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Size Effect upon Solidification of Small Bismuth Particles

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STRUCTURE, PHASE TRANSFORMATIONS,
 AND DIFFUSION

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INTRODUCTION

The liquid–crystal phase transition is a first-order transition. Because of this, both states (liquid and crystalline) are thermodynamically advantageous at the temperature of the transition T_s , this is expressed in the equality of the chemical potentials of the crystal and the melt at this temperature. At T_s , the first-order derivatives of the thermodynamic potential—the entropy and the volume—change jumpwise. The change in the entropy is related to the heat of transition by the equation $\lambda = T_s \Delta S$. Because of this energy barrier, the melting point and the crystallization temperature may not coincide; i.e., the liquid–crystal first-order phase transition is discrete. It is of interest to analyze the parameters, of the liquid–crystal phase transition for small particles, for which the thermodynamic parameters, such as the chemical potential, surface and interface energy, and the temperature of phase transition, depend on the particle size.

It is difficult to reliably analyze numerous experimental data on the solidification of metallic melts; they may not be systematized, because the kinetics of solidification is highly sensitive to impurities. However, the data available indicate the existence of some correlation between the volume of the melt and the supercooling ΔT that is observed upon solidification. For example, a supercooling ΔT of about $0.17T_s$ and $(0.2–0.25)T_s$ may be reached for samples weighing hundreds and tens of grams, respectively, whereas supercooling up to $(0.2–0.3)T_s$ and $(0.3–0.4)T_s$ may be obtained for microdrops about $10^3 \mu\text{m}$ in diameter and particles 10^3nm in diameter, respectively [1]. However, an analysis of the data shows that the tendency to an increase in supercooling of the melt with increasing dispersity of the samples is primarily due to the decrease in the probability of picking up impurities (which may serve as nucleation centers) in the case of microdrops. This con-

clusion is, in particular, confirmed by the data on the solidification of microdrops of bismuth and lead (see table).

A substantial spread in the values of supercooling within each size range also is an argument in favor of the above assumption. Analogous results were obtained for other metals (e.g., In, Sn, Ag, Au, Cu).

It was shown in [2] that the use of island films allows one to control principal parameters of solidification of supercooled islands upon vacuum deposition on a substrate and to obtain reproducible data. For metals such as In, Sn, Bi, Pb, Au, Fe, Co, and Ni, the relative supercooling of islands is equal to $(0.33–0.34)T_s$ and is independent of their diameter in a size range from $100 \mu\text{m}$ to $30–40 \text{nm}$ [2].

On the other hand, an analysis of experimental data shows that the melting point T_R of small particles decreases with decreasing diameter; moreover, the data for different metals may be systematized quantitatively. This is confirmed by the following consideration.

Supercooling upon crystallization of microdrops of various volumes and films with islands of different diameter [1]

Metal	T_s , K	ΔT , ($\Delta T/T_s$)	
		Microdrops with $D < 10^2 \mu\text{m}$	Island films with islands with $D < 10^2 \text{nm}$
Bi	544	90, (0.17)	147, (0.27)
		115, (0.21)	165, (0.3)
		146, (0.27)	200, (0.37)
		227, (0.41)	221, (0.4)
Pb	601	80, (0.13)	158, (0.26)
		84, (0.14)	188, (0.31)
		153, (0.25)	240, (0.39)

According to [3], the use of the thermodynamic model for the solidification of small particles allows one to determine the surface energy of the solid phase σ_s and its temperature coefficient $\partial\sigma_s/\partial T$ and to estimate the activation energy for the formation of monovacancies ϵ_f . The values calculated for metals such as In, Sn, Bi, Pb, and Au agree with experimental data that were obtained using independent techniques.

A combined analysis of data on the crystallization of island films and on the size effect upon melting of small particles shows that the difference between the melting point T_R and the crystallization temperature T_g , representing the temperature hysteresis $\Delta T_{Rg} = T_R - T_g$ at the liquid-crystal phase transition, depends on the diameter of the particles. However, because of the lack of data on the crystallization of supercooled particles less than 30–40 nm in diameter, we cannot follow in much detail the dependence of the temperature hysteresis on the particle diameter for the liquid-crystal phase transition that was suggested for larger particles in [4–6].

