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Short communication

Al_2O_3/diopside ceramic composites and their behaviour in simulated body fluid

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Abstract

Al_2O_3/diopside ceramic composites with good mechanical properties were prepared by uniaxial hot-pressing and their biological activity in simulated body fluid was studied by SEM, XRD, FT-IR and EPMA. SEM micrographs showed a lath-like apatite layer to form on the soaked composite surface, whose good biological activity may be of some promise for biomedical application.

Keywords: Alumina; Diopside; Biological activity; XRD (X-ray diffraction); FT-IR

1. Introduction

Owing to its several special properties e.g. high hardness, high elastic modulus, good chemical inertness, high wear resistance, low friction coefficient and good biocompatibility, alumina is of considerable interest for biomedical engineering applications. In 1970, an artificial hip joint was firstly fabricated using pure alumina and put into clinical applications in 1972. The low fracture toughness of artificial hip joint, however, prevented it to be used at the bone defect sites where heavily loaded [1]. In order to overcome these disadvantages, alumina matrix ceramic composites have been developed [2–6]. Being used as artificial joint material and dental repairing material, pure alumina can not be perfectly interconnected with bone tissues owing to its bad biological activity, which as a result limits its application in biomedical engineering.

Our previous results showed that introduction of diopside in alumina matrix ceramic composites can improve their bending strength and fracture toughness. A composite with high performance vs cost ratio was obtained [7,8]. In this paper, the biological activity of Al_2O_3/diopside ceramic composites is discussed to assess whether the introduction of diopside in alumina can improve its biological activity.

2. Experimental procedure

2.1. Preparation and characterization of Al_2O_3/diopside ceramic composites

Commercial small grain size (0.5–1 μm) 99.9 pure Al_2O_3 powder was used. Diopside ($MgCa(SiO_3)_2$), composed of SiO_2 (55 wt.%), CaO (24 wt.%) and MgO (18 wt.%), was used as an additive. Milling was carried out for 100 h in alcohol using a vibratory ball mill with cemented carbide balls and then metal-mill media impurities were removed by washing in 10 mol.% hydrochloric acid. After drying, densification of the powder was achieved in a graphite die by uniaxial hot-pressing at 1450 °C, at a pressure of 28 MPa in a N_2 atmosphere for 30 min.

The sintered bodies were cut into bars and then standard test pieces (3 mm × 4 mm × 36 mm) were ground and polished with diamond paste. Three-point-bending mode was used to measure the bending strength using an electronic universal experimental instrument (Jinan TEST Co., LTD) with a span of 20 mm at a crosshead speed of 0.5 mm/min. At least twelve

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Table 1
Starting compositions and mechanical properties of Al_2O_3/diopside ceramic composites.

Specimens	Compositions (wt.%)		Mechanical properties		
	Diopside	Al_2O_3	Vickers hardness (GPa)	Flexural strength (MPa)	Fracture toughness (MPa $m^{1/2}$)
D_0	0	100	17.8 ± 1.4	130 ± 55	3.1 ± 0.4
D_1	1	99	18.6 ± 0.8	427 ± 14	4.3 ± 0.2
D_{20}	20	80	14.1 ± 3.5	231 ± 30	3.2 ± 0.8

specimens were tested for each series of composition in air at room temperature. Hardness was measured on the polished surfaces with a load of 9.8 N for 5 s using a micro-hardness tester (Shanghai Hengyi electronic testing instrument corporation). Fracture toughness measurements were performed using the indentation method. The indentations on polished surfaces were generated by a Vickers micro-hardness tester with a diamond pyramid indenter, at a load of 196N and a loading time of 30 s. The formula proposed by Cook and Lawn [9] was used to calculate the final fracture toughness. Data of hardness and fracture toughness were determined using at least 10 indentations on polished surfaces with a Ra of 0.1 μm for each specimen. The starting compositions and mechanical properties of Al_2O_3/diopside ceramic composites are listed in Table 1.

2.2. Ability of Al_2O_3/diopside ceramic composites to form an apatite layer

SBF containing ion concentrations similar to those in human blood plasma was prepared according to the method described by Kokubo [10]. Briefly, reagent-grade $CaCl_2$, $K_2HPO_4{\cdot}3H_2O$, NaCl, KCl, $MgCl_2{\cdot}6H_2O$, $NaHCO_3$, and Na_2SO_4 were dissolved in distilled water and adjusted to pH 7.25. Al_2O_3/diopside ceramic bars were soaked in SBF at 37 °C for 9 days. After soaking, the bars were dried at 100 °C for 0.5 days. The microstructure of the specimens were studied on the original polished surfaces and on the soaked bar surfaces by scanning electron microscopy (HITACHI S-570). The phases of the soaked Al_2O_3/diopside ceramic composites were determined by XRD (D/max-2400). FT-IR (VECTOR) analysis was adopted to identify the appearance of OH^- and PO_4^{3-}. The existence of Ca and P was detected by EPMA (JXA-8800R).

