the resistance jump upon cooling at the temperature T_g to the resistance in the initial solid state at the same temperature becomes, virtually after the second cycle, independent of the number of heating–cooling cycles (Fig. 4).

It should be noted separately that in the $\ln\Delta R/R - 1/T$ coordinates, the decrease in the resistance upon heating with respect to the linear dependence (dot-and-dash line in Fig. 2) with increasing temperature is of a similar character for all subsequent heating–cooling cycles, except for the cycle involving heating immediately

after termination of condensation. This is illustrated conclusively in Fig. 5, which shows these dependences for cycles *3–7* and *9* constructed on the basis of the data from Fig. 2. As follows from Fig. 5, these dependences can be divided into a sufficiently pronounced linear portion below ~400 K with an activation energy of 0.4 eV and a linear portion in the range of ~400–500 K with an activation energy of 0.25 eV. At higher temperatures, the activation energy increases to 0.65 eV and, when approaching the melting temperature of bismuth, to 1.3 eV.

For two-layer Al–Bi films the behavior of electrical resistance in heating–cooling cycles is qualitatively similar to that observed in the three-layer Al/Bi/Al system. As in the three-layer films, a sharp rise in the resistance upon cooling occurs at the same temperature, i.e., 449 K (Fig. 6). The distinction is in the fact that, already in the second cycle, the loss of conduction of the film caused by its fragmentation into separate islands takes place with approaching the melting temperature of the bismuth-based alloy.

In the single-layer Al–Bi films obtained by simultaneous condensation of aluminum and bismuth, the resistance changes quite differently. In this case, unlike three-layer films, the resistance changes most markedly (decreases by a factor of about three) upon heating in the first heating–cooling cycle. With subsequent heating–cooling cycles, the behavior of the single-layer film is analogous to the behavior of the three-layer system subjected to several cycles, i.e., the resistance changes only slightly already after the second and third cycles, and the temperature corresponding to the jump-like rise in the resistance upon cooling is 415 K. In films prepared by simultaneous condensation, the loss of conduction likewise takes place as the number of heating–cooling cycles increases. Thus, in the films with 30 wt % Bi, this is already observed in the third cycle (Fig. 7), which indicates the fragmentation of the film into isolated islands.

Such a qualitatively opposite behavior of electrical resistance in the layered film systems (Al/Bi/Al, Al/Bi), on the one hand, and in the Al–Bi films obtained by simultaneous condensation of Al and Bi, on the other hand, is caused by the following factors. In the layered film systems formed by sequential condensation of the components, only a small amount of bismuth is contained at grain boundaries in the aluminum films because of the condensation-stimulated diffusion [10, 11], i.e., such a system consists of films of practically pure, atomically contacting Al and Bi. Upon the initial heating immediately after condensation is stopped, i.e., after obtaining a layered film system that represents a thermodynamically nonequilibrium system, diffusional processes are intensified due to an elevation of the temperature and give rise to an alloy of a corresponding phase composition determined by the phase diagram and by the ratio between the thicknesses of the contacting films of the components, i.e., by the
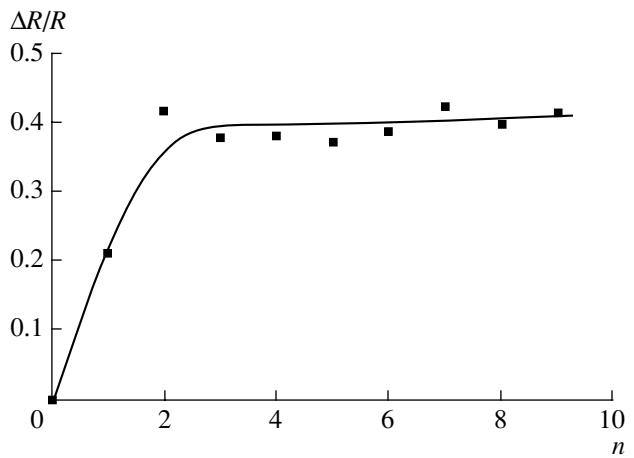