Thus, studying crystallization of small particles from several nanometers to several tens of nanometers in diameter seems to be necessary.

EXPERIMENTAL

To investigate the crystallization of small particles of various sizes, we used a technique [2] based on the electron microscopic study of the morphology of island films that were deposited in a vacuum on a substrate with a temperature gradient. In this case, the crystallization temperature T_g of particles is the temperature of transition from the condensation mechanism of the vapor-crystal type to the vapor-liquid type with increasing substrate temperature. The transition is determined from the change in the morphology of the island films.

The experiments were performed for Bi island films vacuum-deposited on amorphous carbon substrates. The choice of Bi for the investigation was determined by the following: (1) For this metal, there are numerous data on the crystallization of supercooled particles of different diameter [1, 2, 9, 13]. (2) Because of the high anisotropy of the surface energy, crystalline bismuth tends to form planar growth features on solidification, even on amorphous substrates; as a consequence, the boundary between the crystalline region and the region of the supercooled liquid is most clearly observed in this metal in comparison with other low-melting metals such as In, Sn, Pb.

Bismuth samples were prepared by vapor deposition in a vacuum of 10^{-5} – 10^{-6} Pa onto substrates (carbon layer on a cleaved NaCl single crystal) placed in a temperature gradient of 300–600 K. The design of the substrate and the movable screen with a slit allowed us to deposit several (5–6) films differing in “mass thickness” along different “paths” in the same experiment, i.e., under the same conditions. The crystallization tem-

perature for the films with an average island size R of more than 10 nm was determined from the changes in the shape of the islands (Fig. 1) using electron microscopy. For films of smaller mass thicknesses, the difference in the shape of liquid and crystalline islands formed upon deposition via the different mechanisms (vapor-liquid and vapor-crystal) is not so clearly revealed; therefore, the reliability of determining T_g decreases substantially. Taking into account this fact, we developed a special technique to determine the temperature of the changing condensation mechanism for films with an average island size of less than 10 nm. It is based on the study of the temperature evolution of the island size distribution function. Earlier investigations showed that the parameters of the size distribution function (the position of the main maximum and density of particles) change abruptly at the crystallization temperature T_g . For Sn depositions with a fixed mass thickness, displacement of the maximum in the temperature dependence of the island-size distribution is observed at a temperature equal to T_g [7, 8]. With decreasing mass thickness, the displacement decreases; films with an average island size of $R < 5$ nm are virtually indistinguishable in both the shape of the islands (in electron micrographs) and the island-size distribution.

Differences in the histograms of island size distribution for Bi films deposited on carbon substrates are observed down to a particle size of about 3 nm. A distinctive feature of the size distribution for Bi films with low mass thicknesses is the presence of a single maximum in the NR^3 – R histograms. With increasing temperature, the density of islands decreases substantially. For films with $R_{\max} \approx 5.5$ nm deposited at 330, 370, and 440 K, the density of islands is equal to 10000, 5000, and $1200 \mu\text{m}^{-2}$, respectively. For films with the same mass thickness, changes in the density of islands, and therefore, in the average distance between islands, affect their maximum size. Figure 2 shows experimental $R_{\max}(T)$ curves for three series of samples differing in mass thickness. Upon condensation via the vapor-liquid mechanism, the R_{\max} value remains virtually the same, although the density of islands decreases with increasing temperature, because of the reevaporation of atoms. Upon condensation via the vapor-crystal mechanism, a decrease in the density of islands leads to an increase in R_{\max} up to the temperature of change in the mechanism of condensation at which the shape of the islands changes. Near T_g , the visual size of planar crystalline islands is larger than that of spheric liquid islands. For this reason, an abrupt change is observed in the $R_{\max}(T)$ curve (see Fig. 2); the temperature of the abrupt change corresponds to the change in the condensation mechanism. The temperature T_g determined from the $R_{\max}(T)$ curves agrees well with that determined from the changes in the particle shape observed in electron micrographs. The technique described allows us to determine the crystallization temperature for films with islands less than 10 nm in size. The T_g value estimated corresponds to R_{\max} in the NR^3 – R

