INVESTIGATION OF IN-VITRO CORROSION BEHAVIOR OF TiN, CrN AND ZrN HARDCOATINGS ON TiNbTaZr ALLOYS FOR BIOMEDICAL APPLICATIONS

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T.C.
ATATURK UNIVERSITY
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INVESTIGATION OF IN-VITRO CORROSION BEHAVIOR OF TiN, CrN AND ZrN HARD COATINGS ON TiNbTaZr ALLOYS FOR BIOMEDICAL APPLICATIONS

(Biyomedikal uygulamalar için TiNbTaZr alaşımları üzerindeki TiN, CrN ve ZrN sert kaplamaların in vitro korozyon davranışının incelenmesi)

MASTER THESIS

Leila AIT ALI

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FEN BİLİMLERİ ENSTİTÜSÜ
Graduate School of Natural and Applied Sciences

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INVESTIGATION OF IN-VITRO CORROSION BEHAVIOR OF TiN, CrN AND ZrN HARD COATINGS ON TiNbTaZr ALLOYS FOR BIOMEDICAL APPLICATIONS

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Yüksek Lisans Tezi olarak Prof. Dr. Burak DİKİCİ danışmanlığında sunulan "Biyomedikal uygulamalar için TiNbTaZr alaşımları üzerindeki TiN, CrN ve ZrN sert kaplamaların in vitro korozyon davranışının incelenmesi" başlıklı çalışmanın tarafımızdan bilimsel etik ilkelere uyularak yazıldığını, yararlanılan eserlerin kaynakçada gösterildiğini, Fen Bilimleri Enstitüsü tarafından belirlenmiş olan Turnitin Programı benzerlik oranlarının aşılmadığını ve aşağıdaki oranlarda olduğunu beyan ederiz.

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ABSTRACT
MASTER THESIS
INVESTIGATION OF IN-VITRO CORROSION BEHAVIOR OF TiN, CrN AND ZrN HARD COATINGS ON TiNbTaZr ALLOYS FOR BIOMEDICAL APPLICATIONS

Leila AIT ALI

Supervisor: Prof. Dr. Burak DİKİCİ

Purpose: The aim of this thesis is the coating and characterization of TiNbTaZr alloys, which does not contain toxic and allergic elements, with hard TiN, ZrN and CrN PVD coatings to increase their in-vitro corrosion resistance.

Method: The TNTZ alloys were coated using the PVD technique. The adhesion and wettability using pull-off test and contact angle test. In-vitro corrosion resistance of the coatings were measured by using open circuit potential (OCP) and potentiodynamic polarization (PDS) techniques, respectively. The characterizations of the coatings were carried out using scanning electron microscopy (SEM), energy dispersion spectroscopy (EDS) and X-ray diffraction (XRD). In addition, Vickers hardness test was made to evaluate the hardness of the coating.

Findings: The SEM examinations showed all the coatings are homogeneous. All the coatings contributed to harder surface that make the coating suitable for ductile surfaces with good corrosion resistance. It was also conclude that CrN had the highest corrosion resistance followed by ZrN, TiN and last uncoated TNTZ.

Results: It was concluded from the mechanical, corrosive and anti-bacterial results that the ZrN, TiN and CrN coatings can be used to improve the tissue/implant interface properties of biomedical implants.

Keywords: Ti-29Nb-13Ta-4.6Zr (TNTZ), CrN, ZrN, TiN, PVD.

June 2022, 57 pages

ÖZET

YÜKSEK LİSANS TEZİ

BİYOMEDİKAL UYGULAMALAR İÇİN TiNbTaZr ALAŞIMLARI ÜZERİNDEKİ TiN, CrN VE ZrN SERT KAPLAMALARIN İN-VİTRO KOROZYON DAVRANIŞININ İNCELENMESİ

Leila AIT ALI

Danışman: Prof. Dr. Burak DİKİCİ

Amaç: Bu tez çalışmasının amacı, toksik ve alerjik elementler içermeyen TiNbTaZr alaşımlarının in-vitro korozyon dayanımlarının artırılması için sert TiN, ZrN ve CrN PVD kaplamalar ile kaplanması ve karakterizasyonudur.

Yöntem: TNTZ alaşımları PVD tekniği kullanılarak kaplanmıştır. Çekme testi ve temas açısı testi kullanılarak yapışma ve ıslanabilirlik. Kaplamaların in vitro korozyon direnci sırasıyla açık devre potansiyeli (OCP) ve potansiyodinamik polarizasyon (PDS) teknikleri kullanılarak ölçülmüştür. Kaplamaların karakterizasyonları, taramalı elektron mikroskobu (SEM), enerji dağılım spektroskopisi (EDS) ve X-ışını kırınımı (XRD) kullanılarak gerçekleştirilmiştir. Ayrıca kaplamanın sertliğini değerlendirmek için Vickers sertlik testi yapılmıştır.

Bulgular: SEM incelemeleri tüm kaplamaların homojen olduğunu göstermiştir. Tüm kaplamalar iyi korozyon direncine sahip sünek yüzeyler için uygun hale getiren daha sert bir yüzeye katkıda bulunmuştur. Ayrıca CrN'nin en yüksek korozyon direncine sahip olduğu ve bunu ZrN, TiN ve son olarak kaplanmamış TNTZ'nin izlediği sonucuna varılmıştır.

Sonuç: Mekanik, korozif ve anti-bakteriyel sonuçlar birlikte değerlendirildiğinde, ZrN, TiN ve CrN kaplamaların biyomedikal implantların doku/implant arayüzey özelliklerinin iyileştirilmesinde kullanılabileceği görülmüştür.

Anahtar Kelimeler: Ti-29Nb-13Ta-4.6Zr (TNTZ), CrN, ZrN, TiN, PVD.

Haziran 2022, 57 sayfa

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INDEX OF ABBREVIATIONS AND ICONS

Ti : Titanium
Ca : Calcium
Co : Cobalt
Cr : Chromium
Nb : Niobium
Ta : Tantalum
Zr : Zirconium
Ni : Nickel
Ar : Argon
Al : Aluminium
Ag : Silver
α : Alfa
β : Beta
CP–Ti : Pure titanium
TiO_2 : Titanium dioxide
Co-Cr : Cobalt-chromium
SiO_2 : Silicon dioxide
TNTZ : Ti-29Nb-13Ta-4.6Zr
HCP : Closed-Packed hexagonal
BCC : Body centred cubic
°C : Celsius degree
K : Kelvin
µm : Micrometre
nm : Nanometre
ml : Millilitre
sccm : Standard cubic centimetres per minute
HBSS : Hank’s balanced salt solution
IBD : Ion beam assisted deposition
CVD : Chemical vapour deposition
PVD : Physical vapour deposition
PDS : Potentiodynamic scanning
EIS : Electrochemical impedance spectroscopy

EDX : X-ray spectroscopy
XRD : X-ray diffraction
SEM **:** Scanning electron microscopy
TEM **:** Transmission electron spectroscopy
XPS **:** X-ray photoelectron spectroscopy

INTRODUCTION

Nowadays, performance, biocompatibility and resistance to corrosion of materials used as implants are significant. Implants cost over $2.3 billion every year in the biomaterial industry. It is still increasing every year, so providing the desired properties for each type of implant becomes important.

Biomaterials can be classified as ceramics, polymers, composites or metals. Ceramics have high mechanical strength, but their elastic properties are not generally properly beneficial as a body biomaterial. Polymers are easy to produce, but sometimes their strong interaction with the body can cause wear, and also, they can absorb water from the blood. Composites can be tailored for a person according to their need, but their manufacturing is difficult and expensive. Therefore, metal-based implants have high tensile strength and wear and impact resistance, which is why they are suitable for medical applications. However, ion releases from their surfaces to the body can be caused some immunological reactions such as inflammation, clot, allergy, toxicity, corrosion, and cracking of implant.

Thus, different studies focus on surface modification methods and materials that canbe used to find and improve the metallic implant's properties. By the way, they are in constant contact with body fluids and should have high biocompatible properties.

Metallic alloys are classified into 316L, CoCrM alloy and Ti alloys. Stainless steel Co-Cr-Mo has a low corrosion resistance compared to Ti alloys. Due to their high corrosion resistance and passivity films, Ti alloys are more suitable for medical applications.

Considering the interaction feature with bone-like tissues, titanium and its alloys are the most remarkable among the metallic biomaterials. The most important disadvantages of these alloys as biomaterials are that they have a very high elastic modulus compared to bone, and the alloys they contain exhibit toxic or allergic properties.

Titanium alloys are divided into three groups according to the type and amount of alloying elements. Those groups are α such as Ti-6Al-2Sn-4Zr-2Mo, $\alpha + \beta$ such as Ti-6Al-4V and β-type alloys such as Ti–Nb–Ta–Zr. Compared to α+β or α alloys properties, β alloys has remarkable ductility, higher hardenability and corrosion resistance and are more economical. Thus, most significantgest advantage of β-type titanium alloys is that their elastic modulus is considered the closest to the bone.

TiNbTaZr (TNTZ) alloys are noteworthy as alternatives for biological implant applications because they do not show toxic and allergic properties, have high strength, and have a modulus of elasticity close to the bone. TNTZ alloys are suitable materials with these properties, but their use in facial and maxillofacial surgery applications where hardness is at the forefront besides biocompatibility is quite limited. The best way to avoid this problem isto cover the implant surface with hard coatings. Metallic implant materials with a hard surfaceare especially preferred in dental implant applications.

Surface coating is the most common surface technique for obtaining a required improvement for corrosion resistance, wear-resistance and surface hardness. They are divided into four categories: gaseous process as ion beam assisted deposition (IBD), chemical vapour deposition (CVD) and physical vapour deposition (PVD) solution process as Sol-Gel, electrochemical deposition and chemical solution deposition., molten or semi-molten process as welding, thermal spraying and laser, and finally, solid-state process.

In recent years, many non-toxic and non-allergic elements have been brought together and coated on alloy surfaces with PVD techniques. These alloys, called high entropy alloys, are attractive due to their superior performance properties. Many surface coating techniques are used for this purpose. These methods include the PVD technique; It is a widely used thin- film coating technique due to its relatively low production cost, high corrosion and wear resistances, and good adhesion resistance between the coating layer and the substrate (Jannat *et al.*, 2019).

Physical Vapour Deposition can be used to increase corrosion resistance and biocompatibility. PVD coatings are high purity deposits that can be applied on a wide range of substrates at low temperatures with controllable deposition rates knowing that coating performance can change depending on its adhesion, surface chemistry and coating morphology.

This thesis study aims to cover the surface hardness of new generation TNTZ alloys that do not contain toxic and allergic elements with hard coatings such as TiN, ZrN and CrN using the PVD technique and to examine their corrosion behaviour and surface properties in vitro environments. Some studies on the subject are summarized below.

Hove and his friends (Van Hove *et al.*, 2015) reviewed the effect of TiN coating on orthopaedic implants. TiN, famous for its excellent biocompatibility and tribological properties, is generally used for articulating surfaces that need increased hardness and reduced wear. However, some studies showed that delamination and cohesive failure of PVD TiN- coating on Ti-6Al-4V and CoCrMo make third body wear.

Ramoul and his friends (Ramoul *et al.*, 2019) used reactive RF magnetron sputtering to obtain thin films of Zirconium Nitride (ZrN) deposited on Ti6Al-4V and Si (100) substrates. Four samples were deposited by changing Ar/ (N2+O2) ratio; ZrN-01 (O2= 1.5 wt. %), ZrN-02 (O2= 1.8 Wt. %); ZrN-03 (O2= 4.9 Wt. %) and ZrN-04 (O2= 6.1 Wt. %). The tribological behaviour, abrasion, and corrosion properties were evaluated for their potential usage in biomedical applications. All coatings exhibited good wear properties against bovine bone counterparts and good corrosion resistance. However, the lowest oxygen content sample showed the highest corrosion resistance in potentiodynamic scanning (PDS) and electrochemical impedance spectroscopy (EIS). The bioactivity of an uncoated Ti-6A-l4V disc substrate shows a poor antimicrobial effect against the S aureus bacteria. A strong biocide effect was observed with the lowest oxygen content surface of ZrN coating; no microbes were observed after 24 h of contact time.

Chim and her friends (Chim *et al.*, 2009) deposited four different N-based coatings (TiN, CrN, TiAlN and CrAlN) on stainless steel by a lateral rotating cathode arc technique. These coatings' oxidations resistance was compared with annealing for 1 h in the furnace at different temperatures (500, 600, 700, 800, 900 and 1000 °C). The deposited coatings were systematically analysed by energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The EDX results show that in all coating layers with increasing the annealing temperature, nitrogen content decreases while the oxygen content increases in the coating layers. TiN has the least resistance to oxidation and the top layer is almost fully oxidized at 700°C (Figure 1). The oxidation behaviour of each coating was compared with the other coatings, TiAlN has a better oxidation resistance than TiN, as well as CrAlN that was compared to CrN. That is due to the dense alumina (Al_2O_3) layer on the coating which protects the sample from corrosion.

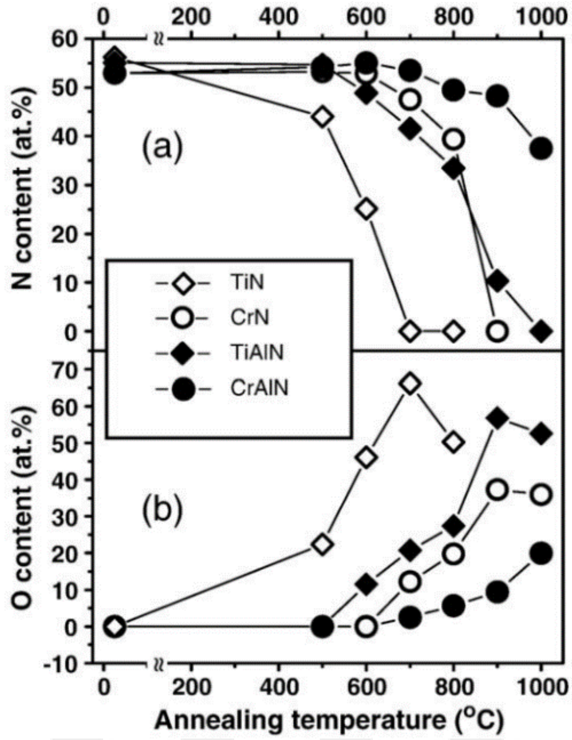


Figure 1. Nitrogen (a) and oxygen (b) content in the four PVD hard coatings after annealing at different temperatures (Chim *et al.*, 2009).

Gu and his friends (Gu *et al.*, 1998) deposited a multilayer nitride coating on Ti-6Al-4V by using the ion implantation technique, and then the wear resistance, corrosion resistance and friction coefficient of the resulting coats were analysed. The results showed that TiN coating improved the wear resistance and corrosion resistance of the Ti-6Al-4V alloy, also that layer properties and homogeneous distribution of coating affect positively TiN resistance to corrosion. The cross-section analysis results of TiN coated samples was conclude that there is a thin layer of oxide film that improves the corrosion resistance when becomes chemically positive.

Subramanian and his friends (Subramanian *et al.*, 2011) deposited TiN, TiON and TiAlN onto CP–Ti substrates using PVD technique. They examined the interaction between blood and the materials in vitro and tested their corrosion resistance. It was concluded that TiAlN has better corrosion resistance then TiN and TiON and that all these coating don't show any toxicity. Due to the formation of thin TiAlON surface layer which is formed when the coating is exposed to the air after deposition.

Yong-yuan and his friends (Yong-yuan *et al.*, 2012) fabricated Ti35Nb2Ta3Zr alloy with low modulus using PVD. Cytotoxicity and corrosion tests showed that Ti35Nb2Ta3Zr is a promising potential biomaterial with higher resistance to corrosion then Ti6Al4V and Ti.

Affi and her friends (Affi *et al.*, 2019) compared the corrosion resistance of TNTZ samples under aged and solution treated conditions , Ti6Al4V ELI, and CP-Ti by immersion tests in 3% NaCl solution for 2, 4, and 6 weeks. Due to the passive oxide film that is a barrier layer for corrosion resistance that is why TNTZ had the lowest corrosion rate as shown in Figure 2. Since corrosion affects the hardness of the material TNTZ under aged condition showed the highest hardness value than other samples.

