

**NOVEL TITANIUM - HYDROXYAPATITE BIOCOSCOMPOSITES  
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**Abstract**

Titanium with nano hydroxyapatite (nHA) as well as with micron size hydroxyapatite was ball milled for various time intervals. The milled powders were characterized using X-Ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM) techniques. The XRD results show peak broadening with increase in milling time indicating the formation of nanocomposite with titanium and HA phases. Relatively, titanium was found to be more reduced in size with increase in milling time than HA in the composite. The EDX results indicated the presence of Ca and P in the titanium matrix. elemental mapping showed homogeneous distribution of Ti, Ca and P after 16 h of ball milling in all the composites. TEM micrographs also revealed the presence of nanocrystals. The powders were compacted, sintered and immersed in simulated body fluid (SBF), which has the same ion concentration as that of the human body plasma, to study bioactivity under physiological condition. After immersion in SBF for 1 week, the compacts were observed in SEM and all the composites were found to be bioactive with the formation of bone like apatite layer on the surface. The morphology of the apatite formed was globular and more dense for the composite prepared using nano HA compared to micron size HA.

**Introduction**

World-wide data reveals that 100 million metallic surgical implants were installed in human beings between 1940 and 1975. Titanium alloys have been the mostly used materials of choice for medical implants. They are generally considered chemically inert, biocompatible with human tissue and resistant to corrosion by human body fluids. There is great interest in the formation of nanosize particles due to their unusual properties [1]. The morphology of the biomaterial is critical to its success as implants, because cells attach, organize, and grow well around fibers with diameters smaller than those of the cells in their natural environment, i.e. cells live in a nano-featured environment of a complex mixture of pores, ridges, and fibers of extracellular matrix (ECM). This information eventually leads to the concept of nanobiomaterials and perceived to be beneficial over conventional biomaterials. For example bone itself is a nanocomposite material consisting of ceramic hydroxyapatite (HA) nanocrystallites in a collagen-rich organic matrix with collagen fibrils of 67 nm periodic microstructure. Both these phases integrate each other into a nano-metric scale to influence cellular activity of osteoblasts (bone forming cells) and osteoclasts (bone resorbing cells) in the formation and remodeling processes

of bone. As cell signaling and processing are essential elements for the formation of the complex and hierarchical structures of bone, the nano morphology of the constituents thus offers another modulation pathway for successful bone implants. Ball milling (BM) was originally employed to produce oxide dispersion strengthened alloys, and then to synthesize different kinds of compounds, amorphous and nanocrystalline materials [2-5].

Synthetic hydroxyapatite (HA,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) has a similar composition and morphology to the mineral content of the bone and hence is extensively used as a bone substitute owing to its excellent bioactivity (ability to form a bond with the bone). However, its poor mechanical properties are the most serious obstacle for load bearing implant applications. The strength of titanium and its alloys are good enough for hard tissue applications such as hip replacement etc., but their bioactivity is very poor than that of HA. A composite of titanium and HA may have the advantage of strength with bioactivity. Since, bone is nanostructured, processing of a novel nanocomposite by ball milling from HA and Ti powders have been attempted.

**Experimental Details**

Different compositions of nano HA (10, 15 and 20 wt. %) or micron size HA (20 wt. %) were ball milled with titanium and were coded as 90Ti10nHA, 85Ti15nHA, 80Ti20nHA and 80Ti20 $\mu$ nHA as shown in Table 1.

**Table1.** EDX results for samples milled for 16h with their composition and code

Sample Code	At%		
	Ca	P	Ti
T1-(90Ti10nHA)	3.00	2.29	94.71
T2-(85Ti15nHA)	6.49	3.78	89.73
T3-(80Ti20nHA)	10.28	6.88	82.84
T4-(80Ti20 $\mu$ nHA)	11.43	6.73	82.84

The powder was ground in a closed vial of tungsten carbide with 10 mm diameter balls. Ethanol was used as the wetting medium. The powder to ball mass ratio was about 1:20 and the rotation speed was maintained at 200 rpm. The milling operation was performed during a cycle of 45 min on and 15 min off for cooling. Milling was done for different time intervals (4, 8, 12, 16, 20 and

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24h). The milled powders were characterized using X-Ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM) techniques. The crystal structure of the as milled powder was characterized by X-Ray powder diffraction analysis [Bruker Discover D8 diffractometer] using  $\text{CuK}_\alpha$  radiation. The diffraction patterns ( $0.02^\circ/\text{step}$  from  $30$  to  $80^\circ$ ) were obtained for samples milled at various time intervals. Scanning Electron Microscope [JEOL] observations were performed to study the morphology of the milled powder. EDX was done in order to assess any phase or contamination occurred during ball milling. Transmission electron microscope [Philips CM12] was done to observe the morphology of the ball milled samples. The ball milled samples were dispersed in ethanol using ultrasonicator and observed in TEM using carbon coated copper grid.

