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Electrophoretic Deposition of Thin Film TiO_2 on Ti6AL4V Alloy Surface for Biomedical Applications

Muslim Idan Hamil[1*], Murtdha Adhab Siyah[2], Mohammed K. Khalaf[3]
[1] *Department of physics, College of Science, University of Misan, Maysan, Iraq*
[2]*Department of Radioactive Waste Treatment and Management, Ministry of Science and Technology, Baghdad, Iraq*
[3]*Department of Plasma, Ministry of Science and Technology, Baghdad, Iraq*

THE electrophoretic deposition technique (EPD) is an effective method to deposit bioactive and biomedical thin films. The EPD technique was used to deposit titanium dioxide (TiO_2) thin films on Ti-6Al-4V substrates under 30 V for 0.5, 1 and 2 min. The films produced in 1 and 2 minutes show the anatase phases TiO_2. The bio corrosion measurement for uncoated and coated films in simulated body fluid (SBF) appears that the samples coated with TiO_2 have more noble behaviors compared with uncoated samples. The corrosion rate was 2.970×10^{-4} mm/y for the sample deposited within the potential range of -273.875 mV.

Keywords: Electrophoretic, Titanium dioxide, Nano TiO_2, a Ti-6Al-4V alloy, Deposition, EPD and biocorrosion.

Introduction

Recently there has been a surge of interest in metallic biomaterials and its alloys owning to their exciting properties such as biocompatibility, corrosion resistance, low density and mechanical strength[1, 2], these properties make titanium and its alloys a potential dental implant material. Ti6A14V is one of the important titanium alloy and it has been mainly used as a biomaterial in the orthopaedic field because it has a good biocompatibility. However the disadvantages of using this alloy are mostly its low wear resistance, as well as its low hardness, in order to improve the corrosion resistance and osseointegration of the titanium and its alloy, many biocompatible ceramics materials were investigated such as titanium, TiO_2, hydroxyapatite, alumina and zirconia [3,4, 19]. Several methods, such as sol-gel process [5], vapor phase deposition [6, 7], micro-arc oxidation [8], and electrophoretic deposition [9] were used to produce TiO_2 coatings. Electrophoretic is considered as a simple, low cost method, and its ability to control the surface morphology and the thickness of the coatings [10]. EPD Consists of the migration of the suspension under an electric field, the particles agglomerate to form a homogeneous layer on the surface of the substrate. In the present study, we studied the deposition of TiO_2 on Ti-6Al-4V alloy substrates by electrophoretic method in synthetic simulated body fluid. The corrosion behavior was investigated by measuring polarization curve (Tafel).

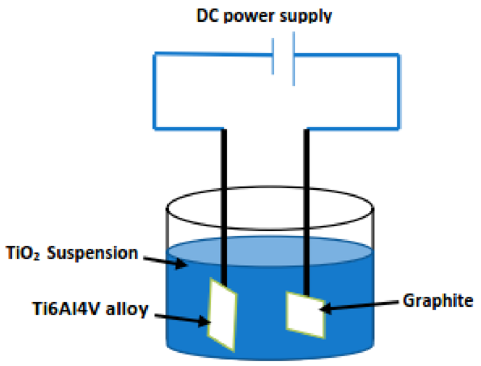

Fig. 1. Electrophoretic deposition cell.

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*Corresponding author e-mail: muslim.iddan@uomisan.edu.iq
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Materials and Method

Preparation of the suspensions

Ti6Al4V substrate were purchased from Bauji, China, the composition of alloy is Ti:90%, Al:6% and V:4% the electrophoretic suspension electrolyte was prepared by the suspension of 6 gm TiO_2 with particle size (10-30 nm) in 50 ml ethanol 99%, 0.1 gm iodine was added to the suspension [11,12]. The suspension was vigorously stirred for 20 minutes using a a magnetic stirrer hot plate. The structure characterization was investigated by X-ray diffraction (Philips Expert MPD, Cu Kα radition) (λ=1.54 A). The corrosion process were determined by using potentiostat (PARSTAT 2273, USA).

