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Review Paper

The Effect of Titanium Nanostructure on Corrosion Resistance as Dental Implants: A Review

Fadhli Muhammad[1], Shintia Novia Sari[1], Bonita Dilasari[1]*

[1] *Department of Metallurgical Engineering, Faculty of Mining and Petroleum Engineering, Institut Teknologi Bandung, Bandung, 40132, Indonesia*
***Corresponding author**: bonita_metallurgy@itb.ac.id

Abstract
Titanium is widely recognized as the most biocompatible metal due to the inert passive oxide layer that forms spontaneously on its surface. However, dental implants made of titanium and its alloys remain susceptible to corrosion when exposed to saliva for extended periods in the oral environment. Additionally, the presence of alloying elements in the alloy may raise concerns about potential toxicity concerns upon release into the human body. Consequently, there is an increasing need for research aimed at improving the mechanical properties and biocompatibility of dental implants made from both commercially pure titanium (CP Ti) and Ti alloys. This article provides a review of recent publications that investigate the impact of grain size reduction on ultrafine-grained and nanocrystalline CP Ti and Ti alloys. The article explores the modification of the oxide layer to nanotube TiO_2 and its influence on corrosion resistance. The analysis of accumulated data provides a comprehensive understanding of the mechanisms underlying corrosion resistance improvement, offering valuable insights into the crucial directions for future research in this field.

Keywords
Dental Implant, Corrosion, Nanocrystalline, Titanium, TiO_2 Nanotube

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1. INTRODUCTION

The material utilize for dental implant must meet specific requirements, including superior biocompatibility, excellent corrosion resistance, reliable mechanical properties (such as fatigue strength and wear resistance), and the ability to osseointegrate (Duraccio et al., 2015; Liu et al., 2004). Titanium is widely recognized as the most biocompatible metal due to the inert passive oxide layer that spontaneously forms on its surface. However, titanium and its alloys still do not fully meet the requirements for the ideal dental implant materials, particularly in terms of shear strength and wear resistance, as well as having a higher modulus of elasticity (103-120 GPa) compared to human bone (10-30 GPa) (Elias et al., 2008). Furthermore, dental implants made of titanium and its alloys remain vulnerable to corrosion over extended exposure to saliva in the oral environment.

According to the American Standard Testing and Material (ASTM), titanium is classified from Grade 1 to Grade 5, with Grade 1 having the lowest strength and Grade 5 having the highest strength. Grades 1 to 4 are unalloyed, while grade 5 is alloyed with 6% aluminum and 4% vanadium (Ti-6Al-4V) (Elias et al., 2008). Ti-6Al-4V is preferred for applications requiring high strength, but the presence of alloying elements may cause potential toxicity when released into the human body (Elias et al., 2013). This drives more research on the modification of both commercially pure titanium (CP Ti) and Ti alloys to provide appropriate mechanical properties as well as excellent biocompatibility for dental implants.

It was reported that reducing the grain size can have a beneficial effect on the mechanical properties of CP Ti. Several studies revealed that reducing the grain size of CP Ti to a few hundred nanometers, known as ultrafine-grained, has significantly increased its strength, making it comparable to that of Ti-6Al-4V (Elias et al., 2013; Garbacz et al., 2018; Greger et al., 2010), while also improving its corrosion resistance (Barjaktarević et al., 2018; Barjaktarević et al., 2019; Barjaktarević et al., 2017; Dimić et al., 2018; Sotniczuk et al., 2019). Efforts were also directed towards developing Ti alloys with less toxic elements, such as niobium, zirconium, molybdenum, and tantalum, to replace aluminum and vanadium (Greger et al., 2010). It has been confirmed that refining the grain of Ti alloys to ultrafine-grained and nanocrystalline sizes (<100 nm) improves their corrosion resistance (Barjaktarević et al., 2018; Dimić et al., 2018; Li et al., 2018). Furthermore, the transformation of the passive layer of titanium oxide (TiO_2) has significantly improved the corrosion resistance of both CP Ti and Ti alloys in a saliva solution (Al-Saady et al., 2020; Alves et al., 2017; Barjaktarević et al., 2019; Benea et al., 2014; Demetrescu et al., 2010; Jiang et al., 2018; Liu et al., 2011; Liu et al., 2012). This article reviews recent publications that investigate the effect of grain size reduction on ultrafine-grained and nanocrystalline CP Ti and Ti alloys. It also discusses the modification of the oxide layer to nanotube TiO_2 and its influence on corrosion resistance. By analyzing accumulated data, a comprehensive understanding of the mechanisms underlying the improvement in corrosion resistance is gained, providing valuable insights into the crucial directions for future research in this field.

