Study of Titanium (ti-6al-4v) and Stainless Steel (316l) Coated with Hydroxyapatite – Nano alumina by PLD Method for Biomedical Applications

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Abstract

This paper reports on the corrosion behavior of HAp + Al_2O_3 nanoparticles coated on Ti-6Al-4V and 316L for orthopedic implant alloy. An adherent thin coating was obtained by Pulsed Laser Deposition (PLD) method. PLD has emerged as an acceptable technique to coat hydroxyapatite and nano-alumina on Ti6Al4V and 316L based permanent implant for the use of orthopedic and dentistry application. It requires the substrate temperature higher than 400°C to form coating of good adhesion and crystallinity, sintered at 850°C. At this range of temperature the mechanical properties of the implant may affected, so the substrate temperature is lowered in order to get the long term performance of the implant. The microstructure of the coated metal is characterized by XRD, SEM analysis. The corrosion behavior of the samples was tested in Simulated Body Fluid (SBF-Hank's solution) using a potentiodynamic polarization studies. Thus the sintered coating implant exhibit higher adhesion, lower porosity and higher corrosion resistance and that is analyzed by using the characterization of SEM, FTIR analysis.

Keywords: Hydroxyapatite, Nano-Alumina, Pulsed Laser Deposition, Titanium alloy, Stainless steel.

1. INTRODUCTION

Nowadays Titanium (Ti-6Al-4V) and stainless steel (316L) are widely used for biomedical implants such as orthopedic and dentistry application. According to the coating thickness the corrosion behavior may vary. Corrosion is defined as an electrochemical process in which a solid metal interacts with its chemical environment which leads to a loss of substance from the materials (e.g., alloy implant) as well as a change in its structural characteristics. During corrosion, alloy release elements into the body over a period of days to months. Corrosion is a concern, particularly when a metallic implant is placed in the hostile electrolytic environment provided by human body. Biocompatibility has been defined as the state of mutual coexistence between the biomaterials and the biological environment such that neither has an undesirable effect on the other (Nikita Zaveri et al. 2010) .An accepted method for providing bioactive surface for titanium alloy and stainless steel is to coat with hydroxyapatite (Hap) and nano-alumina (Al_2O_3) . In this, synthesis ofhydroxyap-atite and nano-alumina by sol-gel method. The characterization of the synthesized nano particle were done by using XRD, SEM. These characterization has- to be done to confirm the synthesized particle is hydroxyapatite and nano-alumina. Plasma spray is the only available method to coat hydroxyapatite on implant metal, hence it has some drawbacks like poor adherence. In past decade, pulsed laser deposition (PLD) technique emerged as a promising alternative for coating titanium and stainless steel implant with hydroxyapatite (Bao et al 2005; Koch et al 2007; Nelea et al 2007) and Nano-alumina. The deposition process in PLD demands a minimum level of substrate temperature for obtaining phase-pure hydroxyapatite. Though calcium phosphate in general are biocompactable, crystalline hydroxyapatite is preferred for in-vivo stability(Koch et al 2007; Nelea et al 2007).In this technique, a dense hydroxyapatite target is ablated by an intense pulsed laser(with wavelength of 355nm or lower)and the substrate metal is kept in front of the radiating plasma plume to acquire the ablated material over its surface and it has more versality and controllability as opposed to plasma spray and other techniques (Manojkomath et al 2011) .It is well known that a thermal treatment of titanium metal will lead to the absorption of hydrogen,carbon ,oxygen and nitrogen from the surrounding atmosphere(Davis 2006).The small atoms enter into the metal lattice interstitially and inhibit deformation ,thereby causing substantial loss in ductility .The hydrogen embrittlement seems to be most detrimental(Manojkomath et al 2011).It is clear that the processing temperature, applied in the PLD processing to obtain the good hydroxyapatite coatings , are likely to affect the bulk mechanical properties of titanium metal and this in turn will reflect adversely in the long term performance of a permanent implant ,this results the effect may be drastic in the case of endosseous implant and joint prostheses which undergoheavy and dynamic loading (Manojkomath et al 2011) .The advantages of PLD technique is the ability to deposit uniform, pure, crystalline and stoichiometric hydroxyapatite films (Mihailescu et al 2005) . However hydoxyapatite itself has some disadvantages like low melting point may lead to loosening and failure of the implant. So only it's being coated with Nano-alumina to increase the adherence of the implant. The major advantages associated with nano-hydroxyapatite and nano alumina are

