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Effect of sodium oxide and magnesia on structure, in vitro bioactivity and degradability of wollastonite

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ABSTRACT

Wollastonite $CaSiO_3$ (W-0) and $CaSiO_3$ doped with Na_2O (W-Na) or MgO (W-Mg) were synthesized by sintering sol–gel derived powders and compacts. The effects of Na_2O and MgO on structure, in vitro bioactivity, degradability and mechanical properties of wollastonite were studied. The main crystal phases of these ceramic powders were β-$CaSiO_3$. In addition, $Na_2Ca_2Si_3O_9$ appeared in sample W-Na and $Ca_3Mg(SiO_4)_2$ appeared in W-Mg. For ceramic block W-Mg, $CaMgSi_2O_6$ appeared. After soaking in simulated body fluid (SBF) for 7 days, the apatite layer was formed on the surface of these ceramics. The addition of Na_2O increased the degradation rate of wollastonite and MgO decreased the degradation rate. Na_2O and MgO improved the bending strength of wollastonite. The elastic moduli of ceramics accorded with that of dense bone of human body.

1. Introduction

Since Hench et al. [1] discovered the first bioactive silicate material, the research works on bioactive calcium phosphate silicate glasses for biomedical applications have received a lot of attention. Soon after Kokubo [2] suggested CaO and SiO_2 are the main cause of bone-bonding with bone tissue. Since then calcium silicate based bioceramics in particular wollastonite ($CaSiO_3$), have been studied as potential substitutes for bone tissue regeneration, because of their superior bioactivity and biocompatibility [3]. However, the dissolution rate of $CaSiO_3$ is relatively fast, which will hinder its clinical applications. The problem can be solved by developing multiphase materials containing highly dissolvable phases and stable phases [4,5]. Hence it is necessary to modify wollastonite by adding other components to obtain biomaterial with excellent properties.

Na^+ can regulate the functions of osteoblasts and Mg^{2+} is essential to bone metabolism [6,7]. They have effects on new bone formation [8,9]. This study chooses $CaSiO_3$ as the base material and the substitution of 5 mol% Na_2O or MgO for CaO in $CaSiO_3$ were synthesized by the sol–gel method and the influences of Na_2O and MgO on the properties of wollastonite were studied.

2. Experimental

$CaSiO_3$ (W-0), $45CaO–5Na_2O–50SiO_2$ (W-Na) and $45CaO–5MgO–50SiO_2$ (W-Mg) (in mol%) were synthesized by the sol–gel method using calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$), tetraethyl orthosilicate ($(C_2H_5O)_4Si$, TEOS), sodium nitrate ($NaNO_3$) and magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$) as raw materials. The detailed processes have been described in our previous work [10]. For preparation of ceramic powders, the precursor powders were firstly stabilized at 700 °C for 1 h and then sintered at 1000 °C for 1 h with a heating rate of 5 °C/min. For preparation of ceramic blocks, the mixture of precursor powders stabilized at 700 °C and polyvinyl alcohol water solution binders was uniaxially pressed at 200 MPa and then the compact samples were also sintered at 1000 °C for 1 h with the same heating rate.

The phases of ceramics were analyzed by X-ray diffraction (Shimadzu, XRD-6100). Scanning electron microscopy (SEM) observations and energy dispersive spectrometer (EDS) analysis were carried out on JEOL JSM-6700F and Hitachi S-3400 scanning. The bioactivity of ceramics was evaluated in simulated body fluid (SBF) at 37 °C in sterile polyethylene containers and the SBF solution was replaced every 2 days. The change in pH values of

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SBF solution was measured by Sartorius PB-10 pH-meter. The degradability of ceramics was evaluated in tris-(hydroxymethyl)-aminomethane and hydrochloric acid (Tris–HCl) buffer solution at 37 °C. The weight of each sample was measured using FA2104 electronic balance and the weight loss was expressed as the percentage of the initial weight. The bending strength and elastic modulus were measured by three-point bending method (RGD-5 type electronic tensile machine). The thermal expansion coefficient (TEC) was measured by thermal expansion coefficient tester (PCY-III-1000). These experiments were repeated three times.

3. Results and discussion

Fig. 1(a) shows the XRD patterns of ceramic powders. The diffraction peaks of these ceramics are indexed on monoclinic wollastonite phase β-$CaSiO_3$ (JCPDS 75-1396). In addition, new phase of $Na_2Ca_2Si_3O_9$ (JCPDS 22-1455) appears in sample W-Na. For sample W-Mg, the peaks of merwinite $Ca_3Mg(SiO_4)_2$ (JCPDS 35-0591) appear. Fig. 1(b) shows the XRD patterns of ceramic blocks. The crystal phases in block samples W-0 and W-Na are consistent with that in ceramic powders. While for sample W-Mg, new strong peaks corresponding to diopside $CaMgSi_2O_6$ (JCPDS 75-1092) appear and $CaMgSi_2O_6$ becomes the main crystal phase. This shows $CaMgSi_2O_6$ tends to precipitate on the surface of ceramic block in the sintering process. The diffraction peak intensity changes significantly compared with Fig. 1(a), which relates to the crystal grain forming and growing, grain size and preferred grain orientation during sintering. Fig. 1(c) shows the XRD patterns of ceramic blocks after immersion in SBF for 7 days. After soaking, the diffraction intensity of matrix phases are significantly reduced and the appreciable slight reflections corresponding to (200), (111), (002) and (211) reflection of hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) phase are observed, indicating the apatite has been induced on ceramics surface. Broadening peak appears at 21–24° (2θ) in these samples, which indicates the crystallinity of apatite is not high. The peak of $CaMgSi_2O_6$ at 31.662° (2θ) overlaps the (211) reflection of hydroxyapatite in sample W-Mg.

