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Fabrication of hydroxyapatite/diopside/alumina composites by hot-press sintering process

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Abstract

Hydroxyapatite/alumina/diopside ceramic composites were fabricated by hot-pressing. The hardness, fracture toughness and bending strength of the new fabricated composites were measured. The compositions of hydroxyapatite matrix ceramic composites were discussed by XRD and FT-IR analysis. Microstructures of the composites were studied on fracture surfaces. The bending strength and fracture toughness of 58 vol.% hydroxyapatite, 40 vol.% alumina and 2 vol.% diopside sample, were 200 MPa and 2.80 MPa $m^{1/2}$, respectively.

Keywords: A. Hot-pressing; Hydroxyapatite; Alumina; Diopside

1. Introduction

Hydroxyapatite is a kind of calcium phosphate that can be attached and proliferated by cells. It has attracted considerable attention with the rapid development of tissue engineering. Although hydroxyapatite has excellent biocompatibility, it is brittle and easier to break down than human body bone [1–3]. Nowadays more and more studies are dealing with the mechanical properties and the cell or tissue ingrowth properties [4–6]. Meanwhile, additives that improve the fracture toughness of pure hydroxyapatite become more various [6–10]. Mullite, an important structural ceramic material, is a solid solution of alumina and silica and has been investigated as a toughening phase for hydroxyapatite by Nath et al. [7]. The authors assessed two issues in their report, one was the chemical interaction between hydroxyapatite and mullite, and another was hydroxyapatite decomposition in the presence of mullite. The report [7] shows the results that the decomposition of hydroxyapatite to β/α-TCP (tricalcium phosphate) is more favored with increase in mullite content. Niu et al. [9] considered that the toughening effect of SiC_W on hydroxyapatite was good, however, the cost of SiC_W was high and it was difficult to distribute SiC_W homogenously in hydroxyapatite matrix. Furthermore, possessing toxicity, SiC_W is bad for researcher's health. A patent (patent number: 03112066.0) reported the process of preparing hydroxyapatite/carbon nanotube composite, the bending strength and fracture toughness of the composite were 90–180 MPa and 1.0–2.8 MPa $m^{1/2}$ [10], the cost of composite was high and its mechanical properties ranged widely. Diopside is cheap and widely applied in toughening alumina matrix ceramic materials [11–14]. There are few articles reporting toughening effect of diopside and alumina on hydroxyapatite. In order to improve the strength and toughness of hydroxyapatite effectively, and to search for an approach for fabricating high performances of hydroxyapatite matrix ceramic composites with low cost, diopside and alumina are introduced in hydroxyapatite in our present work.

2. Experimental procedure

Hydroxyapatite of high purity (99%) and small grain size (1–3 μm) produced by Department of Materials Science and Engineering in Shandong University, was used as the starting material. Commercial diopside and alumina were selected as

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Table 1
Compositions and mechanical properties of the samples.

No.	Compositions (vol.%)	H_v (GPa)	σ_f (MPa)	K_{IC} (MPa m$^{1/2}$)
1	100% HAp	5.8 ± 1.3	26 ± 3	1.00 ± 0.22
2	10%Al_2O_3 + 70%HAp + 20% diopside	6.3 ± 1.0	89 ± 4	1.41 ± 0.12
3	10%Al_2O_3 + 80%HAp + 10% diopside	6.0 ± 1.5	92 ± 5	1.20 ± 0.13
4	10%Al_2O_3 + 88%HAp + 2% diopside	4.7 ± 1.0	113 ± 6	2.63 ± 0.20
5	30%Al_2O_3 + 68%HAp + 2% diopside	5.3 ± 1.2	162 ± 3	2.40 ± 0.16
6	40%Al_2O_3 + 58%HAp + 2% diopside	5.5 ± 1.9	200 ± 2	2.80 ± 0.10

additives. Diopside is composed of SiO_2 (55 wt.%), CaO (24 wt.%) and MgO (18 wt.%).

