Available online at www.sciencedirect.com

ScienceDirect

Materials Research Bulletin 43 (2008) 2643–2651

Materials Research Bulletin

www.elsevier.com/locate/matresbu

Effect of AlF_3, CaF_2 and MgF_2 on hot-pressed hydroxyapatite–nanophase alpha-alumina composites

Zafer Evis [a,*], Robert H. Doremus [b]

[a] *Middle East Technical University, Department of Engineering Sciences, Ankara 06531, Turkey*
[b] *Rensselaer Polytechnic Institute, Materials Science and Engineering, Troy, NY 12180, United States*

Received 15 March 2007; received in revised form 27 April 2007; accepted 29 October 2007
Available online 4 November 2007

Abstract

Nanophase alpha-alumina and hydroxyapatite composites (with and without 5 wt% AlF_3, CaF_2 or MgF_2, added separately) were hot pressed at 1100 °C and 1200 °C to investigate their mechanical properties and phase stability. Hydroxyapatite slightly decomposed to tri-calcium-phosphate when there was no F^- present. With the addition of AlF_3, CaF_2 or MgF_2 into the composite, it improved its thermal stability and mechanical properties. Substitution of OH^- by F^- ions in hydroxyapatite was verified by the change in hydroxyapatite's hexagonal lattice parameters and unit cell volume. A fracture toughness of 2.8 MPa $\sqrt{m}$ and μ-hardness of 8.25 GPa were calculated for the composite containing CaF_2 after the hot pressing at 1200 °C.

Keywords: A. Ceramics; B. Chemical synthesis; C. X-ray diffraction; D. Mechanical properties

---

1. Introduction

Hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) is mainly used as a hard tissue implant because of its similarity to the inorganic part of the bone. However, it can only be used in non-load bearing areas because it is brittle. Composites of HA and alumina can combine the advantages of biocompatibility of HA and high strength of alumina.

When mixtures of HA and alumina powders were sintered in air at temperatures ranging from 1100 °C to 1400 °C, HA decomposed and reacted to form unwanted second phases (i.e. α-tri-calcium phosphate (TCP, $Ca_3(PO_4)_2$)) [1]. The alumina increases the decomposition rate of HA to TCP at temperatures above 1000 °C [1–4] probably because of the formation of calcium aluminates (e.g. $CaAl_2O_4$, $Ca_3Al_2O_6$, $Ca_5Al_6O_{14}$) such as

$$Ca_{10}(PO_4)_6(OH)_2 + Al_2O_3 \rightarrow 3Ca_3(PO_4)_2 + CaAl_2O_4 + H_2O \tag{1}$$

Al_2O_3 completely reacts with HA at temperatures above 1300 °C. However, this reaction can be inhibited by adding a few volume percent of CaF_2 to the powder mixture [5]. Then the HA–alumina composites can be sintered to high

---

[*] Corresponding author. Tel.: +90 312 210 4450; fax: +90 312 210 4462.
E-mail address: evis@metu.edu.tr (Z. Evis).

0025-5408/$ – see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.materresbull.2007.10.032

density at temperatures of 1450 °C and above. The fluoride ions apparently substitute for OH^- in the HA, which reduces its tendency to decompose [5,6].

$$Ca_{10}(PO_4)_6(OH)_2 + CaF_2 \rightarrow Ca_{10}(PO_4)_6F_2 + CaO + H_2O \tag{2}$$

Sintering the mixed powders at intermediate temperatures [7] or using Al_2O_3 platelets instead of equi-axed powders [8] also increased density and improved the mechanical properties of HA–Al_2O_3 composites. HA–alumina composites showed improved Vickers hardness and fracture toughness (K_{1c}) over monolithic HA [7,9,10]. In previous studies, fracture toughness of approximately 1 MPa $\sqrt{m}$ and Vickers hardness of 5 GPa were observed for pure HA [11–17]. For a 23.7 wt% alumina (platelets) and HA composite, mean K_{1c} was 1.95 MPa $\sqrt{m}$ from the measurement of the length of indentation cracks in parallel directions to platelet faces [17]. In another study, a fracture toughness of 2.69 MPa $\sqrt{m}$ was observed for a 23.7 wt% alumina and HA nano-composite [3].

The processing and mechanical properties of HA composites made with micron-sized alumina powder have been studied previously [1,2,5,7]. In the present study, synthesis and characterization of HA and nanophase alumina composites with AlF_3, CaF_2 and MgF_2 were studied for the first time. Composites were hot pressed at 1100 °C and 1200 °C and phase transformations were studied by X-ray diffraction. The hardness and toughness of the composites were determined.

2. Experimental

2.1. Synthesis

HA was synthesized by a precipitation method by mixing reagent grades of calcium nitrate and di-ammonium hydrogen phosphate solutions in the alkaline pH region [18,19]. First, 0.5 M calcium nitrate and 0.3 M di-ammonium hydrogen phosphate were dissolved in distilled water separately. The Ca/P ratio was kept at 1.67 when these solutions were mixed to produce stoichiometric HA. Ammonium hydroxide was added to both of these solutions to bring the pH level to 11–12. Calcium nitrate solution was added dropwise into the continuously stirred ammonium phosphate solution. After stirring the HA solution for 2–3 h, it was heated at 90 °C for 1 h during stirring to decrease the reaction time, and stirred for 1 day at RT. In the next step, the solution was washed repeatedly to remove the remaining ammonia and then filtered through a fine filter paper. The filtered wet cake was dried in an oven at 60–90 °C overnight to remove the excess water. Finally, dried HA particles were ground to $\leq$75 μm (−200 mesh) powder using a mortar and pestle, and calcined at 900 °C for 1 h.

Nanophase Al_2O_3 powder (48 nm size, Nanophase Technologies Inc., Burr Ridge, IL) was mixed with HA powder. The as-received nanophase γ-Al_2O_3 was transformed to nanophase α-Al_2O_3 by heat treatment in a platinum crucible at 1300 °C for 10 min before mixing HA. The ceramic powders were mixed by ball milling. The ball-milled powders were hot pressed in a high temperature—high vacuum furnace (Thermal Technology Inc., Concord, NH). First, 1.4 g of composite powders were put in a graphite mold with a 16 mm inside diameter. Secondly, samples were heated at a rate of 40 °C/min, hot pressed at 1100 °C and 1200 °C under 60 MPa pressure in vacuum and held for 1 h.

The composites designations and descriptions in this study are given in Table 1.

Table 1
Sample designations and descriptions

Sample designation	Description
25AHA	25 wt% alumina + 75 wt% HA
25AHAAF	25 wt% alumina + 70 wt% HA + 5 wt% AlF_3
25AHACF	25 wt% alumina + 70 wt% HA + 5 wt% CaF_2
25AHAMF	25 wt% alumina + 70 wt% HA + 5 wt% MgF_2