

Article

Nanomechanical Behavior, Adhesion and Corrosion Resistance of Hydroxyapatite Coatings for Orthopedic Implant Applications

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Abstract: The aim of this work was to investigate the nanomechanical, adhesion and corrosion resistance of hydroxyapatite (HAP) coatings. The electrodeposition process was used to elaborate the HAP coatings on Ti₆Al₄V alloy. The effect of hydrogen peroxide concentration H₂O₂ on the electrolyte and the heat treatment was studied. Surface morphology of HAP coatings was assessed, before and after heat treatment, by scanning electron microscopy associated with X-ray microanalysis (SEM-EDXS). Moreover, X-ray diffraction (XRD) was performed to identify the coatings' phases and composition. Nanoindentation and scratch tests were performed for nanomechanical and adhesion behavior analysis. The corrosion resistance of the uncoated, the as-deposited, and the heat-treated coatings was investigated by electrochemical test. The obtained results revealed that, with 9% of H₂O₂ and after heat treatment, the HAP film exhibited a compact and homogeneous microstructure. The film also showed a crystal growth: stoichiometric hydroxyapatite (HAP) and β-tricalcium phosphate (β-TCP). After heat treatment, the nanomechanical properties (*H*, *E*) were increased from 117 ± 7 MPa and 24 ± 1 GPa to 171 ± 10 MPa and 38 ± 1.5 GPa respectively. Critical loads (*L*_{C1}, *L*_{C2}, and *L*_{C3}) were increased from 0.78 ± 0.04, 1.6 ± 0.01, and 4 ± 0.23 N to 1.45 ± 0.08, 2.46 ± 0.14, and 4.35 ± 0.25 N (respectively). Furthermore, the adhesion strength increased from 8 to 13 MPa after heat treatment. The HAP heat-treated samples showed higher corrosion resistance (*R*_p = 65.85 kΩ/cm²; *I*_{corr} = 0.63 μA/cm²; *E*_{corr} = −167 mV/ECS) compared to as-deposited and uncoated samples.

Keywords: hydroxyapatite coating; heat treatment; nanoindentation; scratch test; corrosion



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1. Introduction

Biomaterials have been successfully developed and used to improve the quality of human life, not just for an aging population but also for younger people with heart problems. The success of such an implant largely depends on the selection of materials for their manufacture. Titanium and its alloys, such as Ti₆Al₄V, are the most used metal implants because of their corrosion resistance and biocompatibility. These alloys also have a good yield strength and low elastic modulus, which is similar to that of bone [1,2]. However, in recent years, it has been noticed that most metallic materials, including Ti alloy, can undergo degradation in the long term [3]. Many studies [2,4] proved that Ti₆Al₄V implant could cause health problems because of the release of aluminum (Al) and vanadium (V) ions into the human body's fluid system [4]. According to Tlotleng et al. [2], both V and Al ions are associated with long-term health problems, such as Alzheimer's, neuropathy, and Osteomalacia. In addition, Ti₆Al₄V alloy, as a bioinert material, exhibits

poor osteoinductive properties. It cannot form effective bone-bonding between the implant and the human tissue [5]. Currently, these limitations have prompted many researchers to focus on solutions, leading to implant surface modification. Hydroxyapatite has a similar structure to the natural bone component. This similarity makes it the preferred candidate for orthopedic and dental implants [6]. Hence, HAP coating allows for new surface properties such as osteointegration and biocompatibility [6–8], which lead to an improvement in implant functionality. Several techniques have been developed for coating metal implants, including plasma spraying sputtering [2], sol–gel [5], electrophoretic deposition [9], magnetron sputtering [10], LVOF (Low-Velocity Oxyfuel) sprayed [11], and electrodeposition [12,13]. Among the various deposition processes, electrodeposition is widely used in the coating industry, and it is considered to be a simple, quick and low-cost technique. Moreover, this method allows for the coating of substrates that have a complex shape or porous structure [14]. Many studies focus on the various methods used to obtain reliable HAP coatings [15,16], other active research investigate bioactivity [2,11], cytocompatibility, and antibacterial properties [17]. Although the HAP coating should be compatible with the tissue surrounding the implant, it also should possess good mechanical properties, high bonding strength and corrosion resistance. To the best of our knowledge, few works have been done investigating the mechanical properties (the hardness and the elastic modulus) and adhesion behavior of HAP coating obtained by electrodeposition technique [18–20]. Hence, a detailed mechanical and corrosion resistance analysis is indispensable to evaluate the reliability of the HAP deposited thin film. The aim of this work is to study the nanomechanical properties, adhesion behavior and corrosion resistance of HAP coating deposited on Ti₆Al₄V. This work investigates, in detail, the high correlation of the nanomechanical, the adhesion, and the corrosion performances, with the coating morphology, the hydrogen peroxide amount, and the heat treatment.