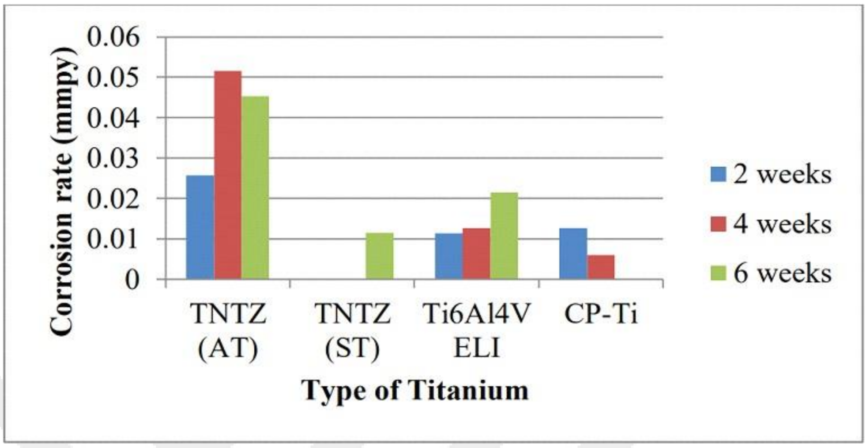


Figure 2. Corrosion rates of samples after immersion test in NaCl 3% (Affi *et al.*, 2019).

Jeong and his friends (Jeong *et al.*, 2007) deposited TiN and ZrN on four samples of Ti-HF alloy (Ti-10wt%, 20wt%, 30wt%, and 40wt% Hf) using PVD. Corrosion test, EDX and SEM were used to study their electrochemical properties. The polarization results showed that sample that is coated with ZrN has the best corrosion resistance since it has the lowest current density due to a stable thin film that protects the surface from corrosion. TiN coatings also made the samples get a better resistance to corrosion then uncoated ones. It was concluded that ZrN and TiN coatings are good for improving corrosion resistance (Figure 3 and Table 1).

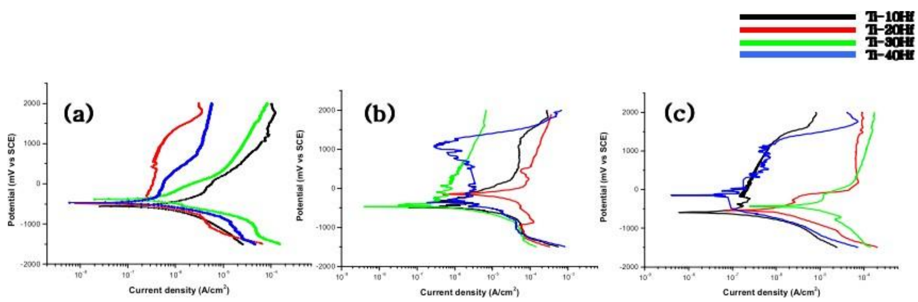


Figure 3. Polarization curves of Ti-xHf alloys after potentiodynamic test in 0.9% NaCl at 36.5±1°C. (a) Non-Coated (b) TiN-Coated (c) ZrN-Coated (Jeong *et al.*, 2007).

Table 1. Corrosion potential and corrosion current density of all the samples at body temperature (Jeong *et al.*, 2007).

	Non-Coated		**TiN-Coated**		**ZrN-Coated**	
	E_{cor}(mV)	I_{cor}(A/cm^2)	E_{cor}(mV)	I_{cor}(A/cm^2)	E_{cor}(mV)	I_{cor}(A/cm^2)
Ti-10HF	-540	2.78x 10^{-7}	-700	1.88x 10^{-5}	-550	2.90x 10^{-5}
Ti-20HF	-490	2.33x 10^{-7}	-640	1.61x 10^{-6}	-480	4.96x 10^{-8}
Ti-30HF	-390	6.98x 10^{-7}	-700	1.57x 10^{-6}	-720	1.18x 10^{-6}
Ti-40HF	-470	2.00x 10^{-7}	-930	1.42x 10^{-6}	-450	3.19x 10^{-7}

Mansoor and her friends (Mansoor *et al.*, 2020) studied the electrochemical behaviour of TiN, CrN and TiN/CrN coatings on nickel-chromium alloy using PVD technique for artificial saliva for dental implant. Resistance of each sample type to corrosion was also measured and compared using EIS. All coated samples had better corrosion resistance the uncoated ones in saliva solution. Furthermore, due to the chromium oxidation that makes denser and protective chromium-containing passive oxide layer, the CrN coated sample had better corrosion resistance that is related to its microstructure and composition comparing coated with TiN and TiN/CrN. Although, the corrosion resistance decreases when the immersion times increase from 1 to 21 days.

Choe and his friends (Choe *et al.*, 2006) coated Ti containing Nb up to 3, 20, and 40 wt.% using PVD with TiN for dental implants. The electrochemical behaviours were investigated using electrochemical behaviours were observed in 0.9% NaCl solution, then the corroded surface was analysed using SEM and X-ray photoelectron spectroscopy (XPS). The TiN coated Ti-40Nb alloy offers good corrosion resistance for dental implants compared with non-TiN coats alloys. The corrosion resistance of Ti-40Nb was higher than that of Ti-10Nb and Ti-20Nb alloy in the 0.9 % NaCl solution. This increased corrosion resistance is attributed to the Ti in the matrix and the formation of a TiN thin film, including oxidation film such as TiO_2 on the surface. The corrosion potential and pitting potential of TiN coated Ti increased with increasing Nb content, because the β-phase and TiN coating layers inhibit Cl^- invasion and thereby increase the corrosion resistance.

Fazel and her friends (Fazel *et al.*, 2020) compared the electrochemical behaviour of TiN singe-layer coating and CrN/TiN multilayer coating. These coatings were applied with PVD method and analysed using XRD, SEM and also EIS for corrosion measurements after immersion of all samples in Hanks' solution for 24 hours. The obtained results from EIS curves in Figure 4. showed multilayer coating has a loop diameter comparing to other coating diameter that means CrN/TiN multilayer coating exhibited better corrosion behaviour 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 which means more interfaces between TiN and CrN single layers coatings with different crystal orientations that postpones the penetration of the corrosive solution to the substrate.

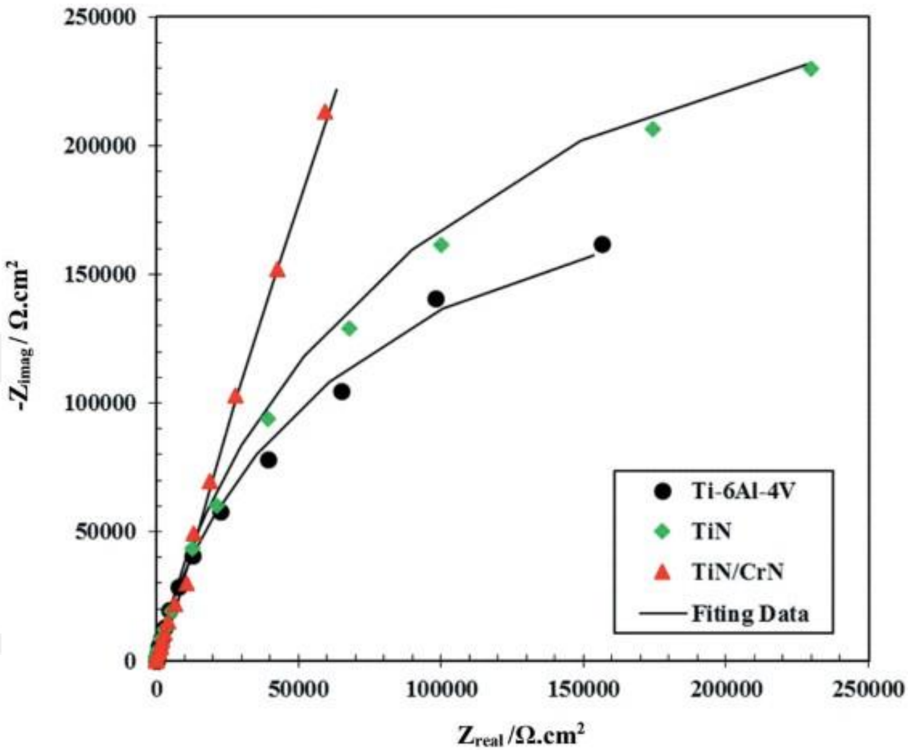


Figure 4. Nyquist plots of CrN/TiN multilayer coating, TiN single-layer coating and substrate in Hank's solution (Fazel *et al.*, 2020).

Wee and his friends (Wee *et al.*, 2005) coated Ti–6Al–4V alloy using PVD with CrN, then coating layer was characterized using XRD, SEM and Vickers hardness test. The hardness test showed that coating layer has three times higher hardness (1390 Hv) value then as-received alloy (402 Hv), and that there was no peeling off on the surface. The results of SEM in Figure 5 show that the coated sample (b) has three times smother surface then as-received sample (a) according to their axis. As a conclusion, CrN layer contributed to smoother and harder surface that make the coating suitable for ductile surfaces.

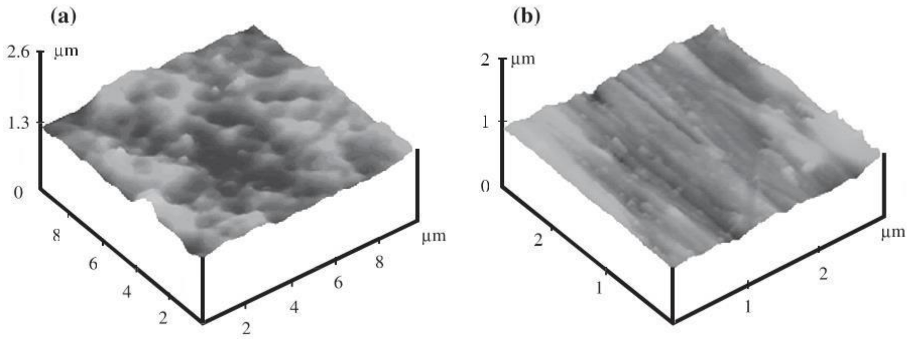


Figure 5. AFM images taken from the Ti–6Al–4V alloys (a) as-received and (b) CrN-coated (Wee *et al.*, 2005).

Chang and his friends (Chang *et al.*, 2011) coated Ti6Al4V alloy with CrN using PVD at various nitrogen pressures (PN_2) to observe the influence of nitrogen on the coating. The coating changes from phase $CrN+Cr_2N+Cr$ to CrN, so Cr layer, a Cr_2N layer and a CrN layer were observed by cross-sectional transmission electron spectroscopy (TEM), X-ray photoelectron spectroscopy and wear test. It was observed that as the nitrogen pressure increases from 0.4 to 1.2 Pa, the micro hardness of CrN films does also from 1550 to 2100. But under a normal load of 3 N some several wear mechanisms as stress cracks, and delamination were observed on CrN coatings as shown on Figure 6.

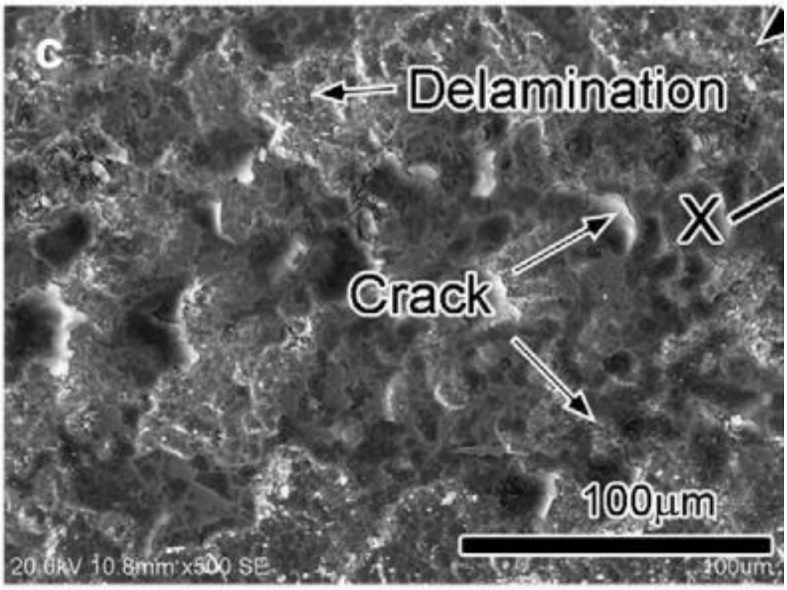


Figure 6. SEM micrographs of wear tracks under normal load of 3 N on CrN/Ti6Al4V coating system (Chang *et al.*, 2011).

Cui and his friends (Cui *et al.*, 2017) coated using PVD nano-TiN on Ti-6Al-4V, then wear performance, biocompatibility and crystalline structure were analysed. The wear test value of the coating was smaller than TiAlN, TiNbN and TiCN coatings showing the excellent anti-wear performance of the gradient coating, and scratch test showed the good resistance of the coating to scratch damage. Figure 7is the result of the analyses of cross-sectional image of the gradient coating. It is clearly seen that the gradient coating was divided into two parts. A light-colour that is a soft (1 and 2) zone with low N and a dark-colour layers that is the "hard" zone (3 and 4) with high N content. The composite of "hard" and "soft" phases exhibits a good combination of high toughness and hardness, low friction and high wear resistance with excellent bonding. General toxicity tests showed that nano-TiN has a good biocompatibility and that is a good candidate to improve the wear resistance of medical implants. General toxicity tests showed that nano-TiN has a good biocompatibility and that is a good candidate to improve the wear resistance of medical implant.

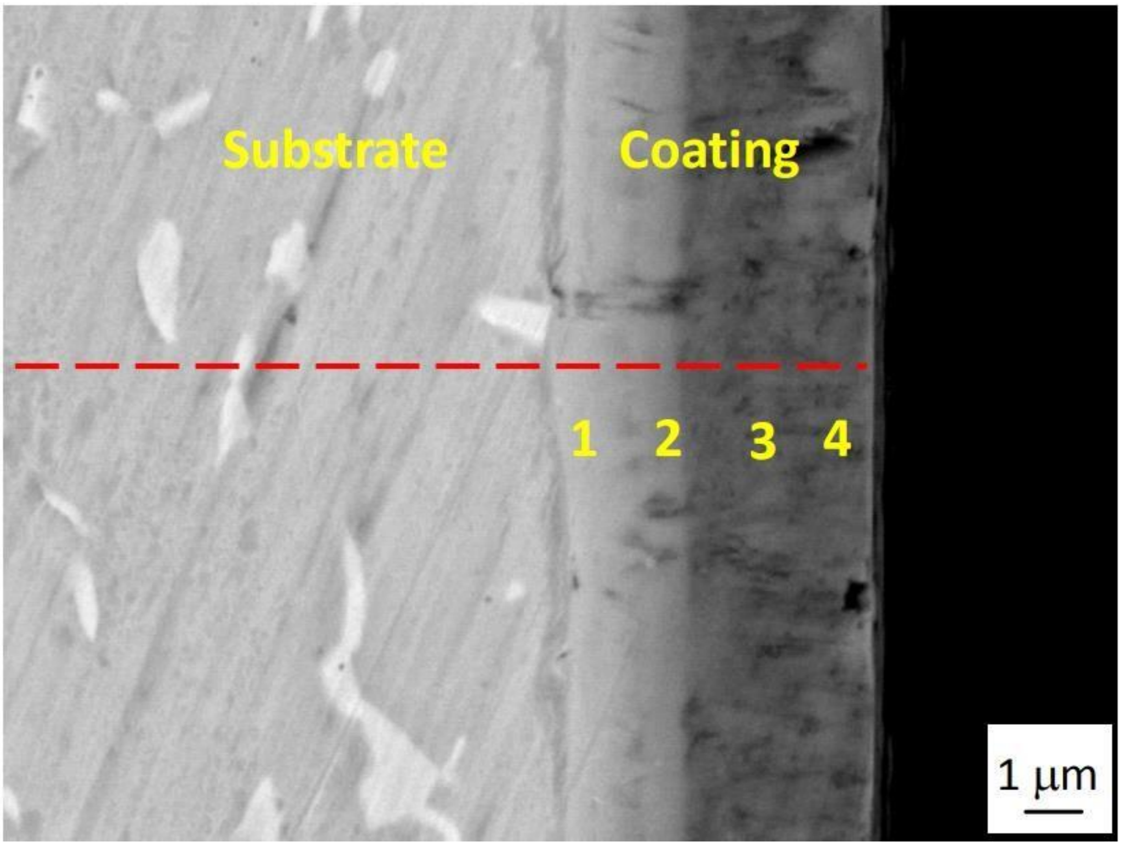


Figure 7. Cross sectional image of the gradient coating (Cui *et al.*, 2017).

