Fabrication And Characterization Of Cerium Substituted Hydroxyapatite/ Polyvinyl Pyrrolidone Coating On Ti-6al-4v Alloy For Orthopedic Applications

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ABSTRACT

Ti-6Al-4V alloys have reaped greater attention as orthopedic implant due to its excellent mechanical properties, corrosion resistance and good biocompatibility. However, its insufficient osseointegration property is a major obstacle for such applications and for this reason, it is important to introduce bioceramic-polymer coatings on the metallic surface to attain true adhesion between the implant and bone. The present work deals with the successful development of cerium substituted hydroxyapatite-polyvinyl pyrrolidone (Ce-HAP/PVP) on Ti-6Al-4V alloy by spin coating. The coatings were characterized by Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). Also, the mechanical behavior of the coatings were analyzed. The corrosion resistance of the obtained coatings was also investigated in simulated body fluid solution by potentiodynamic polarization technique which assured the improved resistivity. Thus, the Ce-HAP/PVP coated Ti-6Al-4V alloy can play a significant role in orthopedic applications.

KEYWORDS: Ti-6Al-4V alloy, Cerium substituted hydroxyapatite, Spin Coating, Polyvinyl pyrrolidone, Potentiodynamic polarization

INTRODUCTION

Metallic biomaterials have been extensively used in orthopedic surgery for replacements of bone till present. Surgical grade 316L SS, Co based alloys, pure titanium and titanium-based alloys are the most widely used metallic materials. Among them, Ti-6Al-4V alloys are garnering attraction and are used clinically as orthopedic surgery implants because of their excellent mechanical properties, their corrosion resistance, and their good biocompatibility. Ti-6Al-4V develop a highly stable surface oxide layer when exposed to air or to aqueous media, which is responsible for bone-bonding characteristics of Ti-6Al-4V implants. Ti-6Al-4V implants provide a bioinert surface for adherence and osseointegration of surrounding bone cells that sparked development of titanium alloy for usage in orthopedics[1]. Titanium alloys are often used in non-weight-bearing surface components such as femoral necks and stems as they have lower modulus of elasticity resulting in less stress shielding of bone[2]. However the osseointegration which is defined as structural and functional bonding between living bone and the surface of implants is still not sufficient to which may ultimately lead to...
mechanical instability and implant failure osseointegration. To enhance implant integration and bone bonding, many strategies are being followed. One among them is the ceramic and polymer coatings on metals.

Ceramic implants for osteogenesis are based mainly on Hydroxyapatite (HAP; Ca$_{10}$(PO$_4$)$_6$(OH)$_2$), since it has a similar chemical composition and structure to the mineral phase of human bone. Therefore, HAP can promote new bone formation and for the firm attachment of bone. HAP coatings on orthopedic implants have gained wide acceptance in orthopedic surgery as it has osteoconductive properties, and that the fixation of HAP-coated implants is better than for uncoated implants following optimal surgical conditions. Owing to the inferior mechanical properties such as brittleness, low tensile strength, low fracture toughness and difficulties in fabrication, HAP cannot withstand under the high physiological loading conditions traditionally associated with orthopedic implants[3]. Furthermore, the HAP structure admits the incorporation of wide range of different ionic substitutions including monovalent (Na$^+$, K$^+$), divalent (Sr$^{2+}$, Pb$^{2+}$, Ba$^{2+}$, Mn$^{2+}$, Mg$^{2+}$, etc.), trivalent (Cr$^{3+}$, Ce$^{3+}$, Al$^{3+}$, F$^{3+}$, etc.) and tetravalent ions (Ti$^{4+}$, Ti$^{4+}$, etc.)[4]. Since, the radius of Ce$^{3+}$ is close to the radius of Ca$^{2+}$, cerium ions can substitute the place of calcium ions in the HA lattice. The small amount Ce ions in human bones can boost up organism’s metabolism and they also have excellent antibacterial property but on the other hand it can also increase the cytotoxicity[5]. To minimize the toxicity, further step is to add a suitable bioactive polymer which is one of the conventional methods with wide-scope. Also, the bioceramic coatings could not maintain long-term stability and may delaminate from the implant surface in certain situations due to lack of mechanical strength which may lead to clinical complications and implant failure.

