Hot pressing of porous alumina matrix biomaterials with diopside and CaF_2

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Diopside and CaF_2 are introduced in alumina matrix. Porous alumina matrix biomaterials are fabricated by uniaxial hot-pressing. The fracture toughness, hardness and bending strength of the biomaterials are tested. The effects of diopside and CaF_2 on fracture mechanism and mechanical properties of porous alumina matrix biomaterials are analyzed as well as the microstructure observations on fracture surfaces the biomaterials. The experiment results show that the introduction of diopside and CaF_2 can contribute to the improvement in mechanical properties and result in porous alumina matrix biomaterials which can be a good candidate for bone tissues.

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1. Introduction

Due to the virtues of good chemical inertness, high hardness and wear resistance, low weight, low cost and coefficient of friction, alumina matrix ceramic materials are widely applied in the fields of refractory materials, grinding media, cutting tools, fine measuring implement, fine sliding way, working platform and high-speed bearing, etc.. The brittleness of pure alumina, however, limits its potential application in many engineering fields. To date, numerous works, focusing on second phases doping, have been carried out to improve the bending strength and fracture toughness of pure alumina [1-6]. The introduction of diopside in alumina matrix ceramic composites can improve their bending strength and fracture toughness [7]. However, the high densification rate of alumina/diopside composites makes them have no biocompatibility and as a result, limit them as candidate for bone tissue regeneration in biomedical industries. In our present study, CaF_2, expected to improve the biocompatibility of alumina/diopside composites, is introduced in alumina/diopside composites. The cooperative toughening effect of diopside and CaF_2 on microstructures and mechanical properties of alumina matrix ceramic materials were analyzed, which was reported by few researchers, and the prepared composite may has potential application in the field of bone tissue regeneration.

2. Experimental procedure

Commercial Al_2O_3 powder of high purity (99.99%) and small grain size (0.5~1μm) was used as the starting materials. Diopside ($MgCa(SiO_3)_2$) and CaF_2 were used as additives. Diopside is composed of SiO_2 (55wt.%), CaO (24wt.%) and MgO (18wt.%). CaF_2, with melting point of 1360℃, was produced by Beijing Yili Fine Chemicals Co., Ltd. The physical characteristics of diopside were listed in Table 1. The compositions of hot-press sintered composites are listed in Table 2.

The raw materials were blended with one other according to certain proportions and ball milled for 60h in an alcohol medium to obtain a homogeneous mixture. Then the slurry was dried in vacuum and screened. Hot-pressing was used to sinter the powder mixture in a graphite die under nitrogen protection. The specimens were heated up to 1400℃ under a pressure of 28MPa for 30min.The sintering parameters are listed in Table 3.

Table 1 Physical characteristic of diopside

Raw materials	Grain size (μm)	Density (g/cm^3)	Impurities (mass fraction, %) <				
diopside	<20	3.3	Al_2O_3	Ni	Ti	Fe	Na
			2.000	0.200	0.200	0.550	0.050

Table 2 Compositions and mechanical properties of hot pressed alumina matrix ceramic materials

Specimens	Compositions (wt.%)	Hardness (HRA)	Bending strength (MPa)	Fracture toughness (MPa·m$^{1/2}$)
A_0	100%Al_2O_3	54.3 ± 1	153 ± 30	3.5 ± 0.4
A_1	98% Al_2O_3 + 1 % diopside +1% CaF_2	90.7 ± 8	381 ± 27	4.7 ± 0.3
A_2	95% Al_2O_3 + 1 % diopside +4% CaF_2	90.4 ± 5	474 ± 12	4.7 ± 0.2
A_3	90% Al_2O_3 + 5 % diopside +5% CaF_2	90.3 ± 5	434 ± 17	4.8 ± 0.3
A_4	90% Al_2O_3 + 2 % diopside +8% CaF_2	90.0 ± 7	443 ± 15	5.4 ± 0.3
A_5	85% Al_2O_3 + 10 % diopside +5% CaF_2	85.0 ± 8	290 ± 30	3.7 ± 0.5

Table 3 Sintering parameters of hot pressed alumina matrix ceramic materials

Temperature [℃]	20-1200	1200-1400	1400	1400-1200	1200-50	50
Speed of heating up and cooling [℃/min]	30	5	30 min holding	40	8	Open the furnace door

The sintered ceramic bodies were cut into pieces and standard test pieces(3mm×4mm×36mm) were obtained through rough grinding, finish diamond grinding and polishing. A three-point-flexural mode was used to measure the bending strength on an electronic universal experimental instrument with a span of 20 mm operating at a crosshead speed of 0.5 mm/min. Twelve samples, taken from a single ceramic body, were used to measure the bending strength of each composition in air at room temperature. The bending strength was calculated by the following formula [8]

$$\sigma_f = \frac{3PL}{2bh^2} \quad (1)$$

where σ_f is bending strength (MPa) and P is load (N) under which the samples break, *b* and *h* are width and height (mm), respectively, and *L* is span (mm).

