Materials Science and Engineering C 51 (2015) 206–215

Contents lists available at ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

A modified milling system, using a bimodal distribution of highly resistant ceramics. Part 1. A natural hydroxyapatite study

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ARTICLE INFO

Article history:
Received 9 October 2014
Received in revised form 31 January 2015
Accepted 5 March 2015
Available online 7 March 2015

Keywords:
Natural hydroxyapatite
Mechanical properties
Sintering
Ball milling
Bioceramics

ABSTRACT

A careful combination of the main parameters controlling natural hydroxyapatite (NHA: $Ca_{10}(PO_4)_6(OH)_2$) production such as milling techniques, sintering temperature and holding time may lead to an interesting NHA based bio-ceramics without any foreign oxide additions. In this way, an original wet milling setup has been proposed to obtain sub-micron sized NHA powders. In order to avoid any possible NHA decomposition, a precise Ca/P ratio of NHA derived from animals was selected accordingly. Also, an alternative direct visual approach of the bone age classification was also proposed. A relative density of about 95% was obtained for powders sintered at 1300 °C for 2 h. The best Vickers micro-hardness and 3 point bending strength values for these sintered samples, using this proposed milling system and without any additions, were 4.7 ± 0.3 GPa and 37 MPa, respectively. Finally, a complete correlation between the powder microstructure and the final product properties has been established.

1. Introduction

Developing new processes are real challenges to replace expensive biomaterial products by others more economic. There are many countries in the world that have abundant raw materials, such as calcite ($CaCO_3$), dolomite ($CaCO_3 \cdot MgCO_3$), bones (natural derived hydroxyapatite (NHA): $Ca_{10}(PO_4)_6(OH)_2$), kaolin, feldspar and quartz. Many works have already been published for valorizing these native raw materials, mainly referring to advanced ceramics [1–3], ceramic membranes [4–10] and bioceramics [11–14]. In this way, an attempt has been made in order to use abundantly available NHA as a local raw material for NHA based biomaterial production.

Because of its close physical and chemical properties to mineral part of bone and teeth [15], hydroxyapatite (HA: $Ca_{10}(PO_4)_6(OH)_2$) is one of the most attractive materials for human hard tissue implants. The biocompatibility of this ceramic, when used as an implant material is good enough to form a direct bonding with the neighboring bone. Nevertheless, its poor mechanical properties are serious obstacles for wider applications [16]. So, they are only used in non-load areas of the human body such as the ossicles in the middle ear. For a full use of bioactive HA-based implants, improvements in their mechanical properties are highly recommended. Consequently, several works have been carried out on structural modifications and mechanical properties of HA in the presence of oxides or metallic dispersions used as reinforcing agents [17–37]. In the literature review, when mechanical property values of pure HA and HA composites are compared between them it can be seen that these different values are closely related to the sample preparation methods [19,22,27,30,36–38]. The densification rate and other microstructure features, such as grain and pore size, which depend on processing parameters (milling) and sintering temperature, may potentially influence the mechanical properties of HA [39,40]. Nevertheless, when the oxides are used as a reinforcing agent for HA, the decomposition of HA to TCP occurs severely [18–21]. The addition of ZrO_2 decreases the decomposition temperature of the reaction HA into TCP (α- or β-TCP) from ~1300–1400 °C to ~1000–1150 °C [20,21]. In fact, the decomposition process itself gives a negative influence on the densification of HA due to the formation of second phases and water steam, and also gives a consequent reduction in the mechanical properties [18–20,28,41]. HA can be synthesized using several methods [42–47] or manufactured from natural materials such as coral [48] or bone after removal of the organic materials by heating [49–52]. The "in vitro" and "in vivo" studies showed that the natural apatite is well tolerated and has better osteoconductive properties than synthetic HA [53]. In addition, the exploitation of natural resource represents an economical way of synthesizing HA by a combustion method. Besides, HA materials manufactured from animal bones may have the advantage of inheriting some properties of the raw material such as its chemical composition and structure [54–56]. For these reasons, the HA was manufactured from cortical bovine bones in all our studies. A first work was done to study the effect of sintering temperature (varied from 800 to 1200 °C) on the process and the kinetics of formation of bonelike apatite on the surface of soaked granules in simulated body fluid (SBF). The results showed that a thicker bonelike apatite film

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http://dx.doi.org/10.1016/j.msec.2015.03.003
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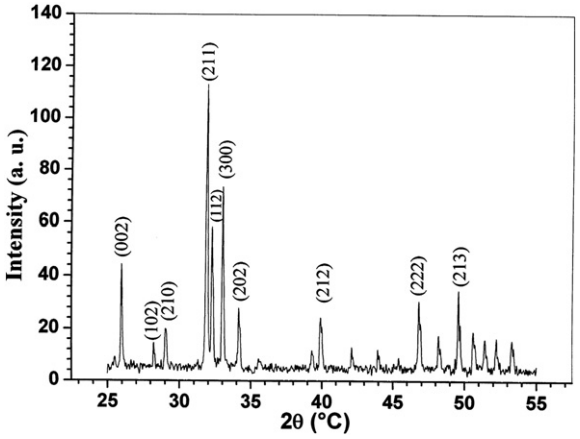

Fig. 1. XRD spectrum of the as prepared NHA powder.

