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Crystal nucleation on glass surfaces. Theory and experiment[1]

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Abstract

It is shown theoretically that the main regularities of spontaneous non-stationary and stationary nucleation on the surface and in the volume of glass are the same. Kinetics of surface nucleation are studied in detail as a function of temperature for the polished surface of cordierite glass. Nucleation occurs mainly on surface defects but spontaneous nucleation on a "perfect" surface takes place simultaneously. The high surface nucleation rate and the high temperature of its maximum $T_m (T_m > T_g)$ is caused mainly by the decrease of the energy barrier Φ^* for the critical nucleus.

Keywords: Cordierite glass; Crystal nucleation kinetics; Non-stationary nucleation; Stationary nucleation

1. Introduction

Glass crystallization begins usually with the surface. The nature and the kinetics of surface nucleation are among the most involved and challenging questions in this field. Surface nucleation is associated directly with the structure of surface layer which in its turn is related to the bulk structure, to the mode of the surface preparation, to the effect of surroundings, and so on. All these factors make the study of surface nucleation fairly complicated. Although one of the first detailed papers devoted to this problem came out in 1927 [1], our knowledge is quite inadequate, in terms of both experimental data and theory. Quantitative research on the surface nucleation rate is very sparse and

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[1] Dedicated to Professor Hiroshi Suga.

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most has been performed only recently. A comprehensive review of the papers published up to 1988 can be found in Ref. [2].

Here we are going to present our effort to give a general theoretical description of surface nucleation kinetics for glass on the basis of primary principles and also correlation of experimental results with theory.

2. Theory

The theory can be built analogously to that for volume crystal nucleation [3]. First spontaneous crystal nucleation on the flat homogeneous glass surface will be considered. The glass and crystals have the same composition. Three cases are possible here.

(1) Surface crystals do not extend over the glass surface (Fig. 1a).
(2) crystals extend partially over the glass surface (Fig. 1b).
(3) crystals extend fully over the glass surface (Fig. 1c).

Crystal growth over the glass surface is possible (Figs. 1b and 1c) if the glass structural units (or their parts, ions, atomic groups) can migrate on the glass surface.

We suppose that structural units have stoichiometric atomic composition but the unit is not a molecule; in general it is a building unit.

We shall consider below case (1) (Fig. 1a). Let us introduce the distribution function $f(g_1, \ldots, g_G, p, T, t)$ of the number of crystals which have G faces, where $g_i (i = 1, 2, \ldots, G)$ is the structural unit number on face i, p is the pressure, T is the temperature, t is the time. The shape and the size of the crystal are given if the numbers g_i are given. One can write for f the following kinetic equation for the change ∂f of f because of the

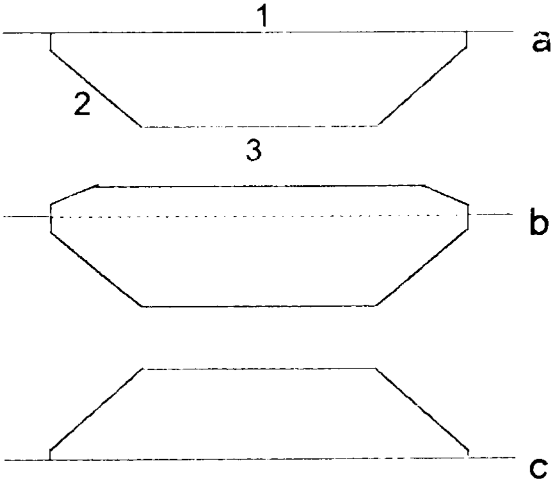

Fig. 1. Possible dispositions of surface crystal nuclei. The nucleus situated under (a), partially under (b), and on (c) the glass surface. *1, 2, 3*—the nucleus faces.

accidental joining and detaching of structural units for faces i per time interval ∂t:

$$\frac{\partial f}{\partial t}=\sum_{i=1}^{G}[I_i(g_i,t)-I_i(g_i+1,t)] \tag{1}$$

$$I_i(g_i)=f(g_i-1)\beta_i(g_i-1)s_i(g_i-1)-f(g_i)\alpha_i(g_i)s_i(g_i) \tag{2}$$

where $\beta_i(g_i)$ is the probability of transition of the structural unit from melt (glass) to crystal through face i per time unit and per surface unit, $\alpha_i(g_i)$ is the similar probability for inverse transition from crystal to melt, s_i is the area of face i; I_i, β_i and α_i depend on all $g_i (i=1,2,\ldots,G)$ but in (2) only variable g_i is written. The complicated system of Eq. (1) can be simplified. In the thermodynamic equilibrium state at $T>T_m$ (T_m is the melting point) the following equality $I_i(g_i)=I_{ie}(g_i)=0$ results from the principle of a detailed thermodynamic equilibrium. This equality gives the relationship

$$\alpha_i(g_i)=\beta_i(g_i-1)\frac{s_i(g_i-1)}{s_i(g_i)}\frac{N(g_i-1)}{N(g_i)},\quad N(g_i)\equiv f_e(g_i) \tag{3}$$

One can suppose that Eq. (3) holds at $T<T_m$ and is valid for non-equilibrium states. We assume that β_i for the external face $i=1$ of the crystal on the interface is equal to zero. Using Eq. (3) one can write

$$I_i(g_i)=N(g_i-1)\beta_i(g_i-1)s_i(g_i-1)\left[\frac{f(g_i-1)}{N(g_i-1)}-\frac{f(g_i)}{N(g_i)}\right] \tag{4}$$

Considering $I_i(g_i)$, $f(g_i)$ as continuous functions of g_i at high enough magnitudes of variables g_i we can substitute the finite differences by differentials. Then we have

$$I_i(g_i)=-N(g_i-1)\beta_i(g_i-1)s_i(g_i-1)\frac{\partial}{\partial g_i}\left(\frac{f(g_i)}{N(g_i)}\right)_{g_i-1}\mathrm{d}g_i,\quad \mathrm{d}g_i=1 \tag{5}$$

$$\frac{\partial f}{\partial t}=\sum_{i=1}^{G}\frac{\partial}{\partial g_i}\beta_i(g_i)N(g_i)s_i(g_i)\frac{\partial}{\partial g_i}\left(\frac{f(g_i)}{N(g_i)}\right) \tag{6}$$

Eq. (6) can be considered as a generalisation of Zeldovich equation [4] for vapour–liquid, liquid–vapour phase transformations. It is necessary to know the values $\beta_i(g_i)$ and $N(g_i)$ for solution of Eq. (6). It is natural to suppose that at high magnitudes of g_i the values β_i are independent of numbers $g_k (k\neq i)$. One can believe that the following formula holds for β_i

$$\beta_i=\frac{1}{\bar{l}^2\tau_i},\quad \tau_i=\tau_{\mathrm{oi}}\exp\left(\frac{\Phi_{\mathrm{ai}}}{kT}\right), \tag{7}$$

where τ_i is the mean time of the expectation of the structural unit transition from the melt to the crystal nucleus on the nucleus–melt interface for face i; $\bar{l}$ is the mean size of the structural unit. Φ_{ai} is the activation free energy of this transition, τ_{oi} is the value of the order of the atomic oscillation period in switching chemical bonds. The value Φ_{ai} is near to the activation free energy Φ_η of the melt viscosity because similar switchings of the chemical bonds are needed for the viscous flow [5] and for structural rearrangements at crystal nucleation.