Fig. 4. Dependence of the relative change in the resistance at the temperature of solidification of the Al/Bi/Al film system on the number of heating–cooling cycles.

component concentrations. Since aluminum and bismuth in the solid state are almost completely insoluble in each other, it is the processes of grain-boundary diffusion that are governing in the initial heating. It is this factor that leads to an excess growth of the resistance above 440 K as compared to the linear dependence (dashed line in Fig. 2). In the $\ln \Delta R/R - 1/T$ coordinates, as follows from Fig. 8, the observed dependence of the resistance increment is, to a first approximation, linear, with an activation energy of 0.28 eV.

When the temperature reaches the melting temperature of the bismuth-based eutectic and that of pure bismuth, an appreciable drop in the resistance is observed (since melting occurs with a decrease in volume), which is accompanied by the activation of processes of dissolution of aluminum in the liquid phase and the formation of corresponding solutions. Upon subsequent cooling of such a system after the attainment of the temperature corresponding to the limiting supercooling for the solidification of the liquid phase in contact with the crystalline aluminum-based phase, a jumplike rise in the resistance occurs, which is probably explained both by the fixation of the arising supersaturated solid solutions and quenching of vacancies and by the fact that in this case the crystallization is accompanied by an increase in volume resulting in the appearance of internal stresses that lead to a further slight increment in the resistance with lowering temperature. The ordinary decrease in the resistance with temperature takes place only below ~ 400 K.

Upon subsequent heating in the next heating–cooling cycle, the resistance begins to decrease from approximately 370 K, which is likely to be caused by vacancy migration, relaxation of internal stresses, and decomposition of supersaturated solid solutions. It seems that the most probable way of relaxation of internal stresses is bismuth diffusion along grain boundaries in the aluminum films. The fact that the resistance
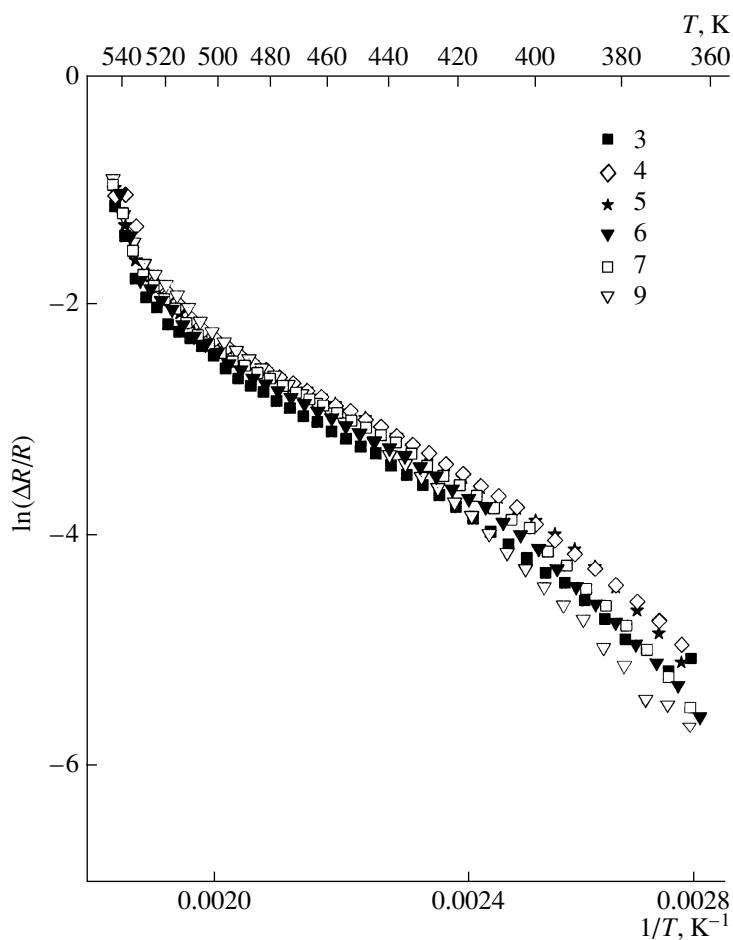
Fig. 5. Dependence of the relative decrement in the resistance on the reciprocal temperature for the Al/Bi/Al system (for *3–7* and *9* cycles).

