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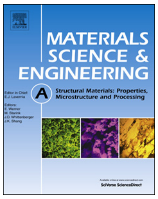

Effects of crystal size on the mechanical properties of a lithium disilicate glass-ceramic

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ABSTRACT

Crystal size of lithium disilicate (LD) phase in a LD glass-ceramic was changed by thermally controlled crystallization of a precursory LD glass at different temperatures. Effects of the crystal size on the mechanical properties of the glass-ceramic were investigated. It was found that the flexural strength presented a hump-like variation trend with increasing the crystal size, the hardness monotonously decreased at the same time. It was further confirmed that micro residual compressive stresses existed inside the LD crystals due to the thermal expansion mismatch between the glass matrix and the crystalline phase. The levels of the residual stresses increased with increasing the crystal size. The crystal size performed dual effects on the flexural strength of the glass-ceramic: an "interlocking effect" caused by larger-sized LD crystals and a "micro residual stress effect" related to the balancing tensile stresses in the glass matrix. Higher residual tensile stresses in the glass matrix induced by larger-sized LD crystals would counteract the "interlocking effect" of the crystals, causing the strength degradation. The hardness of the glass-ceramic was mainly controlled by the "micro residual stress effect".

1. Introduction

Glass-ceramics consisting of glass matrixes and crystalline phases are usually manufactured by thermally controlled crystallization of monolithic glasses [1]. Glass-ceramics combine the properties of crystalline ceramics with those of glasses, showing manifold domestic and technological applications these days [2,3]. Some glass-ceramics are attracting extensive attention in prosthetic dentistry because of their designable mechanical properties combined with translucency and biocompatibility [4–6]. Currently, leucite glass-ceramics based on SiO_2–Al_2O_3–K_2O materials system and lithium disilicate (LD) glass-ceramics based on SiO_2–Li_2O materials system are two important types of commercially available glass-ceramics for dental applications [7,8]. Furthermore, LD glass-ceramics find applications in various other areas such as functional coatings for heat- and corrosion-resistant purposes, advanced materials for hermetic glass-ceramic-to-metal seals at elevated temperatures due to their attractive mechanical, physical and chemical properties [9,10].

There are a lot of works reporting the effects of composition, heat treatment or crystallization behavior on the mechanical properties of glass-ceramics [1,2,11–13]. The key factors for strengthening glass-ceramics have been explored [3–8]. For leucite glass-ceramics with tetragonal leucite as the main crystalline phase, the strengthening mechanism was correlated with a "micro residual stress effect" [5]. Upon cooling after controlled crystallization, a cubic to tetragonal transformation with volume contraction would occurred for the leucite phase [14,15]. The thermal expansion coefficient (TEC) of the tetragonal leucite phase was much higher than that of the corresponding glass matrix [14–16]. These two factors could cause residual tensile stresses inside the crystals along the radial direction at room temperature, which would be balanced by residual compressive stresses in the glass matrix along the tangential direction [3]. The residual compressive stresses in the glass matrix could divert crack forces, resulting in fracture resistance improvement [15]. Thus, the "micro residual stress effect" has been thought to be a key factor for strengthening leucite glass-ceramics [14–18].

For LD glass-ceramics with orthorhombic LD crystals as the main crystalline phase, the strengthening mechanism was correlated with an "interlocking effect" [19]. The peculiar rod-like LD crystals in the glass-ceramics formed interlocking microstructures, which could retard crack progression in the glass-ceramics, resulting in effective strengthening [1,20,21]. Based on the effect, the strength and fracture toughness of LD glass-ceramics are usually much higher than those of leucite glass-ceramics [4,22,23].

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In fact, micro residual stresses could also exist in LD glass-ceramics due to the TEC mismatch between the glass matrix and the crystals, although no phase transformation was observed for the orthorhombic LD phase upon cooling after controlled crystallization [24]. The average linear TECs of orthorhombic LD phase and the corresponding glass matrix were estimated to be 10.1–10.8 × 10^{-6}/K and 12.2–12.8 × 10^{-6}/K respectively [1,24,25]. Residual compressive stresses inside the crystals along the radial direction and the balancing residual tensile stresses in the glass matrix along the tangential direction would arise at room temperature [3,24]. It appears that the micro residual stress state in LD glass-ceramics is just opposite to that in leucite glass-ceramics. The following question is raised: how do the micro residual stresses in LD glass-ceramics affect their mechanical properties? This issue is important for the applications of LD glass-ceramics not only in dentistry but in various other areas such as coatings, glass-ceramic-to-metal seals etc. It was expected that the residual stresses had a negligible effect on the mechanical behavior of LD glass-ceramics duo to the strong “interlocking effect” of the rod-like LD crystals [1]. However, it was reported that distinct strengthening could be achieved in LD glass-ceramics by residual stress relief annealing [13]. The issue is still not clear up to now.

In the present work, LD crystal size in a LD glass-ceramic was changed by thermally controlled crystallization. Effects of the crystal size on the mechanical properties were investigated. The “interlocking effect” and “micro residual stress effect” of the LD crystals were considered simultaneously. The results should be helpful to better understand the strengthening mechanism of LD glass-ceramics.

