

Supercooling during metal crystallization under conditions close to weightlessness using island vacuum condensates

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Island vacuum condensates the properties of which are determined by surface phenomena rather than the force of gravity actually permit to eliminate the effect of alien impurities and own oxides on supercooling ΔT during crystallization. Their application also allows to measure the dependence of ΔT on the contact angle θ between a droplet of a liquid metal and the substrate on which condensation and subsequent crystallization occur. For the metals under study (Au, In, Bi, Pb, Sn, Fe, Co, Ni) the supercooling ΔT is shown to increase with the angle θ growing. With wetting angles $\theta > 130^\circ$ the supercooling ΔT does not depend anymore on the substrate material and for $\theta \rightarrow 180^\circ$ it approaches a value somewhat below $0.4 T_s$, where T_s is the bulk melting temperature.

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Die Anwendung von Inselvakuumkondensaten für die Untersuchung der Unterkühlung bei der Kristallisation von Metallen unter nahezu schwerelosen Bedingungen

Die Beobachtung von Inselvakuumkondensaten, für die der Schwerkrafteinfluß vernachlässigbar klein gegenüber den Oberflächeneigenschaften ist, ermöglicht den Einfluß unlöslicher Fremdstoffe, eigener Oxide und löslicher Beimischungen auf die Unterkühlung ΔT bei der Kristallisation zu vermeiden. So können quantitative Daten über die Abhängigkeit von ΔT vom Benetzungswinkel θ des flüssigen Metalls mit dem Substrat auf dem die Kondensation und die darauffolgende Kristallisation erfolgen, erhalten werden. Es wird gezeigt, daß sich ΔT für die untersuchten Metalle (Au, In, Bi, Pb, Sn, Fe, Co, Ni) bei Erhöhung von θ vergrößert. Bei Benetzungswinkeln über 130° hängt die Unterkühlung nicht vom Unterlagmaterial ab und bei $\theta \rightarrow 180^\circ$ erreicht sie einen Wert von etwas weniger als $0.4 T_s$, wobei T_s der Schmelzpunkt des Volumenmaterials ist.

1 Introduction

The study of supercooling under crystallization is important not only for understanding nucleation phenomena at liquid-crystal phase transition but also for clearing out its effect on the solution of practical problems concerning solidification and determining ways to improve the microstructure and properties of stable and metastable phases. For a deeper

understanding of the nucleation process heterogeneous nucleation should be suppressed to a maximal extent.

For attaining great supercoolings two principally different groups of methods are used [1]. In the first group of methods a very high cooling rate is used to suppress heterogeneous nucleation. However, it is difficult to analyze the results of these measurements because the surface where cooling is taking place is itself a centre of heterogeneous nucleation. In the second group the nucleation process is controlled by removing potential centres of crystallization. Thus, for inactivation of heterogeneous nucleation centres at the melt – container interface, a method of creating amorphous environments called the method of melt fluxing is applied. In this way significant supercoolings in large volumes have been attained for the first time. One of the main methods in this group is the method of microvolumes first applied by Turnbull [2], which is based on separating melts into small drops. For a small drop the probability for alien insoluble impurities to get into the drop is very low and therefore it is easier to approach limiting supercoolings. Later this method was combined with the method of creating amorphous environments by melt fragmentation in a liquid emulsion [3].

It is rather efficient to increase attainable supercooling by performing melting and crystallization in ultrapure environments without any container. Similar conditions occur when a drop is falling in installations with falling samples [4] and also when the melt is being kept in a suspended state by different contactless means (e.g., acoustic or electromagnetic ones). However, the action of acoustic and electromagnetic factors on nucleation even under weightlessness prevents us from attaining the limiting supercooling. Probably this can be overcome, as it has been pointed out by Robinson and Lacy [5], by allowing the sample under weightlessness to float freely in the working chamber. In view of the contaminated atmosphere inside and near the contemporary spaceships one hardly expects to attain the limiting supercoolings with crystallization of chemically active metals aboard them.

Application of island vacuum condensates together with the determination of the supercooling during crystallization is one of the promising directions to investigate the crystallization process [6]. The vacuum condensation method allows to change the size of drops and conditions of their crystallization in wide ranges. The gravitation exerts a negligible influence on such objects due to their small size and

surface phenomena dominate their behaviour. The following estimations support this point. For a droplet of radius R on a nonwetting substrate the ratio of potential energy in the gravitation field $U_g = \frac{4}{3}\pi R^3 \rho g$ (ρ is the density, g is the acceleration of free fall) to its surface energy $U_s = 4\pi R^2 \sigma$ (σ is the surface energy) is $U_g/U_s = \rho g R^2 / 3\sigma$. If we assume $\rho = 10 \text{ g/cm}^3$, $\sigma = 10^3 \text{ erg/cm}^2$ then with $R = 10^{-4} \text{ cm}$ the ratio is $U_g/U_s \approx 3 \cdot 10^{-8}$.