3. Results and discussion

3.1. Microstructure of Al_2O_3/diopside ceramic composites

SEM micrographs of the D_{20} specimen before and after soaking in SBF for 9 days are shown in Figs. 1–3. Those of the D_0 and D_1 specimen after soaking in SBF for 9 days are shown in Figs. 4–6. Compared with Fig. 1, there was an obvious lath-like layer formed in Figs. 2 and 3. The layer on the surfaces of the D_0 specimen, however, was not evident (Fig. 4). The microstructure differed significantly with the different content of diopside. Lath-like layer also appeared on the surfaces of the D_1 specimen after soaking in SBF for 9 days (Figs. 5 and 6) with the layer crystal boundaries of the D_{20} specimen being more evident than for D_0. In order to detect the phases of the lath-like layer, the specimens were characterized by XRD, FT-IR and EPMA, respectively.

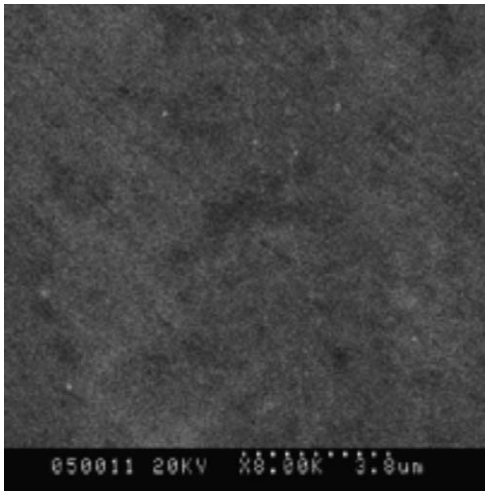

Fig. 1. SEM micrograph of D_{20} specimen before soaking in SBF (8000×).

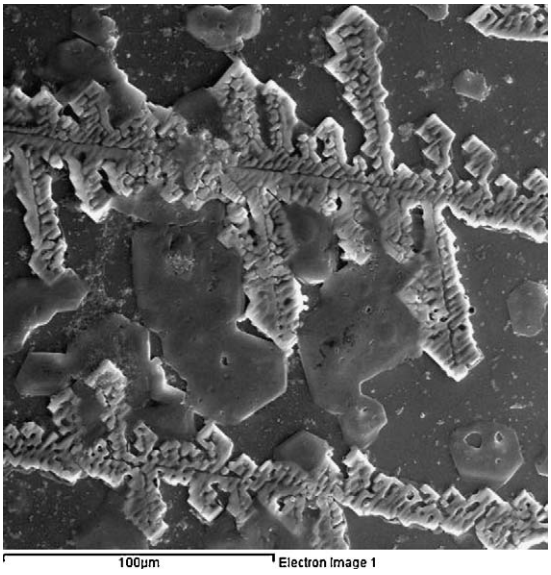

Fig. 2. SEM micrograph of D_{20} specimen after soaking in SBF for 9 days (500×).

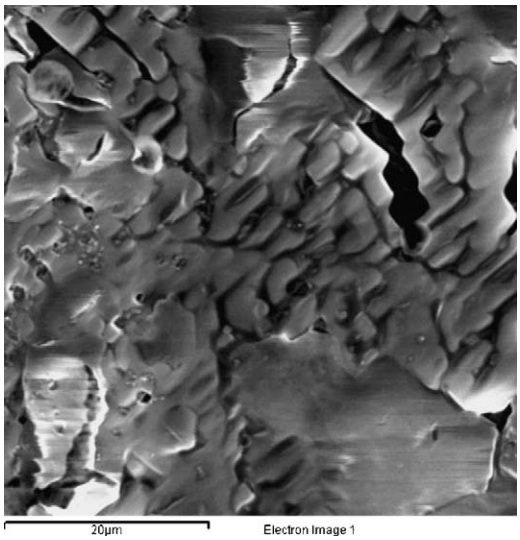

Fig. 3. SEM micrograph of D_{20} specimen after soaking in SBF for 9 days (4000×).

