coatings

Article

HA Coating on Ti6Al7Nb Alloy Using an Electrophoretic Deposition Method and Surface Properties Examination of the Resulting Coatings

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Received: 21 May 2019; Accepted: 18 June 2019; Published: 21 June 2019

Abstract: Ti and its alloys, which are commonly used in biomedical applications, are often preferred due to their proximity to the mechanical properties of bone. In order to increase the biocompatibility and bioactivities of these materials, biomaterials based on ceramic are used in coating operations. In this study, by using an electrophoretic deposition method, instead of on the Ti6Al4V alloy which is commonly used in the literature, a hydroxyapatite (HA) coating operation was applied on the surface of the Ti6Al7Nb alloy, and the surface properties of the coatings were examined. Ti6Al7Nb is a new-generation implant on which there have not been many studies. The voltage values which were used in the coating operation were 50, 100, 150 and 200 V, and the time parameter was stabilized at 1 min. In our method, when preparing the solution, HA, ethanol, and polyvinyl alcohol (PVA) were used. At the end of the study, by using an electron microscope (SEM) the microstructures of the coatings were examined; elemental analyses (EDS) of the coating surfaces were performed; and by using an X-radiation diffraction (XRD) method, the phases which the coatings contained and the concentration of these phases were determined, and the coating thickness, roughness, and hardness values were also determined. Also, by conducting a Scratch test, the strength of the surface combination was examined. At the end of the study, in each parameter, a successful HA coating was seen. By comparing parameters with each other, the ideal voltage value in this coating was determined. It was determined that the most suitable coating was obtained at 100 V voltage and 1 min deposition time.

Keywords: hydroxyapatite (HA); electrophoretic deposition (EPD); Ti6Al7Nb; coating; surface properties

1. Introduction

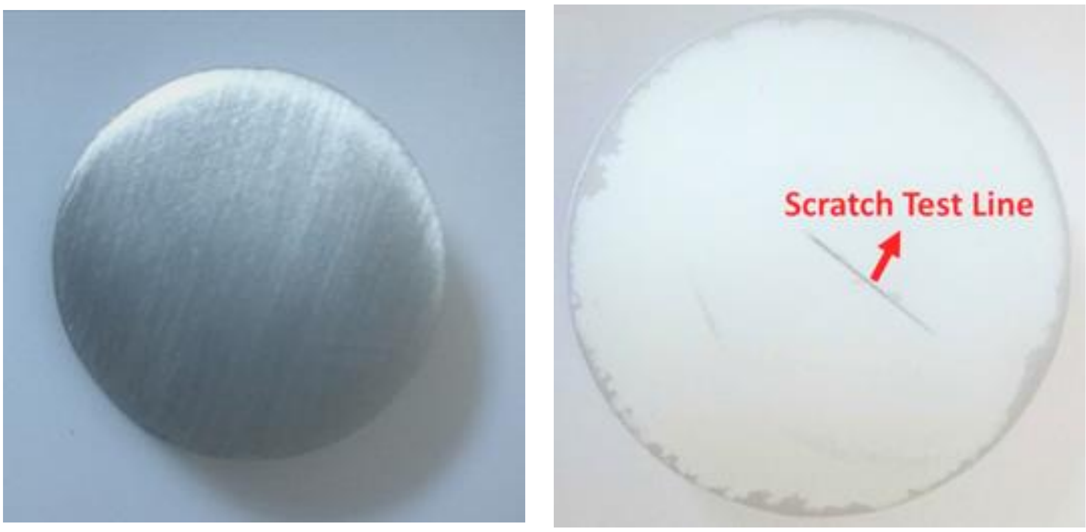
Biomaterials are materials which are used to fulfill the functions of organs and tissues in the human body. These materials are separated into four groups: metals, polymers, ceramics, and composites [1]. Titanium, which is one of the metallic materials, and its alloys are often used in implants due to their high biocompatibility [2–4]. In particular, the Ti6Al7Nb and Ti6AL4V alloys are commonly used in synthetic hip and tooth implants due to their mechanical, chemical, and biological properties [5]. However, the vanadium toxicity of titanium alloy components has become especially worrying. The diffusion of vanadium ions from this alloy causes diseases like peripheral neuropathy, osteomalacia, and Alzheimer's [6]. In our study, Ti6Al7Nb, which we used as the base material, is a new-generation implant material that was developed by the replacement of the controversial vanadium element in Ti6AL4V with niobium [7]. Metallic materials are exposed to corrosion by the fluids which are excreted by the body. Over time, the release of metallic ions in the implant's structure can cause negative effects on the tissues surrounding the implant. Besides this, metallic materials are not bioactive [4]. In order to increase the bioactivity of these implants, a surface operation is needed [4,8]. Because of this, metallic implants are generally subjected to a hydroxyapatite (HA) operation [4,9].