2. Materials and Methods

2.1. Coating Deposition

Cylindrical rods of 12 mm in diameter and 4 mm in thickness of Ti₆Al₄V alloy were used as substrates. Then, a polishing procedure with alumina particles was applied. Substrates were etched with hydrofluoric acid until a smooth metallic surface was exposed with an average roughness of about 2 µm. Before the deposition, surfaces were ultrasonically cleaned into acetone and then into ultra-pure water. The electrodeposition of HAP coatings was carried out in an electrolyte solution prepared by mixing 0.042 M of Ca (NO₃)₂·4H₂O and 0.025 M NH₄(H₂PO₄) with varying amounts (0%, 6%, and 9%) of hydrogen peroxide (H₂O₂). The pH value was adjusted to 4.4 by adding 0.1 M NaOH solution and the temperature fixed at 60 °C. The electrodeposition was performed using a potentiostat/galvanostat instrument (Voltalab PGP 201 Radiometer Analytical (Lyon, France)–VOLTAMASTER software (version 4)). This process was carried out with a typical three-electrode configuration: the cathode (Ti₆Al₄V substrate), the counter electrode in platinum (Pt), and the reference electrode SCE (saturated calomel electrode). Pulsed current electrodeposition with a peak pulse current density $j = 8 \text{ mA/cm}^{-2}$ and a deposition time $t_{\text{ON}} = 1 \text{ mn}$ and $t_{\text{OFF}} = 2 \text{ mn}$ ($j = 0 \text{ mA/cm}^{-2}$) was implemented. The electrodeposition process was detailed in previous work [20,21]. Figure 1 shows the schematic representation of the electrodeposition process.

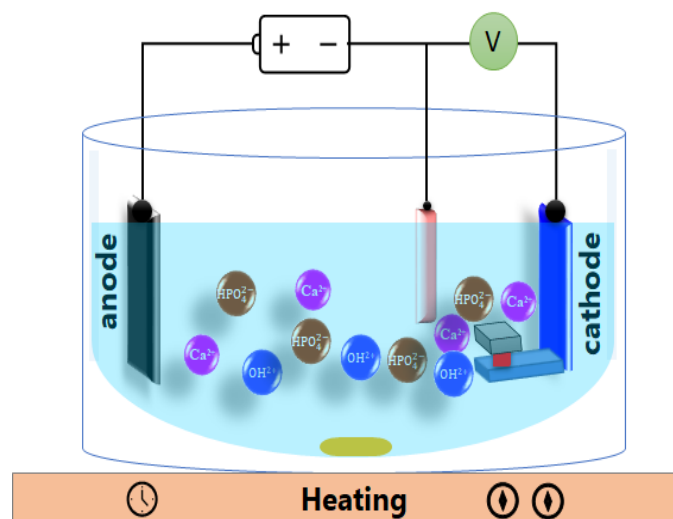


Figure 1. Schematic representation of electrodeposition process.

2.2. Heat Treatment

The HAP coating was thermally treated inside a tubular furnace (Nabertherm RS 80/500/11). Initially, a secondary vacuum of about 10^{-5} mbar was achieved into the working tube with the pumping system. Then, a continuous flow of argon maintained at $100 \text{ L}\cdot\text{h}^{-1}$ was injected, leading to an increase in the pressure to about 10^{-2} mbar. Finally, the temperature was applied in two steps according to the protocol previously developed in our laboratory [20]: a first plateau at 120°C during 1 h for water evaporation followed by a second plateau at 500°C during 1 h. The flow of argon was maintained during the whole heat treatment until complete cooling to room temperature.

2.3. Coating Characterization

The HAP coatings' morphology and the chemical analysis were evaluated using scanning electron microscopy (JEOL JSM-5400LV, JEOL, Tokyo, Japan), associated with X-ray microanalysis (SEM-EDXS) (Éloïse, Tremblay en France, France). To measure the HAP coating thickness, commercial software (ENESIS, Eloïse SARL, Tremblay en France, France) associated with an original procedure for coating analysis developed by Benhayoune H. et al. [22,23] was used. Moreover, X-ray diffraction (XRD) (Bourestnik, Saint Petersburg, Russia) was performed to identify the coatings phases and composition. Nanomechanical behavior was studied using the nano-indentation technique developed by CSM Switzerland Instruments (Anton Paar, Buchs, Switzerland). Tests were conducted using a nano-indenter equipped with a diamond Berkovich tip under a maximum applied load of 100 mN. The film adhesion was investigated using a conventional progressive scratch test with a loading range between 0 and 5 N. The scratch distance and the loading rate were 3 mm and 0.5 N/s, respectively. An electrochemical corrosion test was carried out at room temperature in 3.5 wt.% NaCl solution using Voltalab system. Measurement was performed using the conventional three-electrode cell: reference electrode, platinum auxiliary electrode, and test sample as a working electrode.

3. Results and Discussion

3.1. Morphological and Microstructural Properties

3.1.1. Effect of Hydrogen Peroxide (H_2O_2)

To investigate the effect of hydrogen peroxide, three concentrations (0%, 6% and 9%) were tested. Results of SEM-EDXS and XRD analysis are shown in Figures 2 and 3.

