JAASCI
http://jaasci.com
JOURNAL OF ADVANCED APPLIED SCIENCES
e-ISSN: 2979-9759
PRENSIP
https://prensip.gen.tr

RESEARCH ARTICLE

Coating of Ti6Al4V Alloys by Physical Vapor Deposition Method and Micro-scratch and Corrosion Test Investigations of Coated Samples

Hakan Ada[1✉] • Ahmed Qays Jabbar El Rubaye[2] • Elif Asikuzun Tokeser[3] • Ahmet Mavi[4] • Sinan Aksoz[5]

[1]Gazi University, Faculty of Technology, Department of Metallurgical and Materials Engineering, Ankara/Türkiye
[2]Kastamonu University, Institute of Science, Department of Materials Science and Engineering, Kastamonu/Türkiye
[3]Kastamonu University, Faculty of Engineering and Architecture, Department of Metallurgical and Materials Engineering, Kastamonu/Türkiye
[4]Gazi University, Faculty of Technology, Department of Manufacturing Engineering, Ankara/Türkiye
[5]Pamukkale University, Faculty of Technology, Department of Metallurgical and Materials Engineering, Denizli/Türkiye

ARTICLE INFO

Article History
Received: 25.06.2023
Accepted: 30.06.2023
First Published: 30.06.2023

Keywords
Coating
Corrosion
Micro-scratch
PVD

ABSTRACT

Titanium alloys are one of the most preferred materials in the aerospace industry due to their low density and high mechanical properties. It is also widely preferred in diving and marine equipment due to its excellent corrosion resistance in the marine environment. Due to its high biocompatibility and corrosion resistance, it is also used as a basic component of the biomedical materials sector, especially as implant material. However, titanium alloy has poor wear resistance, so surface treatment is required before use in many applications. In this respect, coated titanium alloys are expected to exhibit higher wear and corrosion resistance. In this study, TiAlN, AlCrN, TiSiN and TiN coatings were applied to the samples using Ti6Al4V alloy as the base material by PVD method at two different coating thicknesses, followed by micro-scratch and corrosion tests on the coated samples. As a result of the micro-scratch tests, it was determined that the indentation depth of the samples increased with the increase in the applied dynamic force, the average friction coefficient values varied between 0.08 and 0.16, and the results of the corrosion tests showed that the cathodic current densities of the coating samples varied considerably compared to the base material. Among the corrosion samples, the closest current density to the base material was observed in the thin AlCrN coating, while the lowest corrosion rate was observed in the thick TiN coating.

Please cite this paper as follows:

Ada, H., El Rubaye, A. Q. J., Asikuzun Tokeser, E., Mavi, A., & Aksoz, S. (2023). Coating of Ti6Al4V alloys by physical vapor deposition method and micro-scratch and corrosion test investigations of coated samples. *Journal of Advanced Applied Sciences*, *2*(1), 36-45. https://doi.org/10.29329/jaasci.2023.562.05

1. Introduction

Titanium has many distinctive properties that lead to its widespread use in many applications and industries such as biomedical, petroleum industries, chemical, aerospace and transportation. Among its most important properties are biocompatibility, high specific strength, corrosion resistance, good fatigue strength (Sha & Malinov, 2009). At normal ambient pressure and temperature, the crystal structure of titanium is tightly packed hexagonal (SPH) α-phase with a c/a ratio of 1.587. At a temperature of about 882 °C, the Ti crystal structure transforms into the β-phase, which is a volume-centered cubic (HMK) structure. This phase remains constant at the melting temperature. There are also some alloying

✉ Corresponding author
E-mail address: hakanada@gazi.edu.tr

elements that increase or decrease the transition temperature from α to β (Luo et al, 2009).

Nitrogen (N), aluminum (Al), gallium (Ga), oxygen (O), germanium (Ge) and carbon (C) are α stabilizers, while silicon (Si), molybdenum (Mo), copper (Cu), vanadium (V), nickel (Ni), tantalum (Ta), cobalt (Co), niobium (Nb), chromium (Cr), manganese (Mn) and iron (Fe) are β stabilizers (Sa'aidi et al, 2022; Ahmad & Zuhailawati, 2020).

Titanium alloys can be divided into three types, α, β and α-β alloys, depending on the two phases of titanium (Li et al, 2019). Due to their superior specific strength, high corrosion resistance, superior melting temperature and low density, titanium alloys are widely used in ship technology, biomedical and space technology (Luo et al, 2009). However, their high sensitivity to adhesive wear and fretting wear, high coefficients of friction, low wear resistance and poor resistance to high-temperature oxidation have limited the application of titanium alloys (Wang et al, 2008). Therefore, many tuning techniques such as ion implantation and deposition, laser surface modification technology and anodic oxidation have been used to solve these problems.

Ti6Al4V has good mechanical and physical properties as well as good formability. Therefore, as Ti6Al4V is developed, it becomes a widely applied Ti alloy. The titanium alloy contains β stabilizers (4 wt% V) and a solid solution strengthener (6 wt% Al).

Materials can lose their mechanical properties as they are used in different situations. Especially wear resistance of parts exposed to wear (tool steels, implant materials, etc.) is very important in terms of durability and long life. In some cases, in order to increase the wear and corrosion resistance of materials, a number of metallurgical and chemical treatments are applied to the material surfaces. The most common of these are nitriding, boriding and carburizing. CVD and PVD add durability to materials with a very thin layer. In recent years, surface treatment with PVD coating has been one of the rapidly developing production methods. In the PVD method, the appropriate material is evaporated from the surface by bombarding high-energy ions with a method called sputtering or by condensing the material as a thin film on the surface of the mold with temperature. So, this process is called physical vapor deposition, or PVD.

