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Effect of the microstructure on the mechanical properties of $CaO–P_2O_5–SiO_2–MgO–F^-$ glass ceramics

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Abstract

$CaO–MgO–P_2O_5–SiO_2–F^-$ glass-ceramic which contains apatite and mica crystalline phases can be used to repair and reconstruct diseased or damaged bones and teeth because of their biocompatibility and bioactivity. Like other glass-ceramics, the mechanical properties of material depend on their microstructure. In this paper, the relationship between the microstructure and the mechanical properties of $CaO–MgO–P_2O_5–SiO_2$ glass-ceramics containing fluorophlogopite and fluorapatite was analyzed with DTA, SEM, XRD techniques and some mechanical testing methods. The results showed that the sample heated at 810 °C for 4 h had smaller crystalline size and less volume fraction of fluorophlogopite, so it had higher bending strength (190 MPa) and higher crack toughness (2.63 $MPa·m^{1/2}$).

Keywords: B. Microstructure; C. Mechanical properties; D. Glass ceramics; Fluorapatite; $CaO–MgO–P_2O_5–SiO_2–F^-$ system

1. Introduction

Research and development investigations on biological glass-ceramic materials have been underway for recent years [1–3]. The development of biomaterials for restorative dentistry is concentrated on fulfilling the high expectations regarding the strength, shade, translucency, chemical resistance, and wear of the material. At the same time, the material must be essy to use for both dental technicians and dentists. Today, dentists may fabricate dental restorations by using special materials and CAD/CAM technology. Bioactive glass-ceramics containing fluorophlogopite and fluorapatite can fulfil the special request. Because in addition to good bioactivity, this kind of glass-ceramics also shows good machinability due to the existence of layered mica phase. Consequently, it is easier to process mica-based glass-ceramics into complex shaped surgical parts by using normal clinical machining methods [4]. This kind of glass-ceramics have also been studied for more than 10 years [5].The relationship between phase separation, nucleation and crystallization had been investigated [6]. But the microstructure-property relationships during crystallization in this kind of glass-ceramics appear rarely investigated.

2. Experimental procedure

The material investigated was produced by mixtures of SiO_2(20–40), Al_2O_3(10–30), MgO(10–30), MgF_2(5–20), $CaHPO_4$(10–30), $CaCO_3$(20–40) and ZrO_2(1–10) (wt.%). Glass batches were ball-milled for 24 h, and thereafter melted in a platinum crucible at 1400∼1450 °C for 3 h. The melts were poured onto a steel plate, annealed for 1 h at 600 °C, and cooled to ambient temperature in the furnace. The resulting glass was crushed and sieved through a 200 mesh to produce a powder suitable for DTA. Measurements (Differential thermal Analyzer, Dupont 2100) were performed with Al_2O_3 powder as a reference material. The samples were heated in air from ambient temperature to 1200 °C at a heating rate of 10 °C/min. XRD experiments were performed using a X-ray powder diffractometer (D8 Advance) operating at 40 kv and 25 mA, using Cu K_α radiation and a Ni filter, with the heattreated samples crushed to a fine powder and scanned at 2°per minute. The bulk specimens of before and after heat-treatment were surface polished with diamond paste to a 0.5 μm finish and acid etched. Then the

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microstructural studies on these specimens were done by scanning electron microscope (6301F). The bulk samples after heat-treatment were cut to the size of 3×4×36 mm^3 and 4×6×30 mm^2. Four point bending strength values were measured, using rectangular specimens (3×4×36 mm^3). Fracture toughness was determined by the SENB method, using rectangular specimens (4×6×30 mm^2). For each sample, six measurements were made in the air for the two experiments.

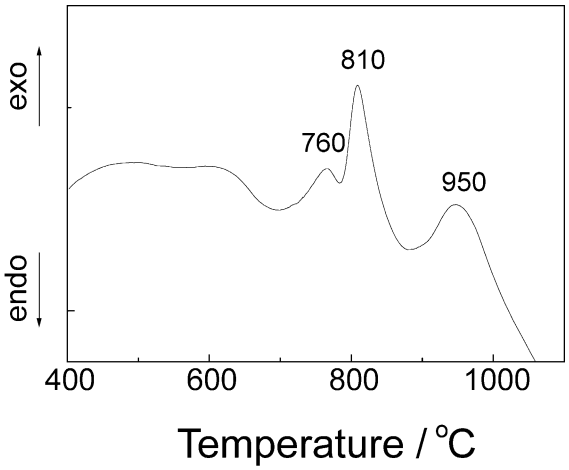


Fig. 1. DTA curve of the sample.

