Comparing electrochemical behavior of applied CrN/TiN nanoscale multilayer and TiN single-layer coatings deposited by CAE-PVD method

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ABSTRACT
The main goal of this study is to compare the electrochemical behavior of CrN/TiN multilayer coating and TiN single-layer coating applied by cathodic arc evaporation (CAE) - physical vapor deposition (PVD) on the substrate of Ti-6Al-4 V in Hank’s solution. So, a TiN single-layer coating was formed using PVD method as well as CrN/TiN multilayer coating under totally the same conditions including deposition temperature, working pressure, bias voltage, cathode current and deposition time. To identify the phases in the coatings, X-ray diffraction (XRD) was utilized in order and field emission scanning electron microscopy (FE-SEM) was used in order to study the microstructure of coating. Potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) tests were also carried out for corrosion measurements. In the corrosion evaluation, the PDP and EIS tests were performed for the samples after immersion in Hank’s solution for 24 hours to reach the steady state. The obtained results from PDP curves showed that the specimen with CrN/TiN multilayer coating exhibited better corrosion behavior than the TiN single-layer coatings. This improvement in corrosion resistance is probably due to the high density of the layers in the CrN/TiN multilayer coating that prevents the penetration of the corrosive solution to the substrate.

KEYWORDS
CrN/TiN coating, Ti-6Al-4V; physical vapor deposition (PVD); electrochemical behavior; Hank’s solution

1. Introduction
The growing demand for implants has made the rapid advancements in the field of biomaterials. So, investigating biomaterials has increased significantly in recent years [1–6]. The main feature of a biomaterial is its biocompatibility that means they should not be toxic or carcinogenic and react chemically unpleasant within body fluids [7–9]. Moreover, they must be mechanically resistant and have a long fatigue life and a high density. The ideal implant for orthopedic applications is supposed to have high corrosion resistance and an elasticity modulus that is proportional to bone modulus [10–13]. Nowadays, metal implants such as stainless steels, Co-Cr and Ti alloys are widely utilized [14–19]. Among these available metal implants, the usage of titanium and its alloys in medicine has significantly increased due to their marvelous properties such as low density, high strength, high corrosion resistance, complete neutrality to the environment, high biocompatibility, low modulus and high capacity for bonding with bone and other tissues. Furthermore, since Ti alloys have lower modulus (55 to 110 GPa) in comparison to stainless steel 316 L (210 GPa) and Co-Cr alloys (240 GPa), their usage has increased in recent years [20]. While exposing to liquid in the body environment, metals and their alloys release metal ions from the implants and cause unwanted reactions in the body because of the chloride ions and highly aggressive proteins existence exposing to some materials having low corrosion resistance [3].

Although titanium alloy especially Ti-6Al-4 V alloy has great corrosion resistance and biocompatibility properties, the long-term performance of these alloys has made some concerns like releasing elements of Al and V from their implants that their releasing can cause problems and diseases like Alzheimer’s and neuropathy [20–22]. Multilayer coatings have received specific attention in order to solve these problems. CAE-PVD coating has received much attention because of the unique characteristics that gives to the coating structure [23–28]. Creating coatings with a dense, uniform, continuous structure, excellent adhesion to the substrate, good control on the morphology of coatings during deposition using parameter modification, possibility of coating for high melting point coatings and above all possibility of deposition in various coating rates ranging from one nanometer per minute to several micrometers per hours are the remarkable features of the CAE method [29–31].

The TiN coating deposited by cathodic arc evaporation method doesn’t have satisfying corrosion resistance due to the columnar morphology and presence of some defects such as pin-holes and macro-particles in the coating. So, the main disadvantage of TiN single-layer coatings is that the

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corrosive solution can easily penetrate the coating and cause the destruction of the substrate [32]. The columnar structure is a suitable path for penetration of the corrosive solution into the substrate. Subsequently, the corrosive solution reaches the substrate and increases corrosion with the pitting mechanism. There are some effective ways to improve the corrosion resistance of the coating such as (1) adding an element to composition of the coating to change the morphology of the coating and (2) changing the architecture of the coating toward multilayer coatings to increase the interface and enhance barriers [33].

