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Structure and compression strength of hydroxyapatite/titania nanocomposites formed by high energy ball milling

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ABSTRACT

Hydroxyapatite/titania (HA/TiO_2; TiO_2 = 0, 5, 10, 15, 20, 25 wt.%) nanocomposites were produced by high energy ball milling (HEBM) at 50 Hz for 1 h from starting materials particle sizes of HA <100 μm and TiO_2 <25 μm. X-ray Diffraction and Field-Emission Scanning Electron Microscopy results indicated that hydroxyapatite and Anatase were the major phases after mechanical milling with particle size less than 100 nm. After 1 h of convenient thermal treatments at 1000–1200 °C, beta-tricalcium phosphate and calcium titanium oxide phases were the main crystalline phases irrespective of the sintering temperature. While Rutile phase was observed at 1200 °C, the presence of Rutile as a secondary phase in the microstructure of the composites has led to an increase of the compressive strength up to 330 MPa in the nanocomposites containing 25% TiO_2. Longer sintering time (3 h) at 1200 °C has not increased the compressive strength. The produced nanocomposites have showed a moderate deformability where a reduction in height (strain) ranging between 1% and 5.6% was attained at the point of the highest compressive stress.

1. Introduction

Hydroxyapatite HA ($Ca_{10}(PO_4)_6(OH)_2$) with a chemical resemblance to the mineral component of bone has intrinsic biocompatibility and osseo integration potential. However, its applications as long bone substitutes and load bearing scaffolds are hindered by the low intrinsic strength exhibited by HA [1,3]. Also, pure HA suffers a relatively high dissolution rate in simulated body fluid that affects its long-term stability [4]. Furthermore, the quick resorption or degradation of HA in biological environments might result in the disintegration of coatings and erosion of the titanium implants [5]. With this knowledge, many efforts have been made to develop methods of processing hydroxyapatite with good mechanical properties and high resistance to corrosion [6]. According to [7,8], ceramic oxides or metallic dispersions have been introduced as reinforcing agents. Based on the interactions between the implant material and the tissues, bioceramics are classified mainly into bioinert, bioactive and bioresorbable materials [9].

Titanium oxide has been extensively investigated as biomaterial due to its excellent biocompatibility and superior corrosion resistance [2], besides, its high stability and erosion resistance [5]. The addition of titania particulates to HA has attracted considerable attention based on the assumption that titania is capable of enhancing osteoblast adhesion and inducing cell growth [10]. Titania have been used to improve the bonding strength of the HA layer and the Ti substrate, as well as the corrosion resistance of Ti [11,12]. Many studies have been carried out to develop stable TiO_2/HA for their capacity to establish a bond with tissues in vivo, and to promote rapid attachment and cell growth in vitro [10,13,14]. It is commonly known that rutile is the most stable titania crystal phase and also the one that is industrially used in many applications while anatase is metastable at room temperature [15]. Crystal structure and some basic properties of rutile and anatase were collected in Ref. [16].

Nanocomposites have received much attention due to their superior mechanical properties in comparison to their large-grained counterparts [17]. Synthesis of calcium phosphate/titania ceramic system with nanometer-sized crystals gets a great attention because titanium oxide is a strengthening agent, which increases the strength and fracture toughness [6,10,11]. Titania/hydroxyapatite composite with mosaic structure was successfully

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synthesized via a facile route without any structure directing agent. It is concluded that, TiO_2/HAp composite has also both excellent adsorption performance and superior photo catalytic redox ability, and can be used as a photo catalyst to effectively degrade pentachlorophenol under UV irradiation [18,19]. It was reported [13] that, the biocompatibility of TiO_2/HA composites were evaluated by means of cytotoxicity and cytocompatibility tests. The results showed that these materials have no toxic effects. The composites of hydroxyapatite and TiO_2 have the ability to adsorb bacteria and organic materials and are considered to be good in antibacterial applications and environmental purifications and also for photo catalytic decomposition of biomaterials, such as proteins and lipids [20].

Mechanical alloying (MA) or high energy ball milling (HEBM) is a potential method for the preparation of various interesting solid state materials and have the advantage of the perturbation of surface bonded species by pressure to enhance thermodynamic and kinetic reactions between solids [21]. Over the past decades, MA or HEBM has been widely developed for the fabrication of a wide range of advanced materials, such as supersaturated solid solutions, metastable crystalline and quasi-crystalline phases, nanostructures, amorphous alloys, ceramic materials, intermetallic, and materials for solar cell applications [21,22,23]. Mechanical alloying/milling is a solid state powder processing technique involving cold welding and fracturing of powder particles. The constituent powder particles are repeatedly fractured and cold welded, so that powder particles with very fine structure can be obtained after milling [15,24]. Recently the effect of high energy ball milling (HEBM) treatment on hydroxyapatite with titanium and silicon has been described [25,26]. During HEBM process, the impacts of the milling balls result in a significant decrease of the HA particle and crystalline size forming nanoscale structure.