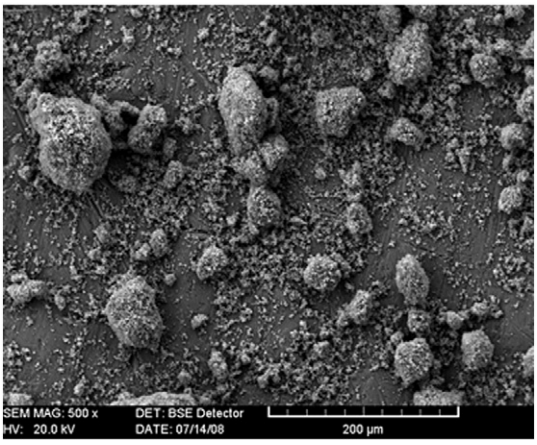

Fig. 3. SEM micrograph of the as prepared NHA powder.

was formed on the surface of granules sintered at higher temperatures (1200 °C) for 2 h [52]. Nevertheless, the sintered samples had lower densities which led to poorer mechanical properties.

However, a careful combination between the main parameters controlling NHA production such as milling techniques, sintering temperatures and holding times may lead to an interesting NHA based bio-ceramics without any foreign oxide additions.

In this way, an original wet milling setup has been used to obtain sub-micron sized NHA powders. In order to avoid any possible NHA decomposition, a precise Ca/P ratio of NHA derived from animals was accordingly selected in this study. It should be remarked that the NHA bioactivity or like apatite layer formation in SBF was already confirmed in a previous work [11,52], using younger animal bones.

Because of the importance of the particle size distributions of starting powders for the sintering process, this study is mainly focused on this property rather than on other physico-chemical properties which were briefly discussed.

2. Materials and methods

2.1. Preparation of specimens

The starting material, used in this work, was NHA obtained by calcination of cortical bovine bone at 800 °C for 4 h to remove the organic materials and then dry milled for 30 min.

Series of NHA powders were wet milled for different times, using a particular homemade vibratory milling system [57]. Afterwards, they were dried and compacted at 75 MPa under cold pressing. Subsequently, the compacted samples were sintered at different temperatures for 2 h [51]. The bulk density was determined using the Archimedes method.

2.2. Characterizations

The tensile strength testing of sintered specimens was done by using a diametral compression test (FORM TEST SEIDNER D 79-40) (Germany). One of the fundamental aspects of this test is the relatively small proportion of the specimen volume which reaches the peak stress at fracture.

In its simplest form, a right circular cylindrical specimen is compressed diametrically between two flat platens. A biaxial stress state is produced within the test specimen and, on the assumption of ideal line loading; the vertical plane is subjected to a uniform horizontal tensile strength of magnitude,

$$\sigma_t = 2P/\pi dt$$

where σ_t (MPa) is the maximum tensile stress, P (N) is the applied load at fracture, d (mm) is the specimen diameter and t (mm) is the specimen thickness.

The correspondence between the measured tensile strength (σ_t) value and its equivalent 3 point flexural strength (σ_f) is given by the following equation:

$$\sigma_f(\text{MPa}) = 2.7\sigma_t(\text{MPa}).$$

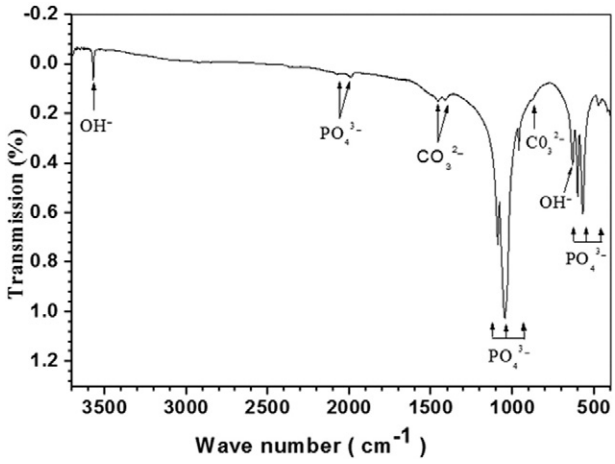

Fig. 2. FTIR spectrum of the as prepared NHA powder.

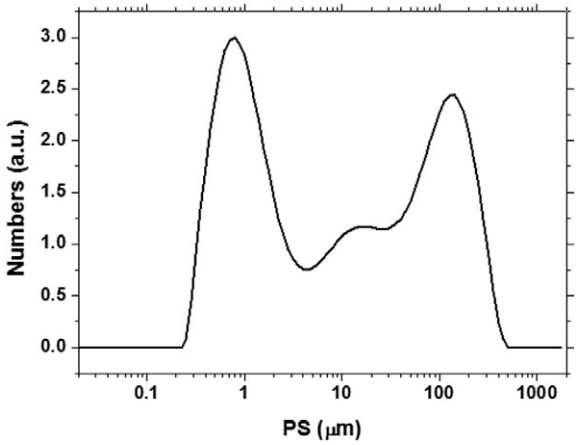

Fig. 4. A particle size distribution of the as prepared NHA powder.