Let us find the equilibrium value $f_e(g_1, g_2, \ldots, g_G) = N(g_1, g_2, \ldots, g_G)(f_e(g_i) = N(g_i))$. We can consider the nucleus as a polymeric molecule having $g_1, g_2, \ldots, g_G$ atoms on its faces and containing $g = g(g_1, g_2, \ldots, g_G)$ atoms. The total number g of structural units is a function of numbers g_i which determine the shape and the volume of the nucleus. For simplicity we shall consider below that all nuclei have the same shape. Under such a condition we can write

$$s_i = \xi_i s, \quad s = \sum_{i=1}^{G} s_i, \quad g_i = \frac{s_i}{\bar{l}^2}, \quad s = \lambda_s g^{2/3}, \quad g = \frac{v}{\bar{l}^3} \tag{8}$$

where $\bar{l}^3$ is the volume per one structural unit; $\bar{l}$ is the mean size of the structural unit; v is the nucleus volume, s is the nucleus surface; ξ_i are parameters which determine the crystal shape; λ_s is the coefficient of the nucleus shape. According to Eq. (8), all values can be considered as functions of one variable; g is the total number of structural units in the nucleus. The equilibrium numbers $N(g_1, g_2, \ldots, g_G) = N(g)$ are only functions of g.

We shall deduce below the formulae for equilibrium nuclei numbers $N_s(g)$ on the glass surface and in the melt (glass) volume $N_v(g)$. The free energy of the system $\Phi(N_1, \ldots, N_s(g), \ldots, N_v(g), \ldots; p, T)$ at a given pressure p and temperature T is a function of N_1, the number of monomeric structural units in the melt, and of $\cdots N_s(g), N_v(g) \cdots$, the numbers of surface nuclei $N_s(g)$ and volume nuclei $N_v(g)$ containing g structural units ($g \geq 2$). In the equilibrium state Φ achieves a minimum value, i.e.

$$\delta\Phi = \frac{\partial\Phi}{\partial N_1}\delta N_1 + \sum_{g \geq 2}\left[\frac{\partial\Phi}{\partial N_s(g)}\delta N_s(g) + \frac{\partial\Phi}{\partial N_v(g)}\delta N_v(g)\right] = 0 \tag{9}$$

where δN_1, $\delta N_s(g)$, $\delta N_v(g)$ are the arbitrary variations of N_1, $N_s(g)$, $N_v(g)$ which obey the condition of conservation of the total number N_o of structural units in the system

$$\begin{aligned} N_o &= N_1 + \sum_{g \geq 2} g[N_s(g) + N_v(g)] = \text{const} \\ \delta N_o &= \delta N_1 + \sum_{g \geq 2} g[\delta N_s(g) + \delta N_v(g)] = 0 \end{aligned} \tag{10}$$

Taking the arbitrariness of δN_s, δN_v into account we obtain from Eqs. (9) and (10)

$$g\mu_1 = \mu_s^c(g), \quad g\mu_1 = \mu_v^c(g), \quad \mu_1 = \frac{\partial\Phi}{\partial N_1}, \quad \mu_s^c(g) = \frac{\partial\Phi}{\partial N_s(g)}, \quad \mu_v^c = \frac{\partial\Phi}{\partial N_v(g)} \tag{11}$$

where μ_1, $\mu_s^c(g)$, $\mu_v^c(g)$ are the chemical potentials of the structural unit in the melt (μ_1) and of the crystal nuclei on the surface ($\mu_s^c(g)$) and in the volume ($\mu_v^c(g)$).

We can write the following relationships

$$\begin{aligned} &\mu_1 = \mu_{1o} + kT\ln(\gamma_1 c_1), \quad \mu_s^c(g) = \mu_o^c(g) + kT\ln[\gamma_s(g)c_s(g)], \\ &\mu_v^c(g) = \mu_o^c(g) + kT[\gamma_v(g)c_v(g)], \quad \mu_o^c(g) = g\mu_{1o}^c \end{aligned} \tag{12}$$

where μ_{1o} is the chemical potential of the structural unit in the melt when its concentration c_1 is equal to unity; μ_{1o}^c is the chemical potential of the structural unit in the crystal; $c_s(g)$ is the surface concentration of nuclei; $c_v(g)$ is the volume concentration of nuclei containing g structural units (the nuclei shape on surface and in volume of the melt can be different); $\gamma_1, \gamma_s(g), \gamma_v(g)$ are the activity coefficients. Concentrations c_1, c_s, c_v are determined by the formulae

$$c_1 = \frac{N_{1v} + N_{1s}}{F_v + F_s}, \quad c_v(g) = \frac{N_v(g)}{F_v}, \quad c_s(g) = \frac{N_s(g)}{F_s},$$
$$F_v = N_{1v} + \sum_{g \geq 2} N_v(g), \quad F_s = N_{1s} + \sum_{g \geq 2} N_s(g) \tag{13}$$

where N_{1s} and N_{1v} are the numbers of structural units on the melt surface and in the melt volume; F_s is the total number of structural units on the melt surface; F_v is the same in the melt volume.

According to Eq. (12), the interface energy is included in the activity coefficients $\gamma_s(g)$, $\gamma_v(g)$

$$kT \ln \gamma_s(g) = \sum_{i=1}^{G} \sigma_i^s s_i^s(g), \quad kT \ln \gamma_v(g) = \sum_{i=1}^{G} \sigma_i^v s_i^v(g), \tag{14}$$

where σ_i^s, σ_i^v are the surface free energies for faces s_i^s, s_i^v. The formation of the external face ($i = 1$) of a nucleus gives rise to the following change in the system free energy

$$\Delta\sigma = \sigma_{1c} - \sigma_{1g} = \sigma_c - \sigma_g \tag{15}$$

where $\sigma_{1g} \equiv \sigma_g$ is the interface energy of the melt (glass)—external medium (atmosphere) interface; $\sigma_{1c} \equiv \sigma_c$ is the free energy of the crystal ($i = 1$)—the external medium interface.

The formula for $\mu_s^c(g)$, Eq. (12), is written for the surface layer of the melt. The thickness of this layer is equal to the mean size of the structural unit $\bar{l}$. We suppose that the external face of every surface nucleus belongs to this layer. The centre of the external face of a nucleus can be placed at any surface structural unit. Therefore, for the surface combinatoric entropy S we can write the usual formula

$$S = k \ln W_s, \quad W_s = \frac{F_s!}{N_{1s}! N_s(2)! \cdots N_s(g)!} \tag{16}$$

We consider in Eq. (16) that the surface nucleus cannot plunge into the volume without a change of its energy but its energy does not depend on its site on the melt surface.