HA is a bioceramic material based on calcium phosphate, which forms most of the inorganic components of bones and teeth [10,11]. Hydroxyapatite is not used as a structural material directly due to its low mechanical properties. Thus, it is used by being applied on a metallic implant material [12]. HA coatings decrease the release of metallic ions by applying a barrier to the metallic implant. Also, with its chemical compound, it increases the bioactivity of the implant [4,13]. Since HA supports bone growth, it is the most used bioactive material [12,14]. In order to coat metallic implants with calcium phosphate material, some methods like immersion coating, electrochemical precipitation, biomimetic method, plasma spraying, and electrophoretic deposition are used [15,16]. Among these, the electrophoretic deposition method is a method which creates a coating of the bioceramic dust particles on the implant material by way of the electric field effect in the suspension [17,18]. One of the highlights of this method is that it is cheaper than other methods like plasma spraying [19,20]. In addition, it is easy to apply, making it very popular in industry [15]. The factors which affect the coating quality in coating operations via the EPD method are the deposition period, the applied voltage, and the suspension concentration [21].

2. Materials and Methods

2.1. Implant Material Selection

In this study, the Ti6Al7Nb alloy, which is often used in biomedical applications as a base material, was chosen. The base material samples used were of dimensions Ø20 × 15 mm with 5 pieces used to test each parameter, giving 20 pieces in total. Pre- and post-coating images of the TiAl7Nb alloys are given in Figure 1. An optical microscope image of the material before the coating was applied is given in Figure 2.



(**a**) (**b**)

Figure 1. TiAl7Nb alloys: (**a**) pre-coating and (**b**) post-coating images.

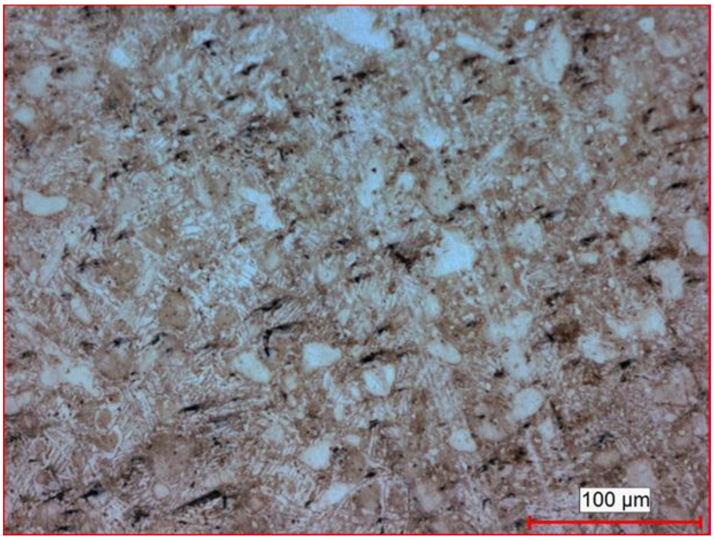


Figure 2. Optical microscope image of the Ti6Al7Nb alloy surface prior to coating.

2.2. Preparation of the Coating

In this study, the Ti6Al7Nb implant material was rubbed using SiC emery paper (P180–P1200 grit) and was washed with detergent and water. Then, the material samples were cleansed in an ultrasonic bath with a wash of pure water for 30 min, with a wash of ethyl alcohol for 30 min, and with another wash of pure water for 30 min, respectively. In order to remove the oxide layers which had occurred on their surfaces, an H_2O–HF–HNO_3 (94:3:3%V) solution was prepared, and the samples were kept in this solution for 5 min. Finally, they were made ready for the coating operation by washing them in an ultrasonic bath with pure water again for 30 min and drying them at 25 °C in an oven.

In the electrophoretic deposition operation, ethanol was used at a purity of 99.8%. In a Teflon beaker, 1 g of HA (Sigma Aldrich, Saint Louis, MO, USA) and 1 g of PVA (Sigma Aldrich) were added to 100 mL of ethanol (Sigma Aldrich) and they were mixed in a magnetic mixer (Cimaron, Guangdong, China) for 30 min; the homogeneous diffusion of HA dust was thus provided. In order to provide suspension stability, the pH value was set at 4 by using HNO_3 and NaOH.