In [6 to 9] the supercoolings exceeding greatly those obtainable by other methods have been reached during the study of the processes of island vacuum condensates formation and crystallization in the condensates. As it is important to attain the limiting supercoolings and in view of the outlined above it seemed expedient to carry out further systematic investigations of supercooling during metal crystallization using island condensates.

2 Methods and Results

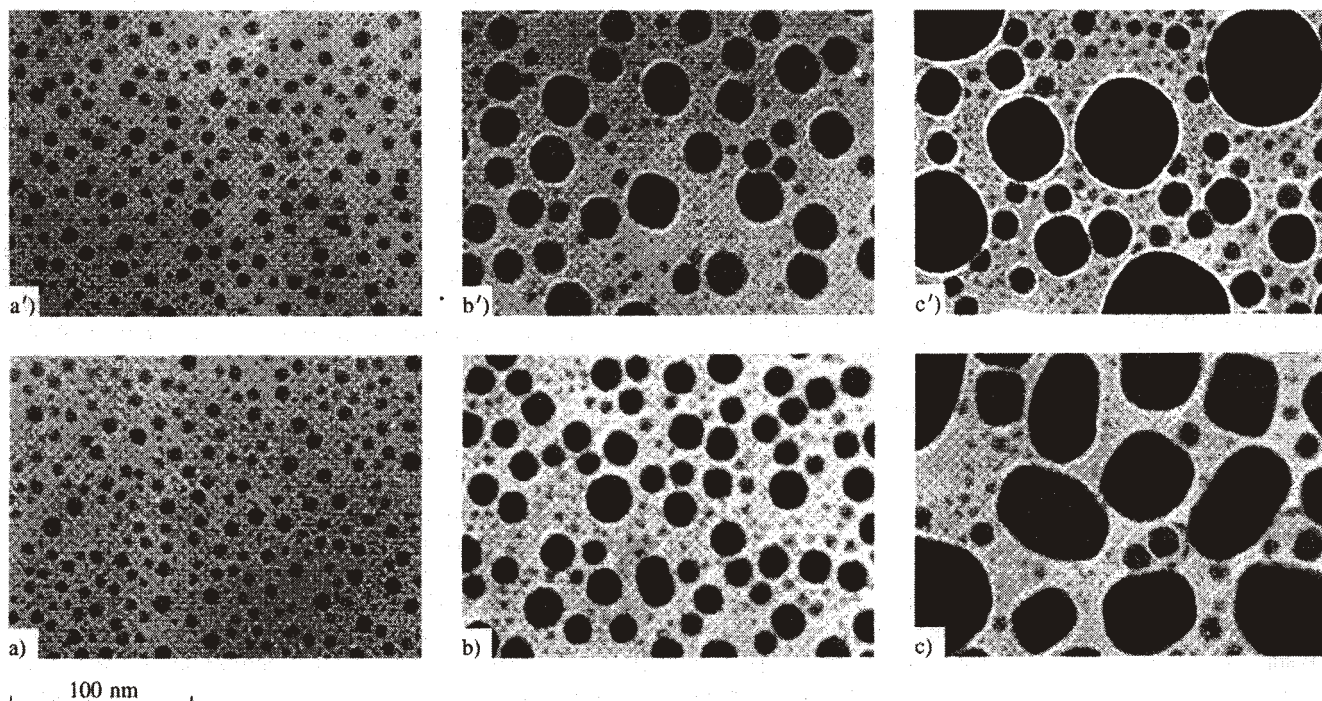
Based on previous investigations of formation of liquid and crystal phases in island vacuum condensates, the following experimental technique has been suggested.