Mansoor and her friends (Mansoor *et al.*, 2019) deposited using PVD TiN, CrN and TiN/CrN ceramic nanolayers on Ni–Cr dental alloys. The coatings were then evaluated with electrochemical tests, using SEM, XRD and dispersion spectroscopy. Surface roughness of coatings was also evaluated and was resulted that CrN coating had better roughness then other surfaces. The potentiodynamic polarization tests showed also passive behaviour of CrN and its high resistance to polarization comparing to the other coatings and the Ni-Cr dental alloy that can be the result of a better passive film must have been formed on its surfaces.

Zhang and her friends (Zhang *et al.*, 2019) deposited CrN and TıN on Ti-6Al-4V alloy using PVD. The fatigue results showed CrN followed by TiN both are good for improving the fatigue resistance of the Ti-6Al-4V. Coated samples showed also better ultimate strength, yield strength, and lower elongation compared with uncoated substrate due to the release of the dislocation in the substrate caused by the hard coating that suppress the initiation of cracks, or also that at a higher velocity the brittle coating can fracture and propagate to the substrate and induce the substrate failure.

Cardenas and her friends (Cardenas-Flechas *et al.*, 2021) deposited (Ti-Zr-Si)N on Ti6Al4V alloy by PVD co-sputtering technique technic using Ti_5Si_2 and Zr targets. Test for coating characterization such as XRD, SEM, UV-Vis spectroscopy, hardness and pin-on-disc tests. The results showed that the roughness, hardness and crystalline size of the coatings can be changed according to the deposit parameters such as RF power temperature or discharge time. For example the highest roughness is measured on the coatings deposited with 170W for 1 hour as in a range of 10-36 nm. Besides the crystalline size of the coating layer was calculated between 20 -25 nm and 13-22 nm for plan 111 and 200 respectively. The presence of silicon gives a greater hardness to the coating due to the synergistic effects of the elements present in the film with a smaller number of pores.

The aim of this thesis is to cover the surface hardness of TiNbTaZr alloys that do not contain toxic and allergic elements with hard coatings such as TiN, ZrN and CrN using the PVD technique, and to examine their corrosion behaviour and surface properties in in-vitro environments using different tests and spectroscopies such as XRD, SEM, EDS, angle contact test, adhesion pull-off test and Knoop hardness test.

THEORETICAL FOUNDATION

History and classification of biomaterials

Before civilization, non-biological materials were used as implants, without understanding biocompatibility, medical devices and process and especially no university courses on biomaterials. The first probable implant was placed in the human body in 1891 by a german surgeon Theodore Gluck who did a hip replacement surgery. Next implant in history was in 1957 by John Abel, who implanted the first artificial of a dog. Even though implants existed centuries before and the proof of their existence is the Maya and their mother-of-pearl teeth from shells (600 AD), the word "biomaterial" started being used until the last 60 years (Ratner, 2013).

Biomaterials are materials that can be used for medical purposes to replace a part or a function of an organ or tissue. These materials are used for different causes of plastic surgery, cardiovascular, ophthalmology, reconstructive surgery, and dentistry (Poovathikkal, 2020). The National Institutes of Health Consensus Development Conference in November 1982 determined biological materials as "any substance derived from synthetic or natural origin. Part of a system that treats, enhances or replaces any organ, tissue or function of the human body". Artificial materials that do not come into contact with the skin at all (such as hearing aids) are not comprehended in our definition of biomaterials because the skin is isolated from the outside world. Traditionally, there are four types of biomaterials: natural materials, ceramics, metals and polymers. Two disparate types of biomaterials can be combined to obtain a fifth type called composite biomaterials. Inert metals and alloys properties and biocompatibility have been discovered, leading to increasedbiomedical applications (Ratner, 2013).

As shown in Figure 8biomedical materials are classified as artificial and natural biomaterials.

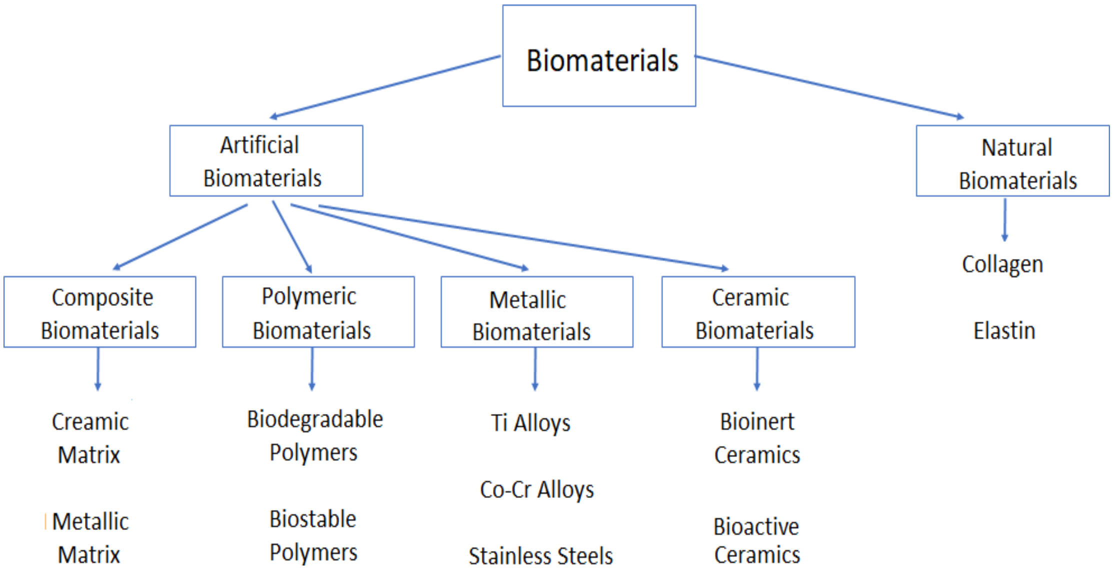


Figure 8. Biomaterials and their types.

The list in Table 2. illustrates various disadvantages, advantages and applications of all types of materials for implantation. Reconstructed natural biomaterial like collagen can be used as replacements as heart valves or arterial walls.

Table 2. Biomaterials comparison.

Material	Example	Advantage	Disadvantage
Metal (Ti and alloys, stainless steels, Co-Cr alloys, Au, Ag.)	Joint prostheses, dental implants, orthopedic screws and bone plates.	High tensile strength, high wear resistance, high impact resistance.	Production difficulty, low corrosion resistance, high density.
Ceramic (Alumina, zirconia, calcium, phosphate)	Dental and orthopedic implants.	High biocompatibility, corrosion resistance.	Low mechanical properties, low elastic properties.
Polymer (Nylon, Silicone, Polyester.)	Stitches blood vessels.	Flexibility, low density.	Low mechanical properties, time-dependent deformation and degradation.
Composite (Wire-or fiber-reinforced bone cement, Carbon-Carbon.)	Bone cement, tooth resin.	High biocompatibility, high mechanical properties, high corrosion resistance.	Production difficulty.

Ceramic-based biomaterials

Ceramics are not the most used materials in medicine compared to metals and polymers. However, alumina, zirconia and pyrolytic carbon are some of the ceramics used as orthopaedics and dental implants because they are strong and chemically inert sometimes biodegradable biomaterials have high compressive strength. Difficulties in manufacturing and affecting negatively bone ingrowth are the main disadvantage next to that the possibility of implant falling off with time (Poovathikkal, 2020).

Polymer-based biomaterials

Polymers are the most used biomaterials due to their easy manufacturing and modification. Although sometimes their strong interaction with the body can cause wear and tear after leaching out, another disadvantage is the possibility of water absorption from blood. Polymers are the main biomaterials of the replacement and enhancement of cardiovascular equipment, coatings for pharmaceutical tablets, various breast implants, soft tissues, heart valves, vascular grafts, artificial hearts, and capsules and blood substitutes (Poovathikkal, 2020).

Composite-based biomaterials

A composite material is the composition of two or more different materials; it is also a material that has a greater phase separation of the atomic scale such as bone, reinforced plastics or fibreglass. Most of the time, natural biological materials are composites. Composites are rigid, strong, lightweight have a high elasticity, and their properties are easy to control. A composite can be used as an implant if all components are biocompatible, and it is also important that the interface should not be reduced while in the human environment (Poovathikkal, 2020).

Metallic-based biomaterials

Metals, and especially metal alloys, are usually used to improve properties such as strength and corrosion resistance. Titanium and its alloys are the most common metal used as a biomaterial. Biomedical metals are mainly composed of three materials such as gold, 316L stainless steel, cobalt-chromium alloys, nickel-titanium alloys, and cobalt-chromium-molybdenum alloys. These metals should be biocompatible, resistant to corrosion, has the needed mechanical properties and should have reasonable cost. Metal is used for knee and hip joint prostheses and fracture fixation lines, artificial heart valves, screws, pins, plates, vascular stents and pacemaker wires. Metals are strongly resistant to fatigue and easy to disinfect but also corrode and can cause ion toxicity (Poovathikkal, 2020).

Usage areas of metallic biomedical materials

A successful biomaterial is a material that respects the aspects of implant properties and biocompatibility, the health of the recipient and surgeon abilities.

Most synthetic biomaterials used for implants are listed in Table 3.

Table 3. Examples of medical and dental materials and their applications (Biomaterial, 2003).

Material	Principal applications
Metals and alloys Co-Cr-Mo, Cr-Ni-Cr-Mo Gold alloys 316L stainless steel Ni-Ti	Dental restorations, bone and joint replacement, heart valves, surgical instruments, stents and orthodontic wires.
Ceramics and glasses Alumina Calcium phosphates Porcelain Carbons	Joint replacement, dental implants, bone repair and surface coatings on metals.
Polymers Silicones Polyethylene Polyesters Hydrogels Polyamides	Ophthalmology, soft-tissue replacement, vascular prostheses, and drug-delivery systems.
Composites	Dental restorations

Titanium alloys

Titanium has been used for many years in aerospace, aircraft and marine industries. Last recent years, with new methods, metals have been used as biomedical products, such as titanium and titanium alloys. Titanium and its alloys are used in the production of surgical splints, dental implants, vascular stents, prosthetic joints, and adhesives (Tirmalar, 2014). The metal's durability and rigid structure, low specific gravity and relatively lightweight, high-temperature resistance and corrosion resistance make it widely used in these particular fields. Titanium alloys attract attention among metallic biomaterials due to their low density, high specific strength and bone-like modulus of elasticity (Sasikumar et al., 2019). Titanium has inert properties, non-toxic structure, antimagnetic properties, easy production of small-sized samples, high biocompatibility, resistance to corrosion and wear, low density and low modulus of elasticity (Tanner, 2002). Low elastic modulus is especially vital, if the biomaterial used has a higher modulus than the bones modulus, stress shielding occurs which means that bone tissue will decrease and won't renew itself easily, and the bone will be then unable to endure the load when an implant is removed (Niinomi & Boehlert, 2015). The main advantages and disadvantages of titanium and its alloys are summarized in Table 4.

Table 4. Titanium and its alloys advantages and disadvantages.(Terlinde et al., 2003)

Advantages	**Disadvantages**
Low density	Production difficulty
High strength	High cost
Low elastic modulus	Inability to interact with bone tissues
Implants chemical stability	Low bioactivity
High biocompatibility	Low osseointegration
Good corrosion resistance	

Depending on the type and amount of alloying elements, titanium alloys are divided into three groups as α, α + β and β-type alloys. CP Ti consists of α-type titanium alloy and is single-phase; Ti-6Al-4V consists of α + β type titanium alloys and is biphasic; TNTZ consists of β-type alloys and consists of a single phase. In Table 5, some properties related to the types of titanium alloys are given.

Table 5. Types and properties of titanium alloys (Obbard et al., 2010).

Alloys	Crystal structure	Specifications	Material examples
α Type	Closed-Packed Hexagonal (HCP)	High resistance to friction, good resistance to plastic deformation and ductility, suitable for high and low temperatures	Ti-6Al-2Sn-4Zr-2Mo CP-Titanium Ti-5Al-2.5Sn Ti-8Al-1Mo-1V
α+β Type		Mix of α and β phases, β phase composition in the range of 10-50% at room temperature, good mechanical strength and low density.	Ti-6Al-4V Ti-5Al-2.5Fe Ti-6Al-7Nb Ti-5Al-3Mo-4Zr
β Type	Body Centered Cubic (BCC)	Low elastic modulus, excellent strain hardening and heat treatment capacity, good mechanical strength and good fatigue resistance.	Ti-42Nb, Ti-30Ta Ti-13Nb-13Zr Ti-35V-15Cr Ti-8Mo-8V-2Fe-3Sn Ti-50Ta-20Zr

Pure titanium has a hexagonal close-packed crystal structure. Due to the allotropic nature of titanium, the hcp crystal structure (α phase) at room temperature will change into a body-centered cubic structure (β phase) structure, when heated to 882°C (1153 K) which is the β transition temperature as, showed in Figure 9 and Figure 10. The β (b) phase is stable from 882°C to the melting point (Soundararajan & Vishnu, n.d.).

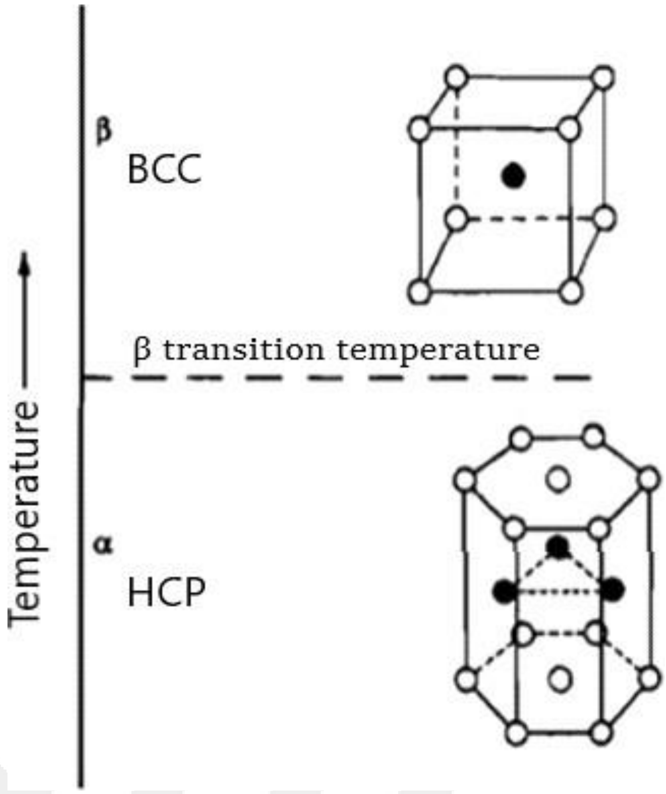


Figure 9. Crystal structure of Titanium (Andersson, 2018).