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similar to tha t of inorganic molecules of the human bone. Here both the synthesized nano particles are coated on Titanium (Ti-6Al-4V) and stainless steel (316L).The coated implant metal is being tested with Hank's solution in order to test the corrosion property of the coated implants. The characterization of XRD and SEM were used to determine the thin layer of Hap and Al_2O_3 on titanium and stainless steel alloy of implant for biomedical application. The present paper describes a Pulsed Laser Deposition (PLD) based method of coating (HaP+Al_2O_3) on titanium alloy and stainless steel metal in order to increase the crystalline and adhesion property in order to enhance the long-term life of the orthopedic implant.

2. MATERIALS AND METHOSDS

2.1 Preparation of Nano-Hydroxyapatite (Hap)

Calcium chloride and aluminium phosphate should be taken at the rate of 4.72g and 8.825g. Add 15ml of ethanol with calcium chloride and 30ml of ethanol with aluminium phosphate. Magnetic stirrer was used to dissolve both the powder separately in ethanol and the stirrer should be rotated at 80rpm for 5-7mins and after that the stirred solutions of calcium chloride and aluminium phosphate is mixed together in a beaker and allowed to get stirred completely for 24hours. Now the well stirred solution were taken into the hot-air over and dried into powder under 70^o for 18hours.Then grind the powdered particle into fine particles by using mortar and pestle.

2.2 Preparation of Nano-Alumina (Al_2O_3)

Nano-Alumina was prepared by using a sol-gel method. According to the molarity ratios, Aluminium Chloride and AluminiumIsopropoxide are taken in the ratios of 0.1g and 0.2g.Add 15ml of ethanol to both the precursor. Magnetic stirrer can be used to dissolve both the precursor finely in the solution. Add 1-3 drops of ammonia to aluminium chloride and is allowed to be kept in room temperature for 30hrs in order to get the gel precipitate and aluminiumisopropoxide should be kept in the stirrer for 18hrs.Now the gel precipitate is allowed to dry in hot-air oven at 70^o,similarly the dried solution of aluminiumisopropoxide also kept for drying under in hot-air oven at 70^o. The dried powder particles of both the precursor should be grinded together in mortar and pestle.

2.3 Pellet Formation and Sintering of Substrate

After the characterization of the Hydroxyapatite and Nano-alumina powder is brought into pellet formation. The pellet of the substrate should be formed by using hydraulic pressing.

The pellet form of Hydroxyapatite should be sintered at 850^o for 72hrs and the Nano-alumina should be sintered at 900^o for 48hrs.Sintering process can be done in order to increase the mechanical strength of the substrate while handling.

2.4 Coated by Pulsed Laser Deposition (PLD) Method

The wide application of thin films Coating in newest technologies has revealed the developing simple methods of obtaining large area of thin films. One of these methods is provided by pulsed laser deposition (PLD). PLD technique is widely used to coat the substrate over the metal.

