Model of Explosive Crystallization in Thin Films Based on the Nucleation and Growth Approach

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1   The problem of adequate kinetic description of explosive crystallization

At present, the phenomenon of explosive crystallization (EC) of thin amorphous films is an experimentally well-studied process that presents a separate class of fast-reaction autowaves driven by the enthalpy difference between the glass (amorphous) and crystalline state of various mono and binary systems [1,2,3]. If a small domain of a glass film is melted, it undergoes crystallization and the evolved heat can lead to the subsequent melting and crystallization of neighboring regions, so an explosive crystallization wave propagates over a film with the velocities up to 20 m/s. As a rule, EC is observed in thin films (~ 1 μm) within a rather narrow range of film thicknesses and substrate temperatures. For a low (subcritical) temperature and film thickness, propagation of the EC wave is suppressed by high heat losses; for a too high temperature and film thickness, the stable glass becomes unstable, and spontaneous multi-zone self-ignition and crystallization occurs. In most cases, the EC wave has two phase transition zones connected in the thermal sense, viz. a leading endothermal zone of glass melting, whose existence is supported by heat-releasing zone of melt crystallization. The conditions for stable EC-wave propagation are determined by complex interaction between thermodynamic, thermophysical and kinetic characteristics of both zones. Prediction of these conditions is of great importance for a variety of technological applications related to semiconductor electronics, solar cell industry, etc. Nevertheless, modern theoretical models of EC should be considered as approximate and not reflecting certain important details of the phenomenon, in particular, the fast crystallization process. For example, in one of the most recent detailed studies [3], the classical Wilson-Frenkel model for the phase boundary velocity [4,5] was applied to both melting and crystallization zones. However, it is known that this model often overestimates the velocity of the crystallization front. It is evident that a more adequate model should be based on a more detailed description of the nucleation kinetics and crystal growth in the crystallization zone.

In the present work, an attempt is made to use the Kolmogorov-Avrami-Mehl-Johnson (KAMJ) formalism [6-8] for the nucleation and growth of product grains in the transient liquid phase which is formed in the EC wave. Another improvement to the model suggested in the present work consists in a more precise calculation of conductive heat losses from the film to the substrate and those to the environment by thermal radiation. Contrary to paper [3], the two dimensional non-steady-state thermal field in the substrate was calculated, which

provided a correct determination of the thermal flux from film to substrate, instead of the introduction of some effective heat transfer coefficient in [3].

2   Nucleation-growth model and some qualitative results

To describe the kinetics of phase formation and heat generation in EC wave, the Kolmogorov-Avrami-Mehl-Jonson (KAMJ) approach is employed. The model includes the nucleation and growth of crystallites and is used in numerous works related to the crystallization of metals in the conditions close to equilibrium [6-9]. The expression for the local conversion of the product (i.e. the volume fraction of crystallized material) in the melt region is written as follows:

$$\eta = 1 - \exp\left[-f \int_{t_0}^{t} I(\tau) \left(\int_{\tau}^{t} V(\zeta) d\zeta \right)^n d\tau \right], \tag{1}$$

where f is the geometrical factor, t_0 is the instant of time when crystallization begins in the given point, I is the rate of heterogeneous nucleus formation, V is the crystal-grain growth velocity, n is the dimension of forming nucleuses.

Time t_0 relates to the instant of complete melting of the film in the given point when the temperature $T=T_m$ is attained.

To formulate a closed problem, it is necessary to determine the kinetic parameters I and V in Eq. (1). Under the assumption of stationary nucleation, the rate (i.e. frequency) of nucleus formation is determined by the following formula [8,9]:

$$I = \frac{K}{\chi} \exp\left(-\frac{E_I}{k_B T} \right), \tag{2}$$

where K is the parameter of nucleus formation rate, χ is the dynamic viscosity of the melt, E_I is the activation energy of nucleation, k_B is Boltzmann constant.

The value of K for the heterogeneous nucleation is estimated in the literature: $K \sim 10^{29}$ Pa/m^3 [9]. The activation energy E_I for a spherical nucleus is determined in the form [8,9]:

$$E_I = \frac{16\pi}{3} f(\theta) \frac{\psi^3}{\Delta G_v^2}, \tag{3}$$

where ψ is the energy of a crystal-melt interface, ΔG_v is the Gibbs energy for product formation in a unit volume, θ is the wetting angle.

Function $f(\theta)$ is given by the following expression [8,9]:

$$f(\theta) = (2 - 3\cos\theta + \cos^3\theta)/4. \tag{4}$$

The growth of the nuclei in the melt proceeds due to diffusion of components in the liquid phase. Because the concentration gradient in the melt is absent due to a high value of the diffusion coefficient, the growth rate of a nucleus, V, is determined by the formula [7]:

$$V(t) = dR_{pr}/dT = D_m/R_{pr}, \tag{5}$$

where R_{pr} is the radius of a product particle, D_m is the difusion coefficient in the melt.

The value of D_m is determined by the Stokes-Einstein formula [10,11]

$$D_m = k_B T/(m\pi r_a \chi), \tag{6}$$

where r_a is the atomic radius of a component, which controls the nucleus growth, m is a numeric factor (m=4-6).

Equation (5) gives the expression for the growth rate of an individual particle:

$$R_{pr}(t) = R_{pr}(t_0) + (2D_m(T)t)^{1/2}, \quad R_{pr}(t_0) = R_{cr} \sim (5\text{-}10)a_{pr}, \tag{7}$$

where R_{cr} is the critical size for a nucleus, a_{pr} is crystal lattice period.

By substituting Eq. (7) into Eq. (5), we arrive to the following expression for V:

$$V(t) = D_m(T)/[R_{cr} + (2D_m(T)t)^{1/2}]. \tag{8}$$

Thus, Eqs. (1-8) give the formulation of a new kinetic model for phase formation during the explosive crystallization phenomenon. Since the general problem, which also includes the equations of heat transfer in the film and substrate is rather complex, the only way to investigate this model is numerical simulation.

Some qualitative results may be obtained by the scaling analysis of general system of equation. Similarly to [13], it can be demonstrated that the main dimensionless parameter for the problem is

$$\chi = \frac{x_* \rho_s c_s}{h \rho_f c_f}, \tag{9}$$

where ρ_f and ρ_s are the densities of the film and substrate, correspondingly, c_s and c_f are the heat capacities, h is the film thickness, x_* is the characteristic length scale for the crystallization zone, which can be estimated from the above-described kinetic model of crystallization. Numerical calculations have shown that stable wave regimes of EC in a thin film on a substrate can exist at rather low values of this parameter, $\chi \sim 0.1$. This condition can be used as a simple tool for finding the limits of EC regimes with respect of the substrate temperature and the film thickness.

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