In vitro comparative study between Alkali Heat Treated and Bio-glass coated on 3D printed Ti-6Al-4V

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ABSTRACT

The present study carries out AHT of 3D printed Ti-6Al-4V samples at two different temperature for Heat Treatment. Soaking the samples in NaOH leads to formation of thin sodium titanium oxide layer which acts as the linking layer between the HA and the surface of Ti-6Al-4V. By increasing the concentration of NaOH the aim was to obtain a better linking layer of sodium titanium oxide which will help in better bonding between the HA and sample surface. After immersion in SBF at 60℃ for different time periods, it was found that the samples were coated with a layer of HA. The bioactive layer thus obtained was characterized by Scanning Electron Microscope (SEM) and X-ray Diffractometer (XRD). HA [$Ca_5(PO_4)_3(OH)$] is basically a form of calcium phosphate. Previous studies have found that HA is one of the best material for biological use due to good bioactivity and biocompatibility. But a major disadvantage lies in the application of HA. As HA it is a brittle material having less tensile strength and impact resistance. Thus, studies are being conducted to alter the strength and toughness of HA or find an alternative material that has increased load bearing capacity but at the same time is as biocompatible as HA. simultaneously in a separate procedure another set of samples were coated with layer of bioglass. Once the bioglass was obtained on the samples, SEM and XRD were conducted to obtain characterization of the bioglass coating.

1. INTRODUCTION

Ti-6Al-4V or Grade 5 Titanium is known as workhorse of the Titanium industry and of the total consumption of Titanium in the world, Ti-6Al-4V has a market share of nearly 50%. In this α-β alloy of Titanium, Aluminum and Vanadium function as phase stabilizers. Aluminum helps in strengthening and stabilizing α and at the same time reduces the density also. Vanadium increases the ductile β phase that allows hot-working. Ti-6Al-4V has stiffness same as that of the commercially pure titanium but is comparatively stronger. The properties of Ti-6Al-4V lie amidst that of steel and aluminium alloys. Ti-6Al-4V possess amazingly high strength-to-weight ratio and is fatigue, corrosion and temperature resistant. Initially, Ti-6Al-4V was used only for aerospace applications but with advancements in technology its application was found in other fields like biomedical, marine, sports etc. This led to an increase in demand of Grade 5 Titanium. Ti-6Al-4V can remain strong and unaltered upto a temperature of 380℃ and resists creep.

While producing this α-β alloy of Titanium a number of factors need to be kept in mind during processes like machining where the microstructure and material properties can undergo a change due to effect of heat and deformation occurring in the course of the process. Due to low thermal conductivity and high mechanical properties traditional machining of Ti-6Al-4V becomes a complicated procedure. Traditional manufacturing of Ti-6Al-4V uses bulk feedstock material and the forging, casting and rolling them followed by machining to get the required design. Like while machining Ti-6Al-4V the deformation causes innate challenges such as increase in tool wear, high stress on tool, undercut portions etc. So if machining is to be done for removing a large volume of material then it becomes a time taking and costly procedure because of machining conditions like low cutting rate and consumption of large amounts of cooling fluid. Quite often separate Ti-6Al-4V parts are joined together by welding methods like plasma arc, laser beam etc. Unfortunately carrying out welding operation to get intricate and functional Ti-6Al-4V parts is a complicated, expensive process and in order to achieve the results it needs to be done with extreme care. Another problem with traditionally produced Grade 5 Titanium is that like most of the other α-β alloy, Ti-6Al-4V also doesn't have good quenchability. But for alloys it is desirable to have quenchability. Ti-6Al-4V is susceptible to strain hardening and is highly reactive to Oxygen. Because of all the mentioned difficulties occurring in producing Ti-6Al-4V using traditional methods nowadays most of the Ti-6Al-4V components are produced by Additive Layer Manufacturing (ALM) or 3D Printing as it is more commonly known as. The Ti-6Al-4V parts produced by ALM possess properties similar to or superior than the traditionally produced parts. Using ALM leads to a decrease in the waste produced while manufacturing along with removing the need to carrying out any welding operation because any required design can be directly 3D printed. Ti-6Al-4V produced by ALM have better quenchability and allow heat treatments to be carried out successfully. Three Additive Manufacturing (AM) techniques being widely used are Directed Energy Deposition (DED), Selective Laser Melting (SLM) and Electron Beam Melting (EBM). The fine powder used for AM is composed of Titanium (85-92%), Aluminium (5.5-6.5%) and Vanadium (3.5-4.5%). Each layer is of 30 to 40 μm and the entire material is light weight but strong. 3D printed Ti-6Al-4V has a slightly rough surface and matte finish.

Ti-6Al-4V not only possess excellent mechanical properties but also has excellent biocompatibility which makes it the most sought after material for making biomedical equipment and implants. But Ti-6Al-4V is bioinert which doesn't allow the implants to have tissue bonding to the bone tissues. In order to have tissue bonding the biocompatibility of the Ti-6Al-4V implants needs to be increased and this can be done by carrying out surface modifications on the implants. For achieving surface modifications and thus increased bioactivity Alkali Heat Treatment (AHT) can be carried out. Also coating the implants by an inorganic material doesn't affect the mechanical properties of the substrate but at the same time leads to an increase in biocompatibility. Now when these implants come in contact with body fluids a layer of hydroxyapatite is formed on the surface of the implants which allows bone tissue bonding at the atomic level.

