

The effect of stresses during crystallization on the crystallite size distributions

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Abstract

In some glasses during thermal annealing, nano crystals are formed, which scarcely grow with time and exhibit a very narrow crystal size distribution. In this paper, considerations on the crystallite size distributions are given. A variant of the nucleation theory including the role of an induction period is included in the model. Since non-isochemical systems are considered, the oversaturation is decreasing with time and therefore a model is chosen according to which the nucleation rate decreases. For the crystal growth velocity, a model recently derived was used which takes into account the stresses formed during the course of the crystallization process. It is found, that a model taking into account decreasing oversaturation, an induction period as well as the occurrence of stresses fully explains the crystallite size distributions experimentally observed which might even be narrower than those according to the theory of Lifshitz, Slyozov and Wagner.

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1. Introduction

Glass-ceramics often exhibit challenging properties, such as low thermal expansion coefficients which enables their utilization for various purposes, such as for cook-top panels or as telescope mirrors.^{1,2} They are also valuable materials for numerous photonic applications. In some cases, it is possible to precipitate crystallites with mean sizes in the nm-range and narrow size distribution. This enables the preparation of transparent glass-ceramics³ which might be used for numerous photonic applications. Recently it has been experimentally shown that the crystallite size distribution⁴ may even be narrower than that according to the well known theory of Lifshitz, Slyozov and Wagner (LSW-theory).⁵ This theory was developed for diluted suspensions and considers an asymmetric size distribution after coarsening by Ostwald-ripening.⁵

Nucleation and subsequently growth of crystals in a glass forming melt has been a challenging topic over the years, mainly due to a very large number of models and approaches that have

been developed in the effort to better understand the microscopic mechanisms of growth in detail.^{6–8} Recently, a new model was suggested combining ideas from percolation theory and the glass forming ability of silicates.^{9–14} Most glass forming systems consist of networks in which the network formers, NF, are connected with oxygen bridges. The network is “floppy” or “rigid”, depending on the number of broken oxygen bridges (NBO) per NF. According to the theoretical model developed by Thorpe and Phillips (see e.g. Refs. [15–20]), as well as from experimental observations,^{9–12} the threshold number for the floppy-to-rigid transition is $NBO_c/NF = 1.6$ for glasses composed of network formers with a coordination number of 4. If NBO/NF is less than this critical value, the network is “rigid”. However, in “rigid” networks there are still some tiny “floppy” regions. It has been shown, that the exact threshold conditions for the rigid/floppy transition depend on the dimensionality of the space and on the coordination number.²⁰

Recently, Monte Carlo Simulations were carried out to simulate the crystallization process in multicomponent systems.²¹ The basic starting assumption was that during the course of the crystallization process, stress energy is developed, which decelerates crystal growth. At a first stage, nuclei are formed inside the “floppy” regions of the glass. The size and concentration

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of these floppy regions in a rigid matrix is a type of percolation problem. It was further expected that the crystal could grow relatively fast until the entire “floppy” region is occupied. Further crystallization has to propagate inside the “rigid” region and it is to be accompanied by stress development. This is of particular importance if the chemical composition of the growing crystal is different from that of the ambient phase. Viscous relaxation could reduce, or even eliminate, the inhibiting effect of elastic stresses.⁴ Hence, in most cases the effect of internal stress is neglected. The common argument is that stress energy is relaxed too fast to affect crystal nucleation or crystal growth. If the two scales (of growth rate and of relaxation rate) are comparable, the stress energy, however, will not have enough time to dissipate completely during the course of the crystallization process. Although the relaxation time is long at the glass transition temperature (around 60 s), the crystallization time is long as well. On the other hand, at elevated temperatures, the relaxation time is short, however, the crystallization time might also be short. Therefore, during the crystallization, residual stress energies cannot be neglected ad hoc.

In the present work we combine the nucleation theory including an induction period with a model taking into account a decreasing driving force for the nucleation process due to decreasing oversaturation as well as a crystal growth velocity which decreases with time. This enables to conclude on the crystal size distributions. It is shown that the formation of stresses during the course of the crystallization leads to much narrower crystal size distributions than those expected by the LSW-theory.

2. Theoretical models

In numerous papers, it has been reported that nucleation rates might depend on time.²² While in a first stage, the nucleation rate is fairly small, it increases with time and finally approaches a constant value. After some time, the nucleation rate reaches a constant value, the steady state; earlier states are non-steady state. The time required until the number of nuclei increases linearly with time is frequently called the non-steady state time lag. The first theoretical description was given by Zeldovich:²³

$$I = I^{ss} \exp\left(-\frac{t_c}{t}\right) \quad (1)$$

with t_c , characteristic time scale; I , nucleation rate; I^{ss} , steady state nucleation rate.