PVD processes are one of the most important and most widely used deposition processes for the deposition of thin films as well as for the deposition of layers or layers with thicknesses ranging from a few nanometers to several micrometers (Leyendecker et al, 1991). The PVD process is also applied by reactive deposition on deposition compounds. The compounding process occurs mostly through interactions between target materials and gases such as nitrogen and oxygen. Arc vapor deposition is a PVD process. This method uses a high current, low voltage arc to deposit solid coatings by vaporizing the target material. The vaporized material is highly ionized and usually the substrate tends to attract the ionized material (Mattox, 2010).

A solid coating is a substance that improves its alloy by adding good properties to it or improving its properties, such as wear-resistant properties, to increase the life and performance of medical materials as well as the productivity of cutting tools (Chim et al, 2009). There are many solid coatings, but the most famous and important ones we will consider in this study are TiN, TiAlN, TiSiN and AlCrN.

This study is based on the production of Ti6Al4V coatings by PVD coating method and the investigation of the corrosion properties of the obtained coatings. The coatings to be applied on Ti6Al4V alloys were realized by PVD method with different types of nitride-containing materials and different thicknesses. In the next stage, micro-scratch and corrosion tests were applied to the samples coated by PVD method.

2. Materials and Methods

In this study; TiAlN, AlCrN, TiSiN and TiN coating processes were applied to the samples using Ti6Al4V alloy as the base material by physical vapor deposition (PVD) method at two different coating thicknesses and it was tried to determine the scratch and corrosion resistance of the coated samples. The samples were subjected to micro-scratch tests to determine the mechanical properties of the samples and corrosion tests to determine the corrosion resistance of the samples.

2.1. Material

In this study, Ti6Al4V alloy was preferred as the main material due to its high biocompatibility and corrosion resistance. The chemical composition and mechanical properties of Ti6Al4V alloy in ASTM F 1472 standard are as shown in Table 1. Cylindrical specimens with a diameter of 12 mm and a height of 30 mm were preferred for coating processes.

AlCrN, TiAlN, TiSiN and TiN were used as coating materials in the coating processes. The properties of AlCrN, TiAlN, TiSiN and TiN coatings are given in Table 2.

2.2. Method

In this study, PVD coating processes of AlCrN, TiAlN, TiSiN and TiN materials were carried out on Ti6Al4V base material by cathodic arc method. The coating processes were carried out on ISYS i90A brand and model device (Figure 1).

Table 1. Chemical and mechanical properties of Ti6Al4V alloy.

Elements	**Al**	**V**	**C**	**Fe**	**O**	**N**	**H**	**Ti**
Wt. %	5.5–6.75	3.5 – 4.5	< 0.1	< 0.3	< 0.2	< 0.05	< 0.015	Remaining

Table 2. Coating properties.

Coating Material	**Microhardness (Hv 0.05)**	**Coefficient of Friction Against Steel (dry)**	**Maximum Operating Temperature (°C)**	**Coating Thickness (µm)**	**Coating Color**
AlCrN	3200	0.35	1100	1-4	Grey
TiAlN	3600	0.55	900	1-4	Black - purple
TiSiN	4200	0.50	1100	1-4	Bronze
TiN	2600	0.40	600	2-5	Golden

Figure 1. PVD coating machine (ISYS Intelligent System I 90A).

2.2.1. Surface cleaning and preparation processes

Since surface cleanliness is important for better coating processes, first of all, a serious surface cleaning and pre-coating preparation process was applied to the 12 mm diameter and 30 mm high specimens. Prior to the coating process, the surfaces of the samples were sanded (ground) using metallographic surface preparation techniques. With the classical metallographic preparation technique, the samples were surface cleaned using 80, 150, 240, 320, 400, 400, 600, 800, 800, 1000, 1200, 1500 and 2000 grit abrasives respectively. Then ultrasonic cleaning was performed by applying high frequency sound waves to the liquid-filled tank, where the samples in the tank were cleaned of dirt and minimal particles were destroyed. Polishing of the samples was also performed at this stage. Abrasive solutions of 6 µm, 3 µm and 1 µm in size for the samples respectively, and polishing processes were carried out by using suitable felt/cloth for these solutions. These processes were applied for surface cleaning before coating and the same processes were repeated during the sample preparation process before micro-scratch and corrosion examinations. After the samples were sanded and ultrasonically cleaned to the desired conditions, the coating process was started. Prior to the coating process, the surface cleaning process was carried out again with a more professional ultrasonic system using more professional devices and solutions. Prior to coating, the samples were subjected to pre-coating surface preparation using an 8-step system shown in Figure 2.

The 4 stages of the 8-stage system are based on the principle of washing with water, and the surface cleaning was carried out with solutions in the other 3 stages. The final stage is the drying stage. The samples were cleaned in the 8 stages we mentioned, respectively, as follows.

1. Washing with water
2. Cleaning with basic solution
3. Rinsing with water
4. Cleaning with acidic solution
5. Rinsing with water
6. Cleaning with neutral (acid + basic) solution
7. Rinsing with water
8. Drying

The pre-coating images of the samples, which were cleaned in 8 stages, are given in Figure 3.

