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Review paper

Hydroxyapatite nanocomposites: Synthesis, sintering and mechanical properties

M. Aminzare[a], A. Eskandari[b,*], M.H. Baroonian[d], A. Berenov[c], Z. Razavi Hesabi[b], M. Taheri[a], S.K. Sadrnezhaad[e]

[a]Department of Materials and Metallurgical Engineering, Iran University of Science and Technology, Tehran, Iran
[b]Department of Materials Engineering, Science and Research branch, Islamic Azad University, Tehran, Iran
[c]Department of Materials, Imperial College London, Exhibition Road, London SW72AZ, UK
[d]Materials and Energy Research Center (MERC), Tehran, Iran
[e]Department of Materials Science and Engineering, Sharif University of Technology, Tehran, Iran

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Abstract

Two different hydroxyapatite based composites reinforced by oxide ceramic (20 wt%) nano crystals were synthesized by high-energy ball milling and sintered by pressure less technique. Alumina and titania nanoparticles as secondary phases improved densification and mechanical behavior of apatite and postponed its decomposition to the tricalcium phosphate (TCP) phases at elevated temperatures. Increasing the relative density of apatite using nano reinforcements leads to enhance the bending strength by more than 40% and 27% (as compared to the pure HA) and increase the hardness from 2.52 to 5.12 (Al_2O_3 composite) and 4.21 (TiO_2 addition) GPa, respectively. Transmission electron microscopy (TEM), scanning electron microscopy (SEM) and X-ray diffraction spectroscopy were employed to study morphologies, fracture surfaces and phase compositions, respectively. The morphological study and micro structural analysis confirm the X-ray diffraction and relative density diagrams.

Keywords: A. Sintering; B. Nanocomposites; C. Mechanical properties; Hydroxyapatite

Contents

1. Introduction

Several paradigm shifts have taken place in different areas such as electronics, robotics, medicine and surgery by the advent of nanomaterials. To some extent, the field of

*Corresponding author. Tel.: +98 912 2388082; fax: +98 21 77240291.
E-mail addresses: arvin.eskandari@yahoo.com, arvin.eskandari86@gmail.com (A. Eskandari).

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medicine and surgery is the most important area because it is related to human's health. In this case, biomaterials play a very important role. Among different categories of biomaterials, bioactive ceramics such as hydroxyapatite are attractive candidates for body's hard tissues replacement [1–4]. Hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) has been widely used as a bulk implant material in non-load bearing areas of the body [5]. Although HA has excellent biocompatibility properties, it is limited in use due to its low strength and brittle nature [6–8]. The main reason of this loss in mechanical properties of HA is decomposition of HA into some calcium phosphate phases such as tricalcium phosphate (TCP) and even tetra-calcium phosphate (TTCP) [9]. Calcium phosphate phases are brittle and have weaker strength. Different techniques have been tried to improve strength and fracture toughness of HA (toughness of pure HA < 1 MPa $m^{1/2}$) [10], such as making composites and using different pressing/sintering methods like underwater shock compaction [10] hot press sintering [3], microwave [5] and spark plasma sintering process [11,12].

Beside the advanced processing routes, bioinert polymer or ceramic materials as reinforcing agents in different forms like whiskers, platelets, fibers and particles have been employed to improve the mechanical properties of HA [13–16]. Moreover, another issue could enhance mechanical properties of apatite is decreasing the grain size, which is well known as Hall–Petch equation [17]. In fact, nanocrystallinity is a key factor for improvement of sinterability and enhancement of compacted specimen behavior owning to high energy and high interface density which are stored in the interfaces of ultrafine grained structures. However, the tendency of nanopowders to agglomeration leads to create some problems in shaping of bodies and there are still challenges in this area. Some effort such as high energy ball milling have been used to overcome/decrease the agglomeration effects [12,18]. The large surface area often dominates the properties of the powders and enhances mechanical, chemical and physical properties, significantly, of the material resulting in interesting and sometimes unexpected behavior of nanoparticles. Nanocrystalline powders of apatite composites can be sintered into well-built osteointegrative ceramic specimens [19].

It has been reported that alumina and titania particles are the best choices for making composite with HA due to their good mechanical properties and bio inertness [1,3,9,15]. As an illustration, Viswanath and Ravishankar [15] have studied the interfacial reactions in hydroxyapatite/alumina nanocomposite. Their work showed that alumina completely reacted with hydroxyapatite and formed alumina-rich calcium aluminates and TCP phases at relatively low temperatures (1000 °C). In contrast, Xihua et al. [3] reported that by introducing diapsoid/alumina and hot pressing the composites under 20 MPa in N_2 atmosphere at 1320 °C, the decomposition of HA was not observed. Que et al. [11] reported that the addition of titania into HA has a major effect on the HA structure and enhanced HA properties. Moreover, because of the introduction of secondary phases, the phase changes in the composites at higher sintering temperatures could take place. Application of the expensive materials processing techniques (e.g. spark plasma sintering) could improve the mechanical properties and bio activity, but the decomposition of HA at 1200 °C results in drastic decreasing the strength of composites. Some attempts have been done to prevent the decomposition. Nath et al. [2], for instance, have tried to inhibit the decomposition reaction of HA into calcium phosphate phases by making HA-Mulite system. Nevertheless, in their study decomposition of HA composites at 1350 °C results in deterioration of the mechanical strength.

The purpose of this work is to study the applicability of a newly devised biomimetic synthesizing technique for the production of the nanocrystalline needle-like apatite powder and subsequent preparation of nanocomposite by high-energy ball milling in order to obtain highly dense objects with desired mechanical properties. The effects of alumina and titania nanoparticles on microstructure, phase decomposition and mechanical properties of the product have also been investigated.

2. Experimental procedure

In the previous study [20], we synthesized the apatite nanocrystals via biomimetic method. In summary, the mixture were composed of acidic calcium phosphate (Merck, 2146) mixed with basic TTCP at 1/1molar ratio and 6 wt% disodium hydrogen phosphate dissolved in distilled water. The solid content of the mixture was 3 g/ml. The hardened paste was maintained in simulated body fluid (SBF) for 7 days. After this period, the material was removed from the SBF, washed with distilled water, dried at 70 °C and ground to fine powder by a planetary mill.

Nanocrystalline alumina powder with the average particle size of 50 nm (Sigma(Aldrich, purity > 99.99%) was used as a secondary phase. Fig. 1 shows X-ray pattern of as-received alumina nanopowder which shows the alpha structure as a predominant phase. To compare the effect of strengthening phases, TiO_2 nanopowder (P25, Degussa Co., Frankfurt, Germany) with a particle size ranging from 11 to 27 nm was employed. TiO_2 powder consisted of 77% anatase and 23% rutile phases. Alumina and titania nanopowders was first mixed with HA nanopowder to obtain 20 wt% mixtures of nanopowders with HA. Powder mixtures were milled in a polymeric ball mill at the speed of 400 rpm, and the weight ratio of ball-to-powder was 10:1. The mixed powders were placed in a cylindrical steel die with 10 mm diameter and pressed uniaxially at 150 MPa.

Non-isothermal sintering was performed upon heating with the rate of 5 °C/min to 1400 °C followed by cooling in an electrical furnace naturally. Sinterability of the compacted powders was determined by bending stresses, Vickers hardness and fractional density measurements.