# Synthesis and characterization of Hydroxyapatite based Nanocomposites for structural applications

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**1.0 Abstract:** Bone is a composite material consisting of hydroxyapatite Ca10(PO4)6(OH)2 [HAp] crystals as a main phase embedded in biologically produced organic matrix. The immune system of the human body exclusively rejects any materials foreign to the body [1]. Synthetic biomaterials need HAp at least in the structure including it to avoid being rejected by living bone. Hydroxyapatite is chemically similar to the mineral component of bones and hard tissues in mammals. It is one of few materials that are classed as bioactive, meaning that it will support bone ingrowths and osteointegration when used in orthopedics, dental and maxillofacial applications. HAp ceramics are reported with osteoconductivity that is being capable of supporting bone apposition and forming a chemical bond with bone [2]. But HAp does not have the mechanical strength to enable it to succeed in long term load bearing applications.

Here in this paper we will discuss, how to increase its mechanical property by using nanoTitania (TiO2) as reinforcing material in Hydroxyapatite (HAp) based composite. Hydroxyapatite (HAp) based nanocomposites were prepared by dispersion of Titania (TiO2) nanoparticles using low energy ball milling and were studied in comparison with coarse particle reinforced composites. The Titania (TiO2) nanoparticle powder was prepared by noval route of mechanical milling at different condition (Dry and Wet Milling) for different time. The Particle obtain and was characterized by using XRD and found that the Dry Mechanical Milling is better than Wet Mechanical milling process in term of Particle size and Hardness, particle size as small as 12 nm was obtain and hence the dry mechanical milling nanoparticle powder was chosen for the experiment. The powders (HAp and TiO2) were consolidated using microwave sintering and then characterized using XRD, SEM, and TEM. It was found that Titania particles exist in the matrix of crystalline calcium phosphate (Ca2P2O7¬). TEM analysis showed the presence of nanoparticles in the composite powders. SEM showed lower porosities in the nanoparticles reinforced composite when compared with its coarse particle counterpart. Micro hardness analysis showed considerable improvement in hardness of HA when reinforced with nanoparticles of Titania.



## 2.0 Introduction

Polymer based nanomaterials have a wide range of applications but their commercial interest has caused a lot of research for structural applications. The areas of applications span wide from biological implants (bone and teeth) to aerospace, marine and military applications. The present work is aimed at obtaining better structural properties by the development of nanocomposites using an inorganic polymer (Hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ ) as the base material.

Hydroxyapatite has the ability to integrate in bone structures and support bone ingrowths, without breaking down or dissolving (i.e. it is bioactive).This property of HA enables it to be used in biological implants [3]. But HA does not have sufficient mechanical strength to enable itself to succeed in long term load bearing applications. This is why researchers all over the world have been developing methods for improving this property of HA and hence enabling its usage in structural applications but popularly has been used as bioceramic coatings and as bone filler materials.

Researchers have also been trying to improve the mechanical strength of HA in the form of nanocomposites by reinforcing the HA matrix with harder, better load bearing materials. Many researchers have been studying the use of metals as fillers [4], [5] and [6]for quite some time now. But this method has become less popular now because of its higher processing cost and complex fabrication methods. However extensive research is being done on the use of ceramic nanomaterials as fillers. There has also been lot of research being conducted for the use of $Al_2O_3$ and $ZrO_2$ as filler materials for HA based composites. But the concern in this field is the biocompatibility of these fillers. Kong et al [7] have done extensive work in improvement of biocompatibility of $Al_2O_3$/HA and $ZrO_2$ / HA composites and also have found optimal compositions for the above composites in load bearing applications.

So in order to find harder, better load bearing ceramic filler materials which is bio compatible and possess better anti-bacterial properties nano-$TiO_2$ is chosen. In almost all of these cases, the size of the titanium dioxide particles is an important factor affecting the final performance of the materials. It is not surprising therefore, that much research has been focused upon the reduction of particle size. Mechanical milling route has been considered as a good method to synthesize ultra-fine metallic oxide [8].Mechanical milling process is a high-energy ball milling operation that involves repetitive welding, fracturing, and re-welding of powder particles. Recently, the process has been regarded as an effective tool to synthesize metastable phases, e.g. supersaturated solid solution amorphous alloys and nano crystalline materials [9-11]. Generally, it is found that the different methods produce different results.