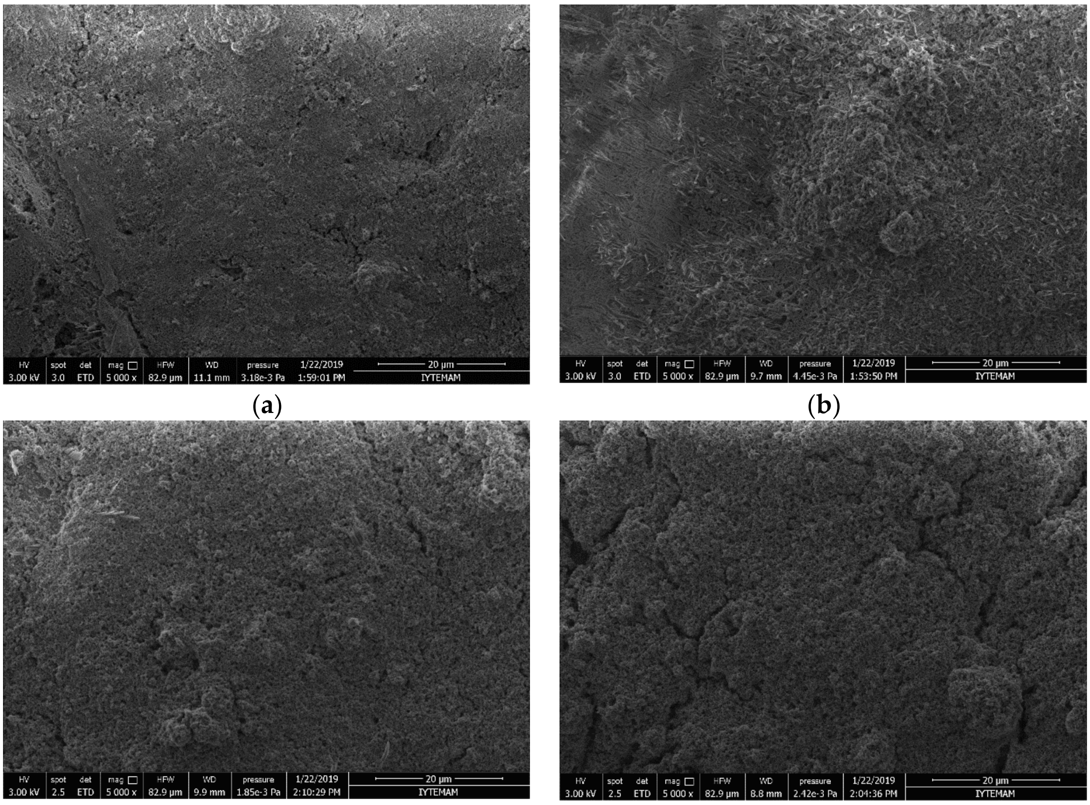
For the coating operation, the Ti6Al7Nb alloy was placed as anode and cathode in positions such that the surfaces to be coated faced each other, and the distance between them was set as 10 mm. The material was dipped into the steady suspension which was prepared in the Teflon beaker and was connected to a DC power supply (Bio RAD Powerpac Basic, Singapore, Singapore). In order to examine the effect of the voltage applied for a constant period on the coating properties, the voltage effect period was kept at a constant value of 1 min and the voltage values were set to 50, 100, 150, and 200 V. The coating operations were performed at these parameters.

In order to increase the bonding strength of the coatings which were formed, the coatings were kept in the oven in the Manisa Celal Bayar University Technical Sciences Vocational School Laboratory at room temperature for 24 h, and then they were heated up to 600 °C at a heating speed of 2 °C/min in a Protherm Furnaces Eco trade mark oven (Protherm Furnaces, Ankara, Turkey) at Manisa Celal Bayar University Technical Sciences Vocational School. They were left to cool after being kept at 600 °C for 1 h.

3. Results

3.1. SEM-EDS

The microstructure examination analyses of the coated samples were performed by using a QUANTA 250 FEG model scanning electron microscope (Fei, Tokyo, Japan) at the İzmir High Technology Institute Material Research Center, İzmir, Turkey, and 5000× images of the results gained in the SEM microstructural examinations are given in Figure 3. Upon examination of the SEM images, it can be seen that the HA structure successfully formed on the surface. It can also be seen that as the voltage value increased, some fractures occurred on the surface.

