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The Heat, Plasma, and Laser Treatments Characteristics of Hydroxyapatite Coatings.

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Abstract

In this work, the study of thermal treatment by laser, plasma glow discharge, and tubular furnace on Ti-6Al-4V alloy coated with hydroxyapatite (HA) by methods of dip coating and electrophoretic deposition. The effect of pulsed Nd:YAG laser , oxygen plasma and tubular furnace treatments on structure, morphology and corrosion resistance of HA coating –Ti6Al4V alloy samples were thermal reported. The samples were tested by optical microscope, XRD, SEM, and the corrosion characteristic with open circuit potential (OCP) and polarization curve (Tafel). The results showed that the samples thermal reported by tubular furnace were the best where the corrosion rate was reduced to 3.567×10^{-4} mm/y for the dip-coated samples and 7.221×10^{-4} mm/y for the electrophoretically deposited samples compared with 9.396×10^{-3}mm/y for uncoated sample. It was found that the heat, laser and plasma treatment enhanced the structure and corrosion resistance properties of the HA coating on Ti6Al4V substrate for use in biomedical applications. This research demonstrates a new low-cost approach to produce high corrosion resistance biocompatible materials.

Keywords: Hydroxyapatite coating, Dip coating, Electrophoretic deposition, Ti6Al4V alloy, Corrosion, Thermal treatments, Laser, Plasma

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1. Introduction

Hydroxyapatite is a biomedical material with multiple and important uses. It is used in medical implants, bone osteoporosis treatment, drug delivery systems [1,2]. All of the coating methods used the heat treatment for the coating layer [3,4] for two reasons; the first is to achieve bonding between the coating layer and the metal, and the second is to achieve the compaction factor and good crystallization of the coating layer [5].The coating layer needs to reduce the corrosion of surgical implants exposed to various body fluids after being implanted in vivo. Therefore, some research has dealt with the effect of thermal treatment performed inside thermal furnaces on the corrosive behaviour of surgical implants coated with hydroxyapatite in different ways [6] or coated with materials other ceramic [7]. The studies also dealt with the effect of specific, but not different, heat treatments on bonding with the bone for hydroxyapatite-coated surgical implants [8], or the effect of specific thermal treatments on mechanical properties [9] Although the laser and plasma techniques were used to coat the bioceramic materials as a thin film form on the surgical veins [10, 11]. In this study, we will use these two techniques as a heat treatment technique to

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study their effect on corrosion resistance behaviour. The hydroxyapatite-coated has done by two different methods, as the dip coating and the electrophoretic deposition, because these methods are easy to apply because they do not need relatively complex systems, and it is easy to control the thickness of the coating layer by controlling the coating time [12, 13]. Many treatment processes have been studied to improve the quality of coatings on substrate, including heat, plasma and ion beam treatment processes. The effect of these operations may alter the surface chemical structure or affect the roughness of the coating [14]. Non melt laser treatment and heat treatment are commonly used for surface modification of materials with the aim of enhancing the properties of thin films. Heat treatment can lead to recrystallization, phase transition, homogenization, and relaxation of internal stresses [15].In this work, the Ti-6Al-4V alloy will be coated with a layer of hydroxyapatite by the two methods mentioned above, and then treated thermally using lasers, glow dc discharge plasma, and thermal furnaces, after which the surface morphology of treated samples will be examined by optical microscope and scanning electron microscopy (SEM) and X-ray diffraction (XRD), then corrosion tests will be performed. Exemplified by measuring the open circuit potential and polarization diagram (Tafel) to determine the annual corrosion rate, and evaluating the results and their impact according to the type of thermal treatment.

