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Biological properties study of bioactive wollastonite containing 5 wt% B_2O_3 prepared from local raw materials

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ABSTRACT

$CaSiO_3$ ceramics have been proposed as a medical material for artificial bone and dental root. In this work, $CaSiO_3$ powders were synthesized by mixture of (CaO) and (SiO_2). The samples were sintered at 1,150˚C for 2 h. Moreover, amounts of B_2O_3 (5.0 wt%) have been added. The *in vitro* bioactivity of both $CaSiO_3$ and B_2O_3–$CaSiO_3$ ceramics was investigated by soaking the powders in simulated body fluid (SBF) for various time periods to analyze the growth of hydroxyapatite (HA) on the surface of the powders. All the materials showed to be highly bioactive through the formation of a homogeneous HA on their surfaces. The B_2O_3–$CaSiO_3$ showed strong hydration in the early stages of soaking in the SBF, when compared with pure $CaSiO_3$, and the hydration was favorable for formation of carbonated HA. The results obtained indicate that the addition of B_2O_3 improved the biological properties of pure wollastonite.

Keywords: Wollastonite; B_2O_3; Apatite formation ability; Bioactivity; SBF solution

1. Introduction

Wollastonite ($CaSiO_3$) is a raw material mainly used for traditional ceramics [1]. Since the discovery of bioglass by Hench and co-workers in 1970 [2], various types of biomaterials containing CaO–SiO_2 such as wollastonite have been investigated as bioactive biomaterials for tissue repair and replacement [3–5]. Moreover, some investigators have reported that wollastonite and pseudowollastonite ceramics are bioactive and observed that the formation of apatite on $CaSiO_3$ ceramics is faster than that on other bioglasses and glass ceramics in simulated body fluid (SBF) solution, whose ion concentration was nearly equal to those of the human body blood plasma [6–10]. Furthermore, there are many wollastonite preparation routes: from its SiO_2 and CaO constituent oxides, sol-gel process, and solid-state reaction method. Because of their potential costs and relatively complicated samples preparation, the first two routes are discarded. For example, when powders

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Table 1
Concentration of SBF in comparison with human blood plasma [31]

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

were synthesized by sol-gel process, many expensive and toxic chemicals (such as acids) are generally used. Consequently, an alternative process is proposed. This process consists of replacing more expensive materials by other raw materials which are less expensive (and non toxics) and which are abundantly available. The main components of these raw materials are: calcite ($CaCO_3$), dolomite ($CaCO_3{\cdot}MgCO_3$), bones (natural derived hydroxyapatite (HA): $Ca_{10}(PO_4)_6(OH)_2$), kaolin, feldspar, and quartz. Many works have already been published in three main interesting research topics for the valorization of these native raw materials. These topics are advanced ceramics [11–15], ceramic membranes [16–23], and bioceramics [24–30]. Replacing the more expensive starting materials, by other low-cost raw materials is significantly important. The generally used starting chemicals price is at least about 100 times more expensive than that of high purities calcite ($CaCO_3$). Another important advantage is the substantial reduction in energy use by decreasing the sintering temperature from about 1,300˚C to about 1,050˚C, when the proposed process is applied.

Consequently, the main goal of this study was to evaluate the B_2O_3–$CaSiO_3$ powders bioactivity by examining HA formation on their surface in SBF.

2. Materials and methods

2.1. *Preparation of specimens*

$CaSiO_3$ powders were synthesized by solid-state reaction method according to our previously published study [26]. The method was based on the mixture of high purities SiO_2 (99.9%) and CaO extracted from local $CaCO_3$, after its calcination at 900˚C for 12 h, then hydrated in distilled water and followed by a second calcination at 800˚C for 2 h. A mixture of CaO and high-purity SiO_2 (99.9%) with CaO–SiO_2 molar ratio equal to one was prepared using wet ball milling for 3 h. Then, the mixture was calcined at 710˚C for 2 h. About 5.0 wt% of B_2O_3 have been added. Subsequently, the powder mixtures were compacted at 150 MPa. Then, the compacts were sintered at 1,150˚C for 2 h.

2.2. In vitro *tests*

The *in vitro* properties of the sintered specimens were investigated by their apatite forming ability in SBF. The wollastonite samples sintered at 1,150˚C for 2 h were ground and sifted through a 40–100 μm sieve, then soaked in SBF solution whose ion concentration was nearly equal to those of the human body blood plasma, as shown in Table 1 [31]. The SBF solution was buffered at pH 7.4 with trimethanol