According to Eqs. (11) and (12) we have

$$\mu_s^c(g) = \mu_v^c(g), \quad \frac{c_s(g)}{c_v(g)} = \frac{\gamma_v(g)}{\gamma_s(g)} \tag{17}$$

By introducing $\mu_s(g)$, $\mu_v(g)$ from Eq. (12) into Eq. (11) we obtain

$$\frac{\gamma_s(g)c_s(g)}{(\gamma_1 c_1)^g} = \exp\left[\frac{g(\mu_{1o} - \mu_{1o}^c)}{kT}\right], \quad \frac{\gamma_v(g)c_v(g)}{(\gamma_1 c_1)^g} = \exp\left[\frac{g(\mu_{1o} - \mu_{1o}^c)}{kT}\right] \tag{18}$$

The total numbers of nuclei $\sum_{g \geq 2} N_s(g), \sum_{g \geq 2} N_v(g)$ are much less than N_{1s} and N_{1v} in Eq. (13), respectively. Hence $F_s \approx N_{1s}$, $F_v \approx N_{1v}, c_1 \approx 1, \gamma_1 \approx 1$, $(\gamma_1 c_1)^g \approx 1$ in Eq. (18).

Besides we have

$$F_{\mathrm{s}} \approx N_{1\mathrm{s}} \approx N_{\mathrm{os}} = \frac{1}{l^2}, \quad F_{\mathrm{v}} \approx N_{1\mathrm{v}} \approx N_{\mathrm{ov}} \approx N_{\mathrm{o}} = \frac{1}{l^3}, \quad N_{\mathrm{so}} = \bar{l} N_{\mathrm{o}} \tag{19}$$

where N_{os} is the total number of structural units on the melt surface. Thus taking Eqs. (13) and (19) into account we obtain from Eqs. (18) and (14)

$$N_{\mathrm{s}}(g) = N_{\mathrm{os}} \exp\left[-\frac{-g(\mu_{1\mathrm{o}} - \mu_{1\mathrm{o}}^{\mathrm{c}}) + \sum\limits_{i} \sigma_i^{\mathrm{s}} s_i^{\mathrm{s}}(g)}{kT} \right] \tag{20}$$

$$N_{\mathrm{v}}(g) = N_{\mathrm{o}} \exp\left[-\frac{-g(\mu_{1\mathrm{o}} - \mu_{1\mathrm{o}}^{\mathrm{c}}) + \sum\limits_{i} \sigma_i^{\mathrm{v}} s_i^{\mathrm{v}}(g)}{kT} \right] \tag{21}$$

Eqs. (20) and (21) were deduced for the thermodynamic equilibrium which takes place at $T > T_{\mathrm{m}}$. These formulae are approximately valid at $T < T_{\mathrm{m}}$ for $g < g^*$, g^* being the critical nucleus size (see below) because subcritical nuclei ($g < g^*$) appear and disappear just at $T > T_{\mathrm{m}}$, and very seldom do they achieve the size $g \geq g^*$ at $T < T_{\mathrm{m}}$.

Under the conditions of Eq. (8) we can write Eqs. (1), (2), (5) and (6) in the following way

$$\frac{\partial f(g,t)}{\partial t} = \sum_{i=1}^{G} [I_i(g,t) - I_i(g+1,t)] = I(g,t) - I(g+1,t) \tag{22}$$

$$I_i(g) = f(g-1)\beta_i(g-1)s_i(g-1) - f(g)\alpha_i(g)s_i(g) \tag{23}$$

$$I(g,t) = \sum_{i=1}^{G} I_i(g,t) = f(g-1)\bar{\beta}(g-1)s(g-1) - f(g)\bar{\alpha}(g)s(g) \tag{24}$$

$$\bar{\beta}(g) = \frac{1}{s(g)} \sum_{i=1}^{G} \beta_i(g)s_i(g), \quad \bar{\alpha}(g) = \frac{1}{s(g)} \sum_{i=1}^{G} \alpha_i(g)s_i(g), \quad s(g) = \sum_{i=1}^{G} s_i(g) \tag{25}$$

$$\bar{\alpha}(g) = \bar{\beta}(g-1)\frac{s(g-1)}{s(g)}\frac{N(g-1)}{N(g)}, \quad I(g) \approx -N(g-1)\bar{\beta}(g-1)s(g-1)\frac{\partial}{\partial g}\left(\frac{f(g)}{N(g)}\right) \tag{26}$$

$$\frac{\partial f}{\partial t} = \frac{\partial}{\partial g}\left[\bar{\beta}(g)N(g)s(g)\frac{\partial}{\partial g}\left(\frac{f(g)}{N(g)}\right)\right] \tag{27}$$

For surface nucleation: $N(g) = N_{\mathrm{s}}(g)$ (Eq. (20)), for volume nucleation: $N(g) = N_{\mathrm{v}}(g)$ (Eq. (21)). For surface nucleation it is convenient to exclude the item s_1 in the sum $s = \sum_{i=1}^{G} s_i$ (Eq. (25)) because $\beta_1 = 0$ for the external face $i = 1$. Eq. (27) is quite similar to the Zeldovich–Frenkel equation [4,6].

Let us consider the simplest model of the isotropic surface nucleus having two faces (Fig. 2a); $i = 1$ is the nucleus—the surrounding medium interface; $i = 2$ is the nucleus—the melt (glass) interface. The nucleus shape is determined by the force equilibrium

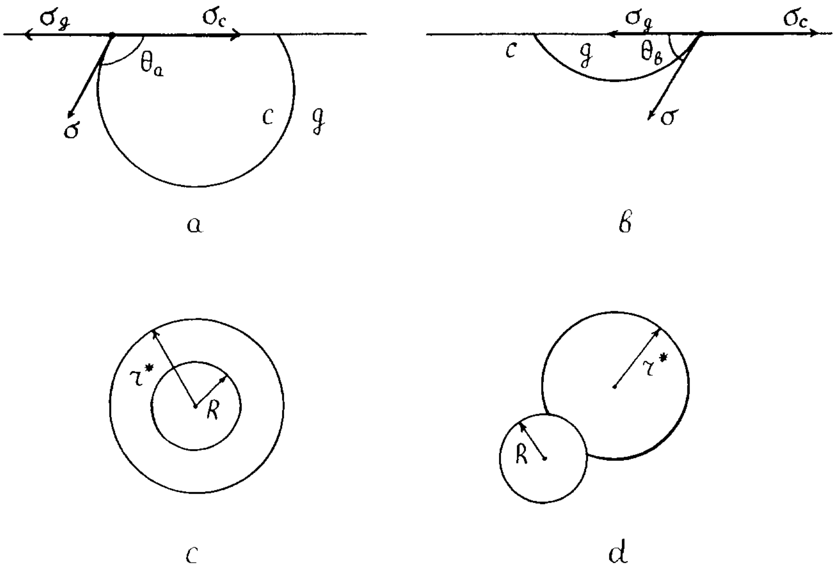

Fig. 2. Isotropic equilibrium surface nuclei: a—crystal nucleus, g—glass, c—crystal, θ—wetting angle, $\sigma_g - \sigma \cos\theta_a = \sigma_c$; b—liquid nucleus, $\sigma_g + \sigma\cos\theta_b = \sigma_c$, $\theta_b = \pi - \theta_a$; c—critical nucleus r^* on particle $R < r^*(\sigma_c < \sigma_g)$; d-critical nucleus r^* on particle $R < r^*(\sigma_c > \sigma_g)$.

