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Effect of calcium fluoride on mechanical behavior and sinterability of nano-hydroxyapatite and titania composites

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Abstract

Composites of nano-hydroxyapatite (HA) – titania (TiO_2) with or without calcium fluoride (CaF_2) were synthesized and sintered at 900 °C, 1100 °C, and 1300 °C. The composites were studied to assess the effect of CaF_2 addition on the sinterability, structure, functional groups, morphology and mechanical behavior of the material. The resultant composites were characterized by XRD, ATR-FTIR, SEM and microhardness measurement, respectively. It was seen that the addition of CaF_2 into HA–TiO_2 composites enhanced the densification via reducing the porosity of the composites. The XRD results showed that as the amount of TiO_2 in the composites was increased, transformation of HA into tricalcium phosphate (TCP) was favored due to the formation of calcium titanate ($CaTiO_3$). On the other hand, the addition of CaF_2 into the composites led to the shrinkage of unit cell volume of HA due to the substitution of F^- ions into HA and suppressed the decomposition of HA in these composites. Moreover, the addition of CaF_2 also improved the microhardness of the composites.

Keywords: A. Sintering; B. Nanocomposites; B. Microstructure-final; C. Thermal Properties; Microhardness

1. Introduction

Hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) is a well known bioceramic and constitutes the majority of human hard tissues [1,2]. In addition to the resemblance to the mineral phase of the bone, its superior bioactivity and biocompatibility properties have enabled HA to be used in clinical medicine as bone fillers or coatings of orthopedic and dental implants [3,4]. HA is also successful in promoting bone growth into the implant matrix and increasing the fixation stability of the implant [5]. However, HA has poor mechanical properties [2,6] and low corrosion resistance in acidic environment [7]. Especially, the mechanical disadvantages of HA restrict its clinical applications as a hard tissue replacement material in load bearing areas of the skeleton. Therefore, in order to improve the mechanical properties of HA based biomaterials such as strength and fracture toughness, many different methods have been proposed. HA composites, HA coating on metallic substrates, various sintering and pressing techniques can be performed by these methods.

Making composites of HA with reinforcement agents, such as bioglass, zirconia (ZrO_2), alumina (Al_2O_3) and titania (TiO_2), is a promising technique to obtain desired mechanical properties. It was reported that the incorporation of biocompatible glass into HA has significant effects on the structure and mechanical properties of HA [8]. Delgado et al. [9] showed that the magnesia partially stabilized ZrO_2 particles could improve the fracture toughness of HA by employing pressing and sintering. The strength of HA was shown to increase steadily with the increasing amount of Al_2O_3 in its structure [10].

Among these different HA based composites, those with TiO_2 have attracted more attention due to the well-known biocompatibility of TiO_2 [11]. TiO_2 is not only a good

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reinforcing agent but also brings HA–TiO_2 composites the ability to adsorb and decompose bacteria to be considered as a good antibacterial material [12]. Besides these biological advantages of TiO_2, it is known to hinder crack propagation, improve the thermal expansion coefficient and the increase interfacial bond strength of HA coatings [13]. On the other hand, HA–TiO_2 composites have also been successfully applied in various non-medical areas. For example, the adsorption properties of HA were combined with the photocatalytic properties of TiO_2 to be used in removal of air pollutants such as volatile organic compounds and nitric oxide [14].

HA–TiO_2 composites were previously synthesized by various techniques such as microwave assisted co-precipitation [4], electrophoretic deposition [13], hydrothermal treatments [12,15] etc. Recently, Al_2O_3 and TiO_2 were successfully added to biomimetically produced nano HA matrix via high-energy ball milling. It is known that the mechanical properties of HA–TiO_2 composites are reduced due to the phase decomposition of HA to tricalcium phosphate (TCP, $Ca_3(PO_4)_2$) at high sintering temperatures [16]. However, incorporation of fluoride (F^-) ions into HA composites was shown to enhance its stability to higher temperatures [17] since F^- ions promote the stabilization of HA crystal structure [18]. It was reported that when CaF_2 was introduced to HA–ZrO_2 composite and sintered at 1350 °C, the decomposition rate of HA to β–TCP was considerably decreased [17].

