Surface characterization of plasma sprayed pure and reinforced hydroxyapatite coating on Ti6Al4V alloy

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Abstract

Hydroxyapatite coatings suffer from poor mechanical properties like fretting fatigue, toughness and abrasive wear resistance. These properties can be enhanced by incorporation of secondary ceramic and metallic reinforcements in HA. An attempt has been made to deposit HA and HA reinforced with 10 wt.% (80Al2O3–20TiO2) by plasma spray process on Ti6Al4V substrate. These coatings have been characterized using SEM, EDAX, XRD and FTIR spectroscopy. Corrosion studies have been done in SBF solution. Bio compatibility study is not included in this work. Reinforcement has enhanced the tensile strength. There is marginal improvement in microhardness and surface roughness with reinforcement. Both pure and reinforced coatings show superior resistance against corrosion in simulated body fluid.

1. Introduction

Hydroxyapatite (HA), having chemical formula Ca10(PO4)6(OH)2 has attracted attention of the researchers in recent years due to its excellent biocompatibility in body environment. Chemical structure (Ca/P ratio) of HA is very close to human bone which makes it compatible to the tissue of human body [1–3]. HA is known to have a simulating effect on bone formation, which is known as osseo-induction. It enhances the osseo-integration, and there are indications that chemical bonding may occur between HA and bone [4,5]. Although it is an attractive choice to be used as implant material due to its biocompatibility and chemical inertness in human body, pure HA has poor mechanical properties like low fracture toughness and bending strength which restricts its use in high load bearing conditions such as orthopedics [6–9]. Metals and alloys have good mechanical properties but these materials may not always be bio compatible in body. It has been revealed from the previous reports that almost all metals and alloys release metallic ions which cause poor fixation of implants and after some time failure takes place [10,11]. Many of the metallic ions may be very toxic to human body [12,13]. The reaction between body fluid and implant material can be minimized by using HA coating. By doing so, one can achieve superior mechanical properties of the substrate and excellent bio compatibility of porous HA coating [26]. Many coating techniques like plasma spray, high velocity oxy fuel spray, sol gel, electroplating and physical vapor deposition etc. are being used to coat HA on metallic implants [14–18]. But plasma spray is the only process which is allowed for biomedical coatings on prosthesis by Food and Drug Administration, (FDA) USA, due to its excellent coating properties like good adhesion strength and crystalline nature of coating [19] as compared to other coating techniques. One problem associated with plasma spray process is that due to the high temperature of plasma jet crystalline HA changes into amorphous calcium phosphate phases like α-tri calcium phosphate, β-tri calcium phosphate, and oxy hydroxyapatite which are non favorable phases and are prone to dissolve in human body environment [3,20,21]. Many studies have been carried out to prevent formation of these phases by varying coating parameters like stand off distance, current and voltage [2,3].

Since plasma spray process involves very high temperature and so reinforcements may have tendency to react with HA at the high temperatures. Viswanath et al. [22] has worked on interfacial reactions in hydroxyapatite/alumina composite. They observed that alumina completely reacted with hydroxyapatite and formed alumina rich calcium aluminates at relatively low temperatures. This has been attributed to the diffusion of Ca2+ from hydroxyapatite into the alumina matrix. This diffusion of Ca2+ leads to formation of TCP. They proposed the following reaction for this.

$$Ca_{10}(PO_4)_{6}(OH)_2 + 6Al_2O_3 \rightarrow CaO.6Al_2O_3 + CaAl_2O_4 + 3Ca_3(PO_4)_2 + H_2O$$

Huxia et al. [23] reinforced HA with Al2O3 20 wt.% and this mixture was sintered at 1200, 1300 and 1400 °C and observed similar reaction. Wenxiu et al. [6] worked on hydroxyapatite/titania nanocomposites derived by combining high-energy ball milling with spark plasma sintering processes. They proposed following chemical
reaction between HA and titania at temperature higher than 900 °C. This reaction also confirms the formation of TCP.

\[
\text{Ca}_{10} (\text{PO}_4)_6 (\text{OH})_2 + \text{TiO}_2 \rightarrow 3 \text{Ca}_3 (\text{PO}_4)_2 + \text{CaTiO}_3 + \text{H}_2\text{O}\t
\]

Similar reaction was reported by Li et al. [24] who worked with HA-TiO₂ composite coatings deposited by HVOF technique.