The ball milled samples were compacted and sintered at  $1100^\circ\text{C}$  for 2 h in a sealed quartz tube with argon gas. Its bioactivity was examined in simulated body fluid (SBF) which simulates the inorganic part of human blood plasma. The SBF solution was prepared by dissolving reagent-grade  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{NaHCO}_3$ ,  $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$ ,  $\text{CaCl}_2$  and  $\text{KH}_2\text{PO}_4$  into distilled water and buffered at  $\text{pH}=7.3$  with tris-hydroxymethyl aminomethane (TRIS) and  $\text{HCl}$  at  $37^\circ\text{C}$  [6]. The samples were exposed to the solutions under static conditions in a constant water bath at  $37^\circ\text{C}$  for a week respectively. After exposure the samples were washed in distilled water and its surface after chemical treatment and soaking in SBF were determined by SEM.

## Results and Discussion

### XRD Characterization

The XRD patterns for the raw HA powder and titanium fines are shown in Fig. 1. The peaks in the diffractogram match with the standard pattern for titanium (JCPDS # 44 – 1294) and HA (JCPDS # 9-432). This shows that both the starting materials have good phase purity. The XRD analysis of 90Ti10nHA and 85Ti15nHA powders after milling for different times is shown in Fig. 2 and Fig. 3.