(Fig. 2a) $\sigma\cos\theta + \sigma_c = \sigma_g$, where σ is the surface free energy of the crystal–melt (glass) interface and θ is the wettability angle:

$$\cos\theta = \frac{\sigma_g - \sigma_c}{\sigma} = -\frac{\Delta\sigma}{\sigma} < 0, \quad \theta > \frac{\pi}{2} \tag{28}$$

$\Delta\sigma = \sigma_c - \sigma_g > 0$ if the surrounding medium is the atmosphere or the vapour of the melt.

The nucleus shape presents a segment of a sphere having radius r, while the segment height is $h = r(1 - \cos\theta)$, $h > r$ at $\Delta\sigma > 0$ (Fig. 2a). The nucleus volume is

$$v_s = \frac{4\pi r^3 \phi(\theta)}{3}, \quad \phi(\theta) = \frac{(2 - 3\cos\theta + \cos^3\theta)}{4} \tag{29}$$

The increment of the free energy of the system is (see Eq. (20))

$$\Delta\Phi(g) = -g(\mu_{1o} - \mu_{1o}^{c}) + \sum_{i=1}^{G} \sigma_i s_i = -v_s \Delta\varphi + s_i \Delta\sigma + s_2\sigma, \quad \Delta\varphi = \frac{\mu_{1o} - \mu_{1o}^{c}}{l^3} \tag{30}$$

Using the formulae for $s_1 = \pi r^2 \sin^2\theta$ and $s_2 = 2\pi r h$ we obtain [3]

$$\Delta\Phi(g) = \Delta\Phi(r,\theta) = \Delta\Phi_v(r)\phi(\theta), \quad \Phi_v(r) = -\frac{4}{3}\pi r^3 \Delta\varphi + 4\pi r^2 \sigma \tag{31}$$

where $\Delta\Phi_v(r)$ is the free energy increment due to the nucleus appearance in the volume of the melt. According to Eqs. (28) and (31) volume nucleation is energetically preferable compared with surface nucleation, if $\Delta\sigma > \sigma$ and conversely, if $\Delta\sigma < \sigma$. The radius $r = r^*$ corresponding to the critical nucleus can be found from the condition of a maximum value of $\Delta\Phi(r, \theta)$

$$\left.\frac{\mathrm{d}\Delta\Phi}{\mathrm{d}r}\right|_{r=r^*} = 0, \quad r^* = \frac{2\sigma}{\Delta\varphi}, \quad \Delta\Phi^* = \Delta\Phi_v^*\,\phi(\theta), \quad \Delta\Phi_v^* = \frac{16\pi\sigma^3}{3(\Delta\varphi)^2} \tag{32}$$

The following formula is valid for $\Delta\varphi(T)$ at small $|T - T_m|$

$$\Delta\varphi = q\left(1 - \frac{T}{T_m}\right), \quad q = -\left(\frac{\partial\Delta\varphi}{\partial T}\right)_{T_m} T_m = S_m T_m \tag{33}$$

where $S_m = -(\partial\Delta\varphi/\partial T)_{T_m}$ is the entropy of melting and q is the heat of melting.

We are coming now to the analysis of Eq. (27) for the model discussed. This equation can approximately be solved analogously to that in Ref. [4]. We obtain the approximate formula for stationary ($\partial f/\partial t = 0$) nucleation rate I_{st}

$$I_{st} = N_s(g^*)D(g^*)\left[\frac{1}{2\pi kT}\left(-\left.\frac{\partial^2\Delta\Phi}{\partial g^2}\right|_{g=g^*}\right)\right]^{1/2}, \quad g^* = \frac{v_s^*}{l^3} \tag{34}$$

$$D(g^*) = \beta_2 s_2(g^*), \quad N_s(g^*) = N_{os}\exp\left(-\frac{\Delta\Phi(g^*)}{kT}\right), \quad s_2(g^*) = 2\pi r^{*2}(1 - \cos\theta), \tag{35}$$

where $\Delta\Phi(g)$ is determined by Eq. (30) or (31).

The period of non-stationary nucleation takes place before the establishment of stationary nucleation. There are two approximate formulae proposed by Zeldovich [4], Eq. (36), and Kashchiev [7], Eq. (37), for volume nucleation

$$I_Z(t) = I_{st}\exp(-\tau/t), \tag{36}$$

$$I_K(t) = I_{st}\left[1 + 2\sum_{n=1}^{\infty}(-1)^n\exp(-n^2t/\tau)\right], \tag{37}$$

where τ is the characteristic time of non-stationary nucleation. Similar formulae can evidently be obtained for surface nucleation.

We see that the main peculiarities of volume nucleation also occur for surface nucleation. The temperature-dependence of I_{st}, Eq. (34), is determined mainly by the exponent $\exp[-(\Phi_a + \Delta\Phi^*)/kT]$, where Φ_a is the activation free energy for face 2 ($\Phi_a = \Phi_{a2}$). The exponent has a maximum at the temperature T_{max}

$$T_{max} = \frac{T_m}{3}\left.\frac{1 + H_a/\Delta\Phi^*}{1 + H_a/3\Delta\Phi^*}\right|_{T = T_{max}}, \quad H_a = \Phi_a + TS_a, \quad S_a = -\frac{\partial\Phi_2}{\partial T}, \tag{38}$$

where Eq. (33) was used for $\Delta\varphi(T)$; H_a and S_a can be called the activation enthalpy and the activation entropy of structural rearrangement, respectively. Eq. (34) for $I_{st} = I_{s,st}$ is different from that for volume nucleation $I_{\mathrm{v,st}}$ by the value $N_{\mathrm{s}}(g^*)$ which is calculated per surface unit but not per volume unit. $N_{\mathrm{s}}(g)$ (Eq. (20)) is related to the surface layer having the volume $S\bar{l}$, where S is the surface area. Consequently, we must multiply the volume crystal nucleation rate I_{v} by $\bar{l}$ to compare I_{v} with the surface nucleation rate I_{s}. The multiplier $N_{\mathrm{o}} = 1/\bar{l}^3$ transforms to $N_{\mathrm{os}} = N_{\mathrm{o}}\bar{l} = 1/\bar{l}^2$ (Eq. (19)). So the surface nucleation rate can be greater than the volume nucleation rate for the following reasons.

(1) The values of the multiplier $\phi(\theta)$ are small ($\phi(\theta) < 1$ (Eq. (29))).