2.Experimental part

2.1 HA coating and Ti-6Al-4V alloy samples treatment Samples were prepared from Ti-6Al-4V alloy and smoothed with smoothing paper composed of silicon carbide with a granular size of 500 microns, and chemically cleaned with a solution of (O_2, HF, and HNO_3) in volume ratios (3: 1: 6), respectively [16]. Samples were washed with 90% ethanol using an ultrasonic bath for 10 minutes and twice, after which the samples were washed with distilled water using an ultrasonic bath for 10 minutes once. Mix 4 g of nano-sized hydroxyapatite, 50 ml of 90% ethanol, and 5 g of phosphorous pentoxide, after which the samples were immersed in the solution for 5 minutes and then left to air dry for one hour. For shipping, a solution consists of 4 g nano-sized hydroxyapatite, 50 ml of ethanol 90% and 2 g of iodine was used, then the samples were used as a cathode and graphite electrode as an anode and connected to a power supply and a voltage of 30 volts for 5 minutes after which the samples were dried with air for 1 hour. Two coated samples by dip coating and electrophoretic method were treated by using the Nd-YAG laser (Portable Q-switch ND YAG Laser, China), and applying pulses distributed on the surface of the two coated eyes in two different ways with energy of 10 mJ. Two coated samples by dipping and the electrophoretic method were treated by using glow discharge oxygen plasma and a voltage of 600 Volts and a distance between the two electrodes 6 cm for five hours. Finally, two coated samples were treated by thermal tube furnace (Carbonite, MTF 10/15/130, England) for one hour at a temperature of 400 ° C under an atmosphere of air.

2.2 HA coating-Ti6Al4V characterization

The surface morphology of the HA coating-Ti6Al4V samples was analysed using a scanning electron microscope (SEM) (Hitachi S-4160, Japan) and optical microscope images using optical microscope (Nikon type 120, Japan). The corrosion characteristics (the open current potential OCP and polarization curve (Tafel) of the samples were performed by (PARSTAT 2273-Danmark) using solutions similar to the body solutions (simulated body fluid, SBF) [17]. Its components are shown in Table 1. X-ray diffraction (XRD) patterns of the deposited HA coatings were recorded using Shimadzu-6000, Japan diffractmeter equipped with Cu-Kα a radiation in the 2θ range 20°–80°.

Reagent	Components g/I
NaCl	**8.035**
$NaHCO_3$	**0.355**
KCL	**0.225**
K_2HPO_4	**0.231**
$MgCl_2 6H_2O$	**0.311**
$CaCl_2$	**0.292**
Na_2SO_4	**0.072**

Table 1. The components of SBF

3. Results and Discussions

The samples that were treated with the laser were very affected, as the laser engraved the coating area and the base metal represented by the Ti-6Al-4V alloy. (No coating was left on the sample despite the use of the relatively weak energy of the laser, as shown in figure 1. The surface of the sample, which is characteristic of titanium and its alloys, is in figure 2. As for the samples coated in two different ways and treated by dc glow discharge of O_2 plasma and in a thermal furnace, it is not clear through optical microscopy images clear differences of the effect of different treatments on the coating. SEM images of the treated HA coatings on Ti6Al4V substrate are shown in Fig. 3. The SEM examination of the samples showed the difference in the shape of the hydroxyapatite crystals coated on the two samples and the extent of their susceptibility to the different treatments. The samples coated by the method of dipping, electrophoretic and the plasma treatment took a combined cryogenic shape. As for the samples treated with the thermal furnace, the hydroxyapatite crystals took the shape of granules (clustered randomness), as shown in figure 3.

The micrograph of the treated HA coating on Ti6Al4V substrate shows an inhomogeneous surface, no cracks, and a lack of uniformity. The surface of the heat, laser and plasma-treated samples was rough surface. The crystallites of the coated sample by dipping and thermal furnace treatment were larger than those of the plasma, and laser treated HA coating - Ti6Al4V substrate, as confirmed by the XRD results.

From the examination of X-ray diffraction (XRD), as shown in Figure 4, it becomes clear that titanium oxide has two phases (Rutile and anatase) on the sample treated with laser, and this supports what was previously seen in optical microscopy images in which multiple colours appeared as an indication of the different types of titanium oxides formed.

It was also noticed that the top of the hydroxyapatite at the angles 2θ = 25.87, 31.77, 46.71, 64.07 for the sample treated with plasma was less severe than that which appeared at the same angle for the sample treated with the heated oven.

This indicates that the crystallization of the coating layer obtained by plasma treatment was weak compared to the strong crystallization of the obtained coating layer by treatment by tube furnace. On the other hand, the XRD pattern of the thermal treated sample showed higher intensity than the laser and plasma, indicating a significant increase in crystallite size.

