Materials Science and Engineering C 70 (2017) 155–160

Contents lists available at ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

Combined effect of magnesia and zirconia on the bioactivity of calcium silicate ceramics at C\S ratio less than unity

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ARTICLE INFO

Article history:
Received 25 December 2015
Received in revised form 29 July 2016
Accepted 22 August 2016
Available online 24 August 2016

Keywords:
Calcia-silica
Magnesia
Zirconia
SBF
Bioactivity
Vickers hardness
Fracture toughness

ABSTRACT

This paper describes the effect of magnesia in the presence of zirconia on the bioactivity, microstructure and physico-mechanical properties of calcium silicate composition adjusted at calcia/silica ratio(C/S) of 0.5. A mixture from calcium carbonate and silica was conducted at C/S of 0.5. 20 wt.% of magnesia and 5-25 wt.% of ZrO_2 were added. Each mixture was mixed with ethanol in a planetary ball mill, dried, formed and fired at a temperature of 1325 ± 5 °C. Phase composition, FE-SEM, and physico-mechanical properties of the fired specimens were determined and explained. The in vitro bioactivities of these specimens were investigated by analysis of their abilities to form apatite in the simulated body fluid (SBF) for a short time (7 days) using SEM-EDS. The findings indicated that the surface of the specimens containing 5 and 15 wt.% ZrO_2 were completely covered by single and multilayered hydroxyapatite (HA) precipitate typical to "cauliflower" morphology, respectively. The surface of the specimen containing 25 wt.% ZrO_2 did not cover, but there are some scattered HA precipitate. The differences among the results were rationalized based on the phase composition. Vickers hardness and fracture toughness of the specimens of highly promised bioactivity were 2.32–2.57 GPa and 1.80–1.50 MPa. $m^{1/2}$, respectively. The properties of these specimens are similar to the properties of human cortical bone. Consequently, these composites might be used as bone implant materials.

1. Introduction

Bioceramics have become an important class of biomaterials in particular bioactive ceramics which directly form chemical bonds with bone tissues. The oldest bioactive material is the glass 45S5 (bioglass) which was first proposed by Hench et al. [1]. The CaO-SiO_2 based ceramics have been regarded as potential candidates for artificial bone due to their excellent bone bioactivity and biocompatibility. However, they cannot be used as implants under a heavy load because of their poor of the mechanical properties, in particular fracture toughness [2, 3]. Thus, the bioceramic materials with high mechanical properties as well as high apatite mineralization have become the bottleneck. Many researchers devoted their efforts to overcome this shortcoming. Magnesia (MgO) was added to CaO-SiO_2 ceramics and the results recorded gave a remarkable improvement in their mechanical properties through the formation of new phases such as akermanite ($Ca_2MgSi_2O_7$) and diopside, ($CaMgSi_2O_6$) [4–9]. However, the developed phases have high mechanical properties, but they have a low apatite formation in SBF compared with calcium silicate ceramics [6]. Other researchers have tried to find new applications that meet these requirements. High strength inert zirconia or metal substrate coating by wollastonite, hydroxyapatite and bioactive glass were proposed to match such purpose [3] [10–15]. On the other hand, zirconia ceramics have attractive properties such as high strength and fracture toughness for biomedical applications [16]. They have been applied in the heads of hip joint prostheses. However, Zirconia does not bond to the living bone. Interestingly, in 2001, Kokubo et al. pointed that zirconia ceramics exhibit a bone bonding ability from apatite formation when their surfaces are functionalized by hydroxyl(−OH) groups [17]. A nano-composite of ceria- stabilized tetragonal zirconia polycrystals (Ce-TZP) and alumina (Al_2O_3) polycrystals induced apatite forming ability via chemical treatments in aqueous solutions of H_3PO_4, H_2SO_4, HCl or NaOH [18]. Thus, the addition of zirconia may improve the biological and mechanical properties together. In this work, additional efforts were added to solve this problem through a systematic study. Designing new specimens containing calcia, magnesia and silica with different additions of zirconia were examined. Physico-mechanical properties and apatite forming ability have been determined. These specimens were constructed to take advantage of the combination of both bioactive phases (diopside, akermanite) and bioinert phase (baddeleyite). The results were compared with the reported data.

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http://dx.doi.org/10.1016/j.msec.2016.08.057
0928-4931/

Table 1
Chemical composition analysis of silica and zirconia as measured by XRF.

Oxides	Chemical composition, Wt%	
	Silica	Zirconia
ZrO_2	–	98.32
SiO_2	97.93	0.75
Al_2O_3	0.85	0.30
Na_2O	0.10	0.13
MgO	0.08	–
P_2O_5	–	0.06
SO_3	–	–
K_2O	0.10	–
CaO	0.84	0.16
TiO_2	0.10	0.11
Fe_2O_3	–	0.12
F	–	–
Cl	–	0.05
L.O.I.	–	–

Table 3
Compositions of A, B, C and D composites.

Mixture	Composition, wt.%			
	SiO_2	$CaCO_3$	MgO	ZrO_2
A	42.16	37.80	20.00	0.00
B	40.05	35.90	19.00	5.00
C	35.84	32.13	17.00	15.00
D	31.62	28.35	15.00	25.00

Table 4
Ion concentrations of SBF and human blood plasma (mM).