(2) Surface layers can be disordered and strained over a distance of the order of the critical nucleus size. Therefore the activation free energy $\Phi_{\mathrm{a2}} = \Phi_{\mathrm{a}} \approx \Phi_{\eta}$ is decreased, the surface viscosity (Φ_{η}) of the melt or of the glass is also decreased. Besides the chemical composition of the glass surface layers can be changed by interaction with the surrounding atmosphere. This can also reduce the value of $\Delta\Phi(g) + \Phi_{\mathrm{a}}$.

The theory of crystal nucleation on the melt (glass) surface can be applied to the inverse process, i.e. to melt nucleation on the crystal surface during the melting process. In the latter case ($T > T_{\mathrm{m}}$) we have from Fig. 2b

$$\cos\theta = \frac{\sigma_{\mathrm{c}} - \sigma_{\mathrm{g}}}{\sigma} = \frac{\Delta\sigma}{\sigma} > 0, \quad \theta < \frac{\pi}{2} \tag{39}$$

One observes experimentally the origin of the melt layer on various crystals, for example on the quartz surface at very small values $T - T_{\mathrm{m}} > 0$. This indicates that $\Delta\Phi^* = \Delta\Phi_{\mathrm{v}}^*\phi(\theta) \to 0$, $\cos\theta \to 1$. If we compare the results from Eqs. (39) and (28), we shall see that they complement one another; the sum of the nuclei volumes is the volume of a sphere (Fig. 2a, b). When $\Delta\Phi^*$ for the melt nucleus tends to zero, $\Delta\Phi^*$ for the crystal nucleus tends to $\Delta\Phi_{\mathrm{v}}^*$. In Ref. [8] the author found that for melt nucleation the inequality $\sigma_{\mathrm{c}} > \sigma_{\mathrm{g}} + \sigma$ takes place whereas for crystal nucleation $\sigma_{\mathrm{c}} < \sigma_{\mathrm{g}} + \sigma$. This contradiction is absent in our consideration where the inequality $\sigma_{\mathrm{c}} < \sigma_{\mathrm{g}} + \sigma$ takes place in both cases (Eqs. (28) and (38)) but $\cos\theta$ has opposite signs.

Let us emphasize that the value $\Delta\Phi^*$ can be increased by elastic strains arising from the difference between the molar volumes glass and of crystal. The elastic energy decreases if the nucleus centre is placed on the glass surface [9]. This promotes surface crystal nucleation. But it is necessary to take into account the possibility of strain relaxation during the appearance of a critical nucleus. It is probable that the relaxation process requires a smaller number of chemical bond switchings than nucleus formation and the main part of elastic strains can relax more quickly than the nucleus will be formed.

We have considered above nucleation on the flat surface. The theory can also be applied to a curved or distorted surface. Such a surface can be generated by the particles of other phases or by bubbles in the glass volume. In this case the interface surface S is equal to the sum $\sum_i S_i$ of interfaces S_i of the particles of a given chemical nature. The nuclei appear on the surfaces S_i and grow into the glass volume.

Let us consider the simplest model of N_R spherical particles with radius R, then

$$S=\sum_i S_i=N_R 4\pi R^2 \tag{40}$$

The particles R play the role of the external medium. The crystal nucleation rate on the surface, Eq. (40), is given by formulae of the type Eq. (20) and Eqs. (34)–(37). Two limiting cases are possible here:

(1) Particles R are great, $R \gg r^*(T)$, where $r^*(T)$ is the critical radius of a nucleus. The interface is practically flat at the site where the nucleus arises. Consequently Eqs. (28), (31), (32) and (39) are valid. It is pertinent to emphasize here that σ_c can be less than σ_g if the external medium is not a gaseous medium. The relationship $\sigma_c < \sigma_g$ is true if the crystalline structure of a particle (parameters of the crystal lattice cell) is near to that of a nucleus. In this case $\cos\theta=(\sigma_g-\sigma_c)/\sigma>0$, the nucleus shape is expressed by Fig. 2b ($\theta<\pi/2$).

(2) Particles R are very small, $R<r^*(T)$ (this case is discussed in Refs. [10] and [11]). The crystalline nucleus can fully cover the particle R (Fig. 2c). Then we have

$$\begin{aligned}\Delta\Phi^* &= -\frac{4\pi}{3}(r^{*3}-R^3)\Delta\varphi+4\pi R^2(\sigma_c-\sigma_g)+4\pi r^{*2}\sigma\\ &=\Delta\Phi^*_v+\frac{4\pi R^3}{3}\Delta\varphi+4\pi R^2(\sigma_c-\sigma_g),\quad \Delta\Phi^*_v=-\frac{4\pi r^{*3}}{3}\Delta\varphi+4\pi r^{*2}\sigma.\end{aligned} \tag{41}$$

In order that the particles R could be active sites for nucleation, the following inequalities must be fulfilled:

$$\Delta\Phi^*<\Delta\Phi^*_v,\quad \sigma_c<\sigma_g,\quad R<\frac{3(\sigma_g-\sigma_c)}{\Delta\varphi}. \tag{42}$$

At $\sigma_c>\sigma_g$ small particles can be active sites for nucleation in the manner shown in Fig. 2d when a part of the surface of the particle R is an interface between this particle and the critical nucleus (similar to Fig. 2a).

It is also necessary to take into account that on every interface the activation barrier Φ_a for structural rearrangements can be lower. This leads to an increase of the interface crystal nucleation rate I.

The model (Eq. (40)) can be used to illustrate catalyzed volume nucleation due to surface crystal nucleation on N_R particles in the glass volume V. The number $\mathrm{d}N$ of particles R on which any nucleus of the matrix crystalline phase has arisen during the time interval from t to $t+\mathrm{d}t$ satisfies the equation

$$\mathrm{d}N=I(t)4\pi R^2(N_R-N(t))\mathrm{d}t \tag{43}$$

$$N(t)=N_R\left\{1-\exp\left[-\int_0^t \mathrm{I}(t')4\pi R^2\mathrm{d}t'\right]\right\},\ \frac{\mathrm{d}N}{\mathrm{d}t}=N_R 4\pi R^2 I(t)\exp\left[-\int_0^t I(t')4\pi R^2\mathrm{d}t'\right]$$

If we accept that the surface crystal nucleation rate $I(t)$ is given by Eq. (36) we have in Eq. (43) (see also Ref. [12])

$$\int_0^t I(t')\mathrm{d}t' = I_{\mathrm{st}}\left[t\exp\left(-\frac{\tau}{t}\right) + \tau\int_{\infty}^{\tau/t}\frac{\mathrm{e}^{-x}}{x}\mathrm{d}x\right] = I_{\mathrm{st}}\left[t\exp\left(-\frac{\tau}{t}\right) + \tau Ei\left(-\frac{\tau}{t}\right)\right] \tag{44}$$

where Ei is the integral exponent.

