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## Letter to the Editor

## Pore formation in glass–ceramics: Influence of the stress energy distribution

A. Karamanov<sup>a,\*</sup>, I. Georgieva<sup>b</sup>, R. Pascova<sup>a</sup>, I. Avramov<sup>a</sup><sup>a</sup>Institute of Physical Chemistry, Bulg. Acad. Sci., 1113 Sofia, Bulgaria<sup>b</sup>Institute of Mathematics and Informatics, Bulg. Acad. Sci., 1113 Sofia, Bulgaria

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## ABSTRACT

In glass–ceramics, the density difference between the new, semi-crystalline system, and the ambient phase requires a deformation of the grains. However, the first stage of surface induced crystallization is the creation of rigid shell, opposing the shrinkage. Therefore, an important stress appears inside the grain. If the average density of the new system is higher than that of the ambient phase, a tensile stress is generated. In the opposite case, a compressive stress is developed. As soon as the system is neither pure elastic body nor pure plastic one, the concentration of the stress energy depends on the distance from the interface. We describe theoretically the distribution profile of the stress energy. Depending on the stress attenuation parameter and the grain size, there are two solutions. The first one predicts a maximum in the middle of the grain. According to the second, there are two maxima close to the crystal/glass interface. This explains the appearance of cabbage like crystals or of crystalline grains with a pore in the center.

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## 1. Introduction

Glass–ceramics production is accompanied by volume changes because the parent glass density is different from the average density of the newly formed material. Nowadays, glass–ceramics are considered as non-porous materials [1,2], which means that the crystallization volume change can lead only to some shrinkage of the products and to variation of the apparent density.

Similar to the ceramic materials, porosity is considered as a negative factor, which significantly reduces the mechanical properties of final products. For this reason it is assumed that the lack of porosity in the glass–ceramics is one of their main advantages.

Studies of the sintered glass–ceramics show that the densification process is hindered after formation of 10–20% crystal phase. The subsequent phase formation leads to no additional volume variations of the samples [3,4]. It was elucidated that the volume change might be transformed in crystallization induced porosity [5,6]. These additional pores are formed in the centers of sinter-crystallized grains, the pore diameter varies between 50 nm and a couple of  $\mu\text{m}$  and depends on particle size, on the nature of crystal phase and percentage of the formed crystals. Later on the formation of crystallization induced porosity was also confirmed by other research groups [7–9]. However, the phenomenon is not yet studied theoretically.

The aim of the present study is to predict the stress energy profile inside the semi-crystalline grain. In this way the position where the breaking strength is reached can be predicted.

## 2. The model

Recently [5,6], pore formation was experimentally found when glassy grains crystallize from the surface. A typical, crystallization induced pore, formed in a grain of diopside–albite composition, is shown in Fig. 1. The crystallization and sintering of this model glass were discussed in detail in previous works [5,6]. Here, we describe the stress profile developed during the process of a surface-initiated crystallization. After the growing crystals form a rigid shell, the process continues inwards. This is accompanied by the accumulation of stress, because the rigid core does not permit volume changes of the grains and stress relaxation. If the volume of the newly formed system tends to have higher volume, further growth of the crystalline shell causes compressive stress inside the grain. In the opposite case, a tensile stress is created.

The stress profile is needed to predict where it is most likely that the breaking strength will be reached for the first time. We expect two cases: either the stress energy will be maximal at the crystal/melt interface, or it will be maximal in the center of the grain.

The grain is neither a pure elastic body nor pure plastic one. Therefore, we assume that the deformation energy decreases with the distance  $r$  from the crystal/melt interface. In line with the findings of Binder et al. [10,11] we assume that the dependence of the stress energy on the distance from a flat surface is described by an exponential decay law:

\* Corresponding author. Tel.: +359 2 979 2552; fax: +359 2 971 2688.  
E-mail address: [karama@ipc.bas.bg](mailto:karama@ipc.bas.bg) (A. Karamanov).

