P2O5 AS AN EFFECTIVE NUCLEATING AGENT OF LITHIUM DISILICATE GLASS-CERAMICS

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Abstract The objective of the study was to control the nucleation and main crystal formation of lithium disilicate, Li2Si2O5, by an effective nucleating agent to develop high-strength, translucent glass-ceramics. The authors used P2O5 as nucleating agent to precipitate lithium disilicate in glasses derived from the SiO2-Li2O-Al2O3-K2O-ZrO2 system. The concentration of P2O5 was up to approx. 3 wt.%. Additives of P2O5 allowed the control of bulk crystallization. Nucleation was catalyzed by Li3PO4 phases. Li3PO4 is the heterogeneous catalyst. The final glass-ceramic is characterized by a dense microstructure with a high crystalline content of more than 70 vol.%. The mechanical strength was determined as biaxial flexural strength of approx. 740 MPa and Weibull factor of 11.3. The glass-ceramic shows the potential to be applied as a biomaterial for dental restorations. The authors conclude the effectiveness of P2O5 as nucleating agent on the basis of a heterogeneous nucleation of nanophases and precipitating main crystal phases by epitaxial growth.

INTRODUCTION

Nucleation of lithium silicate crystals in glass-ceramics was reported by Beall [1], James [2], Headley and Loeman [3]. It was possible to precipitate both lithium metasilicate, Li2SiO3, to develop Fotoform® or lithium disilicate, Li2Si2O5, to develop Fotoceram® as devices for micromechanics (Beall [1]). High strength glass-ceramics with flexural strength of 400 to 500 MPa were developed in multi-component glass-ceramics with the main crystal phase of lithium disilicate as a material with a self glazing effect (Echeverría [4]), or oriented crystals prepared by extrusion (Rüssel [5]), or prepared by pressing an SiO2-Al2O3-ZnO-Li2O-K2O-P2O5 glass-ceramic (Schweiger et al.[6], Höland et al.[7]).

Recently, the authors of this paper reported on nucleation, phase formation and solid state reaction in a colored ZnO-free lithium disilicate glass-ceramic characterized by translucent properties and an unexpected high flexural strength of more than 700 MPa (Höland et al. [8]). The basis of the previous study [8] is also a ZnO-free composition, but without coloring components. The main aim of this present study is the characterization of the mechanical properties using P2O5 as nucleating agent.

EXPERIMENTAL

Based of the fundamental study of nucleation and phase formation processes [8] the composition of 73.8 wt% SiO2, 3.5 Al2O3, 15.3 Li2O, 4.0 K2O and 3.3 P2O5 was
selected. Raw materials as quartz, aluminum oxyhydroxy hydrate, aluminum metaphosphate, lithium carbonate, potassium carbonate were used. Three times melting at 1400 °C to 1500 °C allowed the preparation of an homogeneous base glass. This glass was cast into 20 blocks of approx. 14 mm x 14 mm x 30 mm, annealed at 500 °C for 10 min to nucleate the glass and cooled to room temperature with 3-5 K/min. The nucleated glass samples were annealed at 700° for 20 minutes. Crystallization of Li2SiO3 took place during heat treatment. Three disks of approx. 1.6 mm in thickness and 13 mm in diameter were prepared from each glass-ceramic block by milling with the dental CEREC® 3 apparatus (Sirona, Germany). That is, 60 samples were processed with this technique. To precipitate lithium disilicate, these 60 disks were heat treated at 850 °C for 10 minutes. An grinding procedure (apparatus: Buehler, Metaserv Motopol 12), using SiC-paper of different degrees (600 to 1000) was applied to prepare the final products of samples having a size of 1.2 ± 0.2 mm thickness and 13 mm in diameter. According to a dental standard [9], these samples (with the given specific diameters of the disks) were used to determine the biaxial flexural strength (one point on three balls) using apparatus (Zwick, Universalpruefmaschine 1456, Germany). The fractured surface of the samples was investigated with scanning electron microscope, SEM, apparatus DSM 962 (Zeiss, Germany) to determine the microstructure of the glass-ceramic. The fractured samples were etched with 40% HF vapor for 30 sec. Room temperature X-ray diffraction, XRD, was performed to determine the main crystal phases of the final product with AXS D 5005 (Bruker, Germany). 20 indentations were also used to determine the fracture toughness as KIC according to Evans and Charles [10] by Vickers indentation.

