



Nonstationary nucleation (explosive crystallization) in layers of amorphous ice prepared by low-temperature condensation of supersonic molecular beams



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ABSTRACT

Layers of amorphous ice were prepared by deposition of supersonic molecular beams of rarefied vapor on a substrate cooled by liquid nitrogen. Molecular beam entered a vacuum chamber through Laval nozzle, which accelerated it to a supersonic speed. An adiabatic expansion of molecular beam leads to a decrease in the temperature at the nozzle outlet and formation of crystalline nanoclusters of water. Under heating of nonequilibrium condensates one could observe a glass transition (softening) and subsequent spontaneous crystallization. The presence of water clusters introduced into nonequilibrium condensates artificially ensured conditions for the initiation of “hot” centers and a transition to an explosive regime of crystallization in an amorphous medium. A theoretical analysis has been made of the role of the thermal conditions in which the crystallization of an amorphous substance proceeds, with allowance for the nonstationary nucleation.

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1. Introduction

The crystallization of low-viscosity supercooled liquids is a stationary random process. A distinct manifestation of characteristic effects of nonstationary crystallization must be observed for viscous liquids or in the region of supercooling to which corresponds the low-temperature branch of the dome-like dependence of the nucleation rate. High nonstationary manifests itself as a delay of nucleation, which is observed, for instance, in the case of glass-forming silicate glasses. Nucleation on the low-temperature branch of the dome qualitatively changes the process itself, which is characterized by an avalanche-like increase in the number of crystal-phase nuclei. The time of complete crystallization of a sample in this case is smaller than the characteristic time of nonstationarity, which is equal to several seconds or minutes [1]. The shock regime of crystallization is realized, if in conditions of high viscosity the steady-state nucleation rate is large enough, $J_0 > 10^{16} \text{ s}^{-1} \text{ cm}^{-3}$ (due to the small size of a critical nucleus) at considerable delay times $\tau_0 \sim 10\text{--}100 \text{ s}$, although the crystal growth rate is small. Besides, intensive nucleation is capable of causing a sample self-heating at the cost of generation of crystallization heat and explosive nucleation. An increase in the crystal growth rate

caused by an increase in the temperature will result in a further increase in the heat release, which in its turn may lead to a further increase of the temperature in the system. The process of crystallization of amorphous layers can intensify itself at the cost of the positive feedback between the heat release rate and the decrease of viscosity. In this case there is a certain analogy with the processes of combustion and explosion. Thus, a distinctive feature of crystallization at intensive nucleation in amorphous solids is the possibility of spontaneous initiation of “hot” centers and explosive crystallization at the sites of local accumulation of crystal nuclei that emerge by way of fluctuation.

For amorphous water condensates the credibility of evaluating the parameters of nonstationary nucleation has been checked by independent experiments on the observation of phenomena of structural relaxation close to the temperature interval corresponding to the value of viscosity $\eta \sim 10^{12} \text{ Pa}\cdot\text{s}$ to the glass-transition region [2].

The condition of initiation of “hot” centers and a spontaneous transition to the explosive regime of crystallization in an amorphous medium with frozen-in crystal nuclei requires their high concentrations, which may be achieved both as a result of a natural nucleation process and by way of artificial introduction of additional nuclei into the medium.

In experiments on ultradispersed powders of amorphous germanium explosive crystallization was observed at a content of the crystal phase exceeding 3%, with an increase in the crystal frac-

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tion in the powder leading to an increase in the velocity of propagation of the front of explosive crystallization [3]. The emergence of numerous “hot” centers, i. e. peculiar crystallization nuclei, might be observed visually. The characteristic indentation of the front of explosive crystallization contrasted with fairly smooth boundaries of the region crystallized from different centers.

The aim of the present work is to investigate the phase stability of solid amorphous water layers prepared by low-temperature condensation of supersonic molecular beams in the presence of completed crystallization centers introduced into non-equilibrium condensates.

The method of low-temperature deposition of molecular beams in vacuum makes it possible to achieve high condensation rates and has proved to be efficient for obtaining the substances that cannot be vitrified by cooling a melt in solid amorphous state. This method of amorphization is applicable even for some one-component metals. Solid amorphous films of water and simple organic compounds prepared by condensation of molecular beams on a substrate cooled by liquid nitrogen have proved to be convenient for an experimental investigation of the processes of formation of amorphous layers and their stability against crystallization [1]. When they are heated, glass-transition effects manifest themselves vividly. Vitreous condensates also serve as convenient model objects for experimental investigations of the kinetics of crystal nucleation and growth in conditions that are far from thermodynamic equilibrium.

At low temperatures the stability of nonequilibrium condensates, which are deeply supercooled frozen liquids, is ensured by the high viscosity and the small value of the nucleation rate of a crystal phase. Their heating is accompanied by glass-transition (softening) and subsequent spontaneous crystallization. Glass-transition and crystallization temperatures depend on the rate of temperature change. For instance, for water, by the data of different authors, the values of these temperatures are in the ranges from 130 to 140 K and from 150 to 165 K, respectively [4–8]. The crystallization of amorphous ice leads to the formation of a metastable cubic structure [9]. On further heating, cubic ice turns into hexagonal. This transition proceeds in a wide temperature range from 180 to 200 K without any noticeable changes in the thermophysical properties owing to the low process rate.