Figure 2. Ultrasonic cleaning unit.

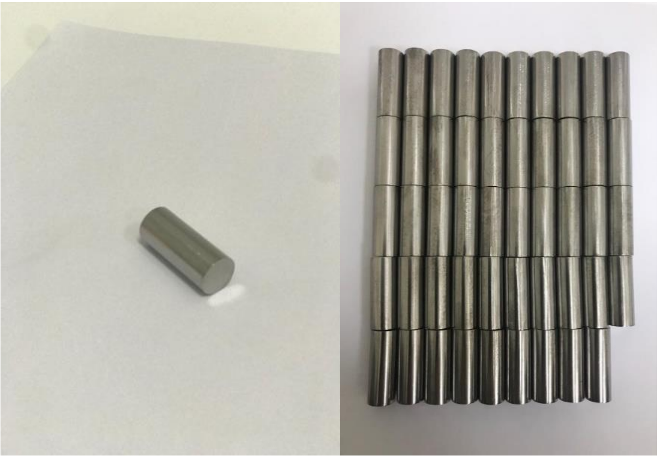

Figure 3. Samples prepared before PVD coating.

2.2.2. Coating process

The samples, whose surface cleaning was completed before the PVD coating processes, were placed in the coating boxes and placed in the device. Separate cathode materials were used for each type of coating for coating processes. The image of the cathode materials produced by the powder metallurgy method is given in Figure 4.

Coating processes were carried out to create two different coating thicknesses at different temperatures and parameters for each coating. Since it has a commercial value, the parameters are kept confidential by the company where the tests are carried out, and only the processing temperature and times are reported. In this context, the processes were carried out based on the temperatures and times given in Table 3.

The coated state of the samples, which were coated within the parameters given in Table 3, is given in Figure 5.

Figure 4. Image of cathode samples used in PVD coating processes.

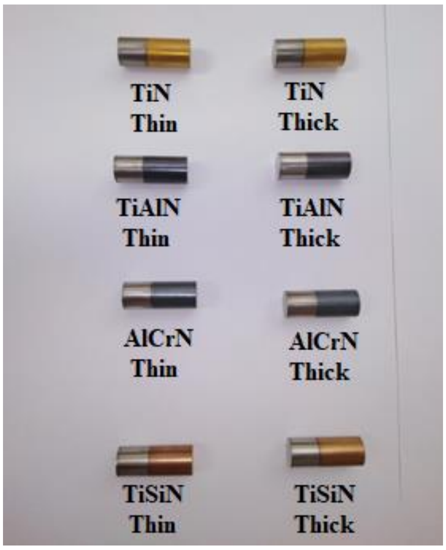

Figure 5. Coated samples.

Table 3. Temperatures and times in PVD coating processes performed with the cathodic arc method.

Sample No	Coating Type	Coating Temperature (ºC)	Pressure (MPa)	Time (Minutes)
1	TiAlN (thin coating)	450	0.5	240
2	TiAlN (thick coating)	450		360
3	AlCrN (thin coating)	500		240
4	AlCrN (thick coating)	500		360
5	TiSiN (thin coating)	500		240
6	TiSiN (thick coating)	500		360
7	TiN (thin coating)	450		240
8	TiN (thick coating)	450		360

2.2.3. Micro-scratch test investigations

The UMT device used in micro-scratch test investigations is a "force-driven static measurement" ultra-micro-indentation device specially designed for the investigation of mechanical properties near the surface of materials. Therefore, it is especially useful in determining the mechanical properties of thin coatings. It is force driven in the sense that the recess is driven into the surface until a resistance equal to a specified force is encountered. The resulting measurement is a static measurement in the sense that penetration is measured at each force step under force balance conditions. The Bruker UMT brand and model device given in Figure 6 is a device whose basic components are an optical imaging system and an indentation column. After choosing a suitable place for the recess with the aid of an optical microscope, the sample is placed on a holder in a positioning stage in a movable manner to a position below the recess so that the recess occurs with the lateral movement of this step.

2.2.4. Corrosion test investigations

Corrosion tests were carried out with a Gamry brand Reference 3000 model device given in Figure 7.a. Before the corrosion test - in the preparation phase, epoxy cold embedding process was applied to the test samples as seen in Figure 7.b, since we can determine the corrosion resistance of the coatings properly and only the coated part of the samples should be exposed to electrical conductivity. After pouring epoxy on the samples, it was left to solidify for about 20-40 minutes. After solidification, the samples were removed from the mold.

Gamry Reference 3000 model device given in Figure 7.a ; it is a potentiodynamic polarizing device that feeds a corrosion cell consisting of a working electrode. The working electrode is the sample and the counter electrode is graphite. The saturated calomel electrode (SCE) was placed as the reference electrode as shown in Figure 7.c. 0.1ml of electrolytic hydrocoloric acid (HCl) was added to the corrosion cell.