Preparation of Ti6Al4V substrate

Ti6Al4V samples were cut to 20mm 20mm diameter was grinded by 500 micron SiC grinding paper. Sonically, cleaned by using ultrasonic, twice in ethanol 96% (Sigma Aldrich, England), then by distilled water for 15 min and allowed to dry in discaiter at room temperature for 24h.

EPD coating

The Ti-6Al-4V alloys samples were coated by connected as cathode to power supply and a graphite sheet 20×80 mm^2 used as anode, the distance between the two electrodes were 15 mm, the voltage was applied at 30 volt [13] and time intervals 0.5, 1, and 2 minutes for each group of samples, as shown in figure (1). The samples were heated at 400 ºC for 1 hr. under air atmosphere by tube furnace. The samples were then tested by using polarization curve (tafel) in synthetic simulated body fluid (SBF) which was prepared by dissolving the chemicals listed in Table (1) in 1 liter deionized water, the pH was adjusted to pH=7.4 using hydrochloric acid or sodium hydroxide as required.

TABLE 1. Chemical composition of synthetic simulated body fluid (SBF)[14].

ITEM	Description	Quantity gm/l
1	NaCl	8.036
2	KCl	0.225
3	$CaCl_2$	0.293
4	$NaHCO_3$	0.352
5	$K_2HPO_4.3H_2O$	0.230
6	$MgCl_2.6H_2O$	0.311
7	Na_2SO_4	0.072

Results and Discussion

The TiO_2 is a polymorphic ceramic material, which could exist, in three well-known structure figures: rutile (tetragonal), anatase (tetragonal), and brooked (orthorhombic). Figure (2) shows the XRD pattern of the Ti-6Al-4V alloy coating with TiO_2 by electrophoretic deposition. We noted by the XRD pattern of sample coated with TiO_2 at time (0.5 min) not any change in crystal structure by compare with uncoated alloy and only the peaks that appeared from the Ti was observed, the diffraction peaks at = 35.13^0 and 40.2^0 correspond to (100) and (101) planes of the titanium, while other materials of alloy not appeared, due to it were percentage in the alloy, could not be refracted. All the peaks are good agreement with the diffraction code 00-044-1294 [15]. The anatase was observed in the diffraction peaks at 2θ= 25.2^0, 36.9^0, 37.7^0, 38.5^0, 48^0, 53.8^0, 55^0, 62.6^0, 68.7^0, 70.2^0 and 75.1^0 correspond to (101), (103), (004), (112), (200), (105), (211), (204), (116), (220) and (215) planes of anatase, respectivity, and all the peaks are agreement with (JCPDS no.:84-1286) [16].

Corrosion measurements

The polarization curve (Tafel) diagram for titanium dioxide covered samples with distinct phases (0.5,1, 2) minutes, the potential polarization curves were presented in Figure(3). When the Ti6Al4V alloy was in immersed in SBF, the corrosion potential was (-395.391) mV. The corrosion potential shifted to the cathode side for samples coated with TiO_2 at deposition time of 0.5,1 and 2 min, the potential values were -361.822, -324.794, and -273.875 mV, respectively.

The electrochemical corrosion measurements of the uncoated Ti6Al4V and the coated Ti6Al4Vsamples prepared in 0.5, 1 and 2 min were obtained using the electrochemical cell configuration in SBF. Coated samples exhibited significant change in corrosion rate. (Fig. 4), the corrosion rate of 2.970×10^{-4} mm/y was observed for sample immerses for 2 min. In contrast, a higher corrosion rate of 8.750×10^{-3} mm/y was obtained for uncoated sample.