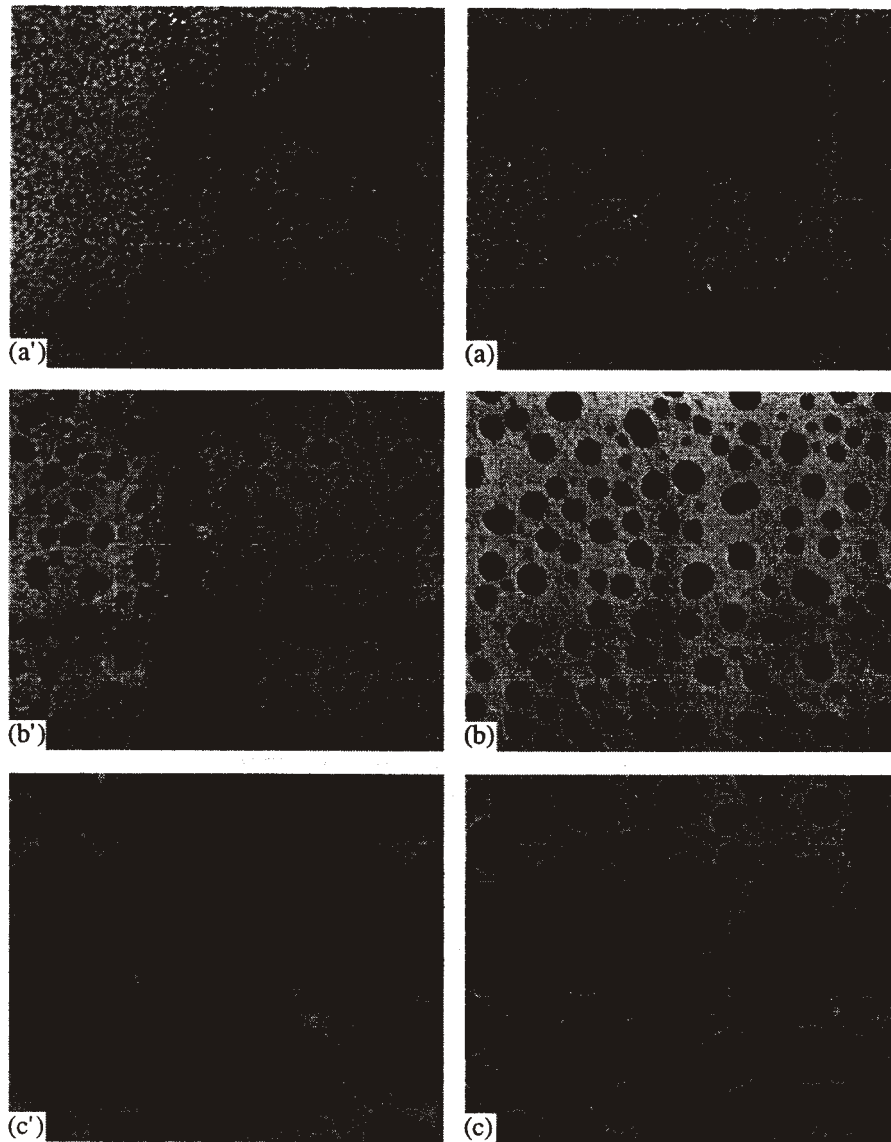


Fig. 1. Microstructure of Bi island films with particles of different average diameter deposited on carbon substrates at various temperatures: (a) $D = 3\text{--}6$ nm, above $T_g = 327$ K; (a') $D = 3\text{--}6$ nm, below $T_g = 327$ K; (b) $D = 10\text{--}13$ nm, above $T_g = 362$ K; (b') $D = 10\text{--}13$ nm, below $T_g = 362$ K; (c) $D = 26\text{--}33$ nm, above $T_g = 353$ K; (c') $D = 26\text{--}33$ nm, below $T_g = 353$ K.

island-size histogram; the error ΔR was assumed to be equal to the half-width of the maximum in the histogram.