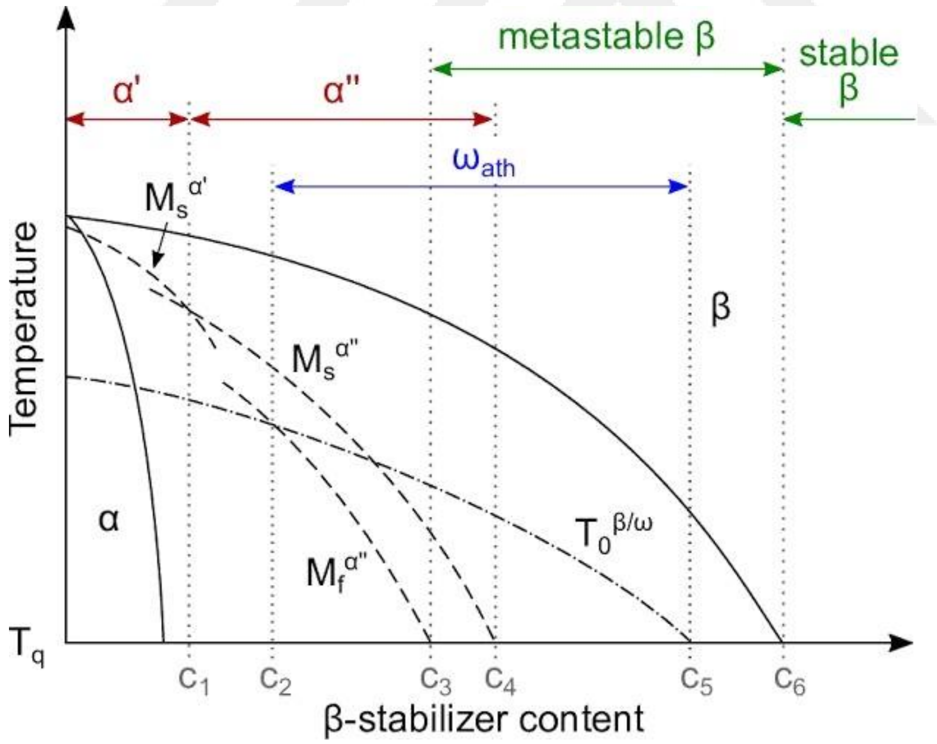


Figure 10. Schematic illustrations of β phase diagram (α'' : α+β) (Bönisch, 2016).

Commercially available β alloys are metastable β alloys, while stable β alloys are not commercially available. β alloys are hardenable and can obtain higher strength levels than α + β alloys and higher specific strengths than many other alloys.

β-type Titanium alloys

Since β alloys is a suitable biomaterial and has better elastic modulus then materials like stainless steel or chrome cobalt alloys more alloys of this type has been studied and improved like Ti–15Mo, Ti–29Nb–13Ta–4.6Zr Ti–12Mo–6Zr–2Fe, Ti–13Nb–13Zr, Ti–35Nb–5Ta–7Zr, and also Ti–Nb–Ta–Zr.

In Figure 11elements like Ta, Nb, and Zr have high biocompatibility. Ti–Nb–Ta–Zr is then an alloy rich of highly biocompatible elements that also stabilize the β phase of titanium and exhibit a lower elastic modulus which makes Ti–Nb–Ta–Zr has an elastic modulus that is closer to bone elastic modulus (48–55 GPa).

TNTZ alloy's mechanical properties were compared with CP Ti a Ti64 alloys and showed in Table 6.

Table 6. Comparison of the Mechanical Properties of TNTZ with CP Ti and Ti64.

Material	Tensile Strength (MPa)	Yield Strength (%0.2) (MPa)	Elongation (%)	Elastic Modulus (GPa)	Atomic Structure
TNTZ	650	615	24	50-120	β
CP Ti	345	275	20	110–130	α
Ti-6Al-4V	895	825	11	110–130	α+β

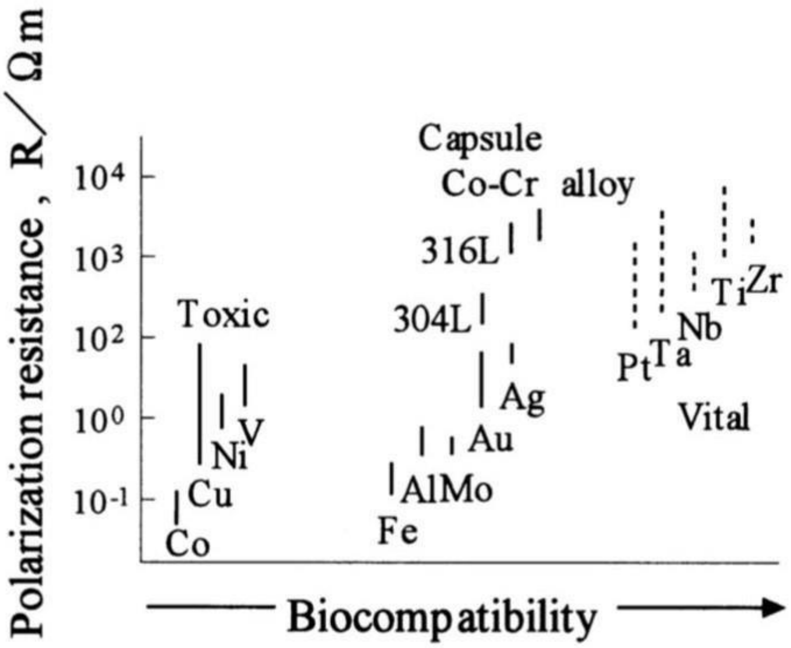


Figure 11. Relationship between polarization resistance and biocompatibility of pure metals (Kuroda et al., 1998).

β alloys has remarkable ductility, heat treatment, higher hardenability and excellent cold rolling properties due to the crystal structure (bcc), higher corrosion resistance than of α+β alloy. The following table presents different advantages and disadvantages of titanium alloys.

Table 7. β-type titanium alloys advantages and disadvantages (Bania, 1994).

Advantages	Disadvantages
High specific strength Low elastic modulus High strength/toughness ratio High friction resistance Good hardening Low forging temperature Cold formability Ease of heat treatment	High density Sensitivity to temperature Difficult and expensive production Inability to stabilize the microstructure

What is biocompatibility?

The human body protects itself from all foreign objects by recognizing and then trying to get rid of them. When a human body does not react and develop an immune response to external material, the material can be called a biocompatible material. Biocompatibility is biological compatibility that makes the interaction between an implant and human tissue occur without producing toxicity, harmful or immune response in living tissues. For a device to be biocompatible, the implant should not possibly break, and sometimes it should be rigid, sometimes the opposite depending on the situation, should have the required surface properties, also the physical and chemical properties of its components, the type, and respects the duration of patient tissue that will be exposed to the device (Poovathikkal, 2020).

Corrosion phenomenon

Corrosion of the metal implant occurs when its components of the alloy are oxidized into ionic form, and dissolved oxygen is reduced to hydroxide ions. Unfortunately, all-metal implants can electrochemically corrode, which makes: the implant dissolution affect the surface, reduction of structural integrity and causes the possibility of reaction between degradation products and host. The corrosion of the metal implant can be controlled by (1) the degree of the thermodynamic driving force that causes corrosion (oxidation/reduction reactions) and (2) physical barriers that limit corrosion kinetics. Depending on different parameters such as geometric, metallurgical, mechanical and solution variables, the corrosion resistance can be improved, which is important because the implant will be in contact with chloride ions and proteins, making the media very corrosive (Viteri & Fuentes, 2013).

Biomedical Material Coating Techniques

Surface coating is a most common surface technique for obtaining a required improvement for wear resistance, corrosion resistance and surface hardness.

Surface coating methods are being applied for different applications and can be divided as follows: (i).Galvanizing, (ii).Conversion Coatings, (iii).Electrochemical Coatings, (iiii).Thermal spraying and (iiiii) Vapor Deposition

Back to 1992a, Rickerby classified these methods into three categories: molten or semi-molten process, gaseous process and solution process. As shown in Table 8. (*Chapter 2 Surface*, n.d.).

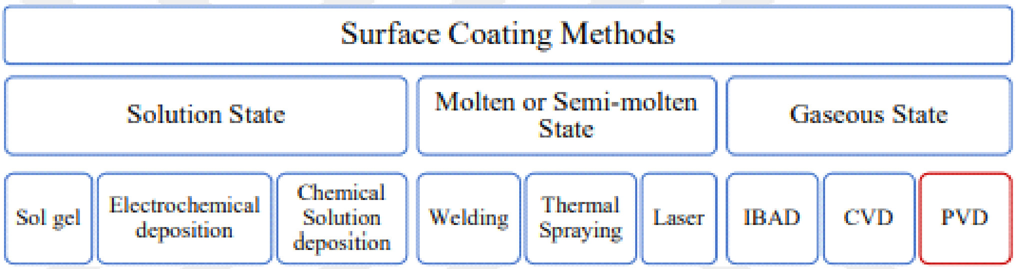


Figure 12. Surface coatings methods (Pinto et al., 2018).In the figures, the following abbreviations are used:

IBAD = Ion Beam Assisted Deposition

CVD = Chemical Vapor Deposition

PVD = Physical Vapor Deposition

In the solution state process, the aqueous solution produces deposits on metal or non-metal substrates. Solution state surface coating methods are generally divided into chemical and electrochemical, but sometimes the chemical reactions can be electrochemical too.

Sol-gel processing is carried out by applying the sol to a substrate, whereupon it undergoes aggregation, gelation and final drying to form a gel. Usually, this technique is used to produce ultra-fine powders, ceramic fibres, thin film coatings, ceramics and glass with different properties.

The molten and semi-molten state process categories may include laser surface treatment, and surface hardening techniques for thermal spraying and welding. Different welding processes can be used to deposit various metals and metal/ceramic composites but is not recommended for non-ferrous metal coatings with melting points below 1100°C. Thermal spraying is a method where the material surface is in a hot gaseous medium at high speed to produce a coating (Scott and Kingswell, 1991). Laser surface treatments can be used for improvement of corrosion, wear.

The gaseous state process are the coating techniques that need to pass through a gas phase before the deposition or modification of the surface. The main coatings are Chemical Vapor Deposition (CVD) And Physical Vapor Deposition (PVD). These two coatings are commonly used for titanium and its alloys for their multiple advantages as improved coating adhesion, uniform coating thicknesses, avoidance of a final machining or polishing stage after coating, controlled coating structures, deposition of a wide range of coating and substrate materials, controllable deposition rates, usually no effluents or pollutants are produced, high purity deposits, lower deposition temperatures, avoidance of the hydrogen embrittlement problems sometimes experienced in electroplating.

Sasikumar and his friends (Sasikumar et al., 2019) reviewed different surface modification techniques for Ti and its alloys and its corrosion behavior for medical applications. These methods are classified into mechanical, chemical, and physical methods as shown in Figure 13.

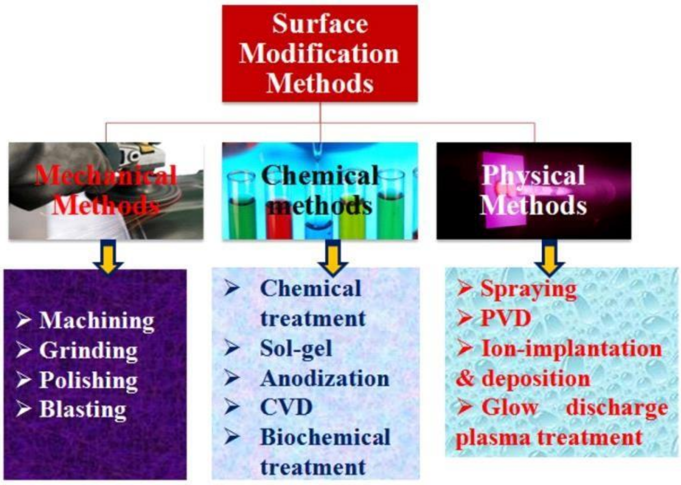


Figure 13. Diagram of all surface modification methods available (Sasikumar et al., 2019).

This review showed that Ti and its alloys prosperities are better after a suitable surface treatment, as improvement in corrosion resistance, wear resistance, surface texture, and biocompatibility. Sasikumar (Sasikumar et al., 2019) also mentioned the importance of studying the corrosion behavior of all modified surfaces and the interaction at the atomic level between the implant's surface, the host and the biological environment inside the human system for obtaining an implant that sustains for an extended period.

The PVD method is a coating method, and in this thesis, this technique improves the surface properties of TNTZ alloys. This method is discussed in detail under the title "**PVD *PVD Coating***

PVD technology is a low temperature process which is very similar to CVD except that in PVD the precursors are in solid form while in CVD they are in gaseous form.

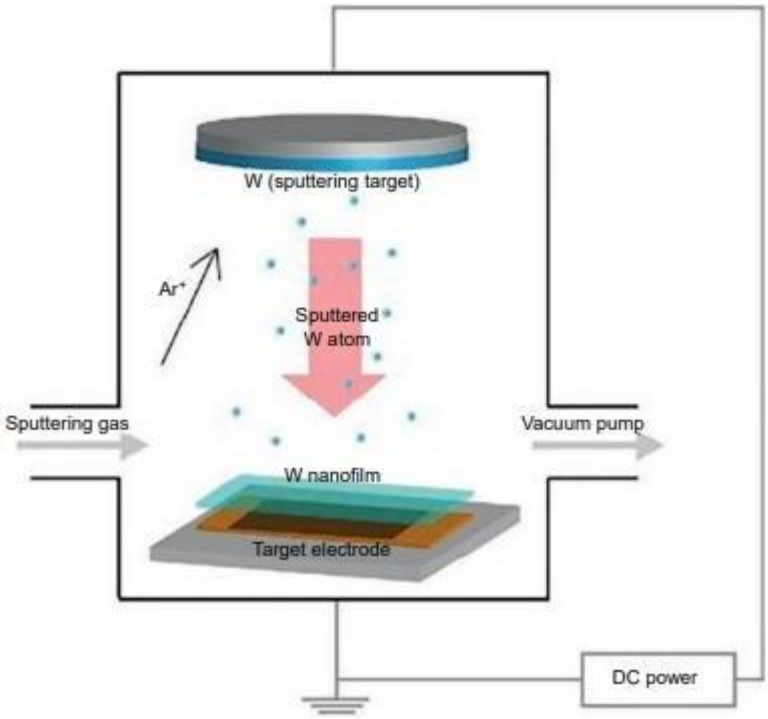


Figure 14. PVD working mechanism (Rafique et al. 2020).

The process involves four steps:

1. Evaporation of the material to be deposited by a high energy

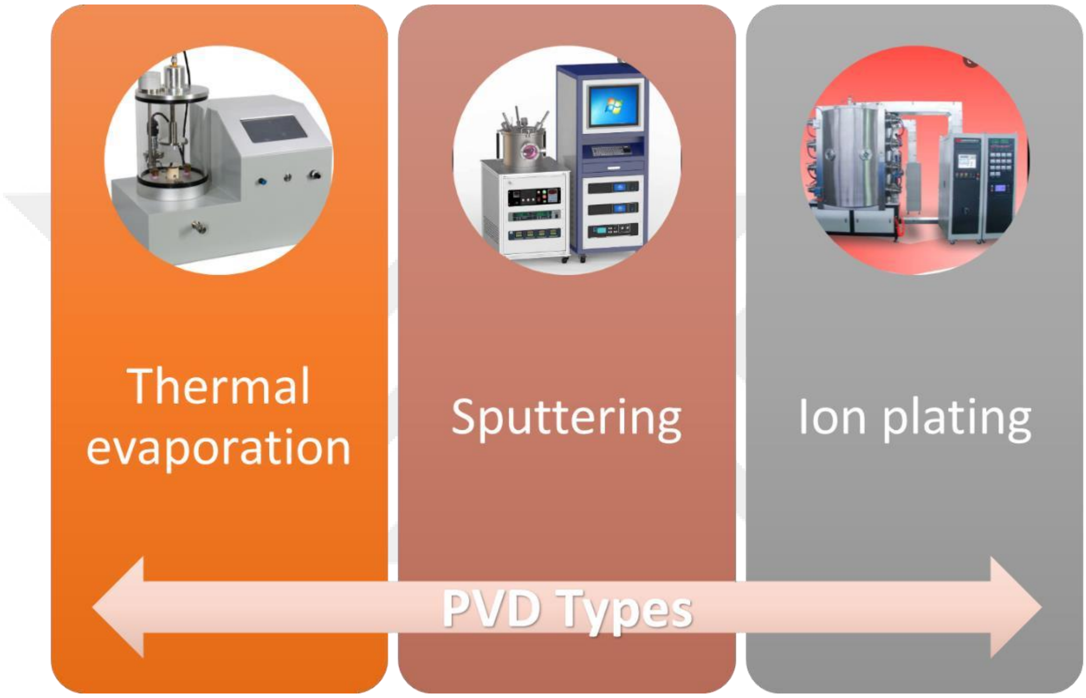
2. Transport of the vapour to the substrate

3. Reaction between the metal atoms and the appropriate reactive gas (such as oxygen, nitrogen or methane) during the transport stage

4. Deposition of the coating at the substrate surface.

In the first step of PVD, a high-energy ion source is used to remove atoms from the target material in the presence of a vacuum and an inert gas (usually argon). A high energy source is supplied to the target material, causing atoms to evaporate from the target surface. The vaporized atoms then move toward the substrate surface and are placed in the chamber. If the deposited material is a metal oxide, carbide or nitrite, the reaction will occur, otherwise, it will not. The evaporated atoms reach the substrate surface and deposit there as a thin layer. The PVD process forms a uniform layer on the surface of a substrate in the nanometer range to the visible range. Less resistance is created in the PVD process, so heterogeneous nucleation leads to the formation of dense layers with improved mechanical properties such as hardness and wear resistance. Figure 14 shows the general mechanism and chamber of the PVD process (Makhlouf 2011).

