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Characterization of CaO-ZrO_2 Reinforced Hap Biocomposite for Strength and Toughness Improvement

Zaw Linn Htun[a,b], Nurazreena Ahmad[a], Aye Aye Thant[b], Ahmad-Fauzi Mohd Noor[a,*]

[a]*School of Materials and Mineral Resources Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Pulau Penang, Malaysia.*

[b]*Department of Physics, University of Yangon, 11041 Kamayut, Yangon, Myanmar.*

Abstract

Hydroxyapatite (HAp) has been used extensively in medical applications for repair or replacement of bone tissues in human body system. It is chemically similar to the mineral component of bone and teeth and will form an artificial bone-like structure with the surrounding bone tissue when implanted. However, sintered hydroxyapatite material exhibits relatively poor mechanical properties than natural bone and as such, improvement of mechanical properties are necessary. One of the candidate materials for the reinforcing phase to HAp is zirconia, ZrO_2. Medical applications of ZrO_2 implants confirmed their satisfactory biocompatibility, although it cannot bond well to bone tissue. In this study, ZrO_2/HApbiocomposites were fabricated with the objective to improve the strength and toughness of the biomaterial. Commercial CaO-ZrO_2 (CZ) was selected as the reinforced material to the HAp matrix. Small amounts of CaF_2 were added to improve sinterability and the phase stability of these biocomposites. Conventional ceramic processing route was used to prepare ZrO_2/HAp samples, which involved milling and mixing, compaction and sintering. X-ray diffraction (XRD), linear shrinkages, density and porosity, flexural strength, Vickers microhardness, toughness, and scanning electron microscopy (SEM) were used to characterize the (ZrO_2/HAp) biocomposites. XRD results indicate phase stability of biocomposites to a temperature of 1200 °C. Shrinkage of fired samples were very uniform with increasing temperature, with slightly lower shrinkage in thickness direction. In general, strength of the reinforced ZrO_2/HAp was successfully increased from 35.70 MPa to 52.88 MPa and the toughness was increased from 0.65 MPa.$m^{1/2}$ to 1.33 MPa.$m^{1/2}$ as well.

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Keywords: Hydroxyapatite; biocomposite; strength and toughness

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* Corresponding author. Tel.: +6045996174; fax: +6045941011.
E-mail address: srafauzi@usm.my

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1. Introduction

HAp is chemically similar to the inorganic mineral component of bone and teeth[1,2] and possesses exceptional biocompatibility and unique bioactivity[3]. Even though HAp offers high biocompatibility, relatively low density, high compressive strength and high hardness, application of HAp as a load bearing implant is limited because of its brittleness and relatively low mechanical properties. Hence, there is a necessity of reinforcement to HAp without hampering its biocompatibility[4]. For these reasons, the biocomposites of HAp and ZrO_2 was conducted in this work in order to combine the biocompatibility of HAp and the high strength and toughness of ZrO_2. ZrO_2 has been found to retain high mechanical strength and toughness without degrading the biocompatibility of HAp when incorporated as a second phase[5–10]. HAp-ZrO_2 composites have shown the improved strength and toughness as compared to monolithic HAp itself[11–14].

However, the reaction between ZrO_2 and HAp will enhance the decomposition of HAp and leads to inhibit densification of the composite resulted in low mechanical properties. Again, the presence of ZrO_2 in the system decreases the decomposition temperature of HAp into tri-calcium phosphate (TCP; α- or β-)[15–18]. With an aim to maintain the phase stability of HAp, CaO-ZrO_2 was chosen in this work in order to provide another source of Ca^{2+}. And, the addition of CaF_2 was also intended to improve sinterability and to retain the HAp phase.

With these contexts, the current study was performed to fabricate HAp and CaO-ZrO_2 composites through the incorporation of CaF_2 by air sintering at temperatures between 1100 to 1350 °C. The effect of the added-CaF2 on sintering behavior of CaO-ZrO2/HAp was investigated.

2. Materials and Method

2.1. Materials fabrication

As starting materials, 90, 95 wt% high-purity HAp (Sigma-Aldrich (M)) and 5, 10 wt% CaO-ZrO_2 (UCM Zirconia Inc., Greeneville Tennessee) powders were used to fabricate (ZrO_2/HAp) biocomposites with the addition of 5 wt% CaF_2(Merck KGaA, Germany) powders, designated as H-5CZ-5CF, H-10CZ-5CF, respectively. The powders were milled and mixed with zirconia balls for 24 h. De-ionized water was used as a mixing media. After milling-mixing, the mixture was dried in an oven at 100 °C for 24 h. Dry aggregates were lightly ground into fine powders using agate mortar and sieved through a 250 µm screen. A 55 mm × 10 mm die was used to form rectangular bar shape sample and a uniaxial pressure of 90 MPa was employed to compact. Sintering was conducted in air atmosphere at six different temperatures (1100, 1150, 1200, 1250, 1300 and 1350 °C) using *LENTON*muffle furnace. The schedule of sintering includes soaking time of 5 h with heating and cooling rate of 5 °C/min. The samples produced are coded as in Table 1.

Table 1. Summary of CaO-ZrO_2/HApcomposition with the study on the effect of CaF_2 addition

Code	CaO-ZrO_2 (wt%)	HAp (wt%)	CaF_2 (wt%) (based on total weight of CaO-ZrO_2/HAp powder (60g))
H-5CZ-5CF	5	95	5
H-10CZ-5CF	10	90	5

2.2. Characterization and mechanical test

Using Archimedes method, the density and apparent porosity of the sintered specimens were measured. The samples were subsequently ground using SiC paper, followed by polishing using 1 µm, 0.3 µm and 0.05 µm alumina powders. After etching at a temperature 100 °C below its sintering temperature for 2 h, their microstructures were analyzed by Zeiss Supra 35VP Field Emission Scanning Electron Microscope (FESEM). The specimens were also characterized by XRD Bruker DX 8 for the phase formed. The scan started from 20° to 80°2θ, using copper (K_α Cu) with wavelength of 1.5406 nm as X-ray source.