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Characterization and Corrosion Behavior of Hydroxyapatite- Coated Titanium Substrates Prepared Through Laser Induced Liquid Deposition Technique

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ABSTRACT

Titanium and titanium alloys are often used in orthopedic surgery and dentistry because of their biocompatibility, mechanical properties, and corrosion resistance. However, their bio- inertness is the most serious drawback for biomedical applications; therefore, in the present study, laser induced liquid deposition (LLD) technique was used to deposit bioactive nanocrystalline HA films on titanium substrates at room temperature and various exposure times (20, 30, and 60 min) were examined. The LLD method was employed via applying a laser irradiation into a liquid precursor and depositing the HA films on titanium substrates immersed in the liquid precursor. According to X-ray diffraction (XRD) and scanning electron microscopy (SEM) results, well crystalline HA coating is prepared and by increasing laser irradiation time, the crystallite size increases from 25 to 41 nm and the morphology changed from rod to mass shape. Also, corrosion behaviors of coating were evaluated by potentiodynamic polarization test in simulated body fluid (SBF). Results showed that by choosing the appropriate exposure time (60 min), the corrosion resistance of coated substrates improved.

1. INTRODUCTION

Titanium and Titanium alloys have been employed in several biomaterials fields such as load-bearing hard tissue replacements and dental implants due to their corrosion resistance and mechanical properties besides their biocompatibility [1- 4]. However, Ti and Ti-based alloys are classified as bio-inert materials which can lead to improper stress distribution, low bond strength and therefore, the implants may separate from host tissues [4-8]; moreover, titanium and other alloying metal ions have a limited corrosion resistance in biological fluids and can accumulate in the nearby tissues. Although the titanium is not toxic, the presence of other alloying elements can lead to allergenic or adverse reactions [9-12].

Accordingly, biocompatibility and corrosion resistance of Ti-based implants are promoted by coating with bioactive materials. Indeed, metallic implants coated by biologically active materials serve the advantages of bioactivity of coated layer and mechanical properties of the metal implant [2]. Among bioactive materials such as hydroxyapatite (HA), calcium phosphates, bioglasses and glass-ceramics [5, 12-14], HA which belongs to calcium phosphates group, is the most biocompatible material; because bone and teeth mineral composition is mainly composed of hydroxyapatite [15-19].

Titanium alloys can be coated by hydroxyapatite via various methods such as ion-beam deposition [20], laser-pulse deposition [21], electrochemical deposition [22], electrophoretic deposition [23], sol–gel deposition [24], plasma spray [25], and magnetron sputtering [26]. Although plasma is widely used in this field, it has drawbacks like poor adherence of coating on metal surface, and HA decomposition at high plasma spray working temperature [27-29].

Laser induced liquid deposition (LLD), a novel approach, is recognized as a simple and clean method for production of nanoparticle colloids and the produced particles are pure, very well suited for further functionalization and therefore, there is no detrimental reaction when they are implanted [30-34]. Hence, in this research, LLD process was utilized for coating HA on Ti- 6Al- 4V substrates as well as LLD exposure time on coating characteristics were studied.

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2. MATERIALS AND METHODS

A Ti- 6Al- 4V substrate with dimensions of 100 × 10 × 2 mm^3 was immersed in 5 M NaOH solution at 60 °C for 24 hours to form sodium titanate hydrogel on the surface of Ti Substrate and enhance apatite nucleation in calcium phosphate solution followed by ultrasonically cleaning and then drying [35]. Also, aqua suspension HA was prepared according to Safronova et.al [36]. It should be mentioned that all the chemicals used in this research are purchased from Merck Company and the chemical composition of Ti-6Al-4V substrate is mentioned in Table 1.

TABLE 1. Chemical composition of Ti-6Al-4V alloy used as substrate in this research.

Element	Wt%
Al	6.3
V	4
C	0.006
Fe	0.17
O	0.166
N	0.006
H	0.002
Ti	Bal

Figure 1. shows the setup used for HA coating by liquid-phase laser. Ti substrate was put on Teflon made specimen holder and then, it was submerged in the hydroxyapatite nanopowder aqua suspension. The coatings were prepared by a CO_2 continuous laser, which has a wavelength, maximum power output, and spot size of 10.6 µm, 150 W, and 1-3 mm, respectively. Temperature of solution was kept constant at 60 °C and various laser deposition times as 20, 30, and 60 minutes were considered to study the laser irradiation time effect on the prepared coatings properties. It must be mentioned that other deposition times such as 10, 120, and 180 min were considered, too. However, these prepared coatings were not as well as others due to lack of coherence; therefore, these deposition times were not considered anymore. Then, the coated substrates were dried over a period of 12 hours at 80 °C. Finally, the samples were sintered at 500 °C for 1 h with heating rate of 5 °C/min.

