Journal of the Mechanical Behavior of Biomedical Materials 78 (2018) 28–35

Contents lists available at ScienceDirect

Journal of the Mechanical Behavior of Biomedical Materials

journal homepage: www.elsevier.com/locate/jmbbm

Understanding the mechanism for the mechanical property degradation of a lithium disilicate glass-ceramic by annealing

D. Li[a], X.C. Li[a], Z.Z. Zhang[b], S.F. Zhang[b,*], L. He[a,*]

[a] State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, China
[b] State Key Laboratory of Military Stomatology, Department of Prosthodontics, School of Stomatology, Fourth Military Medical University, Xi'an 710032, China

ARTICLE INFO

Keywords:
Glass-ceramics
Lithium disilicate
Mechanical characterization
Residual stresses
Annealing

ABSTRACT

Post-crystallization annealing above the T_g was applied to a lithium disilicate glass-ceramic with microstructure consisting of glassy matrix and rod-like lithium disilicate crystals, effect of the annealing on the mechanical behavior was investigated. Flexural strength and VIF toughness of the glass-ceramic unexpectedly decreased after the annealing. The mechanical behavior variation was understood based on residual micro-stress analysis. Coefficient of thermal expansion for the glassy matrix presented a tendency to increase after the annealing, which would enlarge the thermal expansion mismatch between the glassy matrix and the lithium disilicate crystals. As a result, the residual micro-stresses in the glass-ceramic abnormally increased with increasing the annealing time. The mechanical property degradation was attributed to the annealing-induced increase of the residual micro-stresses.

1. Introduction

Glass-ceramics are dual-phase materials consisting of glassy matrix and crystalline phases, which are usually manufactured by thermally controlled crystallization of their parent glasses (Zanotto, 2010). Glass-ceramics combine the properties of crystalline ceramics with those of glasses, finding manifold domestic and technological applications these days (Dittmer et al., 2014; Serbena and Zanotto, 2012). Some glass-ceramics are attracting extensive attention in prosthetic dentistry because of their designable mechanical properties combined with suitable translucency and excellent biocompatibility (Höland et al., 2007). Currently, lithium disilicate (LD) glass-ceramics based on SiO_2–Li_2O materials system have been commercially available glass-ceramics for dental applications via press or CAD/CAM technology (Tang et al., 2014). There are a lot of works reporting the effect of heat treatment or crystallization behavior on the mechanical behavior of LD glass-ceramics (Lien et al., 2015; Monmaturapoj et al., 2013; Serbena et al., 2015; Zhang et al., 2014). The strengthening mechanism was correlated with an "interlocking effect": peculiar rod-like LD crystals in LD glass-ceramics formed interlocking microstructure, which could retard crack progression, resulting in effective strengthening (Höland et al., 2006; Wen et al., 2007; Zhao et al., 2015).

In fact, residual micro-stresses are always present in glass-ceramics upon cooling to room-temperature after crystallization due to thermal expansion mismatch between the glassy matrix and crystalline phases (Pinto et al., 2007; Zanotto, 2010). The stresses certainly affect the overall mechanical performance of this kind of material (Zanotto, 2010). If coefficient of thermal expansion (CTE) for the glassy matrix is smaller than that for the coexisting crystalline phase, tangential compressive stresses can develop in the glassy matrix around the crystals upon cooling and act later as crack deflectors, resulting in toughening of the glass-ceramic (Denry and Holloway, 2004). This was considered responsible for the significant strengthening in leucite glass-ceramics based on SiO_2–Al_2O_3–K_2O materials system (Cattell et al., 2005; Chen et al., 2010, 2011; Denry et al., 1996). For LD glass-ceramics, however, the CTE of the glassy matrix (about 12.2–12.8 $\times$ 10^{-6}/K) is larger than that of the orthorhombic LD crystalline phase (about 10.1–10.8 $\times$ 10^{-6}/K). On the contrary, tangential tensile stresses can develop in the glassy matrix surrounding the LD crystals upon cooling (Mastelaro and Zanotto, 1999; Pinto et al., 2007; Serbena and Zanotto, 2012; Serbena et al., 2015). The tensile micro-stresses might counteract the "interlocking effect" of LD crystals, causing strength decrease (Li et al., 2016). The following question is raised: how can the residual micro-stresses in LD glass-ceramics be affected by the manufacture process?