RESULTS AND DISCUSSION

Figure 3 shows the crystallization temperature T_g as a function of the diameter of supercooled islands in Bi films. It is seen that T_g decreases from 375 K for islands more than 40 nm in diameter to 325 K for particles less than 4–5 nm in diameter. The error of the temperature determination is equal to ± 5 K. Since the diameter is determined from the half-width of the maxima in histograms, the error of determining D for particles crystallizing at a given temperature is estimated as a range of

corresponding particle sizes and is equal to ± 2 , ± 4 , and ± 2 for $D < 10$, 10–40, and > 50 nm, respectively. Actually, these ranges correspond to the different stages of the formation of island films, namely, the nucleation of islands, their growth, and coalescence.

The T_g value for particles with $D > 40$ nm agrees with both the data that were obtained by studying the morphology of Bi films deposited on substrates with a temperature gradient [2] and the data obtained for particles less than 10 nm in diameter using electron diffraction to detect the onset of crystallization [9]

Figure 3 also shows the dependence of the melting point of small Bi particles on their diameter [10–12]. It is seen that in the range of 10–30 nm they differ some-

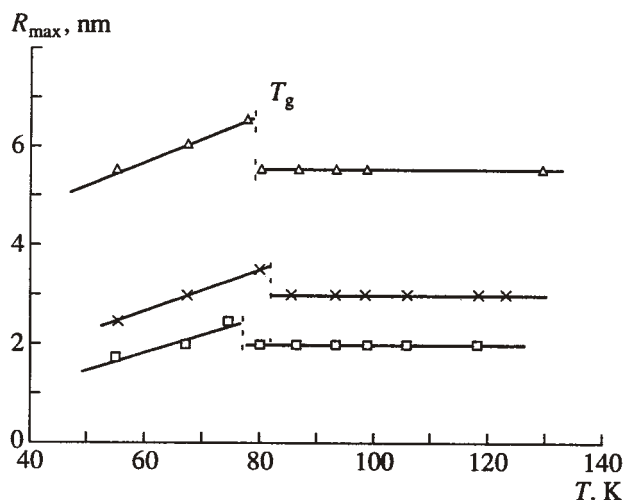


Fig. 2. Temperature dependence of the most probable radius of islands in Bi films with different mass thicknesses.

what. The authors of [10–12] used different techniques to determine the melting points of small particles; these are dark-field electron microscopy *in situ* (in a vacuum of 10^{-5} Pa) [10], transmission electron microscopy *in situ* (in a vacuum of 10^{-4} Pa) [11], and the electron diffraction method of determining the temperature dependences of integrated intensities of reflections (in a vacuum of 10^{-3} Pa) [12]. It is difficult to decide which of these techniques is most reliable [10–12]. However, dark-field electron microscopy [10] is somewhat preferable, because it detects the melting point of isolated particles, rather than melting of an ensemble of particles with diameters varying in a certain range at a fixed temperature [10, 11].

A combined analysis of data on the melting points and crystallization temperatures as functions of the diameter of Bi particles allowed us to construct a quantitative diagram of the liquid–crystal phase transitions for small particles in T – D coordinates (Fig. 3). Three regions can be separated in the diagram, which correspond to the existence of the equilibrium liquid phase (the upper left region above the $T_R(D)$ curve), the supercooled liquid phase (between the $T_R(D)$ and $T_g(D)$ curves), and crystalline phase (below the $T_g(D)$ curve).

