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Effect of magnesia on structure, degradability and in vitro bioactivity of $CaO–MgO–P_2O_5–SiO_2$ system ceramics

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ABSTRACT

$CaO–MgO–P_2O_5–SiO_2$ system ceramics with various magnesia contents (0, 5, 10 and 20 mol%) were successfully prepared by sintering the sol–gel-derived powder compacts. The ceramic degradation was evaluated through the weight loss in the tris-(hydroxymethyl)-aminomethane and hydrochloric acid (Tris–HCl) buffer solution, and their ability to form apatite was determined by soaking in simulated body fluid (SBF). Results indicated that the ceramics structure was greatly influenced by magnesia contents. New crystal phases of $Ca_2MgSi_2O_7$ and SiO_2 were formed when magnesia was added and with an increase of magnesia concentration the phase of $Ca_2MgSi_2O_7$ increased with a simultaneous decline of β-$CaSiO_3$. In addition, studies showed that magnesia played an important role in affecting the degradability and apatite forming ability of $CaO–MgO–P_2O_5–SiO_2$ system ceramics. It is observed that with increasing magnesia concentration, the ceramic degradability gradually decreased and the formation of apatite on samples was delayed.

1. Introduction

Over the last decade or so, $CaO–SiO_2$-system bioceramics, in particular $CaSiO_3$, have attracted more attention as potential bioactive materials for bone repair or regeneration because of their good biocompatibility and bioactivity [1,2]. However, the $CaSiO_3$ bioceramics suffer from their high dissolution rate leading to high pH value and inducing deleterious influence on cell growth [3,4]. It is notable that magnesium, one of the main trace metallic elements, can be observed in human body. Enamel, dentin and bone contain 0.44, 1.23 and 0.72 wt.%, respectively [5]. It has been reported that magnesium plays an important role in human bone development, maintenance and repair through stimulating osteoblast proliferation [6]. Furthermore, previous studies have shown that the incorporating of magnesia into silicate glasses can modify their stability and mechanical properties [7,8].

A group of sol–gel-derived 58S bioglass in the $CaO–P_2O_5–SiO_2$ system has been widely studied, its excellent bioactivity offers great potential for hard tissue surgery [9]. For this reason, in our previous paper [10], the sintering on 58S was performed and $CaSiO_3$-based bioceramics were obtained. In this paper, the incorporation of magnesia into the $CaO–P_2O_5–SiO_2$ system at various concentrations was conducted and the influences of magnesia on ceramic microstructure, degradability and in vitro bioactivity were evaluated.

2. Experimental

$(0.38-x)CaO–xMgO–0.04P_2O_5–0.58SiO_2$ ($x=0$, 0.05, 0.1 and 0.2) powders were synthesized by the sol–gel method using calcium nitrate tetrahydrate ($Ca(NO_3)_2\cdot4H_2O$), magnesium nitrate hexahydrate ($Mg(NO_3)_2\cdot6H_2O$), triethyl phosphate (($OP(C_2H_5O)_3$), TEP) and tetraethyl orthosilicate (($(C_2H_5O)_4Si$, TEOS) as raw materials. The detailed processes have been described in our previous work [11]. For preparation of ceramic disks, the mixture of glass powders (38–74 μm) stabilized at 700 °C and polyvinyl alcohol water solution binders was uniaxially pressed at 200 MPa, and then the green disks of 10 mm diameter and 3 mm height were sintered at 1200 °C for 2 h with a heating rate of 5 °C/min.

The phases of samples were analyzed by X-ray diffraction (XRD, Bruker, D8 Advance), and the microstructure analysis was performed on a scanning electron microscope (SEM, JEOL, JSM 6380LA). The evolution of ceramic degradability was carried out according to the ISO 10993-14 standard. Tests were performed in tris-(hydroxymethyl)-aminomethane and hydrochloric acid (Tris–HCl) buffer solution (pH 7.4) at 37 °C, using triplicate samples. At the end of each period of soaking time, samples were rinsed with deionized water and acetone and dried in air at room temperature. Finally, the weight of each sample was measured using a type of FA2104 electronic balance with an accuracy of 0.1 mg, and the weight loss was expressed as the percentage of the initial weight. In addition, the bioactivity of ceramics was evaluated in simulated body fluid (SBF), proposed by Kokubo et al. [12], at 37 °C in sterile polyethylene containers.