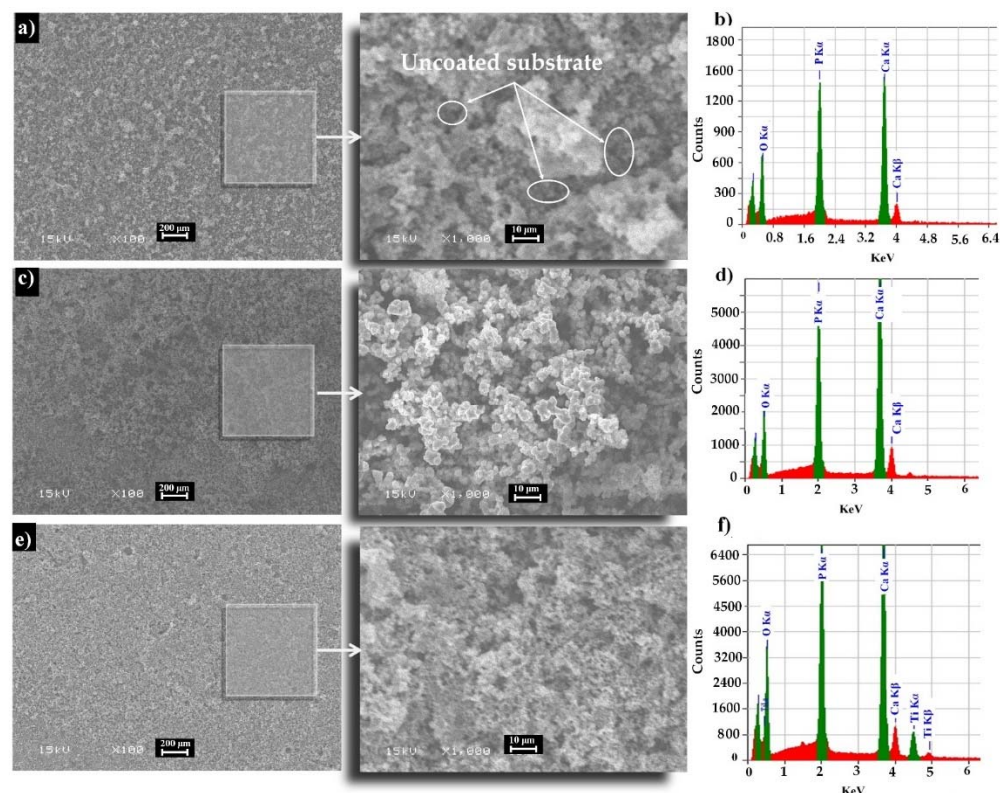


Figure 2. SEM-EDXS analysis of HAP coatings with various amount of H_2O_2 : (a,b) 0%, (c,d) 6% and (e,f) 9%.

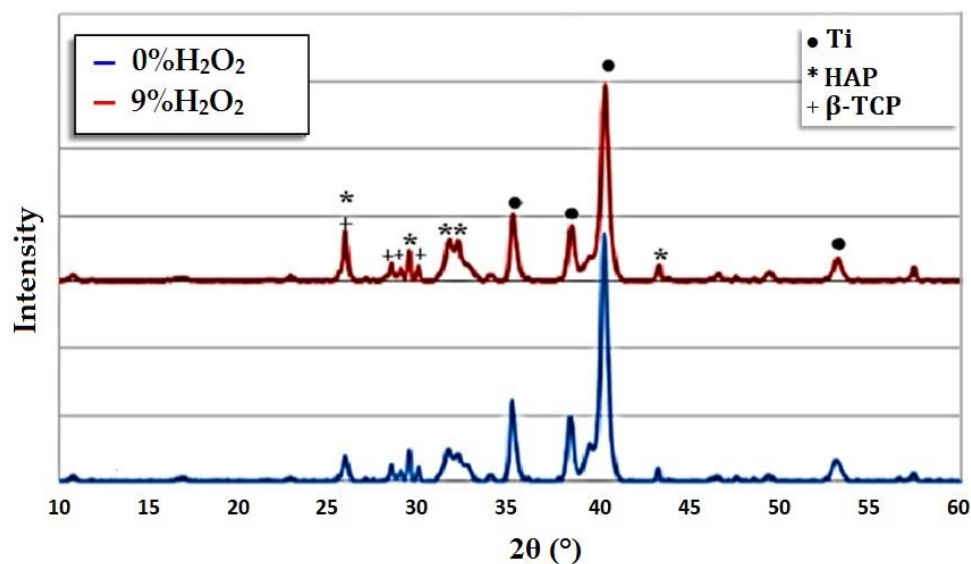


Figure 3. X-ray diffraction (XRD) pattern of HAP coating deposited with 0% and 9% of H_2O_2 .

SEM micrograph indicates that the HAP coating, with a thickness of 15 μm , was composed of small needles and crystallites. The increase of H_2O_2 concentration influences the HAP morphology, with 0% of H_2O_2 . The obtained coating was non-uniform, and certain uncovered substrate zones are observed (Figure 2a,b). When the amounts of H_2O_2 were 6%, the obtained coating (Figure 2c,d) showed that the needles were agglomerated in crystallite spheres, and some porosity was observed. Figure 2e,f shows that the HAP coating morphology, obtained with 9% of H_2O_2 , seems to be similar to that obtained with 6% H_2O_2 but with less porosity. Such a result was found in previous works [21]. The amount of H_2O_2

effect was confirmed by XRD analysis. The increase in H_2O_2 concentration, from 0% to 9%, leads to the appearance of more crystalline phases: hydroxyapatite (HAP) as majority phase and β -tricalcium phosphate (β -TCP) as minority phase. Consequently, the sample with 9% H_2O_2 is retained to analyze the nanomechanical, adhesion, and corrosion behavior.

3.1.2. Heat Treatment Effect

Figure 4 shows the heat treatment protocol as well as the SEM micrograph of HAP coatings with various H_2O_2 concentrations before (Figure 4a) and after heat treatment (Figure 4c).

