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Studio al Microscopio Elettronico a Scansione della porosità indotta dalla cristallizzazione di vetro-ceramici con composizione diopside-albite sinterizzati.

Study of crystallization induced porosity in sintered glass-ceramics with diopside-albite compositions by Scanning Electron Microscopy.

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SUMMARY

Sintered glass-ceramic, belonging to pseudo-binary system diopside - albite, were studied by Scanning Electron Microscopy. The investigated compositions are characterized with formation of crystallization induced porosity and by surface or bulk crystallization in the grains.

The samples were obtained at different heat-treatment and using various glass fractions. The surfaces and fractures of the specimens were observed by SE and BSE techniques and the results were compared with ones, obtained after polishing of the samples and etching with 2 wt % HF for different times.

SEM observations showed the presence of two different types of porosity: intergranular residual pores with irregular shape and smooth surface and intragranular induced crystallization pores with semi-spherical shape and an indented polycrystalline surface.

It was highlighted that some residual porosity always remains in the material after the end of sintering, while the crystallization induced porosity is formed latter and its amount increases as a function of the percentage of crystal phase formed.

These results were confirmed by additional investigations made by pycnometry measurements and XRD.

1. INTRODUCTION

The sinter-crystallization is an alternative method for glass-ceramics production. In this case, materials are obtained by a single heat-treatment, during which processes of densification and phase formations take place simultaneously. However, when the crystallization is very intensive the sintering may be hindered, which leads to the formation of materials with some residual intergranular porosity. At the same time, due to the density variation associated with the phase formation, the crystallisation might also produce an additional intragranular porosity. The formation of this new *induced crystallisation porosity*, P_{CR} , was recently investigated and highlighted in a series of our works (Karamanov and Pelino, 2006a, 2006b, 2008); last year this phenomenon was also confirmed and discussed by other scientific groups (Bernardo et al, 2008; Goel et al., 2008; Yang et al., 2008).

The present study summarises results about P_{CR} formation in a well-studied model composition, belonging to the pseudo-binary system diopside – albite. The reported results were obtained by Scanning Electron Microscopy, applying different techniques and preparative procedures.

2. EXPERIMENTAL

A glass with composition (in mol %) SiO_2 -54, Al_2O_3 -2, CaO -21, MgO -21, Na_2O -2 was melted at 1500°C , the melt was quenched in water in the obtained frits were milled and sieved in different fractions. This glass is characterised by a good sinterability and formation of about 60 wt % diopside by surface crystallization.

"Green" samples with initial size of 7/10/10 were prepared by mixing glass powders with 7.5 % PVA solution and by pressing at 100 MPa.

After drying and a 30 min heat-treatment at 270°C (to eliminate the PVA), the samples were held for times between 1 min and 7 h at different temperatures, using heating and cooling rates of $20^\circ\text{C}/\text{min}$. The densification was evaluated measuring apparent, ρ_a , skeleton, ρ_s , and absolute, ρ_{gc} , densities and estimating the total, P_T , closed, P_C , and open, P_O , porosities:

$$P_T = 100 \frac{\rho_{gc} - \rho_a}{\rho_{gc}} \quad (1) \quad P_C = 100 \frac{\rho_{gc} - \rho_s}{\rho_{gc}} \quad (2)$$

$$P_O = P_T - P_C \quad (3)$$

ρ_a was measured by a dry flow pycnometer (GeoPyc 1360), while ρ_s and ρ_{gc} by He displacement Pycnometer (AccuPyc 1330). Firstly, the skeleton density was measured and then the absolute density after crashing and milling

the samples below 26 μm . Crystalline fraction formed, x (wt %), was also evaluated by the density results through the following expression:

$$x = 100 \frac{\frac{1}{\rho_g} - \frac{1}{\rho_{gc}}}{\frac{1}{\rho_{g(cr)}} - \frac{1}{\rho_{cr}}} \quad (4)$$

ρ_g is absolute density of the parent glass, ρ_{gc} is absolute density of the glass-ceramic, $\rho_{g(cr)}$ is density of a hypothetical glass with composition of the formed crystal phase and ρ_{cr} is density of the crystal phase.