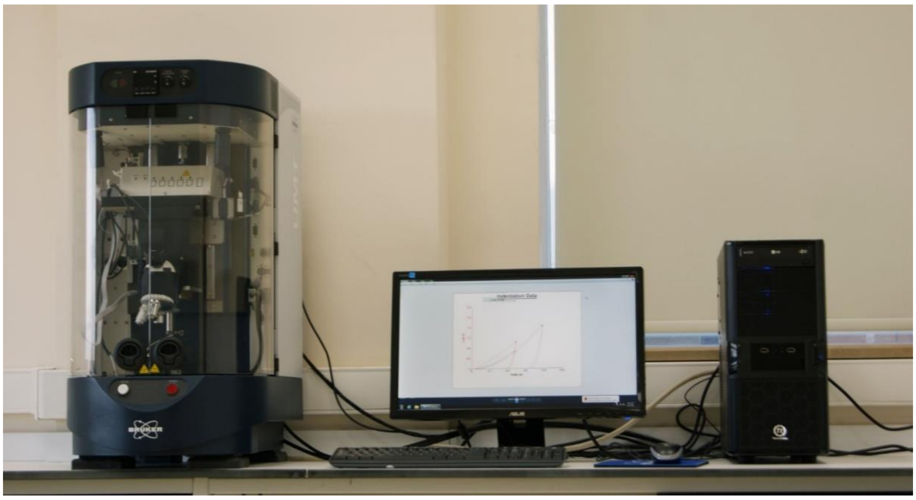

Figure 6. UMT Device.

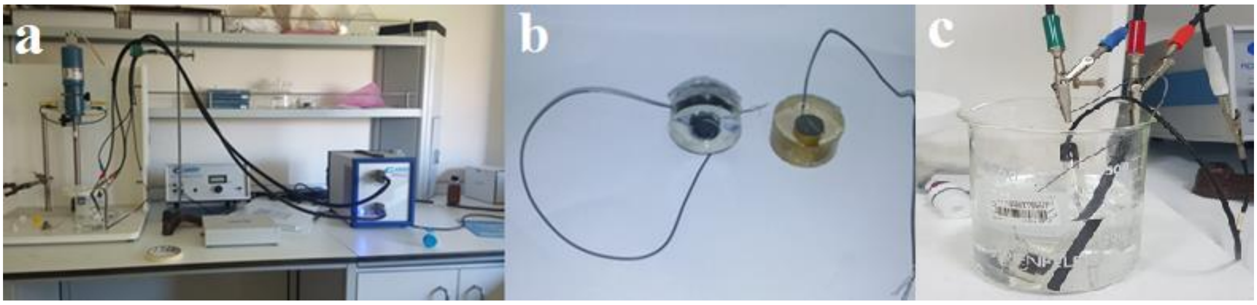

Figure 7. Corrosion equipments; a) Gamry test device b) Samples after molding c) Corrosion cell.

3. Results

Coating processes such as TiAlN, TiSiN, TiN and AlCrN were applied to the samples in order to improve some properties such as hardness, wear and corrosion resistance of Ti6Al4V alloys, which are used extensively in the implant industry due to their biocompatibility with the aerospace industry. In order to determine in detail the effect of the said coatings on the base material properties, the base material and the coated samples were subjected to micro-scratch and corrosion tests. The results obtained within the scope of these tests are explained and interpreted in this section.

3.1. Micro-scratch Test Results

The UMT device used in micro-scratch testing is a "force-driven static measurement" ultra-micro-indentation device specially designed for the investigation of mechanical properties near the surface of materials. Therefore, it is especially useful in determining the mechanical properties of thin coatings. It is force driven in the sense that the recess is driven into the surface until a resistance equal to a specified force is encountered. It is a static measurement in the sense that penetration is measured at each force step under force balance conditions. The UMT tester consists of its key components an optical imaging system and an indentation column. After a suitable location for the recess was selected using the optical microscope system, the sample was placed on a holder in a positioning stage, in a movable manner, to a position below the recess so that the recess would occur with the lateral movement of this step. With micro-scratch tests, friction coefficients, which are an important parameter for the wear resistance of test samples, can be calculated. The graphs obtained from the micro-scratch tests in this study are given in Figures 8-15.

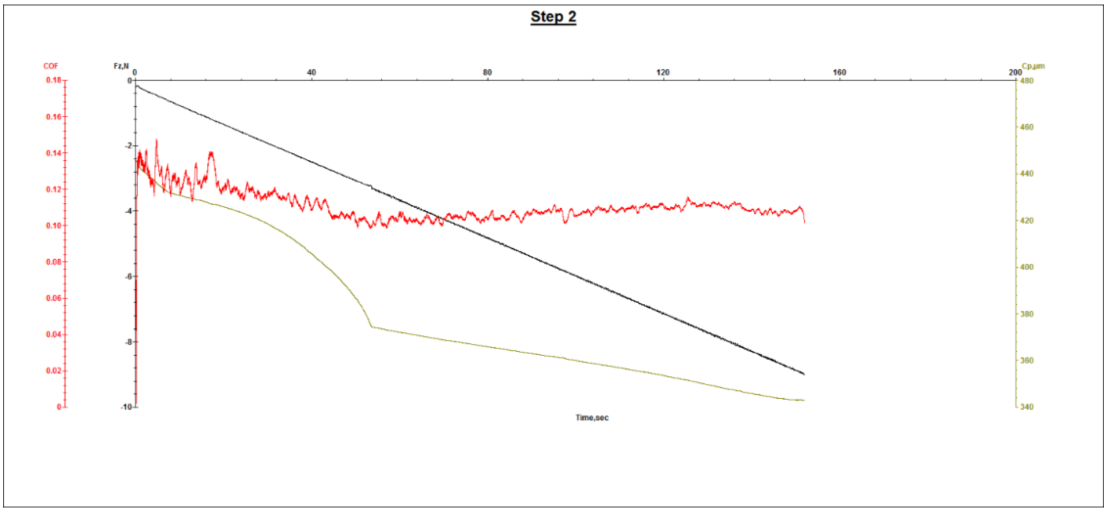

Figure 8. Micro-scratch test results for coating sample number 1 (thin TiAlN).