2. CORROSION BEHAVIOR OF TITANIUM AS DENTAL IMPLANTS

Titanium ($E^0_{Ti^{2+}/Ti}$= -1.63 V vs SHE) has the third lowest standard reduction potential value among commonly used engineering metals, after aluminum and magnesium. This means that titanium and its alloys are readily oxidized when exposed to air or various aqueous media. However, the high affinity of titanium and its alloys for oxygen promotes the spontaneous formation of a naturally stable passive oxide film on their surface, resulting in excellent corrosion resistance (Brunette et al., 2001). The Pourbaix diagram (potential-pH equilibrium diagram) shown in Figure 1 can be used to predict the corrosion behavior of titanium in an aqueous environment. The diagram indicates the thermodynamic stability of titanium as a metal in the "immunity" region. In contrast, the "corrosion" region indicates that titanium will actively dissolve at a high rate under such conditions. The "passivation" region is the area where the stable oxide or hydroxide film protects titanium from further reactions with the environment. The shaded area shows the potential-pH range relevant to the physiological system, indicating that titanium and its alloys are protected by a passive oxide film when exposed to low potential and low pH conditions. Saliva typically has a neutral pH in the range of 5.2 to 7.8 (Noumbissi et al., 2019). However, the pH can decrease with the consumption of acidic foods and beverages. In addition, the pH of saliva can be altered by the presence of bacteria, fungi, and their by-products.

Corrosion types commonly observed in the oral environment include galvanic, pitting, crevice, and fretting corrosion, as shown in Figure 2 (Corne et al., 2016; Gittens et al., 2011; Mellado-Valero et al., 2018; Rodrigues et al., 2013). Galvanic corrosion occurs when dissimilar metals or alloys come into direct contact while exposed to a conductive solution. In vivo galvanic cells can form when titanium-based dental implants come into contact with prosthetic parts or dental restoration components made of other alloys (Noumbissi et al., 2019). The difference in corrosion potential between these alloys can cause an electric current to flow, accelerating corrosion of the less noble metal. If the prosthetic part is made of a less noble alloy than titanium, it can act as an anode and undergo dissolution (Mellado-Valero et al., 2018). Saliva that penetrates the micro-gap between the implant and the abutment acts as a conductive electrolyte.

Pitting corrosion may occur in titanium-based dental implants if the TiO_2 passivation layer is damaged, exposing the base metal (Brunette et al., 2001). Although titanium and its alloys are generally highly resistant to pitting corrosion under various in vivo conditions (Manivasagam et al., 2010), highly concentrated fluoride solutions found in mouthwashes and toothpastes, which are commonly used during oral cleaning procedures. Fluoride ions react strongly with the TiO_2 protective layer, can cause damage. According to Chaturvedi (2009), fluoride ions react strongly with the TiO_2 protective layer, leading to the degradation of the oxide layer. This, in turn, causes corrosion of the exposed base metal, resulting in the formation of small pits or crevices. Crevice corrosion is initiated by a difference in oxygen concentration, which creates an electrochemical potential difference between the confined spaces and the bulk. In small gaps with limited solution flow, the local oxygen concentration decreases, causing the area to become more anodic. This leads to active corrosion, releasing metal ions and electrons. The surface exposed to a higher oxygen concentration acts as a cathode, consuming electrons (Gittens et al., 2011). Meanwhile, fretting corrosion can occur due to friction between implant components caused by repetitive loading, such as chewing, combined with the presence of corrosive electrolytes.