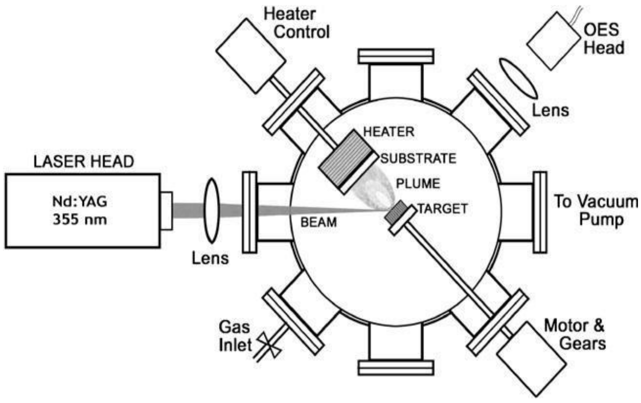


Fig 1 Schematic of deposition

A Nd:YAG with the wavelength of 325 nm and the pulse duration of 3 ns at the rate of 7Hz is used as frequency used for coating.In this the metal is coated under the pressure of 300pascal.The vacuum inside the chamber should be maintained at 99.99% of argon atmosphere. The target for this coating is Titanium (Ti6Al4V) and Stainless steel(316S) and the substrate to be coated is hydroxyapatite and nano-alumina. The substrate was kept at 350^o C before deposition. The laser beam was focused on the target at the incidence angle of 45^o and the target should be rotated for the entire process until it gets to be uniformly coated by the substrate.The vacuum in the chamber was maintained by using the turbo molecular pump. The temperature of the substrate should be maintained at 470^oC-540^oC and the distance of target-substrate is about 20-25mm.The coating process can be done until the fine thin layer of surface over the metal was obtained during the deposition process. Fig 1 Schematic of deposition (Manojkomath et al 2011).

2.5 Testing of Coated Implant by using Hank's Solution

The corrosion behavior of Hydroxyapatite and Nano-Alumina nanoparticle coated on thebioimplantTi-6Al-4V and 316L exposed to hank's solution test. The simulated physiological solution was prepared by adding 8g/L of Nacl,0.14g/L of $CaCl_2$,0.4g/L of KCl,0.35g/L of $NaHCO_3$,1 g/L of Glucose,0.1 g/L of NaH2PO4, 0.1 g/L of MgCl2, 0.06 g/L of Na_2HPO_4 and 0.06 g/L of $MgSO_4$ to 1litres of distilled water (Sathiyanarayanan et al. 2002).Both the coated implant is allowed to dip in the solution for 7-9days. The characterization of the dipped metal should be taken in the periodic interval of time.

3. RESULTS

3.1 XRD Analysis

Phases of the materials in the synthesis were analysed using X-ray diffraction (XRD-Rigaku Dmax model) with radiation(1.267 A^{O}).The phase formed in the nano HAp and nano Alumina were investigated by using XRD analysis and illustrated in the (figure 2,3). The XRD pattern of the synthesized nano HAp powder was compared with (Stoica T et al 2008) which conformed the presence of the hydroxyapatite. In this the presence of calcium phosphate mimic the human bone composition. The XRD analysis of the nano Al_2O3 also confirmed that the presence of alumina is also confirmed .The sharp and clear reflection corresponding to nano-alumina confirm the phase purity and high crystallinity. Hence both the nano particle composite coating contribute to the increase of interfacial bonding strength and high adherence.

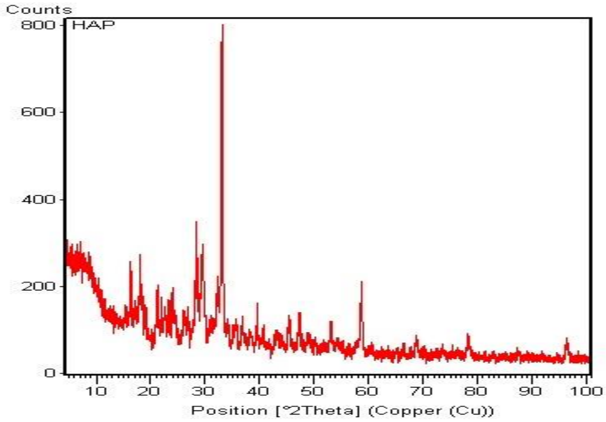


Fig 2 XRD patterns of Hydroxyapatite (HAp)