Post-crystallization annealing treatment above the glass transition temperature, T_g, was usually recommended for glass-ceramic components in order to relieve the residual macro-stresses owing to temperature and/or density gradients across the sections upon cooling (Denry and Holloway, 2004; Fischer et al., 2005; Serbena et al., 2015; Zhang et al., 2014). For dental restorations made of glass-ceramics via

* Corresponding authors.
E-mail addresses: sfzhang@fmmu.edu.cn (S.F. Zhang), helin@mail.xjtu.edu.cn (L. He).

https://doi.org/10.1016/j.jmbbm.2017.11.003
Received 25 September 2017; Received in revised form 31 October 2017; Accepted 2 November 2017
Available online 03 November 2017
1751-6161/

press or CAD/CAM technology, repeated firing above the T_g was usually unavoidable to relieve the residual macro-stresses associated with grinding and polishing procedures, or to achieve color and shape corrections for their esthetic quality (Gozneli et al., 2014). It was expected that residual micro-stresses owing to CTE mismatch in glass-ceramics could not be affected by post-crystallization annealing treatments (Pinto et al., 2007; Serbena et al., 2015). There is no direct evidence for the conclusion up to now. In fact, structural rearrangement in a glass could occur during annealing above the T_g, which caused its physical property change (Wurth et al., 2009; Zeng and Hing, 2002). This type of situation might also occur in the glassy matrix in a glass-ceramic. In the present work, post-crystallization annealing above the T_g was applied to a LD glass-ceramic, effect of the annealing on the mechanical behavior was investigated. Based on residual micro-stress analysis, the mechanical behavior variation was correlated with the annealing response of the CTE mismatch in the LD glass-ceramic. The results should be helpful to better understand the strengthening mechanism in LD glass-ceramics.

2. Material and methods

2.1. Parent glass preparation

Based on previous research works (Höland et al., 2006; Yuan et al., 2013), a dental LD glass with the nominal composition of $65.5SiO_2$–$27.5Li_2O$–$1.2P_2O_5$–$1.8K_2O$–$2.0Al_2O_3$–$1.5ZrO_2$–$0.5CeO_2$ (in mol%) was prepared from reagent grade raw materials of silica, lithium carbonate, aluminium metaphosphate, potassium carbonate, alumina, zirconia and ceria powders. The powders were wet-mixed (with ethanol) in a rotating PTEF jar with agate grinding media for 2 h. The mixture was melted in a Pt-crucible at 1450 °C in an electric furnace for 2 h in air. The molten glass was quenched into cold distilled water to form a glass frit. The frit was dried, and then re-melted in the Pt-crucible at 1450 °C for 1 h and at 1500 °C for 0.5 h. The re-molten glass was cast into shape in a graphite mould, which was pre-heated to 500 °C, to form a block with dimensions of 60 × 22 × 5 mm^3 (length, width and thickness). The glass block was air-cooled down with the graphite mould to room-temperature.

The obtained glass blocks were transparent and homogeneous, their monolithic amorphous nature was confirmed by X-ray diffraction (XRD) using an X'Pert Pro diffractometer with Cu-K_α radiation (λ = 0.15418 nm). The compositional integrity of the glass blocks was checked by means of X-ray fluorescence (XRF) and atomic absorption spectrometry (AAS). Compared with the nominal composition, the maximum relative deviations of the concentration measurement results were ± 3% for SiO_2 and Li_2O, and ± 5% for other oxides. Crystallization characteristic of the parent 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. The glass began glass transition at a temperature of $T_g \sim 463$ °C, and presented two exothermic crystallization peaks on the DSC curve (Li et al., 2016). The double-peak crystallization behavior was considered a particular character for multi-component LD glass-ceramic system containing P_2O_5 as a volume nucleating agent (Höland et al., 2006; Soares et al., 2015).

