Corrosion behaviour of plasma sprayed HA-TiO2 coatings on Ti6Al4V substrate

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ABSTRACT

This study was performed to investigate the corrosion behaviour of plasma sprayed Hydroxyapatite (HA) and HA-TiO2 double layer coatings on Ti4Al6V substrates. The coatings were characterized by X-ray diffraction (XRD) and Scanning electron microscopy (SEM) attached with Energy-Dispersive X-Ray Spectroscopy (EDX). Tafel and Potentiodynamic techniques were used to assess the in-vitro corrosion behaviour of two coatings and un-coated Ti4Al6V substrate. HA coated Ti6Al4V samples showed a good corrosion resistance however uncoated Ti6Al4V, TiO2 and HAP on TiO2 coatings produced comparatively low corrosion resistances.

Keywords: HVOF; Ti6Al4V; Hydroxyapatite; TiO2 coating

1. Introduction

Nowadays, with the increase of the aging human population, the need for biocompatible materials is continuously increasing in order to repair the damages of the bone tissues[1]. Generally, implants used in hard tissues are produced from metallic materials because metallic materials have good mechanical strength and toughness. Stainless steels, Co-Cr alloys, commercially pure titanium (CP Ti) and its alloys are widely used in biomedical application[2, 3]. Ceramic and polymer biocompatible materials are not as mechanically stable as metallic materials, especially under load-bearing conditions. However, metallic materials can corrode the body over time and create toxic effects and mechanical stability can be weakened[4, 5]. To avoid this situation, the surfaces of the metallic materials are coated with biocompatible ceramic HA and the corrosion resistance of the metallic materials can be increased[6]. Recently, various techniques have been applied to deposit HA coatings onto metal substrates such as, sol-gel coating[7], electrophoretic deposition[8], plasma spraying[9], high velocity oxy-fuel (HVOF) spray [10-12], and cold spraying[13, 14]. But plasma spray is the most commercially used technique for producing coatings close to bone tissue with high porosity percentage and good adhesion-cohesion strength. Traditional porosity microstructure accelerates the adaptation of HA coatings to bone tissue[5]. However, the porous structure allows the body fluid to come into contact with the metallic substrate and causes corrosion in the coating-substrate interface, resulting in weakness mechanical strength and adhesion of the coating. To overcome this, researchers suggested that double layer with the bond coat or functionally graded coatings and reinforcing HA coatings with ceramics such as Ti, TiO2, Alumina etc.. In the case of TiO2 being preferred as reinforcing addition, its favourable biological effects and high corrosion resistance were considered[15-19].

In the present study, Ti4Al6V substrate have been coated with the HA and TiO2 as a single and double layer. Microstructures, compositions, phase structures and corrosion behaviour of the coatings were characterized.

2. Experimental Procedures

Ti4Al6V cylindirical shaped samples with a diameter of .25 mm and thickness of 8 mm, were used as a substrate.
Prior to coating process, the substrate was grit blasted using 50-80 mesh alumina particles, in order to remove surface oxides and to improve adhesion of coatings. Commercial Sulzer Metco Amdry 6210 TiO₂ and spray dried HA powder were used to produce bioceramic coating layer. Figure 1 shows SEM image and EDX results of powders. HA powder is spherical shape but TiO₂ powder is angular shape.

![Figure 1](image.png)

**Figure 1.** SEM and EDX analysis results from a) HAP and b) TiO₂ powders [20].

The plasma gun was fastened on a three-axis CNC table and gun speed was selected as 600 mm/min. Grit blasted samples were fixed by using clamps on the turntable and turntable speed was selected to be 100 rpm and number of passes was selected as 12. Three types of coatings were produced by air plasma spray (APS) method by using Sulzer Metco 9MB plasma spray gun.

Gun nozzle is a commercial 730C and powder injection angle was placed perpendicular to plasma flame. Process parameters of plasma spray technique were listed in Table 1. The images of Ti6Al4V alloy before and after plasma spray coating is given in Figure 2.