The compositions of fabricated hydroxyapatite matrix ceramic composites are listed in Table 1. The samples were marked with 1–6. Raw materials were blended with each other according to certain proportions and ball milled in an alcohol medium to obtain a homogeneous mixture. The slurry was dried in vacuum and screened. Hot-pressing was used to sinter the powder mixture in a graphite die under nitrogen atmosphere. The samples were sintered at 1320 °C (heating rate: 20 °C/min) under a pressure of 20 MPa for 60 min.

The sintered bodies were cut into specimens by an inside diameter slicer. Standard test pieces (3 mm × 4 mm × 36 mm) were obtained through rough grinding, finish grinding with diamond wheels and polishing. Three-point-bending mode was used to measure the bending strength on an electronic universal experimental instrument (WD-10) with a span of 20 mm at a crosshead speed of 0.5 mm/min. Six specimens for each composite were used to measure the bending strength in air at room temperature. Vickers hardness was measured on polished surface with a load of 9.8 N for 5 s on a micro-hardness tester (V-Testor2) produced in Germany. Fracture toughness measurement was performed using indentation method. The indentations on the sample surfaces were generated in a hardness tester (H_v-120), and the formula proposed by Cook and Lawn [15] was used to calculate the final fracture toughness. XRD (D/max-2400) analysis was adopted to identify the phases after sintering. Microstructures of the specimens were studied on fracture surfaces by scanning electron microscopy (HITACHI S-570).

3. Results and discussion

3.1. Mechanical properties of hydroxyapatite/alumina/diopside composites

Mechanical properties of the samples are listed in Table 1. We can see from Table 1 that improved bending strength and fracture toughness are obtained when low-content diopside (2 vol.%) are added in hydroxyapatite matrix ceramic material (samples 4–6). The strength and toughness of the composites increase as alumina content is raised. Too high content of alumina (>40 vol.%) will decrease densification of the composites for the reason that the sintering temperature of alumina is high (about 1500 °C) [12].

It is obvious that the fabricated hydroxyapatite matrix ceramic materials, sintered at 1320 °C under a pressure of 20 MPa for 60 min in N_2 atmosphere, exhibit significant improvements in mechanical properties than monolithic hydroxyapatite. Samples 5 and 6 show better comprehensive performances. The bending strengths are 162 MPa and 200 MPa, and fracture toughnesses are 2.40 MPa m$^{1/2}$ and 2.80 MPa m$^{1/2}$, respectively. Generally speaking, the bending strength and fracture toughness of human compact bone are about 160–180 MPa and 2.2–4.6 MPa m$^{1/2}$ [5]. The mechanical properties of samples 5 and 6 can meet the requirement of human body bone.

3.2. XRD and FT-IR analysis of hydroxyapatite/alumina/diopside composites

The X-ray diffraction analysis of monolithic hydroxyapatite (sample 1) is shown in Fig. 1. There exist mainly hydroxyapatite and a little tricalcium phosphate, tricalcium phosphate is from the decomposition of hydroxyapatite at high temperature (1320 °C).

Figs. 2 and 3 show the X-ray diffraction analysis of samples 5 and 6, respectively. It can be clearly seen that the main phases of the composites are HAp, Al_2O_3 and some glass phases composed of SiO_2, anorthite and mullite. Anorthite and mullite may be from the reactions between alumina and diopside [11,13]. The decomposition of hydroxyapatite does not take place when alumina and diopside is introduced in hydroxyapatite matrix.

