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Low temperature fabrication and characterizations of β-$CaSiO_3$ ceramics

L.H. Long [a,c], L.D. Chen [a,*], J. Chang [b]

[a] State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China

[b] Biomaterials and Tissue Engineering Research Center, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China

[c] Graduate School of Chinese Academy of Science, Shanghai 200050, China

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Abstract

Dense β-$CaSiO_3$ (low temperature phase) ceramics were fabricated by spark plasma sintering (SPS) in the temperature range of 700–950 °C using chemically precipitated amorphous powder. The maximum density of the obtained β-$CaSiO_3$ ceramics reached about 2.60 g/cm^3 with grain size of 100–200 nm. The maximum bending strength was 190 MPa. The Young's modulus and fracture toughness reached 62.8 GPa and 1.67 MPa $m^{1/2}$, respectively. The simulated body fluid (SBF) tests showed that HAp grains covered the surface of β-$CaSiO_3$ ceramics completely after 3 days immersion. The thickness of HAp layer was about 15 μm for the 3 days specimen and it reached 25 μm for the 7 days immersion. SPS-sintered β-$CaSiO_3$ ceramics obtained by SPS had both good mechanical properties and excellent bioactivity.

Keywords: C. Mechanical properties; SPS; $CaSiO_3$; Ceramics; Bioactivity

1. Introduction

Since the discovery of Bioglass by Hench et al. in 1971 [1,2], many glasses, glass–ceramics and ceramics have been found to bond to living bone and most of these materials contain CaO–SiO_2 [3,4]. Recent studies showed that $CaSiO_3$ (wollastonite) has good bioactivity and thus exhibits prospective application as biomaterials [5,6]. Since $CaSiO_3$ ceramic is poorly sinterable, many reports so far have only concerned the preparation of $CaSiO_3$ powder, α-$CaSiO_3$ (high temperature phase) coating as well as its composite biomaterials [6–10], while few concerned the preparation and properties of β-$CaSiO_3$ ceramics.

In recent years, a new rapid sintering technique, spark plasma sintering (SPS), has been developed, which is featured with high heating rate and is suitable to densify ceramics at lower temperatures suppressing grain growth. Some biomaterials have also been fabricated by SPS [11,12], and it was reported that the SPS-sintered HAp ceramics have better bioactivity than that obtained by a conventional hot-pressing method [13].

In this study, amorphous $CaSiO_3$ powder was prepared through a chemical precipitation method and β-$CaSiO_3$ ceramics were fabricated by SPS. Their mechanical properties and bioactivity were evaluated.

2. Experimental methods

$CaSiO_3$ powder for the present study was prepared through a chemical precipitation method. $Ca(NO_3)\cdot 4H_2O$ and $Na_2SiO_3\cdot 9H_2O$ were used as raw materials. They were separately dissolved in de-ionized water in the concentration of 0.3 mol/l. The pH value was adjusted to be 12 using NH_4OH. The obtained Na_2SiO_3 solution was dropped into $Ca(NO_3)_2$ solution with vigorous agitation. The reactant mixture was filtered, then washed three times with de-ionized water and finally washed by ethanol. The powder was dried at 80 °C, and then calcined at 700 °C for 2 h.

The obtained $CaSiO_3$ powder was put into a graphite die (30 mm in diameter) and sintered using Spark Plasma

* Corresponding author. Tel.: +86 21 52412520; fax: +86 21 52413122.
E-mail address: cld@mail.sic.ac.cn (L.D. Chen).

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Table 1
Ion concentration of SBF in comparison with human blood plasma

	Concentration (mM)							
	Na^+	K^+	Ca^{2+}	Mg^{2+}	HCO_3^-	Cl^-	HPO_4^{2-}	SO_4^{2-}
SBF	142.0	5.0	2.5	1.5	4.2	148.5	1.0	0.5
Blood plasma	142.0	5.0	2.5	1.5	27.0	103.0	1.0	0.5