Hence, it is necessary to improve the mechanical properties of the HAP coatings without compromising its biocompatibility. As a response to this issue, polymers combined with HAP have been made to tackle the problem and to make it useful for potential applications in bone repair and regeneration. Polyvinyl pyrrolidone (PVP) seems to be a suitable material for this purpose. PVP is characterised by its hydrophilic property, high biocompatibility to human body, non-toxic and corrosion resistance which makes the material a potential candidate for use in orthopedic applications[6].

The use of sol–gel routes to form a bioactive hydroxyapatite layer on metal substrates has recently received greater attention in the development of orthopedic implants. Numerous advantages can be realized through the sol–gel route, as compared to other coating methods such as thermal spraying, electrophoretic deposition, electrochemical deposition, sputter coating, laser deposition. One of the major advantages is inherently low-temperature nature of the sol–gel process. The structural and phase integrity of the coatings can therefore be preserved and a fine, controllable microstructure can be obtained. An atomic level of mixing during sol preparation ensures a significant improvement in the physical and chemical homogeneity of the sol and also allows a complete coverage of the exposed surface area by a thin coating for implants[7].

In this work, Ce-HAP/PVP composite has been prepared and the composite has been coated on Ti-6Al-4V alloy by spin coating technique for the first time. The obtained coatings were examined by a series of means such as Fourier transform infrared spectroscopy (FT-IR), Scanning electron microscopy (SEM). In addition, the mechanical behaviour has been analyzed. Also, the corrosion behavior of the resultant coating was evaluated using potentiodynamic polarization technique in SBF solution.

2. Experimental:
2.1. Materials:
Commercially available calcium nitrate tetrahydrate (Ca(NO$_3$)$_2$·4H$_2$O), cerium nitrate hexahydrate (Ce(NO$_3$)$_3$·6H$_2$O), di-ammonium hydrogen phosphate (NH$_4$_2HPO$_4$), ethanol, acetic acid, and polyvinyl pyrrolidone purchased from Aldrich Chemical Co. (Aldrich, India), were used for the development of Ce-HAP/PVP composite coating on Ti-6Al-4V alloy by sol-gel deposition. All chemicals were of analytical grade and were used as received, and deionized water was used throughout the experiment.

2.2. Specimen Preparation:
Ti-6Al-4V alloy, with composition (wt %) 5.7 Al, 3.85 V, 0.18 Fe, 0.038 C, 0.106 O, 0.035 N, and balance titanium, was used in the present study. Pieces of Ti-6Al-4V alloy with a size of 10 × 10 × 3 mm were cut and used as the substrate for the sol-gel deposition of Ce-HAP/PVP composite. Prior to deposition, the samples were abraded with different grades of SiC emery papers from 400 to 1200 grit, washed with distilled water, degreased with acetone, and then dried at room temperature of 30 °C.

2.3. Synthesis Of Ce-Hap Powder:
For the synthesis of Ce substituted HAP, 0.35 M of Ca(NO$_3$)$_2$·6H$_2$O, 0.15 M of Ce(NO$_3$)$_3$·6H$_2$O and 0.3 M of (NH$_4$)$_2$HPO$_4$ were dissolved separately in DI water. The solutions were mixed in the molar ratio of 1.67. The electrolyte was kept in a magnetic stirrer for 2 h and the pH was adjusted to 4.5 using NH$_4$OH solution. To maintain the uniform concentration, the magnetic stirring of solution was controlled at a speed of 180 rpm. In this process, the electrolyte was deaerated with N$_2$ for 30 min. The resultant Ce-HAP solution was further
ultrasonicated for 2 h to ensure good dispersion. It was then filtered, washed, dried at 80 °C for 12 h, and ground into a fine powder.

