Densification Behavior and Mechanical Properties of Biomimetic Apatite Nanocrystals

A. Eskandari[1], M. Aminzare[1], H. Hassani[1], H. Barounian[1], S. Hesaraki[1] and S.K. Sadrnezhaad[2,*]

[1]*Materials and Energy Research Center, P.O. Box 31787-316, Tehran, Iran,* [2]*Department of Materials Science and Engineering, Sharif University of Technology, P.O. Box 11365-9466, Tehran, Iran*

Abstract: Nanocrystalline hydroxyapatite (nHA) of 50 nm average diameter and length to diameter ratio of >3 was synthesized by biomimetic method. Non-isothermal sintering improved densification behavior and mechanical properties of apatite to 0.88 maximum fractional density, 70MPa bending strength, 148MPa compressive strength and 2.53GPa microhardness at sintering temperature of 1250°C. Higher sintering temperatures resulted in the decomposition of the apatite and in-situ biphasic calcium phosphate HAP/TCP formation. This process lowered apatite densification and weakened mechanical properties of the sintered specimen. Transmission electron microscopy (TEM), x-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM) helped to elucidate the structure/property correlations.

Keywords: Apatite, biomimetic, mechanical properties, nanocrystal, sintering.

INTRODUCTION

Among phosphate groups, a unique biocompatibility feature exists in apatite with formula $Ca_{10}(PO_4)_6X_2$ in which X represents hydroxyapatite (HA) hydroxyl (OH^-) group, fluorapatite fluoride (F^-) group and chlorapatite chloride (Cl^-) group. Dense calcium phosphate is a promising material for biomedical applications. It has been demonstrated that the nanodimensional hydroxyapatite formed in calcium phosphate cements (CPCs) during soaking in SBF solution (Kokubo's solution with ionic concentration similar to that of human plasma [1]) highly resembles the inorganic phase of the human bone [2]. Densification of pure HA is at the same time difficult; tending sometimes to impossible [3, 4]. Stea *et al*. have densified HA compacts forming tight bonds with bone tissue sintering procedure [3]. Alternative additives have been used by Kim *et al.* to obtain high densification [4]. They gained ~20% porosity via sintering of pure hydroxyl apatite at 1450°C; while addition of 5% CaF_2 resulted in production of a full dense body.

Although HA has many advantages to alternative materials [5], it suffers from poor mechanical strength [6] and inability to withstand sever load-bearing conditions [4, 7, 8]. Many attempts have been made to make composite properties superior [9, 10]. Nanocrystallinity is a key factor for improvement of sinterability and enhancement of compacted articles behavior [11]. Large surface area of the nanocrystalline apatite results in lowering of the sintering temperature and improvement of the grain attachment. Nanocrystalline powders of apatite can be sintered into well-built osteointegrative ceramic articles [12].

Decomposition of hydroxyapatite is a negative incident that may occur during the sintering process. Principal outcome is tricalcium phosphate (TCP) [$Ca_3(PO_4)_2$]. This material is a biodegradable ceramic with different α and β polymorphs which can dissolve in physiological media and replace the bone [6]. The decomposition of hydroxyapatite into β-TCP will bring about low density and poor mechanical properties in a sintered body [4]. Xu *et al.* have reported 8.7% decrease in the sample density by increasing the sintering temperature from 1300°C to 1400°C [13]. The dominant phase is β-TCP at 1400°C. Sintering at high temperatures and/or long durations can cause decomposition of the HA phase [14, 15]. Technique of synthesis also affects on the decomposition temperature [16]. Fathi *et al.* have, for example, found TCP at 700°C in nHA powder synthesized via sol-gel [16]; while Que *et al*. have observed TCP at 1200°C in HA produced by wet chemical precipitation [17].

The purpose of this work is to unveil the newly devised biomimetic synthesizing technique easily usable for production of the nanocrystalline hydroxyapatite powder and its subsequent sintering to obtain highly dense objects with appropriate mechanical specifications. Effects of synthesis conditions, microstructural state and phase decomposition on mechanical properties of the product are investigated.

MATERIALS AND METHODS

Calcium phosphate cement was used to produce apatite phase according to the procedure reported in the literature [18]. In summary, The mixture was composed of acidic calcium phosphate (Merck, 2146) mixed with basic TTCP at molar ratio of 1/1 and 6 wt % disodium hydrogen phosphate dissolved in distilled water. The powder-liquid ratio in the mixture was 3 g/mL. The hardened paste was maintained in simulated body fluid 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. The specific surface area of the product analyzed by Brunauer-Emmett-Teller technique (BET, BEL Japan Inc) was 101 m^2/g. The average particle size measured in isopropanol medium by laser particle size analyzer (Fritsch Particle Seizer Analysette 22) was about 0.5 μm. Transmission electron microscopy (TEM, CM200 FEG, Philips, Netherlands) and x-ray diffraction (XRD, Philips, X'Pert) pattern were used to characterize the synthesized sample.

Green bodies were compacted with uni-axial 250 MPa press and then non-isothermally heated at a rate of $5°C.min^{-1}$ within an electric resistance furnace. Sinterability of the compacted powders was determined from compressive and bending stresses, Vickers hardness and fractional density and grain size evaluations. Compressive strength was measured by Zwik/Roell machine at a strain rate of 0.5 mm/min. The bending stress was determined from 3-point bending test using loading rate of 0.5 mm/min. Water displacement (Archimedes method) was used to measure the densities of the sintered specimens. Vickers hardness and toughness were measured by indentation at load of 500 g and dwell time of 20 s. Microstructure and grain size of the specimens were also obtained by using field emission scanning electron microscopy (FESEM, Hitachi, S-4160).

*Address correspondence to this author at the Department of Materials Science and Engineering, Sharif University of Technology, P.O. Box 11365-9466, Tehran, Iran; Tel: +9821-66165215; Fax: +9821-66005717;
E-mail: sadrnezh@sharif.edu

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