2. Material and methods

2.1. Precursory glass preparation

Preparation of bulk LD glasses could be achieved by uniform mixing of raw material powders (e.g., silica, lithium carbonate, metaphosphate, etc), and melting of the mixtures for a long period (e.g., 2 h) even several times to form homogeneous melts and obtain glasses with uniform composition after casting the melts into moulds [1,2,19–21]. In this work, a commercially popular LD glass-ceramic with uniform composition, namely IPS e.max® Press (Ivoclar Vivadent) [8], was used as an original material. The LD glass-ceramic ingots with a same batch number were melted in a Pt-crucible at 1450 °C for a short period of 30 min in air. The melts were cast into shape in a graphite mould, which was pre-heated to 500 °C, to form precursory glass blocks with dimensions of 60 × 22 × 5 mm^3 (length, width and thickness). The glass blocks were immediately annealed at 500 °C for 30 min and subsequently cooled inside furnace to room temperature to minimize the temperature gradients across the glass blocks' sections. The obtained glass blocks were transparent and homogeneous, displaying a very light amber color. The compositional integrity of the glass blocks was checked by means of X-ray fluorescence (XRF) and atomic absorption spectrometry (AAS) [2,26]. Compared with the original glass-ceramic ingots, no detectable change in composition was found for the glass blocks post the short time melting.

Monolithic amorphous nature of the as-prepared glass was confirmed by X-ray diffraction (XRD) using an X'Pert Pro diffractometer with Cu-K_α radiation (λ=0.15418 nm), as shown in the inset in Fig. 1. Crystallization characteristic of the glass was analyzed by differential scanning calorimetry (DSC) in a SETARAM LabsysTM TG DSC, using a high-purity alumina crucible and a heating rate of 40 K/min. Fine glass powders with a maximum particle size of about 3 μm and a mass of 30 ± 1 mg were used for the DSC measurement. The glass powders were obtained by grinding pieces of the glass using an agate mortar, and the particle sizes were estimated by scanning electron microscopy (SEM) using a Hitachi S-4800 microscope. Fig. 1 shows the corresponding DSC curve. It can be seen that the glass presented two exothermic crystallization peaks on the DSC curve with peak temperatures of T_{p1} ~ 610 °C and T_{p2} ~ 799 °C respectively. The double-peak crystallization character was common for the multi-component LD glass-ceramic system containing P_2O_5 as a volume nucleating agent [19,27]: the first peak corresponded to the transformation from glass to lithium metasilicate phase, and the second peak was related to the formation of LD phase. The onset and end temperatures, T_{o2} and T_{e2}, of the second peak were estimated to be ~ 755 °C and ~ 843 °C respectively. The melting point, T_m, was estimated to be ~ 900 °C.

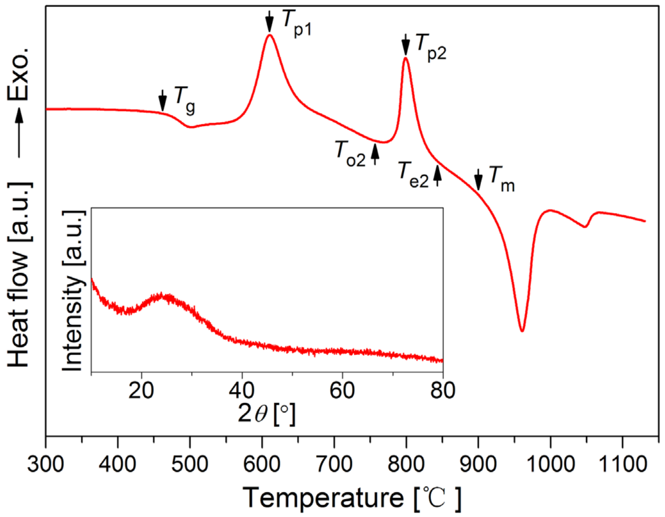

Fig. 1. DSC curve of the precursory glass. The inset shows the corresponding XRD pattern of the glass.

2.2. Glass-ceramic specimen preparation

From the precursory glass blocks, forty plate-shaped glass bars with dimensions of 22 × 4.5 × 2.5 mm^3 (length, width and thickness) were cut using a diamond saw under a well-cooling condition. Based on the characteristic temperature values obtained from the DSC curve in Fig. 1, four groups of the glass bars were heat-treated according to the two-step annealing profiles listed in Table 1 to prepare glass-ceramic specimens. The first step at 610 °C (T_{p1}) for all specimens was designed to form lithium metasilicate phase [19,27]. The second steps at 755 °C, 799 °C, 843 °C and 900 °C (T_{o2}, T_{p2}, T_{e2} and T_m) respectively for specimens G1–G4 were designed to form LD phase. The heating rate used for the heat-treatments was controlled to be consistent with the heating rate for the DSC experiment in Fig. 1 (40 K/min). To achieve equilibrium crystallinities after the second step treatments, the annealing time was increased with decreasing the annealing temperature [28,29]. The specimens were furnace-cooled down to room-temperature after the treatments.

Table 1.
Crystallization annealing profiles for the glass-ceramic specimens.

Group No.	Annealing profiles
G1	610 °C/1 h +755 °C/8 h
G2	610 °C/1 h +799 °C/4 h
G3	610 °C/1 h +843 °C/2 h
G4	610 °C/1 h +900 °C/1 h