Table 2
The properties of $CaSiO_3$ ceramics

Sinter temperature (°C)	Density (g/cm^3)	Water absorption (%)	Fracture strength, σ_f (MPa)	Fracture toughness, K_{1c} (MPa $m^{1/2}$)	Young's modulus (GPa)
700	2.1	19	140 ± 9	0.72 ± 0.03	40.1 ± 4.0
750	2.6	2.1	190 ± 5	1.67 ± 0.05	62.8 ± 5.6
800	2.5	3.4	171 ± 12	1.58 ± 0.03	57.5 ± 8.4
850	2.3	4.5	164 ± 5	1.57 ± 0.06	51.5 ± 5.0
900	2.2	3.1	109 ± 9	1.54 ± 0.04	51.0 ± 4.7
950	2.2	3.2	100 ± 11	1.52 ± 0.05	50.0 ± 5.2

Sintering (Dr Sinter 2040, Sumitomo Coal Mining Co.) in vacuum (less than 10^{-4} Pa) under a pressure of 40 MPa. The heating rate was 150–200 °C/min and holding time at the sintering temperature was 5 min.

The crystalline phases of the chemically precipitated powder and sintered specimen were analyzed by XRD (Rigaku D/max 2200PC). The density was determined according to Archimedes principle. Microstructures were observed by scanning electron microscopy (SEM, JSM-6700F). The bending strength and Young's modulus were measured with a universal tester (Instron-1195) using a three-point test method with a span length of 20 mm and a crosshead speed of 0.5 mm/min. The fracture toughness, K_{1C}, was evaluated by the single-edge notch beam method (Instron-1195, notch width: 0.25 mm, the notch depth: 2 mm) with six samples each data. The distribution of elements was analyzed by electron probe microanalyzer (EPMA, EPMA-8705QH_2, Shimadzu, Japan).

The simulated body fluid (SBF) was prepared by dissolving reagent-grade $CaCl_2$, $K_2HPO_4 \cdot 3H_2O$, NaCl, KCl, $MgCl_2 \cdot 6H_2O$, $NaHCO_3$ and Na_2SO_4 in de-ionized water and the ion concentrations were adjusted to be similar to those in human blood plasma (Table 1). The SBF was buffered at pH 7.4 with trimethanol aminomethane–HCl. The sintered $CaSiO_3$ ceramic (2 mm × 3 mm × 20 mm) was soaked in 21 ml SBF solution and maintained at 36.5 °C. The soaking period was 3 days and 7 days, respectively and SBF was renewed every day.

3. Results and discussions

3.1. Characterization of β-$CaSiO_3$ ceramics

Fig. 1 shows the XRD patterns of $CaSiO_3$ ceramics sintered at various temperatures. The as-prepared powder was mainly in amorphous state with small amount of CaO–SiO_2–nH_2O (Fig. 1). Samples sintered by SPS at 700 °C to 900 °C are of β-$CaSiO_3$ (low temperature phase) ceramics. Sintering temperature and some properties of sintered $CaSiO_3$ ceramics were summarized in Table 2. The density of $CaSiO_3$ ceramic sintered at 700 °C was 2.1 g/cm^3 and it reached 2.60 g/cm^3 for the sample sintered at 750 °C. However, the density decreased gradually and maintained about 2.2 g/cm^3 after 900 °C. The water absorption decreased significantly from 19% for the samples sintered at 700 °C to about 3% for those sintered above 750 °C. The bending strength of $CaSiO_3$ ceramics sintered at 700 °C was 140 MPa, and reached the maximum value of 190 MPa at 750 °C, which was much higher than that of cortical bone and about two times as that of the sintered $CaSiO_3$ reported previously [10,14]. The Young's modulus and fracture strength showed the same changing tendency, which reached maximum value of 62.8 GPa and 1.67 MPa $m^{1/2}$, respectively, at 750 °C.

The alteration of mechanical properties of $CaSiO_3$ was mainly due to the change of the microstructure of the sintered

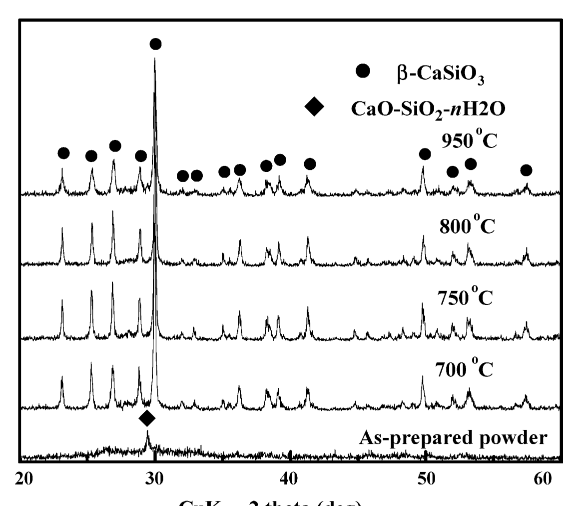

Fig. 1. XRD patterns of $CaSiO_3$ powder and ceramics sintered by SPS at various temperatures.