The obtained glass-ceramics were investigated with Scanning Electron Microscopy (Philips XL30CP) using fractured or polished samples. The polishing procedure was made by two steps: “grinding” and “polishing”. During the first step, the samples were treated consecutively with 600, 1000 and 1200 SiC grid (10-15 min for each grinding); during the second step, the samples were polished for 15-20 min successively with 9, 3 and 1 μm diamond paste suspensions. After each of the treatments the samples were cleaned in ultrasonic bath with alcohol and observed by optical microscopy. After that the samples were etched with 2 % HF solution for 3 or 10 sec. The fractures were observed mainly by SE techniques (after Au metallization), while the polished samples were principally studied by BSE technique (without metallization, at 20 KV and at controlled vacuum of 0.5 mBar).

3. RESULTS

The initial period of sinter-crystallization (at 800 °C for fraction 75-125 μm) is highlighted in Figs. 1-6. Fig. 1 shows a SE image of a fracture after 1 min holding, which elucidates neck formation between the grains (i.e. an earlier stage of densification). Fig. 2 shows a fracture after 1 h step and demonstrates a complete sintering and beginning of surface crystallization.

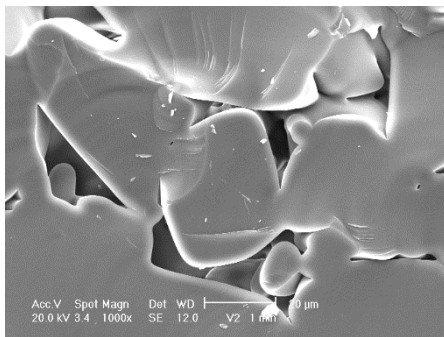


Figure 1. SE image of fracture (1 min at 800°C).

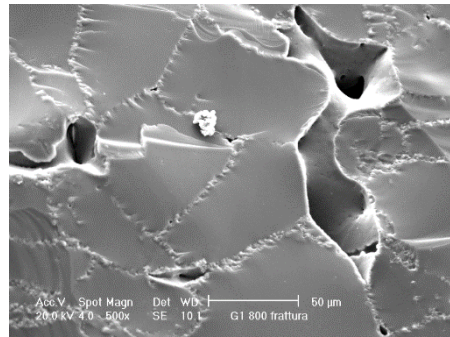


Figure 2. SE image of fracture (1 h at 800°C).

Figures 3 and 4 elucidate the beginning of diopside formation at higher magnifications after 2 h. Fig. 3 shows crystallization, starting from the surface of a residual pore, while Fig. 4 demonstrates the boundary between two well sintered particles.

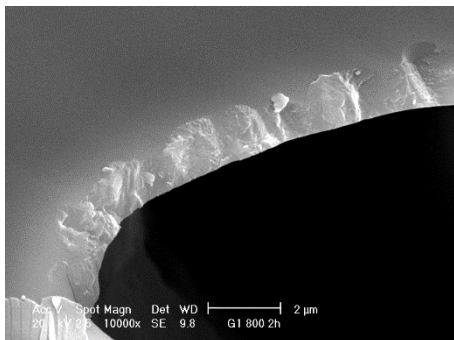


Figure 3. Beginning of surface crystallization from a residual pore (SE, fracture).

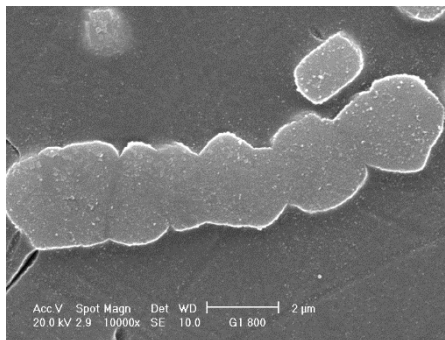


Figure 4. Beginning of surface crystallization between sintered grains (SE, polished)

Figs. 5 and 6 show BSE images of polished sample after 1 h step, obtained after 3 seconds etching. The comparison between photos 2 and 5, as well as between 3 and 6, clearly demonstrate that the SE technique give better information about the structure of sintered samples and the morphology of diopside crystals at the initial stage of phase formation.