	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	HCO_3^-	HPO_4^{2-}
SBF	142.00	5.00	1.50	2.50	148.80	4.20	1.00
Blood Plasma	142.00	5.00	1.50	2.50	103.00	27.00	1.00

2. Materials and experimental procedure

2.1. Materials

Most of the raw materials utilized in this investigation were chemically grade materials. $CaCO_3$ as a source of calcia (C: CaO) (Fisher Chemical, UK), magnesia (M: MgO) (LOBA Chemie for laboratory reagents and fine chemicals, India), zirconia (Z: ZrO_2) (SEPR, France) and quartz as a source of silica (S: SiO_2) (El-Nasr Company for Refractories and Ceramics "Sornaga", Egypt) were used. The chemical analysis of zirconia and silica powders supported by analytical XRF (Model advanced axios Netherlands) was given in Table 1. MgO was a heavy extra powder of purity of 99% and its particle size was <5 μm. The particle size of zirconia and silica was given in Table 2. The particle size distribution of zirconia and silica was measured using a laser light-scattering particle-size analyzer (Model LB500, Horiba. Tokyo).

2.2. Experimental procedure

A mixture of calcium carbonate and silica was conducted at C/S molar ratio of 0.5. 20 wt.% of magnesia and 5–25 wt.% of ZrO_2 were added. The mixtures composition was given in Table 3. The mixtures were wet mixed with ethanol in a planetary mill for 45 min using a zirconia ball to produce a homogenous mixture. The mixtures were dried and ground to pass through a 0.1 mm sieve. The powders were uni-axially pressed (KPD-30 A, Spain) at 60 MPa into a cylindrical shape of 2.3 cm diameter and 1 cm length. The specimens were dried in oven at 110 °C for 24 h and then fired at 1325 ± 5 °C for 2 h in a programmable electric furnace (HT 16/17, Nabertherm, Germany). The temperature of the specimens was raised from room temperature to the targeted firing temperature with a constant rate of 4 °C/min.

2.3. Characterization

Phase composition and crystalline phases in sintered specimens were identified by advanced X-ray powder diffraction using Bruker advanced X-ray diffractometer model D8 Kristalloflex (Ni-filtered Cu Kα radiation; λ = 1.544 Å, Germany). In addition, the Crystallite sizes were calculated from the XRD pattern by applying Scherrer's equation.

Table 2
Particle size distribution of silica and zirconia powders.

Material	Particle size, μm		
	d_{10}	d_{50}	d_{90}
Silica	2.69	25.95	104.70
Zirconia	1.32	5.38	13.95

Microstructural features of the sintered specimens were characterized using a field emission scanning electron microscope (FESEM; QUANTA FEG250 Made in NL). The surfaces of the specimens were examined using backscattered electron signals (BSE). Elemental analysis of each phase was also performed using the energy dispersive X-ray spectroscopy (EDX) equipped in the FESEM.

The apatite-formation ability of the obtained sintered specimens were evaluated by soaking in a simulated body fluid (SBF) solution at pH 7.45 and temperature of 36.5 °C for 7 days. The SBF solution was prepared according to the procedure described by Kokubo and Takadama [19]. Its ion concentrations were similar to those in human blood plasma as shown in Table 4. After soaking for 7 days, the specimens were rinsed with water, dried at ambient conditions and characterized by SEM.

Apparent porosity and bulk density of sintered specimens were determined by an Archimedes immersion technique using kerosene [20].

Vickers hardness (H_V) and fracture toughness (K_{IC}) of the obtained ceramic specimens were determined at room temperature on the polished surface considering an average of five indentations using a Vickers indentation method [21–25] with 20 kg load for 15 s. Vickers hardness was computed using the following relation:

$$Hv = 0.0018544\left(p/d^2\right)$$

where p is the indentation load (N), d is an average length of the two

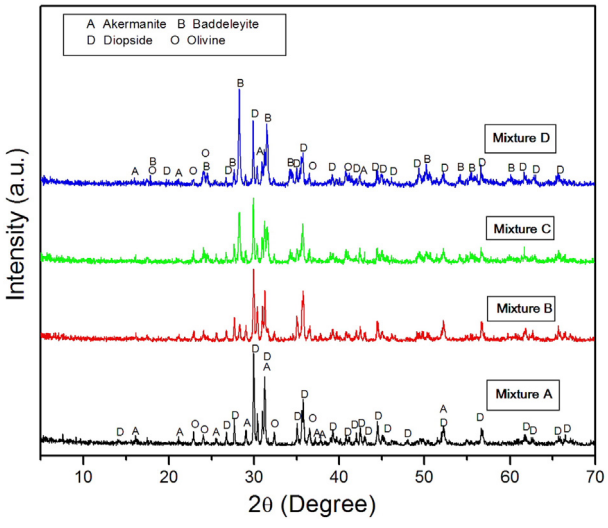

Fig. 1. X ray patterns of the sintered A, B, C and D specimens.