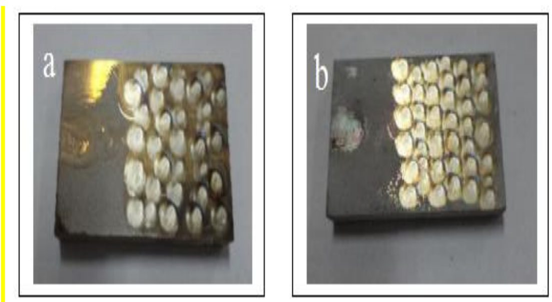


Figure (1): Laser-treated (a) dip-coated samples (b) electrophoretic coated samples

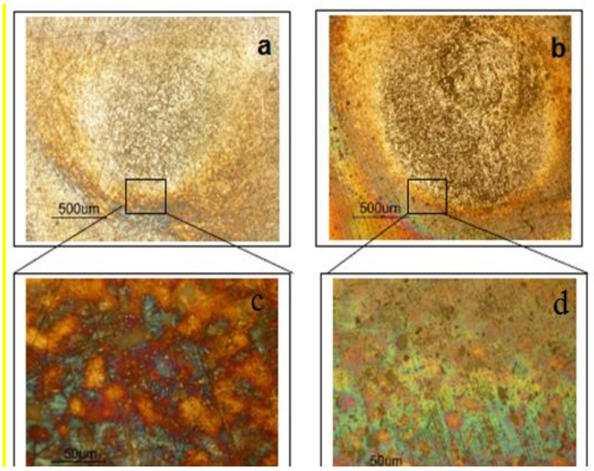


Figure (2): Images of the optical microscope of laser-treated samples (a) the dip-coated sample magnified 50x, (b) magnified 500 x, (c) The sample coated by electrophoretic method magnified 50x, and (d) magnified in the area marked to 500x.

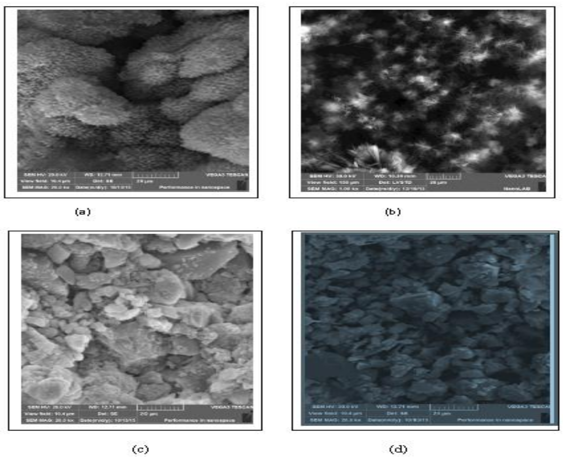


Figure (3) SEM images (a) of the coated sample by dipping and plasma treatment (b) for the coated sample by the electrophoretic method and plasma-treated (c) for the dip coated sample and thermal treated by the thermal tube furnace (d) for the coated sample by the electrophoretic method and the treated by the tube furnace

Corrosion tests for samples coated by dipping and the electrophoretic methods show that the samples treated with a laser were taken to decrease from the starting value of the test and this indicates that the obtained oxidation protection layer was not well connected (un adhesive), which led to the collapse of this layer with time in the examination until it reached the effort to a semi-stable state. As for the samples treated with plasma, the open-circuit voltage was more than the starting value of the test, and this indicates that the coating layer is well stable. The samples treated by the tubular thermal furnace have reached open circuit voltage values higher than that of the plasma-treated as shown in figure (5).

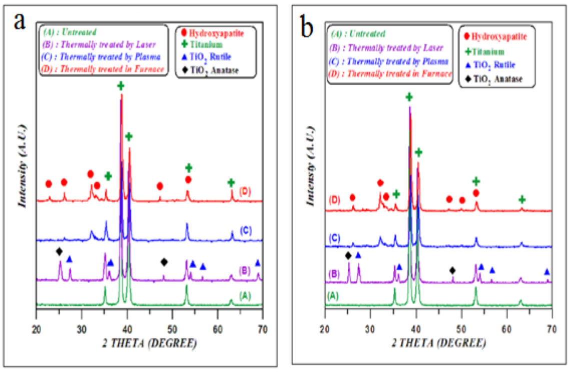
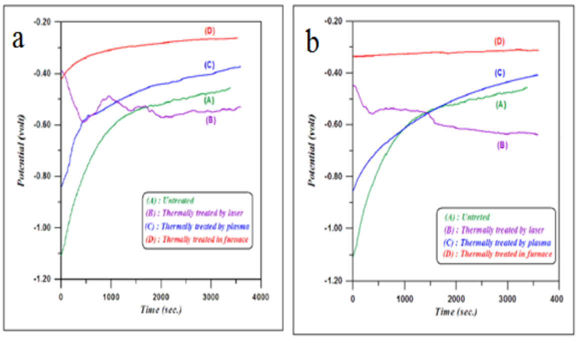