2. Experimental

Hydroxyapatite powder (HA) of particle size in the range of 100–180 μm and having volume mean diameter (particle size distribution) D [3,4] of 150.12 μm was used for experiments. D [2,3] and D [v, 0.5] of the powder was 15.10 μm and 140.30 μm respectively. 10 wt.% (80Al₂O₃–20TiO₂) having grain size 10–40 μm was used as reinforcement by ball milling to enhance mechanical properties of coating. SEM micrographs of pure HA powder, reinforcing material (80Al₂O₃–20TiO₂) and HA reinforced with 80Al₂O₃–20TiO₂ are shown in Fig. 1. SEM micrograph shows that both HA and reinforced materials have crushed angular shape.

Coating of pure and reinforced HA was carried out by Plasma Spray System at Anod Plasma Spray Limited, Kanpur, (India). Ti6Al4V alloy strip (ASTM F 1472) having thickness 3 mm was used as a substrate material. Samples to be coated were grit blasted using alumina having size 60–80 μm at blasting pressure 0.44 MPa for good coating adhesion. Average value of surface roughness of the sample after the sand blasting was 6.45 μm. Parameters of coating are given below in Table 1.

2.1. Characterization techniques

2.1.1. Microstructure and phase analysis

Microstructure analysis was carried out of both feedstock powder as well as coated samples. Coated samples were cut on diamond cutter and mounted in the epoxy resin for the cross sectional analysis. The mounted samples were polished on 800, 1000 grade emery paper followed by 1/0, 2/0, 3/0, 4/0 and 5/0 grade papers and finally polished on cloth with alumina grade II paste. Cross sectional analysis was followed by 1/0, 2/0, 3/0, 4/0 and 5/0 grade papers and mounted in the epoxy resin for the cross sectional analysis. The cross sectional analysis was carried out by SEM/EDAX (FEI Quanta 200F, Made in Czech Republic). X-ray diffraction analysis (Bruker-Binary V3) was carried out to analyze the phase structure of both feedstock powder and coated samples. Coated samples were cut on diamond cutter and mounted samples were polished on 800, 1000 grade emery paper followed by 1/0, 2/0, 3/0, 4/0 and 5/0 grade papers and finally polished on cloth with alumina grade II paste. Cross sectional analysis was carried out by SEM/EDAX (FEI Quanta 200F, Made in Czech Republic). X-ray diffraction analysis of both feedstock powder and coated surface by taking radiation source of CuKα at angle 10° to 60°. Fourier transformed infrared spectroscopy (FTIR) analysis of feedstock and coating were done on (Thermo Nicolet, USA) and (Nicolet 6700, USA) respectively to indentify various types of chemical bonding present in the coating.

2.1.2. Coating crystallinity

There are many methods to determine the crystallinity of HA coatings using X-ray diffraction like Rutland Method, Relative Intensity Method and Rietveld Method. But in previous literature it is reported that Rutland Method is an accurate method for determining crystallinity [2,14]. In this method crystallinity is calculated by comparing the total area under the diffraction pattern with the area of the amorphous region of the pattern. The % crystallinity is determined by using equation as:

\[
\text{Crystallinity} (%) = \left(\frac{\sum A_c}{\sum A_a + \sum A_s}\right) \times 100
\]

Where \(\sum A_c\) is the sum of the areas of all HA crystalline peaks and \(\sum A_s\) is the sum of area under the amorphous peaks.

2.1.3. Surface roughness

Surface roughness pertomether (Wyko NT 1100, USA) was used to measure the surface roughness (Rₐ) and (Rₚ) values of the plasma sprayed coated specimens. Each reported value of surface roughness (Rₐ) and (Rₚ) is the mean of five observations taken at different locations. Each value of Rₐ is the average roughness calculated over the entire measurement array given as \(R_a = \frac{1}{M} \sum_{j=1}^M |Z_j|\), \(Z_j\) is the height of each pixel after the zero is removed. Whereas \(R_p\) value is called ten point height which is the average of ten greatest peak to valley separation on the evaluation area given as \(R_p = 1/10 (H_1 + H_2 + \ldots + H_{10}) - (L_1 + L_2 + \ldots + L_{10})\), where \(H_1\) is peak height relative to the zero mean and \(L_1\) valley depth (positive) relative to zero mean.