3. ELECTROCHEMICAL CORROSION TEST

Various electrochemical corrosion tests are commonly used to investigate the electrochemical properties of CP Ti and Ti alloys in different artificial saliva solutions. This article compares data from the potentiodynamic polarization test, which is a technique that involves shifting the potential at a certain rate and recording the resulting current. The test cell is a three-electrode system comprising a working electrode, a reference electrode, and an auxiliary electrode. The polarization curves illustrate the correlation between the measured potential and current. Analyzing the polarization curve can provide information about the corrosion potential (E_{corr}) and corrosion current density (i_{corr}), which are estimated using the well-known Tafel extrapolation method. For materials that exhibit active-passive behavior, parameters such as current density in the passive region (i_{pass}), potential range in the passive region, and trans-passive potential can be identified for materials that exhibit active-passive behavior (Jones, 1996). In general, a more negative E_{corr} indicates a higher tendency for the material to corrode, while a higher i_{corr} signifies a higher rate of corrosion reaction rate.

4. EFFECT OF GRAIN SIZE REDUCTION

This review examines the impact of grain refinement on the corrosion behavior of CP Ti and Ti alloys, specifically in ultrafine-grained and nanocrystalline states. The data analyzed is based on potentiodynamic polarization tests conducted in an artificial saliva solution. Table 1 summarizes the corrosion potential (E_{corr}) and corrosion current density (i_{corr}) data from recently published papers.

Dimić et al. (2018) investigated the corrosion behavior of ultrafine-grained CP Ti and Ti-13Nb-13Zr alloy, which were obtained through the high-pressure torsion (HPT) process. Electrochemical tests were conducted in an artificial saliva solution with a pH of 7.5 at 37°C. The results confirmed that reducing

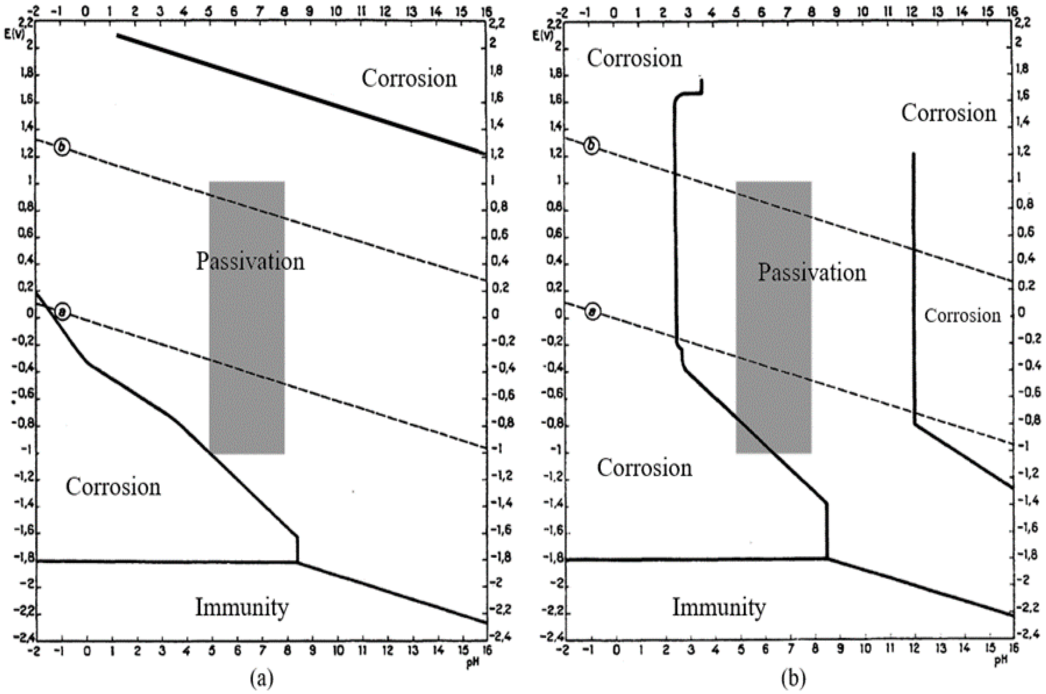

Figure 1. The Pourbaix Diagram for Ti/TiO_2 (Rutile) (a), and Ti/$TiO_2.H_2O$ (b) (Brunette et al., 2001)