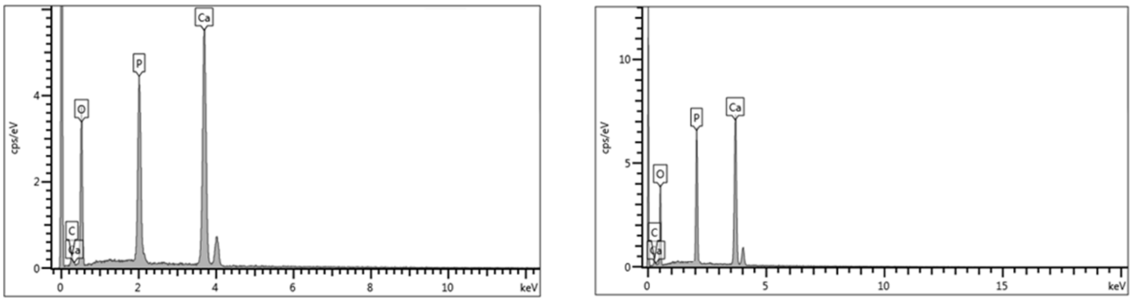


(**a**) (**b**)

(**c**) (**d**)

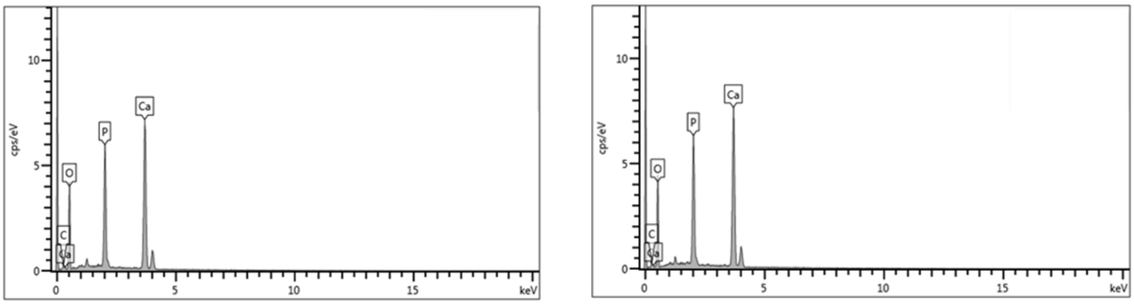
Figure 3. SEM images of hydroxyapatite (HA)-coated Ti6Al7Nb alloys (5000×): (**a**) 50 V/60 s, (**b**) 100 V/60 s, (**c**) 150 V/60 s, (**d**) 200 V/60 s.

The elemental components of the coated sample structures were determined by using an EDX detector on the QUANTA 250 FEG model scanning electron microscope at the İzmir High Technology Institute Material Research Center. The comparative EDS results for different coating voltages are given in Figure 4. When the results are examined, it can be observed that a calcium phosphate structure occurred in all coatings. For each parameter, the Ca/P ratio is given in Table 1.



(**a**) (**b**)

Figure 4. *Cont.*



(**c**) (**d**)

Figure 4. The EDS results of HA-coated Ti6Al7Nb alloys: (**a**) 50 V/60 s, (**b**) 100 V/60 s, (**c**) 150 V/60 s, (**d**) 200 V/60 s.

Table 1. Ca/P ratios for different voltage values.

Voltage	Ca/P
50 V	1.61
100 V	1.65
150 V	1.72
200 V	1.73

3.2. *XRD*

In order to determine which phases the coated samples contained and the concentrations of these phases, a PHILIPS X'PERT PRO X-radiation diffraction device (XRD, Philips, Tokyo, Japan) was used. Figure 5 shows the results of the XRD tests. According to the test results, the HA crystals occurred at peak points of 32.2494°, 34.1778°, 39.9130°, 48.1571°, and 50.5511°.

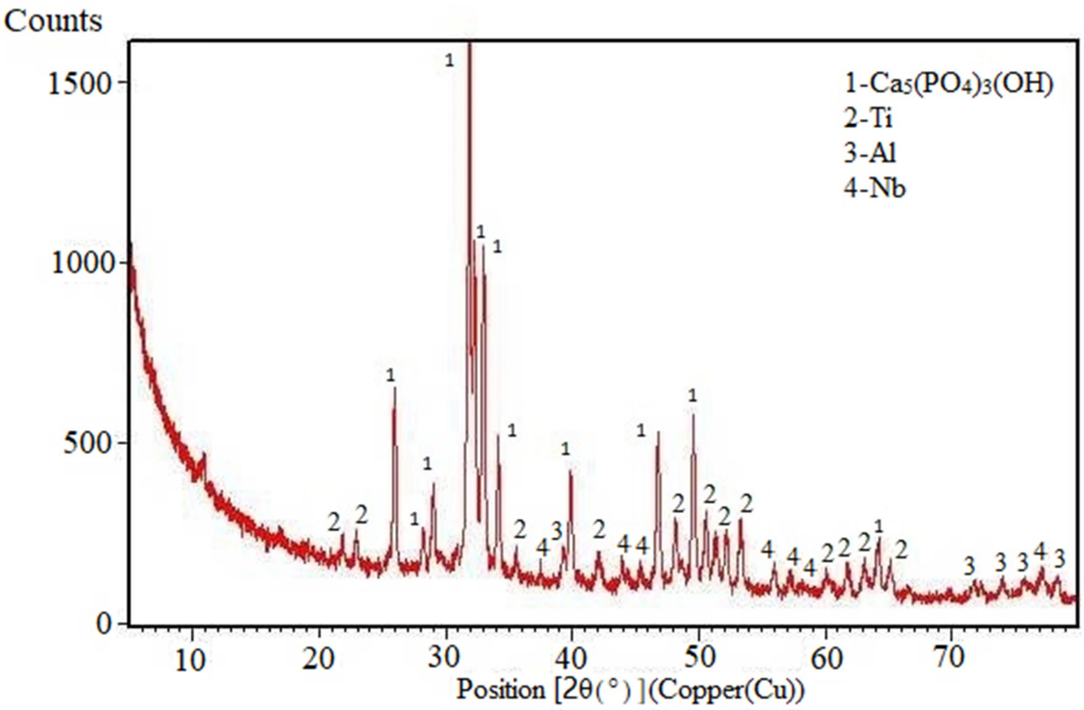


Figure 5. XRD analysis results.

3.3. Coating Thickness

The thickness of the HA coatings formed using the electrophoretic deposition method was evaluated in terms of µm using a ElektroPhysik MiniTest 730/Sensor FN 1.5 HD trademark device (ElektroPhysik, Oakland, NY, USA) at the Manisa Celal Bayar University Technical Sciences Vocational School Laboratory. The averages of the results were taken by performing evaluations on each coating surface five times. For 50, 100, 150, and 200 V values and a deposition period of 1 min, five evaluations were performed for each gained coating, and averages of the results were taken. The average values of the coating thicknesses gained from the evaluation results are given in Table 2.

Table 2. The average thicknesses of HA coatings.

Coating Thicknesses (µm)(60 s)	
50 V	4.38 ± 0.085
100 V	5.43 ± 0.108
150 V	7.60 ± 0.112
200 V	9.42 ± 0.135

3.4. Surface Roughness

For the determination of the surface roughness of the samples gained as the result of the coatings, a Roughness Tester PCE-RT 1200 model device (PCE-RT 1200, Meschede, Germany), which was present in the Manisa Celal Bayar University Technical Sciences Vocational School Laboratory, was used. The evaluation range was determined as 12.5 mm and the evaluation speed was determined as 0.5 mm/s; the results were gained in terms of micrometers. For the coatings formed with 50, 100, 150, and 200 V and a 1 min deposition period, evaluations were performed five times for each coating, and the average of the evaluations was taken. The average roughness values gained from the evaluation results are given in Table 3.

Table 3. The average roughnesses of HA coatings.

Surface Roughnesses (Ra) (µm)(60 s)	
50 V	0.818 ± 0.104
100 V	1.055 ± 0.095
150 V	1.552 ± 0.099
200 V	1.673 ± 0.081

3.5. Scratch Test

In order to evaluate the bonding strength of the HA coatings to the base metal, on the nano scratch test device (CSM Instrument, Needham, MA, USA) present in the Middle East Technical University Central Laboratory, Ankara, Turkey, a load range of 0.05–3 N, a scraping length of 5 mm, and a scraping speed of 5 mm/min were used. In Figures 6–9, the friction coefficient graphics and the scraping marks on the coatings gained with 50, 100, 150 and 200 V and a 1 min deposition period using the electrophoretic deposition method are shown. Upon examination of the figures, it can be seen that the friction coefficient decreases as the voltage value increases.

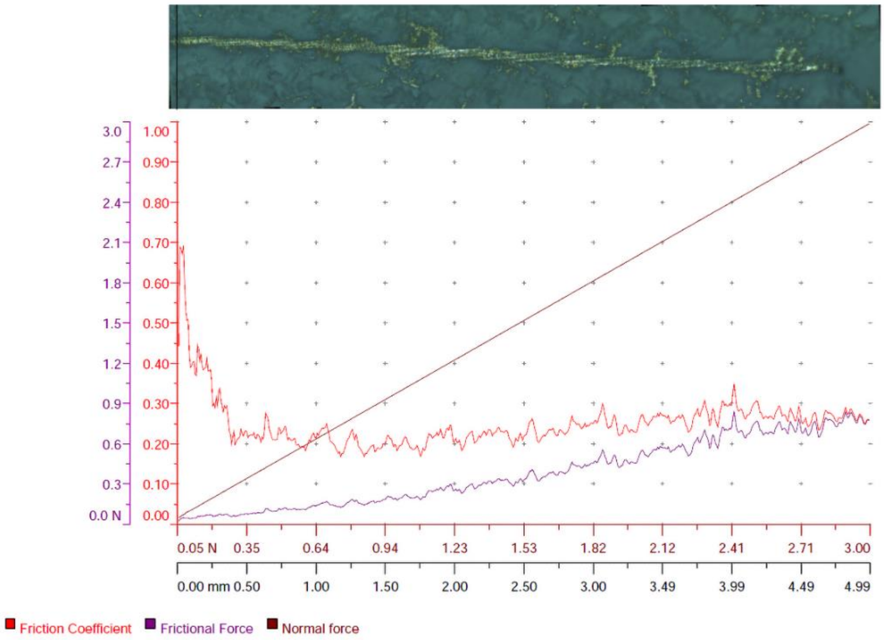


Figure 6. The friction force which occurred under the loads applied during Scratch testing of the coatings formed at 50 V and a 1 min period, and the variation of the friction coefficients.

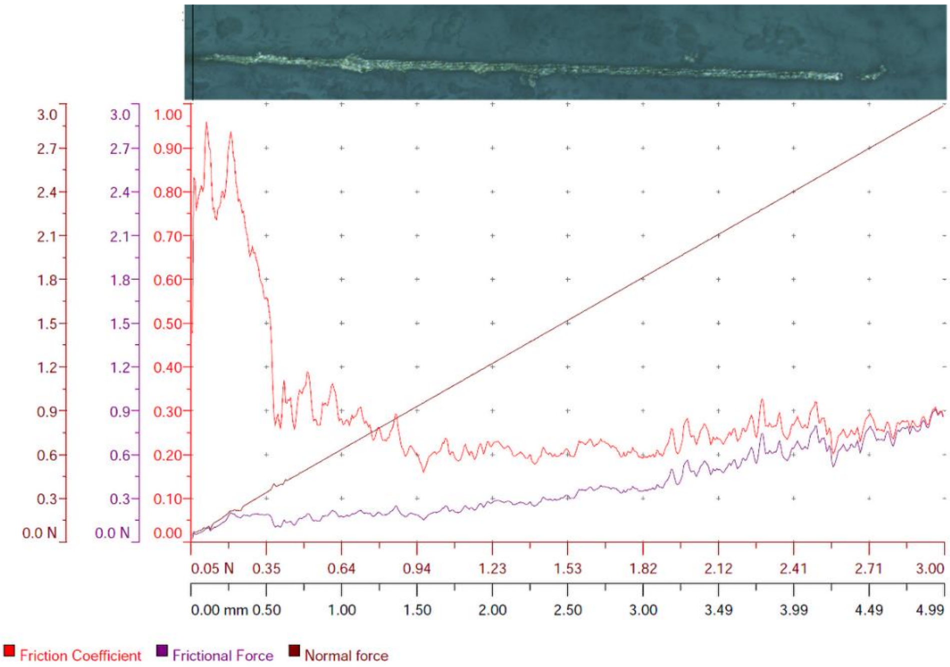


Figure 7. The friction force which occurred under the loads applied during Scratch testing of the coatings formed at 100 V and a 1 min period, and the variation of the friction coefficients.