The diagram shows that, for particles less than 50 nm in diameter, the temperature hysteresis upon melting and crystallization $\Delta T_{Rg} = T_R - T_g$ depends on their diameter. The maximum value $\Delta T_{max} \approx 0.33T_g$ corresponds to particles with $D \geq 50$ nm (these results agree with data [1, 13]); for particles of smaller sizes, ΔT_{Rg} decreases. The decrease in ΔT_{Rg} was observed experimentally for Bi [1], In, and Sn [15]; however, the data are only semiquantitative and do not allow one to precisely determine the $\Delta T(D)$ dependence and the critical diameter of particles D_c . It is seen from Fig. 3 that, with allowance for experimental error, the coordinates

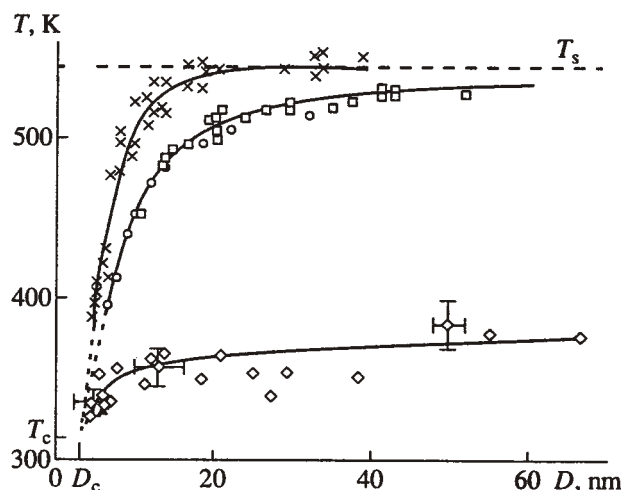


Fig. 3. Crystallization temperature T_g and the melting point as functions of the diameter of Bi particles determined in different works: (\diamond) T_g , present work; (\blacktriangle) T_g [9]; (\square) T_R [10]; (\times) T_R [11]; and (\circ) T_R [12].

of the critical point, where $T_R \rightarrow T_g$, i.e., the supercooling necessary crystallization becomes equal to zero, are $T_c \approx 310 \pm 5$ K and $D_c \approx 2$ –3 nm. Zero supercooling upon crystallization points to the change in the character of the phase transition for small particles; namely, the liquid–crystal phase transition for particles with $D < D_c$ becomes continuous rather than discrete. This fact cannot be explained within the classic theory of solidification, which assumes the existence of an energy barrier between the liquid and solid states. Therefore, we may assume that, for particles with diameters less than D_c , there is no energy barrier for crystallization or it is minimal; correspondingly, the heat of crystallization λ is equal to zero. This also points to the minimum energy of the interphase boundary between the crystal and the melt (σ_{sl}).

The observed decrease in supercooling with decreasing diameter of particles may be analyzed within the classic capillary model of homogeneous nucleation upon crystallization from the melt. According to this theory, the work of formation of a crystalline nucleus with a critical radius of $r^* = 2\sigma_{sl}(T_s/\lambda\Delta T)$ is determined by the following expression:

$$A^* = \frac{16\pi}{3}\sigma_{sl}^3(T_s/\lambda\Delta T)^2 \quad (1)$$

It is shown in [2] that the homogeneous nucleation (when any atom of N atoms of the system may serve, with equal probability, as a nucleation center for the crystalline phase) may be described by the following relationship between ΔT and the energy of the interphase interface σ_{sl} :

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

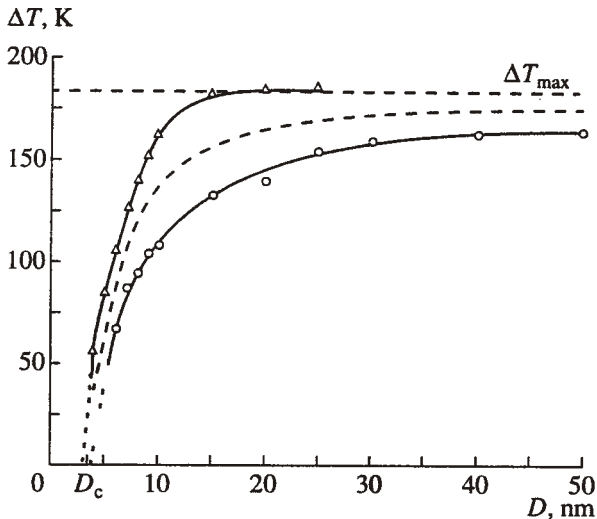


Fig. 4. Supercooling as a function of the diameter of Bi particles, determined with allowance for the data of different works: (Δ) [11]; (\circ) [10, 12], and (---) averaged data [10–12].