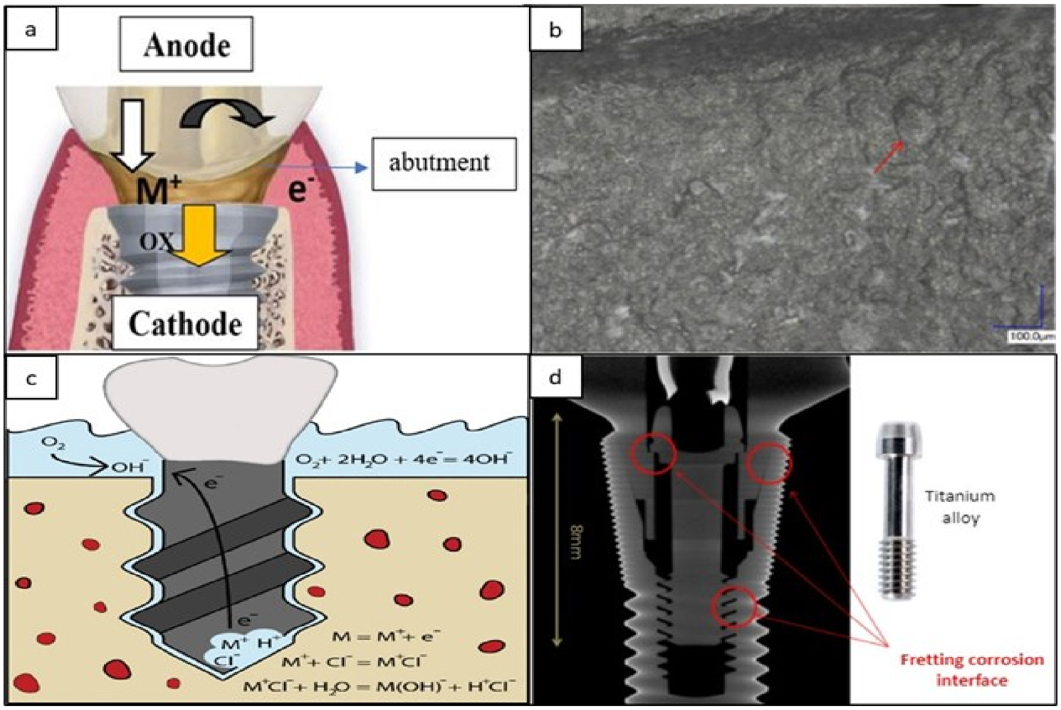

Figure 2. The Most Common Types of Corrosion Observed in Dental Implants (a) Galvanic Corrosion (b) Pitting Corrosion (c) Crevice Corrosion (d) Fretting Corrosion (Corne et al., 2016; Gittens et al., 2011; Mellado-Valero et al., 2018; Rodrigues et al., 2013)

the grain size to ultrafine has a positive effect on the corrosion resistance of the Ti alloy, as indicated by the shift in E_{corr} value from -300 mV to +213 mV vs SCE. The i_{corr} value decreased significantly from 110×10-9 A cm^{-2} to 53×10^{-9} A cm^{-2}. However, the corrosion resistance of CP Ti did not improve after the HPT process.

Table 1. Summary of E_{corr} and i_{corr} Values Obtained from Tafel Extrapolation of Ultrafine-Grained and Nanocrystalline CP Ti and Ti Alloys in Artificial Saliva Solution