Furthermore, the same method using different amount of the starting materials produce powder of different size [12]. Accordingly, it prompted us to investigate the factors in detail which may have important effect upon the particle size.
In this paper, titanium dioxide nano-powders were prepared by the Mechanical milling. X-ray diffraction (XRD) and Transmission electron microscopy (TEM), of milled powders was used to study the effect on the microstructures and grain size. In the later stage of this paper consolidation of composite powders has also been studied and SPS has been studied more popularly. The mechanical properties of spark plasma sintered nano composite powders have produced enhanced indentation and fracture toughness [13]. Thus, SPS compacts of nanoZrO2/ Al2O3-HA composite powders have been considered for load-bearing orthopedic implants because of its unique fracture toughness and strength. Porous HA ceramics have been sintered effectively and this process could get a sintered ceramic more rapidly at much shorter sintering time and lower sintering temperature than that of the conventionally heat sintering process. Furthermore, the microwave-sintered samples showed much smaller grain size and more uniform microstructure and resulted in bio-ceramic with a comparable compressive strength of that obtained in conventional method [14].

## 3.0 Experimental Work

### 3.1 Preparation of nano $TiO_2$ powder:

Commercially available micron sized powders of $TiO_2$ (99%Pure, LOBA Chemic Pvt Ltd, Mumbai) were used. The milling was performed in a planetary ball mill (FRITSCH, GERMANY). Initially the particle size of the $TiO_2$ were measured with the help of a Particle size analyzer (Particle Sizer Annlysett-22,FRITSCH) During milling the weight ratio of the ball to the powder was maintained at 10:1. The balls and vials are made of tungsten carbide. The rotating speed for milling of the vials was maintained at 300 rpm for all the experiment. Primarily acetone was used as the wet milling medium. After milling for a predetermined time e.g. 20h and 35h, a small amount of ball-milled powder were taken out for analysis .Another set of nano $TiO_2$ powders was prepared by dry milling without using any liquid milling medium. Samples were drawn after predetermined time intervals 20h and 35h.



### 3.2 Characterization:

The particle size of the $TiO_2$ before milling was measured with the help of a particle size analyzer (Particle Sizer Annlysett-22,FRITSCH). As receive and milled powders were characterized by X-ray diffraction (XRD) technique. X-ray diffraction analysis was carried out using CuK$\alpha$ radiation on a Philips PW1840 diffractometer using a step size of $0.05^0$ (2$\theta$). Prior to these analyses, XRD peaks were corrected for the effects of the K$\alpha_2$ radiation and instrumental broadening. The particle size of the ball milled $TiO_2$ powders (wet & dry) were computed by the XRD technique using single line profile analysis [15].
The microstructure, crystallite size were studied using the JEM 2100 HRTEM operated at an acceleration voltage of 200 kV in bright field modes. Selected area diffraction (SAD) patterns were obtained to identify the phases at specific locations using appropriate aperture and tilt.

### 3.3 Processing of composites:

HA powder of 99% purity with an average particle size ~20 μm (LobaChemiePvt Ltd, Mumbai) and 5% Coarser size, 5% nanosized $TiO_2$ powder (dry mechanical milling for 35 hr was preferred) were used for preparing (HA+ 5%$TiO_2$) green powder mix.
**TiO2 particles were dispersed in HA powders using ball milling technique. The precursor materials were milled at 300 rpm in tungsten carbide vials with tungsten carbide balls in a toluene environment. The milling was done for duration of 1 hr per composition. Samples with 5 wt % TiO2 coarse powders and 5 wt% TiO2 nanoparticles were separately dispersed in HA and milled to obtain the composites. The powders were commercially procured. The synthesized composites were then consolidated using microwave sintering techniques at temperatures around 1400 ˚C. The composite powders were characterized using TEM. The sintered pellets were characterized using SEM and XRD analysis. Micro hardness measurements were taken and compared with pure HA.**

## 4.0 Results and discussion

### 4.1 $TiO_2$ Nano Powder Preparation:

The particle size distribution of the $TiO_2$ powder prior to mechanical milling is shown in Figure 1. The size distribution profile of the powder clearly shows that the distribution is fairly wide ranging from 0.195μm to 23.08μm.