β-$CaSiO_3$ ceramics as shown in Fig. 2. The SEM micrographs of fractured surface of sintered $CaSiO_3$ ceramics indicated that the average grain size for the sample sintered at 750 °C was 100–200 nm (Fig. 2A). The fracture was mainly due to the intergrain cracking. The grain size increased with sintering temperature (Fig. 2B and C). Some transcrystalline fractures were observed for the sample sintered at 800 °C. For the sample sintered at 900 °C, the grains fully grew (Fig. 2C) and many large pores were enclosed within grains. In addition, the smooth fracture plane of the samples sintered at 950 °C showed that the samples sintered at 900 °C exhibited completely transcrystalline fracture. The rapid releasing of residual hydrone at high temperature is attributed to the increase of pores and decrease of density after sintering at temperatures above 800 °C.

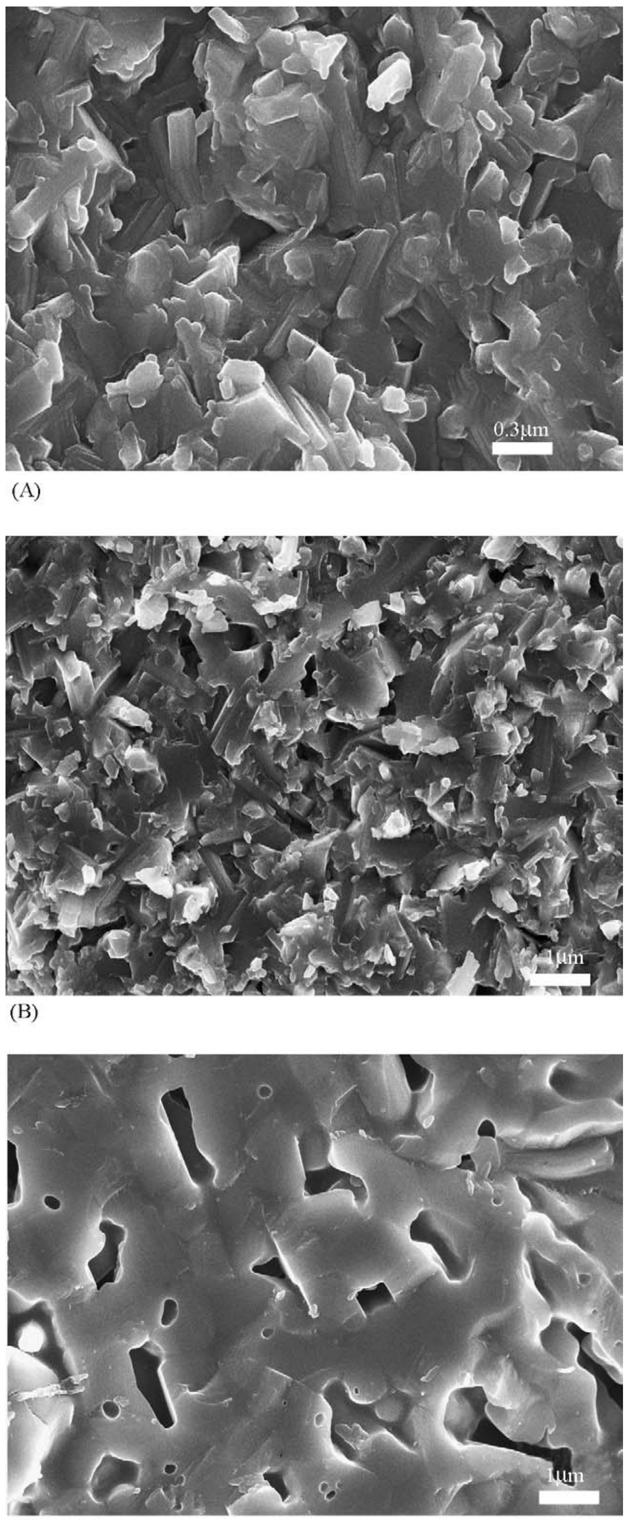

Fig. 2. SEM photographs of the fracture surfaces of $CaSiO_3$ ceramics sintered at different temperatures: (A) 750 °C; (B) 800 °C; (C) 900 °C.