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3. Results and discussion

Fig. 1 shows the XRD patterns of the sintered ceramics. Wollastonite β-$CaSiO_3$ (JCPDS 42-0547) and pseudowollastonite $Ca_3(Si_3O_9)$ (JCPDS 74-0874) phases are observed in the magnesia-free ceramic. For the ceramics containing magnesia, it is indicated that Mg can react with Ca, Si and O forming a new crystal phase of akermanite $Ca_2MgSi_2O_7$ (JCPDS 35-0592) and the incorporation of magnesia induces the formation of cristobalite SiO_2 (JCPDS 27-0605). For Ca^{2+} and Mg^{2+}, the Dietzel's ionic field strength I ($I = Z/r^2$, where Z and r are the cation charge and the radius, respectively) is 2.04 $Å^{-2}$ and 4.73 $Å^{-2}$, respectively, indicating that the glass modifying character of Ca^{2+} is larger than that of Mg^{2+}. It has been reported that part of magnesia acts as a network intermediate and enters into the silicate network as MgO_4 tetrahedral units [13]. Therefore, as magnesia is added at the expense of calcium oxide, the glass network will be tighter and the formation of MgO_4 will increase polymerization, which promotes the crystallization of $Ca_2MgSi_2O_7$ and SiO_2. Furthermore, magnesia concentration greatly affects the ceramic crystal phase composition. With increasing of the magnesia content, the intensity of $Ca_2MgSi_2O_7$ peaks increases with the simultaneous decline of β-$CaSiO_3$.

Fig. 2 shows the weight loss of ceramics after soaking in Tris–HCl solution. As can be seen, the weight loss of each ceramic increases with the soaking time. After soaking for 28 days, the magnesia-free ceramic shows the highest weight loss (16.5%) and the ceramic containing the most magnesia (20 mol%) presents the lowest weight loss (8.5%). It is suggested that the ceramic degradability correlates to the magnesia content. As shown in Fig. 1, for the magnesia-containing ceramics, phases of $Ca_2MgSi_2O_7$ and SiO_2 are also observed besides β-$CaSiO_3$. SiO_2 is a bioinert material, $Ca_2MgSi_2O_7$ has been proved to be bioactive and its degradation rate is significantly lower than that of β-$CaSiO_3$ [14]. Therefore, it is comprehensible that the role of the magnesia content in altering the dissolution of the $CaO–MgO–P_2O_5–SiO_2$ system ceramics is mainly achieved by the formation of $Ca_2MgSi_2O_7$ and SiO_2 phases. Especially, for bone tissue repair applications, bioactive ceramics with various degradation rates are needed, and the desired degradation can be obtained by the adjustment of magnesia contents in $CaO–MgO–P_2O_5–SiO_2$ system ceramics.

XRD patterns of ceramics after 14 days of soaking in SBF are shown in Fig. 3. The diffraction peaks at 25.7, 31.9 and 32.8° (2θ) assigned to the (002), (211) and (300) reflections of hydroxyapatite (HAp, JCPDS 24-0033) are obviously investigated on the magnesia-free ceramic. For other ceramics, with the increase in the magnesia content, it is shown that the intensity of apatite peaks decline and for ceramic with 20 mol% magnesia, most of apatite peaks diminish, only a crystalline peak at 25.7° 2θ corresponding to the (002) reflection of HAp is found, which can be attributed to the c-axis preferred orientation of the HAp crystal [15]. Moreover, compared with the sample before soaking, it is worth noting that the β-$CaSiO_3$ and $Ca_3(Si_3O_9)$ peaks intensity greatly decline after soaking in SBF, which can be attributed to their dissolution and bioactivity behavior [1,16]. It seems that the ceramic apatite-formation ability has some relationship with its degradability. A lower value of degradability indicates a lower formation rate of apatite, this result is in agreement with the research of Ducheyne et al. [17]. The incorporation of magnesia decreases the degradability of $CaO–MgO–P_2O_5–SiO_2$ system ceramics, however, it does not suppress the apatite formation on these ceramics in SBF, especially for the ceramics with 0–10 mol% magnesia, the apatite formation is obvious, as confirmed by Fig. 3. As it is shown, $Ca_2MgSi_2O_7$ possesses a significantly lower ionic release rate than β-$CaSiO_3$, and this effect directly correlates to the apatite formation. Moreover, with the substitution of Mg for Ca and the depletion by crystallization of $Ca_2MgSi_2O_7$, the release of Ca reduces and therefore decreases the apatite crystallization and growth [18]. This is further confirmed by the ceramic morphologies after soaking in SBF. SEM photomicrographs of the ceramics after soaking in SBF for 14 days are shown in Fig. 4. The magnesia-free ceramic surface (Fig. 4(a, b)) is fully covered by a compact apatite layer constituted by numerous aggregates of spherical and lathlike crystals. Such similar behavior can also be