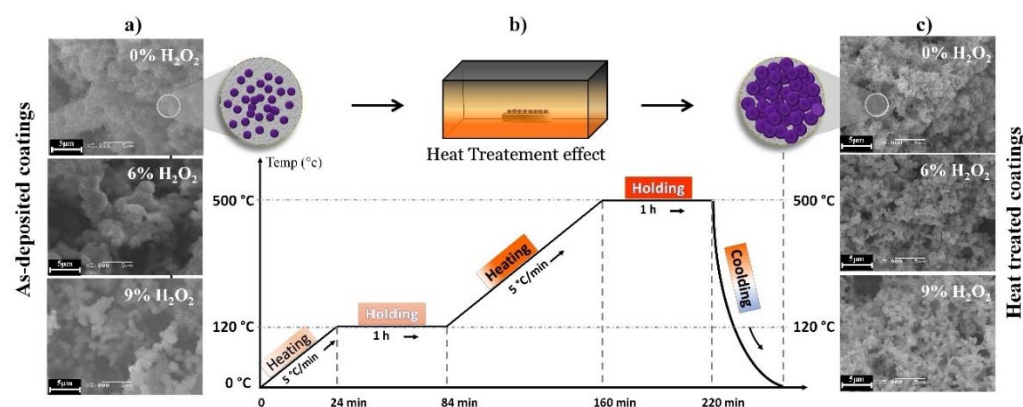


Figure 4. SEM micrograph of HAP coatings with various H_2O_2 concentrations: (a) before heat treatment, (b) heat treatment protocol and (c) after heat treatment.

SEM micrographs show that the heat treatment profoundly influenced the coating morphology (Figure 4a,c). This effect was more noticeable for the coating deposited with 9% H_2O_2 . Figure 5 shows the top-view SEM images of the as-deposited (Figure 5a,b) and heat-treated (Figure 5c,d) HAP coating obtained with 9% H_2O_2 . The coating morphology was dominated by the agglomeration of particles having a spheroid shape. The size of these spheroids increased under the heat treatment, suggesting an improvement in the coating compactness and a decrease of its porosity. Such a result was confirmed in other recent works [6,11]. On the other hand, this morphology is required in biomedical applications to ensure osseointegration and stability of the implant [24]. XRD diffractograms of the heat-treated HAP coating (0% and 9% of H_2O_2) are shown in Figure 6.

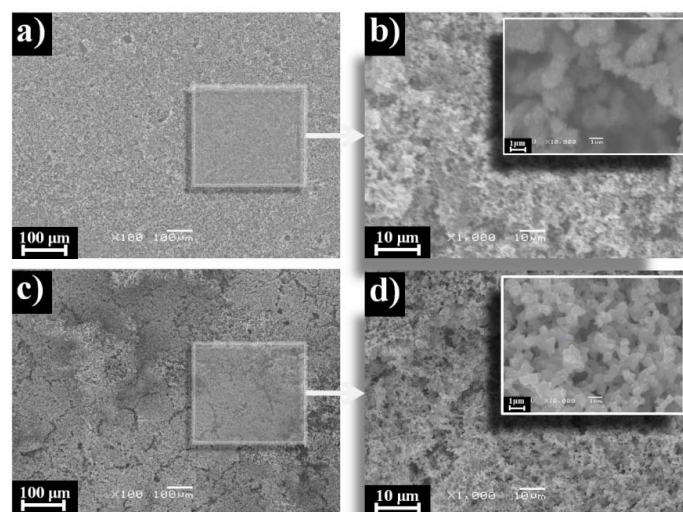


Figure 5. SEM micrographs surface of (a,b) as-deposited and (c,d) heat-treated HAP coating deposited with 9% H_2O_2 .

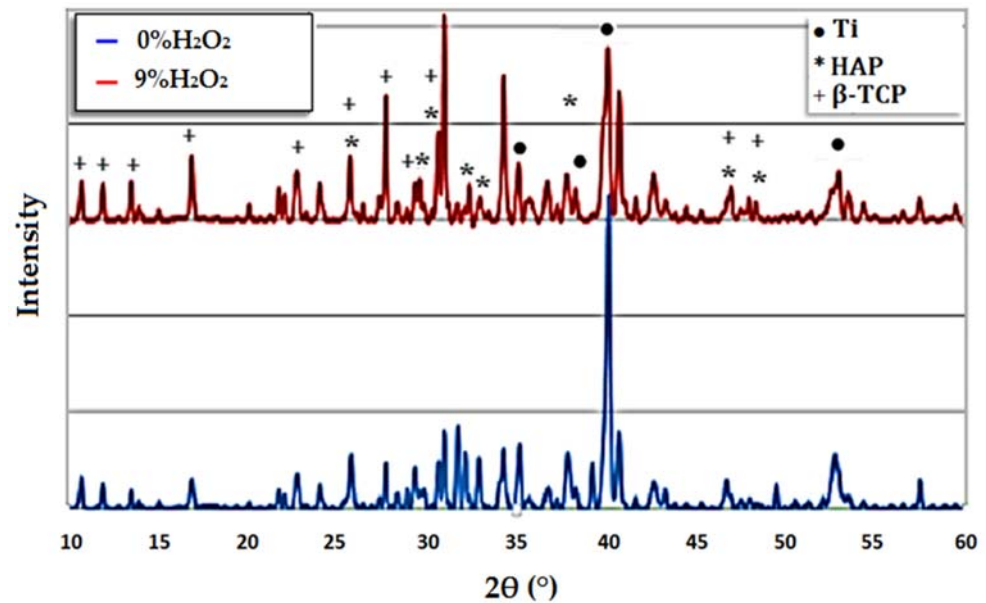


Figure 6. XRD diffractograms of the heat-treated HAP coating obtained with 0% and 9% of H_2O_2 .