In the present study, it was aimed to enhance the sinterability and mechanical properties of HA–TiO_2 composites with the addition of CaF_2 because the effect of CaF_2 on the HA–TiO_2 composites is not studied in the literature. For this purpose, HA–TiO_2 powders were mixed by ball milling with or without CaF_2 for 1 h and then sintered either at 900 °C, 1100 °C or 1300 °C for 1 h. The resultant composites were characterized by X-ray diffraction (XRD) studies, attenuated total reflectance-fourier transform infrared spectroscopy (ATR-FTIR) and scanning electron microscopy (SEM). The effect of CaF_2 addition on the density and microhardness of the composites was also investigated.

2. Materials and methods

The materials used in this study are the composites of HA–TiO_2 and HA with or without CaF_2. The description and the composition of the composites are given in Table 1.

HA was synthesized by mixing reagent grades of calcium nitrate ($Ca(NO_3)_2$) and di-ammonium hydrogen phosphate ($(NH_4)_2HPO_4$) solutions in the alkaline pH region as described previously [19]. The resulting HA powders were mixed with TiO_2 and reagent grade CaF_2 powders. In order to accomplish this, the dried HA particles were first ground to 75 μm (200 mesh) in an agate mortar and then calcined at 600 °C for 10 min. TiO_2 powders were calcined at 1075 °C for 10 min and rutile phase was obtained. The particle size distribution of the raw powders was determined by the Malvern Zetasizer nano-ZS. The powders were mixed to prepare pellets by ball milling for 1 h. The mixed powders were uniaxially pressed to pellets with 13 mm diameter and 4 mm thickness under compressing pressure 50 MPa in a hardened steel die, and then sintered at 900 °C, 1100 °C or 1300 °C for 1 h.

Table 1
The sample designations and descriptions of HA–TiO_2 composites synthesized in this study.

Sample designation	Description
HA	100 wt% HA
HA20T	80 wt% HA + 20 wt% TiO_2
HA40T	60 wt% HA + 40 wt% TiO_2
HA2.5F	97.5 wt% HA + 2.5 wt% CaF_2
HA20T2.5F	77.5 wt% HA + 20 wt% TiO_2 + 2.5 wt% CaF_2
HA40T2.5F	57.5 wt% HA + 40 wt% TiO_2 + 2.5 wt% CaF_2

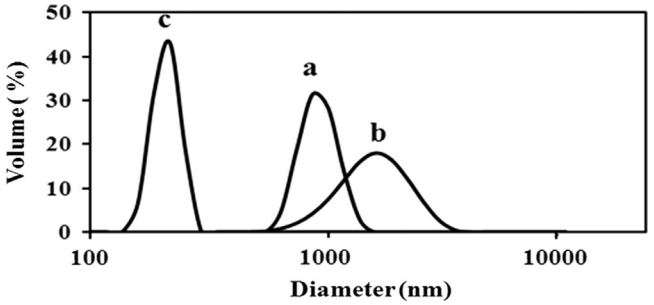

Fig. 1. The particle size distributions of the raw materials (a) HA; (b) TiO_2; (c) CaF_2.

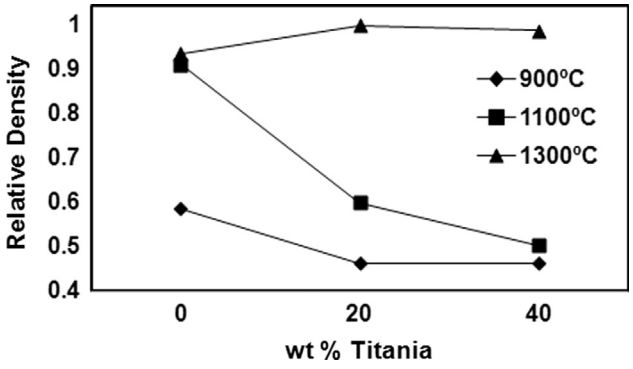

Fig. 2. The relative density as a function of the amount of TiO_2 in the composites without CaF_2 sintered at 900, 1100, and 1300 °C.

The bulk density of the sintered samples was calculated by dividing their weight by volume. The theoretical densities of the composites were calculated from the known weights (W) and densities (ρ), according to the following formula [20]:

$$\text{Theorical Density}(\text{g/cm}^3) = \frac{W_a + W_b + W_c}{((W_a/\rho_a)+(W_b/\rho_b)+(W_c/\rho_c))} \quad (1)$$

where the component "*a*" is HA (and/or TCP), the component "*b*" is TiO_2, and the component "*c*" is CaF_2. For the composite density calculation, the densities of HA, β–TCP and α–TCP are taken as 3.156 g/cm^3, 3.07 g/cm^3 and 2.87 g/cm^3, respectively.