2.1.4. Porosity

Coated samples were subjected to porosity measurement by using Zeiss Axiovert 200 MAT inverted optical microscope, fitted with imaging software Zeiss Axiovision (Release 4.1), which is compatible with ASTM B276 standard. The analysis using image processing software determines the pore area size in the view field by converting the pore areas...
Table 1
Spraying parameters of pure and reinforced HA coating.

<table>
<thead>
<tr>
<th>S. No</th>
<th>Coating parameter</th>
<th>Units</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Current (A)</td>
<td>750</td>
</tr>
<tr>
<td>2</td>
<td>Voltage (V)</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>Arc pressure (MPa)</td>
<td>0.41</td>
</tr>
<tr>
<td>4</td>
<td>Hopper RPM</td>
<td>5.4</td>
</tr>
<tr>
<td>5</td>
<td>Hydrogen pressure (MPa)</td>
<td>0.06</td>
</tr>
<tr>
<td>6</td>
<td>Stand off distance (mm)</td>
<td>105</td>
</tr>
<tr>
<td>7</td>
<td>Powder rate g/min</td>
<td>35</td>
</tr>
<tr>
<td>8</td>
<td>Nozzle diameter (mm)</td>
<td>7</td>
</tr>
</tbody>
</table>

(grey-level areas) into a background color such as red while the rest of the microstructure remains in its original color. The area of one feature is numerically related to the total area of the picture, as the program counts the number of one color type pixels (red) and sets that as a ratio of the total number of pixels in the picture (total area). About twenty (20) separate locations were selected on the surface of coating to avoid the overlap between two locations and determine the area percent porosity.

2.1.5. Tensile strength

Tensile strength of pure and reinforced HA coatings were carried out according to ASTM F-1147-05 standard. The coated samples of 1 cm² were fixed from both sides (i.e. one side coated and other side substrate material). Adhesive material (Araldite) was used to fix the coated piece. The test was performed with tensile machine (Hounsfield, UK) in which one arm was fixed and load was applied with the second. The samples having uniform coating thickness of 150 µm were tested for tensile strength test. The load at which the whole coating got peeled off from the surface was recorded. The test was repeated three times with similar samples and average has been taken for determination of the tensile strength. After the test the samples were examined by the optical microscope to ensure that the whole coating was peeled off. The data was converted for area 5.07 cm² as per the requirement of the above standard.

2.1.6. Micro hardness

To check the micro hardness of the samples the cross-section of the coated parts were mounted in the epoxy resin and polished. The micro hardness of the as sprayed coatings was measured by using Micro hardness Tester (Leitz, Germany) fitted with a Vickers pyramidal diamond indenter with 98.07 mN load. Hardness value was calculated from the relation \( H_v = 1854.4 \times F/d^2 \), where \( F \) is for load in grams and \( d \) is for the diameter of the indenter in micrometer. Each reported value of the micro hardness is the average value of five measurements.

2.1.7. Corrosion behavior in simulated body fluid

Pure and reinforced HA coatings were tested for corrosion in simulated body fluid by electrochemical polarization test. SBF solution was prepared according to the composition suggested by Kokubo [25]. The test was carried out on three electrode corrosion cell interfaced with a potentiostat (PARSTAT, Princeton Applied Research, USA) which consist of Ag/AgCl as reference electrode and counter electrode. Sample which is to be polarized acted as working electrode. The area of the sample exposed to SBF solution was 1 cm². Samples were immersed in the SBF solution for 1 h before starting the measurements. The corrosion current density values were calculated by Tafel slope methods.

3. Results

The coatings with and without reinforceement have nearly same thickness of around 150 µm. Presence of some cracks can be seen on the cross-section of pure HA coating as shown in Fig. 2(a), whereas the coating with reinforcement is observed to be more homogeneous and free of cracks as can be seen in Fig. 2(b). In earlier work Morks [26] has compared pure HA and silica reinforced HA coating and observed that silica reinforced coatings were denser as compared to pure HA coating. White elongated pieces of substrate material are seen at the interface of coating and substrate in Fig. 2(b). The Al₂O₃ and TiO₂ are distributed in a direction parallel to substrate. Al₂O₃ is seen as elongated black stringers and TiO₂ is in the form of white streaks.