Therefore, there have been numerous efforts to enhance or improve the corrosion resistance of the PVD coatings. For example, by altering the composition of the coatings via adding elements such as carbon, the morphology of the coating tend to a-C structure, resulting in a denser coating and increases its corrosion resistance [34]. Also, the morphology of the TiN coating changes to co-axial structure by adding about 8% of Si element into the TiN composition to prevent the penetration of the corrosive solution into the substrate [35].

It has been shown that multilayered coatings containing TiN show better corrosion performance than single-layer coatings [36]. Multilayered coatings such as Ti/TiN, TiN/AiN, TiN/TiCN, TiN/ZrN, and CrN/TiN are of this category [37–39]. The CrN/TiN multilayer coating is one of the best coatings to replace TiN single-layer coating [40]. This coating has a longer and more practical lifetime than other coatings and highly prevents corrosion on account of the high density of the coating and the reduction of defects [41].

Many studies have been carried out so far about the formation of CrN/TiN multilayer coatings on different steel substrates by various methods [42], but no report about the formation of this coating on Ti-6Al-4 V alloy using CAE-PVD has been reported. In this investigation, CrN/TiN multilayer coating having a thickness of two micrometers was coated on Ti-6Al-4 V alloy for implant applications in order to improve the surface properties of titanium alloy and improve its corrosion behavior by CAE-PVD and these properties were studied and also compared with TiN single-layer coating.

2. Experimental procedures

2.1. Coating procedure

The samples were prepared by sandpapers ranging from 120 to 2000 to achieve the appropriate surface conditions and then the surface of the samples was polished using an alumina powder of 50 μm powder size. Then the specimens were imposed on ultrasonic bath in acetone and ethanol for 15 min. The CrN/TiN multilayer coatings and TiN single-layer coatings were deposited using the CAE-PVD method based on the listed conditions in Table 1.

2.2. Characterize equipment

After the coating process, metallographic studies were carried out on the cross-section and the surface of samples. Field emission scanning electron microscopy (FESEM, MIRA3, TESCAN) was used to observe the multilayer coating and the number of layers. Also, the XRD was utilized to study the structure and phases that were formed in the layers. The XRD measurements were carried out by an XRD (Philips PW-1730) and the data processing was done by XPert High Score Software. The diffraction angle 2θ differed from 20°–80°, using the Cu–Kα radiation. Atomic force microscope (Nano compact AFM, PHYWE) has been used to carry out the coated samples (with an image size of 50 μm and time/Line 1 s). The contact angle tool was utilized for the evaluation of wettability in the surface coating. Eventually, the adhesion test was carried out based on the VDI3198 standard. Rockwell-C in 1473 N force for 30 seconds was applied in this method and then an OM was used to evaluate the adhesion of coatings.

2.3. Electrochemical tests

The corrosion measurements were done using PDP and EIS methods. In the corrosion test, the PDP and EIS tests were performed on the samples after immersion in Hank’s solution for 24 hours to reach a steady-state. All measurements were done using a standard three-electrode cell, one Pt electrode as an auxiliary electrode and Ag/AgCl electrode as the reference electrode. PDP test having a scanning rate of 1 mV/s began from −0.25 V toward the open-circuit potential and continued until the failure potential of the passive layer. EIS was done in the frequency range of 100 kHz to 10 mHz with a wavelength of 10 mV. To simulate the EIS experimental results and for gaining the best equivalent circuit, Zview software was utilized. All the measurements were repeated at least three times.

3. Results and discussion

3.1. Microstructure and morphology of the coatings

Figure 1 indicates the XRD pattern of TiN and CrN/TiN coatings. The obtained results from diffraction pattern analysis for TiN and CrN/TiN coated specimens
Figure 1. XRD pattern for TiN (a) and CrN/TiN (b) coatings.

