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Development of hydroxyapatite coatings on laser textured 316 LSS and Ti-6Al-4V and its electrochemical behavior in SBF solution for orthopedic applications

S. Arul Xavier Stango[a], D. Karthick[b], S. Swaroop[b], U. Kamachi Mudali[c], U. Vijayalakshmi[a,*]

[a] Department of Chemistry, School of Advanced Sciences, VIT University, Vellore, Tamil Nadu 632014, India
[b] Department of Physics, School of Advanced Sciences, VIT University, Vellore, Tamil Nadu 632014, India
[c] Corrosion Science and Technology Group, Indira Gandhi Centre for Atomic Research, Kalpakkam 603102, India

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ABSTRACT

The current work focused on the development of hydroxyapatite (HAP) coating on laser textured metallic implants using electrophoretic deposition. HAP was synthesized by sol-gel technique and its phase purity and surface morphology were confirmed by FT-IR, XRD and SEM analysis. 316 L SS and Ti-6Al-4V metal implants were polished and the surface was modified using Nd-YAG laser operating at a pulse interval of 10 ns at various overlapping rate of 0%, 25% and 50%. The laser treated surface was characterized for its surface roughness using surface profilometry and surface morphology. The surface roughness of the metallic implants was increased by increase in the overlapping rate. The prepared HAP powder was electrophoretically deposited on bare and laser textured Ti-6Al-4V and 316 L stainless steel followed by vacuum sintering at 300 °C for 2 h. Scratch analysis results showed an improvement in adhesion strength for the HAP coatings on laser treated specimens than untreated metal. Corrosion efficiency of the coated samples was studied in SBF solution using EIS and potentiodynamic polarization studies. The result from the corrosion experiments proved increased corrosion resistance property of laser textured coated samples when compared to bare alloy due to higher adhesion of HAP coating on the metal surface.

1. Introduction

Over the past few decades metallic implants play major role in bone repairs and replacements in biomedical fields. Metals and its alloys are used in fracture fixation, dental amalgams, and partial to thorough joint replacements. The metallic implants like, stainless steel (316 L SS), titanium and their alloys were broadly used for orthopedic applications due to their properties like high corrosive resistance, mechanical properties, high strength and fracture toughness etc. [1–5]. The lack of bioactive sites on the surface of metallic implants leads to poor attachment of the metallic implants to surrounding tissues. Also the leach out of metal ions such as chromium, vanadium, iron and nickel etc, to the body fluid will lead to toxicity and the adverse biological response which may cause major health risks. These troubles can be overcome by giving bioceramic coatings on the surface of the metal implants. Ceramics with bone-bonding ability are referred as bioactive ceramics, such as calcium phosphate ceramics [6–8], bioactive glasses [9], and glass-ceramics [10] was widely deposited on the metal surface due to their enhanced osteo-integration and osteo-conductive properties. Thus HAP can be deposited on metal surfaces by various techniques such as plasma spraying, electrolytic deposition, dip coating, and electrophoretic deposition etc. For orthopedic applications, compared with other coating approaches, the electrophoretic deposition (EPD) was commonly employed. Because of its simple processing and ability to control the thickness by tuning up the parameters, the deposition of HAP on the implant surface was more uniform [11–16]. Meanwhile, the poor adhesion of HAP coating on the metal implants obtained by the EPD technique will possess low wear resistance which may lead to unwanted wreckage (debris) development. Therefore, adhesion of coating on the metallic implants is one of the important phenomena which have to be considered in load bearing applications.

A strong attachment between the metal substrate and HAP can be achieved by increasing the surface roughness of the implants. The increase in surface roughness will enhance the occupation of the HAP particles into the apertures or cavities created on the surface of implants. This would overcome the corrosion risk and coating malfunction at higher load bearing applications especially in bone fixations. Cell and tissue responses are affected not only by chemical properties of the

* Corresponding author.
E-mail addresses: vijayalakshmi.u@vit.ac.in, lakesminat@yahoo.com (U. Vijayalakshmi).

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implant surface, but also by surface topography or roughness of the implants. Hence, there is a need to increase the surface roughness of the implants through surface modification techniques. There are several methods like chemical (etching), electrochemical (electro polishing, anodization etc.), thermal treatment physical (polishing, sand blasting etc) and laser texturing were employed as surface modification techniques to increase the roughness [17–20]. It has been speculated that a strong coating can be achieved by increasing the bonds on the substrate prior to the coating was formed. Hence, the surface modification of the implants prior to coatings is an important alternative for the successful implants. In recent years, laser surface engineering is a rapidly growing surface modification practice which has advantages over other techniques due to rapid rate of processing, ability to operate at atmospheric pressure, selected areas modification. Laser peening process is a cold processing technique and an effective surface modification process which peen the surface of the metallic implants and create roughness. The process of laser peening irradiates the laser pulses on the samples with short duration (nanoseconds) with low power density. This laser shock peening leads to increase in surface roughness which helps the coating to give higher adhesion and improved corrosion resistance properties [21–26,29].

