Investigation the properties of hip implantation structure based on nanotechnology by using radio frequency magnetron sputtering

Dunya Abdulsahib Hamdi 1, 2

1 Department of Prosthetics & Otorthics Engineering Department, Al Nahrain University, Baghdad, Iraq.
2 Surface Analysis and Materials Engineering Research Group, School of Engineering and Information Technology, Murdoch University, Murdoch, WA 6150, Australia.

Received 20 Jan. 2017; Received in revised form 25 Mar. 2017; Accepted 26 Mar. 2017; Available online 1 Nov. 2017

Abstract
In this research, radio frequency magnetron sputtering was used to prepare the Ti6Al4V alloy by powder ceramic Alumina (Al2O3 has 1um particle size, alpha phase, with purity is 5N (99.999%)) in order to increasing biocompatibility surface alloy. Energy Dispersive X-ray spectroscopy, X-ray diffraction, Scanning Electron Microscopic and Optical microscope were performed to identify phases and microstructure. In vitro studies were carried out in simulated body fluid and HP 7.4 with biomimetic tests to see the efficiency of the biocompatibility of the coated surface. Energy Dispersive X-ray spectroscopy chemical analysis showed increasing in Al2O3 and a reduction in Ti content with increasing time deposition. X-ray diffraction phase analysis agreement with Energy Dispersive X-ray spectroscopy results, increasing intensity phase (110) and crystalline with heat treatment at 500°C. The Al2O3 phase disappeared after immersed and Hydroxyapatite (HAp) phase is very visible with full coated covered the surface with high intensity (002) and (211). Scanning Electron Microscopic showed the Al2O3 good coating and there is no crack appearing with convert particle size to 50nm by using radio frequency sputtering, HAp coated all the surface with particle size 300nm after immersion in SBF that is mean the surfaces is biocompatibility and this confirm by Optical microscopy, according to the result the coating will be compatible with human tissue.

Keywords: Ti-6Al-4V alloy; Radio frequency magnetron sputtering; Ceramic coating; Biomaterial; Simulated body fluid and microstructure.

1. Introduction
Biomaterial is defined by the natural or synthetic material that is suitable for interaction into living tissue especially as part of medical device the, they have many characteristics including mechanical, physical, chemical and biological properties that make it suitable for safe, effective, and reliable use within a physiologic environment, as titanium alloy and ceramic represent the type of biomaterial [1]. Titanium and titanium alloys have been extensively studied for many applications in the area of bone tissue engineering due to the light weight, excellent corrosion resistance, high mechanical strength and low elastic modulus. This structure make the titanium alloys used in biomedical devices including screws, hip
and knee prostheses, plates, for either bone replacement or bone fractures [2]. Different methods were done for enhancing the Osseo integration and bioactivity characteristics of the metallic implants such as the coating of the metallic implants with ceramic [3]. Ceramic materials use to cover the implants which used in medical applications, include bioactive ceramics. Al$_2$O$_3$ molecule is one of the stable oxides belong to ionic and covalent bonds between Al and O atoms. These strong bonds leave the ceramic unaffected by galvanic reactions (absence of corrosion, e.g. absence of ion release from bulk materials and from wear debris). Wear debris reduces by using femoral heads of Al$_2$O$_3$ ceramic bearing against Al$_2$O$_3$ cup sockets [4, 5]. For instance, Al$_2$O$_3$ has thermal expansion coefficient is very close to that of Ti alloy, the thermal expansion coefficient of Ti alloy substrate is 8.7 × 10$^{-6}$/K and for Al$_2$O$_3$ is 8.2 × 10$^{-6}$/K this lead to reduce mismatch between coated layer and substrate also prevent formation cracks when cooled from the evaluated temperature[6]. Substation many researches has been done for growth alumina thin film with deposition by magnetron sputtering. Since alumina is a very good insulator a radio frequency (RF) alternating current is best method to be used. An advantage of sputtering, is that and the properties of film under control the sputtered flux of atoms will, at steady state conditions, have the same composition as the target, also particle size convert from micro to nanosize during sputtering [7]. The Particle with nanosize main reducing the grainsize of film that is lead to improve in mechanical properties like strength, wear resistance and hardness [8]. The α-alumina (which is the thermodynamically stable polymorph and very good mechanical properties) growth with different methods, typically requires temperatures above 1000 °C which limits the choice of substrate material such as titanium alloy to those that can withstand high temperatures. α-Al$_2$O$_3$ films was deposit With a negative bias voltage of 200 V and pre-heating the substrate to a lower temperature of 460 °C [9]. The parameters of double glow plasma technique was control to prepare α-Al$_2$O$_3$ coatings were optimized to get dense and thick α-Alumina coatings on stainless steel 316 L at low temperature of 580 °C [10]. RF magnetron sputtering used to study the effect of heat substrate and under layer effect on the structure of Al$_2$O$_3$ films [11]. The aim of this study to improve the alumina coating, growth with small nano size and lowering temperature for prosthetics application.