M. Todea et al [1] has aimed to study the structure and the effects of different types of surface treatments on the bioactivity of Selective Laser Melting (SLM) manufactured Ti-6Al-7Nb Titanium alloy. The samples underwent three types of treatment: Heat Treatment. Chemical Treatment and infusing with bioactive substance. Later the samples were soaked in Simulated Body Fluid (SBF) to check for apatite forming ability. X-Ray Diffraction (XRD), X-ray Photoelectron Microscopy (XPS) and Scanning Electron Microscope (SEM) was used for to characterize the samples.

Ramy A. Abdelrahim et al [2] conducted experiments on conventionally manufactured Ti-6Al-4V to analyze the effect of anodisation and AHT on the bioactivity of samples. 15 samples were taken initially and divided into 3 groups. First group contained the control samples and the other two groups contained samples undergoing anodisation and AHT respectively. For AHT the samples were dipped in 5M NaOH solution and then heat treatment was carried out at 600℃. The results showed that both anodisation and AHT samples showed apatite inducing ability due to the surface roughness obtained. Titanium oxide anatase was formed on the anodisation samples while titania hydrogel was obtained for AHT samples.

Ezgi Butev et al [3] investigated the bioactivity of Ti-6Al-7Nb alloy foam that had 70% porosity. The alloy was manufactured by space holder method and AHT was performed on it. When dipped in 5M NaOH solution, a homogenous coating of sodium of was formed because the pores on the sample allowed the alkali to reach deep inside the sample. Heat treatment was performed at 600℃. The apatite layer obtained was having flower like structure and the Ca/P ratio was close to that of human bone.

Nurul Hazwani Hanib et al [4] carried out surface characterization of Ti-6Al-4V ELI sample. Ti-6Al-4V ELI, or Grade 23, is the higher purity version of Ti-6Al-4V. It can be made into coils, strands, wires or flat wires. AHT was done by using two different alkali solution: 5M NaOH and 5M KOH. The heat treatment was done at 700℃ for 1 hour. Two sets of sample were taken into study. One set consisted of as received samples and the other set contained samples which were abraded with SiC paper before starting the alkali treatment. After conducting SEM, XRD and Surface roughness tests it was found that as received samples immersed in KOH showed better porous network which is beneficial for apatite growth.

Baek-Hee Lee et al [5] aimed to improve the bone-bonding ability of Titanium alloy implants. A comparison has been done between Ti-6Al-4V ELI alloy and a new alloy Ti-In-Nb-Ta to check for apatite forming ability. For improving the biacivity two types of surface treatment were carried out, AHT and simple thermal treatment. It was found that among the two alloys Ti-In-Nb-Ta showed better bioactivity and AHT was preferable than only thermal treatment.

Chin-Fen Lu et al [6] have aimed at understanding the effect of atmosphere, in which heat treatment is carried out during AHT process, on the apatite forming ability of AHT Ti-6Al-4V samples. For the experiment all the samples were immersed in 5M NaOH at 60℃ for 24hr. Now for carrying out heat treatment two groups were made. One was heat treated under atmospheric condition (1 atm) whie the other group was heat treated at vaccum (0.921 atm). After soaking in SBF for 5 days and then doing SEM, EDX and XRD analysis showed that the samples heat treated under atmospheric condition showed better apatite growth as compared to vaccum treated samples.

Hyun-Min Kim et al [7] have carried out experiments to study the bioactivity of different Titanium alloys. They are Ti-6Al-4V, Ti-6Al-2Nb-Ta and Ti-15Mo-5Zr-3Al. Along with them 2 other alloys, SUS316L and Co-Cr-Mo were also tested. Here the samples were immersed in 10M NaOH at 60℃ for 24hr. and then they were soaked in SBF for 4 weeks. Results showed that all of the Titanium alloys formed sodium titanate hydrogel after NaOH treatment and subsequent soaking in SBF resulted in apatite formation. On the other hand, none of the non-titanium alloys formed sodium hydrogel and thus apatite after SBF soaking. This showed that only Titanium alloys have apatite inducement capability upon carrying out required surface treatment.

Mustafa Kamal et al [8] have reviewed the different surface modifications applied on the Titanium metal implants. The aim of the X-ray study carried out here was to correlate the properties of AHT Titanium implants and the bone so that these implants can be used effectively as dental implants. Variation was done among the samples by changing the time period for which the samples were soaked in 5M NaOH at 60℃. Then the heat treatment was done at three different temperature of 800℃, 882℃ and 900℃. Tests were conducted for structural analysis (phase identification, crystal size etc.), mechanical properties (elastic moduli, hardness etc.), pH value etc. Results indicated that the pH of SBF increased after the samples were dipped inside it. This was mainly due to the movement of ions between the Titanium samples and SBF solution. Increasd corrosion resistance was seen in samples that were immersed in NaOH for 4 days than those immersed for 2 days. Finally it was found that heat treatment at 800℃ was better than at 600℃.

Feng-Huei Lin et al [9] have aimed at analyzing the rate of hydroxyapatite (HA) formation on AHT Ti-6Al-4V sample when soaked in concentrated SBF at high temperatures. Concentrated SBF was made by increasing the concentration of calcium and phosphorous ions in SBF. The concentration of Ca^{2+} was increased from 2.5 mM to 3.75 mM. Two different set of samples were soaked in 5 mL of 10M NaOH at 60℃ and 80℃ respectively. All the samples were heat treated at 600℃ only. The results of SEM and XRD showed presence of HA layer on all the set of samples but samples soaked in concentrated SBF at 80℃ showed the formation of HA layer having maximum thickness of around 50 μm.