Material	Remark	Average Grain Size (nm)	E_{corr} (mV vs SCE)	i_{corr} (nA cm^{-2})	Reference
CP Ti grade 2	Coarse grained	$\pm 10^4$	226	38	(Dimić et al., 2018)
	Ultrafine grained	$\pm 10^2$	134	40	
Ti-13Nb-13Zr	Coarse grained	10×10^3	-300	110	
	Ultrafine grained	200	213	53	
CP Ti	Coarse grained	-	-560	955	(Barjaktarević et al., 2018)
	Ultrafine grained	-	23	67.6	
Ti-13Nb-13Zr	Coarse grained	-	-28	103	
	Ultrafine grained	-	-24	166	
CP Ti grade 2	Coarse grained (in pH 4.0)	15×10^3	-230	3.08	(Barjaktarević et al., 2017)
	Coarse grained (in pH 5.5)	15×10^3	-409	2.19	
	Ultrafine grained (in pH 4.0)	270	-113	0.77	
	Ultrafine grained (in pH 5.5)	270	-115	0.59	
CP Ti grade 2	Coarse grained	35×10^3	-159	340	(Sotniczuk et al., 2019)
	Coarse grained (1500 ppm of F^-)	35×10^3	-239	450	
	Ultrafine grained	420	-119	210	
	Ultrafine grained (1500 ppm of F^-)	420	-229	390	
Ti-24Nb-4Zr-8Sn	Coarse grained	$80\text{-}100\times10^3$	-450	500	(Li et al., 2018)
	Coarse grained (100 ppm of F^-)	$80\text{-}100\times10^3$	-550	800	
	Coarse grained (1000 ppm of F^-)	$80\text{-}100\times10^3$	-625	1000	
	Coarse grained (10000 ppm of F^-)	$80\text{-}100\times10^3$	-800	2350	
	Nanocrystalline	<50	-400	130	
	Nanocrystalline (100 ppm of F^-)	< 50	-550	400	
	Nanocrystalline (1000 ppm of F^-)	<50	-600	500	
	Nanocrystalline (10000 ppm of F^-)	<50	-750	2150	

Barjaktarević et al. (2018) reported a similar grain refinement technique for CP Ti and Ti-13Nb-13Zr alloy, but their results were contradictory. The potentiodynamic polarization test of CP Ti in artificial saliva solution with a pH value of 5.5 showed a significant decrease in the icorr value from 955×10-9 A cm^{-2} to 67.6×10-9 A cm^{-2} and a significant increase in the Ecorr value from -560 mV to +23 mV vs SCE for the coarse and ultrafine-grained samples, respectively. Barjaktarević et al. (2017) studied the effect of pH on the corrosion of coarse-grained CP Ti grade 2 with a grain size of 15 μm and the ultrafine-grained CP Ti with a grain size of 270 nm. The results show that the ultrafine-grained CP Ti has a better corrosion resistance than that of coarse-grained at both pH 4.0 and 5.5, with the icorr slightly lower at pH 5.5.

Sotniczuk et al. (2019) successfully reduced the grain size of CP Ti grade 2 from 35 μm to 422 nm using a multiple pass rolling process. The corrosion test in artificial saliva solution showed a lower icorr and a slightly more positive Ecorr in the ultrafine-grained CP Ti compared to the coarse-grained. Although the presence of aggressive fluoride ions caused a decline in the resistance of the passive layer, the passive layer formed on the ultrafine-grained CP Ti was still superior to that formed on the coarse-grained CP Ti. It is believed that the fluoride ions are incorporated in the oxide layer, resulting in a less protective layer on the alloy surface compared to that formed in a fluoride-free saliva solution (Milošev et al., 2013). Li et al. (2018) concluded similar result for the nanocrystalline Ti-24Nb-4Zr-8Sn alloy. They reported that reducing the grain size to smaller than 50 nm enhances the stability of passive films and accelerates the growth rate of the TiO_2 passive layer. The i_{corr} value in the presence and the absence of fluoride ions was lower for the nanocrystalline alloy compared to the coarse-grained one.

The above explanation demonstrates that CP Ti and Ti alloys with ultrafine-grained or nanocrystalline structures exhibit lower icorr values, indicating a slower corrosion rate, and more positive E_{corr} values, indicating a lower tendency for the metal to corrode. This phenomenon can be attributed to the influence of structural defects, such as dislocations and grain boundaries. Smaller grain size results in a higher volume fraction of the dislocations and the grain boundaries, which are preferential sites for the nucleation of the TiO_2 passive layer (Balyanov et al., 2004; Sotniczuk et al., 2019). The materials with smaller grain sizes showed a more compact oxide layer and thereby higher corrosion resistance.