1.1 Materials
The material was used α Al$_2$O$_3$ (Aluminum has 1um particle size, alpha phase, with purity is 5N (99.999%)) provided from VTFM(Vacuum Thin Film Materials).The substrate was used titanium alloys (Ti-6Al-4V) GR2 ASTM F136 (Baogi Jinsheng Metal Material Co. Ltd). According to the manufacturer, have a chemical composition show in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>Ti</th>
<th>Al</th>
<th>V</th>
<th>Fe</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>89.2</td>
<td>5.5-6.5</td>
<td>3.5-4.5</td>
<td>0.40</td>
<td>0.1</td>
<td>0.05</td>
<td>0.20</td>
<td>0.0125</td>
</tr>
</tbody>
</table>

2. Experimental techniques
The Ti-6Al-4V alloy surface modification by deposited biocompatibility of Al$_2$O$_3$. The coatings were deposited on Ti-6Al-4V alloy from Al$_2$O$_3$ targets, using an radio frequency(RF) magnetron sputtering system with Ar gas. The as-deposited Al$_2$O$_3$ coatings were amorphous, to promote their crystallization, the samples were annealed in an oven for 1 hour at 500°C. The specimens of Ti-6Al-4V alloys were used as substrates in plasma sputtering system with a circular shape of 2 cm diameter and 1.8 mm thickness. The specimen alloys were grained with various grades of SiC paper such as 180, 240, 320, 500, 600, 800, 1000, 1200, 1800 and 2500 μm of grain size and polished using Struers-DAP-U system, Denmark. The polished alloys were etched and ultrasonically cleaned. The vacuum chamber of RF sputtering device was of 1 × 10$^{-7}$ Torr, and operation frequency generator was 13.65 MHz with working pressure was 4 × 10$^{-3}$ Torr with keep all the conditions work constant and change time of sputtering, the process condition was used can be seen in Table2. This condition have been determine by experimental work (pilots study). In vitro studies were carried out in simulated body fluid (SBF), biomimetic are based on the growth of calcium phosphate SBF, to produce an apatite layer on the surface of Ti implants, increasing their consequently favouring Osseo integration and osteoconductivity. Passive conducted the biomimetic tests to see the efficiency of the biocompatibility of the coated surface. The biocompatibility experiments were performed by immersing Ti-6Al-4V alloy samples coated with Al$_2$O$_3$ single layer for one month in SBF with the compositions shown in Table 3.
Table 2. Deposition conditions of (Al₂O₃) films coated onto Ti-6Al-4V alloy using RF sputtering technique.

<table>
<thead>
<tr>
<th>Types of deposition single layer</th>
<th>Al₂O₃ layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power (W)</td>
<td>200</td>
</tr>
<tr>
<td>Working pressure (Torr)</td>
<td>4 × 10⁻³</td>
</tr>
<tr>
<td>Substrate temperature (°C)</td>
<td>250</td>
</tr>
<tr>
<td>Distance between target and substrate (cm)</td>
<td>5</td>
</tr>
<tr>
<td>Time deposition (tD) of Al₂O₃ (hours)</td>
<td>2,4&amp;6</td>
</tr>
</tbody>
</table>

Table 3. The concentration of SBF [7].

<table>
<thead>
<tr>
<th>Materials</th>
<th>Weight in mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium chloride NaCl</td>
<td>8.036</td>
</tr>
<tr>
<td>Calcium chloride CaCl₂</td>
<td>0.293</td>
</tr>
<tr>
<td>Sodium bicarbonate NaHCO₃</td>
<td>0.352</td>
</tr>
<tr>
<td>Potassium chloride KCl</td>
<td>0.225</td>
</tr>
<tr>
<td>Dipotassium hydrogen phosphate trihydrated K₂HPO₄H₂O</td>
<td>0.230</td>
</tr>
<tr>
<td>Magnesium chloride six hydrated MgCl₂H₂O</td>
<td>0.311</td>
</tr>
<tr>
<td>Sodium kpretait Na₂SO₄</td>
<td>0.072</td>
</tr>
</tbody>
</table>