Table 8. PVD coating types .



Physical Vapor Deposition is a thin-film coating process that produces coatings of pure metals, metal alloys and ceramics with thicknesses typically in the 1 to 10 µm range. This deposition involves the physical deposition of atoms, ions or molecules of a coating onto a substrate (Rafique et al. 2020). There are three main types of PVD:

1. Thermal evaporation uses heated material to form a vapour that condenses on the substrate to form a coating. Heating is accomplished by various methods, including hot wires, electrical resistance, electron or laser beams, and electric arcs.

2. Sputtering involves the electrical generation of plasma between the coating material and the substrate.

3. Ion plating is essentially a combination of thermal evaporation and sputtering.

Table 9. Advantages and Disadvantages of PVD Method (Makhlouf 2011).

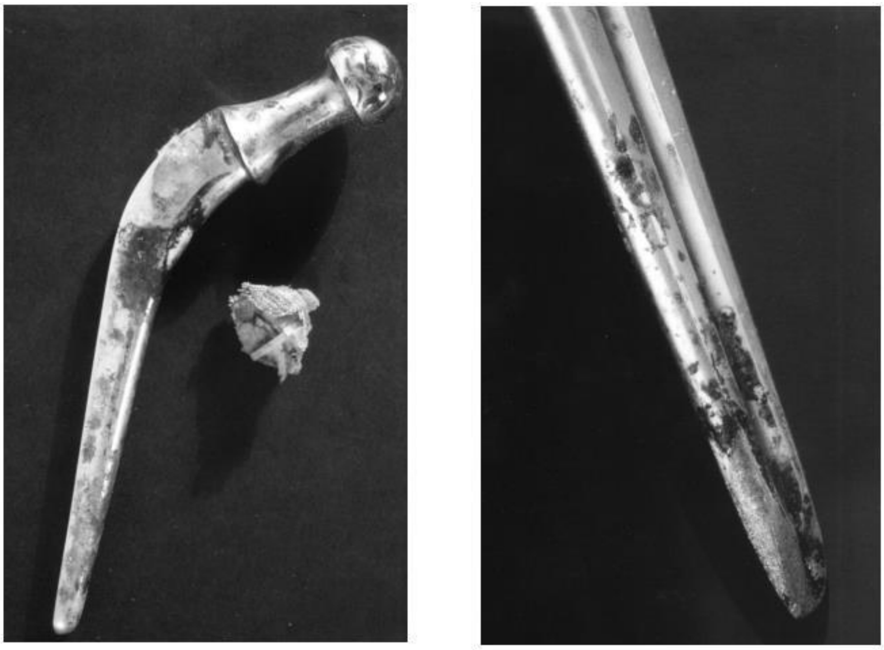
Advantage	Disadvantage
Improve properties, Environmentally friendly compared to other methods, All types of inorganic materials and some types of organic materials can be used.	High cost, Complex processes, Can not be applied to samples with complex shapes.

In-Vitro corrosion

The term "In-vitro corrosion" defines the damage as degradation, dissolution or remineralization of a biomaterial in a laboratory setting representing human body corrosion. Human body corrosion is corrosion that occurs in human body fluids which causes the metal under the decomposition due to the interaction with tissues. The human environment contains a chloride ions and proteins, which makes a highly corrosive environment. All surgical implant surfaces are the spot for various chemical reactions. The metal component of the alloy is oxidized to its ionic form, and the dissolved oxygen is reduced to hydroxide ions. Most metals and alloys that can resist corrosion are in a passive state, titanium and its alloys is a passive metal that has a thin oxide layer TiO_2 (if Ti) on its surface and usually have high corrosion resistance, so it is usually the first choice in other metal biomedical materials. Generally, the thickness of the passivation films formed on these metals is about 3-10 nm, and they are composed of metal oxides (ceramic films).

Due to the existence of the oxide film, at a given potential, the dissolution rate of the passivation metal is much lower than the dissolution rate of the active metal. These thin films spontaneously formed on the metal surface prevent further transport of metal ions and/or electrons through the thin film, depending on the passivation film's characteristics and its solubility in the environment. These films are effective barriers when they are dense, covering the metal completely, have an atomic structure that restricts ions and/or electrons from passing through the metal oxide-solution interface; and they must be able to remain on the surface of these alloys, even in the case of mechanical stress or wear.

Figure 15 shows corrosion of a hip implant from stainless steel. In the long-term implantation process of orthopedics applications, the surrounding tissues degraded due to the release of ions from the implant material into the environment.



tabl 15. Corrosion of a hip joint from stainless steel (J. Walczak et al., 1998).

MATERIAL AND METHOD

Sample Preparation

In this study, the composition of the material used as a base is shown in Table 1. It is a β-type titanium alloy with a chemical composition called Ti-29Nb-13Ta-4.6Zr (TNTZ) alloy. Hereafter TNTZ will be described as substrate.

Preparation of the base titanium sample

A hot-forged Ti–29Nb–13Ta–4.6Zr rod with a diameter of 25 mm and a length of 50 mm was used as substrate. The hot-forged TNTZ was subjected to a solution treatment of 3.6 ks in a vacuum at 790 °C (1063K), followed by quenching. Substrates with 15×10×2 mmsizes were taken from the rod by wire erosion method for coating (Figure 16). The samples were wet sanded up to #4000 and then polished to a mirror surface with a colloidal SiO_2 suspension. After all, the samples were cleaned with ethanol ultrasonically for 15 min and dried with cold air before coating. Materials were produced by micro-arc-melting at Tohoku University, Institute for Materials Research, Department of Biomaterials, Niinomi Laboratory.

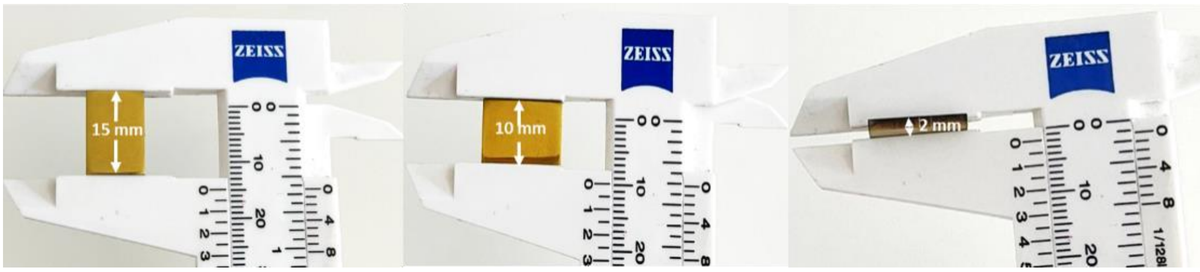


Figure 16. Sample dimensions.

Table 10. Chemical Composition of TNTZ Alloy.

Nb	Ta	Zr	C	N	O	H	Fe	Ti
28.60	12.30	4.75	0.02	0.01	0.09	0.04	0.22	Rest

TNTZ alloys mechanical properties were summarized in Table 12.

Table 11. Mechanical Properties of TNTZ.

Material	Tensile Strength (MPa)	Yield Strength (%0.2) (MPa)	Elongation (%)	Atomic Structure
TNTZ	650	615	24	β

PVD coating

The nitride-based coatings were performed by using cathodic arc deposition method. After the sample was ultrasonically washed using ethanol and acetone, it was then placed on the sample holder. The system was vacuumed to 4 10^{-5} Torr. Before the coating process starts, the coating chamber was heated at 400˚C and the samples were cleaned to remove contamination for 30 min using arc ion bombardment. Cr, Ti and Zr targets with a working atmosphere of high-purity N_2 were applied. The depositions were conducted for 1 h using a bias voltage of -60 V, a target current of 50-100 A and a temperature between 450˚ and 550˚C. The coatings thicknesses were approximately 20 µm average. The coatings process has been done by IONBOND IHI GROUP.

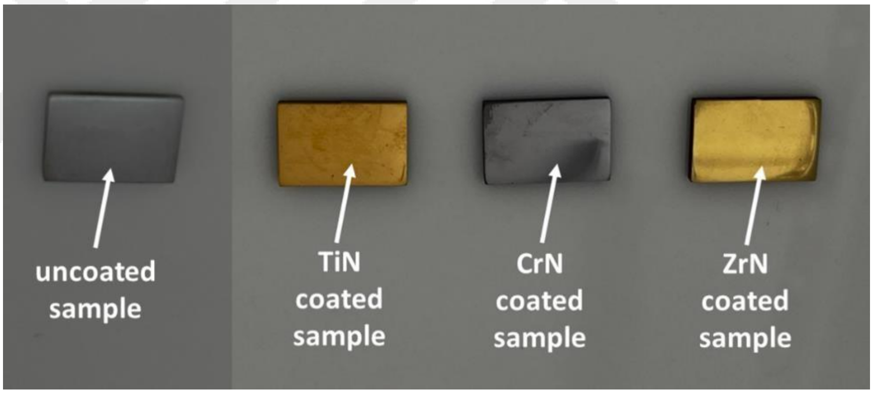


Figure 17. Uncoated sample and PVD coated samples.

Microstructural Characterizations

The morphologies of the samples after coating were analysed by scanning electron microscope (SEM) and X-ray diffraction device (XRD).

Scanning Electron Microscope Surface Analysis

Scanning electron microscope (SEM) is a type of electron microscope that scans the sample surface with an electron beam and displays the data it obtains. Electrons from the beam are scanned across the surface of the material and secondary electrons reflected and emitted from the surface of the material are detected to provide information about the surface morphology of the material. It is a common method to study particle size, magnetic fields, crystal morphology and surface defects. Morphological analysis was performed with the SEM device (HITACHI SU3500) by taking images at various magnifications from the sample surfaces.

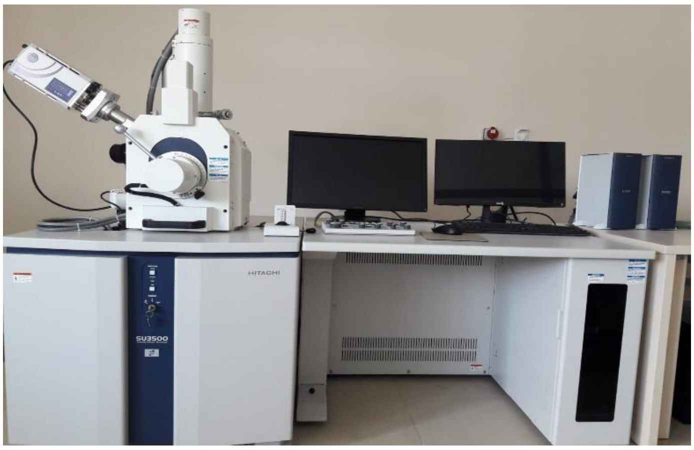


Figure 18. SEM device (HITACHI SU3500).

XRD Phase Analysis

In the XRD system, the characteristic X-ray beam obtained by striking the accelerated electron beam on the copper plate, reflected or diffracted rays sent on the samples were recorded with the help of the detector, and as a result of the examinations, information about the phases, phase amount and changes in the structure in the samples were obtained. Sample analysis was performed in the XRD device (PANalytical EMPYREAN) at a wavelength of 1.5406 and in the range of 10°-90°.

Figure 19. XRD device (PANalytical EMPYREAN).

Wettability angle measurements

The contact angles of the coated and uncoated surfaces were measured using the sessile drop method (Attension® Theta Flex). The angle was read directly from the cross - sectional image by a high-resolution digital camera at 10s.

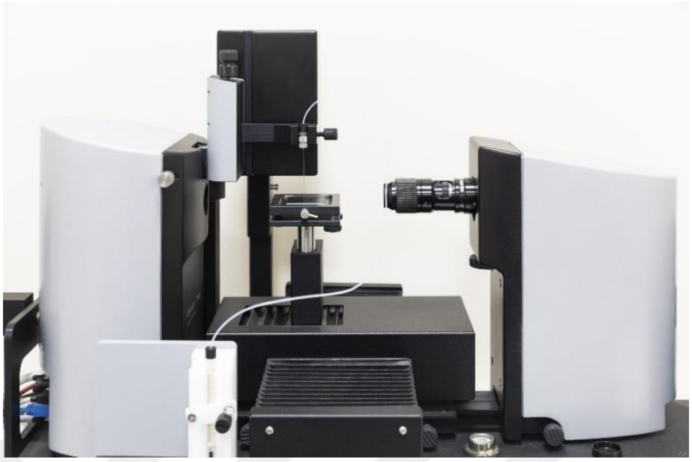


Figure 20. The contact angle instrument.

Pull-off adhesion test

The adhesion strengths of the coatings were evaluated according to ISO 13779-2 standards by using a tensile machine (Shimadzu 100 kN). Coated and uncoated TNTZ samples were bonded by using a strong adhesive glue (DP420 epoxy, 3M). Then, they were dried for 24 h at room temperature and then samples were taken into the oven preheated to 130°C, and kept for 4h. Adhesion tests were performed in the tensile testing device at 0.5 $mm.min^{-1}$ tensile speed after drying. The adhesion strengths of the coatings have been calculated by dividing the rupture forces into cross-sectional surface areas (Figure 21).

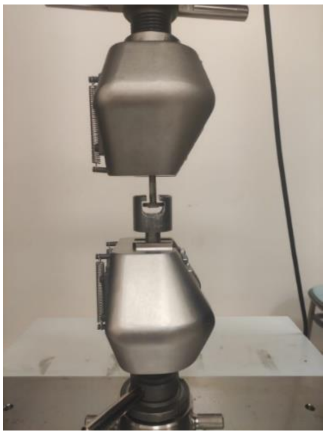


Figure 21. The pull-off test instrument.

Knoop micro-hardness test

In this study, the surface hardness of the samples were measured by using a Universal micro-hardness tester (Shimadzu HMV-G) via the Knoop test method. A force of 250 mN and 100mN were applied to the coated samples and uncoated sample surface respectively during the tests for 15s. All measurements were repeated five times, and the results were presented by average values with std dev. The device used in the Knoop micro-hardness test is given in Figure 22.

Figure 22. Knoop Hardness Testing Machine (SHIMADZU).

In-Vitro corrosion test

For the in-vitro corrosion test, the samples were carried out using a sample holder shown in Figure 23 with a corroded surface area of 0.385 cm^2 produced with a 3D Printer. Thus all results have been normalized according to surface area after the tests. Hanks's solution (hereafter called as HBSS, simulated body fluid) was used as the electrolyte during the corrosion test. The chemical precursors and orders of the preparation of one litre solution are given in Table 13.