Figures 2 and 3 show the results of XRD analysis of the mechanically milled $TiO_2$ powders in dry and wet condition. The pattern clearly shows that initially $TiO_2$ particles possess tetragonal crystal structure, which transform partially to orthorhombic and hexagonal crystal structure with the increase in dry milling and wet milling time. It has been further observed that the XRD pattern gets broadened with the increase in milling time, which suggest reduction in $TiO_2$ particle size and increase in lattice strains in the crystallites. This effect appears to be more prominent in the XRD pattern of the dry milled sample than the XRD pattern of the wet milled $TiO_2$ powder. This can be further corroborated by the results of the XRD pattern of the ball-milled sample by analyzed by the single line profile analysis technique.

Table 1 summarizes results of the single line profile analysis, which shows the variation of particle size and lattice strain with respect to milling condition and time. From the table it is quite clearly evident that with the increase in milling time the particle size of $TiO_2$ powder decreases and corresponding lattice strain increases. It has been also observed that dry milling is more effective technique in reducing the particle size to the nanometric length scale as compared to wet milling.
A bright field TEM image and the corresponding SAD pattern from the powder dry milled after 35 hr are shown in Fig. 4. Examination of the TEM image (Fig. 4a) and inset of the Debye rings in the corresponding SAD pattern (Fig. 4b) indicate that nano-sized. Fig. 5 shows the bright field TEM image and thecorresponding SAD pattern of the dry milled after 35 hr. Comparison of the TEM images in Figs. 4a and 5a suggest that dry milling is the better process for obtaining minimum crystal size $TiO_2$. Infact, the SAD pattern from the powder wet milled after 35 hr (Fig. 5b) showsmany spot with Debye rings which confirm larger crystallite Size.)

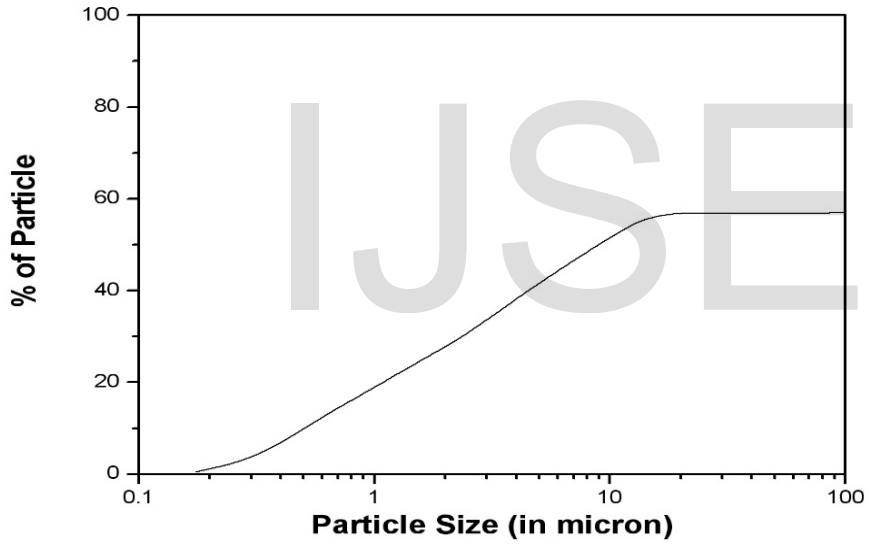





Figure 1 Particle size distribution of $TiO_2$ powder sample before ball milling.