The X-ray Diffraction (XRD- Rigaku Ultima JV, japan, with 20 KV,2mA and 0.04KW with a monochromatic radiation scanned Cu Kα (1.54056 Å)) were performed to measure the identity of the various phases in the films over a 20 range with a step size of 0.01°. The thickness of coatings deposited onto Ti-6Al-4V alloys was estimated using side view of SEM images (SEM, HITACHI 5-4800 japan), while the surface morphology of the films were investigated with Scanning Electron Microscopic (SEM). The SEM was operated at 25 kV. The elemental composition of the films was obtained by energy dispersive spectroscopy EDS (EDS, PHILIPS XL series, japan).

3. Results and discussion
3.1 Before immersion
3.1.1 Microstructure examination (Opticalmicroscopy)
By using the optical microscopy to show that structure of coating in micro size. Figure (1-a) shows the structure of alloy Ti-6Al-4V alloy without coating it is clear from the optical examination that the crystal structure of the alloy is very clear and the grain boundary spirited the grain of Ti alloy. Figure (1-b) shows the structure of the alloy after coating and heat treatment used to obtain the α-Al₂O₃ phase resulting in relative stability of most common Al₂O₃ particle. The growth of α-alumina phase (Al₂O₃) like finger on the surface of Ti alloy is very clear as shown in the Figure (1-b) after 6 hours and also the morphology of the surface does not show any micro crack and porosity in the coating layer by using RF magnetron sputtering.

![Figure 1. The microstructure of Ti6Al4Valloy before and after coated with Al₂O₃ layer.](image)

3.1.2 Energy dispersive X-ray spectroscopy (EDS)
Energy Dispersive X-ray spectroscopy were used to investigate the chemical composition of the Ti-6Al-4V alloy uncoated and coated with Al₂O₃ layers as shown in Figure 2. The energies transition 4.508KeV
and 4.93 KeV belong to Ti Kα and Ti Kβ respectively. 0.5 KeV energy belong to O Kα. The peaks of energy transition of the AlKα that appears at energy of 1.48 KeV which belong to layer of Al2O3 coated and substrate. The EDS patterns of the as resived Ti-6Al-4V alloy uncoated shows in Figure 2.a, the intensity: 0.5 for O Kα, 0.1 for Al Kα and 2.58 for Ti Kα. The chemical analysis report showed low concentration Al2O3 is about 3.9 wt% with a high content Ti to 85.5 wt%. Figure 2 (b, c & d) represent Ti-6Al-4V alloy coated with Al2O3 at different time for tD 2, 4 & 6 hours respectively. The increasing in intensity (0.6, 1.5 & 1.7) for AlKα and decreasing in intensity (2, 1.5 & 0.7) for Ti Kα belong to increasing the time of deposition. The intensity of O Kα increasing (0.4, 0.7 & 0.72) with time deposition belong to oxidation layer. The chemical analysis report in Table 4 showed increasing in Al2O3 particles is about 19.7, 27.4 &30.0 wt% with a reduction in Ti content to 43.5, 29.6&25.1 wt%. The increasing of Al2O3 particles deposition the reduction of Ti particle [12].

Figure 2. EDS spectra of: (a) Ti-6Al-4V alloy uncoated, (b), (c) & (d) single layer Al2O3 for tD 2, 4&6 hours respectively coated on Ti-6Al-4V alloy.
3.1.3 Scanning electron microscopy (SEM)

The experimental part of other studies was focused on growth of phase α alumina thin films at low-temperature below 1000 °C [7]. Figure 3 shown image of Al₂O₃ coated on Ti-6Al-4V alloy at tₖ, 6 hours. The morphology of surface was good coating and there is no crack observed because substrate heated during deposition which is one of most important properties of RF sputtering, during deposition proses the alumina particle and substrate has high temperature so it solidified slowly. Other authors used plasma spray technique for coating, hot Al₂O₃ particle contact with cold NiAlSi substrate, it soldificate very fast which it is lead to crack [18]. The coating growth particles finger-like (like particle which observed by optical Figure (1-b) and diffused is observed after heat treatment, there are no defect in layer but has high porosity. The mechanism via surface diffusion is achieve by the diffusion of atoms along the surface of adjacent particles without shrinkage, this result agreement with Chih-Jen Wang et al worked at 1250 °C for centring alumina [8]. The nanosizs of alumina with particle size approximately 50nm have strong surface charge this lead to aggregation as shown in Figure 3. The SEM photograph has been choosing for the beast result of EDS analysis.

3.1.4 X-ray diffraction (XRD)

Figure 4 shows the X-ray Diffraction (XRD) patterns of the precipitation products for investigation of effects of different time deposition Al₂O₃ coated Ti-6Al-4V alloy. The XRD patterns exhibit the crystal major phase presented in alpha alumina (αAl₂O₃) due to coated layer with diffraction angles (37.7°,76.8°& 77.2°) belong to plans(110,1010&119) and at increasing time deposition (6 hours) the intensity of plan(110) increasing also appear plan(119).The phase δAl₂O₃ at peak (32.7°) belong to alumina coated [13] was found the thickness of film increasing with increasing the content phase δAl₂O₃. The different phase alumina appearing at increasing the thickness of film [14]. This results agreement with X-ray Diffraction XRD pattern of plasma sprayed AlN powder into distilled water [15]. Titania (TiO₂) at angles(32°) with planes (101) belong to natural oxide layer of alloy consist of (TiO₂, Ti₂O₃ and TiO) [16]. It was observed that by increasing in time deposition, the intensity of signals phase Al₂O₃ are increased and agreement with EDS. In this experimental with RF sputtering the peak energy αAl₂O₃ is higher the
same phase result from Al₂O₃–Al composite coatings deposited by plasma spraying [17]. The sharp peaks belong to high crystal and nano size particle alumina and this agreement with result of SEM.

Figure 4. XRD patterns of the Al₂O₃ coated Ti6Al4V alloy for 2, 4 & 6 hours deposition time tD.

3.2 After immersion in SBF
3.2.1 Microstructure examination (Optical microscopy)
Figure 5 shows the microstructure immersing Ti-6Al-4V alloy samples coated with Al₂O₃ single layer for one month in SBF and the layer of HAp is very visible with full coated, the substrate and Al₂O₃ layer approximately disappear. The composite of HAp in solution of SBF attractive to the surface of sample and great thick layer from HAp as shown in Figure 5 this mean the surface is biocompatibility.

Figure 5. The microstructure of Ti-6Al-4V alloy coated with Al₂O₃ layer after immersion in SBF, with full coated HAp layer.

3.2.2 Scanning Electron microscopy (SEM)
The HAp growth on surface of sample this means the surface with biomaterial properties. Apatite was present as aggregates, showed different shapes as rough, granular to dense and its particles, thick-like plates as shown in Figure 6 like shape particles precipitation was observed [4, 20]. Also the particle with nano size approximately 300nm and uniform grain size with a narrow size distribution corresponding to the crystallinity improvement of the HAp powders after heat treatment at 500°C.

3.2.3 X-ray diffraction (XRD)
From Figure 7 the Al₂O₃ peaks disappear due to the high thick of Hydroxyapatite (HAp) layer and the strong HAp was at (112) and (002) at (32.19 and 25.86) respectively with high intensity which demonstrate that the most stable phase is HAp, this mean an improvement in the coating crystallization Al₂O₃ and has good bonds between the particles of Al₂O₃ and HAp by using plasma sputtering. The Al₂O₃ (110) at Figure 4 dissolved and disappear after immersed the sample in SBF. Also other peaks for HAp at (102), (300) and (421) belong to Ca₅H (PO₄) 2.5H₂O other calcium phosphor compound phases. This preferred orientation suggested that high coating and chemical reaction between the different
components were occurred. The purpose from immersing the samples in SBF is to attract the apatite species (Ca &P) spectra from solution. This result is in a good agreement finding [19].

Figure 6. Top-view SEM image of Al₂O₃ coated on Ti-6Al-4V alloy at t₀, 6 hours after immersion.

Figure 7. XRD patterns of the Al₂O₃ coated Ti-6Al-4V alloy for 2, 4 & 6 hours deposition time t₀ after immersion.

4. Conclusions
1. X-ray diffraction shows alumina Al₂O₃ and base metal (Ti-6Al-4V) peaks disappear due to high thickness of coating.
2. There is no crack observe by SEM after deposition because the substrate heated before and during coating process.
3. The alumina nano size particles have strong surface charge which lead to aggregation. The SEM shows different shape of aggregate it is particles like thick plates, the aggregate depend on size of particle and coating method.
4. Uniform grain size distribution due to crystalline improvement after heat treatment at 500 °C.
5. The surface biocompatibility improvement and the piratical size of Al₂O₃ converted from micro to nano size, this agrees with nano size of cell human. According to the result the coating will be compatible with human tissue.

References


