Journal of University of Science and Technology Beijing
Volume 9, Number 3, June 2002, Page 212

Effect of crystallization of $CaO-P_2O_5-SiO_2-MgO-F^-$ glass-ceramics on its mechanical properties

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(Received 2001-12-06)

Abstract: The microstructure of $CaO-P_2O_5-SiO_2-MgO-F$ glass-ceramics during crystallization were investigated and the crystallized phases were identified with DTA (Differential Thermal Analysis), SEM (Scanning Electron Microscope) and XRD (X- ray Diffraction) techniques. The mechanical properties such as bending strength and fracture toughness, as well as their changes with advancing crystallization were determined. The results show that the changes of the mechanical properties are correlated with the microstructures. The sample heated up to 810℃ and soaked for 4 h has smaller crystalline size and less volum fraction of fluorophlogopite, so it has higher bending strength (about 190 MPa), and higher crack toughness (about 2.63 $MPa \cdot m^{1/2}$).

Key words: biologic glass-ceramic; microstructure; $CaO-P_2O_5-SiO_2-MgO-F$ system; crystallization

Bioactive glasses and glass ceramics are very promising biomaterials that have been successfully applied to repair and reconstruction of diseased or damaged hard tissues (bones and teeth) of humans [1-4]. The glass-ceramics containing fluorophlogopite and fluorapatite has been studied for more than ten years [5-7]. This kind of glass-ceramics has not only good bioactivity, but also good machinability due to the existing of layered mica phase. Consequently, it is easier to process mica-based glass-ceramics into surgical parts with various complex shapes by normal clinical machining methods [8-10]. The relationship between phase separation, nucleation and crystallization had been investigated [11]. But the changes of mechanical properties with the microstructures during crystallization in this kind of glass-ceramics have not been reported yet.

In this work, the fluorophlogopite and fluorapatite were identified. The relationship between the mechanical properties and microstructures were investigated.

1 Experimental

1.1 Glass preparation

The material investigated was produced from powders of SiO_2(35), Al_2O_3(15), MgO(8), MgF_2(10), $CaHPO_4$(12), $CaCO_3$(17) and ZrO_2(3), by mass ratio. Glass batches were ball-milled for 24 h, and then melted in a platinum crucible at 1 400-1 450℃ for 3 h . The melting samples were poured onto a steel plate, annealed for 1 h at 600℃, and cooled to ambient temperature in the furnace.

1.2 Differential thermal analysis

Above prepared 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 powders as a reference material. The samples were heated in air from ambient temperature to 1 200℃ at a heating rate of 10 ℃/min.

1.3 Microstructure analysis

The microstructure studies on the glass and the crystallized glass were done by scanning electron microscope (6301F). Crystalline phases in glass-ceramic specimens were identified by X-ray powder diffractometer (D8 Advance).

1.4 Mechanical tests

Bending strength values were measured by four point loading method, using rectangular specimens (3 mm×4 mm×36 mm). Fracture toughness was determined by SENB method, using rectangular specimens (4 mm×6 mm×30 mm). For each sample, six reduplicate measurements were made in the air for the two experiments.

2 Results and discussion

2.1 Thermal analysis

Figure 1 shows the 10 ℃/min linear heating DTA thermogram. Three exothermal peaks were observed. According to the results of X-ray (see section 2.2), the-

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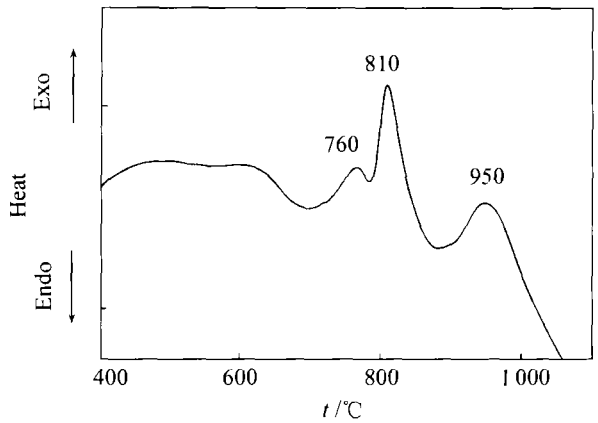

Figure 1 DTA curve of the sample.

se peaks may be associated with the following crystallization steps: Leucite; Fluorapatite; Fluorophlogopite.