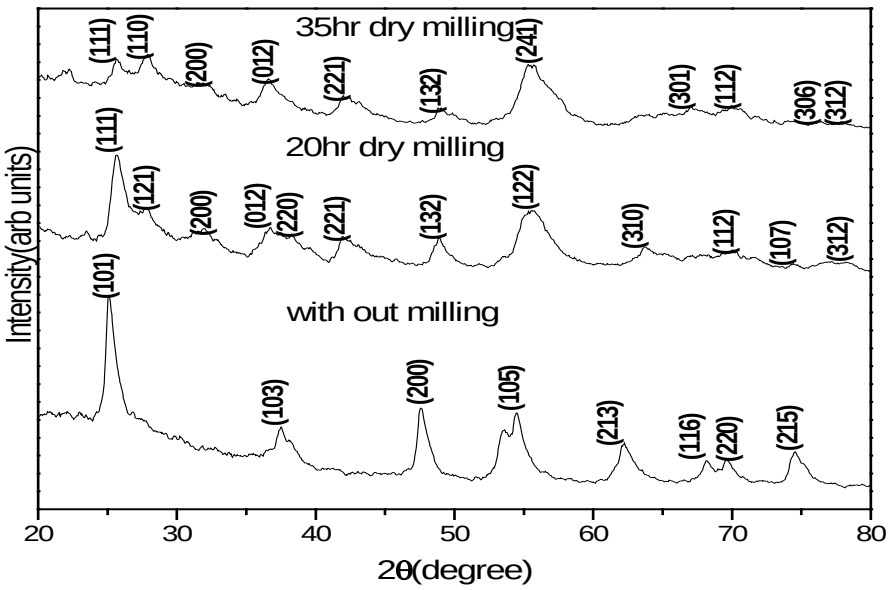



Figure 2 XRD spectra of $TiO_2$powder (a) After 20h dry milling (b) After 35h dry milling (c) without milling.



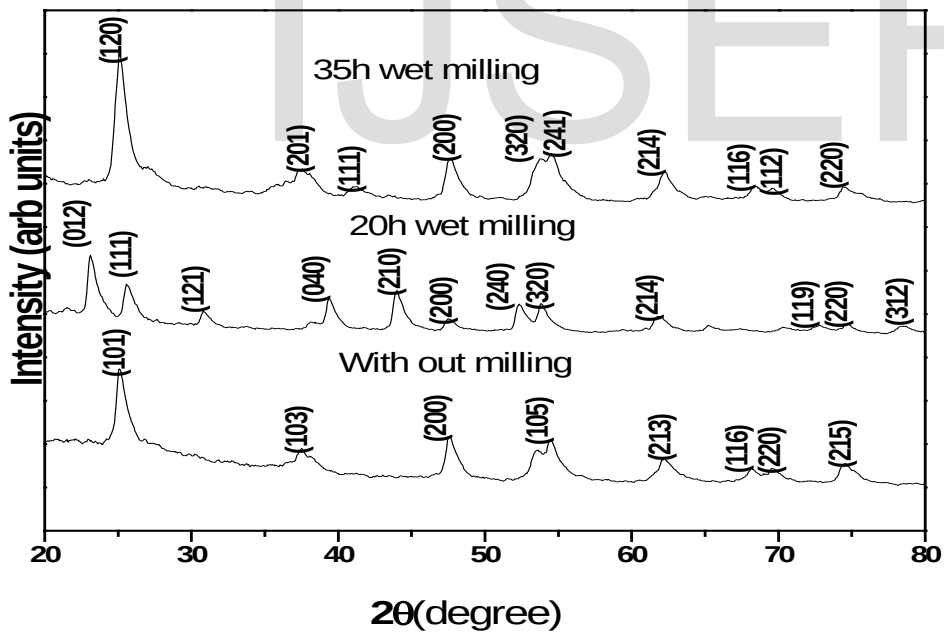



Figure 3 XRD spectra of $TiO_2$powder (a) After 20h wet milling (b) After 35h wet milling (c) without milling.

