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Research paper

Simultaneous mechanical property and biodegradation improvement of wollastonite bioceramic through magnesium dilute doping

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ABSTRACT

The large-area bone defects in head (including calvarial, orbital, and maxillofacial bone) and segmental bone are attracting increased attention in a wide range of clinical departments. A key requirement for the clinical success of the bioactive ceramics is the match of the mechanical behavior of the implants with the specific bone tissue to be filled. This raises the question as to what design strategy might be the best indicators for the balance between mechanical properties and biological performances. Here we go beyond the traditional approaches that use phase conversion or biphasic hybrid; instead, we achieved a simultaneous enhancement of several mechanical parameters and optimalization of biodegradability by using a dilute doping of Mg in a single-phase wollastonite bioceramic. We show that the wollastonite ceramic can be rationally tuned in phase (α or β), mechanical strength (in compression and bending mode), elastic modulus (18–23 GPa), and fracture toughness (>3.2 MPa $m^{1/2}$) through the usage of Mg dopant introduced at precisely defined dilute concentrations (Mg/Ca molar ratio: 1.2–2.1%). Meanwhile, the dilute Mg-doped wollastonite ceramics are shown to exhibit good bioactivity in vitro in SBF but biodegradation in Tris is inversely proportional to Mg content. Consequently, such new highly bioactive ceramics with appreciable strength and toughness are promising for making specific porous scaffolds for enhancing large segmental bone defect and thin-wall bone defect repair.

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1. Introduction

Trauma, infection, and congenital deformity can result in over critical-size bone defects or lost that cause a series of challenges for reconstructive surgeons. In cases where thin-wall calvarial, orbital, and maxillofacial bone defects, as well as load-bearing long bone defects are caused by high-energy trauma or debridement for infected tissues or tumors, the local blood circulation in bone bed is poor, and the specific requirement of mechanical properties and biological performances of the grafts lead to fail to survive (Kilinc and Aytekin, 2014; Kinnunen et al., 2010; Leu et al., 2009; Takumi and Akimoto, 2009; Zhou et al., 2011). Therefore, the materials should be able to fabricate complex shapes with desirable patient-tailored applications, meanwhile the promotion of bone tissue regeneration and in situ repair are the optimal directions in orthopedic research.

Since Hench et al. firstly discovered Bioglass® which was proved to possess excellent bioactivity and osteoconductivity in the early 1970s (Hench et al., 1971), Ca–silicate bioactive glasses, glass–ceramics, and bioceramics have been widely studied for their potential applications as hard tissue repair materials (De Aza et al., 2000; Gerhardt and Boccaccini, 2010; Kokubo et al., 1986; Sprio et al., 2009), special implants or prosthesis (Baino and Vitale-Brovarone, 2014, 2015; Huhtinen et al., 2013), as well as drug delivery (Soundrapandian et al., 2014). For bone regeneration, the artificial materials need to meet the requirements of good osteoconduction, osteoinduction, as well as controllable bioactivity and degradation (Hench and Polak, 2002). Besides, the bone implants should have considerable fracture strength and toughness which match the bone biomechanical requirement in thin-wall bone trauma.

In the last decade, β phase of wollastonite (CSi) has attracted significant attention among the most promising candidates due to its outstanding bioactivity (Siriphannon et al., 2002). De Aza PN and colleagues found that the CSi ceramic exhibited faster apatite formation than other CaP in human parotid saliva (De Aza et al., 2000). Some studies have also shown that Ca and Si ions play important roles in the formation of the apatite layer, and affect the biological metabolism of osteoblastic cells which indirectly influenced the mineralization process and bone-bonding mechanism (Mohammadi et al., 2014). However, the slightly faster degradation rate which mismatches with the bone tissue regeneration during the new bone ingrowth (Xu et al., 2008), especially, the relatively low fracture strength and toughness which fails to meet the specific mechanical requirement in thin-wall bone defects constrains its clinical applications (Bratton and Durairaj, 2011). To reinforce the structure and to enhance the mechanical strength, biopolymer (Shirazi et al., 2014b), metallic oxide (Shirazi et al., 2014a) and many other materials are used to modify the CSi based materials scaffolds (Mehrali et al., 2013).