Scanning electron micrographs of top surfaces of pure and reinforced HA coated specimens are shown in Fig. 3(a) and (b) respectively. It can be observed from the micrographs that both the coating surfaces have some partially melted and few unmelted particles and are free from cracks.

FTIR analysis of pure HA and reinforced HA powders and their coatings have been carried out in range from 4000 cm⁻¹ to 500 cm⁻¹ are shown in Fig. 4(a) and (b). In Fig. 4(a) presence of OH group in case of pure HA powder are observed at 3568 cm⁻¹ and 648 cm⁻¹ whereas in case of coating these are at 3732 cm⁻¹ and 632 cm⁻¹ where as in case of coating these are at 3732 cm⁻¹ and 648 cm⁻¹, spectra shows presence of PO₄²⁻ group at 960 cm⁻¹, 1044 cm⁻¹, 1088 cm⁻¹, 600 cm⁻¹.

![Fig. 2. SEM micrograph along the cross-section of plasma spray coatings on Ti6Al4V (a) pure hydroxyapatite coating; (b) hydroxyapatite reinforced by 10% (80 Al₂O₃–20 TiO₂).](image-url)
and 570 cm\(^{-1}\) in case of HA powder and at 978 cm\(^{-1}\), 1028 cm\(^{-1}\), 1092 cm\(^{-1}\), 577 cm\(^{-1}\) and 596 cm\(^{-1}\) in case of coating. Similarly in Fig. 4 (b) OH group is present at 3568 cm\(^{-1}\) and 632 cm\(^{-1}\) in case of reinforced powder and 3733 cm\(^{-1}\) and 676 cm\(^{-1}\) in case of coating. Presence of PO\(_4^3^−\) group may be observed at 956 cm\(^{-1}\), 1043 cm\(^{-1}\), 1093 cm\(^{-1}\), 601 cm\(^{-1}\) and 569 cm\(^{-1}\) in case of powder and 962 cm\(^{-1}\), 1034 cm\(^{-1}\), 1119 cm\(^{-1}\), 556 cm\(^{-1}\) and 610 cm\(^{-1}\) in case of coating. FTIR spectra of pure and reinforced HA are almost similar. No large variation is observed in both powders and coatings, which is in agreement with existing literature\[27–29\]. At 2360 cm\(^{-1}\) in both pure and reinforced HA coatings presence of CO\(_2\) molecule has been observed which was not present in the original pure and reinforced powders. Same observation has been reported by Li et al.\[30\] and Dey et al.\[31\]. Dey et al.\[31\] have attributed CO\(_2\) presence to absorbance of carbon dioxide (CO\(_2\)) from the atmosphere. Similar observations of CO\(_2\) bond in FTIR spectra have also been reported by other researcher\[32–34\].

Presence of tri calcium phosphate (α-TCP, β-TCP) and tetra calcium phosphate (TTCP) can be observed between 31º and 33º on both pure and reinforced HA coatings in XRD analysis of the coated samples as shown in Fig. 5(a) and (b). These above phases were not present in their original powders. These phases are amorphous in nature and may be rapidly soluble in body environment which may cause failure of bio implant inside the body. Similar amorphous phases have been also reported by earlier researchers\[2,3,6\]. It can also be observed from the XRD analysis that HA peaks of both pure and reinforced powders are sharp and after coating they become broad that indicating conversion of crystalline material to amorphous phase.

### 3.1. Coating crystallinity

Coating crystallinity of HA coating was calculated from XRD between 20º and 60º angle range. Three samples of pure HA and reinforced HA coatings were analyzed for average crystallinity value which was 69.8% in case of pure HA coating whereas 68.5 for reinforced HA coating. These crystallinity values are comparable with the results published in the previous research work\[35\]. The percentage values of amorphous phases (TCP and TTCP) in pure HA and reinforced HA coatings were 11.28% and 14.12% respectively.