Vickers hardness was tested on polished surface of the samples with a load of 9.8N for 5s using a micro-hardness tester (MH-6). Fracture toughness measurement was performed using indentation method with a hardness tester (Hv-120), and calculated using the formula proposed by Cook and Lawn [9]. The X-ray diffraction (XRD) analysis was undertaken to identify the crystal phases present after sintering. Microstructural observations of the fracture surfaces and polished surfaces were examined by scanning electron microscopy (HITACHI S-570).

3. Results and discussion

3.1. X-ray diffraction phase analyse

The X-ray diffraction analyses of A_1, A_3 and A_4 sintered at 1400℃ for 30min, are shown in Figs. 1, 2 and 3, respectively. It can be seen from the figures that there exist Al_2O_3 in A_1 specimen, Al_2O_3 and CaF_2 in A_3 specimen, Al_2O_3, CaF_2 and AlF_3 in A_4 specimen. As shown in Fig. 3, there exists newly formed AlF_3 phase, which is found to be resulted from the reaction of Al_2O_3 and CaF_2:

$$Al_2O_3 + 3CaF_2 \rightarrow 2\,AlF_3 + 3Ca\,O \quad (2)$$

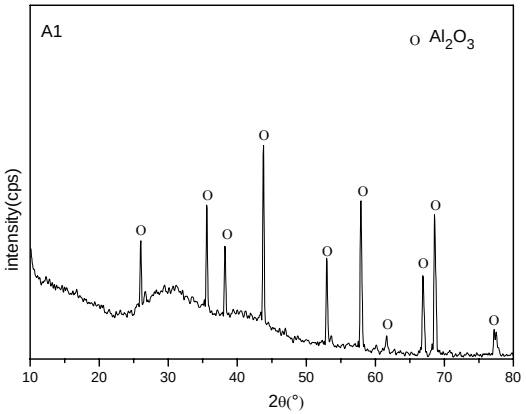

Fig. 1. XRD pattern of A_1 specimen sintered at 1400℃ under 28MPa for30min

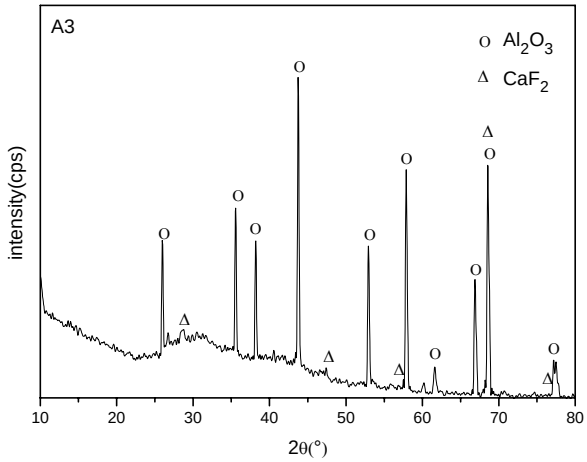

Fig. 2. XRD pattern of A_3 specimen sintered at 1400℃ under 28MPa for30min

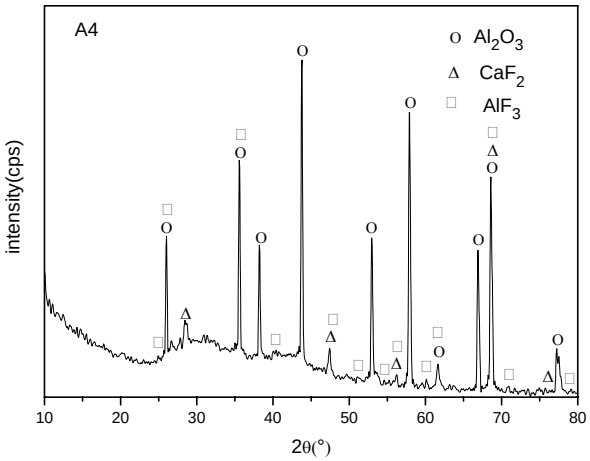

Fig. 3. XRD pattern of A_4 specimen sintered at 1400℃ under 28MPa for30min

Based on thermodynamics analysis of the reactive equation, the following ranking can be expressed:

$$\Delta G^{\theta}{}_{T} < 0 \tag{3}$$

where $\Delta G^{\theta}{}_{T}$ is the Gibbs free energy of the reaction (1). XRD analysis shows that AlF_3 actually exist in A_4 specimen as previously mentioned.