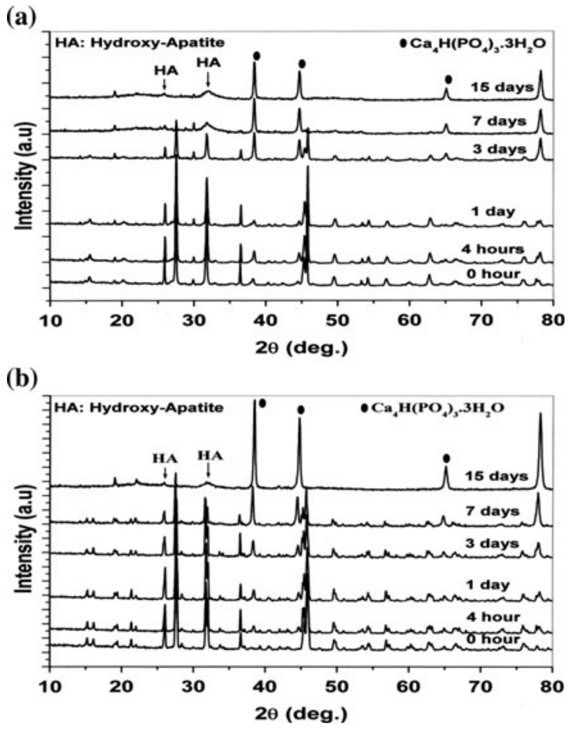

Fig. 1. XRD patterns of (a) α-$CaSiO_3$ powders and (b) α-$CaSiO_3$ with 5 wt% of B_2O_3 sintered at 1,150˚C for 2 h before and after soaking in SBF solution for various periods.

aminomethane–HCl. The samples were immersed in SBF solution at 37˚C for 4 h and 1, 3, 7, and 15 days. After soaking for various periods, the samples were gently removed from the fluids with deionized water, and followed by drying at room temperature for further characterization.

2.3. Characterizations

The surface structure and morphology of specimens before and after soaking in SBF solutions were characterized by: X-ray diffraction (XRD) (BRUKER, D8 ADVANCE) (Karlsruhe, Germany) with a CuK α radiation ($\lambda = 0.154$ nm) and a Ni filter, working voltage 40 kV, and working current 30 mA, scanning electron microscopy (SEM) (HITACHI, JSM-6301 F) (Tokyo, Japan) working at a 7 kV as an accelerating voltage and energy dispersive spectrometry (JEOL JSM-6400). The changes in concentrations of Ca, P, and Si ions in SBF solution after soaking were measured by an inductively coupled plasma (ICP) (Spectro, France).

3. Results and discussion

3.1. Formation of HAp on the surface of B_2O_3–$CaSiO_3$ powders

The XRD patterns of both the pure $CaSiO_3$ and B_2O_3 containing $CaSiO_3$ (B_2O_3–$CaSiO_3$) powders sintered at 1,150˚C before and after soaking in SBF solution for various time periods are shown in (Fig. 1(a) and (b)), respectively. Only α-$CaSiO_3$ peaks appears for the two powders before soaking in SBF solution, which indicates that B_2O_3–$CaSiO_3$ ceramics maintained α-$CaSiO_3$ structure at amounts of 5 wt% B_2O_3.

It is obvious that the characteristic peak intensities of both the pure $CaSiO_3$ and B_2O_3 containing $CaSiO_3$ (B_2O_3–$CaSiO_3$) powders decrease with the increase in soaking time and disappeared after 7 days of soaking. new peaks for $Ca_4H(PO_4)_3.3H_2O$ were apparent after 7 days, while the characteristic peaks of HA appeared after 7 days of soaking, indicating the formation of HA on the surface of α-$CaSiO_3$ powders.

The surface morphology of both the pure $CaSiO_3$ and B_2O_3 containing $CaSiO_3$ (B_2O_3–$CaSiO_3$) powders