According to direct electronographical studies [9, 10], the islands formed on the substrate during the initial period of crystallization are liquid at the temperature below the bulk melting temperature T_s , due to the decrease of the melting temperature for small particles. During the increase of the size of islands their melting temperature increases and at $T_g < T < T_s$ an island film from a supercooled liquid is forming, in accordance with the vapour-supercooled liquid mechanism. The boundary temperature T_g and, correspondingly, the supercooling $\Delta T = T_s - T_g$ depend on vacuum conditions and on the substrate material. Supercooling obtained here coincides with the one observed by methods of scanning electronography [11] and electron microscopy [7] when island films condensed under identical vacuum con-

ditions into a liquid phase at high temperatures ($T > T_s$) were cooled. Below the temperature T_g , after the islands reach the size determined by the size dependence of the melting temperature, they crystallize and then the condensation occurs into a crystal phase. As a result of this, with the growth of mass thickness one rather quickly observes a transition to the formation of continuous polycrystalline films. All this allows to determine simply and reliably a temperature range of existence of the supercooled liquid, i.e., the value of supercooling using condensates prepared on the substrate with a temperature gradient in a wide range ($0.5 T_s$ to T_s) [8].

Experiments were carried out in a heatable vacuum set-up that allowed to create pressures up to 10^{-8} Pa , using oil-free pumps. The composition of residual gases was controlled by a special bleeding system including a mass-spectrometer. A number of metals (Au, In, Bi, Pb, Sn, Fe, Co, Ni) with different melting temperatures and chemical activities with respect to residual gases were studied. In, Bi, Pb, Sn and Au of 99.999 % purity and Fe, Co and Ni of the 99.99 % purity were used for our experiments. The In, Bi, Pb, Sn and Au were evaporated from resistive evaporators whereas Fe, Co and Ni were evaporated by an electron gun with water cooling. The condensation rate and mass thickness of the films were measured with a quartz resonator.

As substrates we used cleavages of NaCl and KCl monocrystals and polished plates of Al_2O_3 polycrystals. We also used carbon and oxide (Al_2O_3 , ZrO_2 , MgO , SiO) films, and also some metal films (W, Ni, Cu) which were prepared by evaporation with different methods in vacuum just before the condensation of the metals under study. A circular substrate holder with a necessary temperature gradient along it provided for the same condensation rate and incidence angle of the molecular beam at all substrate points. Tantalum plates with a variable cross-section to which molybdenum grids with corresponding films-substrates were attached



Figs. 1a to c. Electron micrographs of tin island films of various mass thicknesses condensed onto carbon substrates below, (a)-(c), and above, (a')-(c'), the limiting temperature T_g (mass thickness: (a) 2 nm, (b) 5 nm and (c) 15 nm).

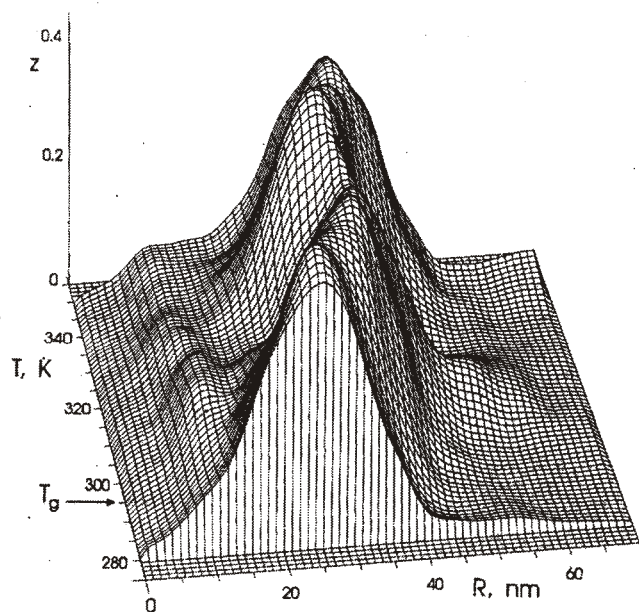


Fig. 2. Distribution of islands over sizes versus the temperature of the carbon substrate during condensation for tin films of 15 nm mass thickness ($z\Delta R$ is the film mass thickness formed by particles with sizes lying in the interval $(R, R + \Delta R)$).

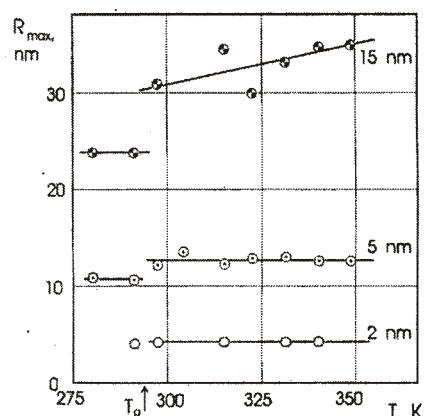


Fig. 3. Temperature dependences of the maximum of the island distribution function for tin condensates with different mass thicknesses.

were used as substrate holders for the preparation of Fe, Co and Ni films. The substrate holder was heated by electric current. To prevent metal condensation on the substrate before a stationary regime of evaporation was established, a mobile screen was provided between the substrate and the evaporator. After the condensation of metals the samples were cooled down to the room temperature and were removed from the vacuum chamber for examination.