FT-IR spectra of the samples were analysed by using Fourier transform infrared spectroscopy (VECTOR, produced in

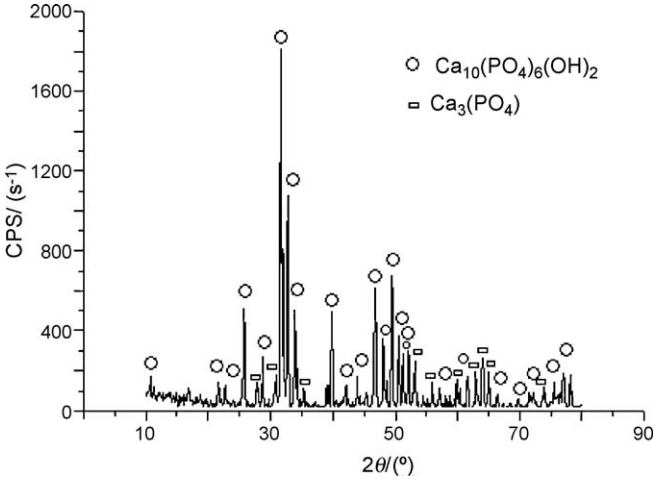

Fig. 1. X-ray diffraction patterns of sample 1.

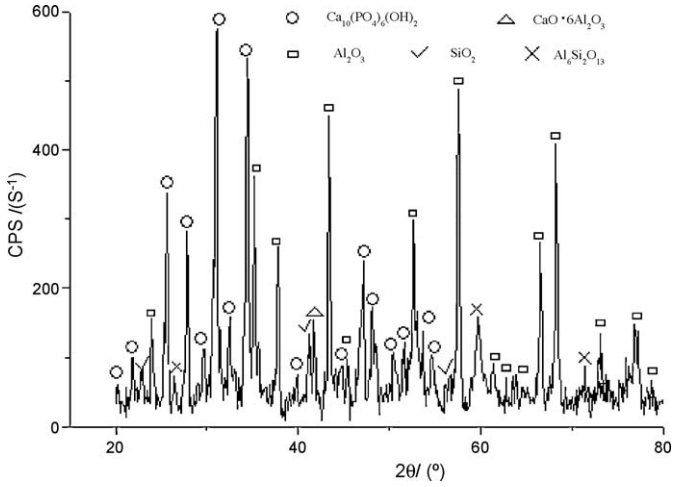

Fig. 2. X-ray diffraction patterns of sample 5.

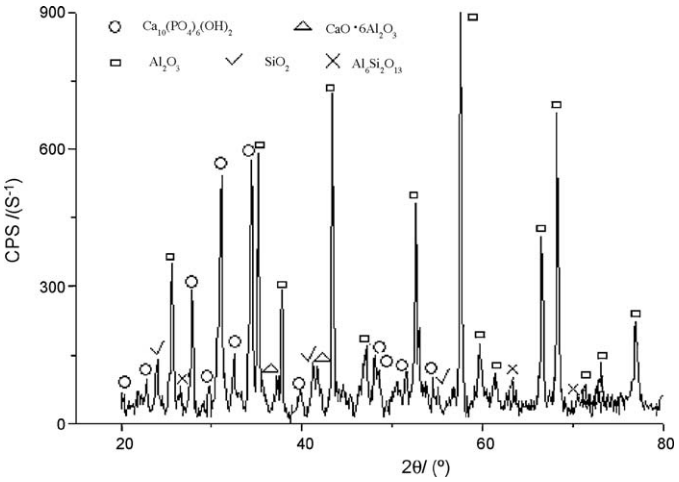

Fig. 3. X-ray diffraction patterns of sample 6.

Germany). As we can see from Fig. 4, the vibration peak of hydroxyl bonds locates at 3442 cm^{-1}, 1646 cm^{-1}, 692 cm^{-1} and 601 cm^{-1}, and that of PO_4^{-3} at 1124 cm^{-1}, 1045 cm^{-1}, 946 cm^{-1}. In Fig. 5, the vibration peak of hydroxyl bonds locates at 3440 cm^{-1}, 1639 cm^{-1}, 603 cm^{-1}, and that of PO_4^{-3}