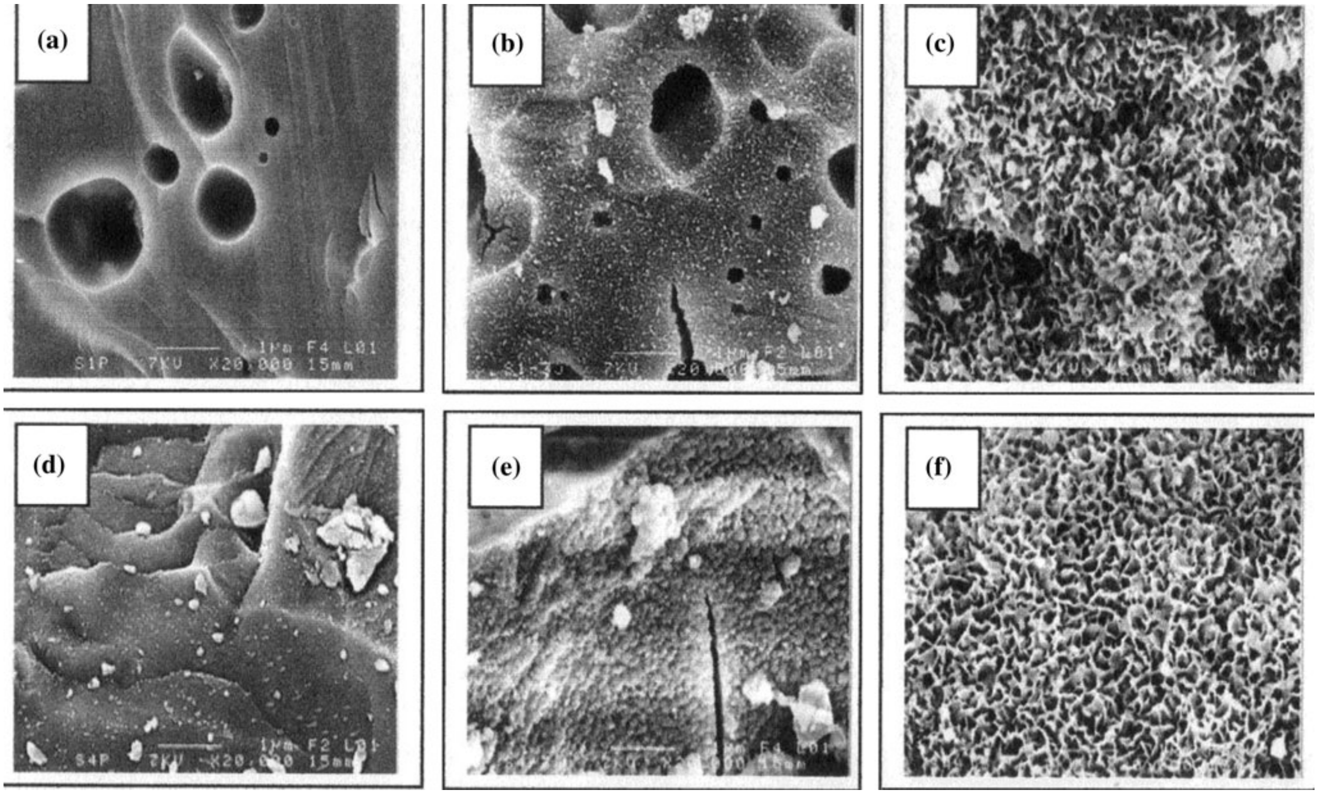

Fig. 2. SEM micrographs of α-$CaSiO_3$ before and after soaking in SBF solution for (a) 0 h, (b) 3 d, (c) 15 d and SEM micrographs of α-$CaSiO_3$ with 5 wt% of B_2O_3 before and after soaking in SBF solution for (d) 0 h, (e) 3 d, (f) 15 d.

before and after soaking in SBF solution for 3 and 15 days are depicted in Fig. 2. In comparison with the particles before soaking in SBF solution (Fig. 2(a)) of pure $CaSiO_3$ and (Fig. 2(d)) of B_2O_3–$CaSiO_3$, small ball-like particles appeared inside the pores, and on the surface of pure $CaSiO_3$ and B_2O_3–$CaSiO_3$ powders soaked in SBF for 3 days (Fig. 2(b)–(e)), respectively. After prolonged soaking for up to 15 days, the surface morphology of powders has changed and a continuous layer of dense deposits formed on the surface of pure $CaSiO_3$ and B_2O_3–$CaSiO_3$ powders (Fig. 2(c)–(f)), respectively.

The formation mechanism of apatite was proposed by Hench et al. [32]. The exchange of calcium ions in pseudowollastonite with H^+ in SBF solution gives rise to the formation of silanol (Si-OH) in the surface layer, an increase in pH value at the pseudowollastonite-SBF, and eventually the production of a negatively charged surface with the functional group ($Si–O^-$). This functional group ($Si–O^-$) had been proposed to be a catalyzing agent and could provide specific favorable sites for the apatite nucleation.

3.2. Concentration changes of Ca, P, and Si in SBF solution

The changes of concentrations of Ca, P, and Si in SBF solutions measured by ICP after soaking for various time periods were studied. It is obvious that the ion concentrations of SBF solutions changed markedly after soaking in SBF solution. The Ca and Si concentrations in SBF increased with an increase in the soaking time to 7 days. Afterwards, the Ca concentration in SBF decreased after 15 days of soaking. In contrast to the increase of Ca and Si, the P concentration of SBF solutions decreased during the soaking periods.

The increases in the calcium and silicon concentrations were attributed to the dissolution of these ions from the $CaSiO_3$ and B_2O_3–$CaSiO_3$ powders. Moreover, the decrease in the calcium ions after 15 days of soaking is due to a faster consumption of Ca ions during the subsequent formation of HAp on the surface of the powders. The decrease in the phosphorus concentration was attributed to the formation of both amorphous calcium phosphate and crystalline apatite on the surface of powders by consuming the P ions from the SBF solutions.

ICP measurement results suggest that Ca and Si concentrations increased, while P concentration decreased due to the formation of HAp on the surface of α-$CaSiO_3$ powders during the soaking in SBF solution.

4. Conclusion

Bioactive ceramics have been known to integrate with living bone by forming HA on their surfaces. The formation of HA is induced by functional groups on the materials, such as Si-OH.

Pure $CaSiO_3$ and B_2O_3–$CaSiO_3$ powders were synthesized using solid-state reaction. The results obtained indicated that pseudowollastonite (α-$CaSiO_3$) present high reactivity in SBF solution by showing strong hydration when soaked in it.

The obtained results suggest that both pure $CaSiO_3$ and B_2O_3–$CaSiO_3$ powders have an excellent reactivity in SBF solution by the formation of HAp in SBF solutions and are potential candidates as tissue repair biomaterials and bone tissue regeneration.

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