In A_3 and A_4 specimen, there are no trace of CaO, SiO_2 and MgO, which react with the matrix, producing $MgO{\cdot}Al_2O_3$, mullite, anorthite, and $CaO{\cdot}6Al_2O_3$ [7], leading to interface reactions and strengthened grain boundaries. $MgO{\cdot}Al_2O_3$, mullite, anorthite, and $CaO{\cdot}6Al_2O_3$ are difficult to be detected by XRD for little content.

3.2. Mechanical properties

Mechanical properties of the composites with different content of diopside and CaF_2 were listed in Table 2. Alumina matrix ceramic materials with addition of diopside and CaF_2 show improved mechanical properties with respect to pure alumina sintered under the same conditions. The fracture toughness of A_4 specimen reaches $5.4MPa{\cdot}m^{1/2}$. The bending strength of A_2 specimen reaches 474MPa. 10 wt. % diopside additions makes A_5 specimen obtain a relative lower mechanical properties, which may be mainly owing to the high content o f glass phases. It is indicated that the prepared composites, after sintering at 1400℃ for 30min in N_2 atmosphere, show obvious enhancements in mechanical properties. Composites with less than 5wt.% diopside addition show better comprehensive performances than pure alumina. The improved mechanical properties correlate with the microstructure of the composite, and that will be analyzed in microstructures section.

3.3. Analysis of microstructures

Fig. 4 shows SEM micrograph on fracture surface of A_0 specimen. The grain shape of pure alumina is regular and almost circular. The fracture mode was mainly intergranular. There exist porosity among incomplete developed alumina particles and the grains boundary is observable. SEM micrographs on fracture surfaces of A_3 and A_4 specimen are shown in Figs.5 and 6, respectively. The fracture mode of A_3 and A_4 specimen is a combination of intergranular and transgranular fracture. The grain boundary almost disappears. The grains are solidly bonded together and they have more contacting area owing to the interface reactions happened during the hot press sintering [7, 10], which may lead to the improved mechanical properties of A_3 and A_4 specimen.

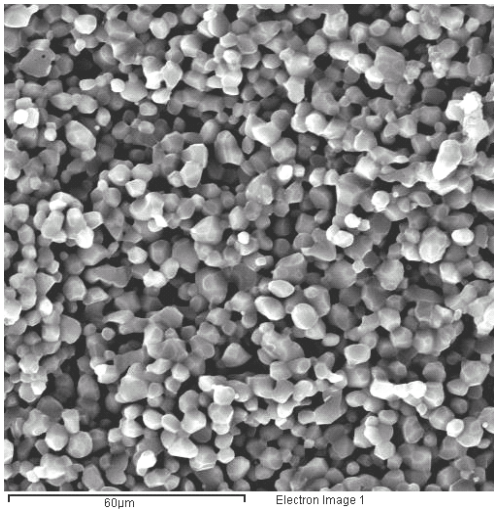

Fig. 4. SEM micrograph on fracture surface of A_0 specimen (800 times)

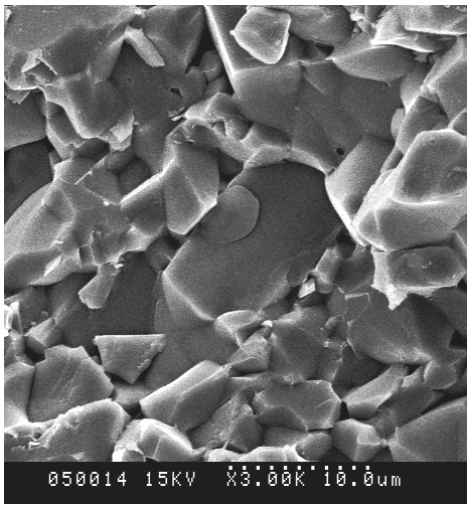

Fig. 5. SEM micrograph on fracture surface of A_3 specimen (3000 times)