5. EFFECT OF TiO_2 NANOTUBES FORMATION

Titanium is a popular biomedical material due to its ability to naturally form protective oxide layers when exposed to air or water. The native oxide layer is amorphous and is attributed to the biocompatibility of the metal. However, for long-term dental implant applications, the native oxide layer is insufficient. One of the surface modification treatments that has been used to improve the properties of the oxide layers is the formation of TiO_2 nanotube arrays by electrochemical anodization (Al-Saady et al., 2020; Jiang et al., 2018; Liu et al., 2011; Liu et al., 2012). This technique involves passing a direct current through a fluoride-containing electrolyte with titanium as the positive electrode to produce a thicker oxide layer than the naturally formed one. The oxidation of the titanium surface to form TiO_2 and chemical dissolution by the aggressive ions resulted in a porous structure, which can be controlled by operational parameters such as applied voltage, time, temperature, electrolyte composition, pH, conductivity, and viscosity to obtain nanotubes. This article reviews the impact of TiO_2 nanotube formation on the corrosion behavior of CP Ti and Ti alloys. The review is based on data obtained from potentiodynamic polarization tests conducted in an artificial saliva solution. Table 2 summarized the E_{corr} and i_{corr} values obtained from the Tafel extrapolation.

Demetrescu et al. (2010) conducted a study that demonstrated the successful formation of TiO_2 nanotubes with a diameter of almost 120 nm. This was achieved through anodization of CP Ti in a mixture of 1 M $(NH_4)_2SO_4$ and 0.5% NH_4F with an applied voltage of 20 V for 2 hours. The untreated sample had nanostructured TiO_2. Both samples were then potentiodynamically polarized in an artificial saliva solution. The data shows that the treated sample has better corrosion resistance than the untreated sample. This is supported by a significant decrease in the icorr value from 7120×10^{-9} A cm^{-2} to 210×10^{-9} A cm^{-2}, as well as a positive shift in the Ecorr value from -399 mV to -274 mV vs SCE.

Al-Saady et al. (2020) conducted anodization on CP Ti by applying voltage variations of 15 V, 20 V, 25 V, and 30 V for 15 min and 30 V for 30 min. The results indicate that CP Ti with TiO_2 nanotubes exhibits better corrosion resistance than that of untreated CP Ti. Furthermore, increasing the applied voltage and anodization time has a positive effect on corrosion resistance, as higher voltage and longer anodizing time lead to lower i_{corr} and more positive E_{corr}. Another study by Jiang et al. (2018) conducted a study on the corrosion behaviors of CP Ti with TiO_2 nanotubes prepared by various anodization procedures. The samples with three-steps and two-steps anodization, in which the second step was conducted in a fluoride-free electrolyte, exhibited superior corrosion resistance among all samples. This was indicated by very low i_{corr} values. The procedure is thought to create a dense oxide layer, known as a barrier layer, between the oxide nanotubes and the titanium substrate, which improves the corrosion resistance.

Barjaktarević et al. (2019) investigated the formation of TiO_2 nanotubes on coarse-grained and ultrafine-grained Ti-13Nb-13Zr alloy. The study concluded that anodized ultrafine-grained Ti alloy exhibits superior corrosion resistance compared to the bare Ti alloy and anodized coarse-grained Ti alloy. Additionally, TiO_2 nanotubes formed on ultrafine-grained Ti alloy were more homogeneous than those formed on the coarse-grained Ti alloy, regardless of the anodization time. Longer anodization time produce more homogenous nanotubes with larger diameters and thinner walls. The ultrafine-grained Ti alloy with 90 minutes of anodization time gives the highest E_{corr} value and lowest i_{corr} value.