<table>
<thead>
<tr>
<th>Before coating</th>
<th>After coating</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image.png" alt="Un-coated" /></td>
<td><img src="image.png" alt="HAP Coated" /></td>
</tr>
</tbody>
</table>

**Figure 2.** Images of specimens and coatings deposited on Ti6Al4V substrate before and after coating process

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current (Ampere)</td>
<td>500</td>
</tr>
<tr>
<td>Primary gas, Ar (scfh)</td>
<td>90</td>
</tr>
<tr>
<td>Secondary gas, H₂ (scfh)</td>
<td>15</td>
</tr>
<tr>
<td>Carrier gas flow rate, Ar (scfh)</td>
<td>13.5</td>
</tr>
<tr>
<td>Number of passes</td>
<td>12</td>
</tr>
<tr>
<td>Spray distance (mm)</td>
<td>75</td>
</tr>
<tr>
<td>Gun speed (mm/min)</td>
<td>600</td>
</tr>
<tr>
<td>Turntable speed (rpm)</td>
<td>100</td>
</tr>
</tbody>
</table>

**Table 1.** Air plasma spray process parameters.

The microstructure, morphology and chemical composition of coatings were examined by Scanning electron microscopy (Leo 1430 VP) which is equipped with EDX. X-ray diffraction technique (Shimadzu 6000) was used to
determine the crystalline structure of the powder and coatings.

Corrosion test of coated and uncoated Ti4Al6V samples were performed in simulated body fluid (SBF) with a time of 1 hour. SBF contained NaHCO3, MgCl2·6H2O, CaCl2·2H2O, K2HPO4·3H2O, Na2SO4, KCl, NaCl and NaN3. At the end of incubation time, the electrochemical-corrosion behaviour of samples was investigated by the electrochemical Tafel extrapolation and linear polarization methods. Corrosion current (Icorr), corrosion rate, polarization resistance (Rp) and corrosion potential (Ecorr) were determined from the current density-potential curves obtained from corrosion tests. Then, the corrosion current density (Icorr) was found by dividing the corrosion current by the surface area of the specimen.

3. Results and discussions

3.1 Characterization and microstructure of coatings

SEM-EDX images and optical cross-sections taken from the surface of the coated Ti6Al4V alloy are given in Fig 3. When Figure 3 is examined, it can be seen that both TiO2 and HAP + TiO2 coatings adhered homogeneously to the surface. The powders that were sprayed and melted through the plasma hit the substrate and then formed a coating with flat and lamellar structure. HAP coated layers were successfully deposited on the substrate without degradation and reaction with the substrate (Ti6Al4V alloy)[20, 21]. Unmelted powders, porosity and oxides are present in the coating layer of TiO2[22]. The microstructural images showed that there is no delamination that will allow any cracks and to separate upper layer from the substrate. Figure 3 also shows the porosities that are generally found in thermal barrier coatings. Porosites, a characteristic feature of plasma spray coatings, can be found in coatings up to 20% depending on the type of powder material used[20].

As a result of EDX analysis from the surface of the coated Ti6Al4V alloy specimens, it was determined that coatings were formed on the surface and their thicknesses were measured to be 42 μm, 65 μm and 165 μm for HAP, TiO2 and HAP + TiO2, respectively. In the HAP + TiO2 coated sample, the TiO2 peaks was not detected because the overall coating thickness was 162 μm (HAP: 77 μm, TiO2: 85 μm). As can be seen in Figure 3a from EDX study that Ca, P and O, which are the main elements of HAP powders, have been detected on the surface [23, 24].

![Figure 3. SEM-EDX and Optic images of a) HA coated Ti6Al4V, b) TiO2 coated Ti6Al4V, c) HA+TiO2 coated Ti6Al4V specimens.](image-url)
### 3.2 Microhardness of coatings

The hardness values obtained in HV with the top coatings at a certain intervals for 15 seconds and 300 g load are shown in Table 2.

<table>
<thead>
<tr>
<th>Material</th>
<th>HV&lt;sub&gt;0,03&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA Coating</td>
<td>573</td>
</tr>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt; Coating</td>
<td>920</td>
</tr>
<tr>
<td>HAP + TiO&lt;sub&gt;2&lt;/sub&gt; Coating</td>
<td>720</td>
</tr>
<tr>
<td>Ti6Al4V alloy</td>
<td>HRC 33</td>
</tr>
<tr>
<td>HA&lt;sup&gt;25, 26&lt;/sup&gt;</td>
<td>537.5-580</td>
</tr>
<tr>
<td>Cortical Bone&lt;sup&gt;25, 26&lt;/sup&gt;</td>
<td>40,4</td>
</tr>
<tr>
<td>Alveolar Bone&lt;sup&gt;25, 26&lt;/sup&gt;</td>
<td>35,2</td>
</tr>
</tbody>
</table>

Table 2. Micro-Hardness Values obtained from specimens.

