Study of Microstructure at Different Sintering Temperatures of Alumina Reinforced Hydroxyapatite Bioceramic Composite

Vaibhav Trivedi[1], Anupam Srivastav[2], Rahul bhatnagar[3], Mohd Javed[4]

[1, 3, 4] *(Department of Mechanical Engineering, IFTM University Moradabad, India)*
[2] *(Middle East College, Knowledge Oasis Muscat, Sultanate of Oman)*

Abstract: *Hydroxyapatite $Ca_{10}(PO_4)_6.OH_2$ (HAp), known for bioactive fixation with the surrounding bone tissues, is one of the most studied and used material for implants. The brittle behavior of HAp due to lower fracture toughness under mechanical loads is improved by addition of a ceramic second phase such as Al_2O_3, SiC, ZrO_2, etc. There is a need to focus on the microstructure of such reinforced biomaterials to understand the relationship between their established mechanical behavior and the microstructure. In this work microstructure of pure HAp and 20wt% Al_2O_3-HAp biocramic composite, sintered at 1050° C, 1150°C and 1250° C temperature range for 02 hours curing time, is studied to establish relationship of strengths and microstructure of these materials.*
Keywords: *Reinforced Hydroxyapatite, Sintering, Microstructure, SEM*

I. Introduction

During the last decades, numerous types of biomaterial of various classes have been developed and synthesized, which either belong to metals, polymers or ceramics, category. In the metallic category of Biomaterials, Titanium alloys are commonly used as implant material, due to high fracture strength associated with their high fracture toughness [1]. As feasible alternative to metals due to many problems associated with them, Ceramic materials are used because of their chemical composition being closer to that of hard tissues, which give rise to a better biocompatibility [2,3]. Chemical composition of the mineral bone is close to that calcium phosphates and therefore maximum attention has been given to bioceramics compounds of this family [4-6].

Hydroxyapatite $Ca_{10}(PO_4)_6.OH_2$ (HAP), which is known for a bioactive fixation with the surrounding bone tissues, has become a most studied and used material for permanent implants. The main problem with bioceramics like hydroxyapatite is its brittle behavior due to lower fracture toughness under mechanical loads [7-10]. The addition of a ceramic second phase such as Al_2O_3, SiC, ZrO_2, etc is known to be a way to improve the mechanical reliability of ceramic matrices [11-13]. In spite of various studies having been devoted to these types of reinforcement of hydroxyapatite matrices, no study has focused on the comparison of microstructure of such reinforced materials, fabricated at different temperatures.

II. Literature Review

A common approach in practice with regard to preparing a stronger bioceramic based biomaterial is the use of bioceramics, whether bioactive or bioinert for its excellent biological behavior and improve the relative weak mechanical properties by reinforcement with an appropriate second phase [14]. To be effective as a reinforcing agent, for a ceramic-matrix composite material, the strength and elastic modulus of the second phase must be higher than those of the matrix [15]. In addition, the reinforcement must be chemically compatible with respect to the matrix. Moreover, the coefficient of thermal expansion of the reinforcing agent should be as close as possible to that of the matrix to avoid the formation of micro cracks around the second phase [16].

Hard bioceramic particle reinforced Hydroxyapatite composite has been investigated by many workers in which acceptable biocompatibility as well as the mechanical strength of these materials has been established. It is also known now that the mechanical properties of hydroxyapatite (HAp) bioceramic material improve significantly by adding tetragonal-zirconia-polycrystalline (TZP) powder coated with Al_2O_3. Composite containing 15 volume % zirconia and 30 volume % alumina, added to the HAp by the coating method shows about 3 times higher strength and the fracture toughness than those of pure HAp [17]. In similar study involving Zirconia toughened HAp composites, the elastic modulus was found to increase from 110 GPa for pure HAp to 171 GPa and the fracture toughness from 1.2 MPa m$^{1/2}$ to 2.1 MPa m$^{1/2}$ for the composite [18].

Among the various reinforcing agents, the Alumina (Al_2O_3) is the most widely investigated [19]. The primary role of alumina as second phase reinforcement is to prevent catastrophic brittle failure by transformation-induced retardation of grain growth and crack deflection toughening mechanism [20]. However, when this oxide is used as a reinforcing agent for HAp, the decomposition of HAp to β-TCP occurs severely, resulting in poor densification and reduced mechanical properties [21]. Therefore, efforts are being made to

produce fully densified HAp–Al_2O_3 composites without the decomposition. The desired property of osteo conductivity remains the dominating effect in these HAp composite materials [22].