2.4. development of ce-hap and ce-doped hap/pvp composite coatings on ti-6al-4v substrates:
Ce-doped HAP/PVP composite coatings were produced by spin coating technique. 1g of Polyvinyl pyrrolidone (PVP) dissolved in equal amount of ethanol-water mixture by stirring for 2 h. The Ce-doped HAP powder sieved by 200 mesh sieves was added into the PVP and the suspension was stirred for 12h till the solution was well mixed. Ce-doped HA/PLA composite coatings were formed on Ti-6Al-4V substrates using Specktrospin - spin coater manufactured by Spektron Instruments Inc. The prepared suspension was dropped on the Ti-6Al-4V specimens which were sticky to the coater. Spin the specimens at the speed of 3000 rpm for 60 s and repeat the former steps for three times to obtain coatings with appropriate thickness. The coatings were dried at room temperature of 30°C. For comparison, Ce-HAP were developed by dissolving 1g of as-synthesized Ce-HAP powder in equal amount of ethanol-water mixture. Further, steps are followed similarly as the development of Ce-HAP/PVP on Ti-6Al-4V substrates.

2.5. Surface Characterization:
Fourier transform infrared (FTIR) spectra of the composite were recorded on a Nicolet 380 FTIR spectrometer (PerkinElmer) over the frequency range from 4000 to 400 cm−1 with 32 scans and spectral resolution of 4 cm−1. The surface morphology and elemental composition of the composite coatings were examined by scanning electron microscopy (SEM) analysis (JEOL JSM-6400). The mechanical performance (Vickers microhardness (HV) tests) of the coated Ti-6Al-4V samples were carried out at a load of 490.3 mN with a Vickers pyramid indenter, using an Akashi AAV-500 series hardness tester.

2.6. Electrochemical Evaluation Of Composite Coatings:
Electrochemical measurements were carried out through potentiodynamic polarization to assess the anticorrosive characteristics of the coatings. A saturated calomel electrode (SCE), platinum electrode, and Ti-6Al-4V alloy were used as the reference, counter, and working electrode, respectively. Simulated body fluid (SBF) solution with ion concentration nearly equal to that of human blood plasma was used as electrolyte medium. This solution was prepared according to the protocol suggested by Kokubo and Takafama[8]. Potentiodynamic polarization studies were measured at a scan rate of 1 mV·s−1 in the potential range between −200 and −2000 mV. The obtained data was recorded by use of internally available software.

RESULTS AND DISCUSSION

3.1. Ft-Ir Analysis:
Figure 1(a) represents the FTIR spectrum of HAP. The characteristic peaks appeared at and 565 cm−1, 473 cm−1 and 945 cm−1 depict the phosphate groups. The absorption peaks observed at 3599 and 600 cm−1 are assigned to the stretching and bending vibration of the OH− group. In addition, the broad band at 3460 cm−1 and a peak at 1639 cm−1 are assigned for the stretching and bending mode of the H2O molecule of HAP, respectively.

![Fig. 1: FT-IR spectra of (a) HAP, (b) Ce-HAP, (c) Ce-HAP/PVP coatings](image-url)
The FT-IR spectrum of Ce-HAP (Figure 1(b)) coating shows a similar structure of HAP, but some changes in IR wavenumber of bands are observed due to the substitution of Ca²⁺ by Ce³⁺ into the apatite lattice where the ionic radius of Ca²⁺ is 0.100 nm and Ce³⁺ is 0.107 nm. The bigger radius of Ce³⁺ consequently decreases the bonding strength of P–O and the OH group[5]. Figure 1(c) indicates the FTIR spectrum of Ce-HAP/PVP. In addition to the peaks of Ce-HAP, the characteristic peaks of C=O stretching vibration can be observed at 1673 cm⁻¹ which denotes the addition of PVP. The bands at 704, 865 and 1281 cm⁻¹ are attributed to C–C stretching, C–N stretching and C–H bending vibrations of the PVP respectively[9]. Thus the FTIR spectra may confirm the formation of Ce-HAP/PVP composite.

3.2. Sem Characterization Of Resultant Coatings:

The SEM images provide direct information about the typical morphology of the Ce-HAP coated and Ce-HAP/PVP specimens (Figure 2).