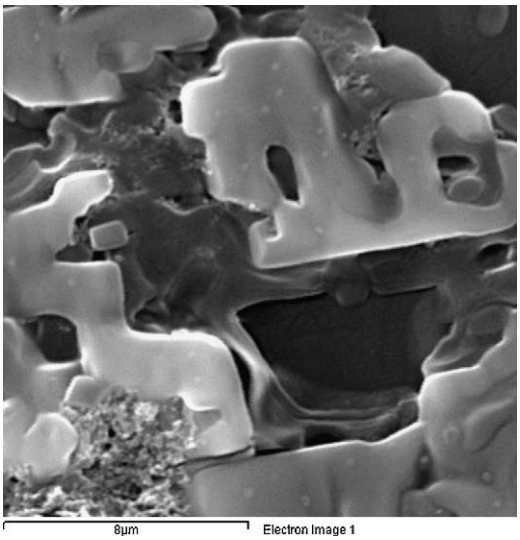

Fig. 5. SEM micrograph of D_1 specimen after soaking in SBF for 9 days (6000×).

3.2. X-ray diffraction phase analysis of Al_2O_3/diopside ceramic composites

XRD patterns of the D_1 and D_{20} specimen after soaking in SBF for 9 days are shown in Figs. 7 and 8. Hydroxyapatite and Al_2O_3 were detected in the soaked D_1 specimen, whereas Al_2O_3, hydroxyapatite, mullite ($Al_6Si_2O_{13}$), anorthite ($CaO{\cdot}Al_2O_3{\cdot}2SiO_2$), Mg_3Al_2 $(SiO_4)_3$ and CA6 ($CaO{\cdot}6Al_2O_3$) were detected in the soaked D_{20} specimen. By a comparison with our previous studies on XRD patterns of the D_1 and D_{20} specimen before soaking in SBF [8], the conclusion can be drawn that hydroxyapatite was formed in the D_1 and D_{20} specimen after soaking in SBF for 9 days.

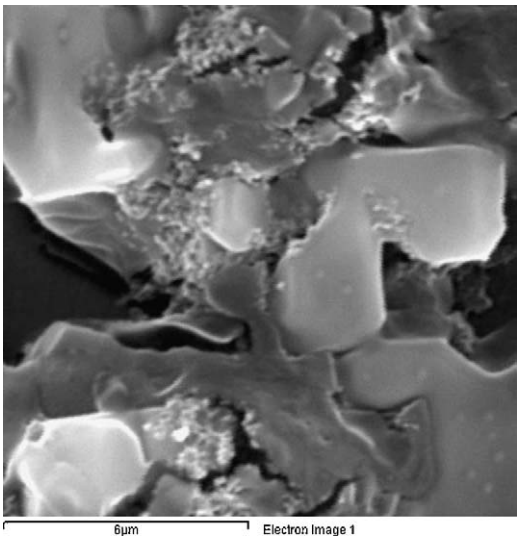

Fig. 6. SEM micrograph of D_1 specimen after soaking in SBF for 9 days (8000×).

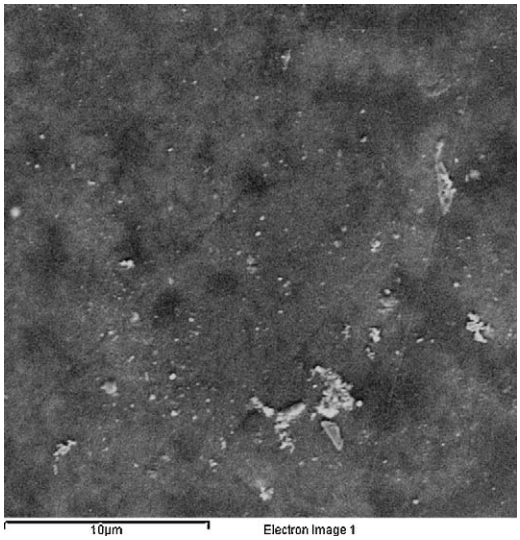

Fig. 4. SEM micrograph of D_0 specimen after soaking in SBF for 9 days (4000×).

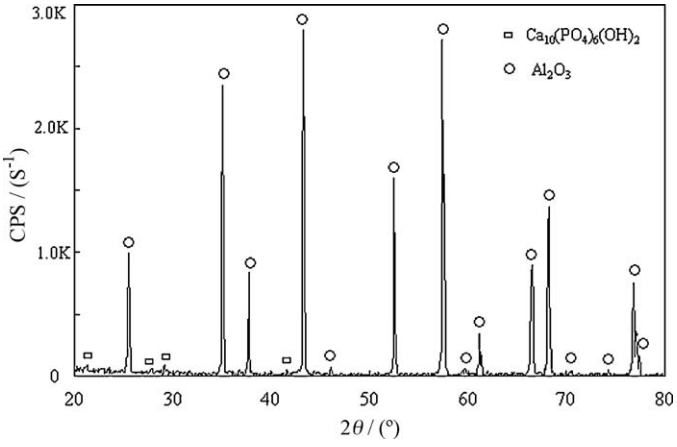

Fig. 7. XRD patterns of the D_1 specimen after soaking in SBF for 9 days.