Figure 2. SEM images of (a) surface of CrN/TiN multilayer coating, (b) surface of TiN single-layer coating, (c) cross-section of CrN/TiN multilayer coating, and (d) cross-section of TiN single-layer coating.
confirmed the face-centered cubic structure (FCC) \cite{43}. Some peaks of the substrate are observed due to the coating thickness of fewer than 2 microns. As can be seen, the peaks (111), (220) and (311) are observed in the crystallographic structure of the CrN/TiN multilayer coatings. It should be considered that the overlap of TiN and CrN phases in CrN/TiN multilayer coatings applied by the CAE method has been confirmed by the researchers \cite{42}. The crystallite size of the TiN single-layer coating is nearly 17 nm based on the Scherrer equation.

Many macro-particles are seen on the surface of both TiN and CrN/TiN coatings by observing the SEM images of the coating surfaces in Figure 2(a,b). Similar macro-particles were observed for TiN \cite{27} and TiN/CrN \cite{26} coatings deposited by CAE-PVD. The size of these macro-particles is approximately the same in both coatings, but they are present in TiN single-layer more than CrN/TiN multilayer. This factor increases the surface roughness of the single-layer coating in comparison to the multilayer coating. Figure 2(c) indicates the FE-SEM image of the CrN/TiN multilayer coating cross-section. Figure 2(d) illustrates the FE-SEM image of the TiN single-layer coating cross-section. As can be seen, the layers have very tightly adhered to each other and no cracks or cavities are observed in the grain boundary that can improve the corrosion behavior of the coating. Also, in this figure, the number of layers and their thickness can be observed.

3.2. Topography and surface properties

Figure 3 indicates the images of atomic force microscope (AFM) scanning on the surface of TiN single-layer and CrN/TiN multilayer specimens. As can be seen, the surface of CrN/TiN coating is a little smoother than the surface of TiN coating. In the other investigations \cite{44}, it has been found out that the growth of CrN coatings is coaxial and this coating has the fewest macro-particles that are likely due to the presence of CrN coatings within TiN layers that causes an increase in the surface smoothness. Also, the two dimensional AFM images are shown in Figure 3 indicate single-layer and multilayer coatings qualitatively and this reveals that surface smoothness in CrN/TiN multilayer coatings is more than TiN single-layer coatings. Table 2 presents the comparison of the surface roughness for TiN and CrN/TiN coatings. In this table $R_a$ is the mean roughness height which is calculated as the arithmetic mean of absolute roughness values within the scanning area.

![AFM scanning image of the sample surface with coating of (a) TiN single-layer and (b) CrN/TiN multilayer.](image-url)
roughness value, $R_z$ is the average of the longest roughness in 5 measurements and $R_{\text{max}}$ is the height of the highest roughness. It can be seen that in the three criteria of $R_a$, $R_z$, and $R_{\text{max}}$, the numerical value of the multilayer coating is less than that of the single-layer coating, indicating a more area of surface smoothness of the CrN/TiN multilayer coating.

Wettability is a very important feature of solid surfaces that affects the application and other properties of surfaces such as corrosion, wear and erosion mechanisms against liquids and surface contamination. For this purpose, a drop-to-surface contact technique was utilized to measure the wettability angle. The wettability angle is specified by the resulting surface energy between the different phases and can vary from 0 to 180 degrees. Increasing the wettability angle raises the hydrophobicity of the surface that probably improves corrosion behavior.

Figure 4 illustrates an example of water drop images and measured wettability angle on TiN single-layer and CrN/TiN multilayer coatings. Based on the results, the wettability angle for the CrN/TiN multilayer coating was 15% more than the TiN single-layer coating. As illustrated in Figure 3, AFM images show that when surface topography changes, the amount of surface energy and height and width of peaks and valleys affect the wettability angle, both phenomena affect the contact angle simultaneously. Indeed, as the surface roughness changes, the phases in contact with the water drop change and so the effective surface energy changes. In addition, topography and surface roughness dimensions (peaks and valleys) are also affected by the position of the water drop and all these factors simultaneously affect the wettability angle [45]. Furthermore, changes in surface dimensions and surface ups and may create conditions that lead to air detention between surface roughness and at last results in changing the wettability angle [46]. Thus and as expected, CrN/TiN multilayer coating has a larger wettability angle due to less roughness that probably affects its corrosion behavior.