In an ideal isochemical system, (the crystal precipitated has the same chemical composition as the melt), the crystal growth velocity once a steady state is reached does no longer depend on time. However, if the system is not isochemical and the crystallizing component has a larger concentration, then also the nucleation rate can no longer be considered as constant. In numerous reports on nucleation and crystallization in the field of metals and alloys^{24–26} the problem of decreasing concentrations of the respective crystal forming components, i.e. decreasing oversaturation, is taken into account. This leads to a decreasing driving force for the nucleation process and hence to decreasing nucleation rates. According to Refs.,^{24–26} Eq. (2) describes the

nucleation rates in non-isochemical systems taking into account the induction period:

$$I = I_0 \exp\left[-A \left(\ln \frac{c(t)}{c_e}\right)^{-2}\right] \exp\left(-\frac{t_c}{t}\right) \quad (2)$$

with $I_0 \exp\left[-A \left(\ln \frac{c(t)}{c_e}\right)^{-2}\right] = I^{ss}$, where I_0 is a numerical constant, A is a parameter related to the energy barrier for nucleation, $c(t)$ is the concentration as a function of time and c_e is the equilibrium concentration, i.e. that concentration below which crystallization does not take place.

In the following, the oversaturation, i.e. concentration as a function of time, is decreasing due to crystallization. The formation of the crystalline volume fraction was assumed to obey the Johnson–Mehl–Avrami–Kolmogorov (JMAK) theory of phase transformation:^{27–31}

$$c(t) = c_{in} + (c_e - c_{in}) \left(1 - e^{-\left(\frac{t}{\tau_A}\right)^n}\right), \quad (3)$$

with c_{in} as the initial concentration of the crystallizing component, characteristic time τ_A determines the time law of decreasing oversaturation and the Avrami parameter n .

Then the nucleation rate shows an exponential decay attributed to decreasing concentration of the crystallizing component.

In general, the distribution of crystal sizes is controlled by three processes: the linear growth rate, the nucleation rate and the process of Ostwald ripening. In the present treatment the third process, Ostwald ripening, will be neglected. This is a reasonably good assumption for the early stages of crystallization as well as in the case of stopping crystal growth of the nano crystals due to the formation of a stress field near the interfaces.

The case when the relaxation time of the stress field τ_R could be different from the time τ_D , that building units need to attach to the crystal, was studied in Refs.²¹ and.³² Recently it has been shown using Monte Carlo simulations that the crystal growth velocity depends on time.²¹ By analogy, theoretical considerations taking into account stresses formed during the course of the crystallization process also resulted in nucleation rates which decrease with time. Using the results from Ref.,³² it can be shown that in this case, after annealing time t_a at constant temperature, the crystal that is formed at moment t has a size L as follows:

$$L(t_a - t) \approx L_S \left(\frac{t_a - t}{\tau_R} + (1 - e^{-\frac{t_a - t}{\tau_D}})\right), \quad (4)$$

with the parameter L_S regarding the size of the crystal at that moment when crystal growth starts to be dominated by the stresses formed, τ_R is the relaxation time of the interface matrix diffusion zone and τ_D is the time of the diffusion controlled growth in the beginning.

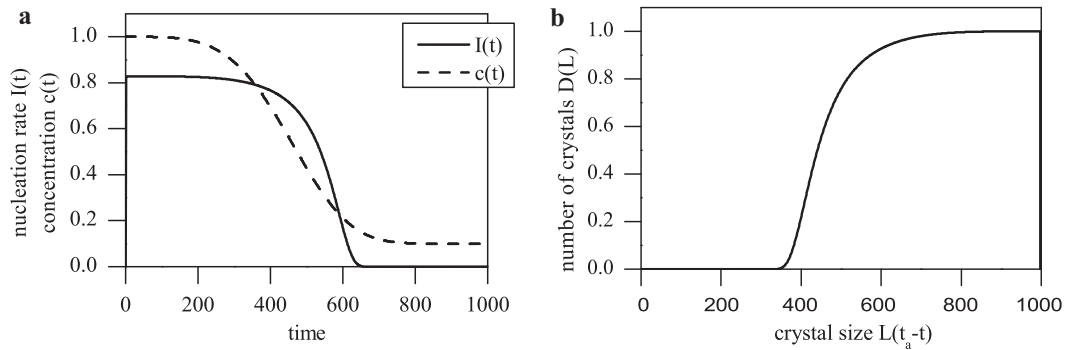


Fig. 1. Nucleation rate and oversaturation for non steady state nucleation in a diluted system (a) and the resulting crystal size distribution assuming a constant crystal growth velocity (b).