Compared to the result given in Figure 3, XRD analysis showed a change in the width and intensities of the peaks for the two concentrations of H_2O_2 . The XRD diffractogram of the untreated sample (Figure 3) presented a broader peak and a small crystallinity. After the heat treatment, the XRD pattern showed peaks of Ti with a clearer biphasic phase structure consisting of HAP and β -tricalcium phosphate (β -TCP). The XRD patterns also exhibited a thinner peak, revealing an improvement in the coating crystallinity with the heat treatment. The results confirm those of other market research studies [12,25], Motofumi et al. [25] indicated that the crystallinity of the HAP coating increased after heat treatment over 350°C . Saman et al. [12] showed a direct relationship between the heat-treatment temperature and crystallinity level.

3.2. Nanomechanical Behavior

The nano-indentation test resulted in a graph showing the relation between the normal applied load and the corresponding penetration depth at two distinct phases: loading and unloading. Figure 7 shows the typical load–penetration depth curve. During the nano-indentation test, the penetration depth increased as a function of the applied load. Moreover, a plastic deformation occurred until the maximum load ($P_{\max}$) corresponded to the maximum penetration depth ($h_{\max}$). A residual penetration depth (h_r) was obtained after the complete removal of the indenter. The area covered under A–B–D–A presents plastic deformation energy (W_p), and the area covered under D–B–C–D presents the elastic-recovering energy (W_e) during the indentation process.

Analysis of the load–Penetration depth (P – h) curves, based on the Oliver–Pharr approach [26], allows the extraction of nanomechanical properties (Hardness H and Young modulus E) of the HAP coating. This method uses power law to fit the unloading curve and takes the tangent at peak load ($P_{\max}$) as the maximum contact stiffness S (Figure 7). According to this method, the hardness is estimated from

$$H = \frac{P}{A} \quad (1)$$

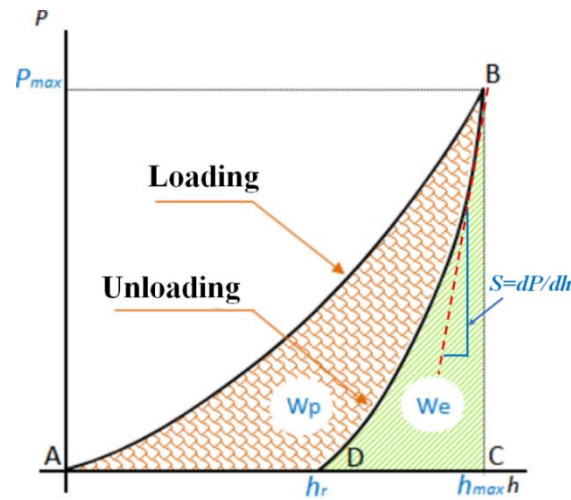


Figure 7. Typical Load vs. Penetration depth curve.

The film elastic modulus can be estimated from the well-known relation between the real projected contact area A_c , the initial unloading slope S (unloading stiffness), and the reduced elastic modulus E_r

$$E_r = \frac{\sqrt{\pi}}{2\beta} \frac{S}{\sqrt{A_c}} \quad (2)$$

where β is a constant that depends on the geometry of the indenter tip. The film elastic modulus E is calculated using the relation

$$\frac{1}{E_r} = \frac{(1 - \vartheta^2)}{E} + \frac{(1 - \vartheta_i^2)}{E_i} \quad (3)$$

where ϑ is the Poisson's ratio of the film, E_i and ϑ_i were the indenter's elastic modulus and Poisson's ratio, respectively.

Figure 8a shows the load–penetration depth curves of HAP coating before and after heat treatment and the obtained nanomechanical properties (H and E) as well as the maximum penetration depth $H_{\max}$ and the residual penetration depth h_r . The H/E and H^3/E^2 ratios are important to predict the HAP coating performance [27]. The H/E ratio, called elastic strain to failure, was used to assess the film resistance to elastic deformation. The H^3/E^2 index predicts the resistance to plastic deformation and the wear resistance of the coating. The obtained values of the H/E and H^3/E^2 index are given in Figure 8b.

As a general interpretation of the results, for both as-deposited and heat-treated HAP coating, the plastic energy (area covered under A–B–D–A) is much higher than the elastic energy (area covered under D–B–C–D) which reveals the plastic behavior of the HAP coating. Moreover, with the heat treatment, the maximum ($H_{\max}$) and the residual (h_r) penetration depth are reduced from 8.7 ± 0.34 and $7.95 \pm 0.3 \mu\text{m}$ to 6.2 ± 0.2 and $5.88 \pm 0.15 \mu\text{m}$, respectively. This result indicated that HAP coating has better resistance to the penetration, which was related to the increase in the hardness and Young's modulus. The enhancement of HAP coating's nanomechanical properties after heat treatment was explained by the increase in coating compactness and a decrease in its porosity, as confirmed by SEM-EDXS analysis (Figures 4–6). The improvement in Young's modulus is necessary for orthopedic implants because it reduces the stress concentration in the bone. The implants with a modulus closer to that of the bone would yield a more homogeneous stress distribution and less micro-motion at the interface [28,29].