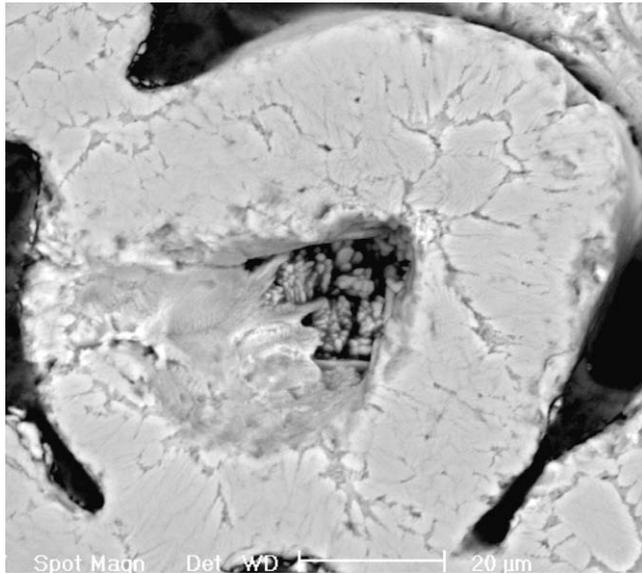


Fig. 1. BSE-SEM image of a crystallization induced pore, formed in the center of a 100  $\mu\text{m}$  grain.

$$\varepsilon = \varepsilon_0 \exp\left(-\frac{r}{r_0}\right). \quad (1)$$

Here  $\varepsilon_0$  is the deformation energy accumulated at the crystal/melt interface and  $r_0$  is a scaling distance. It is a result of the interplay between the elastic constants and the dissipative properties related to the viscosity. As shown in Refs. [12–17], the elastic energy increases with the density difference.

It is seen that  $r_0$  depends on the composition of material as well as on whether there is a tensile stress developed or it is a compressive one. We prefer Eq. (1) to the  $\sim 1/r^6$  law proposed in Refs. [18,19] because the latter diverges for  $r = 0$ . Beyond this limit both approximations give practically identical results.

We consider a point inside the amorphous part of a spherical cluster with coordinates  $M(0, 0, z)$ , as shown in Fig. 2. The grain is partially crystalline. The distance  $r$  between this point and an arbitrary point  $N(X, Y, Z)$  on the crystal/melt interface is determined by the following expression,

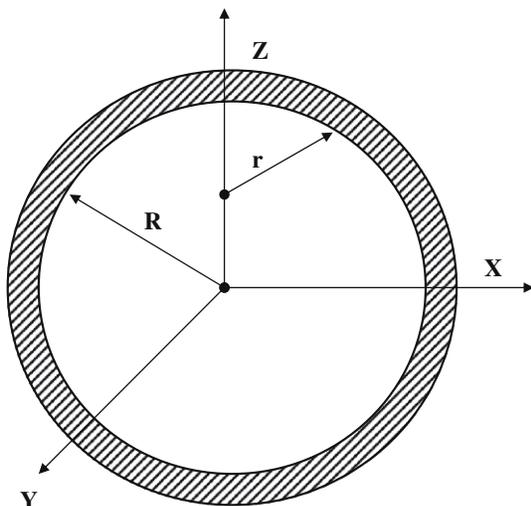


Fig. 2. Semi crystalline grain. The dashed area forms a crystalline shell so that stress energy generated inside cannot relax. Further crystallization leads to a decrease of the radius  $R$ .

$$r^2 = (X - 0)^2 + (Y - 0)^2 + (Z - z)^2. \quad (2)$$

The radius of the crystal/melt interface is  $R = r(0, 0, 0)$ . The total deformation energy  $E(z)$  at the point  $M(0, 0, z)$  is integral over the whole crystal/melt interface  $S$ :

$$E(z) = \frac{\varepsilon_0}{k} \iint_S \exp\left(-\frac{r}{r_0}\right) ds. \quad (3)$$