2.2 XRD analysis

Figure 2(a) is the XRD pattern of the sample before heating treatment. It is found that the sample is fully amorphous. Figure 2(b), (c), and (d) show the X-ray diffraction patterns of the samples after heating up to 760, 810, 950℃ and soaking for 4 h, respectively. Figure 2(b) proves that at 760℃, the leucite and fluorapatite appear, but the most of the sample is still amorphous. According to figure 2(c), at 810℃, the predominant crystalline phase is fluorapatite, and a little of fluorophlogopite appears. Finally figure 2 (d) indicates that there are two crystalline phase in the sample at 950℃ 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 (figure 2).

It is found that at the temperature of the 1st peak in figure 1 about 75% (volume fraction) of the sample is amorphous, the rest is leucite and fluorapatite (figure 2 (b)). The fraction of the amorphous phase decreases during the higher temperature heating treatments. At the temperature of the 2nd peak the amount of fluorophlogopite is half of that of fluorapatite. And about 15% of the sample is amorphous (figure 2(c)). At the 3rd peak, the ratio of fluorapatite and fluorophlogopite are equally about 45% (figure 2(d)).

From the above discussion, it can be concluded that fluorapatite and fluorophlogopite are the predominant crystalline phases of this glass-ceramics. And the fluorapatite is the low-temperature depositional phase (810℃), the fluorophlogopite is the high-temperature depositional phase (950℃).

2.3 Microscopic examination

Figure 3 shows the micrographs of the sample after

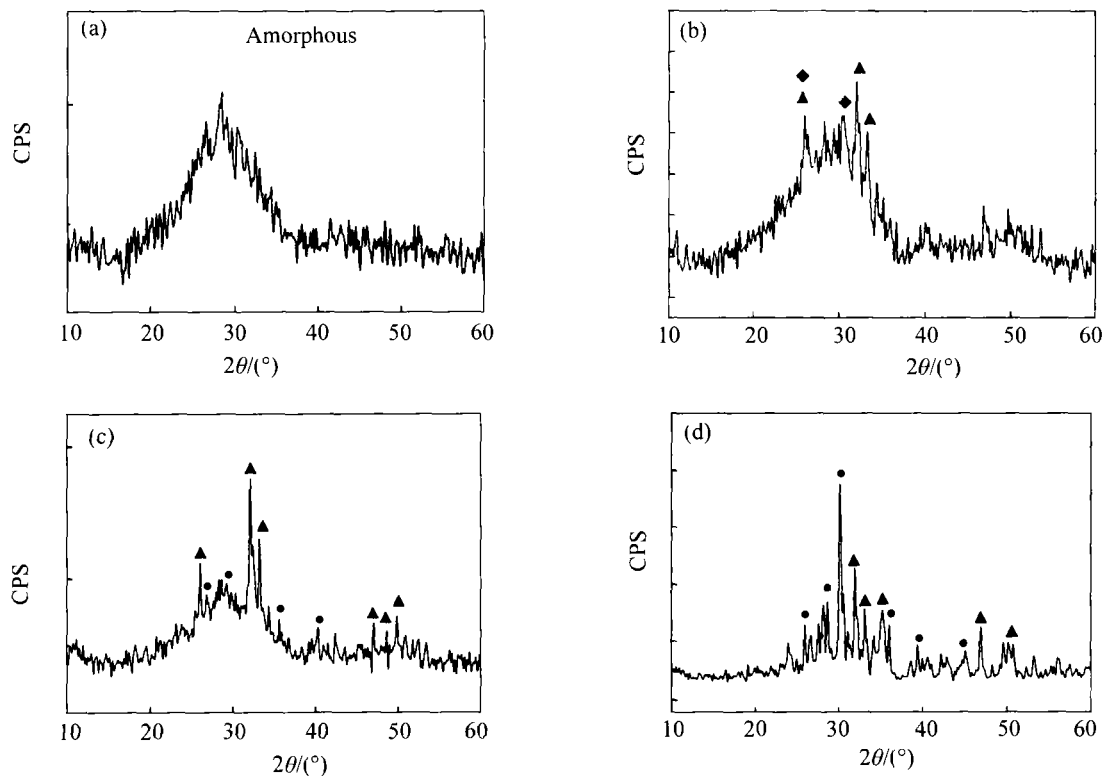

Figure 2 XRD patterns of the specimens, (a) sample before heat treatment; (b) sample soaking for 4 h at 760℃; (c) sample soaking for 4 h at 810℃; (d) sample soaking for4 h at 950℃. ▲—$Ca_5(PO_4)_3F$; ●—$KMg_{2.75}Al_{0.5}O_{10}F_2$; ◆—$KAlSi_2O_6$.