Instead of the value $I(t)4\pi R^2$ we can introduce a concept about the activity of nucleation site $\alpha(t)$ (the probability of crystal nucleation on a single active site (AS) per unit time). The activity $\alpha(t)$ is proportional to the surface s_i ($4\pi R^2$ in Eqs. (43) and (39)) of the active site and it is greater, the greater the degree of structural strains and distortions which decrease the barriers to structural rearrangements. The substitution of Eq. (44) into Eq. (43) gives the following expression

$$N(t) = N_R\left\{1 - \exp\left[-\alpha_{\mathrm{st}}t\left[\exp\left(-\frac{\tau}{t}\right) + \frac{\tau}{t}Ei\left(-\frac{\tau}{t}\right)\right]\right]\right\}, \tag{45}$$

where α_{st} is the stationary value of $\alpha(t)$.

Eq. (43) can be applied to heterogeneous surface nucleation produced by various surface active sites. Such active sites can be caused, for example, by small crystalline or amorphous particles on the glass surface or in surface cracks. These particles can react with the glass surface at high temperature and change the local chemical glass composition inducing the appearance of new small crystalline particles of new phases.

3. Experimental

To date the nucleation rate on the glass surface remains scantily explored [13]. Up to now the kinetics of surface crystal nucleation has been studied in most detail for cordierite glass ($2\mathrm{MgO}\cdot 2\mathrm{Al_2O_3}\cdot 5\mathrm{SiO_2}$). Crystals of μ-cordierite and petalite-like X-phase arise on the cordierite glass surface polished by $\mathrm{CeO_2}$. The kinetic dependences of the nucleated crystal number $N(t)$ were obtained by the "development" method in the case of X-phase crystals [14–16] and by the method based on the analysis of crystal size distribution resulting from simultaneous crystal nucleation and crystal growth for μ-cordierite crystals [17].

The sigmoid form and the saturation of kinetic curves $N(t)$ (Figs. 3a and 3b, curve 1) are typical of non-steady nucleation at the limited number of surface AS. However the nature of the AS is different: the level of saturation (N_{sx}) of the X-phase crystal number decreases rapidly with temperature owing to thermodeactivation of $\mathrm{AS_x}$ but the one of μ-cordierite crystals ($N_{\mathrm{s}\mu}$) does not depend on temperature and is constant within the reproducibility of the surface state (Fig. 4). The appearance of $\mathrm{AS_x}$ results probably from polishing by $\mathrm{CeO_2}$. When the surface is polished

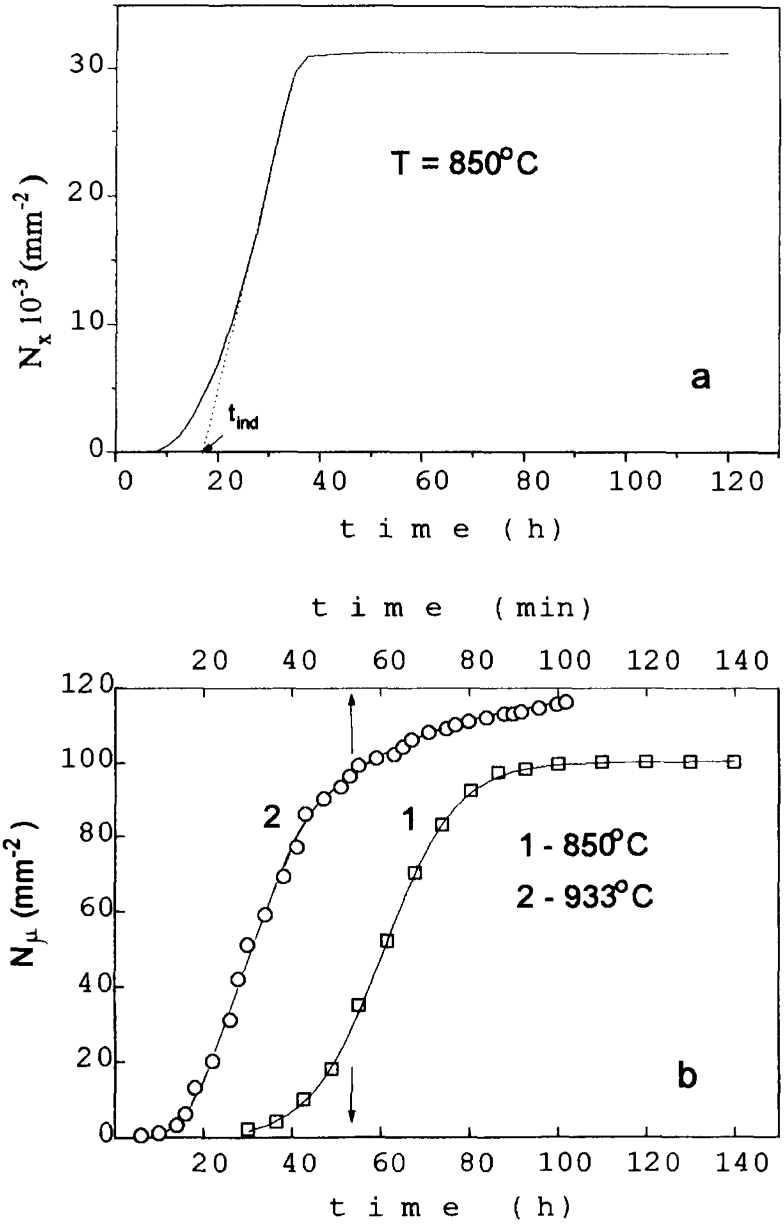

Fig. 3. Kinetic dependences $N(t)$ for surface-nucleated crystals of (a) X-phase and (b) μ-cordierite.

by Cr_2O_3 only μ-cordierite crystals arise on it. It is possible that AS_x containing CeO_2 can transform or dissolve, reacting with cordierite glass at high temperatures. So its activity may decrease at a rate increasing with temperature. In the simple case, when the probability β of AS_x deactivation per unit time does not depend on time

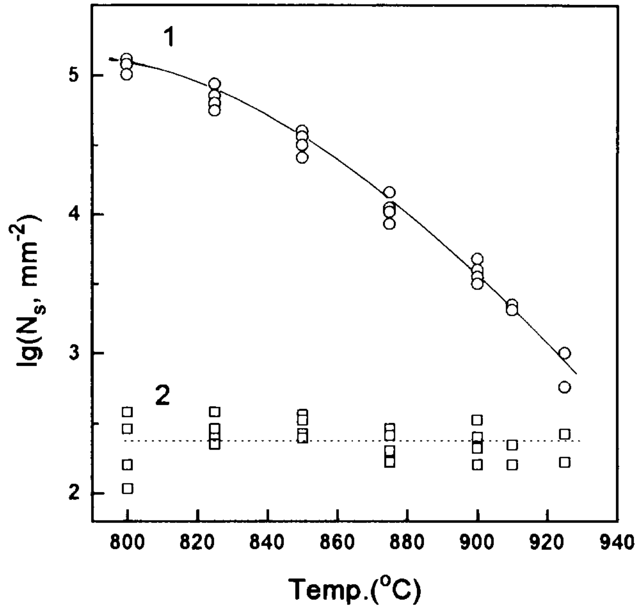

Fig. 4. Graphs of saturation crystal number density plotted against heat-treatment temperature T for (1) X-phase and (2) μ-cordierite.

and the activity of AS_x $\alpha = 0$ at $t < t_{ind}$ (see Fig. 3a) and $\alpha = \alpha_{st}$ at $t \geq t_{ind}$, the following equation was obtained [15]

$$N_x(t) = N'_0 \frac{\alpha}{\alpha + \beta}\{1 - \exp[-(\alpha + \beta)(t - t_{ind})]\}, \quad t \geq t_{ind} \tag{46}$$

$$N'_0 = N_0 \exp(-\beta t_{ind}),$$

where N_0 is the initial number of AS_x.