3. Results and discussion

3.1. Thermal analysis

Fig. 1 shows the 10?/min linear heating DTA thermogram. Three exothermal peaks were observed, which according to the results of X-ray (see Section 3.2), can be associated with the following crystallization steps:

1. Leucite;
2. Fluorapatite;
3. Fluorophlogopite.

3.2. XRD analysis

Fig. 2a is the XRD pattern of the sample before heating treatment. It was found that the sample is fully

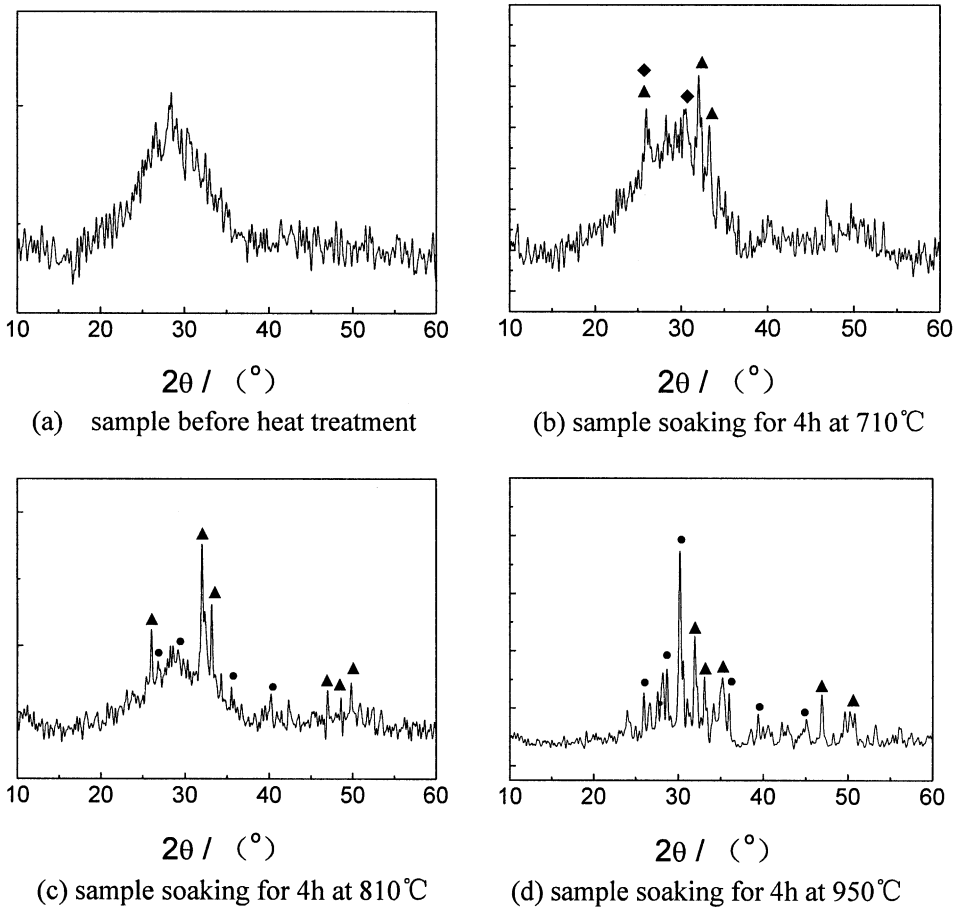


Fig. 2. XRD patterns of the specimens: ▲, $Ca_5(PO_4)_3F$, ●, $KMg_{2.75}Al_{0.5}O_{10}F_2$, ◆, $KAlSi_2O_6$.

amorphous. Fig. 2b, 2c, 2d show the X-ray diffraction patterns of the samples after heating up to 760 °C, 810 °C, 950 °C soaking for 4 h, respectively. Fig. 2b proves that at 710 °C, the leucite and fluorapatite appear, but most of the sample is still amorphous. According to Fig. 2c, at 810 °C, the predominant crystalline phase is fluorapatite, and a little of fluorophlogopite appears. Finally Fig. 2d indicates that there are two crystalline phases in the sample at 950 °C which are fluorapatite and fluorophlogopite.