N.A. Zarifah et al [10] have aimed at analyzing the mechanical and structural characteristics of hydroxyapatite (HA) when mixed with 45S5 bioglass having different composition. Sintering temperatures were also changed for different groups of samples. The Sample Glass (SG) had the following chemical compositions: SiO_2 (45%), $CaCO_3$ (24.5%), Na_2CO_3 (24.5%) and P_2O_5 (6%). Different set of HA samples were reinforced with 20%, 40%, 60% and 80% of the prepared SG respectively. The results obtained showed that due to addition of SG into HA the density of the samples decreased. This can be due to the trapping of air in the HA sample which was reinforced with SG. On comparing the reinforced samples of HA to pure HA samples, it was found that the reinforced samples had various crystalline phases like calcium phosphate silicate, sodium calcium phosphate etc.

The present study carries out AHT of 3D printed Ti-6Al-4V samples at two different temperature for Heat Treatment. For soaking the samples 15M NaOH was taken. Soaking the samples in NaOH leads to formation of thin sodium titanium oxide layer which acts as the linking layer between the HA and the surface of Ti-6Al-4V. By increasing the concentration of NaOH the aim was to obtain a better linking layer of sodium titanium oxide which will help in better bonding between the HA and sample surface. After immersion in SBF at 60℃ for different time periods, it was found that the samples were coated with a layer of HA. The bioactive layer thus obtained was characterized by Scanning Electron Microscope (SEM) and X-ray Diffractometer (XRD).

HA [$Ca_5(PO_4)_3(OH)$] is basically a form of calcium phosphate. Previous studies have found that HA is one of the best material for biological use due to good bioactivity and biocompatibility. HA has found great application for bone repair scaffold. But a major disadvantage lies in the application of HA. As HA it is a brittle material having less tensile strength and impact resistance when compared to natural bone, its cannot be used where the material need to have significant load bearing properties. Thus, studies are being conducted to alter the strength and toughness of HA or find an alternative material that has increased load bearing capacity but at the same time is as biocompatible as HA.

So, simultaneously in a separate procedure another set of samples were coated with layer of bioglass. Once the bioglass was obtained on the samples, SEM and XRD were conducted to obtain characterization of the bioglass coating. Comparison was drawn between the two set of samples, one coated with HA and the other coated with bioglass.

2. MATERIALS AND METHODS

a. Specimen and Surface Preparation for AHT

In the study six samples of Ti-6Al-4V plates (7mm x 7mm x 1mm) were taken and three groups were made having two samples each. Group A consisted of as received 3D printed samples. Group B and Group C samples were mechanically polished using emery paper. After that samples of all the three groups were washed in acetone in an ultrasonic sonicator bath. Then they were washed in distilled water and dried. All the three groups of samples were then soaked in 5mL of 15 M NaOH aqueous solution at 80℃ for 24 hr. After 24 hr. the samples were taken out and washed in distilled water and then dried in oven at 40℃ for a day. Now, the heat treatment was performed in an electric furnace at a rate of 5℃/min. in an Argon atmosphere where the samples were held at the required temperature (different for all 3 groups) for 1 hr. and then cooled to room temperature in the furnace [3]. For group A the hold temperature was kept at 800℃ [8], for group B it was at 600℃ and for group C it was again at 800℃.

b. Specimen and Surface Preparation for Bioglass coating

Initially the precursor solution of bioglass was made. The composition was 60% Si, 34% Ca and 6% P. Two Ti-6Al-4V plates (7mm x 7mm x 1mm) were taken and mechanically polished using grit paper. They were also soaked in 5mL of 15 M NaOH aqueous solution at 80℃ for 24 hr. Now, they were dipped in the precursor solution for 48 hrs. Then the samples were kept in an eppendorf tube and placed in a hot air oven at 60℃ for 3 days so that gelation can take place. After 3 days the temperature was increased to 120℃ and the samples were kept at this temperature for 2 days. After taking out these samples they were heat treated at 600℃ for 1hr. in an electric furnace at a rate of 5℃/min in air atmosphere.

c. Soaking in Simulated Body Fluid (SBF)

Simulated Body Fluid (SBF) have ionic concentration close to that of human blood plasma. The AHT samples (all three groups) were immersed in SBF for a duration of 7 days and 14 days at a temperature of 80℃. Characterization was done first after 7 days and then after 14 days to compare the apatite formation at these intervals.

d. Analysis of the surface

The surface of the samples was analyzed by X-ray diffractometer (XRD). For the XRD Cu Kα radiation was used having a wavelength of 0.154 nm and the operating condition was set at 40kV and 30mA. The scan rate was kept at 1 $^\circ$ min^{-1} and the 2θ range was kept from 10 ˚ to 90˚. In order to conduct morphological study Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS) was used.

3. RESULTS

a. Alkali Heat Treated Group

XRD Pattern of Ti-6Al-4V sample treated with 15M NaOH at 80℃ for 24 hr. is shown in Fig. 1(a). From the XRD pattern it can be seen that along with presence of Titanium α phase, small peaks of rutile (TiO_2) were also detected. These peaks indicate that Titanium was further oxidized and thus formed oxide layer having a rutile structure. Fig. 1(b) and 1(c) shows the XRD pattern for the samples that were heat treated at 600℃ and 800℃ respectively. From the XRD results it can be clearly seen that presence of sodium titanate ($Na_2Ti_6O_{13}$) was detected in both the cases. Presence of rutile was also found in these samples which is due to the fact that rutile dissolves partially when the samples are dipped in NaOH solution. But the samples that were heat treated at 800℃ showed larger amount of sodium titanate ($Na_2Ti_3O_7$) and lower amount of rutile as compared to the sample heat treated at 600℃. Fig. 1(d) shows XRD of samples that were heat treated at 800℃ and then dipped in SBF for 7 days. The XRD pattern showed peaks at 32˚, 45˚ and 54˚ which are characteristic peaks for hydroxyapatite. Thus the formation of HA was found in the samples that were dipped in SBF after heat treatment.