Crystalline phase and crystallite size of prepared coatings were carried out by XRD (Philips PW 3710, Cu Kα, 30 KV, 35 mA) and surface morphology and elemental analysis was considered by SEM (VEGA, TESCAN) equipped EDX.

Polarization potentiodynamic test was performed by (Autolab, Model µIII, Echo-Chemi) in SBF. The SBF solution is prepared according to the method presented by Kokubo et al [37] and its chemical composition is presented in Table 2. A three electrode cell was used in polarization test which consists of sample, saturated calomel electrode (SCE), and a platinum wire as working electrode, reference electrode, and counter electrode, respectively. The corrosion tests were begun after achieving steady open current potential. The anodic and cathodic polarization curves were plotted by scan rate potential of 1 mV/sec going from anodic to cathodic part. Then, by applying Tafel extrapolation method, corrosion current density (icorr), Corrosion potential (Ecorr), and anodic/cathodic Tafel slopes (βa, βc) were determined from corrosion curves; moreover, mean values and standard deviation was calculated.

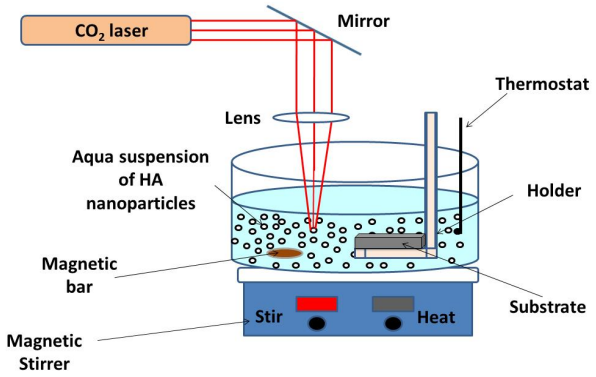

Figure 1. Schematic of HA film coating set up on Ti substrate

TABLE 2. Order and amounts of reagents for preparing 1000 mL of SBF

Order	Reagent	Amount
1	NaCl	8.035 g
2	$NaHCO_3$	0.355 g
3	KCl	0.225
4	$K_2HPO_4.3H_2O$	0.231 g
5	$MgCl_2.6H_2O$	0.311 g
6	1M HCl	39 mL
7	$CaCl_2$	0.292 g
8	Na_2SO_4	0.072 g
9	Tris	6.118 g
10	1M HCl	0-5 mL

3. RESULTS AND DISCUSSION

3.1. PHASE CHARACTERIZATION

Figure 2. depicts the XRD spectra of HA coatings prepared after different laser irradiation time (20, 30,

and 60 min) and sintered at 500 °C. As it is evident in figure 2, in all samples, HA characteristic peaks (standard pdf# 001-1008) have been appeared around 2θ = 25-55°. Also, titanium peaks (standard pdf# 044-1294) originated from Ti substrate is evident in XRD spectrum. Furthermore, intensity of HA peaks decreases by increasing laser irradiation time which shows crystallinity of HA coatings decreases. The crystallite size of HA coatings sintered at 500 °C is calculated by Scherer equation [38] and the results are presented in Table 3.

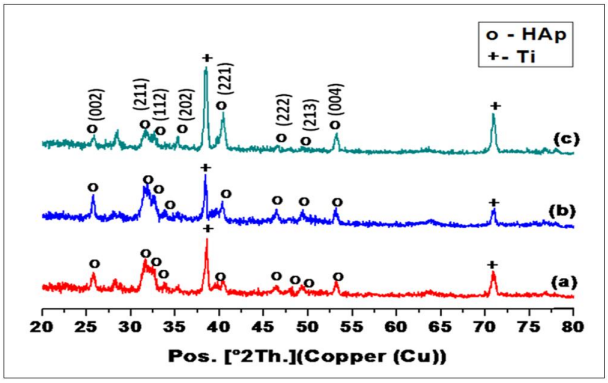

Figure 2. XRD pattern of hydroxyapatite coatings on Ti substrates prepared after (a) 20, (b) 30, and (c) 60 min laser irradiation time and followed by sintering at 500 °C.

As results show, the crystallite size of HA coatings is depended on laser exposure time which increases from ~25 to ~41 nm by increasing irradiation time from 20 to 60 min.