The dimensionless parameter  $k$  is determined from the normalizing condition that on a flat interface the stress energy is equal to  $\varepsilon_0$ , i.e.  $E(z=R)_{R \rightarrow \infty} = \varepsilon_0$ . With this condition, the energy  $E(z)$ , obtained solving Eq. (3), has a form,

$$E(z) = \varepsilon_0 \times \frac{R}{z} \left[ \left(1 + \frac{R-z}{r_0}\right) \exp\left(-\frac{R-z}{r_0}\right) - \left(1 + \frac{R+z}{r_0}\right) \exp\left(-\frac{R+z}{r_0}\right) \right]. \quad (4)$$

### 3. Discussion

The profile of stress energy, respectively, the length of the parameter  $r_0$ , as compared to  $R$ , plays key role. When  $r_0$  is small,

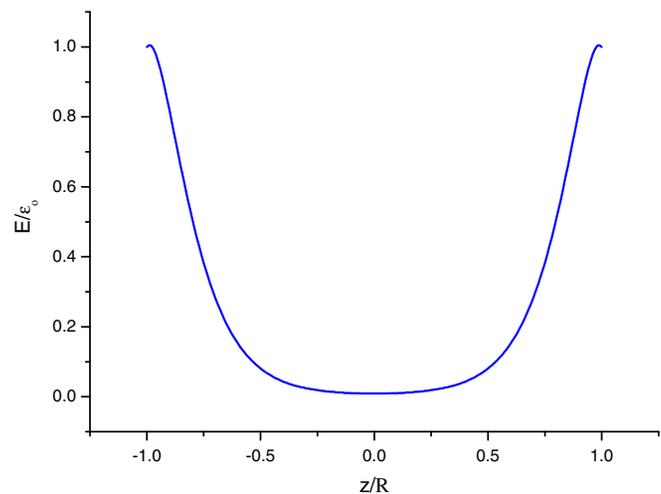


Fig. 3. Energy profile for  $R = 10 r_0$ .

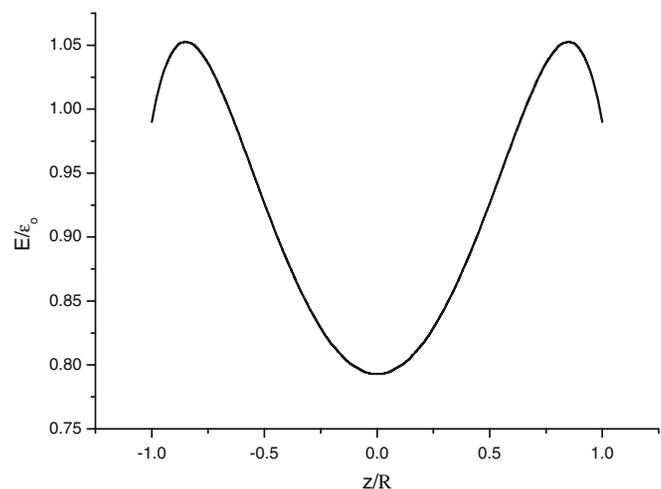


Fig. 4. Energy profile for  $R = 3 r_0$ .

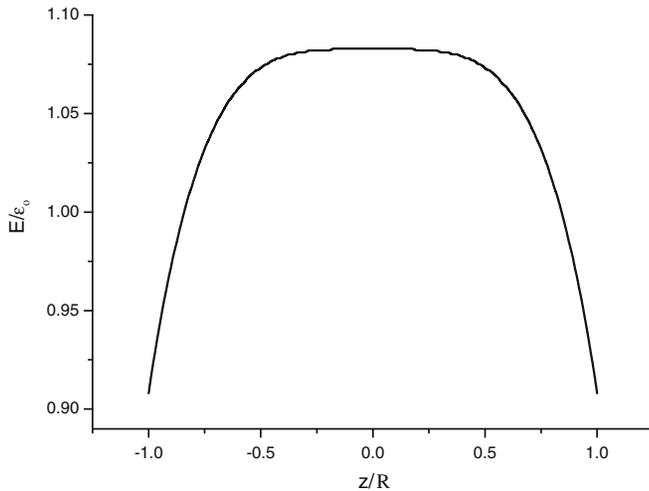


Fig. 5. Energy profile for  $R = 2 r_0$ . A flat plateau is formed.