The structure of island condensates on films-substrates was investigated with an electron microscope with simultaneous electron diffraction patterns analysis. The condensates on massive substrate were studied by replica method and by scanning and optical microscopy. X-ray diffraction analysis was made whenever necessary.

Detailed studies of the influence of mass thickness, pressure and composition of residual gases, condensation rate and substrate material on the metastability limit of supercooling liquid in condensates of the metals mentioned above, i.e., on the value of supercooling during crystallization have been carried out.

For all chosen metals a critical temperature T_g can be defined for the process of condensation on the substrate at the temperatures much lower than T_s . Thus, for island films of In, Sn, Bi, Pb and Au prepared in vacuum of $2 \cdot 10^{-6}$ Pa on amorphous carbon substrates these temperatures are 285, 336, 361, 408 and 891 K, respectively. Above and below these temperatures condensates scatter light rather differently and this difference remains after the films are cooled to room temperature. According to electron microscopic observations above T_g the films have an island structure, the island form being close to spherical. Below T_g rather thick ($> 10^2$ nm) films are completely polycrystalline. According to direct electron diffraction studies made previously this is due to particles being liquid and in a supercooled state above T_g . At very small mass thickness it is difficult to observe the difference in the structure of films above and below T_g with the electron microscope (Fig. 1). With an increase of mass thickness, although the films are still island ones below T_g the difference is well manifested by the shift of the maximum of the function describing particles distribution over sizes at fixed mass thickness (Fig. 2). Also, this difference increases with the mass thickness growing. This is demonstrated in Fig. 3 where the dependence of the maximum of the distribution function on temperature is shown, the mass thickness being the parameter.

The difference in the structure of thin films above and below T_g is manifested in a change of a particle profile pattern. Below T_g particles have a flat form, but above T_g their form is close to spherical.

It should be noted that under sufficiently short cooling the particles formed as the result of crystallization of a supercooled liquid phase are mainly monocrystalline and acquire facets typical to the given metal. This is illustrated in Fig. 4 showing electron micrographs of cobalt particles above and below T_g . Under fairly fast cooling the particles retain a spherical form. For such metals as indium and lead as a result of keeping them at room temperature the particles already acquire the facets and at the same time in lead films the formation of oxides takes place.



Figs. 4a and b. Electron micrographs of cobalt particles formed at temperatures below T_g (a) and above it (b) on Al_2O_3 substrates: (a) Vapour-crystal mechanism, (b) Vapour-supercooled liquid mechanism with subsequent crystallization.

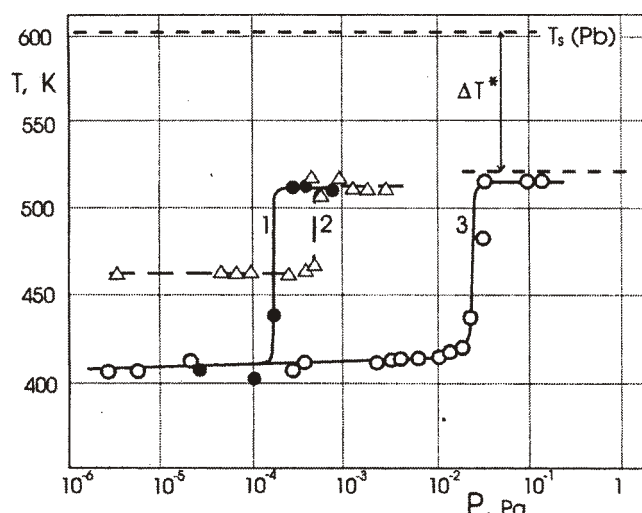


Fig. 5. Limiting temperature T_g versus residual gas pressure for lead on carbon (condensation rate is 0.02 nm/s (1) and 0.5 nm/s (3)) and SiO substrates (curve 2 depicts the data by Fisher and Anderson [12]; ΔT^* is Turnbull's supercooling value [2]).