From the intensities of the X-ray lines the fraction of the different phases formed during the three different heating treatments can be determined approximately (Fig. 2). It is found that at the temperature of the first peak in Fig. 1 about 75% of the sample is amorphous, the rest is leucite and fluorapatite (Fig. 2b). The fraction of the amorphous phase decreases during the higher temperature heating treatments. At the temperature of the second peak, the amount of fluorophlogopite is half of that of fluorapatite, and about 15% of the sample is amorphous (Fig. 2c). At the third peak, the percentages of fluorapatite and fluorophlogopite are equally about 45% (Fig. 2d).

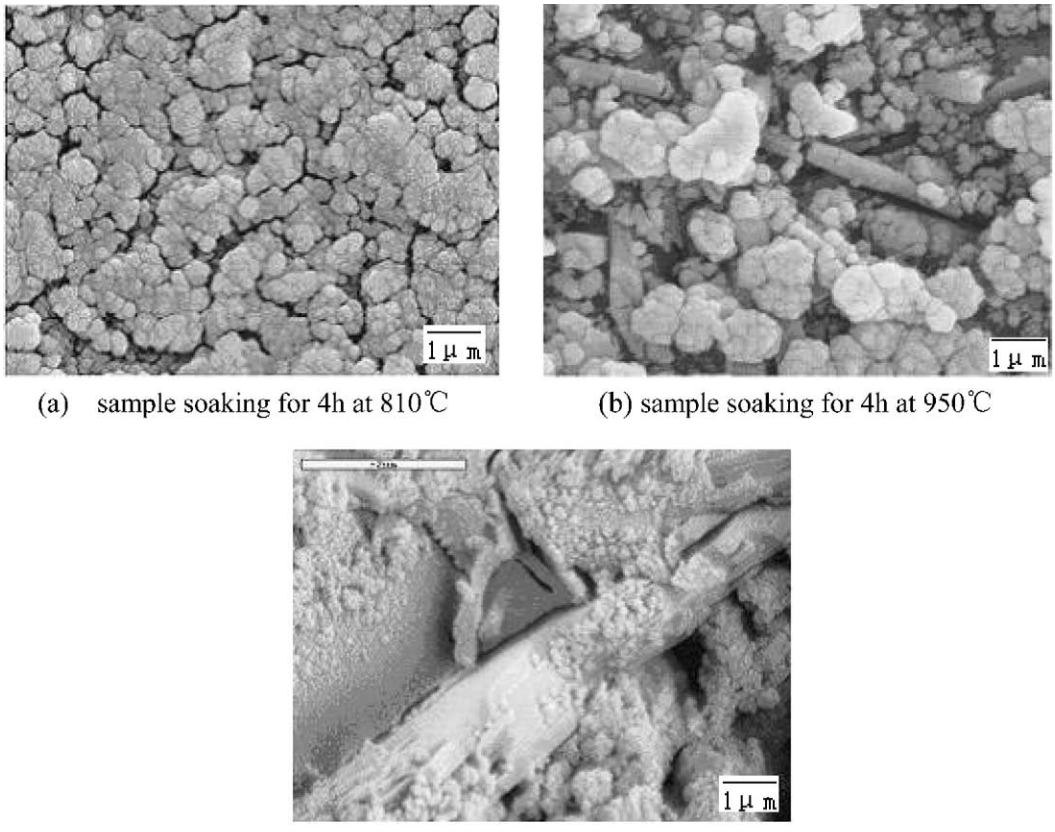
From the above discussion, it can be concluded that fluorapatite and fluorophlogopite are the predominant crystalline phases of this glass-ceramics, fluorapatite being the low-temperature crystallizing phase (810 °C), and fluorophlogopite the high-temperature crystallizing phase (950 °C).

3.3. Microscopic examinations

Fig. 3 shows the micrographs of the sample after crystallization. The microstructure of 810 °C (Fig. 3a) have smaller crystalline size compared with that of 950 °C (Fig. 3b). There exist the lamellar mica phases in the sample soaked for 4 h at 810 °C observed from Fig. 2c. But the crystalline size is too small to be observed in Fig. 3a. When the sample was heated up to 950° and soaked for 4 h, the fluorophlogopite phases can be observed (Fig. 3b). When the sample was heated up to 1100 °C, the very coarse layered fluorophlogopite microstructure appears in the sample, which will result in the rapid decrease of the mechanical properties. The following discussions also approve it.