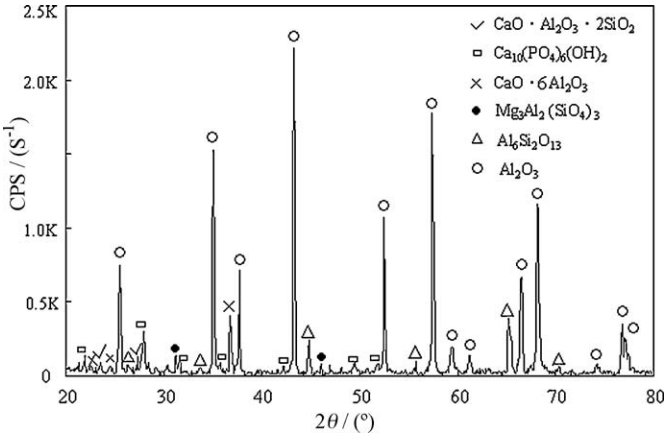

Fig. 8. XRD patterns of the D_{20} specimen after soaking in SBF for 9 days.

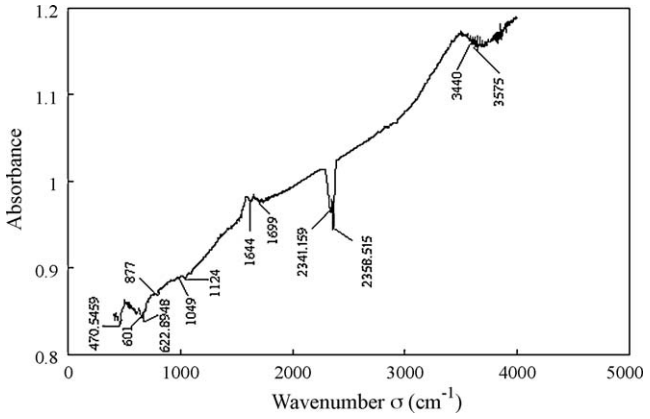

Fig. 9. FT-IR spectra of the D_1 specimen after soaking in SBF for 9 days.

3.3. FT-IR analysis of Al_2O_3/diopside ceramic composites

FT-IR spectra of the D_1 and D_{20} specimen after soaking in SBF for 9 days were analyzed by Fourier transform infrared spectroscopy (VECTOR, Germany) (Figs. 9 and 10). The vibration peak of hydroxyl bonds located at 3575 cm^{-1}, 3440 cm^{-1}, 1699 cm^{-1}, 622 cm^{-1}, 603 cm^{-1} and 601 cm^{-1}, and that of CO_3^{-2} at 1644 cm^{-1} and 877 cm^{-1}. The vibration

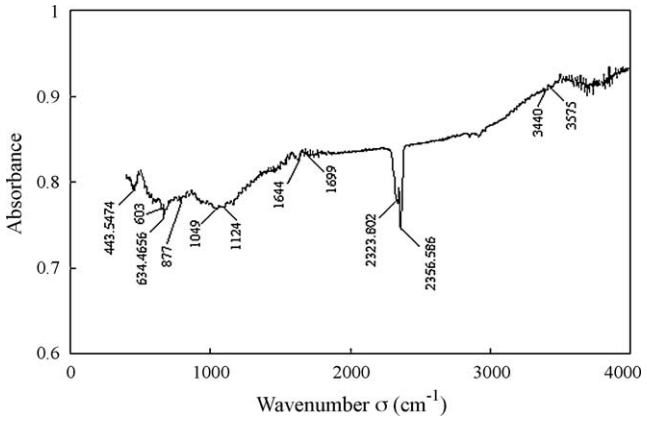

Fig. 10. FT-IR spectra of the D_{20} specimen after soaking in SBF for 9 days.

peak of PO_4^{-3} ranged from 1124 cm^{-1} to 946 cm^{-1}. The analysis of FT-IR spectra makes it sure that the phase of lath-like layer, formed on the surfaces of the D_1 and D_{20} specimens after soaking in SBF for 9 days, are mainly HCA. The vibration peak of CO_3^{-2} for the D_{20} specimen is approximately more intense than for the D_1 specimen, a possible evidence that the biological activity of Al_2O_3/diopside ceramic composites increased with the increase of diopside content.