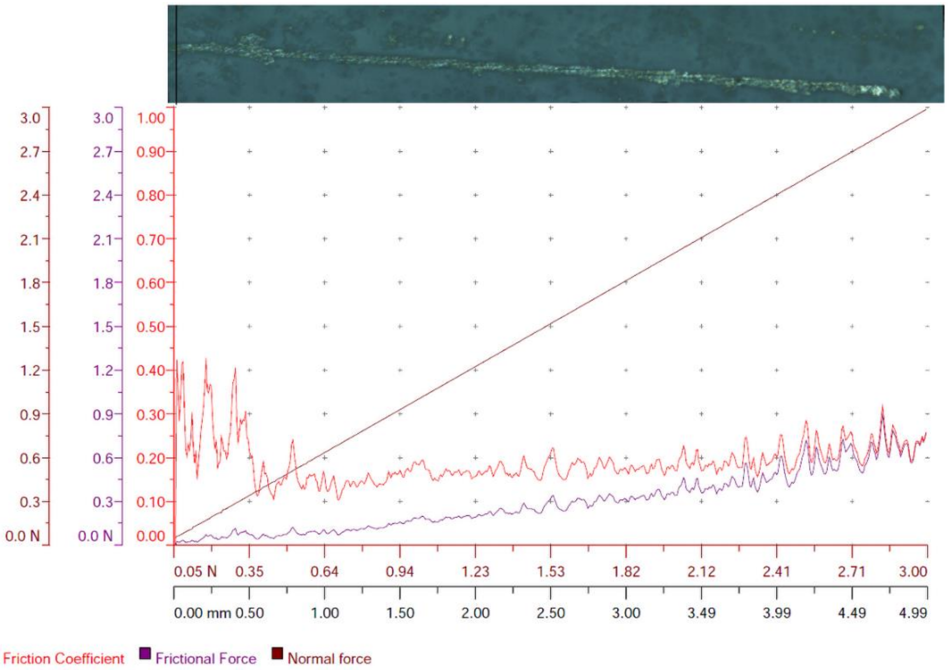


Figure 8. The friction force which occurred under the loads applied during Scratch testing of the coatings formed at 150 V and a 1 min period, and the variation of the friction coefficients.

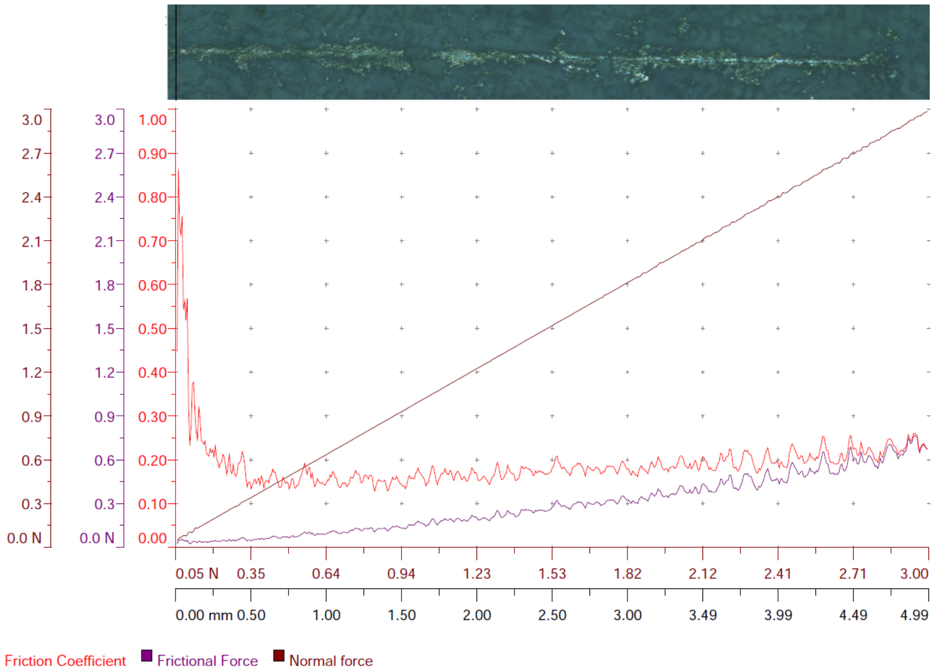


Figure 9. The friction force which occurred under the loads applied during Scratch testing of the coatings formed at 200 V and a 1 min period, and the variation of the friction coefficients.