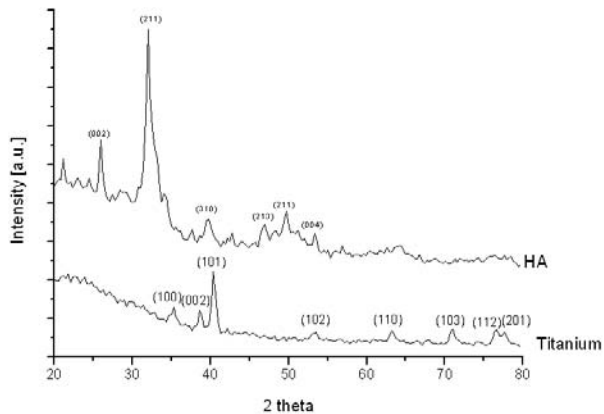


Figure 1. XRD pattern of starting materials, CP-Ti and nHA

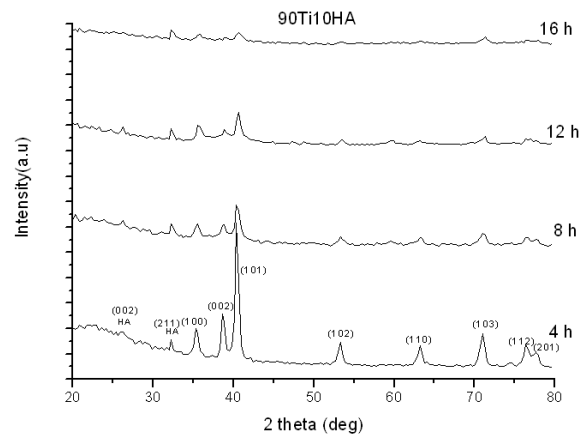


Figure 2. XRD patterns of 90Ti10HA for various milling times

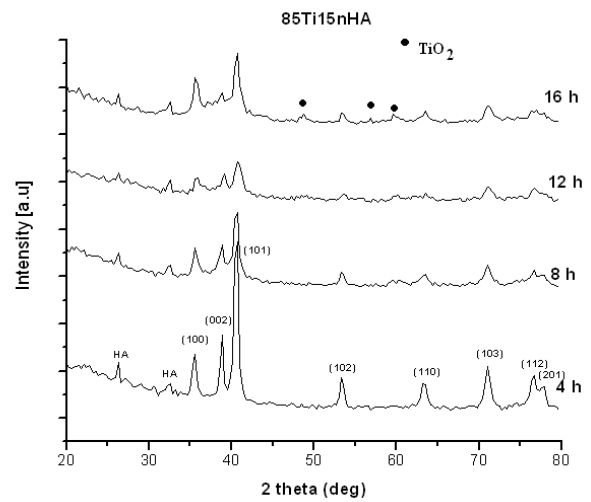


Figure 3. XRD patterns of 85Ti15nHA for various milling times

It can be seen (Fig. 2 and Fig. 3) that the microstructure of the powder undergoes severe changes where as the diffraction peak broadens with increase in milling time. Diffraction peaks of Ti broaden faster than those of nHA. Titania ( $\text{TiO}_2$ , Rutile) peaks were observed after 16 h of ball milling for the 85Ti15nHA sample. This may be due to opening the vial for sample collection for every 4 h. Titanium is prone to form oxides during ball milling in contact with atmospheric oxygen and this may be the reason for observation of rutile phase. However, oxide peaks were not detected by XRD in 90Ti10nHA. The T3 and T4 samples were run continuously for 16 h without opening the vial to avoid any atmospheric oxygen contamination. T3 and T4 contain the same composition of HA (20 wt %) where the former contains nHA and the later contains  $\mu\text{HA}$ . Oxide peaks were not observed in T3 and T4 after milling for 16 h. Figure 4 shows the variation of particle size of titanium as measured by Scherrer equation.

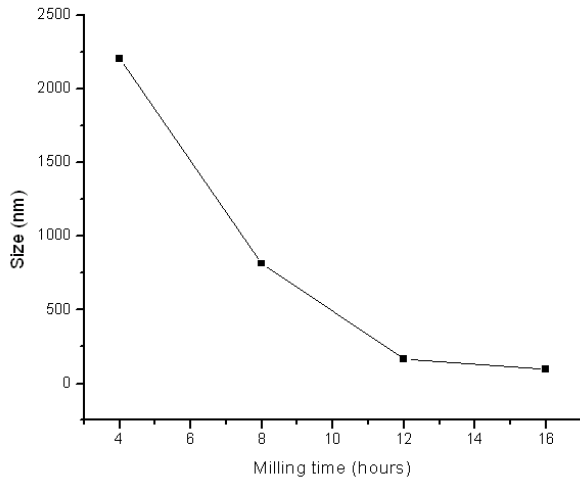


Figure 4. Particle size of Titanium in 80Ti20nHA with milling time

### SEM Characterization

The SEM micrographs in Fig. 5(a) and 5(b) show the change in morphology of 90Ti10nHA powder particles with 8 and 16 h milling time. It is observed that the Ti particles, which are significantly larger than the nHA particles after 8 h of milling, undergo significant reduction in size and became comparable in size with nHA particles after 16 h of milling. This is due to high energy ball milling during which mechanical impactation of hard balls onto titanium and HA takes place. This includes severe plastic deformation, cold welding and fracture of the ductile phase (Ti), disintegration of brittle phase (nHA) via rolling, grinding and shearing of hard balls. The micrographs, Fig. 5(c)-(e) show that HA becomes homogeneously distributed with increasing milling time. The statement that the nHA particles do not undergo any reduction in size with time is also supported by these SEM micrographs.

It is observed that HA in 80Ti20nHA is more homogeneously distributed than 80Ti $\mu$ nHA in the titanium matrix. From Fig. 5, it is also observed that the distribution of HA particles into Ti matrix increases with increase in the weight % of HA. By comparing these two figures, Fig. 5(d) and Fig. 5(e) it is seen that the nano hydroxyapatite diffuses more into the titanium matrix compared to micron sized hydroxyapatite. Figure 5(f) shows the EDX results of the composite 90Ti10nHA powder milled for 16 h. The atomic and weight percentages of the different powders obtained from EDX is shown in Table 1. Spot EDX was taken at three different spots for the same composition. Elements such as Ti, Ca and P were detected and are tabulated in Table 1. From EDX it is evident that an in-situ composite has been formed. With increase in HA content the % of Ca and P also found to increase. Figure 6 shows the elemental mapping of compacts made from the composite 80Ti20nHA milled for 16 h. Mappings show the distribution of Ca, P and Ti elements. It was observed that all the three elements are homogeneously distributed. In all the four trials, no agglomeration of any particular element was found after 16 h of ball milling.