2.2. Glass-ceramic specimen preparation

From the parent glass blocks, 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 crystallization characteristic, all the glass bars were thermally crystallized by a two-step heat treatment process of 610 °C/1 h + 900 °C/1 h to prepare the glass-ceramic specimens (Li et al., 2016). The first step at 610 °C corresponded to lithium metasilicate phase precipitation in the parent glass, and the second step at 900 °C was designed to form LD phase (Höland et al., 2006; Soares et al., 2015). The specimens were air-cooled down to room-temperature after the thermally controlled crystallization. After this, post-crystallization annealing treatments at 500 °C (above the T_g) were applied to some of the obtained glass-ceramic specimens for 15 and 180 min respectively to investigate the annealing effect on the mechanical behavior. The specimens were furnace-cooled down to room-temperature after the post-crystallization annealing.

Following the guidelines of ISO 6872, (2008), the lateral faces of the plate-shaped glass-ceramic specimens were wet-ground using SiC grinding papers and polished with diamond suspensions. Final dimensions of 22 × 4 × 2 mm^3 (length, width and thickness) were obtained for all the specimens.

Using the X'Pert Pro diffractometer, structure of the glass-ceramic specimens was checked directly on their wider lateral surfaces. The microstructure was observed by scanning electron microscopy (SEM) using a Hitachi S-4800 microscope on the same surfaces. The observed surfaces were etched with 5% hydrofluoric acid solution for 4 min, and sputtered with Pt.

2.3. Mechanical testing

Three-point bending method can be used to evaluate the flexural strength of glass-ceramics (ISO 6872, 2008). Flexural strength of the LD glass-ceramic was investigated by three-point bending test using the prepared plate-shaped specimens. The test was performed on a screw-driven SUNS CMT4204 testing machine at a constant cross-head displacement rate of 0.5 mm/min. The flexural strength, σ_f, was calculated by the following relation (ISO 6872, 2008):

$$\sigma_f = \frac{3Pl}{2wt^2} \quad (1)$$

where P is the breaking load, l is the test span (15 mm), w and t are the width and thickness of the specimens respectively.

Intrinsic fracture resistance of glass-ceramics can be accurately and reliably evaluated by the internationally standardized fracture toughness methods for ceramics and other brittle materials (Quinn and Bradt, 2007). In addition, the Vickers indentation fracture (VIF) method has also been employed to estimate the fracture resistance of glass-ceramics because of its expediency (Huang et al., 2013; Monmaturapoj et al., 2013; Serbena et al., 2015; Tang et al., 2014). Although the VIF method was discredited due to its ill-defined crack arrest condition (Quinn and Bradt, 2007), it is still a popular experimental technique for estimating the fracture toughness of brittle materials up to now (Huang et al., 2013). In the present work, fractured segments of the three-point bending specimens were used for the indentation measurements using a Vickers micro-hardness tester. It is generally known that the VIF results may be strongly affected by residual stresses in the near-surface zones of the specimens. The residual stresses may be introduced also by the grinding and polishing processes, which are often solved by additional stress relief treatment before the VIF testing (Serbena et al., 2015). Under the subject and purpose of this study, it is not appropriate to apply additional stress relief treatment to the specimens in different annealing states. To decrease the effect of surface condition on the VIF results, all the specimens were finally mirror-polished with a 0.5 μm diamond suspension to achieve similarly high surface finish. Topographic features of the surfaces were acquired using a NANOVEA PS50 3D optical profilometer with scanning step-sizes of 10 μm in X and Y directions and a resolution of 2 nm in Z direction. The roughness values, S_a (ISO 25178-2, 2012), of the surfaces were controlled as 0.101 ± 0.012 μm (0.8 mm cutoff length). The indentation measurements were conducted on the surfaces with two loads of 5 N and 50 N respectively, the dwell time was 15 s. The lower load 5 N was employed to determine the Vickers hardness of the glass-ceramic, no cracking formed around the Vickers impressions under the load. The higher load 50 N was chosen to generate cracks along the diagonals of the square Vickers impressions, no spalling around the impressions was observed.