Based on VDI-3198 [47], the adhesion of the coatings is qualitatively specified by a Rockwell-C indenter effect on the surface of the coatings. There are several cracks around the indenter effect according to this standard in classes HF1 to HF2 where the adhesion of the coating to the substrate is acceptable. But in the HF4 to HF6 classes, where the adhesion of the coating to the substrate is unacceptable, it gradually increased the delamination area of the coating around the indenter effect. Figure 5 indicates an image of the Rockwell-C indenter effect by an optical microscope for both TiN and CrN/TiN coatings. Comparing the created indenter effect with the relevant standard, it is observed that the single-layer and multilayer coatings are located in the HF1 class. Therefore, both coatings have excellent adhesion to the substrate.

### 3.3. PDP Measurements

Figure 6 shows the PDP curve for CrN/TiN multilayer coating and TiN single-layer coating and steel substrate in Hank’s solution. As it is clear, applying ceramic coatings on titanium alloy led the PDP curves of the single-layer and multilayer nitride coatings to be shifted toward the nobler potential and lower corrosion current density than the substrate. This shows that applying ceramic coatings reduces the thermodynamic tendency for corrosion occurrence as well as the tendency for corrosion kinetics. Similar PDP plots were noticed in Artificial Saliva solution for TiN, CrN and TiN/CrN coatings deposited by CAE-PVD [40]. Table 3 shows the obtained results from these plots by considering Tafel extrapolation [48–51]. These results

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**Table 2. Surface roughness specifications for the TiN and CrN/TiN coatings.**

| TiN coating | CrN coating | Target material | Working pressure (torr) | Target current (A) | Target-substrate distance (cm) | Deposition time (min) | Rotational speed of specimens (RPM) | Bios voltage (V) | Duty cycle (%) | Coating temperature (ºC) |
|-------------|-------------|-----------------|------------------------|-------------------|-----------------------------|----------------------|----------------------------------|----------------|----------------|------------------------|
| Titanium (99/6%) | Chromium (99/6%) | 5 x 10^{-3} | 5 x 10^{-3} | 120 | 120 | 15 | 15 | 90 | 90 | 5 | 5 | -150 | -150 | 50 | 50 | 250 | 250 |
include corrosion potential ($E_{corr}$), corrosion current density ($i_{corr}$) and polarization resistance ($R_p$). The obtained results indicated that the samples with coatings had higher polarization resistance than the titanium substrate. It can be seen that the polarization resistance was 86 times more than that of the titanium substrate and also 10 times more than that of TiN single-layer coating in the CrN/TiN multilayer coating. The CrN/TiN multilayer coating has the least corrosion current density ($6.53 \times 10^{-6} A/cm^2$) and the highest corrosion potential ($-0.268 V_{Ag/AgCl}$) that indicates the least thermodynamic tendency for the corrosion to occur than other specimens. The cavities from the coating process and the existence of obtained macro-particles are the most significant defects of coatings.

So, the corrosive solution can penetrate into the coating via these pores and finally reach the substrate by destroying the coating. Consequently, porosities play an important role in different properties of the coating, especially in its corrosion resistance.

### 3.4. EIS measurements

Figure 7 shows the obtained Nyquist plots from the EIS tests. All the Nyquist curves have similar profiles. Similar Nyquist plots were noticed for TiN, CrN and TiN/CrN coatings deposited by CAE-PVD in Artificial Saliva solution [40]. The Nyquist plots show imperfect semicircles. According to the Nyquist plots shown in Figure 7, the non-ideal capacitance behavior of all the samples studied in Hank’s solution is evident. It can be seen that the sample having CrN/TiN multilayer coating has the most loop diameter and so the highest most corrosion resistance by comparing the diameter of the curves loop in the Nyquist plots. This behavior is ascribed to the existence of the large number of CrN/TiN coating layers that postpones the corrosion process. Increasing the number

**Table 3.** Obtained electrochemical results from the potentiodynamic polarization curves of substrate and coated samples.

| Sample          | $i_{corr}$ (A.cm$^{-2}$) | $E_{corr}$ (V$_{Ag/AgCl}$) | $R_p$ (MΩ.cm$^2$) |
|-----------------|--------------------------|-----------------------------|-------------------|
| Ti-6Al-4 V      | $5.12 \times 10^{-4}$    | $-0.363$                    | 0.04              |
| TiN             | $6.01 \times 10^{-5}$    | $-0.279$                    | 0.37              |
| CrN/TiN         | $6.53 \times 10^{-6}$    | $-0.268$                    | 3.44              |

**Figure 5.** Optical microscope images of the Rockwell-C test for qualitative evaluation of coating adhesion of (a) CrN/TiN and (b) TiN.