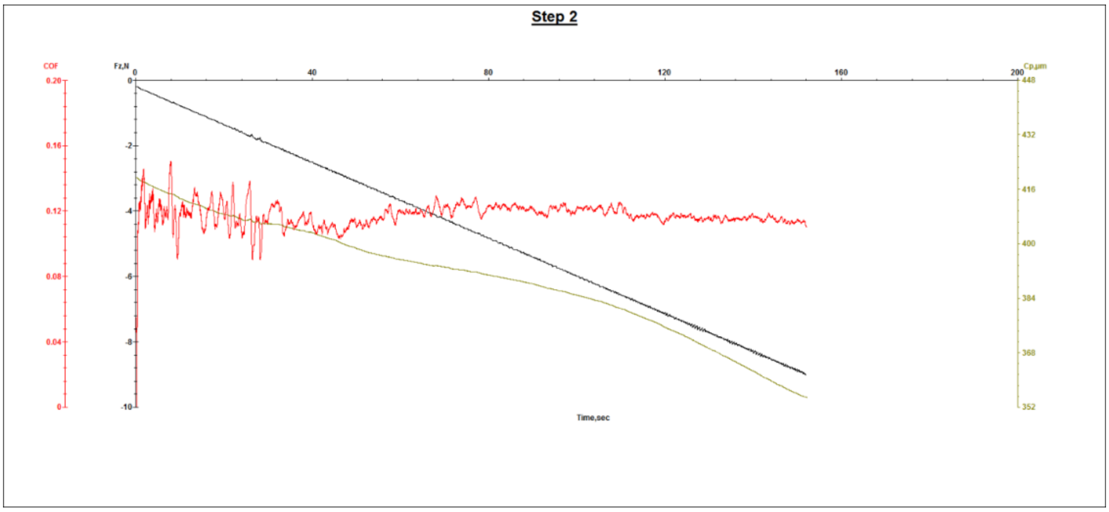

Figure 9. Micro-scratch test results for coating sample number 2 (thick TiAlN).

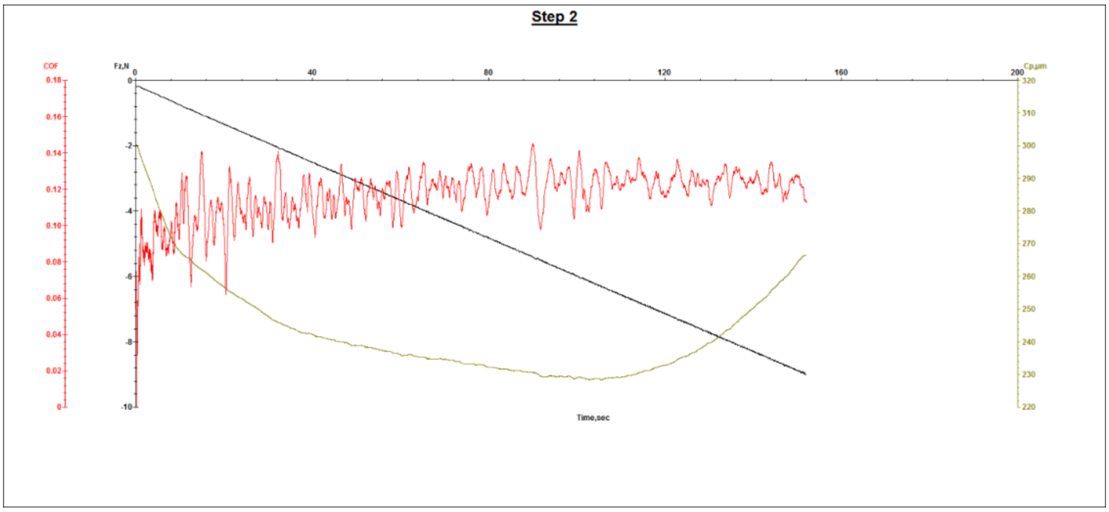

Figure 10. Micro-scratch test results for coating sample number 3 (thin AlCrN).