3. Results

In the following, crystal size distributions $D(L)$ are calculated from the derivative of the number $N(t) = \int_0^t I(x)dx$ of crystals to the size $L(t_a - t) = \int_0^{t_a-t} U(x)dx$.^{33,34}

$$D(L) = \frac{I(t)}{U(t_a - t)} \quad (5)$$

with the crystal growth velocity $U(t_a - t)$

$$U(t_a - t) = L_S \left(\frac{1}{\tau_R} + \frac{1}{\tau_D} e^{-\frac{t_a-t}{\tau_D}} \right). \quad (6)$$

Note that the nominator in Eq. (5) is a function of t (because it counts for the number of nuclei formed in this moment), while the denominator is a function of $t_a - t$ (because it counts the further development of these nuclei). Subsequently, the size distributions were normalized in order to obtain a maximum equal to unity.

First, the most simplified case is considered where the nucleation rate is constant, i.e. does not depend on time $I(t) = I^{SS}$ and the crystal growth velocity is constant:

$$U(t_a - t) = U^{SS} = \frac{d_0}{\tau} \quad (7)$$

Here d_0 is the intermolecular distance in the crystal and τ is the time for which the crystal front propagates to this distance. In the following, this model is denoted as model A. As a trivial result, the size distribution is also constant. There is a constant number of crystals at any size between zero and the maximum size obtained during the annealing period.

In the next model (model B) it is taken into account that the concentration of the crystallizing component is a function of time. In multicomponent glass systems where one component is crystallized, the matrix surrounding the crystal will be depleted in the crystal forming units. Therefore, the concentration will decrease with time and the driving force for nucleation will also decrease due to the decreasing oversaturation.

In Fig. 1(a), the concentration and the resulting nucleation rate are shown as a function of time. The time scale was set from 0 to 1000 arbitrary units. As parameters for the concentration profile, the initial concentration c_{in} was set to one and the equilibrium concentration c_e to 0.1. The Avrami parameter n was

set to four which is attributed to a three dimensional growth,³¹ e.g. observed in a cubic system. The characteristic time t_A was set to 500 in arbitrary units in order to obtain an observable effect in the chosen time interval. For the nucleation rate I_0 was set to unity and t_c to zero. It should be noted that in this model, an induction period does not occur and the crystal growth velocity does not depend on time. It can be seen, that the nucleation rate starts to decrease after approximately 400 time steps and approaches zero at time point 650. In Fig. 1(b), the crystal size distribution is shown. Crystals smaller than about 350 arbitrary units do not exist, because according to the nucleation rate curve shown in Fig. 1(a) after a certain time limit, practically no further nuclei are formed, and hence crystals which grew only for a comparable short time are not observed. On the other hand there is a large number of large crystals because the nucleation rate at the beginning is maximum and these crystals grew for the longest time and hence to the maximum size. Practically, the crystal size distribution is similar to the mirrored nucleation rate curve because of the linear assumption of the crystal growth.

In some multicomponent glass systems, the crystal size remains nearly constant after a certain time. This is due to a crystal growth velocity which decreases with time. The next model (model C) includes decreasing oversaturation as well as a time dependency of the crystal growth velocity as described in Eq. (4). Fig. 2(a) shows the crystal size as a function of time using Eq. (4). Here, the ratio of τ_R/τ_D was varied. The time τ_D was kept constant (100 time arbitrary units), while τ_R was varied from 200 to 5000 time units. The size L_S was set to unity. In a good approximation, the crystals grow rapidly with a nearly constant crystal growth velocity until a certain crystal size is reached. Then increasing stresses are formed, which decelerates further crystal growth. The latter leads to a decrease in the crystal growth velocity which, however, approaches another approximately constant value. By using the same parameter set for concentration and nucleation rate as in Fig. 1, the resulting crystal size distributions are shown in Fig. 2(b). Each graph exhibits a maximum, the curves are getting much steeper with increasing the ratio τ_R/τ_D from 2 to 50 and the maximum is shifted to smaller crystal sizes.