increment slows down after the number of heating–cooling cycles increases indicates that, probably, the process of the formation of quasicrystalline alloy across the whole thickness of the layered system originally being nonequilibrium is mainly completed.

The fact that the relative increment in the resistance slows down with increasing number of heating–cooling cycles and then goes to a nearly constant level and that the dependences in the $\ln\Delta R/R - 1/T$ coordinates (see Fig. 5) are virtually coincident for all heating–cooling cycles after the initial cycle, seems natural for the following reasons. As was already noted, a layered film system after condensation consists of films of practically pure components contacting at the atomic level. In the process of heating upon subsequent heating–cooling cycles, the alloy is formed due to the interaction of these films of pure components. In reality, this process is completed within several cycles. The formation of a liquid bismuth-based phase, a partial dissolution of aluminum in the liquid phase, and grain-boundary diffusion take place at each heating–cooling cycle. Upon cooling, compressive stresses arise owing to the solidification of the supercooled bismuth-based melt which

is accompanied by increasing the volume. At the same time, quenching of vacancies and of supersaturated solid solutions occurs upon crystallization due to the supercooling. Since the physical processes are replicated in the already formed quasicrystalline alloy based on the layered film system during repeated heating–cooling cycles, the corresponding dependences of resistance likewise are replicated.

The above considerations and the coincidence of the activation energies in a temperature range of 400–500 K that are calculated from the resistance increment upon the initial heating (0.28 eV) and from the drop in resistance upon subsequent heatings in heating–cooling cycles (0.26 eV) allow one to conclude that the obtained values of the activation energy are likely to correspond to the activation energy for grain-boundary diffusion of bismuth in the film system under study. The activation energy 0.4 eV appears to be connected with the migration to sinks, which are primarily the intergranular boundaries, of nonequilibrium vacancies formed upon quenching of the bismuth-based phase from the liquid state. The large activation energies at high temperatures probably correspond to the decom-

position of the supersaturated solid solution of aluminum in bismuth (0.65 eV) and to the bulk diffusion of aluminum (1.3 eV). In order to obtain a one-to-one correspondence between the obtained values of the activation energy and the observed physical processes, additional studies should be conducted [12].

Upon obtaining films by the simultaneous condensation, the alloy is in a strongly nonequilibrium state because of mixing at the atomic level, which is mainly associated with the quenching of the supersaturated solid solution. This is evidenced by a marked decrease in the resistance in the process of the first heating after termination of condensation. After reaching the melting temperature of bismuth-based eutectic and subsequent cooling, the resistance increases sharply at the solidification temperature but, nevertheless, this value remains significantly smaller than the initial value. With subsequent heating–cooling cycles, such films behave similarly to the layered systems after 4–5 cycles. This indicates that the formation of a quasi-equilibrium alloy is virtually completed after the first heating to the melting temperature of the eutectic.

The above considerations about the structure of the examined layered film systems and films prepared by simultaneous condensation of the components, which are related to their initial state and states after subsequent heating–cooling cycles, are in agreement with the available literature data and structural studies. Thus, the presence of an appreciable solubility upon simultaneous condensation of aluminum and bismuth on a substrate at room temperature was reported as early as in 1959 [9].

