Preparation of Fluoramphibole Glass Ceramics by The Mechanochemistry Method

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Abstract: The fluoramphibole glass ceramics were successfully prepared by mechano-chemistry method using waste glass and fluormica powder. The effects of ball milling parameters on synthesis of fluoramphibole glass ceramics were studied by means of XRD and SEM. The mechanical properties of the samples were discussed. The results show that the optimum preparation conditions were as follows: the processing of 10 to 1 ball to powder weight ratio, rotation speed of 800 rpm and milling of 45 minutes. Under these conditions, the highest value of modulus of rupture for fluoramphibole glass ceramics is 41.73 MPa.

1. Introduction
High energy ball milling can crush the powder to micron or nanometer particles through strong impacting, grinding and agitating, to increase the density of the prepared samples and improve the performance of the samples[1-3]. The sintering-reactive crystallization method, to fabricate a fluoramphibole glass ceramics[4-6] using waste glass powder as the main raw material by adding fluormica crystals into the glass powder. The fluoramphibole glass ceramics can widely applied in environmental protection building materials, because of its good possessing machinability [7].

The fluoramphibole crystals are randomly staggered and connected by the residual glass to form the crystal framework of the glass ceramics, which strengthens the mechanical properties of the fluoramphibole glass ceramics[8]. Fluoramphibole glass ceramics can produce compressive stress and have good thermal shock resistance. At first, people didn't find the processability of fluoramphibole glass ceramics. With the further research on this kind of glass ceramics, it was found that apart from the excellent mechanical properties, fluoramphibole glass ceramics also has good processability, which can be used as dental restorative materials. The fluoramphibole-fluorapatite glass ceramics prepared by adding P₂O₅ also has biological activity and was a potential artificial bone material. The solvability of fluoramphibole crystal makes the fluoramphibole glass ceramics machinable, being similar to the fluoramphibole glass ceramics.

Up to now, the preparation method of fluoroamphibole glass ceramics is still melting method, using two-step heat treatment for crystallization. The research on the mechanism of fluoramphibole crystallization in fluoramphibole glass ceramics was still in its infancy. The influence of the type of nucleating agent and glass composition on fluoramphibole crystallization and the growth law of fluoramphibole crystal was still under further study[9].
In this study, fluoramphibole glass ceramics was prepared by high energy ball milling with mixed powder of waste glass and fluormica. The effects of ball milling parameters on synthesis of fluoramphibole glass ceramics were studied. The mechanical property of the samples was discussed.

2. Experimental

Preparation of fluoramphibole glass ceramics. The fluoramphibole glass ceramics were prepared by mechanochemistry method using waste glass powder (size of 100 mesh) and fluormica powder (size of 130 mesh). The effects of different preparation processes on the fluoramphibole glass ceramics were investigated by changing the ball material ratio (5:1, 10:1, 15:1), rotating speed (400 rpm, 600 rpm, 800 rpm) and milling time (15 min, 30 min, 45 min). The 6 wt% PVA water solution as a binder was added by drop to the mixed powder, then press the powder into a square compacts at 5 MPa. The square compacts (size of 60 mm×60 mm×5 mm) were sintered with temperature of 900 ºC and holding time with 2 h.

Characterization of fluoramphibole glass ceramics. The crystalline phase of the fluoramphibole glass ceramics was characterized by x-ray diffraction (XRD, Empyrean) with Cu Kα radiation. The morphology of the fluoramphibole glass ceramics were coated with a thin film of gold and were observed by scanning electron microscopy (SEM, JSM-6360LV). The mechanical properties of the fluoramphibole glass ceramics were determined by anti-snapped experiment instrument (DPK-500). The calculation formula was as follows:

$$R = \frac{3}{2} \times \frac{FL}{bh^2}$$

R—Fracture modulus, MPa;  
F—Maximum failure load, N;  
L—Distance between fulcrum, mm;  
b—Specimen width, mm;  
h—Minimum thickness of specimen at break, mm

3. Results and Discussion

Fig.1 shows the XRD patterns of glass ceramics obtained from waste glass and fluormica powder with different ball material ratio. The XRD patterns indicate that fluoramphibole were the only crystallized component at different ball material ratio, which consistedent with the standard diffraction lines of fluoramphibole (JCPDS No.41-1429)[10]. As the XRD patterns show that nothing changes in diffraction peaks and diffraction intensity at higher ball material ratio.