It follows from (2) that, given the $T_g(D)$ and, naturally, the $\Delta T(D)$ dependences, we may experimentally estimate the $\sigma_{sl}(D)$ dependence for small particles. Figure 4 shows the $\Delta T(D)$ dependences for Bi particles calculated from the T - D diagram. The upper curve was obtained from the melting data for Bi [11], and the lower curve is based on the data from [10, 12], whereas the dotted curve displays the averaged data.

As was mentioned above, no definitive criteria are available to quantitatively estimate the reliability of the data on melting of small particles that were obtained by different techniques; therefore, subsequent analysis is based on the averaged data. Figure 5 shows the $\sigma_{sl}(D)$ dependence calculated by equation (2) using the experimental $T_g(D)$ (present work) and $T_R(D)$ (averaged data [10–12]) dependences. The σ_{sl} value decreases with decreasing diameter; this points to the decrease in the energy barrier between the liquid and crystalline phases. The $\sigma_{sl}(D)$ curve obtained may be approximated by the expression

$$\sigma_{sl} = \sigma_{sl}^{\infty}(1 - 2\delta/R) \quad (3)$$

for the following values of the parameters: $\sigma_{sl}^{\infty} = 80 \text{ mJ/m}^2$ and $\delta \approx 1.8 \text{ nm}$ (δ has the meaning of the width of the intermediate layer between a crystalline particle and the melt.) According to [14], σ_{sl}^{∞} determined from the dihedral angle of grain misorientation at the solid–liquid interface is equal to 82 mJ/m^2 . Note that the decrease in the interphase energy for small particles described by equation (3) was predicted theoretically on the basis of the statistical electron theory of the surface energy of metals [16]. The radius of a critical nucleus (r^*) for particles with diameters close to the

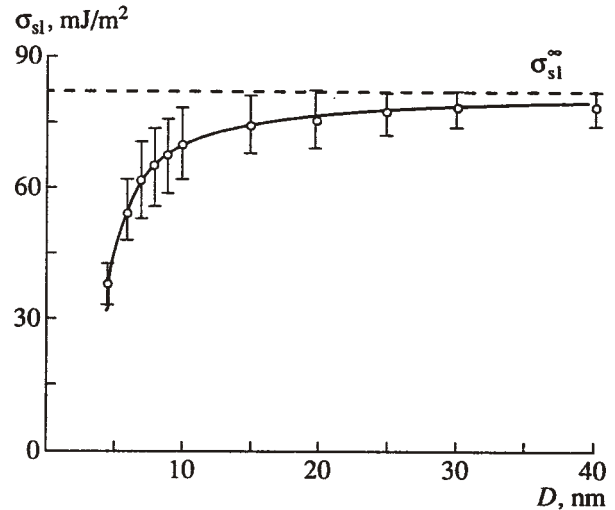


Fig. 5. Interphase energy at the crystal–liquid interface as a function of the diameter of Bi particles.

critical size D_c is about 1.1 nm. The estimations show that supercooling upon crystallization becomes equal to zero for islands with diameters close to that of the smallest nuclei capable of growth, i.e., $2(r^* + \delta) \approx D_c$.

CONCLUSION

The experimental data discussed above show that, with decreasing particle diameter, the difference between the liquid and solid states disappears; the critical diameter of the particles is close to the size of short-range ordered regions in the liquid. For the smallest particles, the liquid–crystal phase transition is continuous, whereas for larger particles, it is discrete.

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