The investigations performed with unchanged material of the substrate have shown that changes of pressure of residual gases and condensation rates have a different influence on the supercooling. So for island condensates of gold on carbon films an increase of pressure of residual gases p from 10^{-7} to 10^{-1} Pa has no effect on the temperature T_g . At the same time for island films of bismuth and lead on carbon substrates a dependence of T_g (supercooling ΔT) on pressure of residual gases with fixed rate of condensation is clearly observed (Fig. 5 gives the data on lead). Under some critical pressure p_c one observes a sharp increase of T_g from the value 361 K for bismuth and 400 K for lead to 430 and 518 K, respectively. As it follows from Fig. 5, the critical pressure p_c depends on condensation rate. In the same Fig. 5 the data [12] on T_g dependence on p for lead on the SiO-substrate are shown. From Fig. 5 one sees that the value of T_g at $p > p_c$ does not depend on the substrate material and coincides with the value down to which drops of lead were supercooled in Turnbull's experiments (ΔT^*) [2].

Along with electron diffraction patterns of the metal one obtains the lines of condensation oxides (e. g., $\gamma\text{-Bi}_2\text{O}_3$) in

films of bismuth and lead condensed at pressure of residual gases exceeding p_c . For island films of bismuth on the oxide Bi_2O_3 substrate the value of T_g coincides with that for the carbon substrate at $p > p_c$. This indicates that the oxide formation is the cause of a sharp increase of T_g at $p > p_c$. For island films of tin and pressure of residual gases $p > 10^{-2}$ Pa an increase of T_g (a decrease of supercooling) from 335 K to 400 K also takes place, although such a direct relation between p_c , condensation rate and temperature T_g is not observed. With the increase of T_g the lines of SnO_2 oxide are found in the diffraction patterns of the films.

Film deposition is determined not by the absolute values of residual gas pressure and condensation rate but by the ratio of the number of molecules of residual gases getting on the substrate per unit time, n_o , to the number of molecules of the condensing metal, n_m . Therefore experiments studying the n_m/n_o effect on T_g for tin on carbon substrate with controlled change of residual atmosphere composition have been carried out.

Estimations of T_g were made with a change of pressure from $3 \cdot 10^{-7}$ up to 10^{-2} Pa when the condensation rate changed from 0.01 to 10 nm/s. Figure 6 shows the corresponding dependences of the temperature T_g on n_m/n_o obtained under the assumption that the adhesion coefficient of gases is unity. It is seen that the highest supercooling under tin crystallization on the amorphous carbon substrate is achieved most easily in the residual atmosphere consisting mainly of noble gases. Assuming that the adhesion coefficient of gases is less than 0.1, the content of impurities determined by the ratio n_m/n_o in fact is much lower than the one given in Fig. 6 (the relevant actual ratio exceeds one in Fig. 6). That is why for determining T_g for the metals under study it is sufficient to carry out experiments under pressures of $5 \cdot 10^{-7}$ to $5 \cdot 10^{-6}$ Pa with the condensation rate of some nanometers per second.

Basing on this, the influence of the substrate material on the supercooling was studied under the above mentioned conditions with simultaneous electron diffraction study of the films. Traces of oxides were not observed. The contact angle θ between the substrate and a liquid droplet of the condensing metal was chosen as a parameter determining the influence of a substrate material on supercooling during a liquid phase crystallization. Depending on the size of islands (10 to 10^4 nm), the substrate material and the value of the contact angle we used specially developed different methods [13] for their determination using electron, scanning and optical microscopic techniques.

Figure 7 presents the data obtained on the dependence of a liquid phase supercooling during crystallization on the substrate on the wetting angle (the substrate material) for the metals under study. It is seen that at small θ supercooling is low and it increases with θ increasing. Thus for Co on oxide substrate (Al_2O_3 , ZrO_2) the wetting angle is $\theta = 140$ to 145° . For Fe and Ni on Al_2O_3 -substrates the angle θ is 135 to 140° . The obtained supercooling are 670, 595 and 598 K for Fe, Ni and Co, respectively and they are much higher than those obtained previously by other methods [1, 2]. At the same time for Co on tantalum substrate the value of supercooling is less and equals 450 K. When wetting is poorer, namely with θ increasing, supercooling increases and approaches some limiting value, i.e. supercooling at $\theta \rightarrow 180^\circ$ tends to a constant value for all metals studied of $\Delta T = \frac{1}{3} T_s$.