**Figure 6.** PDP plots of Ti-6Al-4 V substrate, TiN single-layer coating and CrN/TiN multilayer coating in Hank’s solution.

**Figure 7.** Nyquist plots of CrN/TiN multilayer coating, TiN single-layer coating and substrate in Hank’s solution.
of coating layers causes an increase in the number of interfaces between TiN and CrN single-layer coatings that the crystal orientations will change in these interfaces and it takes the corrosive solution a long time to reach the substrate from the surface [52]. Furthermore, the corrosion resistance increased by the presence of chromium in the multilayer coating.

The equivalent electrical circuit (EEC) of Figure 8 was used to model the EIS [53,54]. The obtained values of elements were from modeling the electrochemical behavior of the substrates and coatings are presented in Table 4. Dissembling the differences in coatings, it should be noted that the solution resistance is almost the same for all three samples because of using the same corrosion solution whereas the resistance of coatings inner layer is much greater than the resistance of outer layer. This shows that the coatings play an important role against passing destructive ions because of their fewer defects and denser structure. The CrN/TiN multilayer coating has the most resistance of inner layer ($8.23 \times 10^5 \Omega \text{cm}^2$) and outer layer ($2.56 \times 10^3 \Omega \text{cm}^2$) and as a result the best corrosion behavior.

The titanium substrate having no coating and with the least resistance of inner layer ($2.07 \times 10^5 \Omega \text{cm}^2$) and outer layer ($0.8 \times 10^3 \Omega \text{cm}^2$) has the most unpleasant behavior. As described before, the SEM images indicate fewer macro-particles and cavities on the multilayer coating than the single-layer coating and therefore the roughness of the multilayer coating is less than the roughness of single-layer coating. So, the corrosion resistance decreases due to the formation of larger cavities according to the investigations because, the corrosive solution containing destructive ions can easily pass through the pores and reduce the corrosion resistance [55].

4. Conclusion

CrN/TiN multilayer nanostructured and TiN single-layer coatings were successfully deposited on the Ti-6Al-4 V substrate by the CAE-PVD technique. Microstructural characteristics and electrochemical behavior of these coatings were compared to the Ti-6Al-4 V substrate in Hank's solution. The main results out of the current study are as follows:

1. The surface morphology of the coatings indicated that TiN and CrN/TiN coatings had the most and least amount of needle cavities and macro-particle, respectively. Also, according to the SEM images, due to the existence of a large number of interfaces in the CrN/TiN multilayer coating, it directly affected the corrosion behavior.

2. The results of PDP curves showed that the current density of CrN/TiN multilayer coating, TiN single-layer coating, and the bare sample were $6.53 \times 10^{-6}$, $6.1 \times 10^{-5}$ and $5.12 \times 10^{-4} \text{A/cm}^2$, respectively and also have a corrosion potential of $-0.268$, $-0.279$ and $-0.363 \text{V}_{\text{Ag/AgCl}}$ respectively. This decrease in corrosion current density and the increase in corrosion potential indicates the improvement in corrosion behavior of CrN/TiN multilayer coatings in comparison to the TiN single-layer coating and the bare sample.

3. Also, the results of the PDP test showed that in CrN/TiN multilayer coating, the polarization resistance was 86 times more than the Ti-6Al-
4 V substrate and 10 times more than the TiN single-layer coating and CrN/TiN coating had the least corrosion current density and the most corrosion potential.

(4) This improvement in corrosion resistance is perhaps owing to the high density of the layers in the CrN/TiN multilayer coating that prevents the corrosive solution penetration into the substrate. Also, another factor that causes an increase in corrosion of the single-layer coating than the multilayer is the high surface roughness of the single-layer coating due to the presence of macro-particles.

Disclosure statement

No potential conflict of interest was reported by the authors.

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