In this current study, pure hydroxyapatite was synthesized by sol-gel technique and was characterized by FT-IR, XRD and SEM analysis. We have increased the surface roughness of both 316 L SS and Ti-6Al-4V metallic implants by laser texturing method, HAP synthesized by sol-gel method was deposited on the metal surfaces by EPD method and their adhesion analyses were studied. Electrochemical behavior of the developed HAP coatings were performed in stimulated body fluid (SBF) solution to prove the corrosion resistance behavior for better clinical applications.

2. Experimental procedure

2.1. Synthesis of sol-gel derived HAP

Hydroxyapatite was prepared by sol-gel method using 0.6 M of Triethyl phosphite (Phosphorous precursor) and the resultant solution was hydrolyzed at 90 °C for 16 h, 1 M of calcium nitrate tetrahydrate is used as Calcium precursor and the solution was added to the refluxed phosphorus solution by dropwise and finally refluxed at 90 °C for 24 h. Then the solution was evaporated in water bath at 60 °C to form gel. After gelation, it was dried in a hot air oven at 100 °C followed by sintering in muffle furnace at 900 °C for 2 h. Further the sintered powder was characterized using FT-IR (Shimadzu –IR Affinity-1 Spectrometer, Japan), XRD (Bruker D8 Model, Germany) for determination of functional groups and phase purity. The surface morphology of the sol-gel derived HAP was analyzed using SEM (Zeiss EVO 18 Research, Germany).

2.2. Substrate preparation

316 L Stainless steel and Ti-6Al-4V were taken for these studies which were extensively used in bone tissue engineering. The metal specimens with dimension of 10 × 10 × 5 mm thickness (316 L SS and Ti-6Al-4V) were polished sequentially using silicon carbide sheets from grade 120 to 1200. Further, the polished specimens were ultrasonically cleaned and degreased using acetone for 15 min. Then the samples were again washed with deionised water and stored in vacuum desiccator to prevent it from oxidation. The polished specimens were further used for laser patterning followed by electrophoretic deposition of HAP particles at the voltage of 70 V at a constant duration of 3 min.

2.3. Laser surface patterning of metallic implants

The polished specimens were treated in perpendicular with Q-switched, Nd-YAG laser at the fundamental wavelength of 1064 nm (Green light) operating at the pulse interval of 10 ns, at 150 mJ of energy at various overlapping rate of 0%, 25% and 50% with the spot diameter of 800 μm in perpendicular direction. Additionally, the laser textured implants were characterized for surface roughness using surface profilometry, surface morphology and elemental analysis by SEM-EDAX Phase analysis after laser treatment was characterized by XRD analysis.

2.4. Fabrication of HAP coatings

The coating of hydroxyapatite on polished metallic transplants and laser treated metallic specimens were attained by electrophoretic deposition. Prior to coating, the prepared hydroxyapatite powder was dispersed in isopropyl alcohol (3 g in 75 mL) by means of ultra-sonication and kept stirring for overnight to get uniform dispersion of the HAP particles. The deposition of HAP particles was done by applying DC power supply of 70 V for 180 S to the polished and laser textured metal specimens (Ti-6Al-4V, 316 L SS). For EPD deposition, the metal specimen is acted as cathode and stainless steel is treated as anode. Further, the coated specimens were removed, dried and vacuum sintered at 300 °C for 2 h under N_2 atmosphere to avoid oxidation of coated samples and used for further studies.

2.5. Adhesion test for HAP coatings

The adhesive nature of the HAP coatings between untreated and laser treated metal surfaces can be determined by scratch analysis. The scratch tests were performed using DUCOM scratch tester with a Rockwell C diamond indenter with a tip diameter of 200 μm (Model TR-101) by applying ramp load of 1 N with the stroke length of 5 mm at scratch velocity of 0.5 mm/s. Here, “C” attributes to the Rockwell testing load range from a Preliminary force of 10 kg f to maximum 150 kg f. The data were acquired using computer operated WINDUCOM software. The nature of scratch for the HAP coated implants were examined for its different type of defects (spalling, buckling, chipping,) conformal cracking and tensile cracking by an optical microscope (OM ZEWASSCLEMAX, VWASION).

2.6. Corrosion studies

The corrosion performance of the bare, laser textured and coated specimens were studied using electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization technique (TAFEL). The experiments were carried out using the electrochemical work station (Biologic SA model SP-150, France) with three electrode arrangements, wherein the specimen of area with 1 × 1 cm^2 was kept as working electrode (WE), Platinum wire as counter electrode (CE), Silver/silver chloride (Ag/AgCl/Satd (KCl)) electrode as reference (RE) and Stimulated body fluid (SBF) with pH maintained at 7.4 was used as electrolyte. The electrochemical impedance studies were conducted with a frequency ranging from 100,000 Hz to 0.01 Hz by applying AC signal with the small amplitude of 10 mV at the scan speed of 10 points per decade. The polarization studies were carried out by sweeping the electrode potential from −0.300 V to +0.300 V at the scan rate of 1 mV per minutes. All the experiments were repeated for three times to minimize the error.

3. Results and discussions

3.1. Sol-gel synthesized HAP

Fig. 1a shows the FT-IR pattern of as synthesized (Raw) and the powder sintered at 900 °C for 2 h. The broad band formed in raw powder at around 3550 cm^{-1} was found to be decreased after sintering which indicates the removal of water molecules on sintering at higher temperature. The characteristic bands formed at 3604 cm^{-1} and