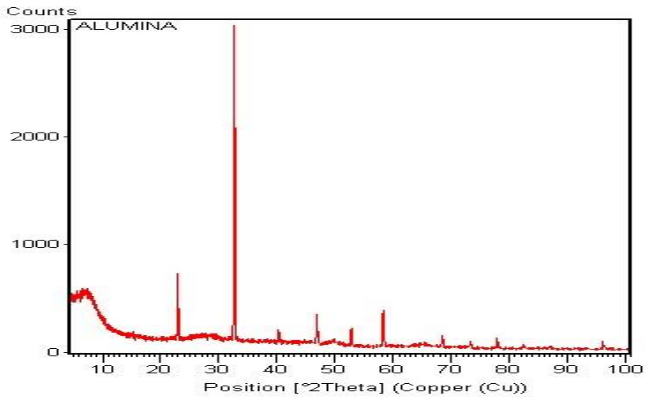


Fig 3 XRD patterns of Nano-Alumina (Al_2O_3)

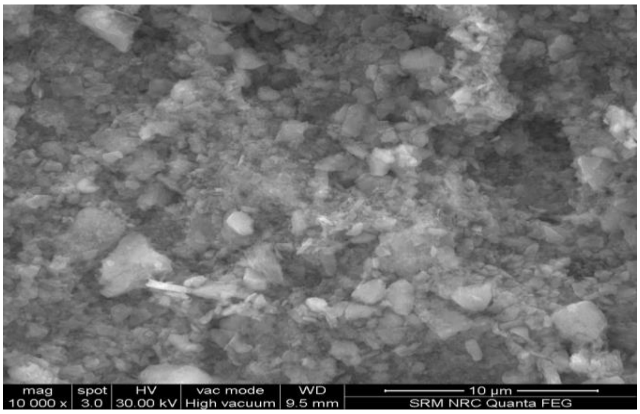
3.2 SEM Analysis of the Coated Implant

Scanning electron microscopy of the samples were taken in low vacuum mode. The SEM result demonstrated that the surface was coated uniformly by using Pulsed Laser Deposition (PLD). SEM results describes that the surface of the coated materials. The surface of the coated implant metal is only analyzed by the morphological characterization. SEM analysis only reveals the coating levels of the substrate on implant alloy.

3.3 FTIR Analysis of the Coated Implant

The FTIR results shows that the as-deposited coating is composed of the Aluminium chloride and calcium phosphate. The infrared absorption spectrum of the as-deposited on the implant contains the major peak represents the coated category of the substrate on the implant. The FTIR spectrum of the samples in the wave number range of 3800-200 cm^{-1} which covers the bending and stretching regions of the aluminium chloride and calcium chloride. The inset contains part of the spectrum in the wave number range (2200-1800 cm^{-1}),this region helps to conform the characteristic of the aluminium isopropoxide specifically and reports that the traces of the aluminium phosphate in the implant.The bands corresponding to the aluminium chloride (2800-2400 cm^{-1}), aluminium isopropoxide (2200-1800 cm^{-1}), calcium chloride(1400-1200 cm^{-1}) and aluminium phosphate(1000-600 cm^{-1}).Thus the FTIR results reports that the peak of the particles conforms the presence of the substrate.

Fig 4 SEM images of the surface morphology of Coated and tested



Titanium (Ti-6Al-4V)

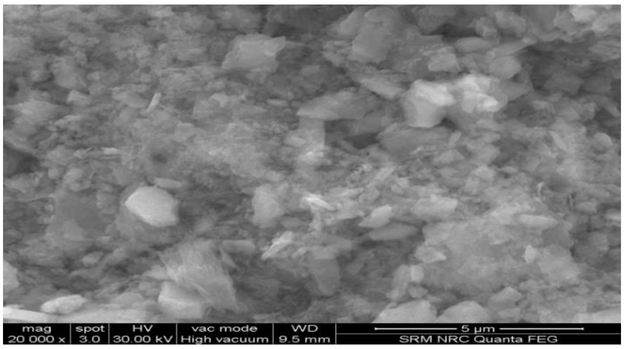


Fig 5 SEM images of the surface morphology of Coated and tested Stainless steel (316L)

The coated materials were HAp and Al_2O_3 on titanium alloy(Ti-6Al-4V) and stainless steel (316L) were shown in the figure(3,4) .In this coated titanium analysis implies that dense coating of the substrate on the metal and in stainless steel it is coated as a primarily smoothern. SEM analysis of the coated implants are highly smooth surface and uniformly phased, so it has been proven that it can be beneficial for mechanical anchoring of the human bone. The calcium phosphate present in the HAp has same properties of the human bone.