crystallization. The microstructure of 810℃ soaked specimen (figure 3 (a)) have smaller crystalline size compared with that of 950℃ soaked (figure 3 (b)). There exist the lamellar mica phases in the sample soaked for 4 h at 810℃ according to figure 2(c). But the crystalline size is too small to be observed in figure 3 (a). When the sample was heated up to 950℃ and soaked for 4 h, the fluorophlogopite phases can be observed as shown in figure 3(b). When the sample was heated up to 1 100℃, very coarse layered fluorophlogopite microstructure appears in the sample, which will result in the rapid decrease of the mechanical properties. The following results also approve it.

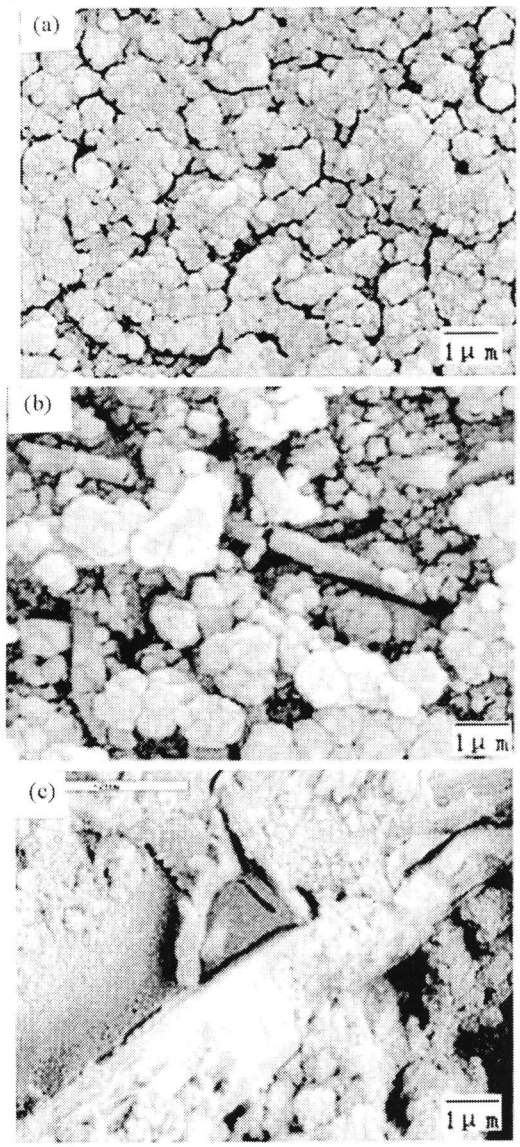

Figure 3 SEM micrographs of samples, (a) sample soaking for 4 h at 810℃; (b) sample soaking for 4 h at 950℃; (c) sample soaking for 4 h at 1 100℃.

2.4 Mechanical test

The variation of bending strength and fracture toughness *versus* temperature is shown in **figure 4**. Generally, the fluorophlogopite has the layered microstructure, so it has good machinability. But the mechanical properties of the sample containing mica phase will decrease with the increase of the crystalline size and the

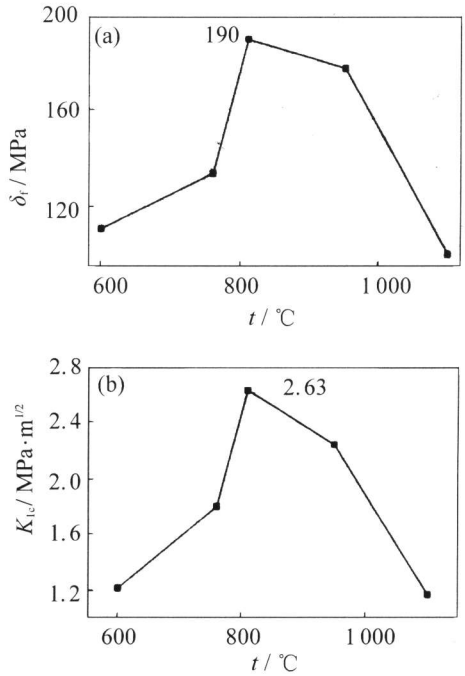

Figure 4 Curves of the relationship between δ_f, K_{1c} and soaked temperature, (a) bending strength; (b) fracture toughness.