In models A to C, the second term in the Zeldovich-equation (Eq. (2)) was neglected. So far, the nucleation rate did not show an induction period. In model D, the variation of parameter t_c

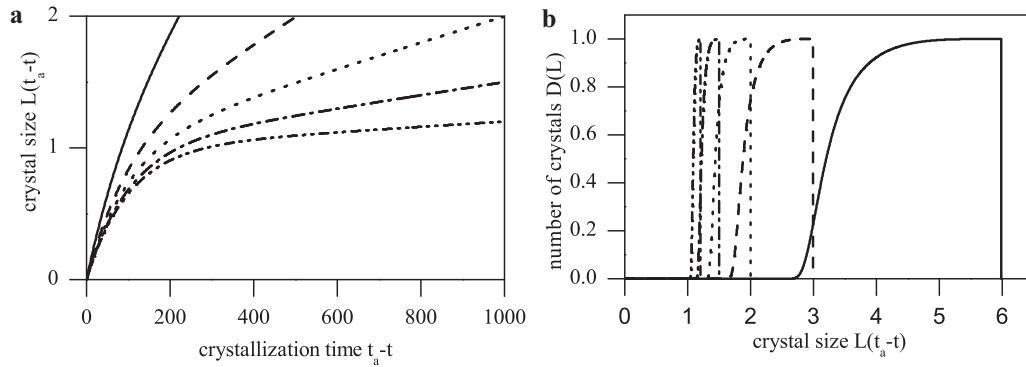


Fig. 2. Linear size L of the cluster versus time for different relaxation times. For $\tau_R/\tau_D = 2$ (solid line), 5 (dashed line), 10 (pointed line), 20 (dash-dotted line) and 50 (dash-double dotted line) (a) and the resulting crystal size distributions (b).

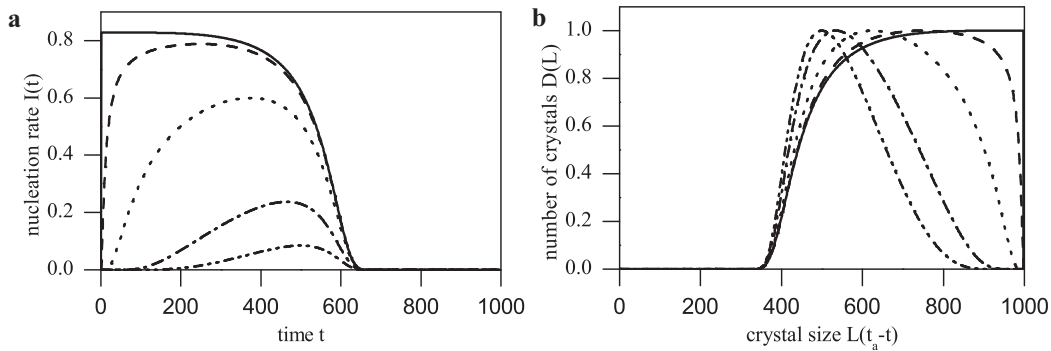


Fig. 3. Nucleation rate in a diluted system with $t_c = 0$ (solid line), 10 (dashed line), 100 (pointed line), 500 (dash-dotted line) and 1000 (dash-double dotted line) (a) and the resulting crystal size distributions with linear crystal growth (b).

was taken into account while a constant crystal growth rate was assumed. In Fig. 3(a) nucleation rates are shown as a function of time while the parameter t_c was varied from zero to 1000. For $t_c > 0$, the nucleation rate exhibits a maximum which gets narrower with increasing t_c . The resulting crystal size distributions are shown in Fig. 3(b). It is seen, that the crystal size distributions exhibit a pronounced maximum when t_c increases and the width of the curve decreases with increasing t_c . The maximum crystal size is shifted to smaller values with increasing t_c and it should be noted that at larger t_c the curve shows a log-normal shape.

In Fig. 4, the models C and D are combined to model E. Again t_c is varied from zero to 1000 but in comparison to Fig. 3(b) the crystal growth is a function of time according to Eq. (4) with the parameters $\tau_R/\tau_D = 50$. It is seen, that only small crystals are observed which possess a very narrow size distribution slightly above the set parameter of L_S with unity. There are no crystals smaller than approximately one arbitrary unit and no crystals larger than 1.2 arbitrary units. It should be noted that the size distribution approaches a Gaussian shape when t_c increases.