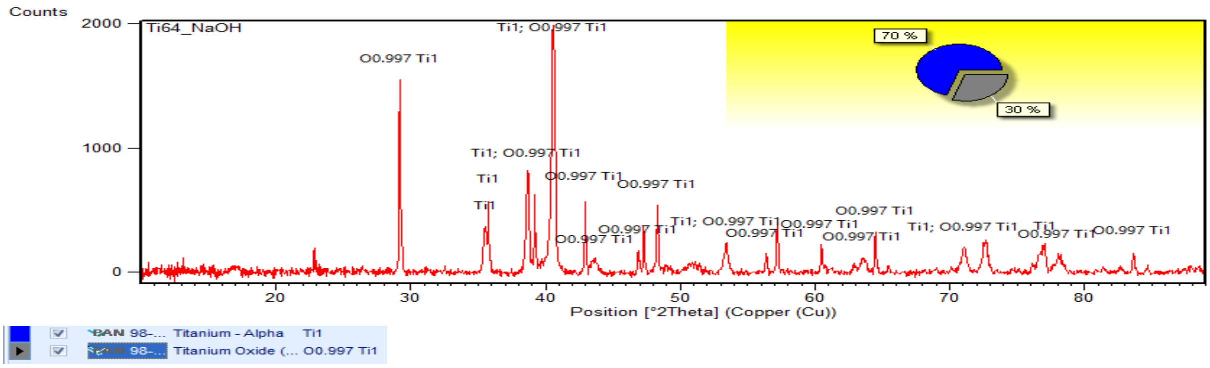

Figure 1(a). Ti-6Al-4V NaOH treated only

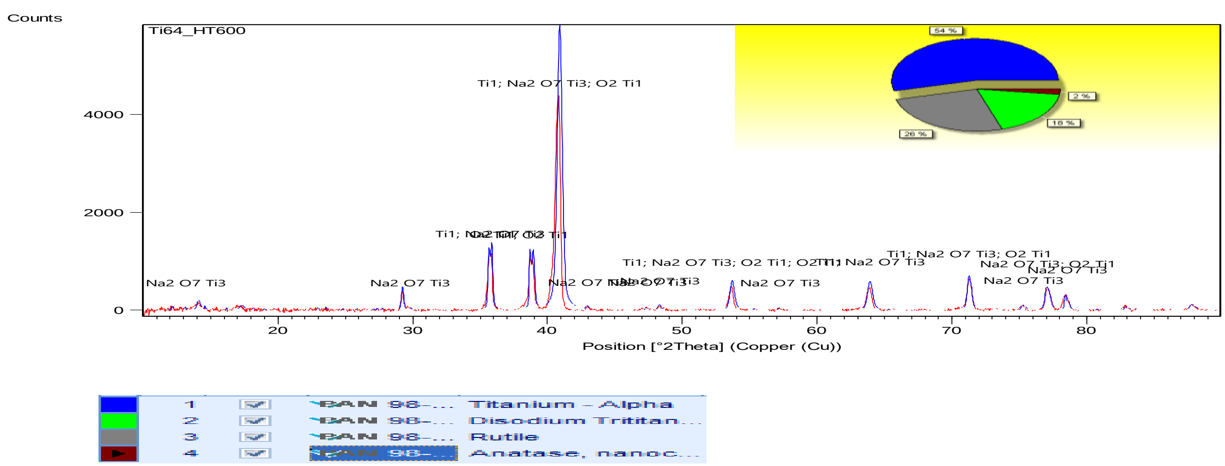

Figure 1(b). Ti-6Al-4V heat treated at 600℃ after NaOH treatment

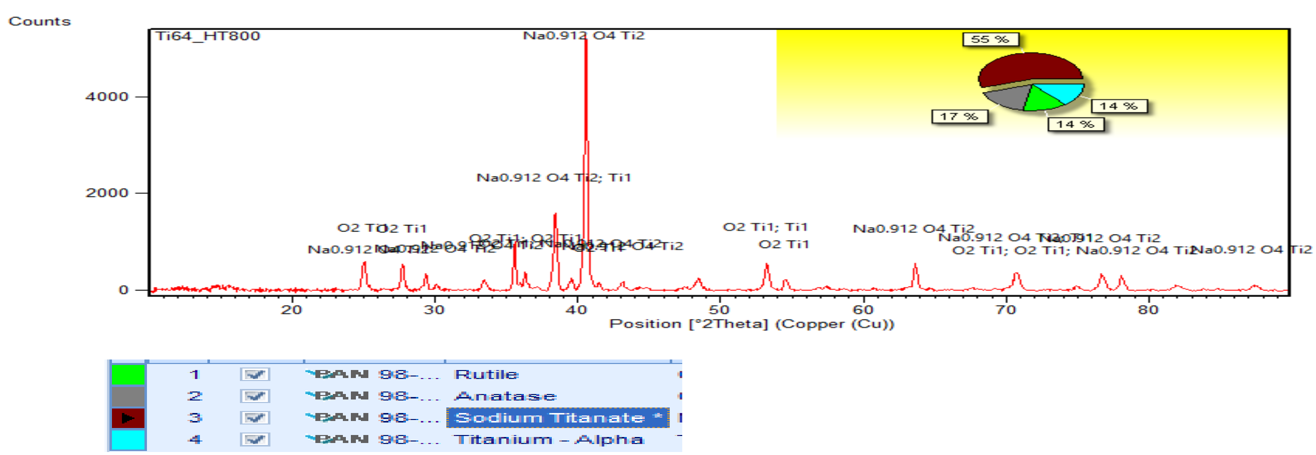

Figure 1(c). Ti-6Al-4V heat treated at 800℃ after NaOH treatment

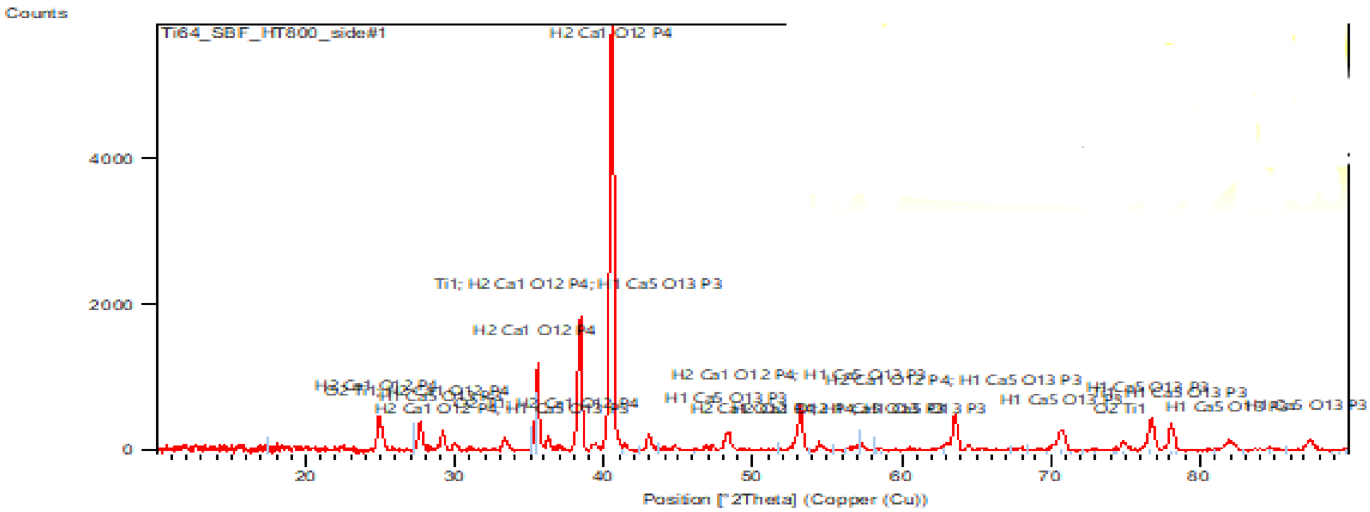

Figure 1(d). Ti-6Al-4V heat treated at 800℃ and then immersed in SBF for 7 days at 60℃