Table (3) contain on some of corrosion characteristics of coating TiO_2 on Ti6Al4V alloys at different time periods shows the passivation current (the current of passivation region in tafle curve) and weight loss for the samples. We see that the passivation current become less with increasing

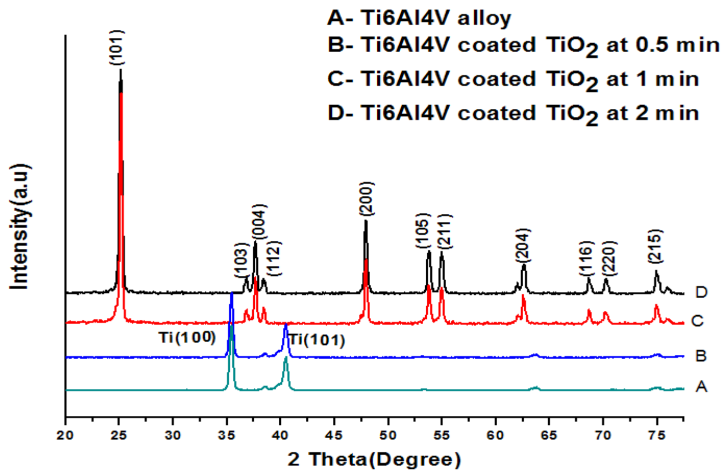

Fig. 2. XRD pattern for Ti-6Al-4V coated samples with TiO$_2$.

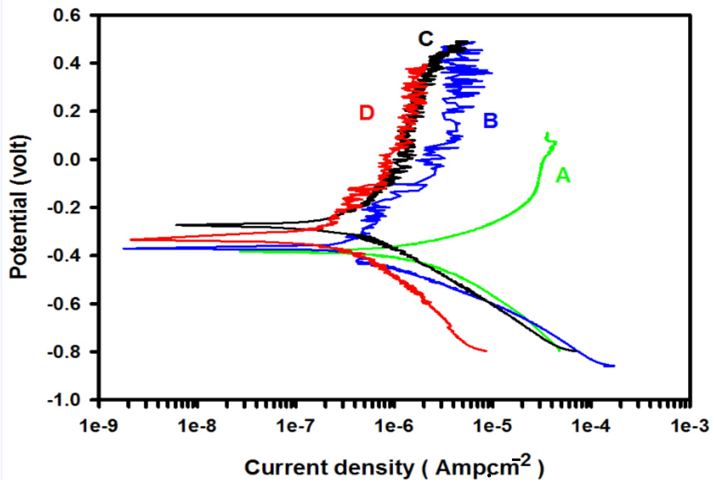

Fig. 3. Polarization curves (Tafel) for Ti-6Al-4V alloy, A: uncoated. B: coated at 0.5mim. C: coated at 1min. D: coated at 2min.

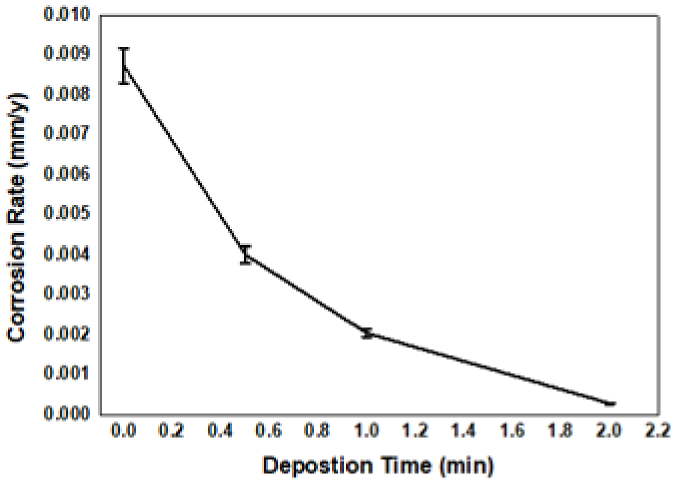

Fig. 4. Corrosion Rate of coating TiO$_2$ on Ti6Al4V alloys, a:uncoated ,b: coated at 0.5 min., c:coated at 1 min. and d: coated at 2 min.

TABLE 2. Corrosion characteristics of Ti6Al4V samples coated with titanium dioxide a: un coated ,b: coated at 0.5 min., c:coated at 1 min. and d: coated at 2 min.