4. Discussion

HA crystals were observed at peak points of 2Theta = 26.06° and 31.62° in the XRD results of the coatings Kumar et al. gained in the HA coating operation that they performed on a Mg-3Zn alloy surface via the electrophoretic deposition method at 20 V/cm for 10 min [14]. Iqbal et al. observed HA crystals at peak points of 25.91°, 28.94°, 31.78°, 32.19°, 32.93°, 34.10°, 39.80°, 46.71° and 49.49° in the coating operation they performed on 316L stainless steel [15].

As a result of the performed evaluations, when the coating thicknesses are examined, it can be seen that due to increasing voltage value, the value of the surface roughness increased. Kwok et al. found a coating thickness of approximately 10 µm in the HA coating operation which they performed on Ti6Al4V bases at 200 V for 3 min [4]. Bartmanski et al. performed an HA coating operation on Ti13Zr13Nb bases in a solution which they prepared using 0.5 g of HA in 100 mL of ethanol at 50 V for a 1 min period, and they observed a coating thickness of approximately 29.35 µm [8]. Dudek et al. performed HA coating operations on NiTi shape memory alloy at different voltages and periods, and they observed coating thicknesses of 2.6 µm at 80 V over a 1 min period, 2.8 µm at 100 V over a 1 min period, and 4.2 µm at 80 V over a 2 min period [19].

As a result of the performed evaluations of the roughness values, it was observed that the surface roughness value increased with increasing voltage value. Bartmanski et al. evaluated the surface roughness value as 1.26 µm in the solution they prepared using 0.5 g HA in 100 mL ethanol for HA coating operations on Ti13Zr13Nb bases at 50 V and a 1 min period [8]. Javidi et al. formed coatings at different periods and voltages in HA coating operations they performed on 316 L stainless steel; they found the surface roughness on the coating they formed at 90 V and at a 180 s deposition period to be 1.8 µm. They also determined that surface roughness increased with increasing voltage [13].

5. Result

In this study, an HA coating operation was performed by using an electrophoretic deposition method on Ti6Al7Nb alloy. When the mechanical and metallographic test results performed after the coating were examined, it was observed that for all of the applied parameters, successful results were achieved. By the end of the study, upon examination of SEM images, it was observed that the coatings gained by applying 50 and 100 V did not have any cracks and the coatings gained by applying 150 and 200 V showed the same cracks. As a result, it was determined that with increasing voltage, cracking of the coating surfaces increased. Besides this, at all parameters, homogeneous coatings were gained.

The Ca/P ratios of the HA coatings formed at different voltage values were determined from the EDS analysis results. These were determined as 1.61 at 50 V, 1.65 at 100 V, 1.72 at 150 V, and 1.73 at 200 V. It can be seen that the value of 1.67, which is the ideal Ca/P ratio in this context, was approximately gained at 100 V.

When the coating thickness results were examined, the lowest coating thickness was evaluated as 4.38 µm at 50 V, and the highest coating thickness was evaluated as 9.42 µm at 200 V. It was determined that the coating thickness increases with increasing voltage. When the surface roughness results were examined, the lowest surface roughness was evaluated as 0.818 at 50 V, and the highest surface roughness was evaluated as 1.673 µm at 200 V. It was determined that with increasing voltage, the surface roughness value increased.

Upon examination of the plots of the friction force and friction coefficient, the highest friction coefficient was evaluated as an average of 0.25 at 50 V, and the lowest friction coefficient was evaluated as an average of 0.18 at 200 V. It was determined that with increasing voltage, the friction coefficient decreased.

The microscopic images showed that the coating with the lowest bonding strength was formed at 50 V, and the coating with the highest bonding strength was formed at 200 V. It was determined that with increasing voltage, the bonding strength increased.

At the conclusion of the study, when all analysis results were examined, it was determined that the most appropriate parameters were gained at 100 V and a 1 min period of deposition due to the facts that the coating does not comparatively have any cracks; its Ca/P ratio is the closest to the ideal value; and its coating thickness, surface roughness value, friction coefficient, and coating bonding strength are ideal.

Author Contributions: İ.A. and A.İ.B. conceived and designed the experiments; İ.A. and M.K. performed the experiments; İ.A. and M.A.C. analyzed the data; İ.A., M.K. and A.İ.B. wrote the paper.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

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