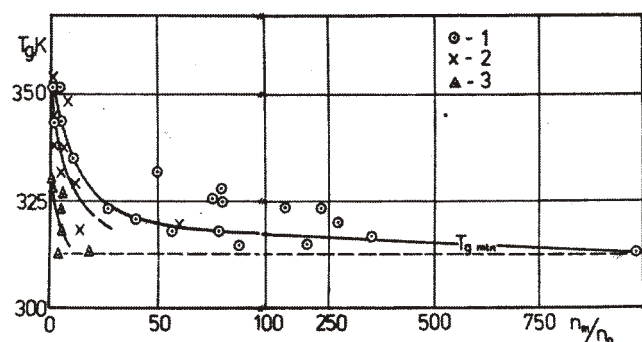


Fig. 6. Temperature T_g versus n_m/n_o for tin island films condensed onto carbon substrates in an initial residual atmosphere (1) and in atmosphere enriched with oxygen (2) and noble gases (3).

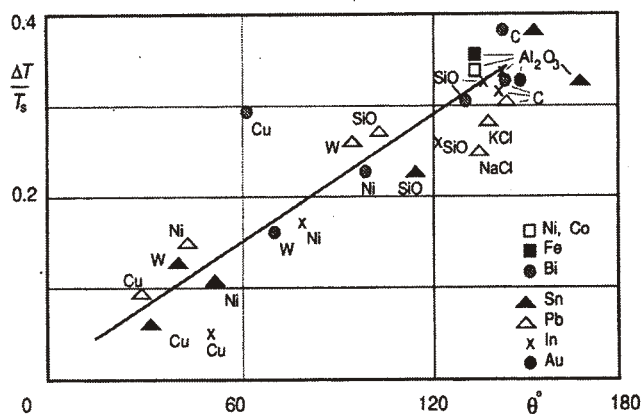


Fig. 7. Relative magnitude of supercooling versus contact angle for the wetting of the substrates by the condensates for various metals (the points are labeled with the substrate material).

3 Discussion

The results obtained on supercooling of a number of metals using island vacuum condensates, can be explained in terms of the classical theory of condensation and crystallization [2, 14].

According to the capillary theory of condensation [14] to form a critical nucleus of the condensed phase in the form of a spherical segment with the contact angle θ one should perform the work

$$\Delta G^* = \frac{16\pi}{3} \frac{\sigma_{cv}^3}{\Delta G_v^2} \Phi(\theta) \quad (1)$$

The radius of the critical nucleus is

$$r^* = 2\sigma_{cv}/\Delta G_v \quad (2)$$

Here $\Phi(\theta) = (2 - 3\cos\theta + \cos^3\theta)/4$, σ_{cv} is the free surface energy of the condensate–vapour interface. The change of the specific (per volume) free energy during condensation ΔG_v equals $(kT/V_a)\ln(p/p_e)$, where V_a is the atomic (molecular) volume, p is the pressure of supersaturated vapour and p_e is the equilibrium pressure of vapour.

From (1) it follows that $\Delta G^* = 0$ at $\theta = 0$, i.e. the activation barrier of nucleation is absent, and at $\theta = 180^\circ$ (complete nonwetting) $\Phi(\theta) = 1$ and the substrate is not active in the process of nucleation. Then islands of the condensed phase will be formed having practically a point contact with the substrate. Usually for island condensates on neutral amorphous substrates one has $\pi/2 < \theta < \pi$.

For forming island condensates at initial stages at small sizes there is a substantial contribution of a surface term into the free energy, which leads to lowering their melting temperatures. Simple thermodynamic considerations lead to the known relation for melting temperature of a particle with R radius [15]

$$T_R = T_s(1 - 3\Delta\Omega/\lambda R), \quad (3)$$

where $\Delta\Omega$ is a change of surface energy during melting defined as $\Delta\Omega = \sigma_s - \sigma_l(\rho_l/\rho_s)^{1/3}$ (σ_s , σ_l and ρ_s , ρ_l are specific surface energies and densities in liquid and solid states at T_R), λ is the melting enthalpy.

The melting temperature is also determined by Eq. (3) for a particle in the form of a spherical segment of radius R situated on the substrate and forming a contact angle θ

with it (under the assumption that the angle does not change during melting). However, the volume of the melting particle is $\Phi(\theta)$ times less than the volume of a free particle with the same radius and with $\theta \rightarrow 180^\circ$ the volume of melting particles on the substrate is close to the volume of free particles.

A comparative analysis of Eqs. (2) and (3) shows that due to a small size initially formed nuclei of a condensed phase are liquid. Later with their growth in the process of condensation they may be in the supercooled state at $T < T_s$ if supercooling is less than the one required for the crystallization on a given substrate.