3.2. SBF immersion tests

Bioactivity was evaluated for β-$CaSiO_3$ ceramics sintered at 750 °C. Fig. 3 showed SEM micrographs of β-$CaSiO_3$ ceramics immersed in SBF for 3 days. The specimen surface was completely covered by rod-shaped, 50 nm width and 200 nm length (Fig. 3A and B) HAp grains. Also micro-cracks appeared on the surface (Fig. 3A). These indicated that HAp

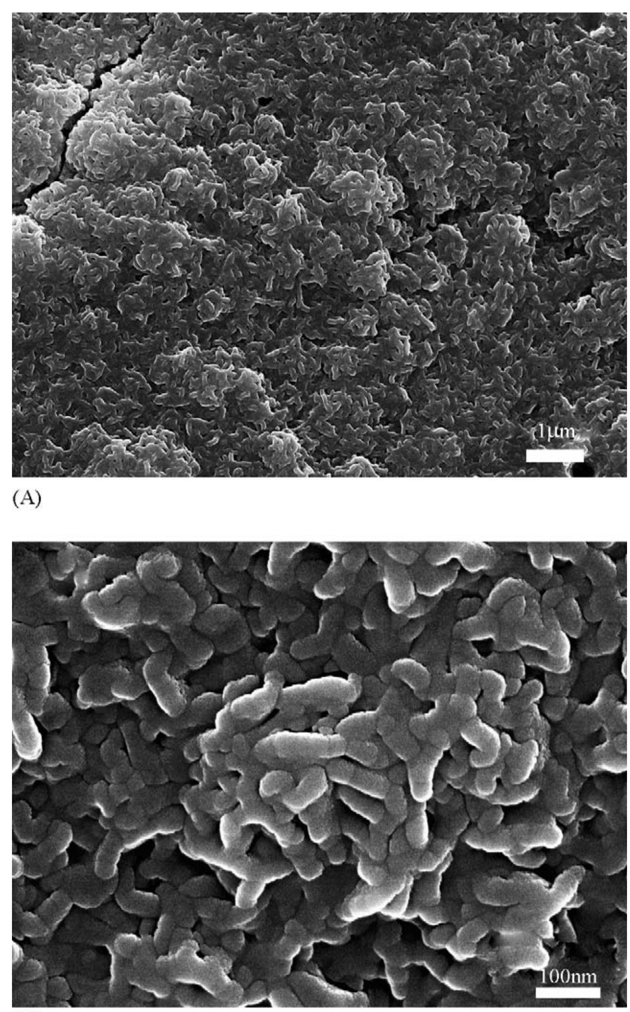

Fig. 3. SEM photographs of the surface of $CaSiO_3$ ceramics immersed in SBF for 3 days. (B) is a magnification of (A).

deposited on β-$CaSiO_3$ ceramic immersed in SBF after 3 days. The thickness of HAp layer was about 15 μm for the 3 days specimen and it reached 25 μm for the 7 days immersion. The speed of HAp formation was faster than those previously reported [5,7], which might be attributed to the nano-structure of β-$CaSiO_3$ ceramic sintered by SPS at 750 °C.

4. Conclusions

β-$CaSiO_3$ ceramics were densified by SPS at low temperature as 750 °C from amorphous $CaSiO_3$ powder synthesized through a chemical precipitation method. β-$CaSiO_3$ ceramics with grains of 100–200 nm were obtained at 750 °C. The obtained β-$CaSiO_3$ ceramics had good mechanical properties with bending strength of 190 MPa and fracture toughness of 1.67 MPa $m^{1/2}$. HAp deposited rapidly on the surface of β-$CaSiO_3$ ceramic in SBF. Therefore, β-$CaSiO_3$ ceramics sintered by SPS at 750 °C had good mechanical properties and bioactivity and might be a good candidate material for biomaterials.

Acknowledgements

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