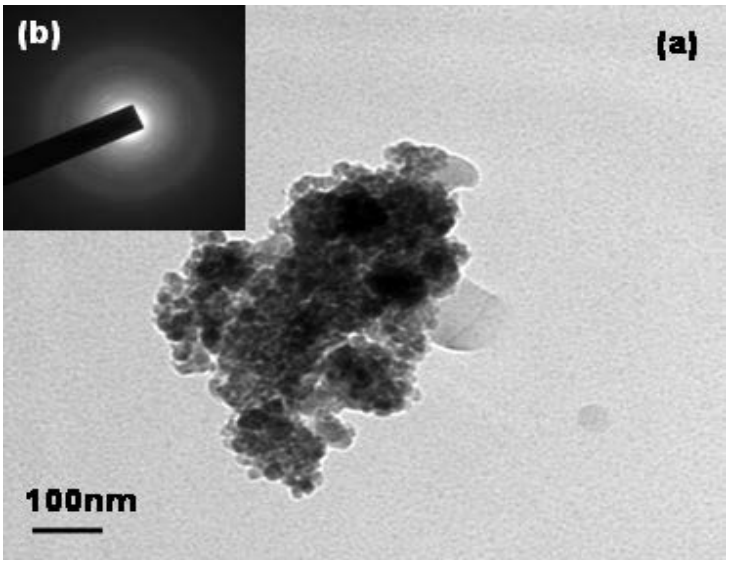



Figure 4(a) Bright field TEM image and inset (b) the corresponding SAD pattern of the powder dry milled after 35 hr.

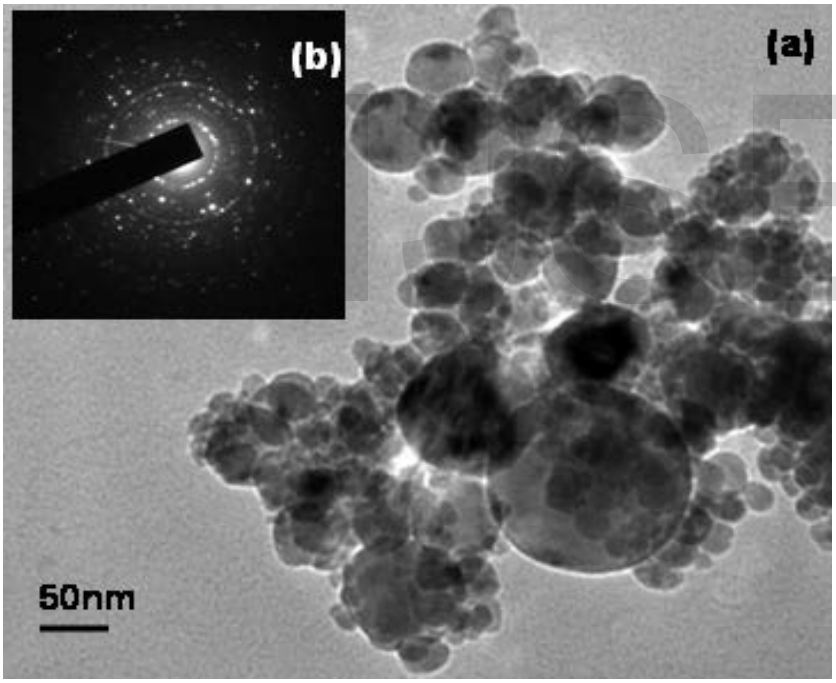



Figure 5(a) Bright field TEM image and inset (b) the corresponding SAD pattern of the powder wet milled after 35 hr.