Further, it has been reported that the particle size of these reinforcements are the major factor affecting the mechanical properties. When large alumina platelets are added, the improvement in strength is minimal because of formation of micro cracks around the platelets due to large difference in coefficient of thermal expansion between HAp and Al_2O_3. On the other hand, when fine Al_2O_3 was used as reinforcements, the strength improved steadily with increasing amount of Al_2O_3 [23].

In all such studies, major emphasis has been given to the phases present and mechanical property improvements. Not much work is found which gives the the comparison of the microstructure of Alumina-HAp biocermics composite to correlates with the reported mechanical improvements. This work establishes these relationships of microstructure of bioceramic composite with the sintering temperatures which in turn have direct relations with the strengths. For this study 20 wt% Al_2O_3-HAp composite has been selected, based on reports of work [24-25] in which compositions ranging from 10 wt% to 40 wt% have been investigated over 1050° C to 1250° C temperature range.

III. Materials And Methods

Raw materials used for the study were analytical grade reagents and chemicals (99% pure). The raw materials used are:

3.1 Hydroxyapetite {$Ca_{10}(PO_4)_6(OH)_2$}
The matrix material for the different composite materials prepared and investigated was pure and synthetic hydroxyapatite (HAp) (Fisons, Philadelphia, USA make having 502.32 as Molecular Weight. The particle size of the powder was in the range of 0.5 μm to 2.0 μm).

3.2 Alumina (Al_2O_3)
For preparation of 20 wt% alumina-HAp composites, α-Al_2O_3 powder (Merc, Germany, having particle size <20 μm) was taken as reinforcing particles.

3.3 Polyvinyl Alcohol
It was procured from C.D.H., New Delhi, and used as an organic binder for the compaction of the powders.

IV. Specimen Preparation And Sintering

For the micro structural studies involving the selected materials, one composition containing pure Hydroxyapatite and other containing 20 wt% Alumina-Hydroxyapatite composite were prepared by first mixing the powder well in agate mortar in presence of acetone for 3 hours. 2 wt% of PVA was added as binder to this powder and the mixture was again mixed for 1 hour. The thoroughly mixed powders having different compositions were then compacted in a rectangular die under a hydraulic press at pressure 25 KN/cm^2. All the specimens were prepared in a shape of rectangular bar of dimension 25 mm x 5 mm x 3 mm. These green specimens were then sintered at 1050° C, 1150° C and 1250° C in a microprocessor controlled programmable super kanthal furnace (Eurotherm P818 programmable temperature controller Baishakh & Co. Ltd., Calcutta) maintaining 07 ^{o}C/min heating and cooling rates, and keeping a curing time of 2 hours at each temperature.

4.1 Xrd And Microstructural Analysis
All the different composites to be investigated in this study as well as pure HAp, pure alumina, all sintered at different temperatures (along with un-sintered starting powders of pure HAp, alumina, 20% alumina-HAp mixture) is characterized for phase identification using XRD. For the study of type of microstructure and size and distribution of pores, etc., the sintered as well as fractured samples of each type (without polishing the surface) were examined under SEM. All the samples were coated with Gold-Palladium film to improve its electron conductivity during Scanning Electron Micrographs.

V. Results And Discussion

The Scanning Electron Microscopy (SEM) was done to analyze the microstructure of pure HAp as well 20 wt% alumina-HAp composites specimens, sintered at 1050° C, 1150° C and 1250° C temperature for the 02 hours curing time, studying both, the sintered surface and the fractured surface of each specimen. The SEM micrographs of these specimens are shown in Figure 1 to Figure 12. Figure 1 to Figure 3 shows sintered surface of pure HAp specimens sintered for 02 hrs at the three selected temperatures. These micrographs reveal that good sintering is achieved even at 1050° C, which increases at 1250° C. However, at 1250° C, irregular surface with bubble like structures is visible, which is indicator of decomposition of HAp (as confirmed through XRD given in Figure 18), as has also been reported in such previous work by other authors, mentioned in literature