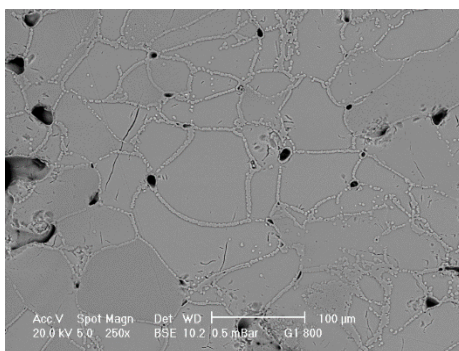


Figure 5. BSE image (1 h at 850°C, 3 sec etching) (low magnification).

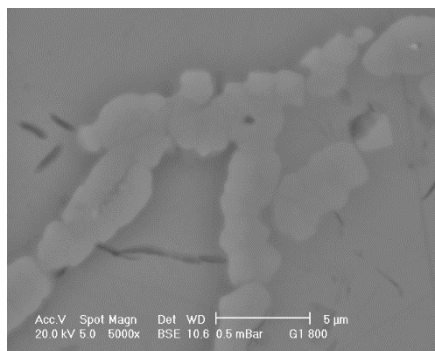


Figure 6. BSE image (1 h at 850°C, 3 sec etching) (high magnification).

The structure of glass-ceramic with a complete sinter-crystallization (fraction 75-125 μm after 1 h at 900°C) is shown in Fig. 7-10. Figs. 7 and 8 present SE images of a fractured sample and a crystallization induced pore in the centre of particle, respectively. The last object, studied by BSE after 3 seconds etching, is also shown in Fig. 9, whereas Fig. 10 presents another crystallization induced pore, observed after 10 seconds etching with 2 % HF. In this case, the comparison between SE and BSE images highlight that the

BSE technique is more appropriated to study the final structure of sinter-crystallized samples.

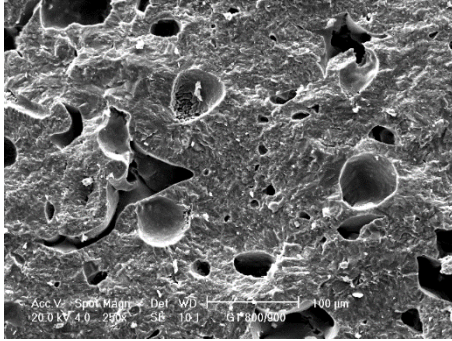


Figure 7. SE image (fracture, 1 h at 900°C).

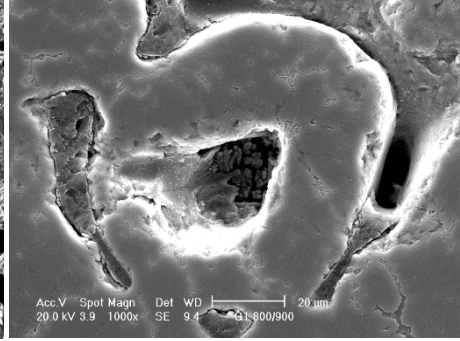


Figure 8. SE image (polished, 1 h at 900°C).

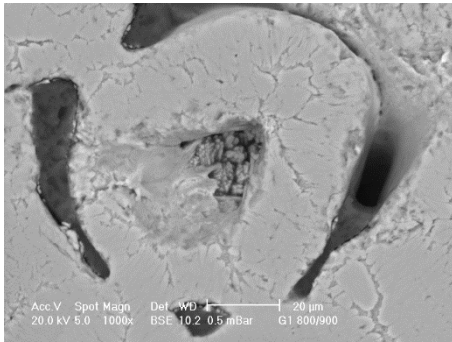


Figure 9. BSE image (1 h at 900°C, 3 sec etching).



Figure 10. BSE image (1 h at 900°C, 10 sec etching).

Figs. 11, 12 and 13 demonstrate the increasing of crystallinity vs. time for fraction 0.53-0.75 μm at 800 oC (after 1, 4 and 7 h holding, respectively). Fig. 11 shows that during the initial stage of crystallization no additional intragranular porosity is formed, while Fig. 14 demonstrates a typical crystallization induced pores in the end of heat-treatment (after 7 h step), which shows that the morphology of new pores at lower temperature is not “well-distinguished” as ones at higher temperature (Fig. 9 and 10).