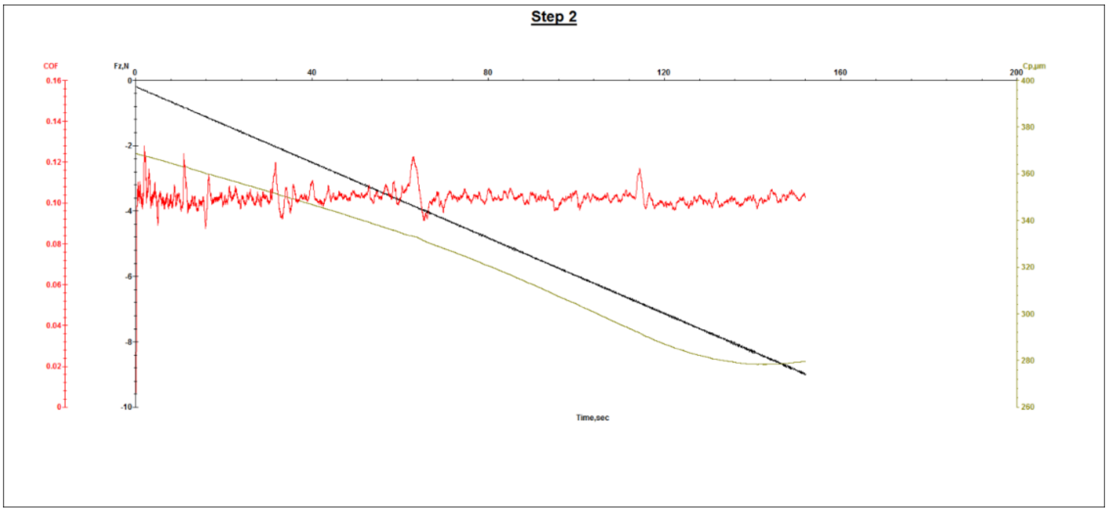

Figure 11. Micro-scratch test results for coating sample number 4 (thick AlCrN).

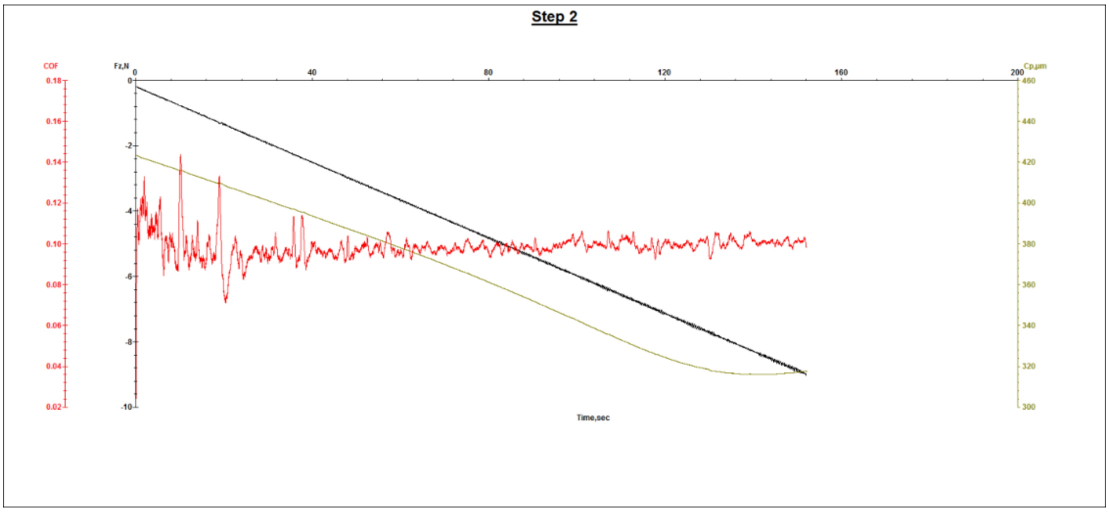

Figure 12. Micro-scratch test results for coating sample number 5 (thin TiSiN).

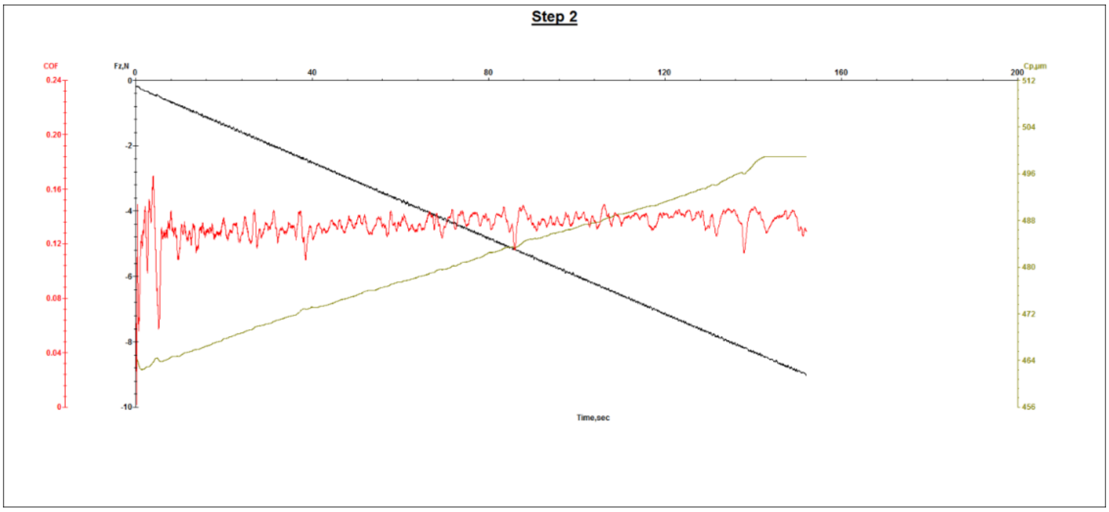

Figure 13. Micro-scratch test results for coating sample number 6 (thick TiSiN).