ITEM	i Cor. (Amp)/cm^2	E Cor. (volt)	Cor. Rate (mm/y)
Uncoated	1.006×10^{-6}	-0.385	8.750×10^{-3}
0.5 min	4.627×10^{-7}	-0.363	4.024×10^{-3}
1 min	2.365×10^{-7}	-0.269	2.057×10^{-3}
2 min	3.002×10^{-8}	-0.330	2.970×10^{-4}

coating time period, because the increasing in coating thickness make the corrosive ions does not easily penetrate the coating layer , so that the current which result from liberating electrons in the surface of the metal and cause less current pass during the corrosion process. The Faraday's low shows the proportionality between the current pass during electrochemical reaction (I) and mass reacted (w) with time (corrosion rate) is given by the equations (1,2,3) [17]. The weight loss calculated from corrosion rate depended on the equations:

$$dw/dt = (I\ t\ M)/ZF \qquad (1)$$

Where M is the molecular weight, Z is the number of reciprocal charge and F is faraday constant. And by dividing the equation by area, eq.(1) will be:

$$w/At = ItM/ZFA \qquad (2)$$

Where M/Z was the equivalent weight Eq and I /A was the current density i, so that the relation (2) will be:

$$w/At = iEq/F \qquad (3)$$

The weight loss w/At (W) was in gram per cm^2 second), but the corrosion rate can also calculate by unit millimeter/year (mmy), as follows: $g/((cm^2\times sec)\times 3600\ sec/hr. \times 24\ hr/d \times 365d/y \times (1/100)\ cm^2/mm^2) =$ cor. rate $g/(mm^2\times y)$

By dividing the relation by density ρ (g/cm^3) the corrosion rate will be:

$W/\rho = cor.rate / (\rho\ g/cm^3 \times 0.001 cm^2/mm^2) =$ cor. Rate mm/y

$$W = cor.\ Rate\ mm/y \times \rho \times 3.171 \times 10^{-9} \qquad (4)$$

Table (3) shows the reduction of weight loss value with increasing coating time. This was expected because of the reduction in corrosion rate means the reduction in weight loss from samples material.

The polarization resistance (Rp) calculated from the slopes of cathodic and anodic slopes (bc and ba) by relation (5) below to evaluate how the coating impede and remedy the corrosion. The polarization resistance increased with increasing coating time as shown in table(4), i.e. the increasing in coating thickness lead to increasing in polarization resistance and hinder the corrosion [18].

$$R_p = \Delta E/\Delta i \qquad (bc \times ba)/(2.303 \times icor.\times(bc+ba)) \ (5)$$

Conclusion

The coating of increasing period of Ti6Al4V alloy with TiO_2 layer by EPD improved the corrosion properties, such as the corrosion rate (Cor. rate) and the polarization resistance (R_p). The corrosion rate decreased, where was $8.750x10^{-3}$ mm/y for uncoated sample, while be $2.9750x10^{-4}$ for 2 min period coated sample, and also, the polarization resistance increased, (RP) be 303.919 KΩ/cm^2 for 2min coated, while was 33.264 KΩ/cm^2 for uncoated sample. All the coated sample appeared to be more noble in corrosion behaviors and decreased the value of corrosion values MPY (corrosion velocity) and current, meaning the TiO_2 coating has good protection for Ti6Al4V alloy in SBF and could be used in biomedical applications.

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TABLE 3. Shows the reduction of weight loss value with increasing coating time.

ITEM	Passivation current (Amp)	Weight loss ($mg.cm^{-2}.s^{-1}$)
Uncoated	5.652×10^{-5}	1.248×10^{-10}
0.5 min	6.132×10^{-6}	5.742×10^{-11}
1 min	1.053×10^{-6}	2.935×10^{-11}
2 min	9.046×10^{-7}	4.238×10^{-12}

TABLE 4.Calculated polarization resistance for Ti6Al4V samples coated with titanium dioxide a: uncoated, b: coated at 0.5 min., c: coated at 1 min. and d: coated at 2 min.

ITEM	i Cor. (Amp)/cm^2	bc (volt)	Ba(volt)	R_p (Kohm)/cm^2
Uncoated	1.006×10^{-6}	0.162	0.147	33.264
0.5 min	4.627×10^{-7}	0.177	0.843	137.279
1 min	2.365×10^{-7}	0.168	0.313	200.716
2 min	3.002×10^{-8}	0.038	0.047	303.919

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