Along with the possibility of employment of solid amorphous water layers for an experimental study of the crystallization kinetics of supercooled liquids the interest in its properties is caused by their unusual behavior both in the region of deep supercooling, where water is in a vitreous state, and in the temperature region moderately lower than the equilibrium melting point, where water is still in a liquid state (approximately before -40°C at 1 bar). Numerous experimental and theoretical works are devoted to investigation of the anomalous behavior of the properties of supercooled liquid water and the polymorphism of the solid amorphous water state (see, for example Ref. [7,10–14]). However, the understanding of peculiarities in the behavior of many of its properties remains vague.

2. Thermal regime of crystal growth in an amorphous layer

The possibility of initiation and development of explosive crystallization in amorphous media is determined by the thermal conditions at the boundary of an isolated growing crystal nucleus. The case of transition to an explosive crystal growth has been investigated in detail theoretically. The conditions of an accelerated crystal growth have been found in Ref. [15–17], when the crystallization heat release leads to an increase in the temperature and an abrupt increase in the crystal growth rate. The formulation of the problem in this case includes the heat conductivity equation

for a crystal growing in an amorphous medium with a heat source at the boundary. For instance, for a spherical crystal of radius R growing in an amorphous phase the temperature field $T(r, t)$ is described by the heat conductivity equation

$$\frac{1}{a} \frac{\partial^2 T}{\partial t^2} = \frac{\partial^2 T}{\partial r^2} + \frac{2}{r} \frac{\partial T}{\partial r}, \quad (1)$$

which must be supplemented with the condition of heat balance at the crystallization front:

$$\chi_s \left(\frac{\partial T}{\partial r} \right)_{r=R-0} - \chi_l \left(\frac{\partial T}{\partial r} \right)_{r=R+0} = \frac{\Delta h u}{v_s} \quad (2)$$

and boundary conditions

$$\left(\frac{\partial T}{\partial r} \right)_{r \rightarrow \infty} = 0, \quad T(\infty, t) = T_\infty \quad (3)$$

Here Δh is the specific heat of crystallization, v_s is the specific volume of a crystal phase, a is the thermal diffusivity, and χ_s and χ_l are the thermal conductivities of a crystal and an amorphous phase. In solving it is assumed that the temperature dependence of the crystal growth rate $u = dR/dt$ is nonmonotonic. It increases with temperature in the region of existence of an amorphous state, reaches the maximum, and then decays to zero at the temperature of the crystal-melt equilibrium. Such a dependence is given by the relation [18]

$$u = f d \left(\frac{kT}{h} \right) \exp \left(- \frac{E}{kT} \right) \left[1 - \exp \left(\frac{\Delta h \Delta T}{T_0 kT} \right) \right], \quad (4)$$

where f is the fraction of locations at the surface of a growing crystal to which molecules from liquid phase may adhere, d is the linear size of molecules, E is the activation energy of the process of molecule transfer from the liquid to the surface of a growing nucleus (in calculations E is taken to be equal to the activation energy of a viscous flow), T_0 is the melting temperature, $\Delta T = T_0 - T$ is the supercooling, k and h are the Boltzmann and Planck constants, respectively.

If it is assumed for simplicity that the values of thermal conductivity, thermal diffusivity, heat capacity and density are little different in both phases, and the temperature inside a crystal is equal to that of its surface T_s , then instead of condition (2) we have

$$\frac{R}{3} \frac{\partial T_s}{\partial R} u - a \left(\frac{\partial T}{\partial r} \right)_{r=R+0} = u T_q, \quad (5)$$

where $T_q = \Delta h/c$, c is the heat capacity.

Methods of solution of the heat conductivity equation as applied to the problems of crystallization are examined in detail in Ref. [19] A self-similar solution of Eq. (1) that satisfies condition (5) and boundary conditions (3) leads to the following expression for the temperature of the crystallization front:

$$T_s = T_\infty + \left(T_q - \frac{R}{3} \frac{\partial T_s}{\partial R} \right) \frac{uR}{a} \left[1 + \frac{uR}{a} \text{Ei} \left(- \frac{uR}{a} \right) \exp \left(- \frac{uR}{a} \right) \right], \quad (6)$$

where Ei is the integral exponential function.

The relation between the radius of a growing crystal and the temperature of its surface at a given temperature of the amorphous matrix is shown schematically in Fig. 1. Small crystals grow at the temperature of the amorphous matrix until they reach the size R_* . After that one occurs an abrupt heating of the crystal and an increase in the rate of its growth, i. e. transformation into a “hot” crystallization center. If the thermal effect of crystallization T_q exceeds the initial supercooling $\Delta T = T_0 - T_\infty$, then in the process of the crystal growth the temperature at its surface T_s tends to T_0 . But if $T_q < \Delta T$, the asymptotic value of T_s is equal $T_\infty + T_q$.

A “hot” crystallization center in an amorphous layer may appear as a result of an external action which causes a local heating

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