SEM and EDS analysis was conducted for the samples. Fig.2 (a) and 2(b) shows the SEM image of sample heat treated at 800℃ and then immersed in SBF at 60℃ for 7 days and 20 days respectively. SEM images showed the presence of coating over the surface of samples and it was seen that for the samples dipped in SBF for 20 days showed a more dense coating than the sample dipped for 7 days.

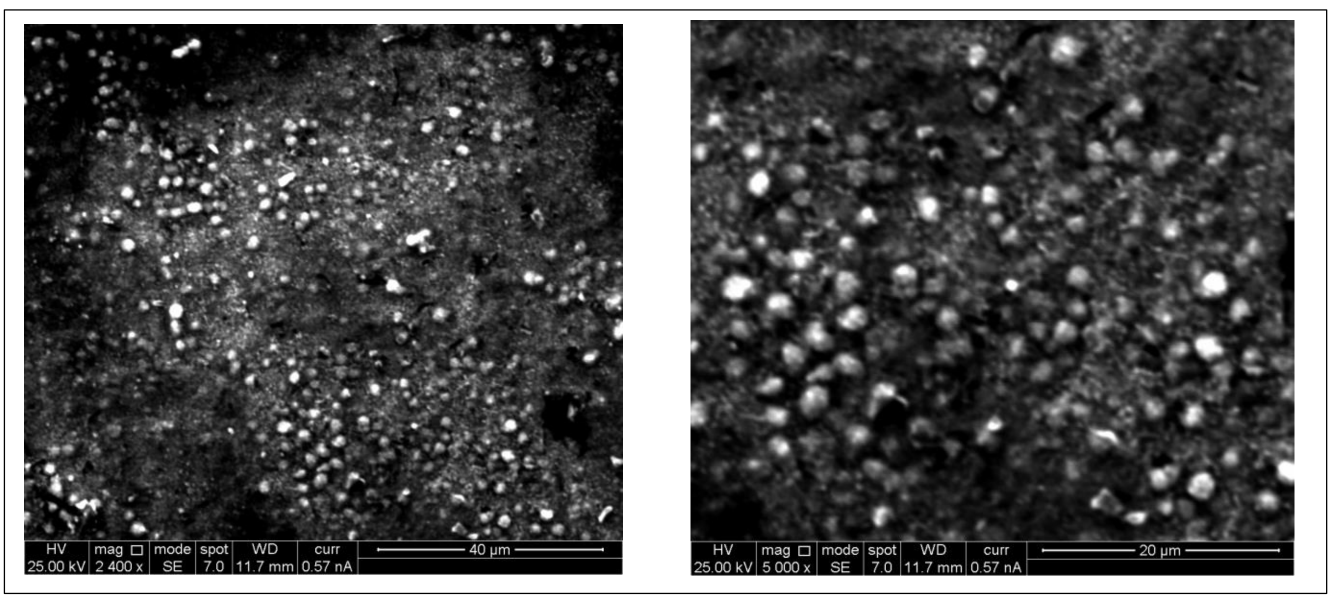

Figure 2(a). SEM of Ti-6Al-4V heat treated at 800℃ and immersed in SBF for 7 days at 60℃