In this manuscript, the application of a high energy ball milling technique to produce hydroxyapatite/titania nanocomposites ceramic was studied. The effect of titania addition and sintering temperature and time on the formed phases and their influence on the compressive strength of HA were investigated.

2. Materials and investigation procedure

The initial materials are Hydroxyapatite powder (Sigma–Aldrich) having a particle size of <25 μm and titanium oxides (Anatase) of a particle size <100 μm. Batches from HA and titania were fed into a 20 cm^3 high energy vibratory ball milling chamber which vibrated with a frequency of 50 Hz. HA/TiO_2 nanocomposites was prepared by adding TiO_2 to HA in different percentages of 0, 5, 10, 15, 20 and 25wt. %. The powders were milled using hardened steel balls for 1 h with balls to a powder ratio of 20:1. After high energy ball milling, the milled powder samples were cold compacted into cylindrical tablets (diameter; $D_o = 7.5$ mm and height; $H_o = 5$ mm) under a pressure of 100 bars for a dwell time of 150 s in order to consolidate the specimens for further sintering. Sintering was performed in normal atmosphere using electric resistance muffle furnace at 1000 °C for a heating time of 1 h and 1200 °C for one and 3 h. The specimens were fed into the furnace and heated up to desired temperature. The heating time was calculated from the point at which the desired temperature has been reached. All the sintered samples were furnace cooled.

XRD analysis was performed using a Siemens D5000 powder diffractometer equipped with Cu K_α radiation (wavelength $\lambda = 0.15406$ nm) with a nickel filter at 40 kV and 30 mA. The diffractometer was operated within the range of $20° < 2\theta < 60°$ using a step time of 3 s and a step size of 0.01°. A wider diffractometer angle ranging up to 90° was tested, but no further new phases were detected so that the XRD analysis was further performed until 60°. Diffraction signal intensity throughout the scan was monitored and processed by DIFFRAC-plus software. Topas 2.1 Profile fit software was used to extract the peak parameters and the pseudo Voigt function was used to model the peak shape. The microstructural features of the as-milled and sintered samples have been investigated using a Field-Emission Scanning Electron Microscopy (FE-SEM) ZEISS LEO SUPRA-55 VP. The sample composition was analyzed by energy dispersive X-ray spectroscopy (EDX) using Oxford INCA X-sight.

Compression tests were carried out at the quasi-static loading range, where the initial strain rate ($\varepsilon^\bullet = d\varepsilon/dt$) was set to 0.001 s^{-1}, i.e. the machine cross head speed ($v = \varepsilon^\bullet h_o$) was 0.005 mm/s, where h_o is the specimen's initial height. The universal testing machine type “Instron” model 4210 was used. The sintered specimens were loaded until complete fracture; the load–displacement curves were exported and processed to determine the stress–strain curves. The samples were macro-photographed after fracture to document the mode of fracture.

3. Results and discussion

3.1. XRD patterns of the HA/TiO_2 composites

The function of HA in all of its applications is largely determined by its morphology, composition, crystal structure, and crystal size distribution [27]. Thus, to control the mechanical properties of hydroxyapatite, the influence of synthesis conditions on such characteristics as particles' morphology and size distribution, as well as agglomeration were studied.

The XRD patterns shown in Fig. 1 illustrate the effect of mechanical treatment on the structure of HA and TiO_2 milled powder mixture. The TiO_2 content was 5, 10, 15, 20 and 25 wt.%, besides, the TiO_2-free HA material. Such a range of composition range was chosen in order to investigate the contribution of the different crystalline phases to the microstructure and mechanical behavior of the sintered composites. After 1 h of high energy ball milling, the HA peaks showed a notable intensity reduction as a result of severe plastic deformation. Due to titania structural stability, the intensities of its diffraction pattern got strengthened with increasing titania content. No additional new phases were detected after high energy mechanical milling except a small shift of XRD patterns to a lower angle with mechanical milling due to accumulated strain.

Field Emission Scanning Electron Microscopy (FE-SEM) was used to analyze the morphology of the powders after high energy ball milling (HEBM). Fig. 2(a,b) shows the representative images recorded at different magnifications of HA/10wt.% titania and Fig. 2(c,d) for HA/25wt. % titania, confirming that the particle size in the as milled samples is of the order of tens of nanometers (<100 nm). The morphology of the initial large particles was significantly changed due to fracture, agglomeration, and de-agglomeration processes. The mechanism of fragmentation and formation of nonsized material by HEBM is controlled by the following three stages [21,28]: *i)* in the first stage, the particles are subjected to deformation localization in shear bands that resulted in high dislocation density, *ii)* in the second stage, the cell/sub grain structure with nanoscale dimensions are produced through dislocation annihilation, recombination or rearrangement to reach a lower energy of the system, and *iii)* the final stage, the high angle grain boundaries replace the low angle grain boundaries by boundary rotation or sliding and the grain boundaries near the sample edge are broken and single crystal nanoparticles are peeled off the edge of the samples. This fragmentation process is time dependent and the resultant crystallite size can be controlled by the relationship [29]: