The role of stress on initial stages of crystal growth

I. Avramov *
Institute of Physical Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

Abstract

Crystallization in undercooled melts is accompanied by development of stress energy, due to the difference in volume of the new system as compared to the ambient phase. Therefore, the growth rate decreases with time. Here, the non-stationary differential equation is solved, accounting for the production of energy of stress deformation as well as its reduction caused by relaxation. In this way the growth rate and the dependence of crystal size on time are obtained. The change of the growth rate is significant when new formed phase has composition different from the ambient phase, so that particles, creating the new phase can move much faster the main molecules of the matrix. A steady state is determined by the condition that the rate of stress energy production is equal the rate of stress energy consumption. The degree to which the stationary growth rate \( U_{\text{max}} \) is controlled mainly by the ratio of the self-diffusion coefficient of the building units to the diffusion coefficient of the building units creating the new phase. A clear break in the size versus time dependence of the growing crystal is seen.

1. Introduction

When melts are annealed at temperatures slightly above the glass transition region, crystallization is accompanied by stress development and stress relaxation. In particular, this is important when the chemical composition of the growing crystals is different from that of the ambient phase. Note that viscous relaxation could reduce, or even eliminate, the inhibiting effect of elastic stresses. Therefore, in most publications, the effect of internal stress is neglected. The common argument is that stresses are relaxing too fast to affect crystal nucleation or crystal growth. If the two scales are comparable, the stress energy will not have enough time to dissipate completely while crystallization process takes place. Although the relaxation time is large near the glass transition temperature, the crystallization time is large as well. On the other hand, at elevated temperatures where relaxation time is short, the same happens to crystallization time. Therefore, during the crystallization, the possibility of appearance of certain residual stress energy cannot be neglected ad hoc. A quantitative description of the time evolution of elastic stress during isothermal crystallization involves interplay between the kinetics of stress development, was described by Nabarro [1], Christian [2] and Schmelzer et al. [3–6]. Strains can be of different types and magnitude, depending on the kinetics of crystal growth. The resulting stress depends on kinetics of crystal growth as well as on the rate of viscous relaxation. Such relaxation and its influence on crystal growth were investigated in Refs. [4,7] using numerical methods. Here we extend results of [4,7] and develop a generalized formalism for the description of growth of a new phase in viscoelastic media.

2. The model

Due to crystallization, sample volume is changed causing a development of stress energy. As the process proceeds in viscoelastic media, this energy diminishes via relaxation. At every moment, the stress energy \( \varepsilon \), per molecule, is determined by the balance of the energy production and energy relaxation. The crystal growth rate \( U \) depends on the thermodynamic driving force \( \Delta \mu \) (see Refs. [8,9]) as follows:

\[
U = \frac{W d_0}{\tau_0} \left[ 1 - \exp\left( \frac{-\Delta \mu RT}{RT} \right) \right] + \frac{W d_0}{\tau_0} \frac{\Delta \mu RT}{RT},
\]

where \( W \leq 0.5 \) is a dimensionless parameter accounting for the concentration of kink places. In Eq. (1) \( R \) is the ideal gas constant, \( d_0 \) is the intermolecular distance and \( \tau_0 \) is the time for transport of the building units across the interface. Usually, it is determined by the diffusion coefficient, \( \tau_0 = d_0^2/D \). In deriving Eq. (1) no limitations on the nature of \( \Delta \mu \) were introduced. The supersaturation \( \Delta \mu \) accounts for the change in the free energy of the system when a molecule is attached to the growing crystal. Actually, it is change of thermodynamic potential \( \Delta \mu \), when a molecule is attached to the new phase in absence of elastic stress and the corresponding energy \( \varepsilon \) of stress of elastic deformation:

\[
\Delta \mu = \Delta \mu_c - \varepsilon.
\]
For purely elastic body, the instantaneous deformation energy $e_0$ can be written [7,9,10] as

$$e_0 = \frac{GV_m}{9(1-\gamma)\delta^2}, \quad \delta = \frac{\Delta V}{V_m}$$

where $G$ is Young’s modulus, $\gamma$ is Poisson’s number, and $\Delta V$ the volume change. If the new phase is formed by relatively fast diffusion of one of dissolved component forming new phase with molar volume $V_c$, then $\Delta V = aV$; $a \ll 1$. Generally, due to viscous relaxation, $\varepsilon \ll e_0$ holds. We connect the number $n$ of particles incorporated into the unit area of the crystalline phase via the intermolecular distance $d_o$ as

$$\frac{\partial n}{\partial t} = \frac{U}{d_o^2}.$$  

(4)

The stored elastic energy may change due to two sorts of processes: (i) instantaneous increase when new molecule is incorporated into the crystal; (ii) decrease $e_0$, of elastic energy due to viscous relaxation. The best known approximation for relaxation kinetics is the assumption of Maxwell according to which stress depends on relaxation time $\tau_R$ as follows:

$$\left(\frac{\partial e}{\partial t}\right)_n = -\frac{\varepsilon}{\tau_R}.$$  

(5)

Therefore, in accordance with Ref. [7] we obtain

$$\frac{\partial \varepsilon}{\partial t} = \left(\frac{\partial e}{\partial t}\right)_n + \varepsilon \frac{dn}{dt} = \frac{\varepsilon}{\tau_R} + \varepsilon \frac{U}{d_o^2}.$$  

(6)

The final form of differential equation controlling $\varepsilon$ is obtained by introducing Eq. (1) into Eq. (6)

$$\frac{\partial \varepsilon}{\partial t} = \Omega \frac{\Delta \mu_c}{\tau_R} \frac{\varepsilon}{\tau_R}(1 + \Omega),$$  

(7)

where

$$\Omega \equiv \frac{W \varepsilon o \tau_R}{RT}$$

(8)

is a dimensionless parameter responsible for the role of stress development. The solution of Eq. (7) under the initial condition $\varepsilon = 0$ at $t = 0$ is

$$\varepsilon = \Delta \mu_c \frac{\Omega}{(1 + \Omega)} \left[1 - \exp\left(-\frac{\Omega}{\tau_R} t\right)\right].$$

(9)

The reason to assume the above initial condition is because nucleation is a fluctuation process. Due to density fluctuations the critical nuclei are formed in “floppy” regions of the matrix. Moreover, the nucleation time is much larger the relaxation time such that $\varepsilon = 0$ at the initial stage.