Table Caption

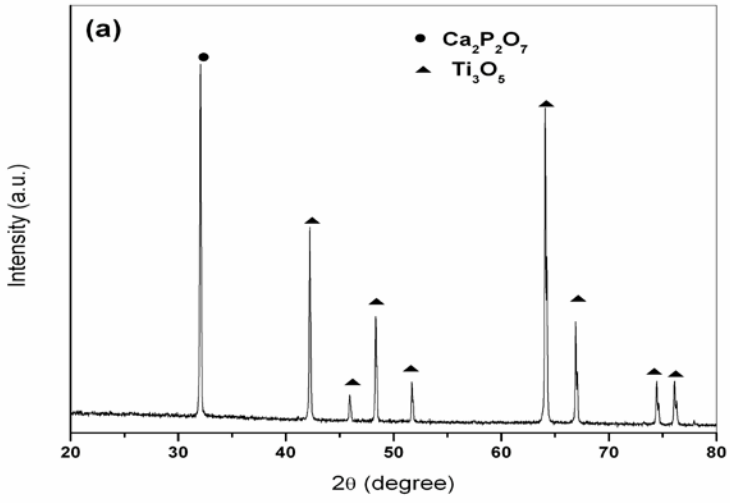
Table-1. *Influence of different milling condition and time on the variation of particle size and strain as measured by single line profile analysis of XRD spectra.*

| Milling time (hrs) | Milling condition | Particle size (nm) | Strain |
|---|---|---|---|
| 20 | Dry | 16.15 | 0.012 |
| 35 | Dry | 11.86 | 0.0109 |
| 20 | Wet | 18.93 | 0.0019 |
| 35 | Wet | 16.17 | 0.0091 |

Table 1: Influence of different milling condition and time on the variation of particle size and strain as measured by single line profile analysis of XRD spectra.

**4.2 Processing of Composite:**

The sintered samples were characterized using XRD technique. Fig 6 shows the XRD plots obtained for the samples. It can be seen from figure 6 (a) that the titania nanoparticles reinforced HA pellet shows all the characteristic peaks of crystalline TiO2 but rest of the peaks were identified to be a crystalline phase of calcium phosphate $Ca_2P_2O_7$. The formation of this phase can be attributed to the loss of water upon sintering. Fig 6(b) of coarse particle reinforced composite also indicates the formation of $Ca_2P_2O_7$ by the identification of all its characteristic peaks. However the titania phase in the coarse particle composite exists in $Ti_3O_5$ form thereby indicating the occurrence of a phase transformation during sintering. All the peaks were identified using JCPDS standards and it can be seen that there is a good match both in terms of intensity and position of the peaks.



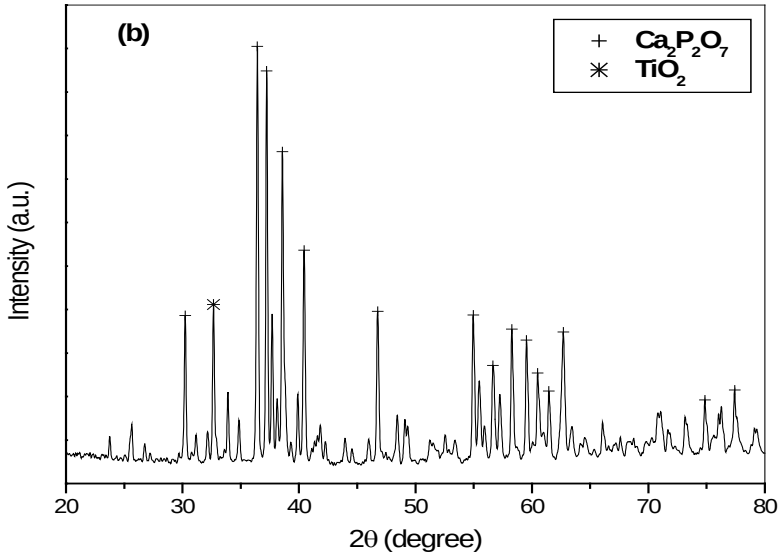
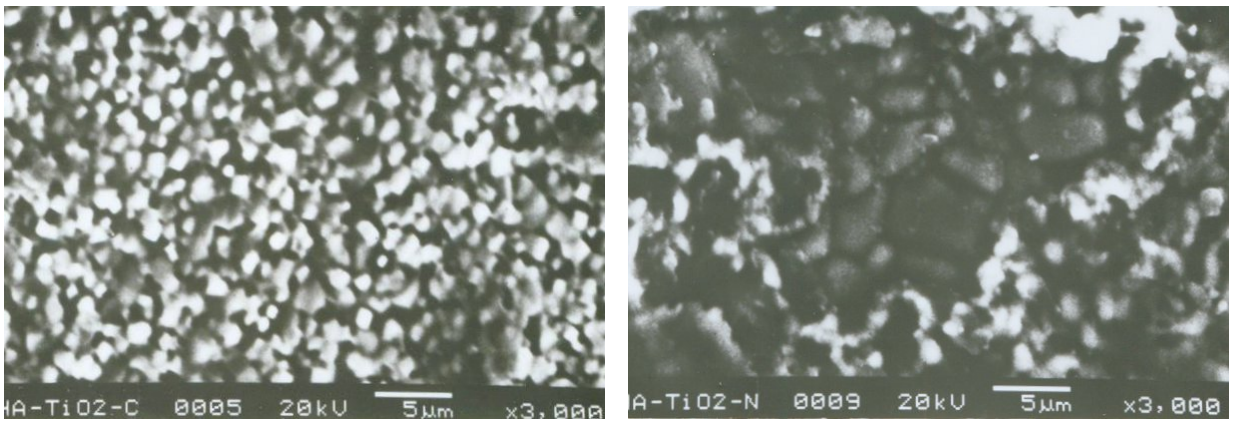