### 3.2. Surface roughness

Surface roughness plays an important role in case of body implant. The main requirement of the bio implant is to facilitate easy cell growth on its surface as soon as it is implanted in the body. For easy cell growth the coating must be rough. Surface roughness of pure and reinforced HA coating was observed between 5.30 \(\mu\)m to 6.49 \(\mu\)m and 5.53 \(\mu\)m to 7.31 \(\mu\)m respectively. Average values of eight readings in both cases are plotted in the graph. Average surface roughness of reinforced HA coating was found to be 6.06 \(\mu\)m which is slightly higher than that of pure HA coating (i.e. 5.81) as shown in Fig. 6. Slight increase in surface roughness may be due to presence of alumina–titania reinforcement.

### 3.3. Porosity

Porosity of HA coating is very important since the coated metallic sample has to be in human blood plasma. Hence the coating should be
free of through porosity so that the metallic substrate should not react in body environment resulting in toxic metal ion dissolution in human blood plasma [10,21]. Porosity of reinforced HA coating was found to be lower than that of pure HA coating. That may be due to the small size of reinforced material. In 10 readings highest value and lowest value of porosity in case of pure HA coating was 1.90 and 0.58% whereas in reinforced HA coating it was 0.78 and 0.57%. Average values of both coatings are shown in the Fig. 6. Similar effect of reinforcement in the form of decrease in porosity was observed by the Morks [26] when he reinforced silica in pure HA coating.

3.4. Tensile strength test

Tensile strength test is very important since bio implant may have application in high load bearing conditions such as orthopedics. In order to achieve longer life of bio implant the tensile strength of the porous coating must be sufficient to hold the coating with the metallic substrate. As shown in Fig. 7(a) tensile strength of reinforced HA coated sample was observed to be higher (32.2 MPa) than that of pure HA coated sample (28.6 MPa). Tensile strength results are close agreement with the previous result presented by Silva et al., [36].

3.5. Micro hardness

Micro hardness of the pure HA and reinforced HA coatings were determined across the cross-sectioned samples. The effect of reinforcement on the hardness of HA coatings are shown in the Fig. 7(b). It is observed that hardness of the reinforced coating is slightly higher. This may attributed to decrease in coating porosity and role of reinforcement.

![Fig. 4](image_url) FTIR analysis of (a) pure HA powder and coating, (b) reinforced HA powder and coating on Ti6Al4V.

![Fig. 5](image_url) XRD analysis of (a) pure HA powder and its coating on Ti6Al4V, (b) reinforced HA powder and its coating on Ti6Al4V.

![Fig. 6](image_url) Surface roughness (µm) and porosity (%) of pure and reinforced HA coating.
of polarization test are reported in Table 2. Corrosion current density coating is in Fig. 8. The range of passivation potential for pure HA and reinforced HA 3.6. Electrochemical polarization test

Tafel polarization curves of pure and reinforced coating are presented in Fig. 8. The range of passivation potential for pure HA and reinforced HA coating is $-0.72 \text{ V to } -0.38 \text{ V and } -0.5 \text{ V to } -0 \text{ V}$ respectively. Results of polarization test are reported in Table 2. Corrosion current density value of pure HA coating is slightly lesser than reinforced HA coating. From this it can be assumed that pure HA coating has marginally higher resistance to corrosion in SBF as compared to reinforced HA coating.

4. Conclusions

Pure and 10 wt.% (80Al2O3–20TiO2) reinforced hydroxyapatite coating was successfully deposited on Ti6Al4V substrate by plasma spray process. Following conclusions may be drawn from the characterization and measured mechanical properties corrosion behavior of in SBF.

1. Reinforcement by 10 wt.% (80Al2O3–20TiO2) leads to a denser and crack free coating.
2. Presence of some non crystalline phases like α-TCP, β-TCP and TTCP were observed to be 11.28% and 14.12% for pure and reinforced HA coating respectively.
3. Surface roughness with reinforcement.
4. Porosity of reinforced HA coating is decreased slightly.
5. Reinforcement has led to improvement in tensile strength of coating from 26.6 MPa to 32.2 MPa.
6. Improvement in micro hardness was observed with reinforcement as compared to pure HA coating.
7. Corrosion current density in reinforced HA coating was slightly higher i.e. 1.59 $\mu$A as compared to HA coating i.e. 1.53 $\mu$A.

Reinforcement with 10% (80Al2O3–20TiO2) has improved most desirable properties for coating for bio implants. However with reinforcement, it led to increase in non favorable phases like TCP and TTCP, these phases are prone to dissolution in body environment rapidly which may be deleterious.

References