Available online at www.sciencedirect.com

ScienceDirect

Materials Today: Proceedings 3 (2016) 1923–1932

www.materialstoday.com/proceedings

Recent Advances In Nano Science And Technology 2015 (RAINSAT2015)

Investigation on Mechanical Behavior and Bioactivity of Fluorohydroxyapatite Toughened by Zirconium–Cerium ions Additions

Vijayalakshmi Sanyal, R. Kesavamoorthi, C. Ramachandra Raja*

Department of Physics, Government Arts College (Autonomous), Kumbakonam, India - 612002.

Abstract

Ceria stabilized zirconia (CSZ) in fluorohydroxyapatite (FHA) are prepared by sol-gel method, their phase transition, mechanical and biological properties are reported in this technical paper. Powder samples of pure HA, YZr/5Ce-FHA (where Y=5, 15, 40 mol% of Zirconium ions (Zr)) and 40Zr / XCe –FHA (where X = 5, 10, 20 mol% of Cerium ions (Ce)) compositions are prepared. The powders are uniaxially pressed at 100MPa to form pellets and sintered at 1200˚C for 2 hrs. Mechanical properties such as Vickers microhardness [H_v], fracture toughness [K_{1c}] and brittleness index [H_v / K_{1c}] are evaluated through Vicker's microhardness testing. Microhardness of pure HA was found to be 4.16 GPa, further additions of Zr-Ce ions in FHA increased the H_v value to 7.4 GPa. Sample 40 Zr/10Ce-FHA recorded the highest fracture toughness as 1.87 MPa $m^{1/2}$, which is 2.8 times higher than pure HA. The lowest brittleness index 4.2 $\mu m^{-0.5}$ for this sample confirms the transformation into tough material. The XRD pattern confirmed the presence of t-ZrO_2 and m-ZrO_2 phases. The characteristic of the surface that favours osteogenic bone formation was analysed in vitro, by immersing the sample in simulated body fluid (SBF) solution for 14 days. The apatite layers on the surface prove the osteoconductive nature and is analysed by FESEM-EDAX. Experimental results suggest that the addition of CSZ in FHA increased the toughness of the material suitable for load-bearing applications and confirmed the osteoconductivity.

Selection and Peer-review under responsibility of [Conference Committee Members of Recent Advances In Nano Science and Technology 2015

Keywords: Hydroxyapatite; XRD; Micro hardness; Fracture toughness; Osteoconductive.

---

* Corresponding author. *E-mail address:*crraja_phy@yahoo.com , crrajaphy@gmail.com

Selection and Peer-review under responsibility of [Conference Committee Members of Recent Advances In Nano Science and Technology 2015.].

1. Introduction

Mechanical and biological properties of Hydroxyapatite (HA), an excellent bioceramic material can be modified by substitution of ions in its structure [1]. HA used in repair and replacements of bones for past three decades has a remarkable success for its biological response at the interface of the implant material. But the poor mechanical properties of HA has restricted its use in load bearing applications. Zirconia (ZrO2) is a bioinert ceramic material which poses excellent mechanical properties. Researchers now concentrate in preparing composites of HA-ZrO2 [2-5]. Zirconia has monoclinic structure at room temperature and converts to tetragonal above 1000°C. This tetragonal phase of zirconia transforms to monoclinic during cooling accompanied by an expansion and is called transformation toughening. Thermally induced transformation controls the amount of phases that can be retained after thermal cycling and enhances the toughness of the material. Composites of HA-ZrO2 partially stabilized by Y2O3, Ce2O3 and MgO, enhances the mechanical property through the mechanism of transformation toughening which is resistance to crack growth. The crack cannot propagate as its motion is inhibited by strain field around transformed reinforcement and exhibit 3-6 times fracture toughness higher than HA. Ceria stabilized Zirconia (CSZ) gives rise to a stress induced transformation from t-ZrO2 (tetragonal phase) to m-ZrO2 (monoclinic phase) when cooled after sintering. The resultant transformation is toughened ceramic and is confirmed with the existence of t-ZrO2 and m-ZrO2 phases. HA-ZrO2 composites which are generally prepared by physical mixing or by colloidal dispersion at higher temperature (1100˚C-1300˚C) thermally decompose into undesirable phases such as β-TCP and calcium zirconate. These phases are biodegradable and reduce the mechanical properties of the composites [6]. Nagarajan et al. have studied the partially stabilized zirconia with yttria and ceria which enhanced the mechanical properties but showed the presence of β-TCP and calcium zirconate phase [7]. Zirconium ion incorporated HA nanopowders by sol-gel method has been reported to minimize the undesirable phases and has resulted with excellent biological properties [8]. Recent studies have proved that co-substitution of ions in nano HA facilitates the improvement in mechanical and biological properties. Zirconia has excellent mechanical properties which are suitable for load bearing applications and its bioinertness makes it biocompatible [9]. Bacterial adhesion on implant surfaces is a frequent problem occurring in dentistry and orthopedic field which leads to infection and do not regulate bone bonding and further results in removal of implants. It is proposed that the addition of metal ions which are also antibacterial agents such as Ag+, Cu+, Zn2+, Ce3+,etc can solve this problem. In recent days the dental and medical field utilizes cerium ions to control the bacterial growth. Cerium (Ce3+), the rare earth element has good bioactivity and is also an antibacterial agent. Cerium ions when structurally incorporated in HA results in reduction of particle size while increases the interaction with bacteria and thus acquire enhanced antibacterial property. Moreover the reinforcement of ceria not only stabilizes zirconia, but also increases the material toughness by crack bridging and crack shielding mechanisms resulting in improved mechanical properties. Higher concentration of cerium ions in HA increases the dissolution rate and when used as implant result in adverse reaction. Addition of fluorine ions as anionic substitution in HA, enhances the thermal, chemical stability and also decreases the dissolution rate of apatite over pure HA. Moreover the thin outer layer in the teeth is fluoridated to control the dissolving rate of minerals and it also plays major role in improvement of the mechanical strength of the implant. [10-14]. Sol-gel process yields molecular level mixing, purity and low temperature synthesis of the samples. This method also avoids formation of undesirable phase transformation and thus enhances the mechanical property. The hardness and fracture toughness of the natural apatite is ~ 4.3GPa and 1.16 MPa m1/2. Studies have reported that by reinforcing silver, tetragonal zirconia polycrystal (TZP), SiC and titanium-dioxide in HA, the fracture toughness of the material can be improved to 0.70, 2.45, 0.96 and 1.95 MPa m1/2 respectively. The low brittleness index and high fracture energy result in a tough material [14, 15]. Chen et al. has discussed the mechanical properties for incorporation of various weight percent of Zr4+ (YTZP) in HA and has concluded that 20 wt % of Zr4+ additions has a Knoop hardness of 6.7 GPa and fracture toughness as 2 MPa m1/2 [16]. Prabhakaran et.al., has reported that 40 and 60 % Zr4+ in HA is suitable for orthopedic applications using spectral studies [17]. Osteoconductive nature is decided by the apatite layer formed on the surface which accelerates the tissue on growth and bone bonding ability of the implants. In vitro tests provide more information about the implant materials before proceeding with the in vivo tests in the live animals. The in vitro study of Zr-HA composites soaked in simulated body fluid (SBF) confirms the apatite forming ability by deposition of calcium phosphate layers and thus is osteoconductive in nature [18,19].The present study investigates the effect of different concentrations of zirconium