Effects of silica sol on the microstructure and mechanical properties of CaSiO₃ bioceramics

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ABSTRACT

CaSiO₃ ceramics were fabricated with silica sol addition by pressureless sintering. The effects of silica sol on phase composition, microstructure and mechanical properties of CaSiO₃ ceramics were investigated. The silica sol additive was found to be effective in speeding up pore elimination, improving the grain growth, decreasing the sintering temperature and shortening the sintering time. When the amount of SiO_2 was 5 wt%, a flexural strength of 186.2 MPa was achieved with an open porosity of 3.9%. The main crystal phase was β-CaSiO₃ below sintering temperature of 1150 °C.

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1. Introduction

As one of the most important calcium silicate, CaSiO₃ (CS) is widely used as industrial ceramics. In recent years, CS has been investigated as biomaterial for hard tissue repair substituent, and has drawn growing attentions for its promising applications in bone tissue regeneration because of its superior bone bioactivity compared to hydroxyapatite (HA) [1–6]. Nevertheless, a major drawback of CS ceramics is their inadequate mechanical strength, which limits the extensive use in bone tissue engineering applications. The low mechanical properties of CS ceramics make them suitable only for low load-bearing applications [7,8].

Generally, it has been believed that using sintering additive is an effective method to adjust the sintering process and improve the mechanical properties of ceramics [9]. The use of SiO_2 [10] and other oxides such as ZrO_2, B_2O_3, and Cr_2O_3 as sintering aids was often reported to increase the densification kinetics in ceramic composites [5,11–16]. As demonstrated by Shokrollahi [17], nano-SiO_2 promoted grain growth, thereby increasing the grain size at lower sintering temperatures [18]. Moreover, silicon (Si) is an important trace element for bone tissue formation. It can stimulate cellular activities such as the proliferation and differentiation of osteoblast-like cells [19,20]. Researchers have studied the effect of SiO_2 doping on the mechanical and biological properties of bioceramics. They proved that SiO_2 doping increased the mechanical strength and facilitated

cellular proliferation [21–23]. However, silica additives used in these literatures were all solid SiO_2 particles [10,21,24].

In the present paper, silica was added as the state of silica sol. Silica sol is a aqueous solution and contains 30 wt% colloid silicon dioxide. It enables the nano-SiO_2 particles to be more uniformly dispersed into ceramic powders. The objective of this work was to investigate the effects of silica sol as a sintering additive on the mechanical strength and microstructure of CS ceramics.

2. Materials and methods

2.1. Experimental procedure

CS powder was synthesized by the chemical precipitation method. $Na_2SiO_3 \cdot 9H_2O$ and $Ca(NO_3)_2 \cdot 4H_2O$ were used as the source of Si and Ca, respectively [8]. Commercially available silica sol (30 wt%, Kangda Co., Jiangsu, China) was used as sintering additive. 1 wt% PVB (Polyvinyl Butyral, 7 wt%) was employed as binder.

CS, silica sol, binder (PVB) and ethanol were placed in a polyethylene bottle and ball milled for 4 h to obtain homogeneous slurries. Solid contents of the suspensions were fixed at 50 vol%. Compositions of β-CS powder and SiO_2 were listed in Table 1. It should be mentioned that the content of silica sol was designed based on the SiO_2 content (0–5 wt%). The slurry was dried at 70 °C and then sieved through a 100-mesh screen. The mixed powders were uniaxially pressed into rectangular-shaped specimens in a stainless steel die followed by cold isostatic pressing at 200 MPa. The specimens were sintered in air at temperatures ranging from 1000 °C to 1150 °C for 1–3 h at a heating rate of 2 °C/min and finally naturally cooled in the furnace. During the

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Table 1
Composition of the starting powders.

Specimen code	CS content (wt%)	SiO$_2$ content (wt%)
S0	100	0
S1	99	1
S2	97	3
S3	95	5

processing, silica sol was also sintered separately below 1150 °C to investigate its changes during sintering.

2.2. Characterization of the ceramic samples

Specimens were machined into the dimensions of 3.0 mm × 4.0 mm × 36.0 mm to measure the flexural strength via the three-point bending test (Instron 5566, INSTRON, Norwood, MA) with a support distance of 30.0 mm and a cross-head speed of 0.5 mm/min. Phase analysis was conducted by X-ray diffractometry (XRD, D/MAX-RBX, Rigaku, Osaka, Japan) with Cu K_α radiation ($\lambda = 0.15418$ nm). Microstructure was observed by scanning electron microscopy (SEM, JSM-6700F, JEOL, Akishima, Japan). Thermogravimetric differential thermal analysis (TG-DTA) experiment was performed for determining thermal behavior of green powders using a simultaneous thermalanalysis (STA) instrument (Thermoplus EVO II, Rigaku, Japan) at a heating rate of 10 °C/min and air flow of 30 ml/min. Open porosity was determined by the Archimedes method using distilled water as liquid medium. Moreover, all samples were measured before and after the sintering processing to calculate the linear shrinkage. Five samples each were tested to determine the average values of mechanical properties, open porosity and linear shrinkage.