![SEM micrographs of (a, a') Ce-HAP, (b, b') Ce-HAP/PVP coatings](image)

The Ce-HAP particles were uniformly distributed on the metal surface as shown by SEM micrographs (Figure 2a, 2a’), which will result in an improved corrosion performance. Figure 2b & 2b’ shows irregular microspheres with certain levels of agglomeration when PVP is added to Ce substituted HAP. Thus the as-coated Ce-HAP/PVP coated Ti-6Al-4V depicts slight agglomeration and crack free pores which favors the cell adhesion and growth and therefore can be used in orthopedic implant.

3.3. Potentiodynamic Polarization Measurements:

Potentiodynamic polarization curves of uncoated Ti-6Al-4V alloy, Ce-HAP coated, Ce-HAP/PVP composite coated Ti-6Al-4V alloy in SBF solution are shown in Figure 3. The corrosion potential (E_{corr}) and corrosion current density (i_{corr}) values for uncoated and coated samples were found and are summarized in Table 1.

![Potentiodynamic polarization curves for uncoated, Ce-HAP and Ce-HAP/PVP coated Ti-6Al-4V alloy](image)
As inferred from the table, the Ce-HAP coated Ti-6Al-4V alloy showed more positive $E_{\text{corr}}$ and much lower $i_{\text{corr}}$ compared to the uncoated Ti-6Al-4V alloy, whereas the addition of PVP as composite coating Ti-6Al-4V alloy enhanced the corrosion resistance, which can be viewed from the obtained $E_{\text{corr}}$ and $i_{\text{corr}}$ values (Table 1). Thus, potentiodynamic polarization studies denotes that the corrosion resistance of the Ti-6Al-4V alloy was significantly improved due to the Ce-HAP/PVP composite coating.

Table 1: Electrochemical parameters and Hardness values of uncoated, Ce-HAP coated and Ce-HAP/PVP coated Ti-6Al-4V alloy

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>$E_{\text{corr}}$ (mV)</th>
<th>$I_{\text{corr}}$ ($\mu$A.cm$^{-2}$)</th>
<th>Vicker microhardness (Hv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated Ti-6Al-4V alloy</td>
<td>-12 ±0.5</td>
<td>1.29 ±0.04</td>
<td>-</td>
</tr>
<tr>
<td>Ce-HAP coated Ti-6Al-4V alloy</td>
<td>72 ±0.10</td>
<td>0.78 ±0.07</td>
<td>317±11.7</td>
</tr>
<tr>
<td>Ce-HAP/PVP coated Ti-6Al-4V alloy</td>
<td>141 ±0.7</td>
<td>0.63 ±0.04</td>
<td>394.8±12.4</td>
</tr>
</tbody>
</table>

3.5. Vickers Microhardness:

The microhardness ($H_V$) of the coating is one of the basic requirements for the implants to provide the details about the ability of their load bearing capacity when it is implanted into human body under stress. In our present study, the hardness values of the uncoated Ti-6Al-4V, Ce-HAP and Ce-HAP/PVP composite coated Ti-6Al-4V alloy were evaluated using the Vickers microhardness test, and the values are given in Table 1. The Ce-HAP coated Ti-6Al-4V exhibited higher hardness values of $317 \pm 11.7$ H$_V$. The $H_V$ value for the Ce-HAP/PVP composite coated Ti-6Al-4V was observed to be $394.8 \pm 12.4$ H$_V$, which is still higher than that of the Ce-HAP coated substrates. This is subjected to the bonding strength between the Ce-HAP/PVP composite coating and Ti-6Al-4V substrate.

Conclusion:

Fabrication of Ce-HAP/PVP on Ti-6Al-4V alloy was successfully performed by spin coating. The FT-IR analysis confirmed the functional groups of Ce-HAP/PVP. Morphological results revealed the formation of composite coatings with increased uniform morphology which denotes the protection of the Ti-6Al-4V alloy as implants. The corrosion resistance of Ce-HAP/PVP coated Ti-6Al-4V alloy assured the improved corrosion protection in SBF solution. Hence, the developed Ce-HAP/PVP coated Ti-6Al-4V alloy can be a more potential candidate in orthopedic applications.

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