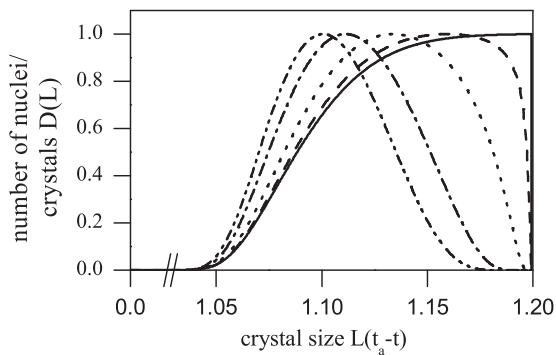


Fig. 4. Crystal size distributions when t_c in the nucleation rate is 0 (solid line), 10 (dashed line), 100 (pointed line), 500 (dash-dotted line) and 1000 (dash-double dotted line) and the crystal growth according to equation 4 with $\tau_R/\tau_D = 50$.

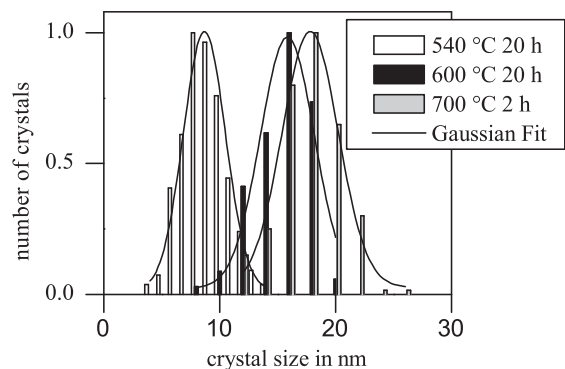


Fig. 5. From TEM-micrographs experimentally obtained crystal size distributions of BaF_2 crystals in the glass system $\text{Na}_2\text{O}/\text{K}_2\text{O}/\text{Al}_2\text{O}_3/\text{SiO}_2/\text{BaF}_2$.

4. Discussion

In the numerical simulation of the crystallization process, the following effects were taken into account: (1) decreasing oversaturation during the course of the crystallization process, (2) a crystal growth velocity which decelerates with time and (3) an induction period of the nucleation process.

If all three effects were not taken into account (model A), the number of crystals for any size is equal up to a maximum value and then is equal to zero. If the decreasing oversaturation is taken into account (model B), the number of crystals increases with increasing size and then approaches a nearly constant value until a maximum crystal size is reached (see Fig. 1(b)). Crystals larger than attributed to this maximum value do not exist. If a crystal velocity is taken into account which after reaching a certain value, decreases with time (model C), the number of crystals increases first exponentially and then goes into saturation until a maximum is reached. If an induction period is taken into account and the crystal growth velocity is constant (model D), an approximately exponential increase is observed for crystal sizes smaller than the maximum. Then it decreases again and approaches zero. Crystal sizes below a certain limit practically do not exist. The curves show approximately a log-normal shape which is reported for some nano particles instead of the LSW-function.^{35,36}

In the literature, experimental studies on the crystal size distribution of crystals with sizes in the nanometer range are scarcely reported. Nevertheless, in Ref. [4] crystal size distributions of BaF₂ nano crystals from an oxyfluoride glass system are reported. They were experimentally obtained using transmission electron microscopy.⁴ This system represents a multicomponent and non-isochemical system. Using X-ray diffraction, it has been shown from the line broadening that the crystals in this system and similar ones do scarcely grow with time. In the initial state of the crystallization process, the glass transition temperature of the residual glassy phases increases until the transition temperature and the annealing temperature are equal. In those systems, the crystallite sizes are usually in the 5–20 nm range.^{4,14,37}

In Fig. 5, the size distributions of the three samples from Ref.⁴ after annealing at different temperatures and for different times are shown. The number of crystals is normalized to unity. It is seen that the size distributions are fairly narrow and as shown in Ref.⁴ may even be narrower than that according to the LSW-theory. Their Gaussian shape fits best with model E where all three effects are taken into account. It can hence be concluded that the model introduced may fully explain the narrow size distributions observed in glass-ceramics containing BaF₂ nano crystals.

5. Conclusion

The nano crystallization in multicomponent glass systems is explained by a model that takes into account a decreasing oversaturation as well as an induction period during the nucleation process and their effects on the nucleation rate. Furthermore, the crystal growth rate is a function of time which is in agreement to

experimental observations in some oxyfluoride glass-ceramics. By means of numerical calculations, crystal size distributions for various parameters of the nucleation rate and crystal growth velocity are obtained. From the trivial case with a constant nucleation rate and crystal growth velocity to the time depended case, the crystal size distributions are calculated. It is shown, that with increasing relaxation time of the matrix during the crystallization and hence hindered in crystal growth, the crystal size distributions become narrower and finally similar to a curve of Gaussian shape. This model explains the formation of nano crystals with a Gaussian crystal size distribution that is even narrower than the LSW-theory predicts.

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