Thus, if a nucleus of a crystal phase in the form of a spherical segment is formed on the liquid–substrate interface, its contact angle with the substrate (ψ) is determined, as it is seen from Fig. 8, by the condition $\sigma_{lu} = \sigma_{sl} + \sigma_{sl}\cos\psi$ (σ_{sl} is the energy of the interface between the crystal and its melt). This leads, together with the independence of the radius of the critical nucleus $r^* = 2\sigma_{sl}T_s/\lambda\Delta T$ of the angle ψ , to a $\Phi(\psi)$ times decrease of its volume compared with the spherical nucleus of the same radius.

Correspondingly, the work for its formation reduces by the same factor, i.e.,

$$\Delta G_{het}^* = \Delta G^* \Phi(\psi) \quad (4)$$

compared with the work to form the critical nucleus under homogeneous nucleation, determined by the expression

$$\Delta G^* = (16/3)\pi\sigma_{sl}^3T_s^2/(\lambda\Delta T)^2 \quad (5)$$

Owing to this, there decreases the supercooling required under heterogeneous nucleation for a liquid crystallized on the substrate.

From Eq. (4) it is seen that for $\psi \rightarrow 0$ crystallization proceeds almost without supercooling. With an increase of angle ψ supercooling will increase and $\Delta G_{het}^* \rightarrow \Delta G^*$ at $\psi \rightarrow 180^\circ$, i.e. the substrate will not actually affect the crystallization of the liquid and the system will be in a state in which nuclei are formed homogeneously.

Naturally, the given phenomenological consideration of the substrate influence on crystallization using angle ψ is mainly applicable to amorphous substrates. Besides, measurements of ψ are impossible to perform at least for metals and that is why the dependence of supercooling on angle ψ cannot be established. One can still draw an important conclusion from reasoning above that with increasing angle ψ the substrate influence decreases as does its influence on the condensation process with an increase of angle θ . Hence, we can expect that for $\theta \rightarrow 180^\circ$ the substrate will practically not affect the crystallization process as well. Thus, studying

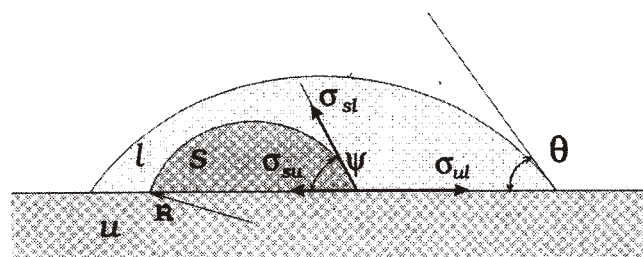


Fig. 8. Formation of a crystal phase nucleus in the liquid on a substrate.

supercooling on different substrates and choosing the contact angle θ to be a parameter determining the substrate influence on ΔT , it is possible for $\theta \rightarrow 180^\circ$ to approach the maximal supercooling with homogeneous crystallization of free liquid drops.

On considering heterogeneous crystallization it should be noted that active insoluble impurities facilitating nucleation are usually insoluble refractory particles. The same activity with respect to many melted metals (e.g., Pb, Bi) is exhibited by their own oxides. This fact fully agrees with data obtained on the influence of own oxides on the supercooling value in island condensates of tin, lead and bismuth. These results also indicate, that the values of supercooling for these metals obtained in Ref. [2] refer not to homogeneous but to heterogeneous nucleation on their own oxides.

If one applies island vacuum condensates for determining supercooling, then the role of insoluble impurities is practically excluded, the only controlled insoluble impurity being the substrate. Making experiments under fairly pure vacuum conditions also prevents the own oxide influence on crystallization.

Along with insoluble impurities, soluble ones also affect supercooling during crystallization, causing a change of the surface tension of a melted substance relative to its crystals. Here the surface-active soluble impurities, i.e. those which decrease the surface tension, are concentrated near the interface and are adsorbed by it. Correspondingly, they decrease the work of formation of nuclei with critical sizes and draw the metastability limit of the supercooled melt towards melting temperature. At the same time insoluble impurities that increase the surface tension, do not concentrate near surfaces of emerging crystals but rather tend to leave these surfaces. Hence, their influence on crystallization should be rather insignificant. Thus, for island condensates of tin and lead it is well seen from Figs. 5 and 6 that when formation of oxides is not observed there is a slight lowering of temperature T_g (increase of supercooling) with an increased content of impurities (including oxygen) coming from residual atmosphere. This can be due to the influence of active components of residual gases on the crystal-melt interphase energy. But in the case of residual atmosphere enriched by noble gases (He and Ar) such dependence is practically not observed and maximal supercooling for tin crystallization on the carbon substrate is reached at substantially higher pressures in the process of condensation (at significantly less values of n_m/n_0 , Fig. 6).