The importance of magnesium (Mg) in human body, its key role in mineralization of calcined bone tissues and indirectly influences mineral metabolism (Althoff et al., 1982), in addition to its application to improve and modify physical, thermal, and mechanical properties of bioactive glasses and ceramics, make Mg a very interesting element as a component of bioactive materials for medical applications (Diba et al., 2014, 2012). In vivo studies have also proved that appropriate concentration of Mg ion is beneficial to vascularization (Witte et al., 2005). According to the above consideration, intensive research has been devoted to developing Ca–Mg–silicate ceramics to improve the osteogensis (Hoppe et al., 2011), strength, and compositions of the bone implants. Chang's group (Wu and Chang, 2006; Wu et al., 2005; Wu and Chang, 2013) and other researchers (Chen et al., 2008, 2010; Nonami and Tsutsumi, 1999) have investigated a series of studies involving stoichiometric compounds with Mg content increased from 3.61% for bredigite ($Ca_7Mg(SiO_4)_4$), 7.39% for merwinite ($Ca_3Mg(SiO_4)_2$), 8.92% for akermanite ($Ca_2MgSi_2O_7$), 11.22% for diopside ($CaMgSi_2O_6$), to 15.53% for monticellite ($CaMgSiO_4$). These ceramics showed acceptable bioactivity, whereas the dissatisfactory mechanical strength and fracture toughness mismatch limited their applications.

In this work, we aimed to develop the Mg dilute doping CSi ceramics with varied Mg/Ca molar ratio of 3–10%, and studied their sintering behavior and mechanical properties. As expected, as Mg dilute doping may retain the crystalline phase of CSi when below 10% of Ca is substituted by Mg. The new bioceramics with appropriate Young's modulus, high flexural strength and fracture toughness were obtained by using presureless sintering technique. This study suggests that the Mg dilute doping is perfect for making new bioceramic products with exceptionally improved mechanical properties for some challengeable bone defect repair.

2. Materials and methods

2.1. Preparation of ceramic powders

The Mg-doped CSi (CSi–Mg*x*) powders with different Mg/CaO ratio, *x* (*x*=3, 6, 10, 14 mol%), were synthesized through a chemical precipitation method. Briefly, $Ca(NO_3)_2 \cdot 4\ H_2O$ and $Na_2SiO_3 \cdot 9H_2O$ were separately dissolved in de-ionized water in the concentration of 0.6 mol l^{-1} with certain proportion of $Ca(NO_3)_2$ replaced by $Mg(NO_3)_2$. Then the Na_2SiO_3 solution was dropped into the $Ca(NO_3)_2$/$Mg(NO_3)_2$ solution mixture under continuous stirring and the pH value maintained at 10.0–10.5. The powder precipitate was filtered, washed four times with de-ionized water, and finally washed by ethanol. The powder was dried at 80 °C, and then calcined at 950 °C for 150 min. The pure CSi powder was also synthesized as control while the other conditions remain the same. The ceramic powders were ground in a planetary ball miller (MP-2L; Chishun Sci&Tech Co., China) with 320 rpm, using 3.5 mm diameter Zirconia ball media in ethanol to obtain superfine powders (below 10 μm).

2.2. Preparation of CSi and CSi–Mg*x* ceramics

The CSi–Mg*x* green compacts with cylindrical (Ø6 × 2 mm, Ø8 × 10 mm, Ø25 × 4 mm) and cuboid (45 × 5 × 8 mm^3) shapes were prepared with a pressure of 8 MPa. Specifically, the polyvinyl alcohol (PVA; ~6 kDa) solution (3.0% v/v) was prepared under magnetic stirring at 45 °C. Then the PVA