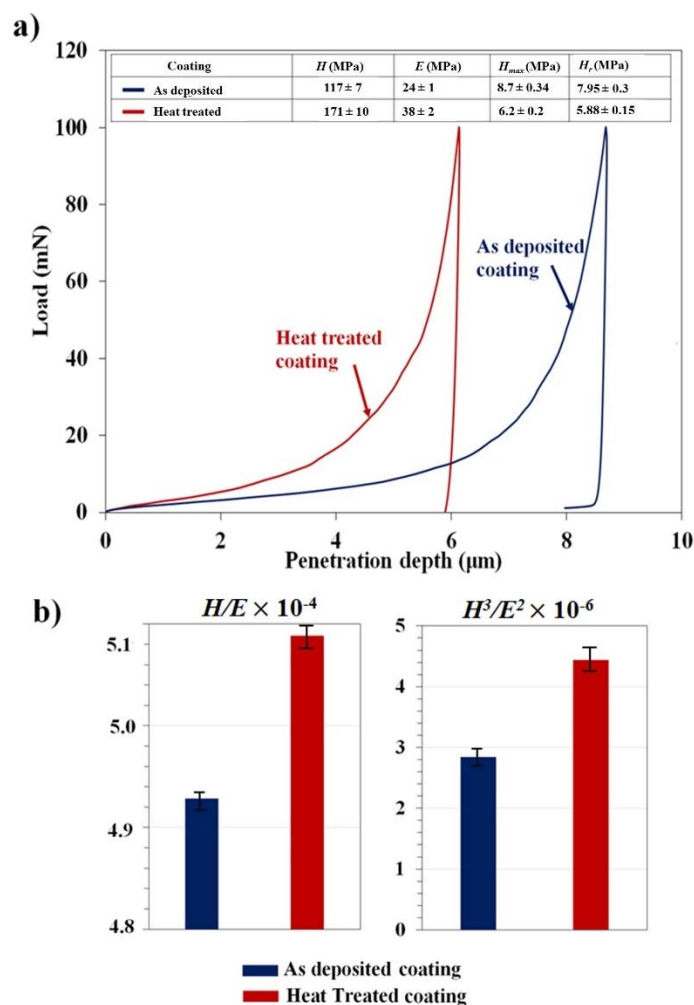


Figure 8. Nanoindentation results: (a) Load-Penetration depth curves and (b) the values of H/E and H^3/E^2 indexes for as-deposited and heat-treated coating.

3.3. Adhesion Behavior

To investigate the adhesion behavior of HAP coating, a conventional scratch test was applied. Both quantitative and qualitative analyses were carried out. The graphs, representing the variation in the friction force and penetration depth as a function of the normal load, were superposed to the corresponding optic microscope images of the scratch tracks of the HAP coatings (Figures 9 and 10).

Critical loads were determined by combining the observations of the scratch tracks and the measurements of normal and tangential loads, as well as the penetration depth. As demonstrated in Figures 9 and 10, the friction force and the penetration depth increase linearly by augmenting the normal load. The first sudden slope change indicated the appearance of the first cracks corresponding to L_{C1} , representing a cohesive failure (Figures 9a and 10a). At a second slope change corresponding to L_{C2} , a first spallation and interfacial delamination were observed, revealing an adhesive failure (Figures 9b and 10b). When the normally applied load increases, the track showed a propagation of micro-cracks caused by the high compressive stress developed in front of the indenter and tensile stress behind the indenter. Then, the highest critical load value L_{C3} was obtained when 50% damage of the film occurred (Figures 9c and 10c). It is also noticeable that the heat-treated HAP coating showed less scratch damage than the as-deposited one. Critical loads obtained before and after heat treatment are given in Table 1.

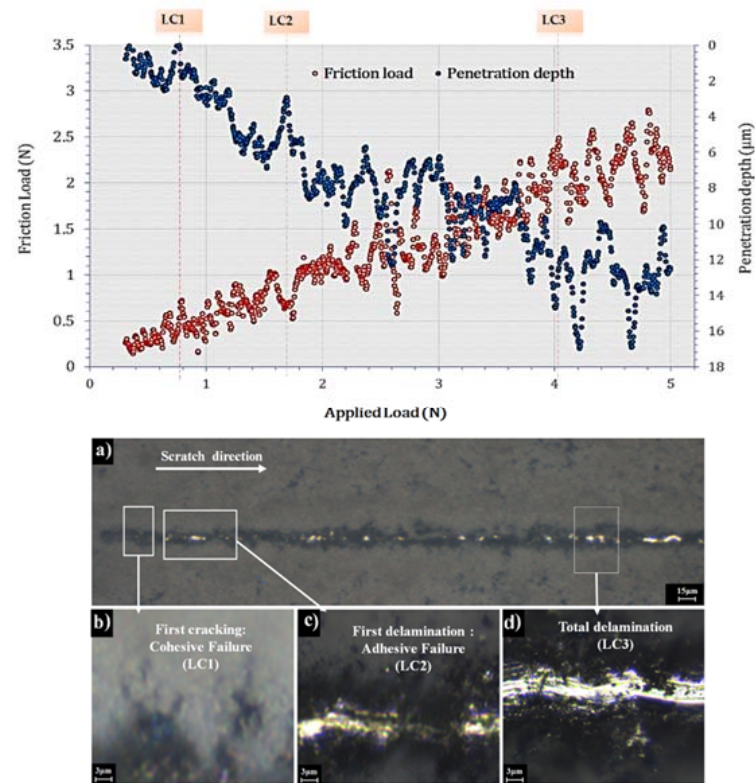


Figure 9. Friction load and penetration depth as a function of the applied load and the corresponding optical micrographs of scratch tracks of as-deposited HAP coating: (a) scratch track; (b) first cracking; (c) first delamination; (d) total delamination.