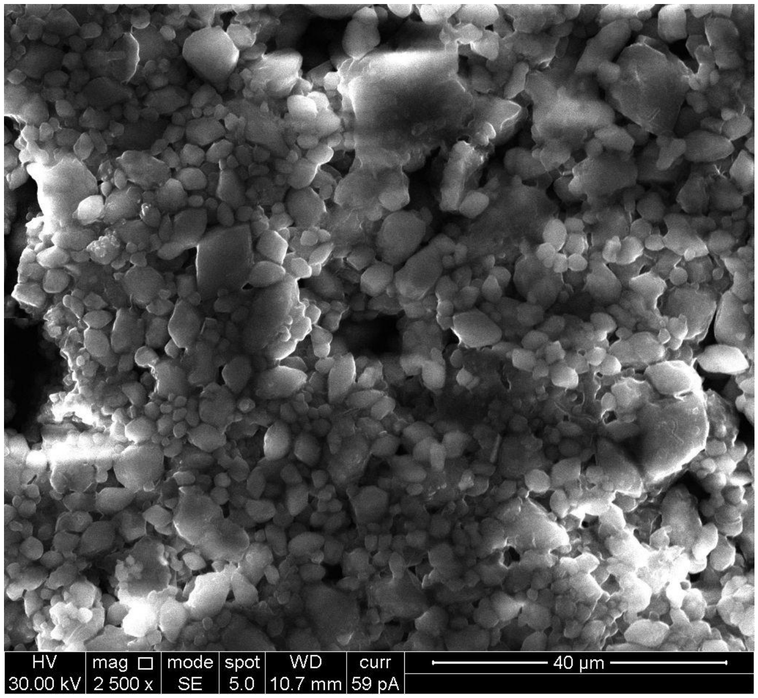

Figure 2(b). SEM of Ti-6Al-4V heat treated at 800℃ and immersed in SBF for 20 days at 60

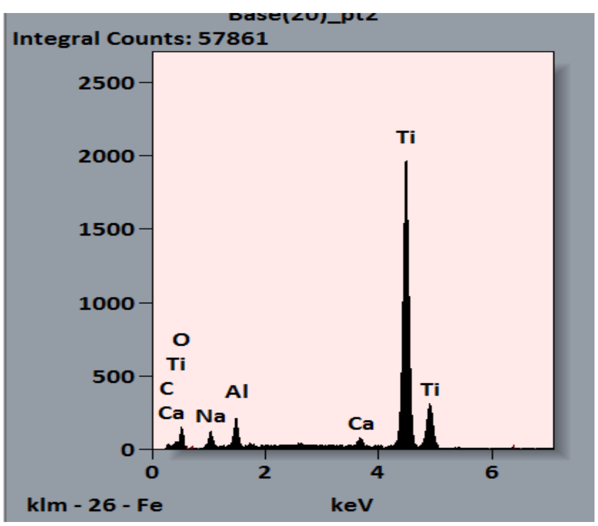

Figure 2(c). EDS of Ti-6Al-4V heat treated at 800℃ and immersed in SBF for 7 days at 60℃

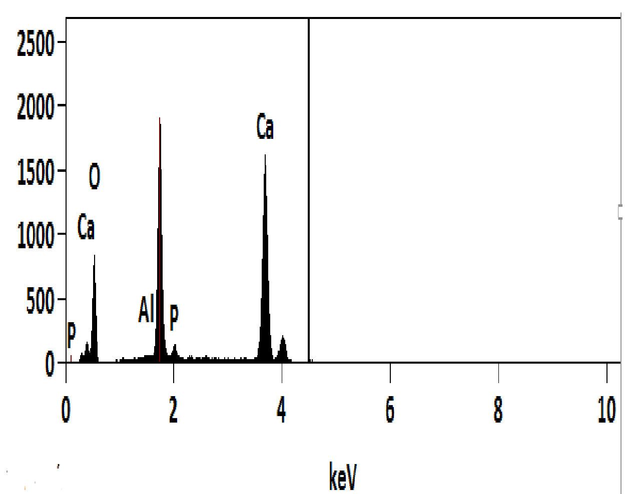

Figure 2(d). EDS of Ti-6Al-4V heat treated at 800℃ and immersed in SBF for 20 days at 60℃

Fig. 2(c) and 2(d) show the EDS spectrum of the samples dipped in SBF, after 800℃ heat treatment, for 7 days and 20 days respectively. In both the spectrum we can find presence of calcium showing the formation of HA on the samples.

b. Bioglass coated Group

In Fig. 3(a), XRD of sample on which the bioglass precursor solution was dropped can be seen. In Fig. 3(b) and 3(c) the sample which were dipped in the precursor solution is shown. The sample in Fig. 3(b) was not soaked in NaOH before dipping in bioglass precursor solution.