From the dependences $N_x(t, T)$ the nucleation rate $I_{xm} = (dN_x(t)/dt)_{max}$ was obtained and the probability of stationary nucleation on the single AS_x was calculated from Eq. (47) [15].

$$\alpha_x = \frac{I_{xm}}{N_0 \exp(-\beta t_{ind})} \tag{47}$$

Instead of saturation, at temperatures from about 870 to 990°C the kinetic dependences $N_\mu(t)$ have an inflexion after which the number of μ-cordierite crystals continues to grow linearly with a rate $I_\mu = dN_\mu/dt$ (Fig. 3b, curve 2). This part of the dependence corresponds to nucleation at the surface between the above-mentioned AS_μ. These crystals can be assumed to nucleate at the "perfect" glass surface free from defects catalysing nucleation. This assumption is not contradictory to the theory. It is possible also that we are dealing here with nucleation at the other active sites (AS'_μ). In any case there are two types of μ-cordierite crystal nucleation. A pure heterogeneous part was separated from the total kinetic curves and described with help of Eq. (45).

The values of $\alpha_\mu \equiv \alpha_{st}$ and τ were chosen to give a good fit to the experimental kinetic curves. It should be noted that to the time when crystals have nucleated at all AS_μ the activity $\alpha(t)$ does not reach its stationary value α_{st}.

The values of I, α, t_{ind} and τ for the X-phase and μ-cordierite crystals are plotted in Fig. 5 as a function of temperature. Here are also shown the values of α_μ and τ obtained in Ref. [18] by fitting Eq. (45) for μ-cordierite crystal nucleation at fractured glass surface.

According to Fig. 5 the temperatures, corresponding to the maximum nucleation rates are quite different not only for the X-phase and μ-cordierite crystals but for the μ-cordierite crystals nucleated at AS_μ and also at the "perfect" surface (or at the AS'_μ). The latter point gives also evidence for the existence of two types of μ-cordierite nucleation at the polished surface. Similar results were obtained in Ref. [19] for the nucleation rate of cristobalite crystals at the atmosphere side of the float glass (Fig. 6). The nucleation rates were calculated from the kinetic dependences $N(t)$ exhibiting an induction period followed by the linear growth of N at low temperatures and the saturation effect at higher temperatures.

As a rule, a maximum of the bulk homogeneous nucleation rate occurs near the glass transition temperature T_g [20]. At the same time the temperatures T_{max} of the surface nucleation rate maxima greatly exceed $T_g \approx T_{13} = 819°C$ (Fig. 5). So in the case of nucleation of X-phase at AS_x, of μ-cordierite at the "perfect" polished surface and at AS_μ and also at the active sites of fractured surface, the value $\Delta T = T_{max} - T_g$ is equal to 70, 130°C and exceeds 180 and 230°C, respectively. For cristobalite crystals (Fig. 6) the value of ΔT is equal to 130°C for low-temperature nucleation and is more than 330°C for another type of nucleation at higher temperatures.

One can assume that in the case of soda-lime–silica glass studied in Ref. [21] the maximum of the surface nucleation rate for $Na_2O \cdot 2CaO \cdot 3SiO_2$ crystals at the fire-polished surface is also placed at higher temperatures compared to that of the volume nucleation rate (Fig. 7). In Ref. [22] the high temperature of the maximum of $Na_2O \cdot 2SiO_2$ crystal nucleation rate at the platinum–melt interface exceeding T_g by about 150°C was reported. The high temperatures of $BaO \cdot 2SiO_2$ crystal nucleation at the crucible wall were observed in Ref. [23]. In this case the rougher wall surface was used, the higher nucleation temperatures were noted.

The high temperatures T_{max} of surface nucleation rate are most likely associated with a decrease in the energy barrier $\Delta\Phi^*$ of surface nucleation compared with that of the volume homogeneous nucleation. According to Eq. (38), T_{max} increases with $K = H_a/\Delta\ \Phi^*$ (Fig. 8). Believing that in the case of homogeneous volume nucleation $T_{max} \approx T_g$ and using the enthalpy of viscous flow activation instead of H_a, the estimates of the ratio $A = \Delta\Phi^*_s/\Delta\Phi^*_v$ needed for the experimentally observed