Figure 6, XRD plots of (a) coarse particle reinforced (b) nano particle reinforced $TiO_2$-HA composite.

Scanning electron microscopy of the sintered pellets was performed fig 7(a) shows the presence of low porosities in the nanoparticle reinforced $TiO_2$-HA composite indicating very good sintering. However the coarse particle reinforced composite does not show good sintering fig 7(b). It can be clearly seen that the samples had fairly high porosity with clearly visible isolated particles sticking to each other. This can be attributed to the fact that the nanoparticles, due to its high surface area to volume ratio and also higher diffusivity shows better sintering capability than that of its coarse counterparts. EDAX results confirm the presence of titania and crystalline calcium phosphate. The scanning electron micrographs were taken using JKOL JSM-5800 scanning electron microscope. The presence of titania and HA were confirmed using EDAX measurements.






(a) (b)

Figure 7, SEM micrographs of (a) coarse particle reinforced (b) nano particle reinforced $TiO_2$-HA composite.

Transmission electron microscopy was performed on the composite powders and the presence of titanianano particles was confirmed. It can be clearly seen from fig 8 that the particles are nanosized with sizes in the range of 30-40 nm. Also agglomerates with higher sizes

can be seen but which would push the average size towards the higher side. The TEM images were taken using JEM 3000 transmission electron microscope.