RESULTS

The flexural strength of the glass ceramics could be characterized with an average value of 740.8 MPa and an standard deviation of ±79.7 MPa. Figure 1(a and b) shows the Weibull statistics of these samples. According to Fig. 1 b the Weibull factor was determined as m=11.3. The fracture toughness, as KIC was measured with 3.13 MPa·m1/2 and standard deviation of ±0.25 MPa·m1/2.

Because of the very high flexural strength of the material, it was a special interest to study the microstructure of the final glass-ceramic. The SEM investigation demonstrated an interlocking microstructure of the crystal phase lithium disilicate in the glassy matrix (Figure 2). The black parts of this figure represent the glassy phase that was surrounded by lithium disilicate crystals. Li3PO4 crystals are located as nanophases in the bulk of lithium disilicate crystals.

The XRD investigations were concentrated on crystal phase formation an a careful study of secondary crystal phases in the volume or the surface areas of the glass-ceramic. Figure 3 shows the XRD pattern of the glass-ceramic with the main crystal phase of lithium disilicate and lithium orthophosphate, Li3PO4, as a secondary phase. But no other phases were determined, neither in the bulk, nor in surface areas. In other words the XRD pattern were equal in surface and bulk areas.
Figure 1 Flexural strength of a lithium disilicate glass-ceramics

a) survival rate

b) Weibull plot
Figure 2 Microstructure of an lithium disilicate glass-ceramic with P₂O₅ as nucleating agent. Etched sample. SEM.

Figure 3 XRD pattern of a lithium disilicate glass-ceramic. Li₃PO₄ represents the secondary phase.
DISCUSSION

The short term heat treatment of the glass-ceramic in the nucleation range for 10 min and the 20 min, respectively 10 min annealing to precipitate crystals in the glassy matrix was very effective and resulted in a dens microstructure. Compared to other types of glass-ceramics shown in a general overview by Höland and Beall [11], the microstructure has to be characterized as an interlocking microstructure. It turns out that a primary crystal growth is dominating the crystal precipitation with the effect that crystals came into contact with each other. The glassy matrix is isolated into islands. Therefore, crack propagation in the glassy matrix is inhibited by crystals. This special microstructure is the reason for a very high flexural strength of more than 700 MPa combined with a translucency of the material. It is well known that the surface quality of the material influences the flexural strength. But such high flexural strength is close to those of sintered ceramics of Al₂O₃-type. This effect is surprising, because the flexural strength was reached without ion exchange in surface areas of the glass ceramic. In the 70th and 80th, glass-ceramics were developed with ion exchange reactions resulted in high strength. But these materials was sensitive to small surface cracks and the material failed and was limited applied in industry (Höland and Beall [11]).

XRD studies of this glass-ceramic also demonstrated lithium disilicate as main and Li₃PO₄ as secondary phase. Therefore, as shown in previous studies [8] Li₃PO₄ reacts as heterogeneous catalyst in the glass-ceramic. But no additional crystal phase formation was determined in surface areas of the glass-ceramic.

The Weibull factor of 11.3 gives the option of a good reliability of the material and allows a practical application as biomaterial for dental restoration, especially as metal-free framework for dental crowns or dental bridges. It is possible to veneer this glass-ceramic with an other type of glass-ceramic, e.g. an fluorapatite containing glass-ceramic.

CONCLUSION

The authors conclude P₂O₅ as a very effective nucleating agent to develop high strength glass-ceramics with lithium disilicate as the main crystal phase. The very high flexural strength combined with translucency and high fracture toughness is a result of an interlocking microstructure of the material.

REFERENCES