X-ray diffraction studies of the layered Al/Bi/Al system showed that the films in the initial state consist of practically pure aluminum and bismuth. In bismuth films, texture with the (001) plane parallel to the substrate is observed in part. After heating to above the melting temperature of the bismuth-based eutectic and cooling to room temperature, the lattice parameters of the phases based on aluminum and bismuth somewhat changed. Thus, the lattice parameter of the aluminum-based phase near the melting temperature and slightly above it after cooling to room temperature is $a = 4.045$ Å and $a = 4.042$ Å, respectively ($a_{tab} = 4.0496$ Å [13]). The lattice parameters of the bismuth-based phase at these temperatures are $a = 4.556$ Å; $c = 11.898$ Å and $a = 4.557$ Å, $c = 11.892$ Å, respectively ($a_{tab} = 4.55$ Å and $c_{tab} = 11.86$ Å [13]). This may be connected both with the formation of supersaturated solutions and with the appearance of internal stresses upon crystallization.

Since the bismuth-based phase, as follows from electron-microscopic studies, is largely located at grain boundaries of the aluminum-based phase, this leads to the fragmentation of continuous films into separate islands upon melting when the content of the bismuth-based phase is considerable because of the reduction of volume and incomplete wetting. Because of the weak mutual solubility of the components, these islands prac-
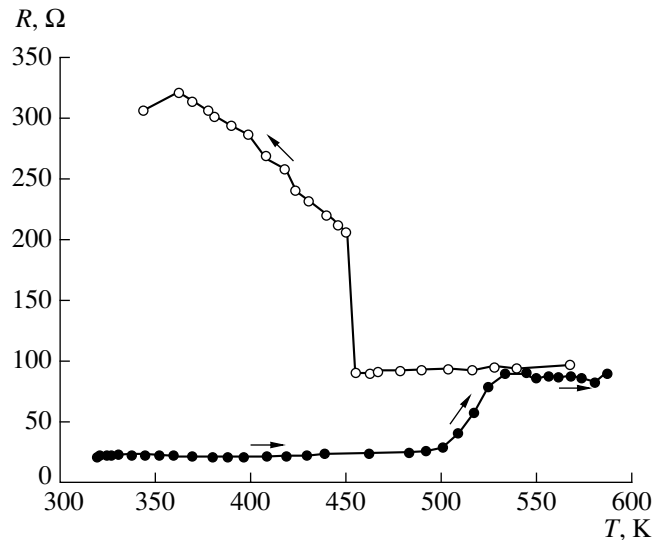

Fig. 6. Variations of the resistance with temperature in the process of heating– cooling cycle for the two-layer Al/Bi film system (thickness of the Al and Bi films is ~500 and ~300 Å, respectively): (●) heating and (○) cooling.
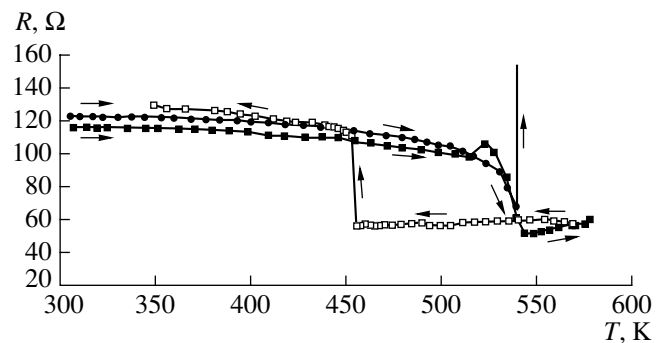