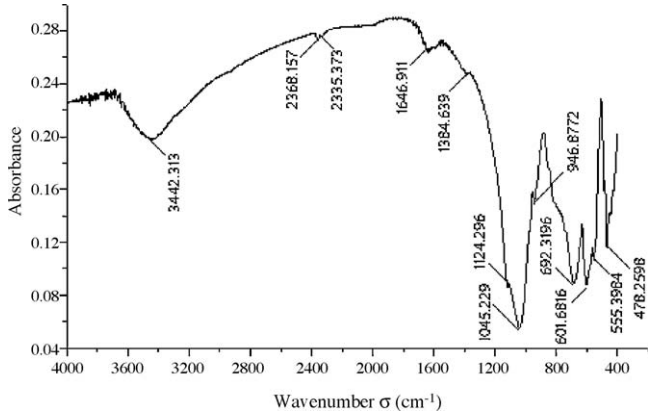

Fig. 4. FT-IR spectra of sample 5.

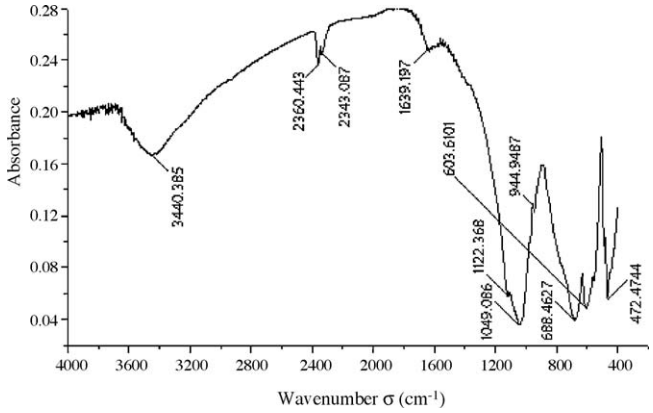

Fig. 5. FT-IR spectra of sample 6.

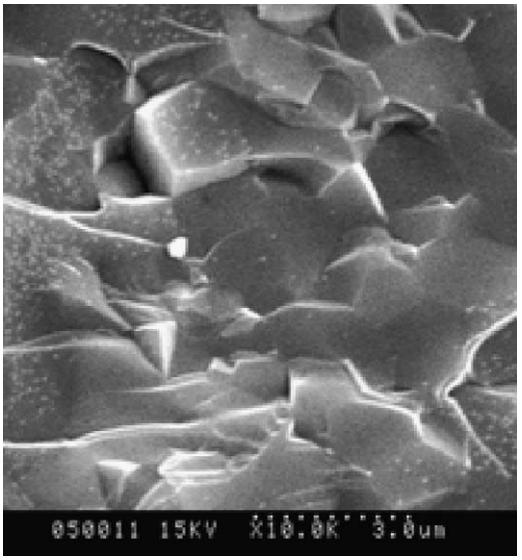

Fig. 6. SEM photomicrograph on fracture surface of sample 1 (10,000 times).

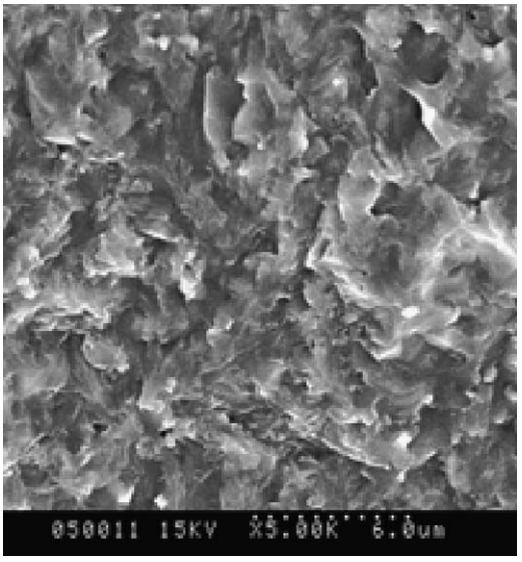

Fig. 7. SEM photomicrograph on fracture surface of sample 3 (5000 times).