Figure 4: XRD plots of heat, laser and plasma treated coated samples: (a) dip coated (b) coated with an electrophoretic



. **Figure 5:** OCP plots of thermaltreated samples with different techniques: (a) dip coated (b) coated with an electrophoretic.

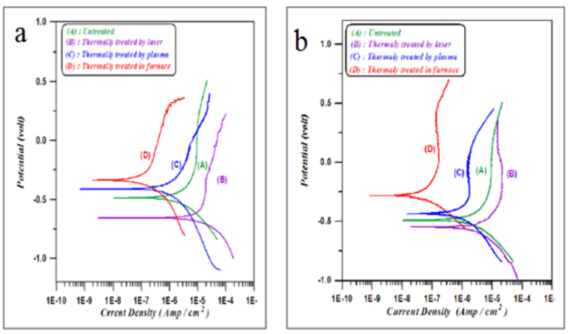


Figure 6: Tafle plots of thermal treated samples with different techniques: (a) dip coated (b) coated with an electrophoretic.

By examining the polarization voltage (Tafel curve), it was found that the annual corrosion rate value increased for the samples treated with a laser than for the untreated and uncoated samples, and this is expected from the results of previous tests of the open-circuit voltage.

The results also indicated that the value of the annual corrosion rate of the samples treated with plasma was less than that of the uncoated samples, meaning that the annual corrosion decreased. Likewise, for the samples treated with the tubular furnace, the value of the annual corrosion rate has decreased significantly, indicating that this type of treatment is the best, and this is also expected as a result of previous tests of the open-circuit voltage.

Figure 6 shows the polarization voltage (Tafel) curves of samples coated with both methods and treated with different thermal parameters. Table 2 shows the results of the corrosion tests for the samples coated by dip coating and heat treatment with different techniques of treatments. Table 3 shows the results of the corrosion assays for the samples coated with the electrophoretic and heat-treated with different techniques of treatment.

Table 2. Corrosion parameters of thermal treated samples with different techniques: dip coated.

E. Corr	I.Corrµ Amp/Cm^2	Corr. Rate mm/y	OCP Volt
-0.492	1.08	$9.396*10^{-3}$	-0.461
-0.658	3.2	$2.784*10^{-2}$	-0.661
-0.397	0.52	$4.350*10^{-3}$	-0.418
-0.289	0.04	$3.567*10^{-4}$	-0.324

Table3. Corrosion parameters of thermal treated samples with different techniques: coated with an electrophoretic.

E. Corr	I.Corrµ Amp/Cm^2	Corr. Rate mm/y	OCP Volt
-0.492	1.08	$9.396*10^{-3}$	-0.461
-0.574	8.1	$7.047*10^{-2}$	-0.542
-0.392	0.61	$5.307*10^{-3}$	-0.418
-0.321	0.08	$7.221*10^{-4}$	-0.324

The corrosion resistance of the treated HA coatings –Ti6Al4V alloy substrates increased with increasing crystallite size, representing an inverse

Hall–Petch (H–P) effect [18]. This may be because the crystallite size of the tested films was smaller than the critical value. These results imply that the thermal furnace treatment applied was sufficient to improve the properties of the HA coatings on Ti6Al4V alloy substrate for use in biomedical applications

4. Conclusion

It is evident, that the laser treatment of samples has damaged the coating layer and increased the annual corrosion rate of the alloy, and that the thermal treatments by plasma and the thermal furnace have improved the surface properties of the alloy, as the corrosion rate decreased to 3.567×10^{-4} mm / y for the dip-coated samples and 7.221×10^{-4} mm / y for coated samples with electrophoretic compared to the corrosion rate of 9.396×10^{-3} mm / y for the uncoated sample. The treatment with a tubular furnace was the best for both of the two coating methods (dipping and electrophoretic) used to treat bone fractures, pacemakers and catheters.

5. Conflicts of interest

"There are no conflicts to declare".

6. Acknowledgments

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