review. The fractured surfaces of these specimens given in Figure 4 to Figure 6 do not show any cracks or pores within the specimen at lower temperature of 1050° C . But at 1150° C and 1250^oC well distributed network of pores is seen, which correlates well with decrease in strength of HAp at higher temperatures reported in other work [25-27].
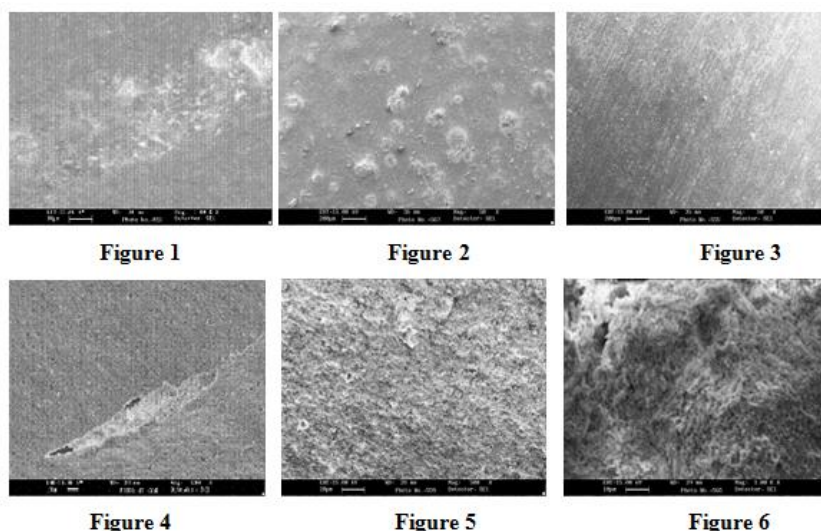

Figure 1   **Figure 2**   **Figure 3**

Figure 4   **Figure 5**   **Figure 6**

Figure 1-3: Sintered surface of pure HAp at 1050 ^{o}C, 1150 ^{o}C and 1250 ^{o}C respectively;
Figure 4-6 Fractured surface of pure HAp at 1050 ^{o}C, 1150 ^{o}C and 1250 ^{o}C respectively;
Figure 7- 9 shows dense Al_2O_3-HAp composite sintered at the three selected temperatures. In case of specimen sintered at 1250 ^{o}C too, well pronounced surface cracks are visible across the surface. These cracks are due to decomposition of HAp and formation of Calcium Aluminates as confirmed by XRD shown in Figure 21.

The internal microstructure revealed in the SEM of fractured surfaces of Al_2O_3-HAp composite sintered at 1050 ^{o}C , 1150 ^{o}C , 1250 ^{o}C (Figure 10 to Figure 12) also confirms dense core with pore size less than 2-3 μm in all the specimens. The fact that the pore size does not increase to any significant level even at 1250°C enables the Al_2O_3-HAp composite to exhibit higher strength (as reported in [25]) than compared to pure HAp at all temperature ranges. It is therefore confirmed through these micrographs that the addition of Al_2O_3 in HAp matrix not only strengthens the matrix but also retain small pore size even at elevated temperatures, thereby negating the effect of HAp decomposition.
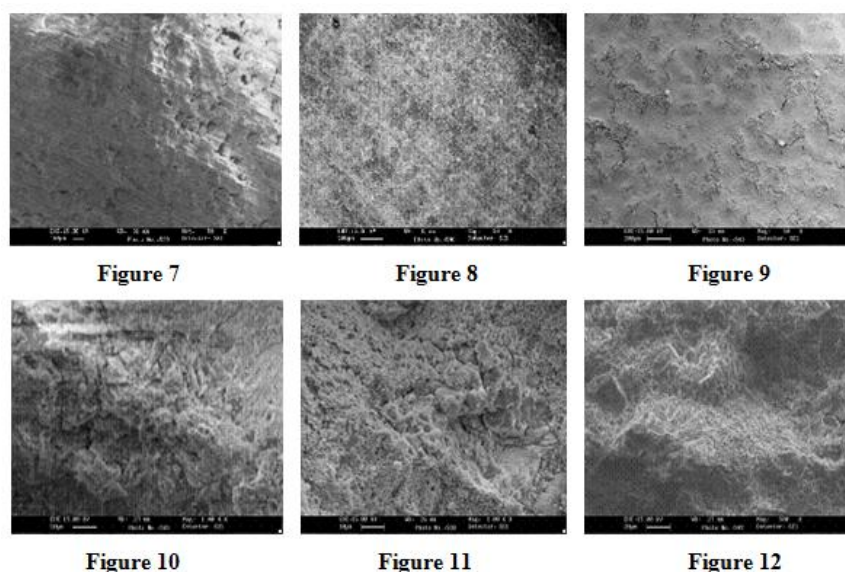