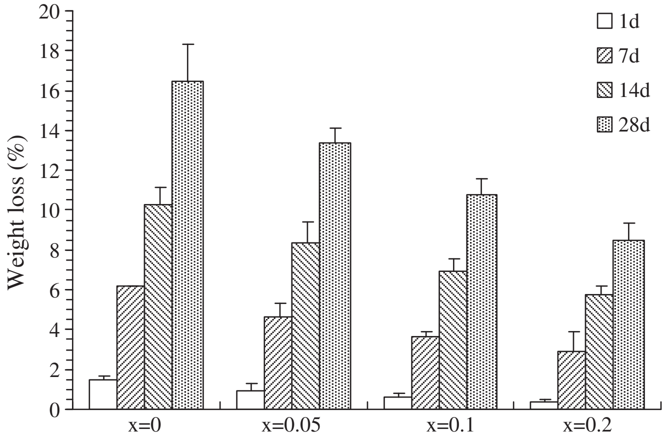

Fig. 2. Weight loss in Tris–HCl as a function of soaking time for $(0.38-x)CaO–xMgO–0.04P_2O_5–0.58SiO_2$ ceramics.

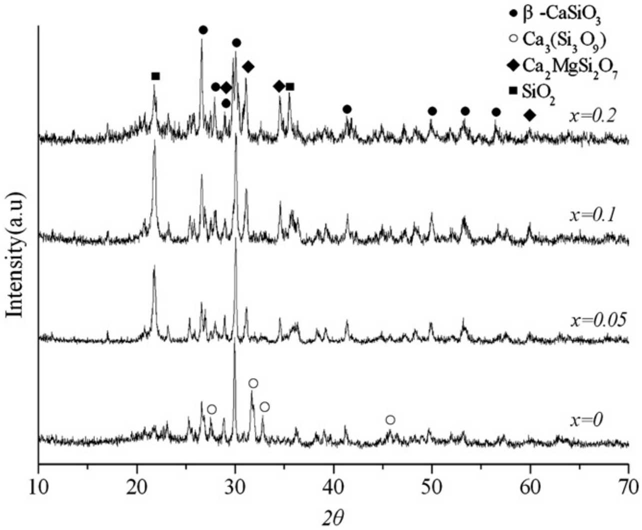

Fig. 1. XRD patterns of $(0.38-x)CaO–xMgO–0.04P_2O_5–0.58SiO_2$ ceramics.

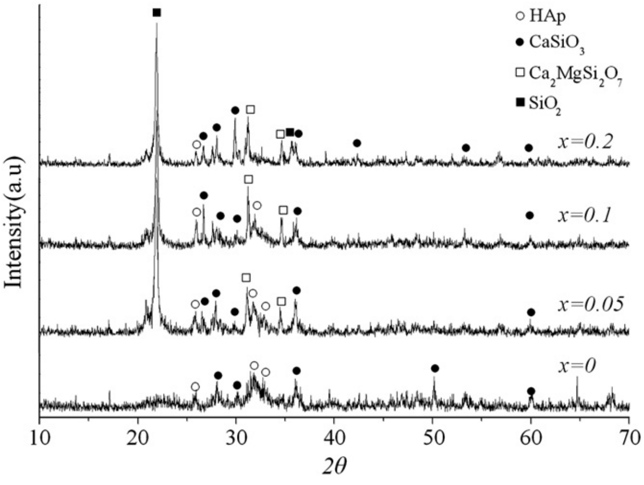

Fig. 3. XRD patterns of $(0.38-x)CaO–xMgO–0.04P_2O_5–0.58SiO_2$ ceramics after soaking in SBF for 14 days.