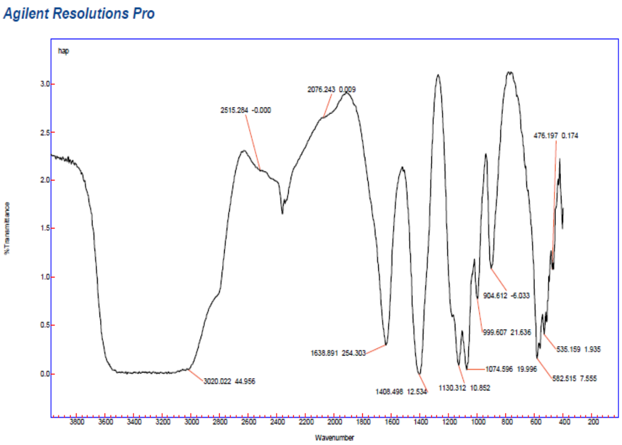


Fig 6 FTIR analysis of coated implant

4. DISCUSSION

The present experiment is an attempt to deposit alumina and hydroxyapatite stainless steel and titanium substrate through the pulsed laser deposition at a temperature of 400^oC. We are using this technique because of the uniform thin coating of the substrate on the metal. We may also use the spray coating and spin coating, but there are many disadvantages of this techniques. The main disadvantages of this technique is the substrate is sprinkled and not uniformly coated .The formation of the amorphous calcium chloride could be anticipated as the chamber environment and the substrate temperature should be favor for the coating. Thus the deposited material is found slightly porous formation and hence we have to increase the temperature of the coating .The XRD results of the HaP and nano alumina implies that the synthesized nano particles are reflects the same characteristics. Thus the coating process can be done by pulsed laser deposition and it is been followed by testing with the hank's solution. The hank's solution is similar to the properties of the human blood and the coated implant should be dipped on the solution and the characterization can be done to check the corrosion tolerance of the implant. The analysis of the coated implant were reported by the SEM image, the results implies that the coating of the substrate is uniformly deposited. The diffused particle on the implant seems like as porous nature. The FTIR results defines that the presence of the calcium chloride and aluminium isopropoxide. The peak detection of the substrate defines the presence of the synthesized nano-particles.

5. RESULTS

The above SEM images of the two implant metal such as Titanium and stainless steel was uniformly coated by Hydroxyapatite (HAp) and Nano-Alumina (Al_2O_3). So far only the hrodroxyapatite coated implant only used for orthopedic and dentistry application but that implant has poor adherence and low mechanical strength. The coating of the implant should be done under the wavelength of 325nm for 3ns of pulsed duration and the argon temperature should be kept at 99.99% under vacuum condition. If the wavelength may exceed to 375 and above may lead to contaminate of the substrate. In this (HAp+Al_2O_3) coated on titanium and stainless steel was tested with hank's solution for 7-9 days. The FTIR results implies that the peak wave number range implies that the presence of the coated substrate has the exact peak value ranges from 3800-200 cm-1.The SEM and FTIR images of the coated and tested implants reflects the same and it had been proven that the implant has high corrosion resistance and good biocompactibility which leads to long life of the implant.

6. CONCLUSION

Thus the implant has uniform distribution of the coated nano particle of (HAp+Al_2O_3) on titanium and stainless steel alloy.This helps to increase the tensile strength of implant .Compared with the coating of HAp on titanium alloy, the HAp+Al_2O_3 coated implant has higher bond strength and it lead to good biocompactibility of the implants used for orthopedic and dentistry application purpose. The future aspect of this work is going to be extended as addition of the zirconia on this coated implant.

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