Figure 7   **Figure 8**   **Figure 9**

Figure 10   **Figure 11**   **Figure 12**

Figure7-9 Sintered surface of 20 wt% Al_2O_3-HAp at 1050 ^{o}C, 1150 ^{o}C and 1250 ^{o}C;
Figure 10-12 Fractured surface of 20 wt% Al_2O_3-HAp at 1050 ^{o}C, 1150 ^{o}C and 1250 ^{o}C
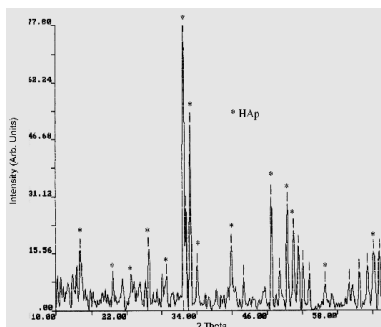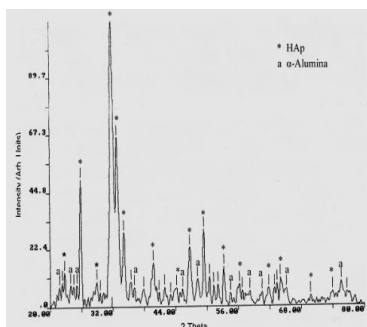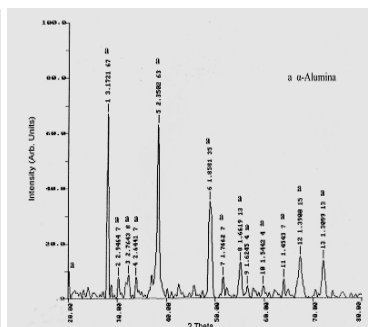
Figure 13 **Figure 14** **Figure 15**

Figure13-15 XRD of un-sintered starting powders of pure HAp, Alumina and 20 wt% Al_2O_3-HAp respectively
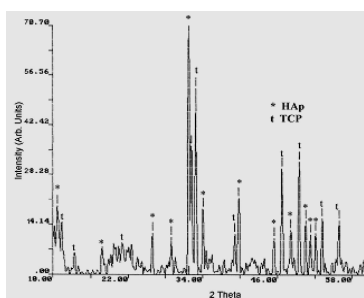

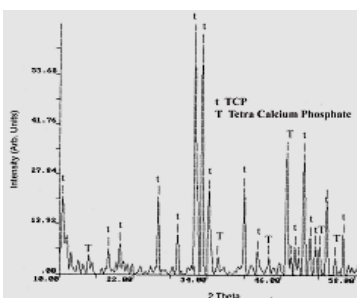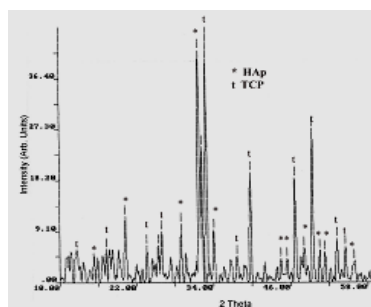**Figure 16** **Figure 17** **Figure 18**
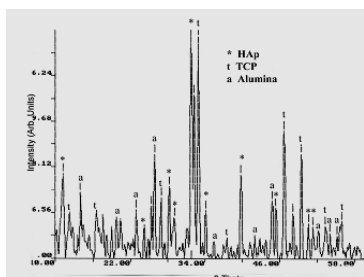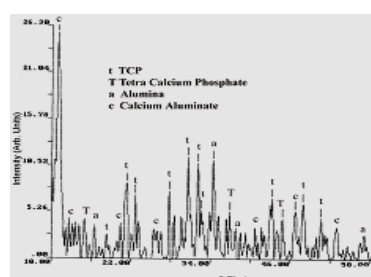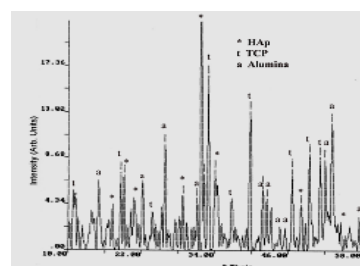
Figure 19 **Figure 20** **Figure 21**

Figure16-18 XRD of pure HAp sintered at 1050°C, 1150°C, 1250°C for 02 hours respectively
Figure19-21 XRD of 20wt% Al_2O_3-HAp composite sintered at 1050°C, 1150°C, 1250°C for 02 hours respectively.

VI. Conclusion
The microstructural studies using SEM, carried out on pure HAp and 20 wt% Al_2O_3-HAp composite sintered at 1050°C, 1150°C, 1250°C temperatures for 02 hours curing time establishes that the decomposition of pure HAp at higher temperature (1250°C) leads to formation of rough and irregular sintered surface and porous internal structure, which is the reason of decrease in strength of HAp with temperature beyond 1050°C. Also, the presence of 20 wt% Al_2O_3 in HAp bioceramics, which is known to increase the strength, does not allow pore size in the bulk to increase in this material, thereby showing higher strengths compared to pure HAp and Al_2O_3-HAp composites sintered at lower temperatures.

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