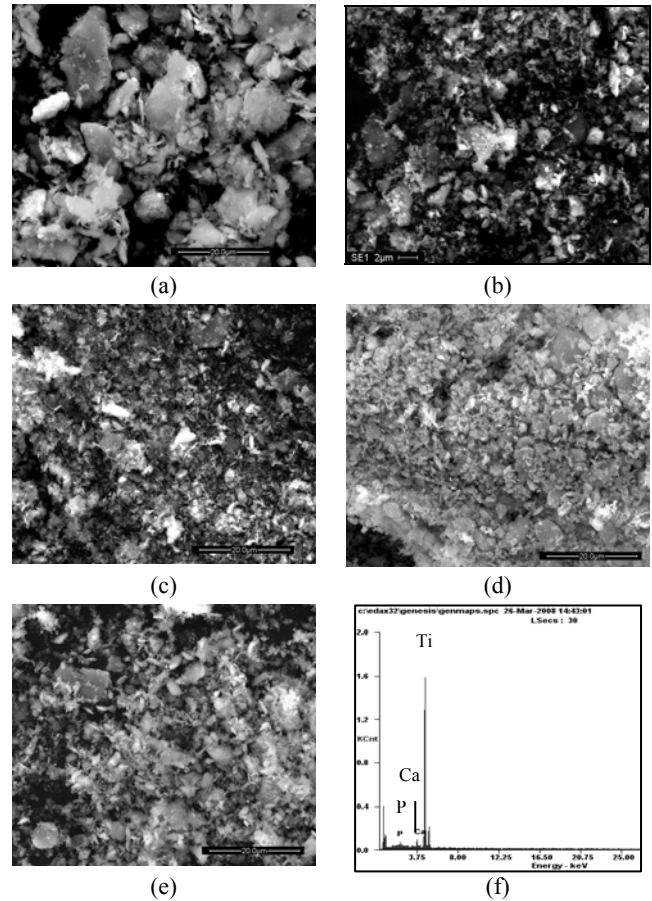


Figure 5. SEM micrographs of (a) 90Ti10nHA, 8h (b) 90Ti10nHA, 16h (c) 85Ti15nHA, 16h (d) 80Ti20nHA, 16h (e) 80Ti20 $\mu$ nHA, 16h and (f) EDX for 90Ti10nHA, 16h

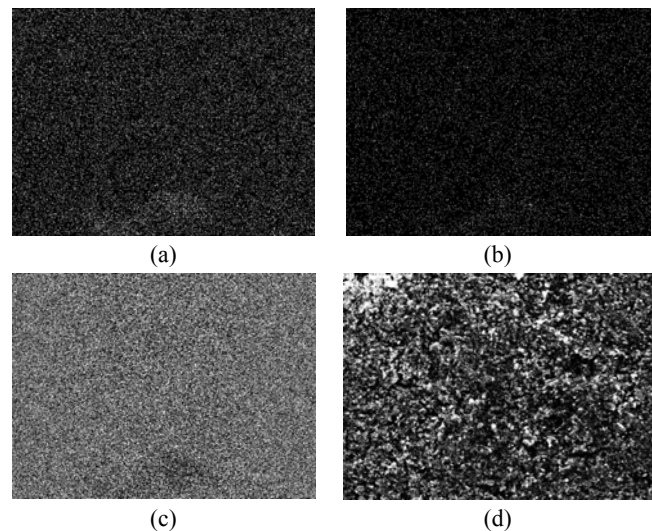


Figure 6. Elemental mapping of T3 (80Ti20nHA) for (a) Ca (b) P (c) Ti and the (d) corresponding SEM micrograph taken at 100X magnification

## TEM Characterization

Figure 7 shows the bright and dark field images of the composite 80Ti20nHA milled for 16 h. It was found that the particles were agglomerated and it was difficult to distinguish between Ti and HA. In the bright field image the crystallites were not distinguishable. The dark field image shows white spots which correspond to nano crystallites agglomerated in the material. Spot EDX on any spot on the agglomerate revealed the presence of Ti, Ca and P elements.