![Fig.1 XRD patterns of glass ceramics with different ball material ratio](image)

The morphologies of fluoramphibole glass ceramics with different ball material ratio were shown in Fig.2, they were rodlike in the glass matrix. As can be seen clearly in the Fig.2, there were fine rod-shaped fluoramphibole crystals distributed in the three figures, intersecting vertically and horizontally, forming a dense structure.
The fluoramphibole glass ceramics prepared with different ball-to-material ratios as variables were sintered at 900°C. The calculated modulus of fracture of each group were shown in Table 1. According to the fracture modulus data, the fracture modulus of the fluoramphibole glass ceramics prepared at a ball-to-material ratio of 10:1 were the biggest, but it was closed to that of the fluoramphibole glass ceramics under the other two conditions.

Table 1 Fracture modulus of fluoramphibole glass ceramics with different ball-to-material ratio

| The ball-to-material ratio | No. | Maximum load (N) | Specimen width (mm) | Minimum thickness when specimen breaks (mm) | Fracture modulus (Mpa) | Average modulus of rupture (Mpa) |
|---------------------------|-----|------------------|---------------------|--------------------------------------------|-----------------------|---------------------------------|
| 5:1                       | 1   | 607.8            | 55.25               | 4.54                                       | 32.02                 |                                 |
|                           | 2   | 698.7            | 55.32               | 4.60                                       | 35.81                 | 33.04                           |
|                           | 3   | 532.5            | 55.00               | 4.31                                       | 31.27                 |                                 |
|                           | 1   | 615.0            | 54.93               | 4.41                                       | 34.54                 |                                 |
| 10:1                      | 2   | 607.8            | 55.18               | 4.27                                       | 36.25                 | 35.51                           |
|                           | 3   | 602.3            | 55.20               | 4.28                                       | 35.74                 |                                 |
|                           | 1   | 604.5            | 53.50               | 4.48                                       | 33.78                 |                                 |
| 15:1                      | 2   | 618.9            | 53.57               | 4.25                                       | 38.38                 | 35.46                           |
|                           | 3   | 609.2            | 53.93               | 4.45                                       | 34.23                 |                                 |

Fig.3 shows the XRD patterns of glass ceramics obtained from waste glass and fluormica powder with different rotating speed. The XRD patterns indicate that fluoramphibole were the only crystallized component at different rotating speed. As the XRD patterns show that nothing changes in diffraction peaks and diffraction intensity at higher rotating speed.
The morphologies of fluoramphibole glass ceramics with different rotating speed were shown in Fig.4. It can be seen that the dispersion of samples were better when the rotating speed was higher.

The fluoramphibole glass ceramics prepared with different ball milling speed as variables were sintered at 900 ℃. The calculated modulus of rupture of each group were shown in Table 2. Under this condition, the modulus of rupture were the largest at 800 rpm, but the modulus of rupture were significantly reduced at 400 rpm. This was because the smaller the speed of ball milling lead to the uneven the mixing, the worse the performance of the obtained fluoramphibole glass ceramics. It can be seen from the SEM photos that the dispersion of fluoramphibole glass ceramics was the best when the rotating speed was 800 rpm, so it is more appropriate to choose the rotating speed of 800 rpm.