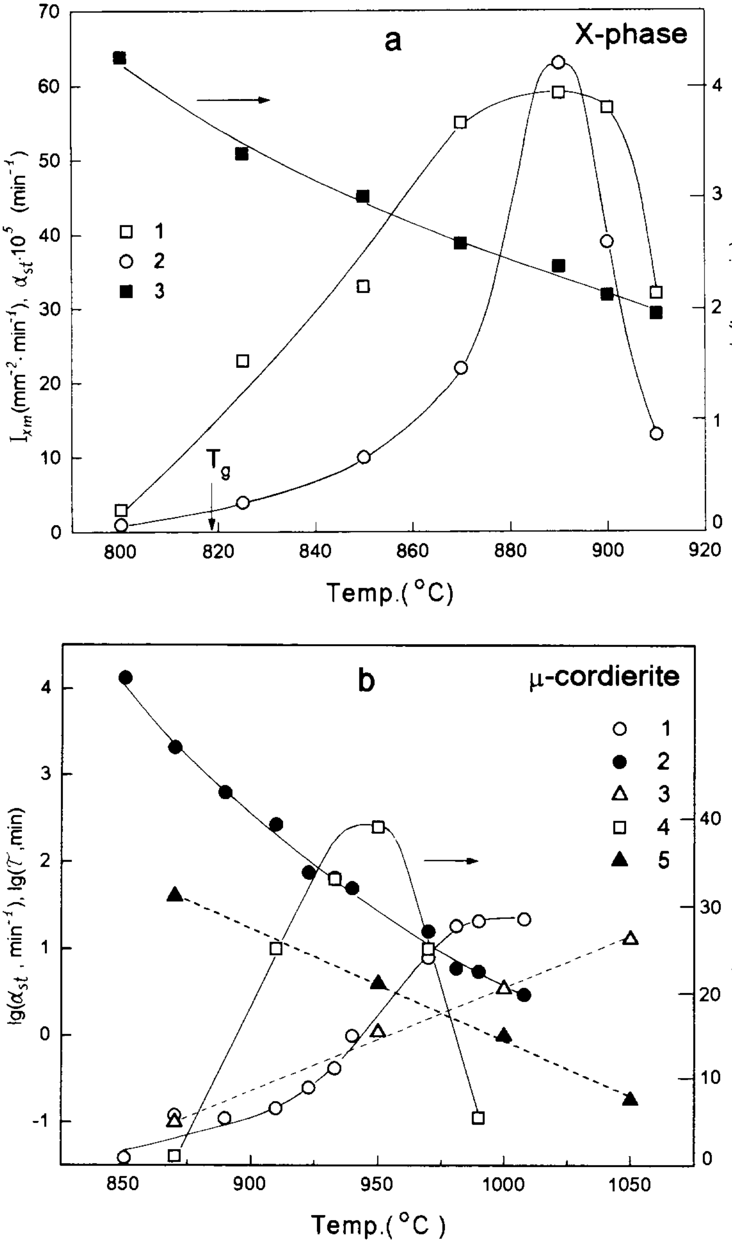

Fig. 5. Temperature-dependences of the nucleation rates and the activities of AS for crystals of X-phase (a) and μ-cordierite (b). (a) 1 — the nucleation rate I_{xm} on AS_x; 2 — the activity of AS_x; 3 — the induction time t_{ind}. (b) 1 — the activity of AS_μ; 2 — the time lag τ; 4 — the nucleation rate on a "perfect" surface (or on AS'_μ); 3, 5 — the activity and the time lag for a fractured surface [18].

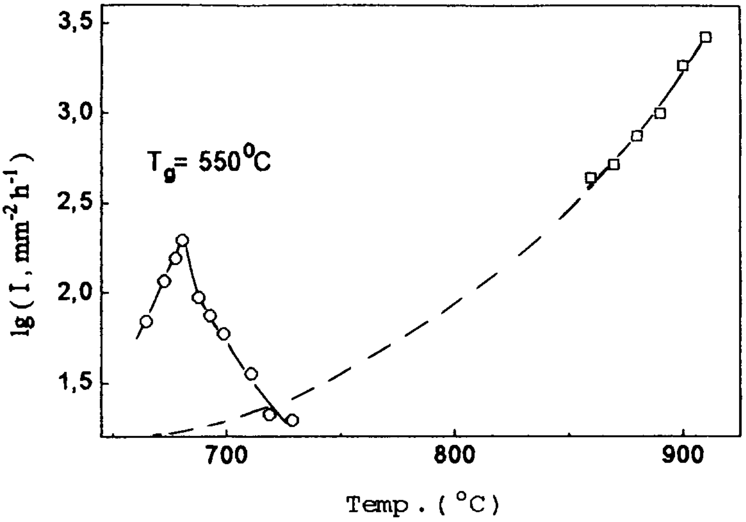

Fig. 6. The temperature-dependence of surface nucleation rates of crystobalite crystals at the atmosphere side of float glass [19].

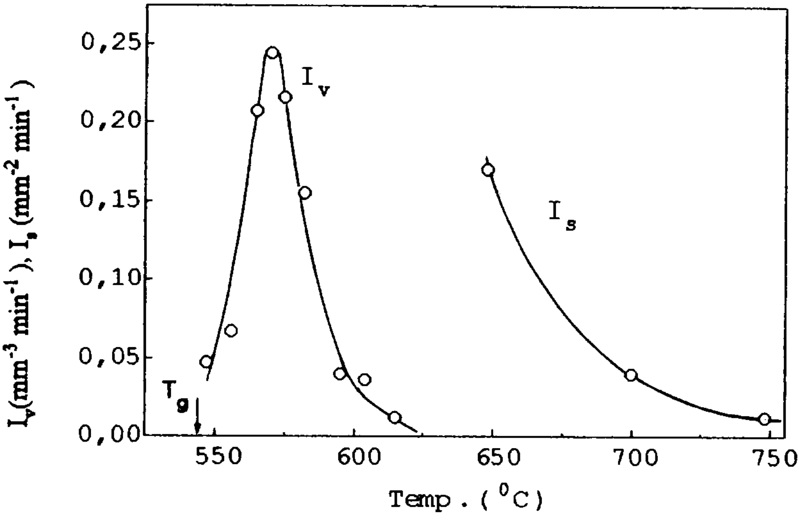

Fig. 7. The temperature dependences of nucleation rate of $Na_2O \cdot 2CaO \cdot 3SiO_2$ crystals in the volume (I_v) and at the surface (I_s) of glass of composition 21.25 Na_2O, 21.25 CaO, 57.5 SiO_2 (mol.%) [21].

shift $\Delta T = T_{max} - T_g$ were performed. At temperatures of the maxima of surface nucleation rates the value A is approximately equal to 0.3, 0.1 and 0.02 for nucleation of the X-phase crystals on AS_x, of μ-cordierite crystals on the "perfect" glass surface and on AS_μ, respectively.

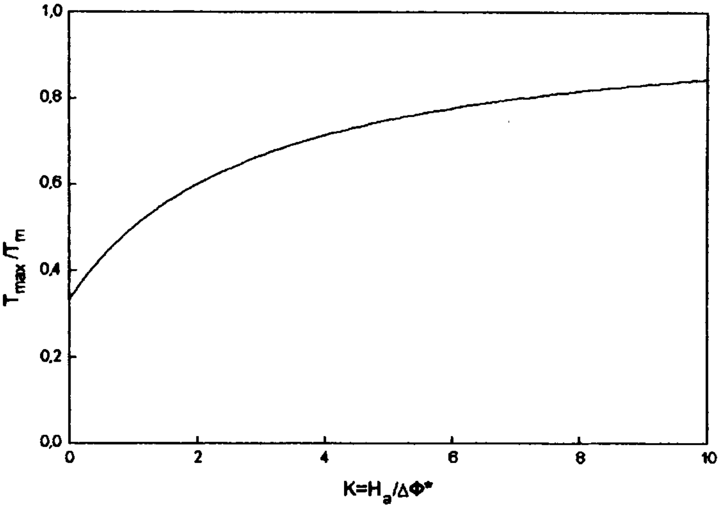

Fig. 8. The dependence of T_{max}/T_m on $K = H_a/\Delta\Phi^*$.

4. Conclusions

It is shown theoretically that the main regularities of spontaneous non-stationary and stationary crystal nucleation on the surface and in the volume of glass are the same.

The non-stationary character of crystal nucleation on the glass surface is experimentally established.

It is shown that nucleation at different kinds of active surface sites dominates, at the same time nucleation on the "perfect" glass surface is also possible.

The nucleation rates of two crystal phases on the surface of cordierite glass were obtained as functions of temperature. Based on our own and literature data, it was concluded that, as a rule, the temperature of the surface nucleation rate maximum lies at a temperature considerably higher than glass transition temperature. This is because of the decrease in the energy barrier of surface nucleation as compared with that of volume homogeneous nucleation.

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