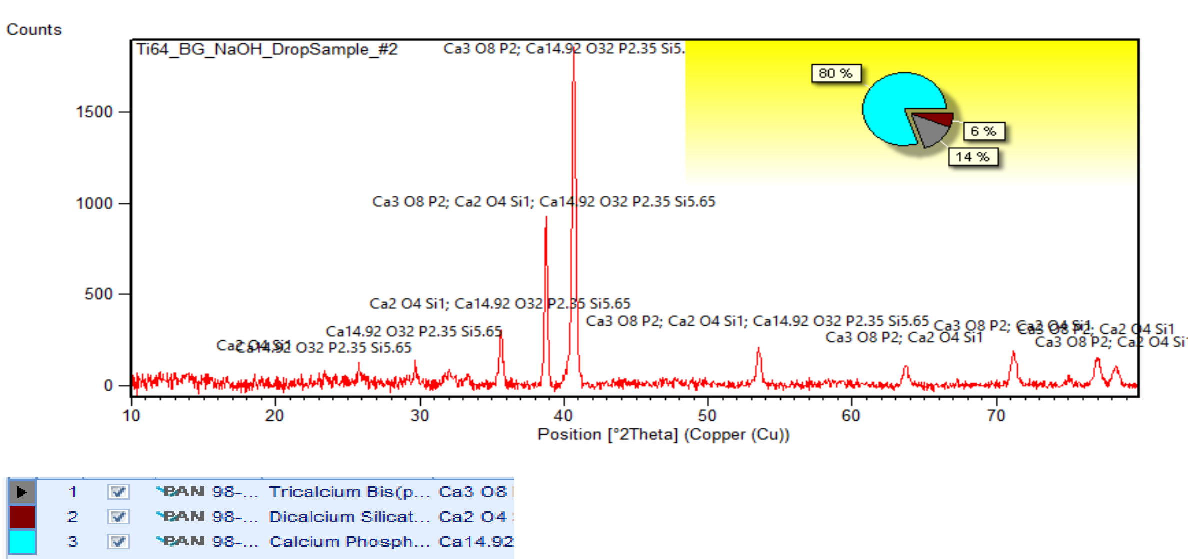

Figure 3(a). Ti-6Al-4V DROP sample (NaOH treated)

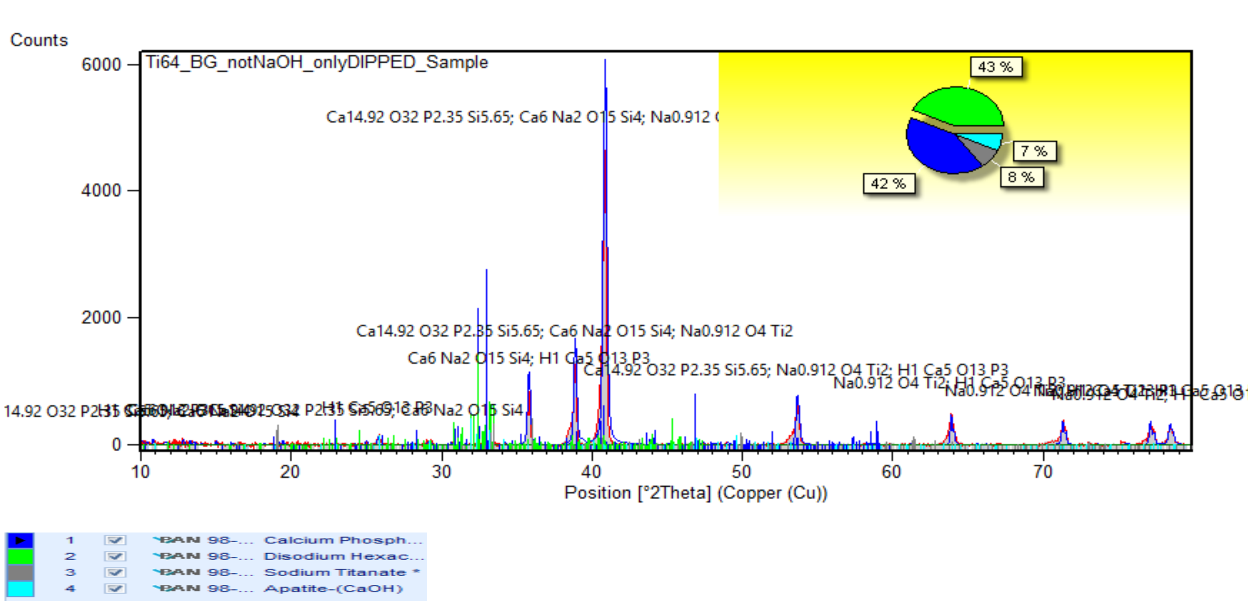

Figure 3(b). Ti-6Al-4V DIPPED sample (Not NaOH treated)

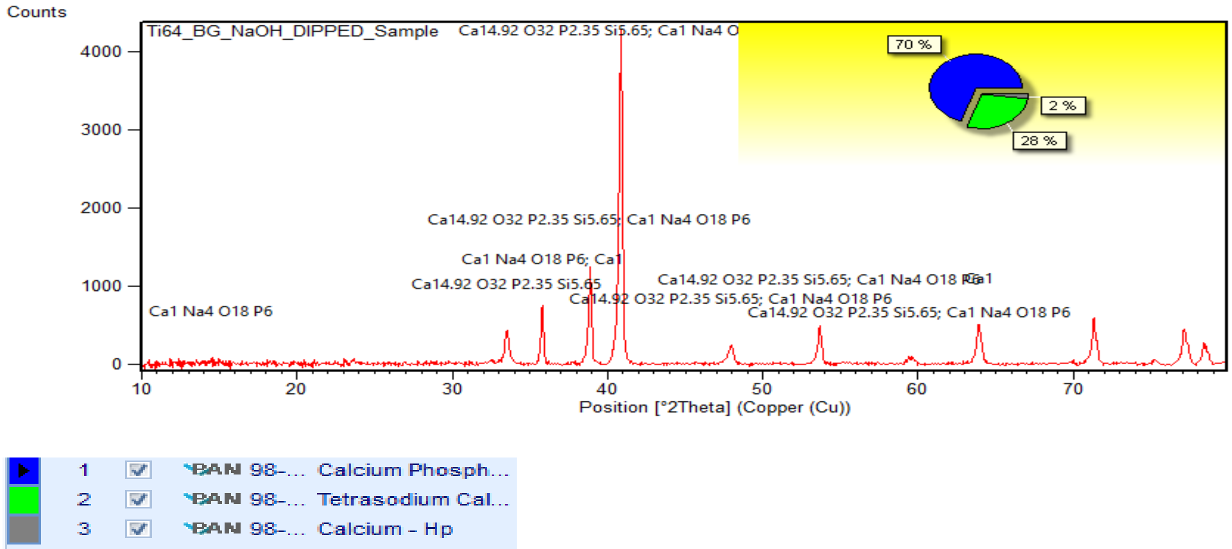

Figure 3(c). Ti-6Al-4V DIPPED sample (NaOH treated)