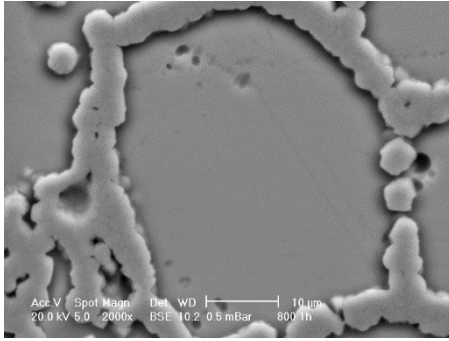


Figure 11. BSE image (1 h at 800°C).

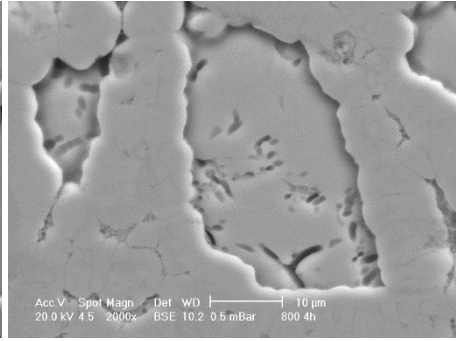


Figure 12. BSE images (4 h at 800°C).

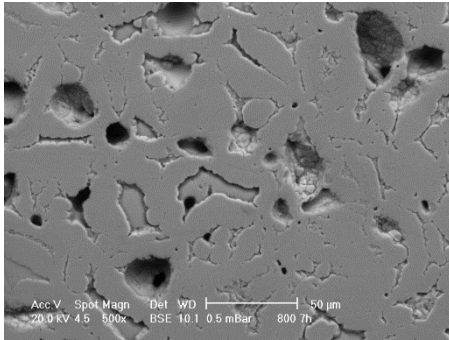


Figure 13. BSE images (7 h at 800°C).

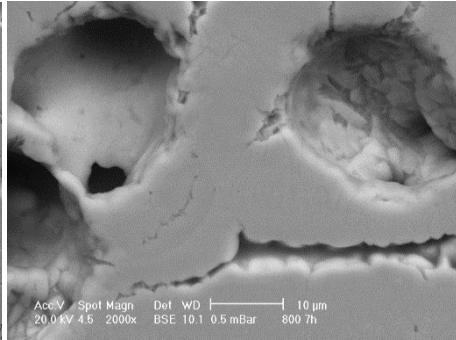


Figure 14. BSE images of crystallization induced pore formed at 7 h at 800°C.

Fig. 15 demonstrates variations of crystallinity, open and closed porosity, obtained by pycnometry for fraction 0.53-0.75 μm at 800°C, which confirm the SEM observations. In fact, assuming that about 4% residual closed porosity always remain in samples, it follows that the formation of additional intragranular crystallization induced porosity starts after the formation of 25-30 % diopside. The difference between structures of crystallization pores, formed at 800 and 900°C, might be partially explained by “classical” diagram of glass transitions (Fig. 16), which shows that an additional dilatational shrinkage, ΔL_{DEL} , can be added to the crystallization shrinkage, ΔL_{CR} , when phase formation carries out at higher temperature.

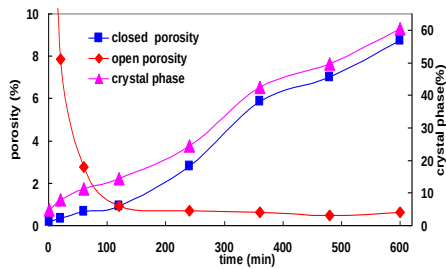


Figure 15. Crystallinity and porosity vs. time.

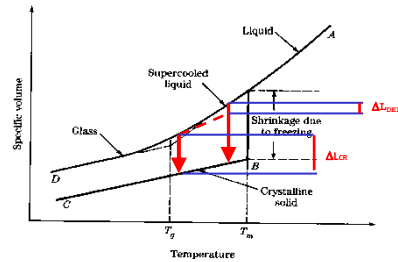


Figure 16. Glass transition diagram.

AKNOWLEDGMENTS

The authors acknowledge the financial support within Project TK-X-1713/07.

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