| The rotating speed (rpm) | No. | Maximum load (N) | Specimen width (mm) | Minimum thickness when specimen breaks (mm) | Fracture modulus (Mpa) | Average modulus of rupture (Mpa) |
|-------------------------|-----|------------------|---------------------|--------------------------------------------|-----------------------|---------------------------------|
| 400                     | 1   | 723.5            | 5.19                | 28.90                                      | 28.90                 | 28.90                           |
|                         | 2   | 787.1            | 5.21                | 31.12                                      | 31.12                 | 28.53                           |
|                         | 3   | 604.3            | 5.07                | 25.56                                      | 25.56                 |                                  |
|                         | 1   | 604.1            | 55.07               | 4.48                                       | 32.79                 |                                  |
| 600                     | 2   | 654.7            | 54.86               | 4.56                                       | 34.44                 | 33.75                           |
|                         | 3   | 748.3            | 55.19               | 4.89                                       | 34.02                 |                                  |
|                         | 1   | 615.0            | 54.93               | 4.41                                       | 34.54                 |                                  |
| 800                     | 2   | 607.8            | 55.18               | 4.27                                       | 36.25                 | 35.51                           |
|                         | 3   | 602.3            | 55.20               | 4.28                                       | 35.74                 |                                  |

Fig.5 shows the XRD patterns of glass ceramics obtained from waste glass and fluormica powder with different ball milling time. The XRD patterns indicate that fluoramphibole were the only crystallized component at different rotating speed. As the XRD patterns show that nothing changes in diffraction peaks and diffraction intensity at longer ball milling time.

The morphologies of fluoramphibole glass ceramics with different ball milling time were shown in Fig.6. It can be seen that the reaction crystallization of samples were better when the ball milling time was longer. A large number of elongated rod-shaped crystals were generated from the glass matrix when milling time is 45 minutes.

The fluoramphibole glass ceramics prepared with different ball milling time as variables were sintered at 900 ℃. The modulus of rupture were shown in Table 3. Under these conditions, the fracture modulus were similar from 15 min to 30 min of ball milling, but it was the largest after 45 min of ball milling, the highest value of modulus of rupture for fluoramphibole glass ceramics was 41.73 MPa.
Fig. 5 XRD patterns of glass ceramics with different ball milling time

Fig. 6 SEM images of glass ceramics with different ball milling time (a) 15 min (b) 30 min (c) 45 min

Table 3 Fracture modulus of fluoramphibole glass ceramics with different ball milling time

| The ball milling time (min) | No. | Maximum load (N) | Specimen width (mm) | Minimum thickness when specimen breaks (mm) | Fracture modulus (Mpa) | Average modulus of rupture (Mpa) |
|---------------------------|-----|------------------|---------------------|---------------------------------------------|------------------------|----------------------------------|
|                           | 1   | 707.0            | 54.57               | 4.60                                        | 36.74                  |                                  |
|                           | 15  | 2                | 601.9               | 4.46                                        | 33.16                  | 34.66                            |
|                           | 3   | 689.1            | 54.93               | 4.70                                        | 34.07                  |                                  |
|                           | 1   | 615.0            | 54.93               | 4.41                                        | 34.54                  |                                  |
|                           | 30  | 2                | 607.8               | 4.27                                        | 36.25                  | 35.51                            |
|                           | 3   | 602.3            | 55.18               | 4.28                                        | 35.74                  |                                  |
|                           | 1   | 609.1            | 53.89               | 4.26                                        | 37.37                  |                                  |
|                           | 45  | 2                | 730.1               | 4.36                                        | 42.75                  | 41.73                            |
|                           | 3   | 726.7            | 53.91               | 4.22                                        | 45.07                  |                                  |

4. Summary
The pure phase fluoramphibole glass ceramics can be obtained by changing the ball material ratio, rotating speed and ball milling time with mixed powder of waste glass and fluormica use mechanochemistry method. The optimum preparation conditions were as follows: the processing of 10 to 1 ball to powder weight ratio, rotation speed of 800 rpm and milling of 45 minutes. Under these conditions, the highest value of modulus of rupture for fluoramphibole glass ceramics is 41.73 MPa, which indicates that mechanochemical method can be applied to the prepare high-performance glass ceramics.
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