TABLE 3. Average crystallite size of HA coatings on Ti substrates as a term of laser exposure time

Time (min)	(2θ)	Crystallite size (nm)
20	31.739	24.7
30	31.913	30.2
60	31.519	41.1

Figure 3. shows the characteristic adsorption peaks of HA nanoparticles. The broad bands at 3436 and 1637 cm^{-1} are assigned to the adsorbed water. The peak observed at 1420 cm^{-1} is attributed to carbonate groups. The band at 1040 cm^{-1} is due to υ_3 PO4 and the bands at 603 and 561 cm^{-1} are because of υ_4 PO4 [19, 38, and 39]. Therefore, XRD and FTIR results indicate that the synthesized nanoparticles are composed of hydroxyapatite (HA).

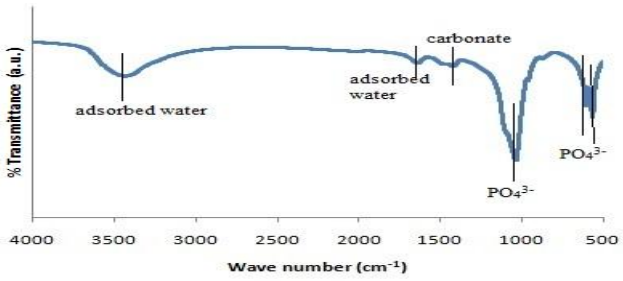

Figure 3. FTIR spectrum of HA coatings.

3.2. MICROSTRUCTURE AND MORPHOLOGY

Figure 4 shows SEM-EDS images of hydroxyapatite coatings on Ti substrates prepared by different laser irradiation time and sintered at 500 °C. As it can be seen, surface morphology of coating was changed from rod-like to mass shape (i.e., which present a molten aspect) by increasing irradiation time. It seems that these variations are due to evaporation of solution and increasing solution concentration by increasing laser irradiation time which contributes to the disordering of the film structure and amorphous-like structure [28].

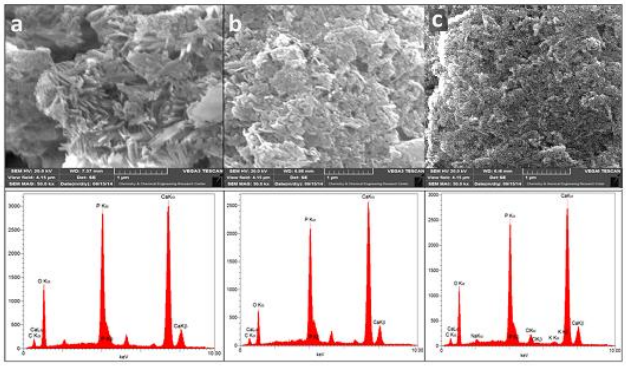

Figure 4. SEM-EDS images of HA coatings on Ti substrates via different laser irradiation time and sintered at 500 °C; (a) 20 min; (b) 30 min; (c) 60 min.

Table 4 shows Ca/P molar ratio calculated from EDX results. The Ca/P ratio calculated for all three samples is about 2.3 - 2.6. It must be mentioned that EDX analysis shows the chemical composition of HA coating approximately. Also, Mhin et al [34] reported that Ca/P ratio in laser ablation in vacuum and liquid medium is approximately about 2.1 and 3, respectively and the Ca/P molar ratio of HA synthesized by laser process in liquid medium is relatively similar to its stoichiometric ratio (Ca/P = 1.67). Besides, laser energy and sintering of HA coatings at 500 °C prepares the required energy for evaporation of P element in the HA structure [40-42] and therefore, Ca/P ratio increases. However, it has

been reported that HA with higher Ca/P ratio has more tendencies to bond to bone [43].

TABLE 4. Ca/P molar ratio extracted by EDX spectra.

Laser irradion time (min)	20	30	60
Ca/P molar ratio	2.3	2.6	2.5

SEM observations of different HA coatings cross sections are presented in figure 5. SEM cross section shows that the coating thickness is a function of laser irradiation time and the coating thickness of samples prepared via 20, 30 and 60 min laser irradiation is almost 1, 3 and 12 µm.