volume fraction of mica. The sample treated at 810℃ has the smaller crystalline size and less volume fraction of mica phase compared with that of 950℃, so it shows higher bending strength and fracture toughness. When the sample heated up to 1 100℃ and soaked for 4 h, very coarse crystal resulted in the rapid decreasing of the mechanical properties, from 190 MPa and 2.63 MPa·m$^{1/2}$ of 810℃ soaked to 101 MPa and 1.17 MPa·m$^{1/2}$of 1 100℃ soaked. And the sample treated at 810℃ has less amorphous compared with that of 600℃ and 710℃, so it has higher mechanical properties.

Figure 5 gives the microstructure of the fracture surface of the samples. The fracture mode is layered crack, due to the existing of the mica cleavage plane. The lamella of sample soaked for 4 h at 810℃ is the smallest and the most homogeneous out of the all samples observed in figure 5, correspondingly the sample has the smallest crystalline size (figure 3(a)). So its fracture toughness is the highest (2.63 MPa·m$^{1/2}$).

4 Conclusions

(1) To study glass-ceramics, the fluorapatite is the low-temperature depositional phase (810℃), the fluorophlogopite is the high-temperature depositional phase (950℃). This rule is important to the future research and application of this glass-ceramics.

(2) The mechanical properties are related to the microstructure. When the sample is all amorphous, the bending strength and fracture toughness are all very

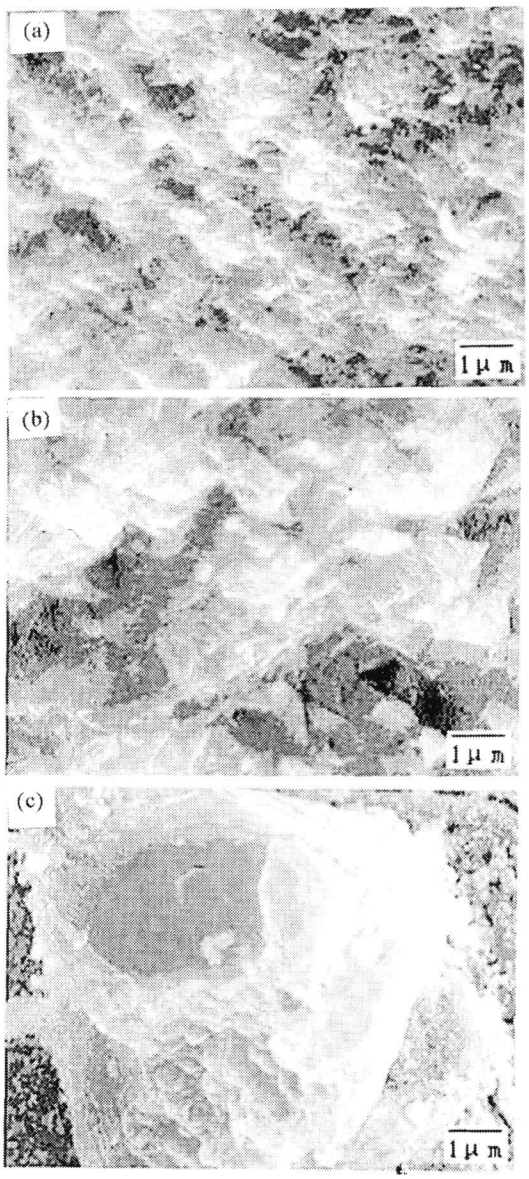

Figure 5 SEM micrographs of cracked samples, (a) sample soaking for 4 h at 810℃; (b) sample soaking for 4 h at 950℃; (c) sample soaking for 4 h at 1 100℃.

low. After crystallization, the mechanical properties decrease with the increase of the crystallization size and the volume fraction of fluorophlogopite phase. The results show that the sample soaked for 4 h at 810℃ has the highest values of mechanical properties.

(3) The SEM micrographs of the fracture surface show that the fracture mode is layered crack. The reason is that there exist lamellar fluorophlogopite phases in the samples.

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