For $t \to \infty$, the steady state stress energy value $\varepsilon_{ss}$ is

$$\varepsilon_{ss} = \Delta \mu_c \frac{\Omega}{(1 + \Omega)}.$$  

(10)

The linear growth rate $U$ is obtained by substituting Eqs. (8) and (2) into Eq. (1) in the form:

$$U = U_{max}\left[1 - \frac{\Omega}{(1 + \Omega)} \left[1 - \exp\left(-\frac{\Omega}{\tau_R} t\right)\right]\right],$$

(11)

where $U_{max}$ is the maximal possible value of the growth rate, i.e. the growth rate when no stress is developed:

$$U_{max} = W \frac{d_o \Delta \mu_c}{\tau_0 \rho_f} \frac{d_o \Delta \mu_c}{\tau_0 \rho_0} \Omega.$$  

(12)

It is seen that crystallization begins at a growth rate $U_{max}$ and decreases continuously to the steady state value $U_{ss}$ determined as

$$U_{ss} = \frac{U_{max}}{\Omega + 1}.$$  

(13)

If a stress energy free $\varepsilon = 0$ complex starts to crystallize at initial moment $t = 0$, the time dependence of the increase of crystal size

$$\Delta L(t) = 2(R - R_0) = 2 \int_0^t U dt$$

is given by

$$\Delta L = 2U_{ss}\left(1 + \frac{\Omega}{(\Omega + 1)} \left[1 - \exp\left(-\frac{\Omega}{\tau_R} t\right)\right]\right).$$

(14)

In the following we determine the supersaturation $\Delta \mu_c$ through the concentration $C$ and the equilibrium concentration $C_e$ of molecules of the new phase in ambient matrix as follows:

$$\Delta \mu_c = RT \ln \frac{C}{C_e}.$$  

(15)

3. Discussion

The main parameter determining the role of stress on the growth kinetics is $\Omega$. It consists has two components, see Eq. (8).

First parameter is the product of the dimensionless parameter $0 < W \lesssim 0.5$ accounting for the mode of growth and $\frac{\rho_0}{\rho_f}$. In the following considerations we use the value $W = 0.1$. Estimations of Eq. (3) show that the value of instantaneous energy of elastic deformation $e_0$ is of the order of thermal energy, i.e. $\frac{\Delta e}{\Delta t} \approx 1$.

Second parameter accounts for the relaxation time $\tau_R = \frac{\tau_0}{\rho_f}$ and the diffusion time $\tau_d$. The ratio $\frac{\tau_0}{\tau_d} \geq 1$ could be very large if molecules creating the growing crystal move faster then the building units of the ambient phase.

The two limiting cases of Eqs. (9) and (10) are readily seen: When $\Omega < 1$, the stress energy changes with time according to $\varepsilon \approx \Omega \Delta \mu_c \left[1 - \exp\left(-\frac{t}{\tau_R}\right)\right]$, so that the limiting value $\varepsilon_{ss}$ remains small.

If a new phase consisting of fast moving particles is growing in an immobile matrix, $\frac{\tau_0}{\tau_d} \approx \frac{W \varepsilon_o \rho_0}{\rho_f}$, the value of $\Omega$ is sufficiently large, $\Omega \gg 1$, so that the stress energy changes fast to the limiting condition $\varepsilon_{ss} = \Delta \mu_c$. Therefore, significant stress is developed inhibiting further crystallization. The time to change to stationary regime is about $t_{ss} \approx \frac{\Delta e}{\Delta \mu_c} = \frac{\Omega}{\rho_f} \tau_0$.

The time dependence of the increase of crystal size $\Delta L(t)$ is given in Fig. 1 according to Eq. (14) for $\frac{\Delta e}{\Delta \mu_c} = 1000$ (solid line); $\frac{\Delta e}{\Delta \mu_c} = 100$ (dotted line) and $\frac{\Delta e}{\Delta \mu_c} = 10$ (dashed line). The dimensionless time is in $t_{ss}$ units. The increase $\Delta L$ of the cluster size is in $d_o$ units. The curves are determined according to Eq. (14) with $\Omega = 0.5$.

Fig. 1. Time dependence of the size (in $d_o$ units) of the growing crystal according to Eq. (1). The dimensionless time is in relaxation time, $\tau_0$ units. Solid line is for $\tau_0/t_{ss} = 1000$, dotted line is for $\tau_0/t_{ss} = 500$ and dashed line is for $\tau_0/t_{ss} = 100$. 

and $c = 9$. It is seen that the initial stage of fast growth is soon replaced by a second step of slow growth. In the limiting case of growth in a matrix of high viscosity, the rate in the second period is so low that it is almost impossible to follow the growth. As a result, nanocrystals are formed.

4. Concluding remarks

Strictly speaking the chemical potential depends on the size of crystals. However, no analytical solution was found so far, accounting simultaneously for the dependence of supersaturation on size and stress. Eqs. (1) and (14) are correct if the starting crystal is sufficiently large.

Acknowledgment

The author gratefully acknowledge the financial support of Project INTERCONY.

References