3.4. EPMA analysis of Al_2O_3/diopside ceramic composites

EDS spectra of the D_1 and D_{20} specimen after soaking in SBF for 9 days are shown in Figs. 11 and 12, respectively. Ca appeared on the surfaces of D_{20} specimen after soaking in SBF for 9 days (Fig. 12). Therefore, it also can be concluded that the phase of lath-like layer is mainly HCA.

Kokubo et al. [11,12] reported silicon to play an important role for the nucleation and growth mechanism of the apatite-like layer on bioactive composites. In our study, an interchange is suggested to take place between the Ca^{2+} ions of the alumina/diopside ceramic composites and the H_3O^+ of the simulated body fluid, which may promote the formation of Si–OH groups on the alumina/diopside ceramic composite surface and induce apatite nucleation. The nuclei thus formed grow at the expense of the ions in the solution that has been saturated with respect to

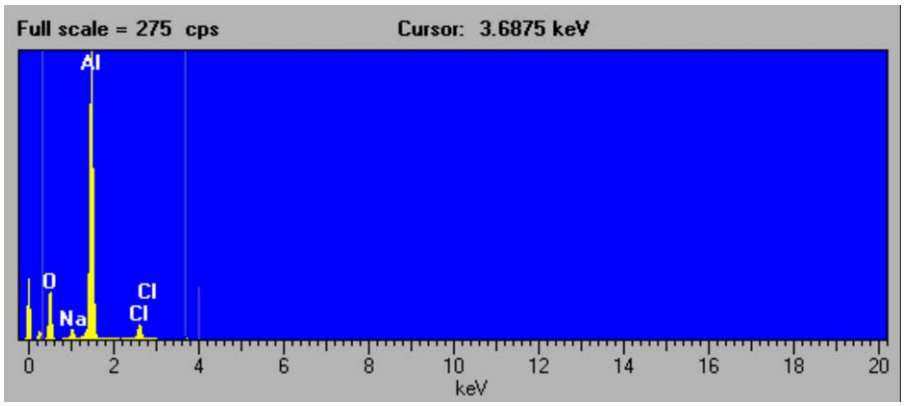

Fig. 11. EDS spectra of the D_0 specimen after soaking in SBF for 9 days.

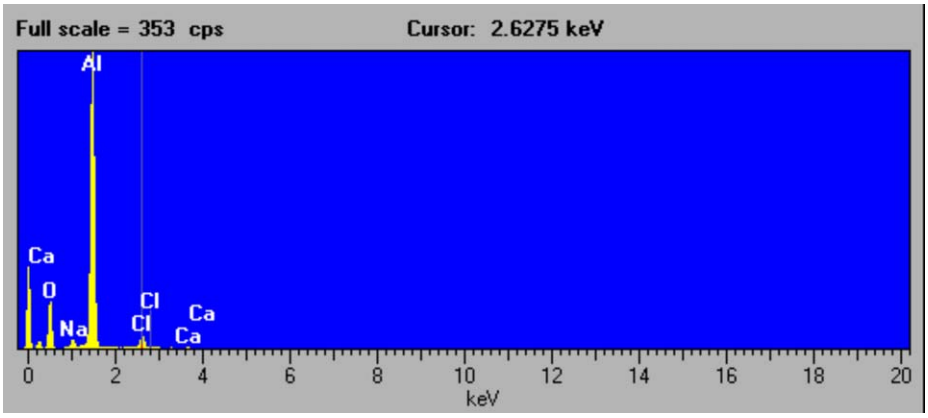

Fig. 12. EDS spectra of the D_1 specimen after soaking in SBF for 9 days.

apatite. Therefore, silicon seems to be very important in increasing the in vitro bioactive behaviour of alumina/diopside ceramic composites.

4. Conclusions

Al_2O_3/diopside ceramic composites with good mechanical properties and expected good biological activity were fabricated by uniaxial hot-pressing. Ca and P were detected on the surface of Al_2O_3/diopside ceramic composites after soaking in SBF for 9 days with formation of an apatite lath-like layer. The addition of an excess of diopside, however, resulted in poor mechanical properties of the Al_2O_3/diopside ceramic composites. So an appropriate amount of diopside should be introduced in alumina to make the composite to possess both good mechanical properties and perspective good biological activity.

Acknowledgements

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