Mater. Res. Soc. Symp. Proc. Vol. 845 © 2005 Materials Research Society AA5.31

Synthesis, Sintering and Microstructural Characterization of Nanocrystalline Hydroxyapatite Composites

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ABSTRACT

Nanocrystalline hydroxyapatite (HAp) exhibits better bioactivity and biocompatibility with enhanced mechanical properties compared to the microcrystalline counterpart. In the present work, nanocrystalline hydroxyapatite was synthesized by wet chemical method. Sintering was carried out with nanocrystalline alumina as additive, the content of alumina being varied from 10 to 30 wt% in the composite. For 20 and 30 wt % Al_2O_3, hydroxyapatite decomposed into tricalcium phosphate (TCP) above the sintering temperature of 1100°C. The fracture toughness of nano HAp-nano Al_2O_3 composite is anisotropic in nature and reached a maximum value of 6.9 MPa $m^{1/2}$.

INTRODUCTION

Nanocrystalline hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ is known to possess unique biological and physical properties that makes it an ideal substitute for human bone. Its chemical similarity with the bone makes it a biocompatible ceramic [1]. Nano HAp provides excellent bioactivity arising from the very high surface area for integration into bone[2] but cannot be used as a implant for load bearing applications due to its poor mechanical properties such as toughness and bending strength. Recently, nanocomposites have received much attention due to the advantage of simultaneous increase in toughness and strength. It is reported that nanosize alumina provides bioactivity where as alumina is bioinert in conventional polycrystalline form [3]. Various reinforcing agents have been employed in the earlier studies to improve the mechanical properties of the HAp composites. Among those, alumina is one of the most widely investigated reinforcement material for HAp composites. However, very few reports are available in the literature on hydroxyapatite based nanocomposites[4-6]. Many questions such as the effect of particle size on the phase stability of HAp in composites and change in mechanical properties such as toughness remain unanswered. The synthesis, sintering and characterization of HAp-Al_2O_3 composites, prepared from nanoparticles of both alumina and HAp, has been carried out in the current investigation.

EXPERIMENTAL PROCEDURE

Hydroxyapatite nano powder was prepared by drop wise addition of diammonium hydrogen phosphate into a calcium nitrate solution and the pH of the mixture was adjusted to 11 with the addition of ammonium hydroxide solution. After the completion of the precipitation reaction, the precipitate was kept at room temperature for 48 hours. Then, the precipitate was washed, filtered and dried at 100°C for 12 hours. Similarly, alumina nanoparticles were also prepared by the wet chemical method. An aqueous solution of ammonium nitrate was added into the aqueous solution of aluminium nitrate. 30 ml of ammonium hydroxide solution was added to

raise the pH around 11. The precipitate was washed, filtered and dried and then the powder was calcined at 900° C for 1 hour.

Crystalline phases in the composites were determined by the x ray powder diffraction (XRD). Composite mixtures containing 10, 20, and 30 wt% of calcined alumina and hydroxyapatite powders were ball milled in agate container with acetone as a media for 5 hours. Green compacts were prepared by uniaxial die pressing and the compacts were sintered at different temperatures varied from 1000°C to 1200°C for a constant duration of 1 hour. Theoretical densities of HAp-Al_2O_3 nanocomposites were calculated from the rule of mixtures. HAp and Al_2O_3 theoretical densities are taken as 3.156 and 3.99gcm^{-3} respectively.

The grain size of the as prepared powder and nanocomposites were determined by using scanning electron microscopy (SEM, Cambridge S360) and transmission electron microscopic studies. For scanning electron microscopy, the sintered specimens were polished and etched in 0.1% HF for 30 seconds. Sintered specimens were ground and the powder was ultrasonically dispersed in acetone for transmission electron microscopy (JEOL JEM 200 CX) studies.

The fracture toughness was determined by measuring the length of the crack generated when the polished surface of the pellet was indented with a Vickers indenter with an applied load of 60N by universal testing machine attached with Vickers indenter (UTM, ZWICK/Roell Z005) The toughness values were calculated using the equation proposed by Evans and Charles[7].

RESULTS AND DISCUSSIONS

The crystalline phases of as prepared HAp and alumina were confirmed by powder XRD pattern. In the sintered nanocomposites, no alumina peaks were detected up to the sintering temperature of 1200°C. Moreover, third phases such as $AlPO_4$ were observed above 1100°C [8]. Hap in nanocomposites containing 20wt% and 30wt% of alumina decomposed into tricalcium phosphate (TCP). The addition of alumina beyond 10wt % reduced the decomposition temperature.