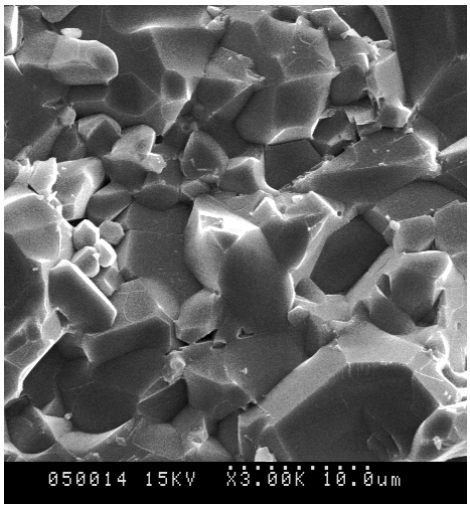

Fig. 6. SEM micrograph on fracture surface of A_4 specimen (3000 times)

Fig.7 and Fig.8 show SEM micrograph on polished surfaces of A_3 and A_4 specimen. Obvious porosity exists on polished surfaces of A_3 and A_4 specimen. The radius of F^{-1} is 0.136 nm, which is nearly equal to that of O^{-2} (0.140 nm). So F^{-1} and O^{-2} can be the replacement of each other and AlF_3 phase is produce as previously mentioned. Due to its low boiling point of 1272℃, some AlF_3 will sublime and become gas at the sintering temperature of 1400℃, which contributes to the formation of porosities for A_3 and A_4 specimen. There is more porosity in A_4 specimen than that in A_3 specimen as shown in Figs.7 and 8 as more content of CaF_2 can react with alumina to produce more AlF_3. Some AlF_3 will sublime and become gas, another may be leaved on for too short sintering time to sublime. Therefore the amount of porosity is controlled by the content of CaF_2 and the sintering parameters. The existing of F^{-1} can promote the sediment of hydroxyapatite crystals and contribute to the adhesion of cells [11, 12].

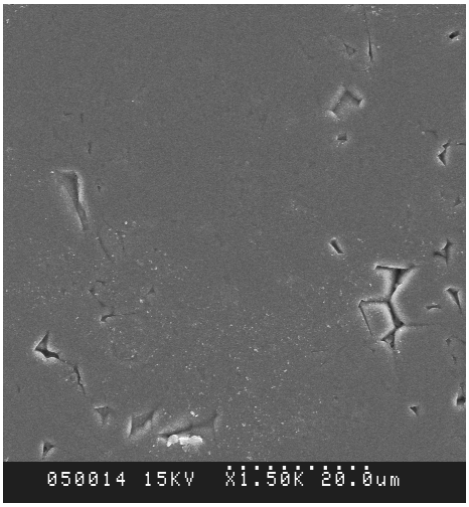

Fig.7. SEM micrograph on polished surface of A_3 specimen (1500 times)

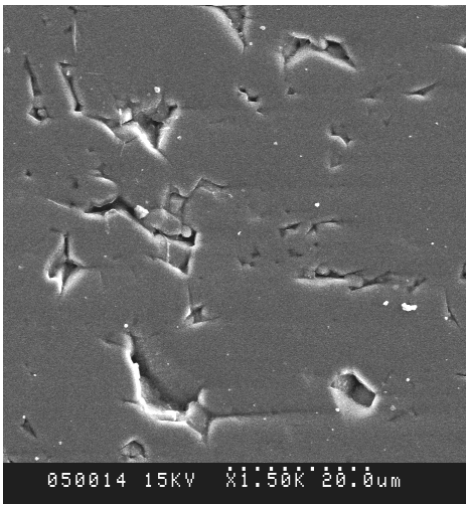

Fig.8 SEM micrograph on polished surface of A_4 specimen (1500 times)

4. Conclusion

The addition of diopside and CaF_2 induces transgranular fracture and the strengthened grain bonding, which may be the principal reason that results in the enhancements in performances of the porous alumina matrix biomaterials. The toughness and strength of the composite with addition of 1wt.% diopside and 4wt.% CaF_2 reach 4.7MPa·$m^{1/2}$ and 474MPa, respectively. Those of the composite with addition of 2wt.% diopside and 8wt.% CaF_2 reach 443MPa and 5.4MPa·$m^{1/2}$, respectively. SEM micrographs on polished surface of the porous alumina matrix biomaterials show that there exist porosities, which is produce by the sublime of AlF_3, among the solidly bonded particles. The porosities and the

left AlF_3 in porous alumina matrix biomaterials may promote the sediment of hydroxyapatite crystals and contribute to cell adhesion.

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