SEM images of the Bioglass samples are shown in Fig. 4(a), 4(b) and 4(c). Fig. 4(a) contains the sample on which the bioglass precursor solution was dropped. Fig. 4(b) and 4(c) show the sample which were dipped in the precursor solution is shown and Fig. 4(b) has the sample that was not soaked in NaOH before dipping in precursor solution.

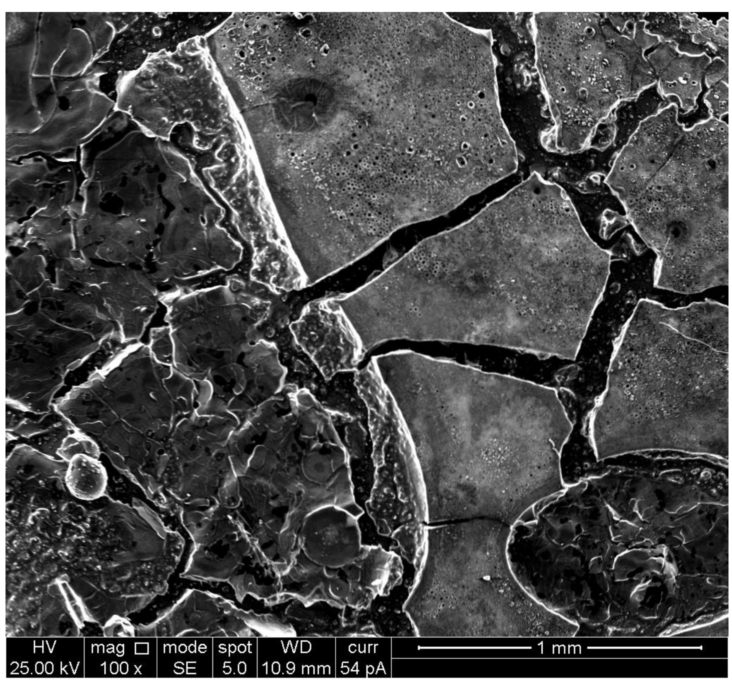

Figure 4(a). Ti-6Al-4V DROP sample (NaOH treated)

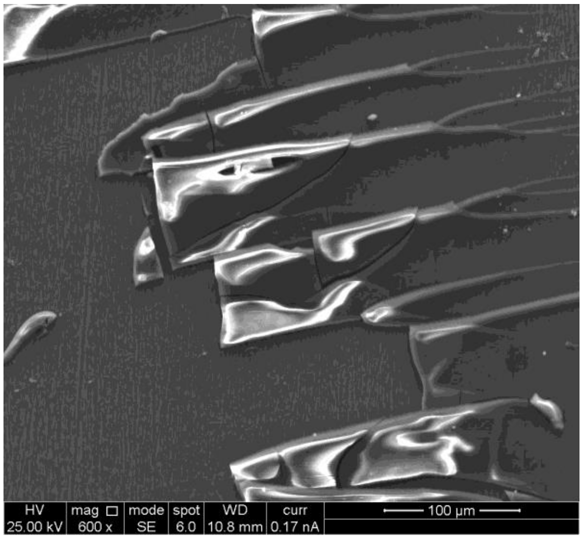

Figure 4(b). Ti-6Al-4V DIPPED sample (Not NaOH treated)

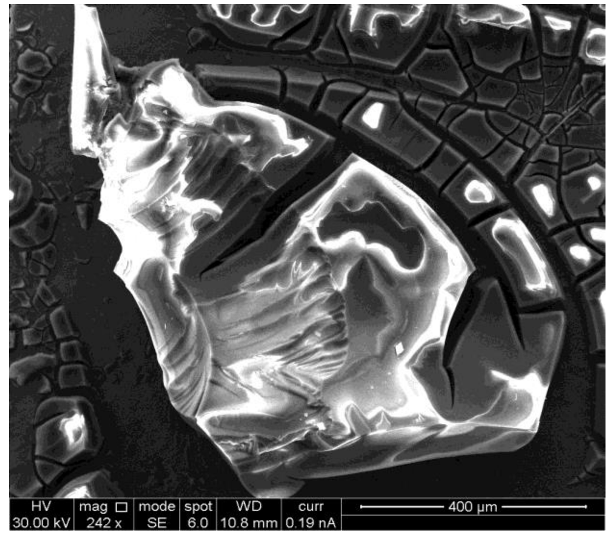

Figure 4(c). Ti-6Al-4V DIPPED sample (NaOH treated)

4. CONCLUSION

From the results obtained in XRD and SEM it can be seen that the samples that were heat treated at 800˚C and then dipped for 20 days in SBF showed maximum growth of HA on their surface. The SEM images showed presence of flowery shaped circular crystals of HA over the surface. The crystal were more clear and visible compared to the samples heat treated at 600˚C. Also the EDS spectrums showed presence of higher amount of calcium in the samples that wee heat treated at 800˚C and then dipped for 20 days in SBF. For the Bioglass samples a significant and uniform coating was obtained for samples that were soaked in NaOH and then dipped in the precursor solution.

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