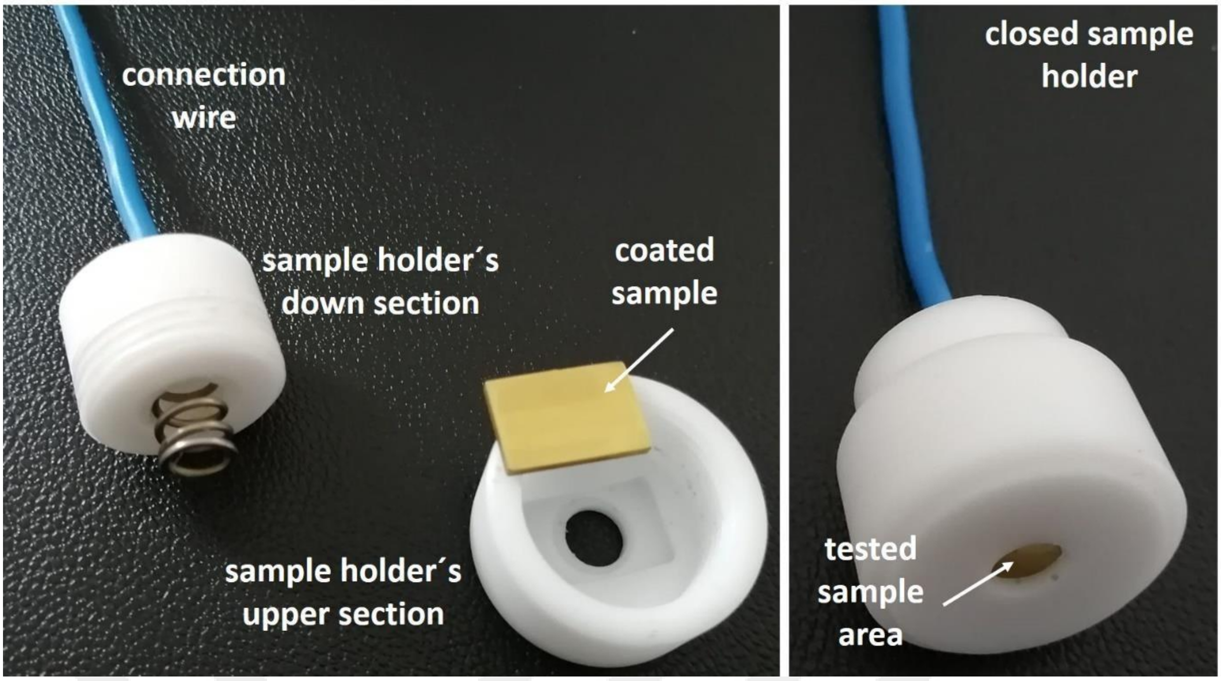


Figure 23. Used sample holder for corrosion test.

Table 12. Components used for preparing HBSS.

COMPONENT	AMOUNT
NaCl	8g
KCl	400mg
$CaCl_2$	140mg
$MgSO_2.7H_2O$	100mg
$MgCl_2.6H_2O$	100mg
$Na_2HPO_4.2H_2O$	60mg
KH_2PO_4	60mg
D-Glucose	1g
$NaHCO_3$	350mg

The pH value of the solution was measured as approximately 7.28. Hanks's solution, which is the electrolyte in corrosion tests, was placed in a 400 ml beaker, heated to 37 °C (body temperature) in a water bath filled with pure water and fixed at this value (Figure 24). Tests were performed on the GAMRY PCII4/750 (USA) Potentiostat/galvanostat instrument. Analyses were performed using three electrodes Ag/AgCl, Platinum wire (Pt) and TNTZ samples coated with PVD of various compositions as reference electrode (RE), counter electrode (CE) and working electrode (WE) respectively.

The first analysis was the open circuit potential test (OCP), which was applied to stabilize the solution potential, and the variation of the potential with time was examined. After the OCP test is completed, the corrosion behaviour of the sample is determined by the potentiodynamic polarization test (PDS) the used density and equivalent weight were 7.27gm/cm^3 and 17.370 respectively. The unit of the corrosion test were given in Figure 25. After corrosion test, the samples are ultrasonically cleaned in ethyl alcohol for 2 minutes (Figure 26) and dried with dry air.

Figure 24. Used devices for preparation of HBSS, (a) precision balance, (b) heating magnetic stirrer and (c) Ph meter.

Figure 25. In-vitro corrosion test.

Figure 26. Ultrasonic cleaner.

RESEARCH FINDINGS AND DISCUSSION

Coating Characterization

SEM

From Figure 27 to Figure 29 SEM surface morphologies of the coatings at different magnifications are presented. The results show that the coating process has been performed successfully. The coatings show a uniform distribution of the constituent element.

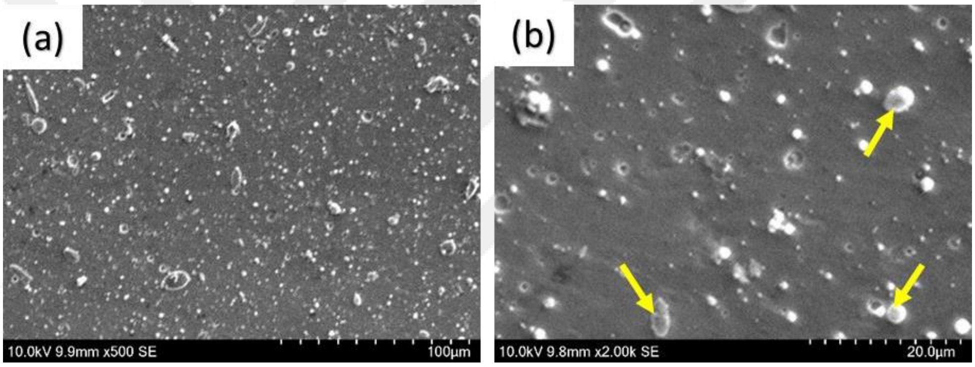


Figure 27. SEM images of TiN coated samples at different magnifications at (a) ×500 and (b) ×2000.

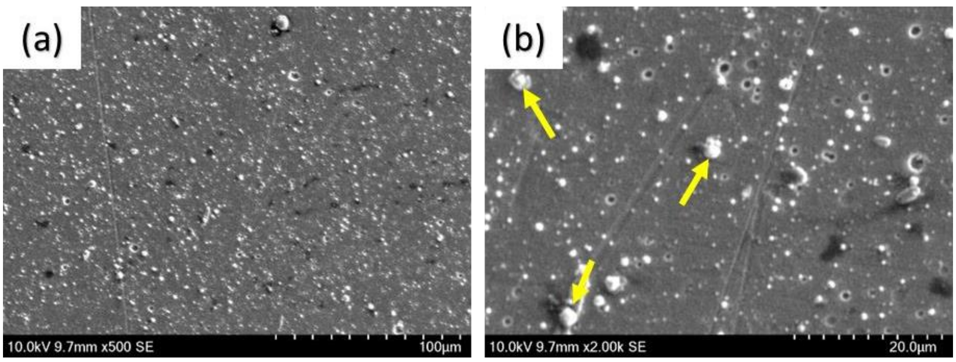


Figure 28. SEM images of CrN coated samples at different magnifications at (a) ×500 and (b) ×2000.

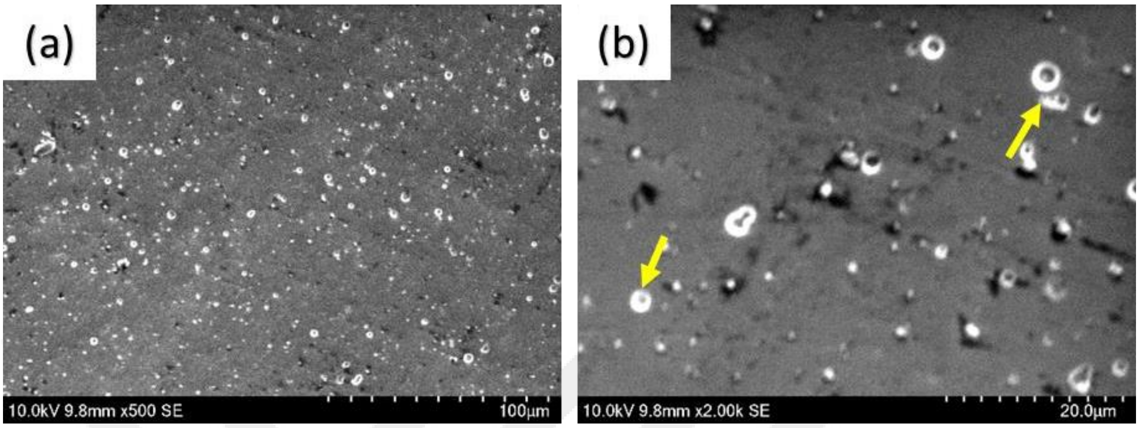
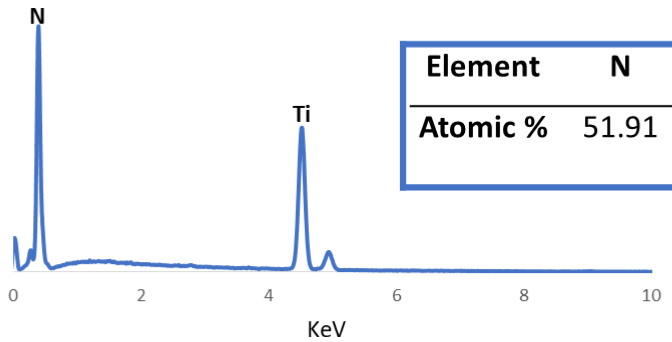


Figure 29. SEM images of ZrN coated samples at different magnification at (a) ×500 and (b) ×2000.

The surface morphologies of the coatings are very similar to each other, many agglomerations are seen on the surface of TiN, CrN and ZnN coatings by observing the SEM images of the coating surfaces in Figure 27, Figure 28 and Figure 29, as it was observed in Fazel and her friends' work, where they found also macro-particles on TiN coated Ti-6Al-4 V (Fazel et al. 2020) and also Kuznetsova and her friends that found that ZrN coating is a smooth surface, with a small numbr of macroparticles (Kuznetsova et al. 2020). This factor increases the surface hardness of the coatings. Also, all films have been uniformed.

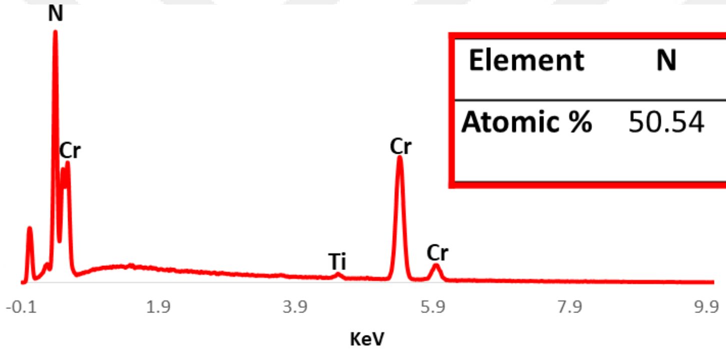
EDS

Before corrosion EDS analysis results of all coatings made on TNTZ are given in Figures 30-32.



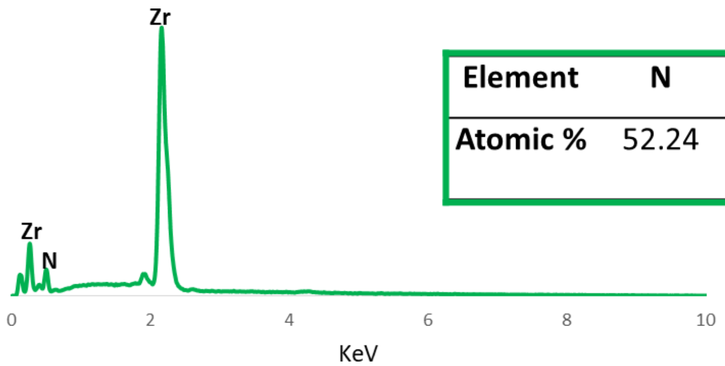
Element	N	Ti	Total
Atomic %	51.91	48.09	100.00

Figure 30. EDS analysis of TiN coated TNTZ.



Element	N	Cr	Total
Atomic %	50.54	49.46	100.00

Figure 31. EDS analysis of CrN coated TNTZ.



Element	N	Zr	Total
Atomic %	52.24	47.76	100.00

Figure 32. EDS analysis of ZrN coated TNTZ.

All EDS results confirmed the composition of the three different coatings.

XRD

XRD results of CrN, TiN and ZrN are summarized n in Figure 33.

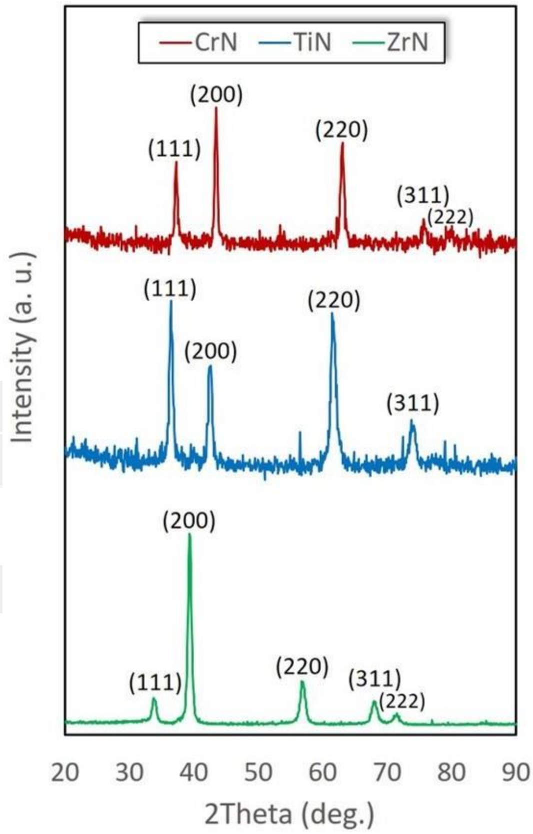


Figure 33. XRD results of all coating.

XRD analyses were taken only from the coatings made on TNTZ to distinguish the major peaks. As a result of the analysis, major peaks (111) for TiN and (200) for CrN and ZrN were detected in the coating layer. No different phases were formed except TiN, CrN and ZrN. All coating had a crystalline structure, and all picks the picks could be defined.

Wettability (Contact Angle) Analysis

The wettability test of the ZrN, CrN and TiN coatings is given in Figure 34.

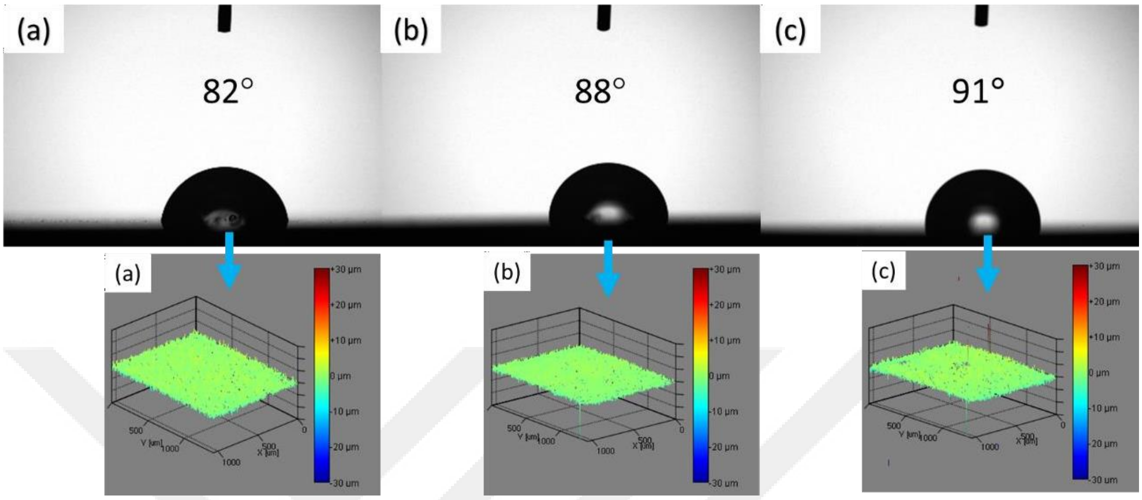


Figure 34. Wettability analysis of coated samples and their 3D images (a)-TiN, (b)-CrN and (c)-ZrN.

While the contact angle of the ZrN coating was 91°, the contact angles of the CrN and TiN coatings were measured as 88° and 82°, respectively. A high water contact angle indicates a hydrophobic character of the surface. While CrN and TiN are hydrophilic, ZrN is hydrophobic making CrN and TiN better biomedical candidates than ZrN. Generally, low surface energy, high surface roughness and low surface texture are favorable to enhance surface hydrophobicity. As it is observed from 3D images, all coatings are homogenous.

The pull-off test

All surfaces of the samples after pull-off test are shown in Figure 35 and their values are summarized in Figure 36.