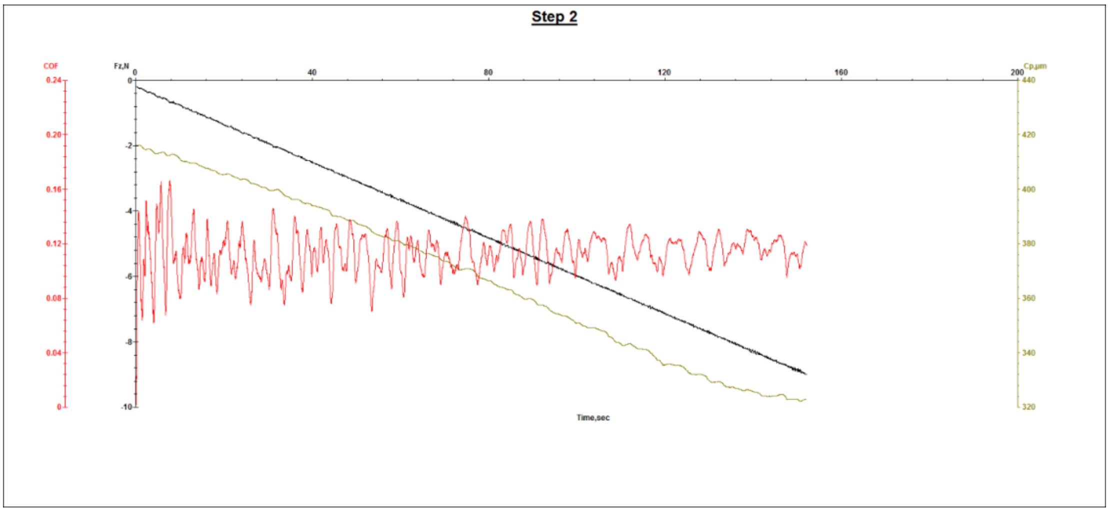

Figure 14. Micro-scratch test results for coating sample number 7 (thin TiN).

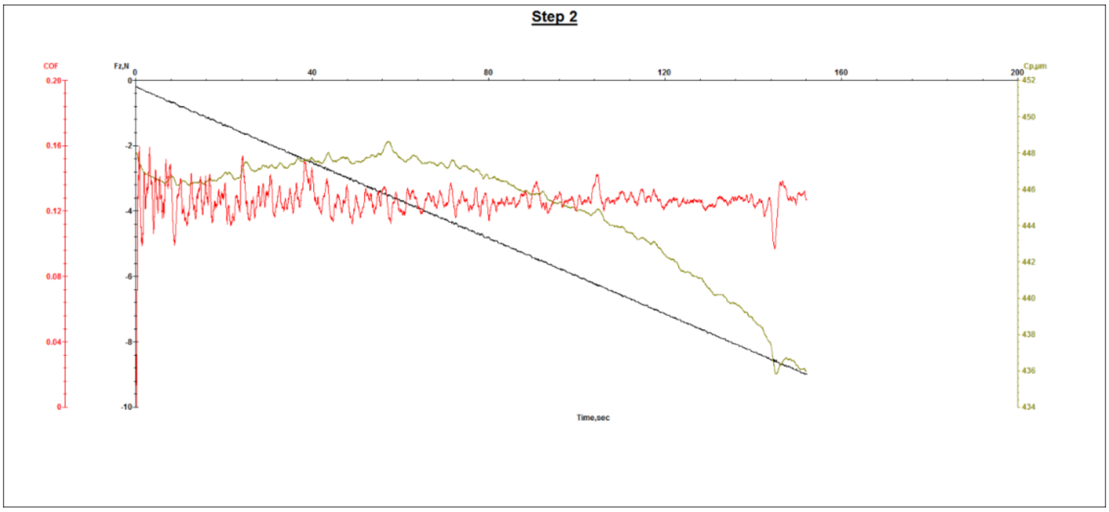

Figure 15. Micro-scratch test results for coating sample number 8 (thick TiN).

3.2. Corrosion Test Results

The corrosion test was carried out with a custom-built (Gamry) instrument, a potentiodynamic polarization device in which the instrument feeds a corrosion cell consisting of the working electrode. This is the measured sample and the counter electrode is graphite. A saturated calomel electrode (SCE) was placed as a reference electrode. Electrolyte (0.1m HCl solution) was added to the corrosion cell. The cables of all electrodes were then connected to the Gamry Reference 3000. The data generated after scanning was analyzed by Gamry Frame Work software installed on the computer.

It is almost impossible to prevent oxide formation in highly active titanium and its alloys due to their oxygen affinity. Even if the oxide films formed on the surface of titanium alloys are damaged, they continue to form oxide films as long as oxygen is present in the environment. Titanium can corrode in an oxygen-free environment. For this reason, nitrogen gas was passed through the 0.1M HCL solution to remove oxygen and OCP measurements were made at a scan rate of 2 mV/s at a range of ±0.3 mV to break the oxide layer. The corrosion rate of the samples was then determined by the Tafel Extrapolation method. Corrosion potentials and corrosion current density were determined from polarization curves. The electrochemical values obtained are listed in Table 4.

Table 4. Corrosion test results.