Fig. 7. Temperature dependence of the resistance of Al/Bi films 1000 Å thick obtained by simultaneous condensation of the components (30 wt % Bi) in the second cycle after preparation ((■) heating and (□) cooling) and (●) the third cycle (heating).
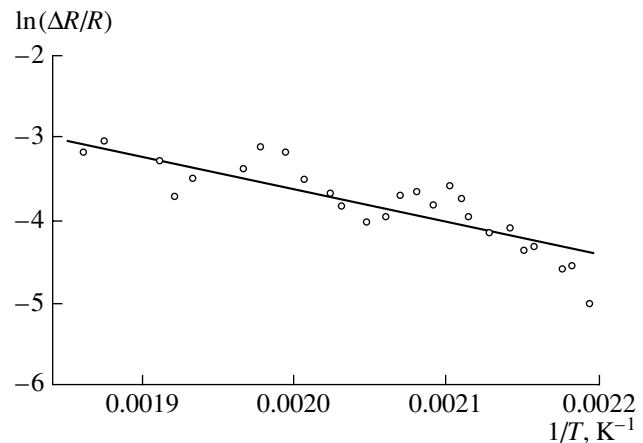

Fig. 8. Dependence of the relative increment in the resistance of a three-layer Al/Bi/Al film system on the reciprocal temperature upon the first heating immediately after termination of condensation.

tically consist of pure aluminum and their surface is coated with the bismuth-based phase. It is natural that the transition to an island film is accompanied by a decrease in its electrical conduction, which was observed experimentally.

It should be emphasized that a feature common to all the investigations performed is that, in the wide variety of measurements of three-layer and two-layer films and films obtained by simultaneous condensation, the temperature corresponding to a jumplike rise in the resistance upon cooling lies in a range of 441–457 K, i.e., the average value is about 449 K.

The behavior of electrical resistance observed in the layered film Al/Bi/Al system, namely, the occurrence of a melting–crystallization temperature hysteresis upon heating-cooling, agrees with the obtained results on the mechanism of condensation of bismuth on an aluminum substrate and with the available literature data. Comparison of these results shows that the temperature at which a jumplike rise in resistance is observed upon cooling of the layered film system is coincident with the boundary temperature T_g corresponding to the lower boundary of stability of the supercooled liquid phase in bismuth condensates on the aluminum substrate. This is connected with the following circumstances. Upon deposition of bismuth on a substrate representing an aluminum film with a temperature gradient, nuclei of a bismuth-based Al–Bi alloy are formed at the initial stage because of the condensation-stimulated diffusion. This is also favored by the fact that these nuclei, in view of their small size, are liquid, and aluminum that serves as a substrate is dissolved in them. Liquid islands of the alloy formed in the process of condensation are retained in the supercooling state down to the temperature corresponding to the ultimate supercooling upon their solidification on the aluminum substrate. Consequently, this temperature corresponds to the ultimate supercooling upon crystallization of bismuth-based Al–Bi alloys in an aluminum matrix.

It should be noted that, as was shown when investigating condensation of bismuth on an amorphous carbon substrate, the boundary temperature T_g is very sensitive to the conditions of sample preparation and especially to the conditions of the performance of subsequent heating–cooling cycles dealing with the already formed condensates. As a rule, when the vacuum conditions of condensation are impaired, this temperature increases to the value corresponding to the crystallization on native oxides.

In the layered systems considered, as follows from the above results, the value of T_g is retained upon multiple subsequent cycles of heating and cooling. Such a behavior seems natural when the layered film systems are obtained by sequential condensation, since this method prevents the ingress of insoluble solid impurities and, correspondingly, the only natural solid impurity that determines nucleation and supercooling upon

crystallization is the aluminum film. Since the bismuth film is bounded from two sides by thick aluminum films, this prevents the appearance of oxides upon crystallization as a result of the interaction with residual gases in the zone where the supercooled melt is formed.

As follows from the obtained average value of the boundary temperature T_g = 449 K, the supercooling upon the solidification of the bismuth-based melt in contact with solid aluminum is ΔT = 95 K. These values can be used to estimate the contact angle of a nucleation center of the bismuth-based eutectic upon its crystallization on the aluminum-substrate surface.