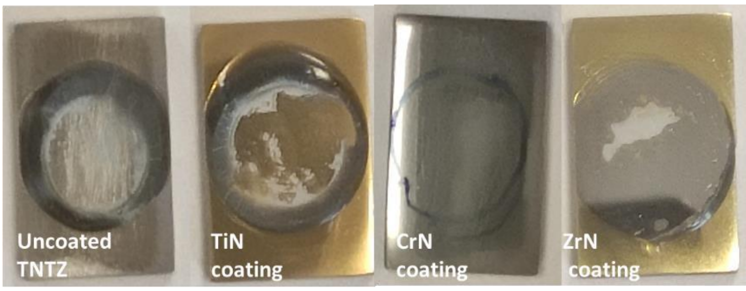


Figure 35. Pull-off test result.

The maximum strength of the adhesive used is between 35-40 MPa. The adhesion strength of CrN and TiN coatings was quite good. The rupture on the surfaces is very low. As can be seen from Figure 36 CrN coating on TNTZ substrate exhibited increasing adhesion strength followed by TiN then ZrN and uncoated sample. The coating adhesion strengths remained between 25 MPa for uncoated TNTZ to 38 MPa for CrN. The desired value for biomedical application of adhesion strength is around 15 MPa which is close to the values resulting in this study.

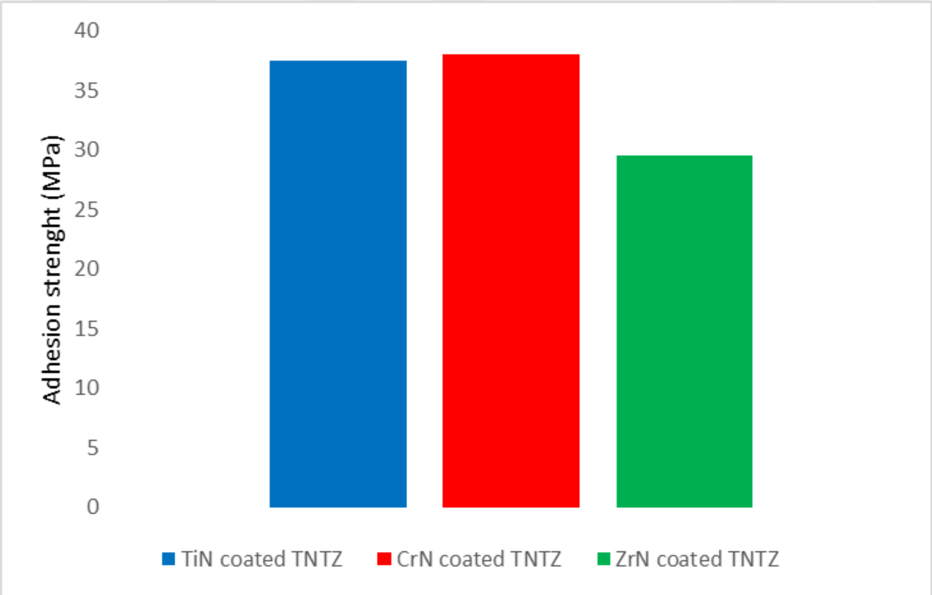


Figure 36. Adhesion test result values of all type of coating

Hardness test (Knoop)

Knoop microhardness test results are shown in Figure 37.

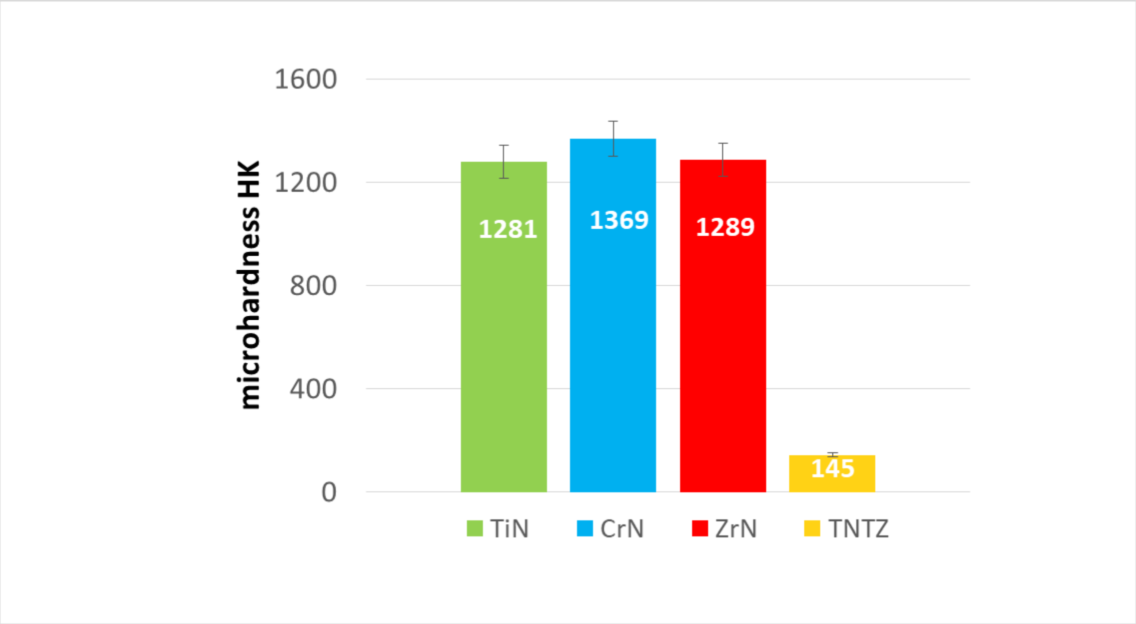


Figure 37. Hardness test results of all type of samples.

All coatings showed higher resistance to the penetration then uncoated TNTZ sample that was 145HK for a 100mN used load which was supposed because of the low elastic modulus of TNTZ that is close to the bone elastic modulus, thus the surface of the implant must have higher hardness due to the high loads and wear that the implant will be confront to. The hardness of 1369 HK, 1289 HK and 1281 HK, were measured from the CrN, ZrN and TiN respectively which are almost nine times higher than 145 HK from the as received alloy, which indicated the successful deposition of all coatings on the surface of the substrate. These results match with Mansoor and his friends (Mansoor et al. 2019), CrN and TiN Vickers hardness test results showed that CrN had better micro hardness strength then TiN. It was also found in Heinrich and his friends where the hardness of ZrN was higher the of TiN (Heinrich et al. 2008).

In-Vitro Corrosion Test Results

Corrosion test studies were performed in SBF 'Hanks's' solution at 37 °C. OCP values of coatings produced in various compositions on TNTZ substrate are given in Figure 38.

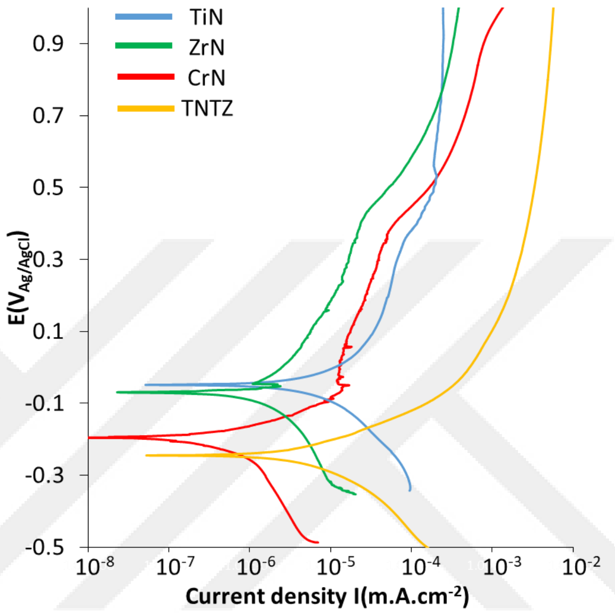


Figure 38. Potentiodynamic polarization curves of coated and uncoated samples in HBSS.

Table 13. Corrosion Parameters of Potentiodynamic Polarization Curves.

Samples	E_{corr} (mV)	I_{corr} ($\mu A/cm^2$)	β_a (mV/decade)	β_c (mV/dec.)	Rp (Ω.cm-2)	Corrosion rate (mpy)
CrN	-195	0.56	85	282	52780	0.174
TiN	-48	33.06	896	541	4449	10.17
ZrN	-69	6.44	826	769	23880	1.983
Uncoated TNTZ	-244	27.20	304	559	3083	8.369

From The table 14 and the Figure 38 due to its low I_{corr} value it is seen that the highest Rp and belongs to CrN followed by ZrN, TiN and last TNTZ. TNTZ had the highest corrosion rate, which means the lowest resistance to corrosion followed by TiN, ZrN and CrN.

Post-Corrosion Surface Morphologies of Coatings

SEM

From Figure 39 to Figure 41 SEM surface morphologies of the coatings after corrosion test at different magnifications are presented.

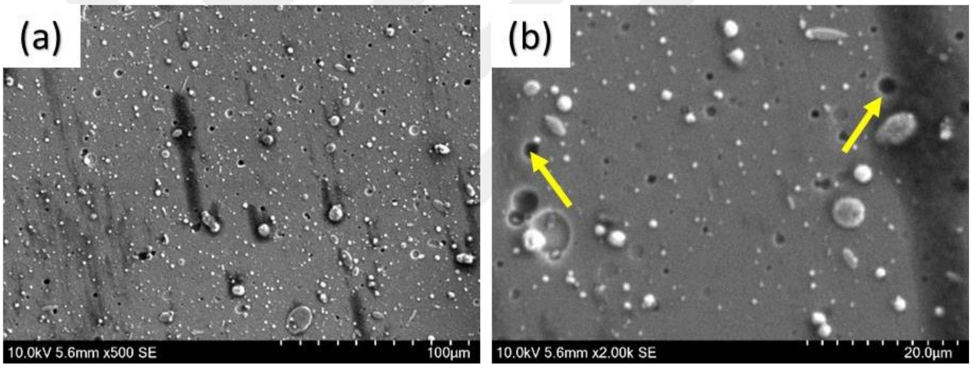


Figure 39. SEM images of TiN coated samples at different magnification at (a) ×500 and (b) ×2000.

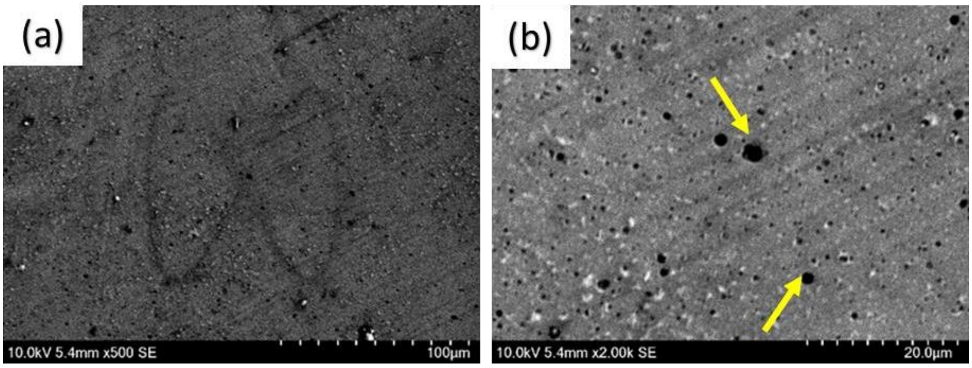


Figure 40. SEM images of CrN coated samples at different magnification at (a) ×500 and (b) ×2000.

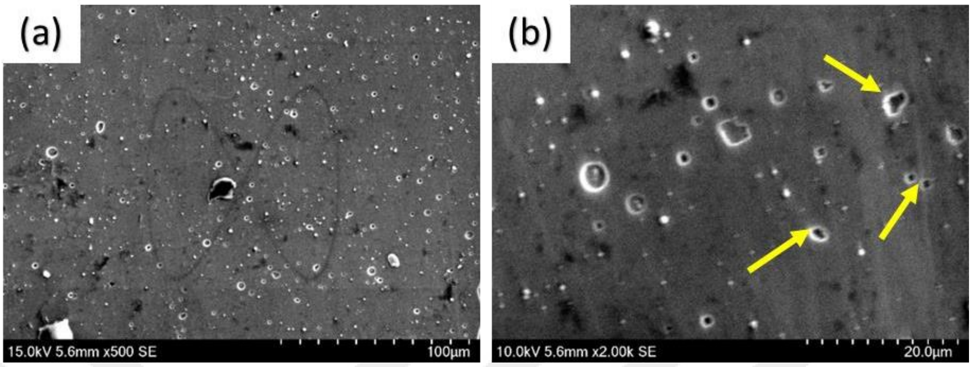
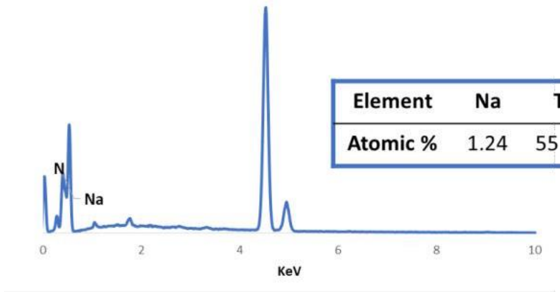


Figure 41. SEM images of ZrN coated samples at different magnification at (a) ×500 and (b) ×2000.

The obtained results indicated that the samples with coatings had higher polarization resistance than the uncoated substrate and it was seen some pits on the surface that indicates that pitting phenomenon occurred.

EDS

Surface EDS maps of TiN, CrN and ZrN coatings on TNTZ substrate are shown in Figure 42, Figure 45 and Figure 47 respectively. From Figure 48, it is obvious that Ti and N particles concentrations are higher than other concentrations. It was also observed Nb, Ta, Na and Zr from substrate that are clear in the pitting caused of corrosion. The same for CrN and ZrN SEM images where the highest concentrations were coating elements (Cr and N for CrN; Zr and N for ZrN) and Oxygen. That indicate the formation of oxide layer to protect the surface from the corrosion which was found by Chipatecua and his friends that suggested that a Cr_2O_3 film is formed from CrN when the corrosion occurs to protect the surface (Chipatecua, Olaya, and Arias 2012). The same for Brown and his friend that found that as a protection to corrosion, from ZrN a thin layer of ZrO_2 is formed (Brown, Alias, and Fontana 1993).



Element	Na	Ti	N	Ta	Nb	Zr	TOTAL
Atomic %	1.24	55.58	42.44	0.34	0.10	0.29	100.00

Figure 42. EDS analysis of TiN coated TNTZ after corrosion**.**

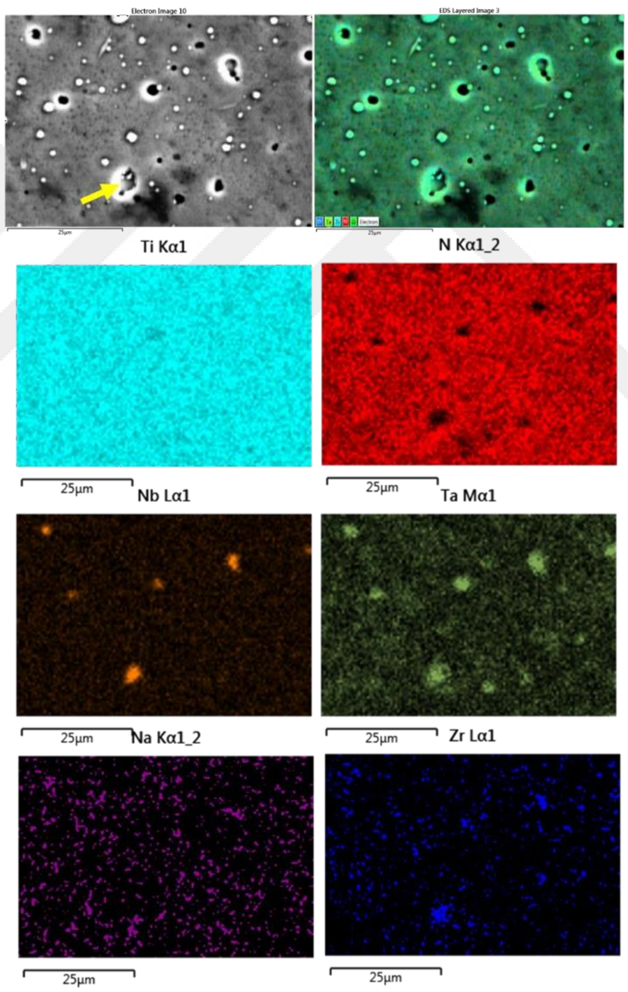
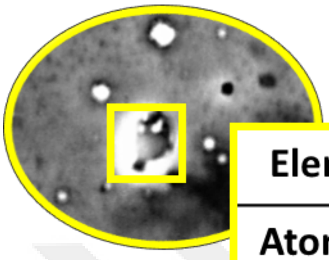


Figure 43. Surface element maps of TiN coating on TNTZ substrate.

