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Sinter-crystallization in the diopside–albite system
Part II. Kinetics of crystallization and sintering

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Abstract

The formation of intragranular pores, induced by diopside crystallization in diopside–albite glasses, was highlighted in a previous study and here confirmed by SEM observation. The sinter-crystallization kinetics of four glass compositions, labelled G1, G2, G3 and G2-Cr, characterized by the formation of *induced crystallisation porosity*, P_{CR}, was investigated. The activation energies of crystallisation, E_C, and sintering, E_S, were evaluated by differential thermal analysis (DTA) and by contact differential dilatometer in non-isothermal conditions, respectively.

The results highlighted that the kinetics of the crystallization process was not influenced by the P_{CR} formation and that the E_C values are in agreement with the corresponding activation energies of viscous flow.

The sintering was evaluated up to 24% linear shrinkage of the samples. In the initial stage of the densification, up to 8% shrinkage, the measured E_S values are comparable for all glasses while, between 9 and 24% shrinkage, E_S increase as a function of the crystallisation ability of each glass. Bulk nucleation occurred in G2-Cr: the rate of phase formation resulted to be higher, the densification was inhibited by the formation of 6 ± 3 wt.% diopside and significant open porosity remained in the sintered glass-ceramic.

Keywords: Sintering; Crystallization; Glass-ceramics; Diopside; Albite

1. Introduction

Glass-ceramics materials have been obtained by sinter-crystallisation technique, using glass powders or frits.[1,2] However, since the densification and the phase formation occur simultaneously, the existing theoretical models, applied to this method, are not able to explain all complex aspects arising during the heat-treatment.[3]

Due to the increasing of the apparent viscosity, the crystallization may reduce or even hinder the sintering, leading to the formation of materials with a residual porosity. At the same time, the formation of crystal phases might avoid the deformation at higher sintering temperature.

The crystallisation lowers the sintering rate and, due to the density variation associated with the phase formation, might also produce an additional porosity. The formation of this *induced crystallisation porosity*, P_{CR}, was highlighted and investigated in the first part of present work.[3] It was demonstrated that the volume variation due to crystallization is partly transformed into shrinkage of the sample and partly into the formation of intragranular spherical pores. The higher is the crystallisation ability of the glass, the lower is the shrinkage and the higher is P_{CR} formation.

In the first part of this study the role played by the formation of the *induced crystallisation porosity* on the crystal growth mechanism was not clarified. In order to highlight this aspect, the crystallisation was investigated by DTA and the obtained activation energies of crystallization were compared with the corresponding activation energies of viscous flow. These results are discussed in the present work, together with the variations of the activation energies of sintering, evaluated by non-isothermal dilatometry. The influence of the crystal phase formation on the densification rate was studied by XRD and SEM techniques.

1.1. Crystallization kinetics

The kinetics of isothermal crystallization in glasses is usually investigated by the KJMA (Kolmogorov, Johnson, Mehl,

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Avrami) equation in the form[1,2,4]:

$$\alpha(\tau) = 1 - \exp(-\text{const}\, I_o U^n \tau^{n+1}) \quad (1)$$

where $\alpha(\tau)$ is the degree of transformation at time τ, I_o the rate of steady-state nucleation, U the rate of crystal growth and n a parameter depending on the crystal growth mechanism and morphology. When no nucleation takes place and the crystals grow on a fixed number of previously formed nuclei, N, Eq. (1) becomes:

$$\alpha(\tau) = 1 - \exp(-\text{const}\, N U^n \tau^n) \quad (2)$$

In the common case of normal growth mechanism, U may be represented by the following relationship[2,4]:

$$U(T) \approx \frac{\text{const}\,\Delta T}{\eta} \quad (3)$$

where ΔT is the degree of supercooling (i.e., the difference between the liquidus, T_l, and the experimental, T_e, temperatures) and η the viscosity. At high temperatures, i.e., close to T_l, U mainly depends on ΔT, while at low temperatures it is a function of the viscosity variation. At high supercooling, the ΔT variation becomes negligible and it may be assumed that the activation energies of crystal growth, E_G, has a value, similar to the corresponding activation energy of the viscous flow, E_η.[2,4] In the glass forming melts E_η decreases with increasing temperature[5,6] but, for a relatively short temperature interval, it may be assumed as constant and evaluated through an Arrhenius equation:

$$\eta(T) = \eta_o \exp\left(\frac{E_\eta}{RT}\right) \quad (4)$$

In the case of non-isothermal crystallization, carried out by DTA or DSC, it is assumed that Eqs. (1) and (2) can be applied in non-isothermal conditions.[7] The non-isothermal kinetics are usually investigated by experiments carried out at different heating rates, v, and the activation energy of crystallization, E_C, may be evaluated by Chen's equation[8]:

$$\frac{E_C}{RT_\alpha} = \ln\left(\frac{T_\alpha^2}{v}\right) \quad (5)$$

where T_α is the temperature, at which α attains equal value at different heating rates. Usually T_α is evaluated at the crystallisation onset temperature, T_o, (corresponding to the beginning of the phase formation) and the peak temperature, T_P, (corresponding to α of 0.63).[4,7] In the last case, Eq. (5) becomes identical to the widely applied Kissinger equation.[9] Using the variation of the glass transition temperature, T_g, with the heating rate, the energy of viscous flow in the glass transition range, E_{Tg}, may also be estimated by Eq. (5).[5,8]

When surface crystallization takes place or when the crystals grow on a fixed number of nuclei, the E_C value corresponds to the activation energy of crystal growth, E_G; when nucleation takes place during heating, E_C has a lower value.[7,10] This is a consequence of the fact that the number of formed nuclei depends on the heating rate: the lower is the rate, the bigger is the number of formed nuclei and the faster will be the phase formation.

1.2. Sintering kinetics

The sintering of glass powders is accompanied by a shrinkage, which depends on the initial porosity, P, of the sample. At 35–40% P the linear shrinkage, $\Delta L/L_o$, corresponding to the formation of a non-porous material, is 13.5–15.5%. The first 10–12.5% are related to neck formation and growth[11,12] and may be expressed by the Frenkel equation[13]:

$$\frac{d(\Delta L/L_o)}{dt} = \frac{3\sigma}{8r\eta(T)} \quad (6)$$

where σ is the surface tension, η the viscosity and r the radius of the particles. Since σ varies little with the temperature, the sintering kinetics depend on the viscosity (i.e., it may be assumed that the activation energy of the sintering, E_S, is equal to E_η). Rewriting Eq. (6) for the case of non-isothermal sintering (i.e., $T = vt$) and expressing η by Eq. (4) the following relationship is obtained:

$$\frac{d(\Delta L/L_o)}{dT} = \frac{\text{const}}{v}\exp\left(\frac{-E_{\sin}}{RT}\right) \quad (7)$$

After integration[8] this relationship gives Chen's equation in the form:

$$\frac{E_{\sin}}{RT_X} = \ln\left(\frac{T_X^2}{v}\right) \quad (8)$$

where T_X is the temperature at which the sintering process attains a fixed shrinkage value X.

2. Experimental

The theoretical compositions of the studied glasses (labelled G1, G2, G2-Cr and G3) are reported in Table 1. In G2-Cr a 0.3 mol% Cr_2O_3 was added in order to favour bulk crystallization.

The energy of viscous flow in the glass transition range and the activation energies of crystallisation were evaluated by DTA results (Linseiz L81), obtained at 2.5, 5, 7.5, 10 and 20 °C/min using 100–110 mg powder samples (75–125 μm). E_{Tg} was evaluated by T_g variations while the activation energies E_o and E_P—by the variations of T_o and T_P, respectively.

The sintering was studied by 7.5/4.0/4.0 mm^3 "green" samples, prepared by 75–125 μm glass powder fractions, pressed at 100 MPa. After 30 min holding at 270 °C (to eliminate the PVA binder) the samples were heated at 2.5, 5, 10 and 20 °C/min in a differential dilatometer (Netzsch 402 ED). In this instrument,

Table 1
Chemical compositions of the studied glasses (mol%)

	G1	G2	G2-Cr	G3
SiO_2	54	58	58	62
Al_2O_3	2	4	4	6
Cr_2O_3	–	–	0.3	–
CaO	21	17	17	13
MgO	21	17	17	13
Na_2O	2	4	4	6