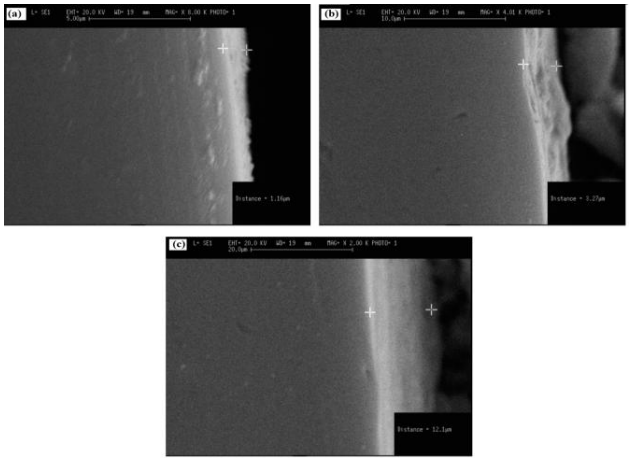

Figure 5. SEM cross section of HA coatings on Ti substrates via different laser irradiation time time and sintered at 500 °C; (a) 20 min; (b) 30 min; (c) 60 min.

3.3. CORROSION TEST

Figure 6 represents the potentiodynamic polarization curves of prepared samples in SBF and Table 5 shows corrosion potential (E_{corr}), corrosion current density (i_{corr}), and Tafel slopes based on figure 6. As results show, untreated titanium corrodes rapidly in SBF due to attack of chlorine ions [2]. When Ti substrates are chemically treated by NaOH solution, the corrosion potential of Ti substrate becomes more noble (increases from -0.497 ± 0.005 vs. SCE to -0.054 ± 0.005 V vs. SCE) and its corrosion current density decreases remarkably from 59.5 ± 2 µA/cm^2 to 6.3 ± 1 µA/cm^2. So, the corrosion resistance of Ti substrates increases. According to the results of other researchers, it seems that under alkaline treatment of Ti and Ti alloys, Na and oxygen ions diffuse and form sodium hydrogen titanate passive layer on Ti substrate which enhances the corrosion resistivity of Ti substrate, increases its bioactivity, and improves the adhesion of biocoatings to Ti substrates [44-49]. Hence, the HA coatings were deposited on NaOH- treated Ti substrates.

As figure 6 and Table 5 show that, in comparison to NaOH treated substrates, the corrosion current density of HA coatings prepared via 20 min laser irradiation time increases to 38.8 ± 1 µA/cm^2 and the corrosion potential slightly increases to -0.050 ± 0.001 V vs. SCE and by increasing laser irradiation time to 30 min, the corrosion current tends to increase and the corrosion potential tends to decrease; therefore, the corrosion resistance of coated samples decreases up until coating for 30 min; because the coating time was not enough to prepare a smooth coatings on substrate and the coatings are porous

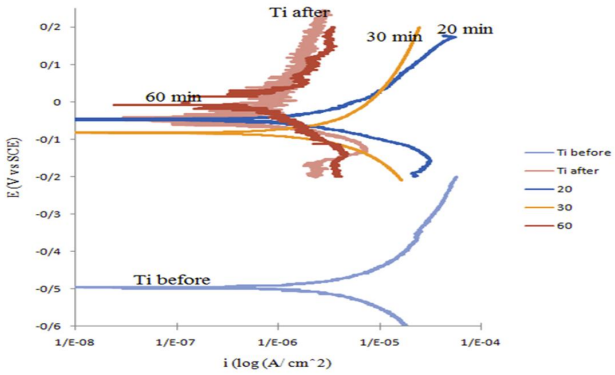

Figure 6. Potentiodynamic polarization curves for bare and treated Ti and HA coated Ti in SBF after 1 h immersion.

TABLE 5. Mean values (standard deviation) of corrosion parameters accordong to potentiodynamic polarization curves of bare and HA coated samples in SBF after 1 h immersion.

Sample	E_{corr} (V vs. SCE)	I_{corr} (µA/cm^2)	B_c (V/dec)	B_a (V/dec)
Ti	-0.497 ± 0.005	59.5 ± 2	0.89	0.65
Pre-treated Ti	-0.054 ± 0.005	6.3 ± 1	0.66	0.72
20	-0.050 ± 0.001	38.8 ± 1	0.31	0.22
30	-0.083 ± 0.005	49.9 ± 2	0.77	0.97
60	-0.006 ± 0.004	4.7 ± 1	0.16	0.26

However, by increasing time to 60 min, the corrosion potential becomes more noble (-0.006 ± 0.004 V vs. SCE), the corrosion current density decreases to 4.7 ± 1 µA/cm^2 and the corrosion resistance increases significantly. It should be mentioned that by increasing laser irradiation time, denser and smoother HA coatings with higher thickness (figure 5) are synthesized and as SEM images show, the coating porosity decreases that all these factors lead to better corrosion resistance in SBF.

4. CONCLUSION

In many stochastic systems, there may occur a situation in which the first service is essential to all arrivals whereas second service is needed by only some of them.

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