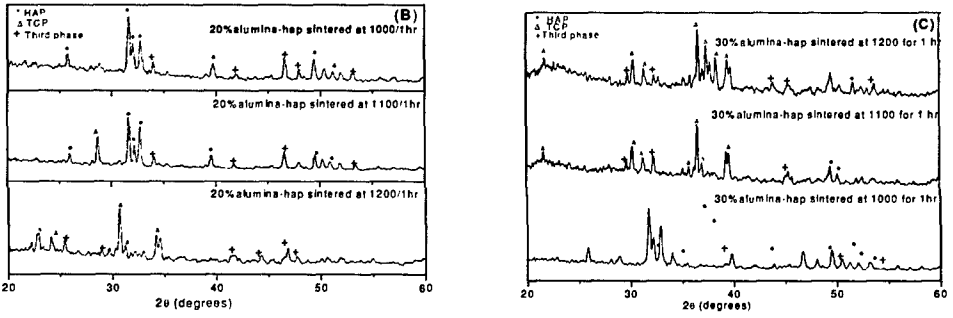

Fig.1. Powder XRD patterns of HAp- Al_2O_3 nanocomposites with A) 10 wt %, B) 20 wt % and C) 30 wt % of Al_2O_3, sintered at various temperatures.

The HAp-Al_2O_3 nanocomposite samples showed the percentage theoretical density in the range of 63-79% when sintered in the temperature range 1000°-1200°C for 1 hour. This decrease in density of composite can be attributed to the differential shrinkage of the HAp, TCP and other unidentified crystalline phases present in the composite[9]. Pure HAp specimens were sintered to near theoretical density, where as the composites have higher porosity which is another requirement for bone in growth [10]. Theoretical densities of the composites are plotted against temperature (Fig. 2).

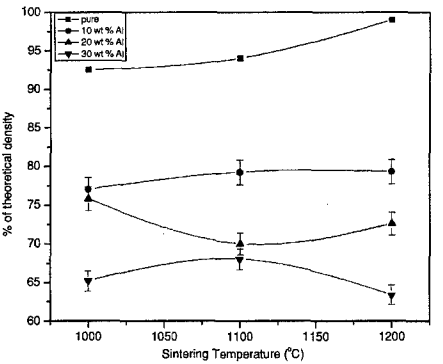

Fig.2. The % theoretical densities of HAp-Al_2O_3 nanocomposites plotted against the sintering temperatures for various compositions.

The particle size of the hydroxyapatite and alumina nano crystalline powders were 20-30 nm and 10 nm respectively. Particle size of pure hydroxyapatie and HAp-Alumina nanocomposites were measured with the help of SEM and TEM micrographs shown in Fig.3.

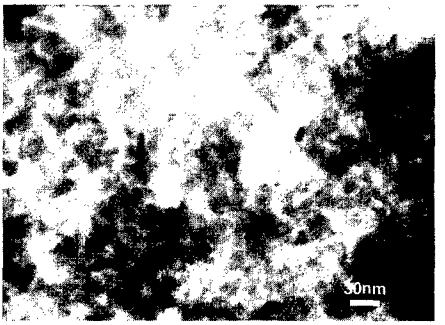

Fig.3.a. TEM micrograph of HAp powder as prepared.

Fig.3.b. TEM micrograph of HAp powder calcined at 800°C for 30 min.

Fig.3.c. TEM micrograph of HAp sintered at 1100°C for 1 hour.

Fig. 3.d. SEM micrograph of HAp at 1200°C for 1 hour.