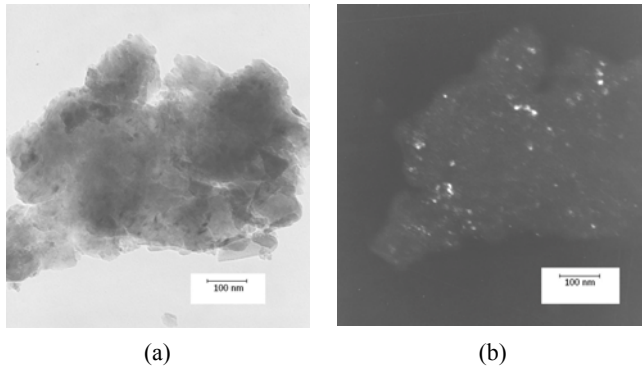


Figure 7. TEM (a) bright field and (b) dark field micrographs of the composite 80Ti20nHA milled for 16h

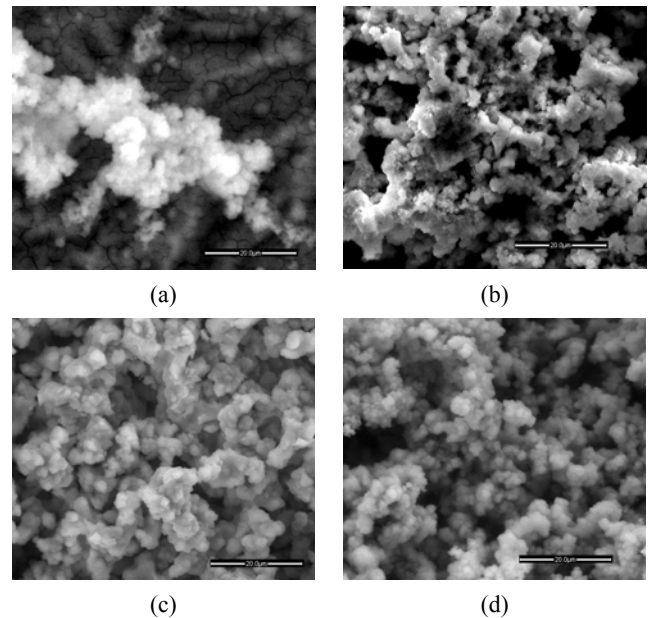
## Bioactivity Characterization using SEM

The powders milled for 16hrs are compacted and sintered in sealed quartz tube with argon gas. The sintered pellets were immersed in SBF for one week. The compacts are then taken out, washed using distilled water and dried. It can be seen that after immersion in SBF, large globular apatite particles have grown on the surface of the specimen as shown in Fig. 8.

It is also observed that a more dense and uniform layer of apatite has formed on the surface of the compact shown in Fig. 8(c) which contains 20% by weight of nHA. However, the nHA showed slightly denser apatite when compared to HA. Figure 8(e) shows the EDX spectra of the apatite layer formed on the 80Ti20nHA composite. Titanium element was not detected on the surface of the apatite layer. Only Ca, P, O were present, which indicates the presence of a thick layer of apatite on the surface. Trace intensities corresponding to Cl and Mg were also observed which may have come from the SBF solution. The Ca/P atomic ratio of the apatite layer formed was found to be approximately 1.62 which is close to that of human bone.

## Conclusions

From the present study it can be concluded that the biocomposite fabricated from HA and titanium powder by ball milling has the ability to enhance apatite nucleation and growth on its surface when immersed in SBF solution. With increase in ball milling time, particle size of titanium was reduced while there was no significant reduction in the particle size of HA. Among all the four compositions, 80%Ti-20% nanoHA was found to induce dense uniform apatite layer formation when compared to other compositions.



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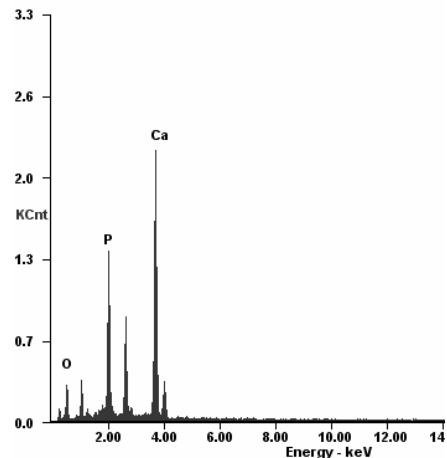


Figure 8. SEM micrographs of compacts immersed in SBF for 1 week (a) 90Ti10nHA (b) 85Ti15nHA (c) 80Ti20nHA (d) 80Ti20 $\mu$ HA (e) EDX of 80Ti20nHA

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