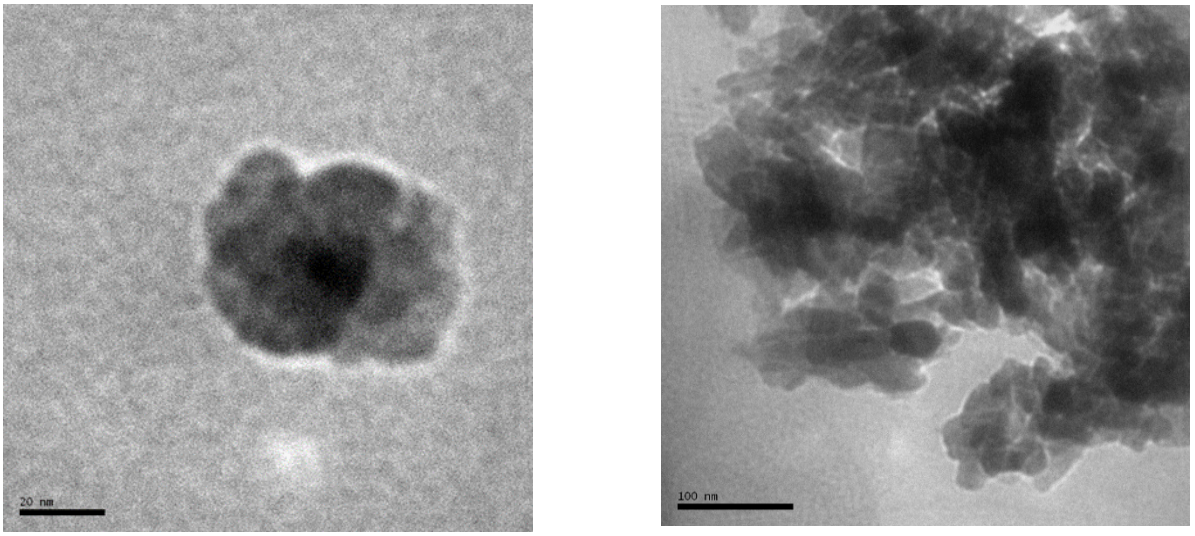



Figure 8, TEM images of nano particles reinforced in $TiO_2$-HA composite.



Microhardness testing was performed using Leica microhardness tester on the two samples viz. nanoparticle reinforced and coarse particle reinforced. The Vickers microhardness of the coarse particle composite sample was measured to be 466 HV and that of the nano particle composite was 631 HV. Both the composites show better hardness than the hardness of pure HA. As shown in Figure 9.

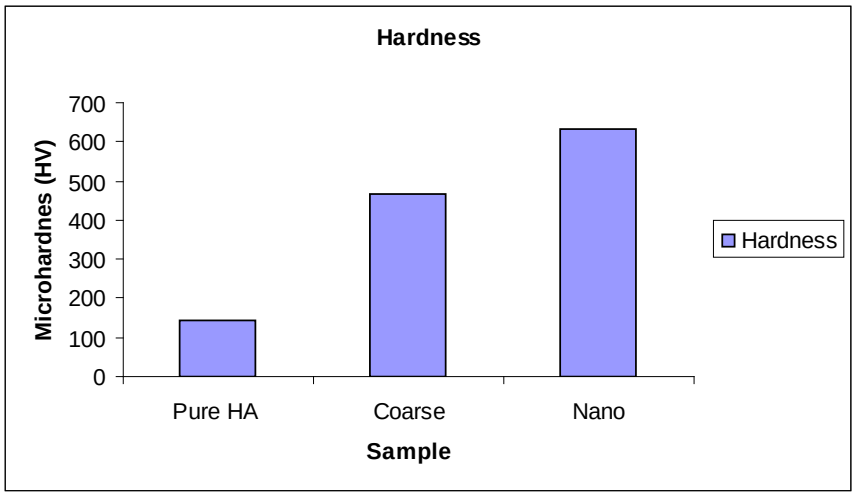



Figure 9:

This fact can be attributed to the better sintering due to nanoparticle reinforcements of titania due to its higher diffusivity and more surface area to volume ratio. It can also be attributed to the large grain boundary area because in ceramics the grain boundary diffusion dominates in solid state sintering. High hardness in nanocomposites results from the suppression of dislocation activity in nanometric grains surrounded by a thin amorphous layer that reduces crack formation and propagation [16] and [17].

**5.0 Conclusion**:

Nano-$TiO_2$ powders have been prepared by mechanical milling method successfully. By controlling the conditions properly, nano-$TiO_2$ powders with the grain size less than 12 nm could be obtained successfully and easily by Dry milling technique then the wet milling technique. Micron sized $TiO_2$ particles which initially possesses a tetragonal crystal structure, transform partially to orthorhombic and hexagonal crystal structure with the increase in milling time.

The ball milling method provides a novel way for the dispersion of Titania particles into an HA matrix. The high rate of heating provided by the usage of microwave sintering enables faster, more efficient and better sintering. The Titania nanoparticles reinforced composite showed much higher hardness at lower concentrations of filler materials (5 % $TiO_2$ nanoparticles in HA and 10 % coarse TiO2 particles in HA.) and both the composites were considerably harder than the pure HA hardness (obtained from literature). This fact can be attributed to the suppression of dislocation movement due to the reinforcements and also to the better sintering due to the enhanced diffusivity of nanoparticles.

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