Measured data in Fig. 7 on the dependence of relative supercooling on the value of the contact angle between the substrate and a liquid metal agrees with the mentioned considerations about the substrate influence on supercooling qualitatively well. This statement is justified because the results were obtained with the minimum influence of insoluble impurities in the form of own oxides and soluble impurities due to residual gases. However, there are no significant grounds for application of a linear extrapolation for determining $\Delta T/T_s$, at $\theta = 180^\circ$, because already at $\theta > 130^\circ$ the function $\Phi(\theta)$ tends to unity, as does the function $\Phi(\psi)$ at $\psi > 130^\circ$. That is why one can probably assume that the value of the relative supercooling $\Delta T/T_s \approx 1/3$ obtained for the metals under study at angles $\theta > 130^\circ$ is close enough to the maximum in the case of the homogeneous nucleation. The measured maximal supercoolings for the mentioned metals are approximately con-

stant and do not depend on island sizes in the range under study (10 to 10^4 nm). At least qualitatively, this can be explained via a thermodynamic approach not requiring the data on the nucleation rate versus supercooling. Specifically, such an approach has been applied in [16] to treat Turnbull's data on metal supercooling.

According to [16], the number of critical nuclei in a melt can be calculated from the formula

$$n^* = N \exp(-\Delta G^*/kT) \quad (6)$$

if one knows the critical nucleus formation work ΔG^* . Here N is the number of equivalent areas in which the crystallization centres are formed. If the nuclei are very small and every atom can serve as a crystallization centre, then N equals the number of melt atoms. This is just the case for homogeneous nucleation and ΔG^* for a spherical nucleus can be calculated with Eq. (5). One sees from Eq. (5) that ΔG^* is infinitely large with $\Delta T = 0$ and no nucleus formation occurs. With ΔT increasing the quantity ΔG^* decreases, however, at sufficiently large supercoolings the intensity of thermal fluctuations and atom mobility are observed to decrease suppressing the formation of nuclei. This is observed, e.g. for glass that can remain in the state of the supercooled liquid with very high viscosity for a long time. Such a state is, probably, unattainable for typical metals at achieved supercoolings, therefore, the decrease of thermal fluctuations and atom mobility cannot limit metal crystallization.

For the crystallization to start not less than one nucleus should be formed in the liquid. Therefore with $n^* = 1$ it follows from Eq. (6) that the work for the critical nucleus formation cannot exceed $kT \ln N$. Consequently, if the nucleation is homogeneous then the crystallization occurs when the work ΔG^* decreases to this value with supercooling increasing. Then in view of Eq. (5) one obtains with $n^* = 1$ the expression

$$\left(\frac{\Delta T}{T_s}\right)^2 \frac{T}{T_s} = \frac{16\pi}{3k \ln N} \left(\frac{\sigma_{sl}}{\lambda}\right)^3 \frac{\lambda}{T_s} \quad (7)$$

In agreement with the law of respective states the ratios σ_{sl}/λ and λ/T_s for metals with the same type of crystal structure are constant [2, 17], but for different types of structure they change in such a way that their product remains constant. This circumstance is the reason for the observed limiting relative supercoolings to be approximately constant.

Conclusion

The experiments have shown that application of island vacuum condensates allows to exclude practically completely the influence of uncontrolled alien insoluble impurities on supercooling during crystallization. For soluble impurities and own oxides it can be done by optimal choice of the relationship between the condensation rate and the pressure of residual gases and their composition. Under these conditions the only controlled solid impurity is the substrate material and by changing it we can perform the aimed control of the value of supercooling in a wide range. For the metals studied (Au, In, Bi, Pb, Sn, Fe, Co, Ni) we have for the first time obtained quantitative data on supercooling versus wetting angle under the conditions when the influence of gas-

eous soluble impurities from residual atmosphere is reduced to a minimum. In island condensates on nonwetted substrates at wetting angles $\theta > 130^\circ$ the supercooling does not anymore depend on the substrate material and with $\theta \rightarrow 180^\circ$ it approaches a value somewhat below $0.4 T_s$. This value is probably sufficiently close to a maximum for the homogeneous nucleation.

Thus, application of island vacuum condensates allows to approach maximal supercooling during crystallization of metals under normal gravity conditions without making complicated experiments under weightlessness in space.

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