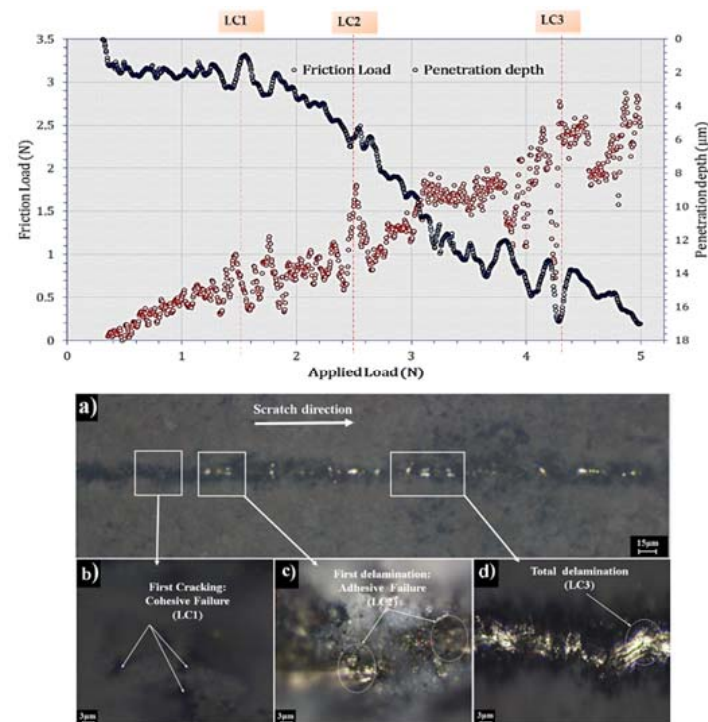


Figure 10. Variation in the friction load and penetration depth as a function of the applied load and the corresponding optical micrographs of scratch tracks of the heat coated HAP coating: (a) scratch track; (b) first cracking; (c) first delamination; (d) total delamination.

Table 1. Critical loads and adhesion strength of the as-deposited and heat-treated HAP coatings.

Coatings	L_{C1} (N)	L_{C2} (N)	L_{C3} (N)	σ_c (MPa)
As deposited	0.78 ± 0.04	1.6 ± 0.08	4 ± 0.23	8
Heat treated	1.45 ± 0.08	2.46 ± 0.14	4.35 ± 0.25	13

During the scratch test, when the interfacial shear stresses were accumulated and sufficiently higher than adhesion forces, the delamination of the film occurred [30]. The adhesion strength obtained with the scratch test was calculated using the following equation

$$\sigma_c = \left(\frac{2P_c}{\pi d_c^2} \right) \left[\frac{(4 + \nu_f)3\pi\mu}{8} - (1 - 2\nu_f) \right] \quad (4)$$

where P_c is the critical load of spalling, d_c is the critical width of the scratch, μ is the friction coefficient, ν_f is the Poisson's ratio of the film.

The obtained values of the adhesion strength of as-deposited and heat-treated HAP coatings are given in Table 1.

Barnes et al. [31] have used scratch testing to measure the adhesion strength of HAP coatings, and they found strength adhesion values with the same order of magnitude. Furthermore, such a result was found by Sopcak et al. [32] using the standard tensile adhesion test ISO 13779-4. On the other hand, the critical loads and adhesion strength increase with the heat treatment. According to Rocha et al. [33], the heat treatment leads to high crystallinity and the formation of chemical bonding between coating and substrate, which explained the strong coating adhesion. In addition, a high temperature promotes the formation of chemical bonds in a large atomic zone mixed at the interface between the coating and the substrate [33]. Tiwari et al. [11] noticed a slight deformation in the interface film/substrate, which was probably related to the mismatch in the coefficient of thermal expansion between the substrate and HAP coating. This phenomenon contributed to an imperfect interface. Hence, the heat treatment leads to an improvement in interface adhesion. In our previous work [34], we also found that the heat treatment of Bioglass coating deposited on Ti₆Al₄V improved the adhesion behavior.

3.4. Corrosion Resistance

The electrochemical corrosion tests of Ti₆Al₄V, as-deposited and heat-treated HAP coatings were carried out in a 3.5 wt.% NaCl solution. Tafel polarization curves are given in Figure 11. Tafel extrapolation method allowed the determination of corrosion parameters such as corrosion potential (E_{corr}), corrosion current density (i_{corr}), cathodic Tafel slopes (β_a and β_c), and the polarization resistance (R_p). These parameters are important data to investigate the kinetics of corrosion resistance.