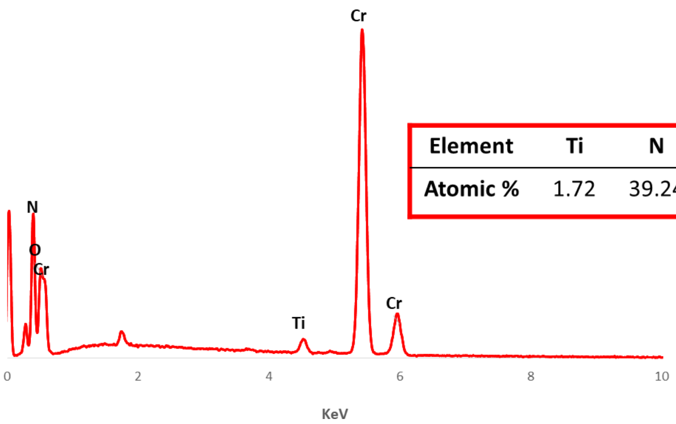
From the Figure 44 the pit area circled in yellow was also examined using EDS and the results were summarized in the table below.



Element	O	Ti	Nb	Ta	TOTAL
Atomic %	52.48	40.63	5.52	1.37	100.00

Figure 44. EDS analysis of a pit from TiN coated TNTZ sample after corrosion.

Elements from the substrate were observed from the pit and also oxygen that indicates the formation of a layer. The thin layer is supposed to be TiO_2 for TiN coating as Chloe and her friends found in their research (Choe, Ko, and Park 2006) .



Element	Ti	N	O	Cr	TOTAL
Atomic %	1.72	39.24	10.17	48.87	100.00

Figure 45. EDS analysis of CrN coated TNTZ after corrosion.

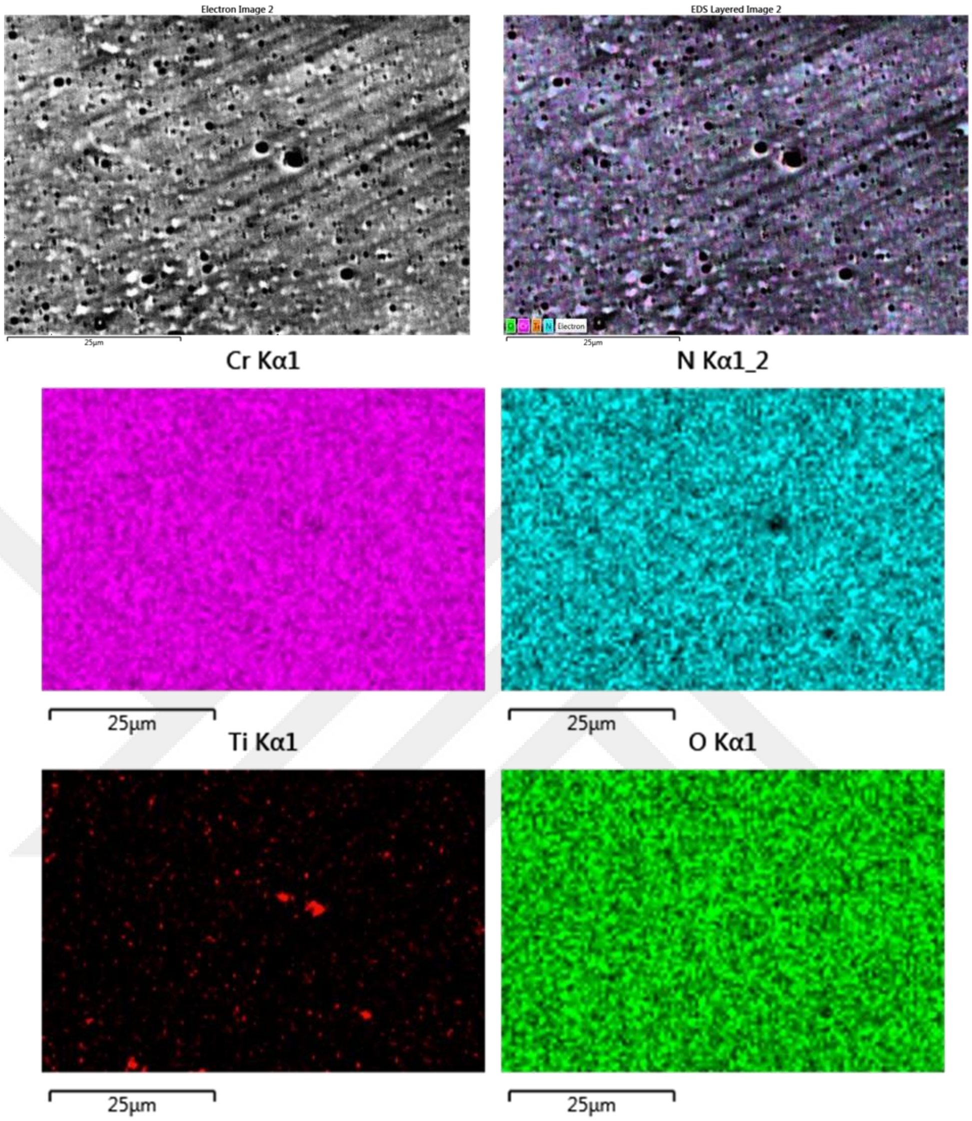
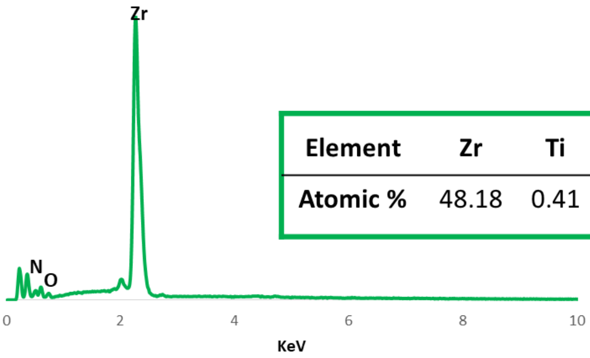


Figure 46. Surface element maps of CrN coating on TNTZ substrate.



Element	Zr	Ti	O	N	TOTAL
Atomic %	48.18	0.41	15.04	36.37	100.00

Figure 47. EDS analysis of ZrN coated TNTZ after corrosion.

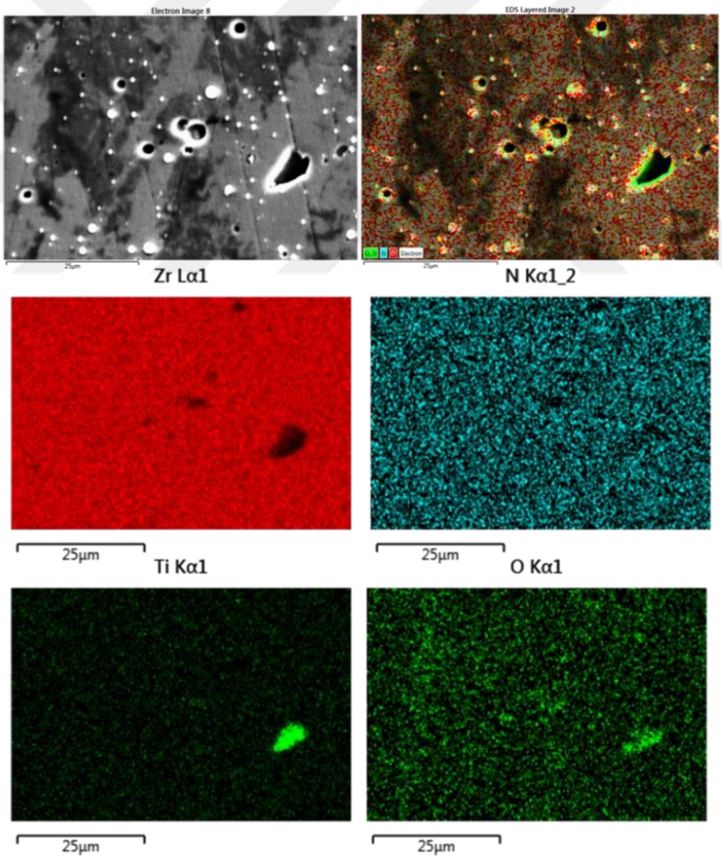


Figure 48. Surface element maps of ZrN coating on TNTZ substrate.

As shown in Figure 48. after the removal of the thin layer, corrosion start occurring on the substrate that is not coated anymore and not protected. The same phenomenon was observed on the surfaces of all coatings after corrosion (Figure 50), it was also observed that the type of corrosion that occurs is filiform corrosion that is a crevice corrosion that attacks the coated surfaces.

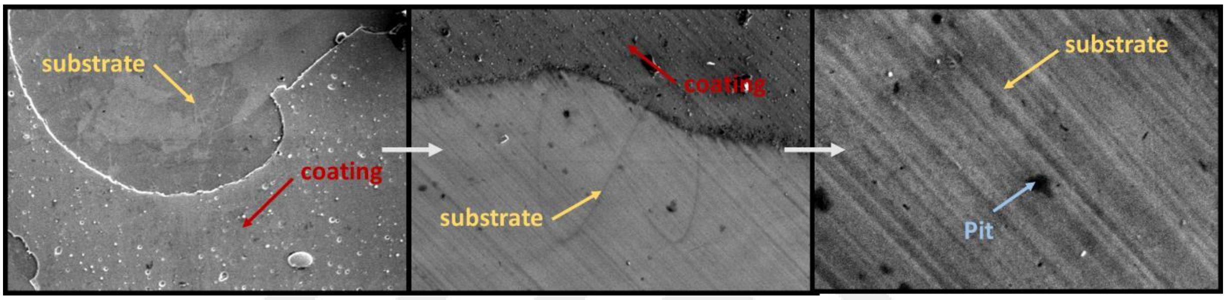


Figure 49. Extensive stage of corrosion.

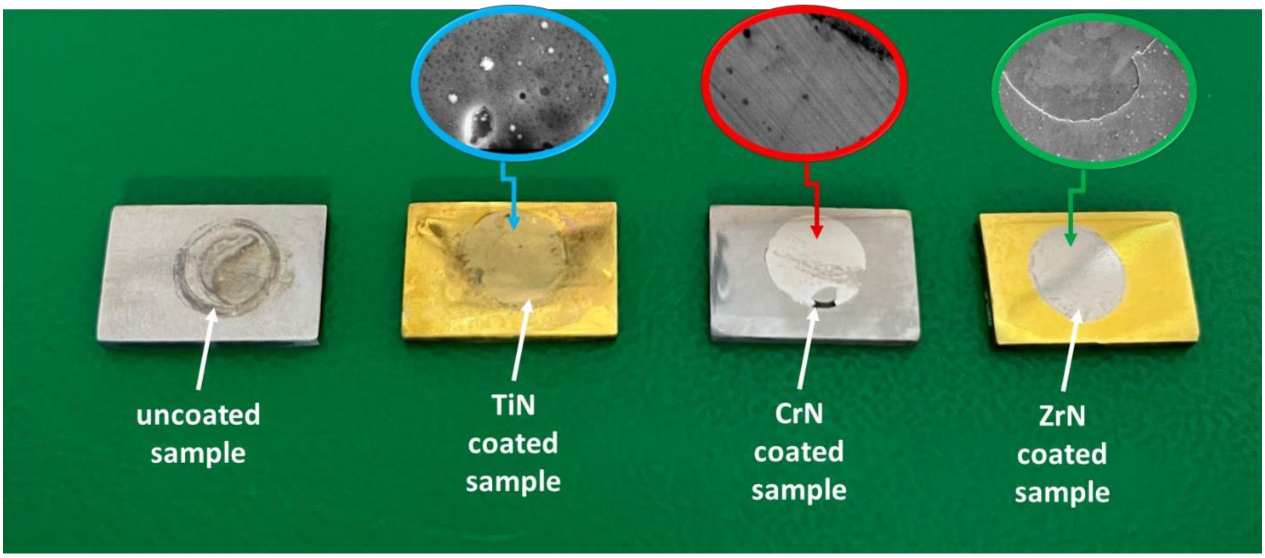


Figure 50. Macroscopic images of coated samples after corrosion.

RESULTS

In this study, TiN, CrN and ZrN coatings were produced to improve the tissue interaction and increase the biocompatibility of the TNTZ alloy by using the PVD method; it is aimed to reveal the optimum conditions in terms of mechanical and tribological characterization and in-vitro corrosion and increase its applicability in the biomedical field. Test results for this purpose are given below.

In the data obtained from the SEM results, the surface distributions of all the coatings were homogeneously coated on the surface and uniform, with macro-particles that increase the surface roughness of the coatings. No cracks or cavities are observed in the grain boundary that can improve the corrosion behaviour of the coating.

In the EDS analysis of the coatings, the components of the coating series (Ti, Cr, Zr, N, etc.) were determined. In XRD analyses, peaks of all coatings were found.

In wettability (contact angle) analyses, the lowest contact angle is the TiN coating, while the contact angle is 82°, while the highest contact angle is 91°, which belongs to the ZrN coating. The high contact angle is a result of smooth surface morphologies, which in this case belongs to ZrN.

The adhesion strength of the coatings was measured in the pull-off tests. TiN coating on TNTZ substrate exhibited increasing adhesion strength followed by CrN,, ZrN and uncoated sample. Complete separation of the coating from the surface was observed after the test. The highest adhesion value of the coatings is CrN with 38MPa, while the lowest value is as-received with 25.17MPa.

Considering the potentiodynamic test results, the coating with the lowest I_{corr} value is CrN with a value of 0.56 μA.cm^{-2}, while the coating with the highest I_{corr} with a value of 33.06 μA.cm^{-2} is from TiN. The coatings generally exhibited good corrosion resistance.

SEM and EDS analyses of the coatings were carried out to observe the post-corrosion surface morphologies, and as a result of the examinations, it was observed that the samples were subjected to pitting corrosion. Again, the presence of the elements (Ta, Nb, etc.) belonging to the base material in the EDS analysis proves that the coatings are dissolved in the Hanks solution. In addition, the presence of O peaks in the coatings proves the formation of oxide layers. On TiN coating, oxygen was observed,, indicating the thin layer of TiO_2 as Chloe and her friends found in their research (Choe, Ko, and Park 2006). It was also observed that TiN coating improved the corrosion resistance of the TNTZ alloy, with a homogeneous layer distribution as observed in Gu and his friends (Gu *et al.*, 1998) study. The same for CrN and ZrN, the formation of an oxide layer to protect the surface from corrosion was found by Chipatecua and his friends, that suggested that a Cr_2O_3 film is formed from CrN when the corrosion occurs to protect the surface (Chipatecua, Olaya, and Arias 2012). The same for Brown and his friend, that found that as protection against corrosion, from ZrN, a thin layer of ZrO_2 is formed (Brown, Alias, and Fontana 1993).

TNTZ had the highest corrosion rate, meaning the lowest corrosion resistance followed by TiN, ZrN and CrN. Mansoor and her friends (Mansoor *et al.*, 2020) studied the electrochemical behaviour of TiN, CrN and TiN/CrN and found that the CrN coated sample had better corrosion resistance then TiN and TiN/CrN. Jeong and his friends (Jeong *et al.*, 2007) deposited TiN and ZrN on Ti-HF alloy and concluded that ZrN has better corrosion resistance then TiN.

It was also observed that all coatings dissolved party or totally after corrosion and that pitting phenomenon started on the substrate.

As a result of the observations and evaluations , it is predicted that coating the implants expecteintended to be used as biomaterials in the biomedical field with biocompatible materials will increase their mechanical and corrosive resistance in in-body use. For this reason, it aims to improve the tissue-implant interaction further by enhancing the additives and considering biocompatibility in future studies.

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