Indeed, when a nucleation center of a crystalline phase in the form of a spherical segment is formed at the liquid–substrate interface, its contact angle with the substrate, ψ, is determined from the condition [14]

$$\sigma_{ul} = \sigma_{us} + \sigma_{ls}\cos\psi ,$$

where σ_{ul} and σ_{us} are the interphase energies of the interphase boundary between the melt (*l*) or crystal (*s*) and the substrate *u*, respectively; and σ_{ls} is the energy of interface between the crystal and the native melt. For this reason, at the same radius of a critical nucleation center, its volume decreases by a factor of $\Phi(\psi)$ $\Big[\Phi(\psi)$

$= 0.25(2 - \frac{1}{4}(2-3\cos\psi + \cos^3\psi)\Big]$ as compared to the

volume of a free spherical nucleation center. Therefore, the activation barrier also decreases by the same factor [14], i.e.,

$$\Delta G^*_{het} = \Delta G^*_{hom}\Phi(\psi),$$

where the work of the formation of a spherical nucleation center upon homogeneous solidification is

$$\Delta G^*_{hom} = \frac{16}{3}\pi\sigma^3_{sl}\left(\frac{T_s}{\lambda\Delta T}\right)^2.$$

Here, λ is the heat of melting. Combination of this expression with the relationship for the number of critical nucleation centers n^*,

$$n^* = N\exp(-\Delta G^*_{het}/kT),$$

arising in the system with N nucleation centers yields, at $n^* = 1$, the relationship between the magnitude of supercooling and the angle ψ

$$\left(\frac{\Delta T}{T_s}\right)^2\frac{T_g}{T_s} = \frac{16\pi}{3k\ln N}\left(\frac{\sigma_{sl}}{\lambda}\right)^3\frac{\lambda}{T_s}\Phi(\psi).$$

Substituting the obtained experimental values T_g = 449 K and ΔT = 95 K and the corresponding literature data T_s = 544 K, λ = 10 885.68 J/mol, σ_{sl} = 80 erg/cm^2 [13], and ρ = 9.84 g/cm^3 into this expression, we obtain that the contact angle of the bismuth-based eutectic upon its crystallization on the aluminum substrate is $\psi = 75°$.

It should be noted that in [7] for bismuth nanoparticles in an aluminum matrix produced by mechanical milling of corresponding powders in a ball mill for several hours with subsequent pressing and sintering, the obtained supercooling is $\Delta T = 171$ K, which substantially exceeds the supercooling in the layered Al/Bi/Al film system observed in this work. The wetting angle of liquid bismuth on solid aluminum calculated in [7] from a decrease in the temperature of melting of Bi particles in the Al matrix is equal to 45°. According to the available literature data [3], this value of the wetting angle must correspond to a supercooling of ~70 K. The high magnitudes of supercooling (171 K) cited in [7] are likely to be connected with the presence of a very thin layer of aluminum oxide on the particles of the initial aluminum powder. When a mixture of powders is subjected to subsequent milling, pressing, and sintering, the aluminum oxide is seemingly concentrated around bismuth particles. In reality, the supercooling observed in [7] is related to the supercooling in the case of solidification of bismuth in contact with aluminum oxide. The supercoolings obtained in [3] ($\Delta T = 183$ K) are close to the above supercooling and were reached upon crystallization of bismuth on Al_2O_3 substrate at a wetting angle of $\cong 146°$.

CONCLUSIONS

Thus, in the layered Al/Bi/Al film system, a melting–crystallization temperature hysteresis was revealed for the bismuth-based phase in contact with a solid aluminum-based phase. The results obtained and their analysis show that the layered film systems may be employed for estimation of supercooling upon crystallization of binary alloys whose components in the solid state are practically insoluble in one another and form a eutectic-type phase diagram with an immiscibility bay in the liquid state, at the stage when the melt based on the lower-melting-point component is crystallized in contact with the solid phase based on the second, more refractory component. It is also shown that the magnitude of supercooling in such layered film systems is well reproducible in repeating heating–cooling cycles.

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