The polarization resistance (R_p) was calculated with Stern–Geary Equation (5) [35].

$$R_p = \left(\frac{\beta_a \beta_c}{2.303 \times (\beta_a + \beta_c) i_{corr}} \right) \quad (5)$$

The results of the polarization test are presented in Table 2.

Table 2. Polarization parameters obtained from Tafel curves.

Samples	E_{corr} (mV/ECS)	i_{corr} (μ A/cm ²)	β_a (mV)	β_c (mV)	R_p (Ω /cm ²)
Substrate	−237	3.78	113.1	271.8	9.17
As deposited	−211	1.98	196.3	241.2	23.73
Heat treated	−167	0.63	233.6	161.7	65.85

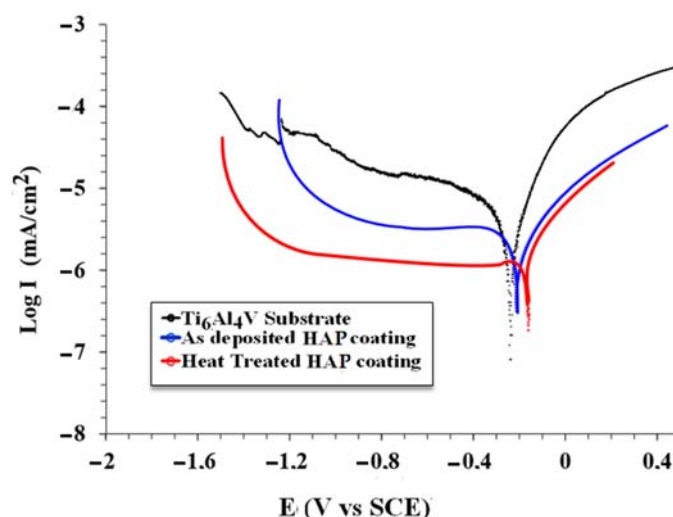


Figure 11. Tafel polarization curves.

Figure 11 shows that the HAP-coated sample exhibits a more significant shift towards the nobler direction compared to the untreated sample and Ti alloy substrate. In addition, the heat-treated HAP coating was characterized by the lower I_{corr} and E_{corr} and the higher polarization resistance R_p compared to as-deposited and uncoated sample (see Table 2). Results were confirmed by optical micrographs of the corroded coating surfaces obtained after four days of immersion in NaCl solution (Figure 12).

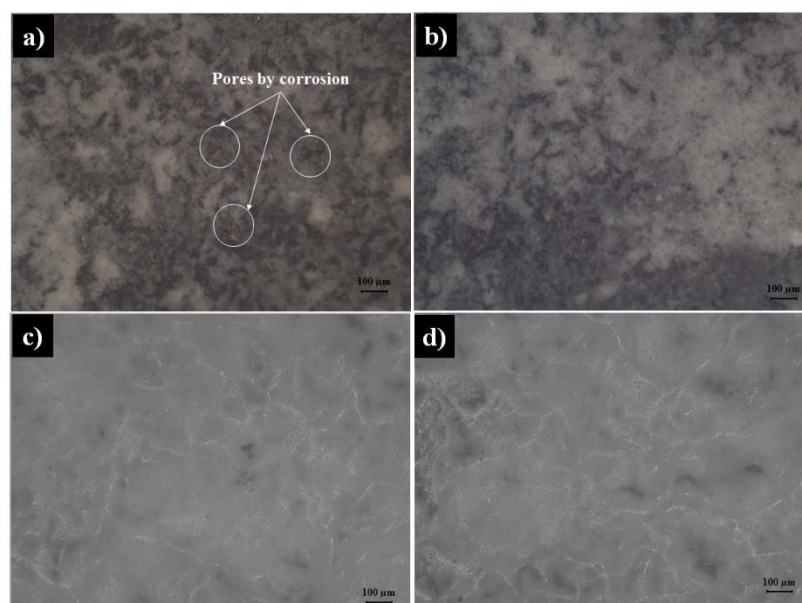


Figure 12. Optical micrograph of corroded samples: (a,b) as-deposited and heat-treated (c,d) HAP coatings.

The optical micrographs of the corroded coating surface morphologies reveal the elimination of the films due to the diffusion of corrosive elements. Results showed that the heat-treated sample had better corrosion resistance compared to the untreated coating. After heat treatment, the coating was compact and well crystallized, and the particles were distributed densely and homogeneously, which presents a barrier against the corrosion mechanism. In addition, the HAP heat-treated coating morphology had a minimal number of pores and cracks, which favors the corrosion protecting ability.

4. Conclusions

The objective of this work was the investigation of nanomechanical properties, adhesion, and corrosion resistance of HAP coating deposited by electrodeposition method on Ti₆Al₄V. The effect of the amount of H₂O₂ and the heat treatment on the coating microstructure and morphology was studied. SEM-EDXS and XRD results showed that the heat-treated HAP coatings deposited with 9% of H₂O₂ exhibited a compact and homogeneous microstructure. The heat-treated coating revealed a crystal growth which is stoichiometric hydroxyapatite (HAP) and β -tricalcium phosphate (β -TCP). An improvement of the nanomechanical and adhesion properties of HAP coatings was found after the heat treatment. The corrosion results indicate that the coatings act as a protective layer and improve the corrosion resistance of the substrate. The corrosion behavior of HAP coatings was also improved by heat treatment.

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