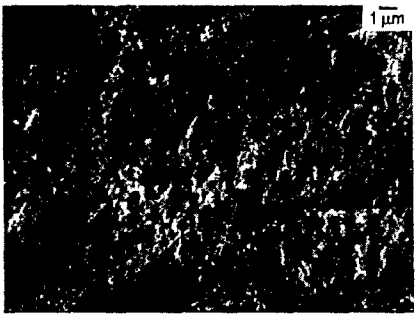

Fig.3.e. SEM micrograph of 10%Al_2O_3-HAp composite sintered at 1000°C for 1 hr

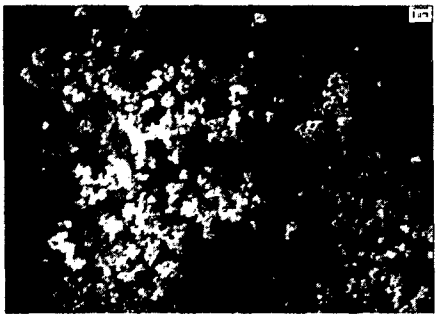

Fig.3.f. SEM micrograph of 10%Al_2O_3-HAp composite sintered at 1200°C for 1 hr

Even though, the grain size of the as prepared HAp powder was around 20 nm, it was found that there was an appreciable amount of grain growth, up to few micron size during sintering in both pure Hap as well as Hap-alumina composite. Inclusion of nanoparticles of alumina into the HAp does not suppress the grain growth of HAp. Alumina remained in nm size while the HAp was in the micron size range. Hence the nano HAp-nano Al_2O_3 composite became micron HAp-nano alumina composite after sintering.

The Vickers hardness values are plotted against the wt% of alumina is shown in Fig.4. Beyond 20 wt% of alumina, the hardness decreased drastically due to the inhomogeneous mixing of alumina with HAp which can form a cluster of particles which sometimes could form interconnected clusters leading to the formation of defects. This is in agreement with the earlier reported work [5]. The toughness of the 20 wt% alumina-hydroxyapatite nanocomposite is anisotropic in nature due to the presence of different phases and compositions which leads to the difference in crack length in different directions as shown in Fig.5. The crack length and fracture toughness values for this nanocomposite along four directions of the indentation are listed in Table1.

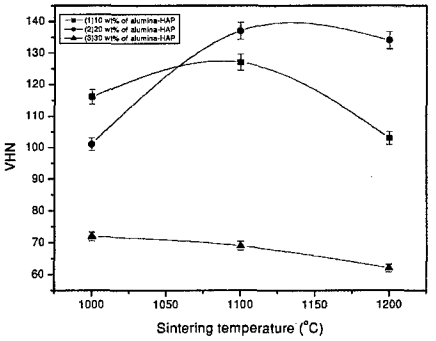

Fig.4. Hardness of HAp-Al_2O_3 nanocomposite plotted against the sintering temperature for various compositions studied.

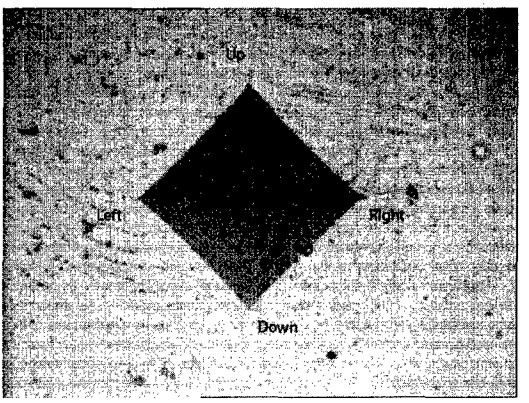

Fig.5 Vickers indentation with cracks along four directions for 20 wt% alumina-HAp nanocomposite sintered at 1100°C for 1 hr

	Up	Down	Right	Left
Crack Length (μm)	121	101	150	80
Toughness (MPa $m^{1/2}$)	3.7	4.87	2.69	6.9

Table1. Crack length and toughness values for 20 wt% alumina-HAp nanocomposite sintered at 1100°C for 1 hour along the four directions of the indentation for a constant load of 60N.

CONCLUSIONS

The synthesis of nanocomposite of HAp and Al_2O_3 followed by sintering has enhanced the mechanical properties. The nano HAp-nano Al_2O_3 composite increased the toughness value up to 6.9 M pa $m^{1/2}$. This value is relatively high when compared to the values reported in the literature, where fracture toughness was found to be 2.95 (±0.45) MPa $m^{1/2}$[5]. Moreover, it has higher porosity which will satisfy the bone ingrowth requirement. The decomposition of hydroxyapatite to tricalcium phosphate is thought to be an undesirable effect but recently there is a growing interest in developing biphasic calcium phosphate ceramics as they are more effective in bone repair or regeneration. However, the thermal stability of this nanocomposite should be investigated further. Moreover by achieving the homogeneity in the composite, toughness value can be made uniform through the composite.

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