Fig. 2 is the SEM micrographs and EDS analysis of ceramic blocks before and after soaking in SBF for 7 days. Before soaking, a lot of spherical particles are compactly distributed on W-0 surface and a small amount of agglomerated particles are observed (Fig. 2a_1). When adding Na_2O, the surface becomes compact but has a large number of micropores (Fig. 2b_1). The presence of MgO in ceramic seems to make the surface more compact and smooth. In addition, a small number of holes are observed (Fig. 2c_1). After soaking, the surface of W-0 is fully covered by numerous apatite particles and the particle agglomeration are observed in some zones (Fig. 2a_2). When Na_2O was incorporated, the surface is fully covered by closely arranged spherical particles and spherical agglomerates on apatite layer are more apparent (Fig. 2b_2). Some small particles that not fully connected generate on W-Mg surface and obvious cracks emerged on drying appear on sample surface (Fig. 2c_2). The results of EDS analysis of ceramics after immersion show that the layer formed on sample surface mainly contains Ca, P and O.

Fig. 3 shows the change in pH values of SBF solution for ceramic blocks with immersion time. The change in pH values of different ceramics basically follows the same pattern and it relates to the exchange rate of ions. In the beginning of immersion time, pH value rises rapidly with the reason that the rapid ion exchange between Ca^{2+}, Na^+ or Mg^{2+} in ceramics and H^+ or H_3O^+ in SBF takes place. The rapid ion exchange leads to SiO_2-rich layer formation on ceramic surface and then Ca^{2+}, PO_4^{3-} and OH^- are migrated onto SiO_2-rich layer to grow into apatite [11]. The SBF solution is replaced every 2 days and the apatite can grow continuously.

Fig.4 shows the weight loss of ceramic blocks after soaking in the Tris–HCl solution. As can be seen, the weight loss of each ceramic increases with the increase of soaking time and the degradation rate of early period is faster than that of latter. The degradation rate of W-Na is faster than that of W-0 in early period and the degradation rate of W-Mg is the slowest. After soaking 7 days, sample W-0 shows the weight loss of 4.17%, W-Na shows a slightly higher weight loss of 4.29% and W-Mg presents the lowest weight loss of 3.02%. Na_2O reduces oxygen concentration in material and destroys the structural integrity, which can improve the ion release rate [12]. Therefore, the degradation rate accelerates and the apatite layer can be quickly formed on ceramic surface. Part of magnesia can enter into silicate network and the modifying character of Mg^{2+} is smaller than that of Ca^{2+} (Dietzel's ionic field strength of Mg^{2+} is larger than that of Ca^{2+}), which makes the structure tight and then reduces the ion exchange rate [13]. Consequently, MgO causes a decrease of degradation rate. In addition, the presence of more than one crystalline phase in sample W-Na and W-Mg can also affect the degradability and bioactivity of ceramics.

The bending strength and elastic modulus of ceramics are tested. The bending strength of W-0, W-Na and W-Mg are 25.33 ± 1.75, 29.51 ± 1.62 and 35.06 ± 2.11 MPa, respectively. Na_2O and MgO improve the bending strength of wollastonite, especially the effect of MgO on bending strength is more obvious. Many factors cause the enhancement of bending strength, such as density, grain size and shape, the uniformity of grain structure, porosity, micro-cracks and crystalline phases [14]. The presence of multiple phases in ceramics can also affect the mechanical behavior. The elastic moduli of W-0, W-Na and W-Mg are 5.03 ± 0.61, 6.47 ± 0.72 and 6.23 ± 0.77 GPa, respectively, which accord with that of cancellous bone (3.2–7.8 GPa) and dense bone (3.9–11.7 GPa) of human body. These bioceramics are recommended as bone replacement materials.

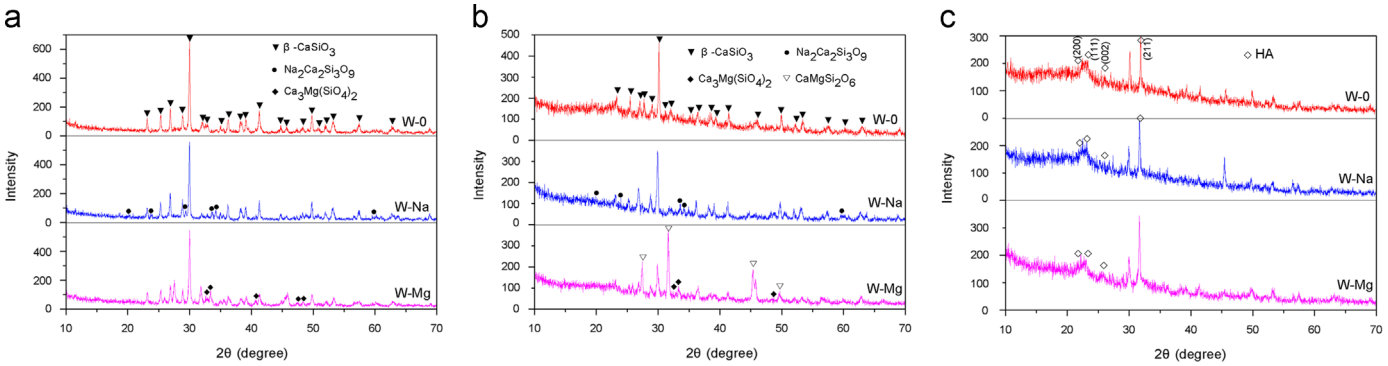

Fig. 1. XRD patterns of ceramic powders (a), ceramic blocks before (b) and after (c) immersion in SBF for 7 days.