3.4. Mechanical test

The variations of bending strength and fracture toughness versus temperature are shown in Fig. 4. Generally, the fluorophlogopite has the layered microstructure, so it has good machinability. But the bending

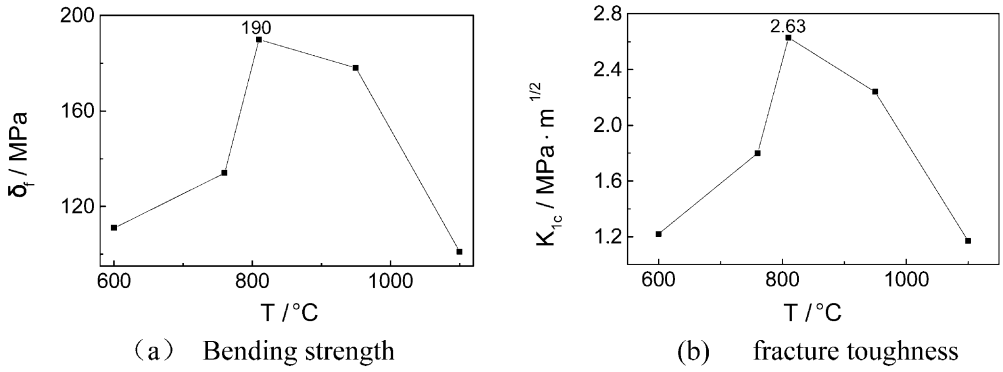


(a) sample soaking for 4h at 810℃

(b) sample soaking for 4h at 950℃

(c) sample soaking for 4h at 1100℃

Fig. 3. SEM micrographs of samples.



(a) Bending strength (b) fracture toughness

Fig. 4. The curves of the relationship between δ_f, K_{1c} and temperature.

strength and the fracture toughness of the sample containing mica phase will decline with the increase of the crystalline size and the volume fraction of mica. Fig. 4 proves it. The sample treated at 810 °C has the smaller crystalline size and less volume fraction of mica phase compared with that of 950 °C, so it shows higher bending strength and fracture toughness. When the sample heated at 1100 °C for 4 h, the very coarse crystal will result in the rapid decrease of the strength and toughness, from 190 MPa and 2.63 MPa $m^{1/2}$ at 810 °C to 101 MPa and 1.17 MPa $m^{1/2}$ at 1100 °C. And the sample treated at 810 °C has less amorphous compared with that of 600 °C and 710 °C, so it has higher mechanical properties.

4. Conclusions

For the studied glass-ceramics, fluorapatite is the low-temperature crystallizing phase (810 °C), fluorophlogopite is the high-temperature crystallizing phase (950 °C). This rule is important for the future research and application of this glass-ceramics. The mechanical properties are related to the microstructure. When the sample is all amorphous, the bending strength and fracture toughness are all very low. After crystallization, the mechanical properties decrease with the increase of the crystal size and the volume fraction of fluorophlogopite phase. The results show that the sample soaking for 4 h at 810 °C has the highest values of mechanical properties.

References

[1] V.K. Marghussian, A. Mesgar, Sheikh-Mehdi, Effects of composition on crystallization behaviour and mechanical properties of bioactive glass-ceramics in the MgO–CaO–SiO_2–P_2O_5 system, Ceram. Int. 26 (2000) 415–420.

[2] M. Laczka, K. Cholewa-Kowalska, A. Laczka-Osyczka, M. Tworzydlo, B. Turyna, Gel-derived materials of a CaO–P_2O_5–SiO_2 system modified by boron, sodium, magnesium, aluminum, and fluorine compounds, J. Biomed. Mater. Res. 52 (2000) 601–612.

[3] M. Laczka, K. Cholewa, Laczka-Osyczka A, Gel-derived powders of CaO–P_2O_5–SiO_2 system as a starting material to production of bioactive ceramics, J. Alloys Compounds 248 (1997) 42–51.

[4] W. Holand, W. Vogle, An Introduction to Bioceramics, World Scientific, Singapore, 1993, pp. 125–137.

[5] W. Hoeland, K. Naumann, W. Vogel, Machinable, Bioactive glass ceramics material, German Patent, DE 3306648A, 22 September 1983.

[6] X.F. Chen, L.L. Hench, D. Greenspan, Investigation on phase separation, nucleation and crystallization in bioactive glass-ceramics containing fluorophlogopite and fluorapatite, Ceram. Int. 24 (1998) 401–410.