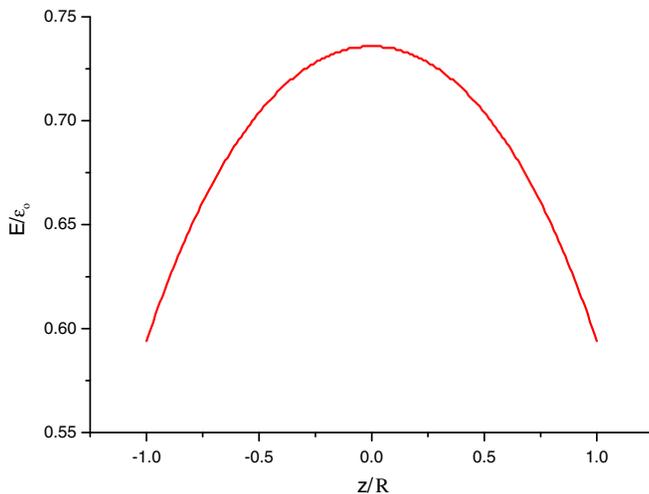


Fig. 6. Energy profile for  $R = r_0$ .

as compared to the grain size  $R$ , the stress energy will decay fast so that the main part will be concentrated near the crystal/melt interface. Fig. 3 shows the stored energy profile for a grain size  $R = 10 r_0$  in dimensionless coordinates  $E(z)/\varepsilon_0$  against  $z/R$ . When  $R$  is large there are two maxima close to the walls. As soon as the maximal value of the stress energy exceeds the breaking strength a break will appear that may lead to the formation of cabbage-shaped crystalline aggregates like observed in Refs. [20–23].

When  $R$  decreases the two maxima move inwards, away from the walls of the grain, as demonstrated in Fig. 4 for  $R = 3 r_0$ . Upon further decrease of  $R$  the minimum in the grain middle and the two maxima near the walls are replaced by a large plateau as shown in Fig. 5 for  $R = 2 r_0$ . When  $R$  decreases further, a sharp maximum in the middle of the grain appears as shown in Fig. 6. The lower is the  $R$  value the sharper is the peak. For a given composi-

tion the parameter  $r_0$  is a material constant. Unlike it, both  $R$  and  $\varepsilon_0$  change with time. As soon as  $R$  is the radius of the inner interface boundary, not the grain size, crystallization leads to continuous decrease of  $R$  and to a simultaneous increase of the generated stress energy parameter  $\varepsilon_0$ . As soon as the maximal value of the stress energy exceeds the breaking strength a crack will be formed at this point. In this way a porous grain (see Refs. [5,6]) will be expected.

During crystallization the crystalline shell (shaded area in Fig. 2) is getting thicker. This is accompanied by an increase of the generated stress energy  $\varepsilon_0$  as well as by a decrease of the radius  $R$  of the inner amorphous part of the grain. Therefore, the ratio  $r_0/R$  increases with time, unless the breaking strength is reached and a crack is formed.

#### 4. Conclusions

A theoretical model is proposed for calculating the distribution profile of the strain energy, generated when surface-initiated crystallization encapsulates the glass inside the grain. It is shown that depending on the grain size  $R$  the stored energy profile can be quite different. For small grains (grain radius  $R \leq 2 r_0$  where  $r_0$  is the scaling distance) the stress profile has a maximum in the middle of the grain and in this case a formation of a pore in the grain center could be expected. When  $R$  increases a flat plateau replaces the peak. Upon further increase of  $R$  two maxima appear moving towards the grain surface while a minimum is formed in the grain center. For very large  $R$  values the two maxima of the stress profile are practically close to the walls of the grain.

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