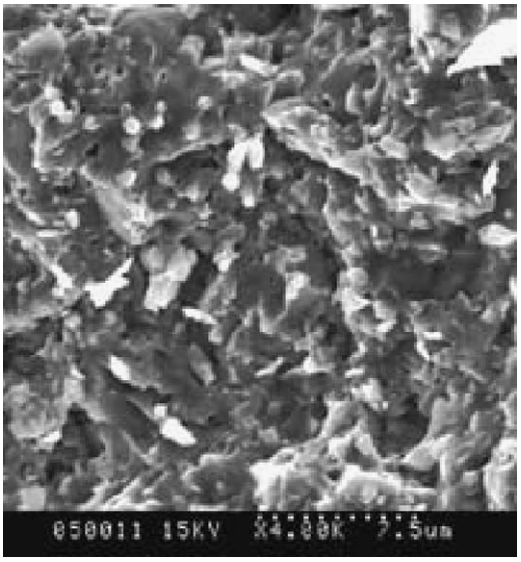

Fig. 8. SEM photomicrograph on fracture surface of sample 5 (4000 times).

at 1122 cm^{-1}, 1049 cm^{-1} and 944 cm^{-1}. The analysis of FT-IR spectra makes it sure that the phase of the fabricated composites are mainly HAp.

3.3. Microstructure analysis of hydroxyapatite/alumina/diopside composites

SEM micrograph on fracture surface of monolithic hydroxyapatite is shown in Fig. 6, and that of samples 3, 5 and 6 are shown in Figs. 7–9, respectively. It can be clearly seen that the fracture surfaces of monolithic hydroxyapatite are smooth. The grain boundaries of monolithic hydroxyapatite are unobservable and the fracture mode is mainly transgranular. However, the grain shapes of hydroxyapatite/alumina/diopside composites are irregular and the fracture mode changes from transgranular fracture to a combination of intergranular and transgranular fracture, which may be the main reason that results in enhanced bending strength and fracture toughness.

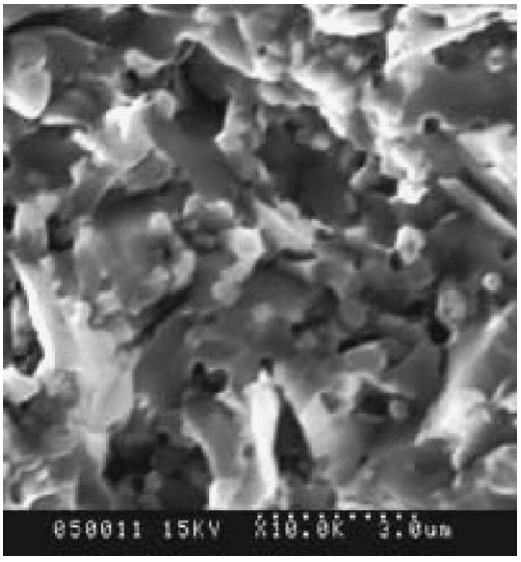

Fig. 9. SEM photomicrograph on fracture surface of sample 6 (10,000 times).

4. Conclusion

Hydroxyapatite matrix ceramic materials are fabricated at 1320 °C under a pressure of 20 MPa for 60 min in N_2 atmosphere. Sample 6 exhibits better comprehensive performances, the bending strength and fracture toughness are 200 MPa and 2.80 MPa $m^{1/2}$, respectively. XRD and FT-IR analysis show that the phase of the fabricated composites is mainly hydroxyapatite, the decomposition of hydroxyapatite does not take place when alumina and diopside is introduced in hydroxyapatite matrix. The irregular-shape grains, the fracture mode of combination of intergranular and transgranular contribute to the improvements in bending strength and fracture toughness of hydroxyapatite/alumina/diopside composites.

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