3. Results and discussion

3.1. Phase analysis

The XRD pattern of the prepared CS powder is shown in Fig. 1 (a). It revealed that the as-prepared powder was β-CS and no other phases were detected. Fig. 1 (b) gives a typical SEM image of the as-prepared powder. The as-prepared powder was composed of irregularly shaped particles, and the grain size was below 5 μm.

Fig. 2 illustrates the phase composition of silica sol sintered at different temperatures. When the sintering temperature increased to 800 °C, silica sol transformed from amorphous state to cristobalite. Above 900 °C, tridymite peaks were detected and the diffraction intensities increased as the sintering temperature increase. All these results indicated that silica sol underwent complex changes during processing.

Fig. 3 shows the TG-DTA curves of β-CS green powder with 5 wt% SiO$_2$. During the processing, silica sol was dispersed uniformly as an initial state of nanometer sized SiO$_2$ particles. After being dried in the oven, silica sol was gelated. Further increasing the temperature caused the dehydration-condensation reaction of silica gel. And the process
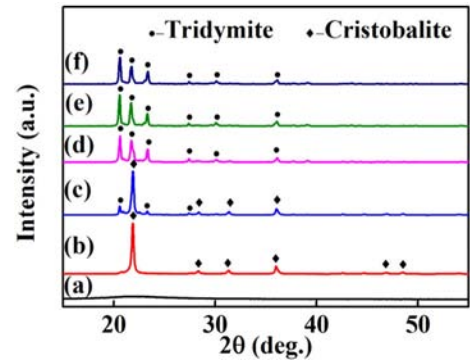

Fig. 2. XRD patterns of raw silica sol sintered at (a) 80 °C, (b) 800 °C, (c) 900 °C, (d) 1000 °C, (e) 1100 °C, (f) 1150 °C.
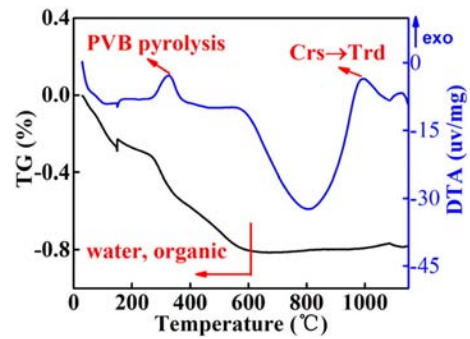

Fig. 3. TG-DTA curves of CS powder with 5 wt% SiO$_2$.

completed at around 800 °C, forming amorphous SiO$_2$. As the sintering temperature continued to increase, the crystallization of SiO$_2$ began. The mass loss below 600 °C was ascribed to the de-bonding of the bonded H$_2$O in the silica gel and the decomposition of PVB. The first exothermic peak around 310 °C in DTA curves was assigned to the decomposition of PVB. The second exothermic peak around 1000 °C originated from the crystallization of SiO$_2$ transforming from cristobalite to tridymite. The TG-DTA results were consistent with the phase composition analysis.

Fig. 4 (a, b) shows the XRD patterns of the specimens with different SiO$_2$ contents sintered at 1100 °C and 1150 °C, respectively. All the sintered specimens (S0-S3) showed the same crystal structure (β-CS) at 1100 °C and no other crystalline phases were detected because of little amount of sintering additive as shown in Fig. 4a. However, α-CS peaks can be observed in the XRD patterns of S1 to S3 sintered at 1150 °C as shown in Fig. 4b. In addition, the intensities of a-CS peaks increased gradually as the amount of SiO$_2$ increased. It suggested that silica sol promoted the phase transformation from β-CS to α-CS. The presence of α phase was closely related to the declining of mechanical
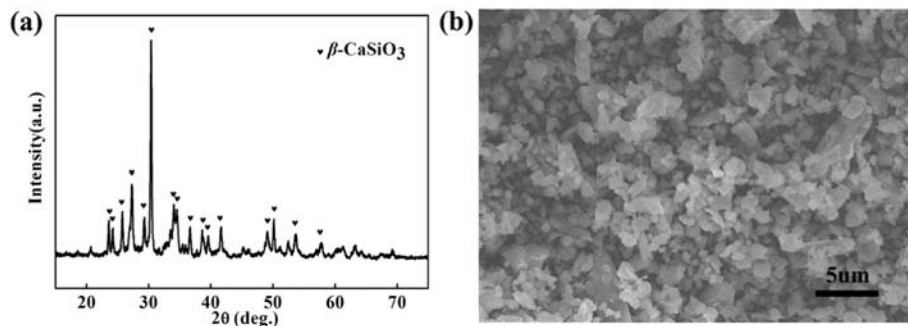

Fig. 1. (a) X-ray diffraction patterns and (b) SEM micrograph of the as-prepared CS powder.