Sample Name	Ba (v/decade)	Bc (v/decade)	Icor (µAcm^{-2})	E Corr (mV)	Corrosion Speed (mpy)
Base material	0.0145	0.0037	15.20	-47.80	19.19
Sample number 1 (TiAlN - thin)	0.4556	0.1744	0.4690x10^{-3}	-184.0	0.5934x10^{-3}
Sample number 2 (TiAlN - thick)	0.6772	0.0758	0.02180	102.0	0.0276
Sample number 3 (AlCrN - thin)	0.1066	0.2294	0.9930	-227.0	1.257
Sample number 4 (AlCrN - thick)	0.07280	0.0524	0.0031	12.10	0.0039
Sample number 5 (TiSiN - thin)	0.4386	0.0372	0.0020	131.0	0.0258
Sample number 6 (TiSiN - thick)	0.0010	0.0193	0.0050	-45.40	0.0640
Sample number 7 (TiN - thin)	0.4742	0.1343	0.137	55.20	0.1728
Sample number 8 (TiN - thick)	0.7818	0.1362	0.4590x10^{-4}	-239.0	0.0581x10^{-3}

4. Discussion

4.1. Discussion of Micro-scratch Test Results

As a result of the graphs obtained from the micro-scratch tests given between Figure 8 and Figure 15; it was determined that the scratch depth created on the samples increased with the increase in the applied force. In the graphs, the red axis represents the coefficient of friction (COF), the black vertical axis represents the normal force (Fz), the black horizontal axis represents the time (sec) and the green vertical axis represents the contact point (Cp). With the dynamic load applied in the tests, depths between 100 and 140 µm were reached for approximately 150 seconds and 9.5 N force. At these depths, it was observed that the coefficient of friction values were similar at values between 0.08 and 0.16. Fluctuations in the coefficient of friction values of the coating layer were observed. This was attributed to the fact that the phases were not homogeneously distributed in some regions of the coating (Islak & Ozorak, 2018).

4.2. Discussion of Corrosion Test Results

When the experimental data given in Table 4 are examined, it has been determined that the cathodic current densities of the alloy samples vary considerably when compared to the base material. Among the samples, the current density closest to the base material was determined in sample 3 (thin AlCrN). Corrosion potential (Ekor) values were found to have a negative shift compared to the base material in sample 8 (thick TiN), sample number 3 (fine AlCrN), sample number 1 (thin TiAlN). The lowest corrosion rate among all samples was determined in sample 2 (thick TiN).

5. Conclusion

As a result of micro-scratch tests; It was determined that the depth of the indentation formed in the samples increased with the increase of the applied dynamic force.

In micro-scratch tests, depths between 100 - 140 μm were reached for approximately 150 seconds and 9.5 N force. It was observed that the friction coefficient values at these depths were close to each other at values between 0.08 and 0.16.

When the experimental data obtained from corrosion tests were examined, it was found that the cathodic current densities of the coating samples varied considerably compared to the base material.

Among the samples, it was determined that the closest current density to the base material occurred in the thinly coated AlCrN sample number 3.

Corrosion potential (Ecorr) values were found to have a negative shift compared to the base material in thick coated TiN sample number 8, thinly coated AlCrN sample number 3 and thinly coated TiAlN sample number 1.

The lowest corrosion rate among all samples was determined in the thick coated TiN sample number 2.

Acknowledgment

As the authors, we would like to thank Kastamonu University Scientific Research Projects Coordination Unit for supporting this study with the project numbered KÜ-BAP01/2018-83, and İnan Coting company, where PVD coating processes were carried out.

Conflict of Interest

The authors declare that they have no conflict of interest.

References

Ahmad, F. N., & Zuhailawati, H. (2020). A brief review on the properties of titanium as a metallic biomaterials. *International Journal of Electroactive Materials*, *8*(2020), 63-67.

Chim, Y. C., Ding, X. Z., Zeng, X. T., & Zhang, S. (2009). Oxidation resistance of TiN, CrN, TiAlN and CrAlN coatings deposited by lateral rotating cathode arc. *Thin Solid Films*, *517*(17), 4845-4849. https://doi.org/10.1016/j.tsf.2009.03.038

Islak, S., & Ozorak, C. (2018). Microstructure, corrosion and wear properties of FeCrNiMo based coating produced on AISI 1040 steel by using laser coating technique. *Hittite Journal of Science and Engineering*, *5*(3), 219-223. https://doi.org/10.17350/HJSE19030000098

Leyendecker, T., Lemmer, O., Esser, S., & Ebberink, J. (1991). The development of the PVD coating TiAlN as a commercial coating for cutting tools. *Surface and Coatings Technology*, *48*(2), 175-178. https://doi.org/10.1016/0257-8972(91)90142-J

Li, N., Xiong, Y., Xiong, H., Shi, G., Blackburn, J., Liu, W., & Qin, R. (2019). Microstructure, formation mechanism and property characterization of Ti+ SiC laser cladded coatings on Ti6Al4V alloy. *Materials Characterization*, *148*, 43-51. https://doi.org/10.1016/j.matchar.2018.11.032

Luo, Y., Ge, S., Liu, H., & Jin, Z. (2009). Microstructure analysis and wear behavior of titanium cermet femoral head with hard TiC layer. *Journal of Biomechanics*, *42*(16), 2708–2711. https://doi.org/10.1016/j.jbiomech.2009.08.003

Mattox, D. M. (2010). *Physical vapour deposition (PVD) processing*. Elsevier Publishing.

Sa'aidi, A. F., Ahmad, F. N., & Zuhailawati H. (2022). Influence of processing parameters on dehydrogenation of TiH2in thepreparation of Ti–Nb: A review. *Heliyon*, *8*(11), e11602. https://doi.org/10.1016/j.heliyon.2022.e11602

Sha, W., & Malinov, S. (2009). *Titanium alloys: Modelling of microstructure, properties and applications*. Woodhead Publishing.

Wang, D., Tian, Z., Shen, L., Liu, Z., & Huang, Y. (2008). Research states of laser surface modification technology on titanium alloys. *Laser and Optoelectronics Progress*, *45*, 24-32.