In general, the hardnesses of the coating deposited by plasma spray are higher than those in natural form or uncoated conditions. The hardness of synthetic HAP appears to be relatively high if we compare the hardness of natural bone microhardness with that of synthetically produced HAP<sup>25, 26</sup>. The hardness of the TiO<sub>2</sub> layer is the highest amongst all specimens and TiO<sub>2</sub> coated specimens can be used where corrosion resistance is high and static strength is needed at the same time <sup>27</sup>.

3.3 Electrochemical corrosion tests

Corrosion of HAP, TiO<sub>2</sub> and HAP + TiO<sub>2</sub> Coated and Uncoated Ti6Al4V alloy characteristics obtained by Tafel and linear polarization method as a result of 1 hour holding time in SBF environment are given in Table 3 and Tafel curves are given in Figure 4.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Solution</th>
<th>Icorr. (µA)</th>
<th>Ecorr. (mV)</th>
<th>Corrosion Rate x 10&lt;sup&gt;-3&lt;/sup&gt; (mpy)</th>
<th>Rp Değeri (kΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated</td>
<td>SBF</td>
<td>1.460</td>
<td>-440</td>
<td>407.5</td>
<td>105.7</td>
</tr>
<tr>
<td>HAP</td>
<td></td>
<td>0.503</td>
<td>-305</td>
<td>62.16</td>
<td>187</td>
</tr>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td></td>
<td>9.520</td>
<td>-352</td>
<td>1176</td>
<td>10.81</td>
</tr>
<tr>
<td>HAP + TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td></td>
<td>1.870</td>
<td>-448</td>
<td>231.1</td>
<td>34.79</td>
</tr>
</tbody>
</table>

Table 3. Corrosion characteristics obtained in SBF medium.

When Table 3 and Figure 4 are examined, the polarization current density (iCorr) values of TiO<sub>2</sub> and HAP + TiO<sub>2</sub> coated samples increased after 1 hour of incubation in SBF medium while the current density values of HAP coated samples decreased. The values of the polarization current density are 1.460 µA / cm<sup>2</sup> in the uncoated state, while the polarization current density values in the coated samples vary between 0.503-9.520 µA / cm<sup>2</sup> depending on the type of coating. The best corrosion resistance was obtained in HAP coated specimens <sup>24</sup>.

The expected improvement in corrosion resistance from TiO<sub>2</sub> and HAP + TiO<sub>2</sub> was not achieved because the icorr values of the TiO<sub>2</sub> and HAP + TiO<sub>2</sub> coatings on the Ti6Al4V alloy surface were higher than the uncoated state and the Rp values were very low compared to the uncoated condition. It is believed that during the TiO<sub>2</sub> and HAP + TiO<sub>2</sub> coating, the coating layer is not fully adhered and also due to the porosity formed between the coating layer and the substrate.

![Figure 4. The Tafel curves obtained in SBF solution for 1 h holding time.](image)

Figure 5 shows SEM images taken from the surfaces after the electrochemical corrosion test. Salt crystals from the SBF solution appear on the surface of the uncoated Ti6Al4V alloy. Cracks are seen on the surface of the TiO<sub>2</sub> coating which has the worst corrosion resistance amongst all the specimens. It can be said that SBF solution dissolves the
matrix around these cracks and reduces corrosion resistance.

4. Conclusions

The following results were obtained as a result of single layer and double layer coatings using HAP and TiO2 powders by the plasma spray coating method on the surface of the Ti6Al4V alloy. 
In the SEM-EDX examinations after plasma spray coating, HA, TiO2 and HAP + TiO2 coatings were found to have formed a homogeneous thickness on the surface. 
Surface hardness of Ti6Al4V alloy increased after plasma spray coating. The HAP coated samples showed an improvement of about 50% in the SBF solution in the corrosion resistance during the 1 hour hold time, but the expected improvement in corrosion resistance in the TiO2 and HAP + TiO2 coatings was not achieved.
The worst corrosion resistances were obtained in TiO2 coated specimens due probably to the formation of reactions leading to the erosion of matrix around the cracks that are intrinsically present in the coating.

References

10. Khor KA, Li H, Cheang P. Processing-microstructure-property relations in HVOF sprayed calcium