Liu et al. (2011) prepared TiO_2 nanotubes on 99.5% Ti foils using various applied voltages. The results indicated that the diameter of the TiO_2 nanotubes increased with higher voltage, as demonstrated in Figure 3. The open circuit potential measurement in artificial saliva revealed that the titanium with nanotubes had a more positive potential than the untreated sample. The electrochemical stability of TiO_2 nanotubes was tested at different anodization voltages. The results indicate that the nanotubes anodized at 15 V exhibited the best performance, followed by those anodized at 10 V, 5 V, and 20 V, respectively. It is possible that the nanotubes produced at 20 V exceeded the critical diameter size, providing more area for the corrosion reaction. The higher surface area of TiO_2 nanotubes also enabled the adsorption of protein that may exist in the saliva, which eventually enhanced the corrosion resistance of the TiO_2 nanotube's outer layer (2012).

Alves et al. (2017) found that anodization in electrolytes containing calcium (Ca) and phosphorous (P) produces Ca/P-doped TiO_2 with a better corrosion resistance than the regular nanotubes and untreated CP Ti. An anodic polarization test in artificial saliva showed that the sample with TiO_2 nanotubes has a wider passive potential range than the untreated. However, the passive current density (i_{pass}) value is almost the same for the regular nanotubes and the untreated CP Ti. Meanwhile, the Ca/P-doped TiO_2 showed a significantly lower i_{pass} value, which was 104 times lower. Previous research by Zhu et al. (2004) also reported that enriching the oxide layer with Ca/P improved the biochemical bonding between bone and anodized surfaces. Therefore, anodizing titanium in Ca/P-containing electrolytes

Table 2. Summary of E_{corr} and i_{corr} Values Obtained from Tafel Extrapolation Before and After Fabrication of TiO_2 Nanotube in Artificial Saliva Solution

Material	Remark	Average Diameter (nm)	E_{corr} (mV vs SCE)	i_{corr} (nA cm^{-2})	Reference
CP Ti grade 1	Untreated	-	-399	7120	(Demetrescu et al., 2010)
	TiO_2 Nanotube (20 V - 120 min)	120±15	-274	210	
CP Ti grade 1	Untreated	-	-209.2	579	(Al-Saady et al., 2020)
	TiO_2 Nanotube (15 V - 15 min)	-	-171	100	
	TiO_2 Nanotube (20 V - 15 min)	-	-162	90	
	TiO_2 Nanotube (25 V - 15 min)	-	-145	80	
	TiO_2 Nanotube (30 V - 15 min)	80	-138	76	
	TiO_2 Nanotube (30 V - 30 min)	-	-130	66	
CP Ti grade 1	Untreated	-	-661	15.1	(Jiang et al., 2018)
	TiO_2 Nanotube (single-step; 30 V - 10 min)	38	-244	12	
	TiO_2 Nanotube (two-steps; 30 V - 10 min)	38	-177	9.1	
	TiO_2 Nanotube (two-steps; first-step 30 V - 10 min, second-step 60 V - 5 min in fluoride-free electrolyte)	-	-173	7.9	
	TiO_2 Nanotube (three-steps; first-step 30 V - 5 min, second-step 60 V - 5 min in fluoride-free electrolyte, third-step 30 V - 5 min)	-	-194	4.6	
	TiO_2 Nanotube (two-steps; first-step 30 V - 9 min, second-step 20 V - 5 min)	-	-293	13.1	
Coarse-grained Ti−13Nb−13Zr	Untreated	-	-28.0	103	(Barjaktarević et al., 2019)
	TiO_2 Nanotube (60 min)	55.43	48.0	47.9	
	TiO_2 Nanotube (90 min)	76.44	61.0	34	
Ultrafine-grained Ti−13Nb−13Zr	Untreated	-	-24.0	166	
	TiO_2 Nanotube (60 min)	56.22	-21.0	41.6	
	TiO_2 Nanotube (90 min)	90.17	80.0	8.9	

might be an attractive method for producing dental implant materials with high biocompatibility and minimal corrosion degradation.

Benea et al. (2014) investigated the surface modification of Ti-6Al-4V alloy to create a nanoporous oxide layer. The study found that anodized Ti alloys exhibit superior corrosion resistance compared to untreated Ti alloy. This was demonstrated by a more positive and stable open circuit potential during a 1-hour immersion in a simulated saliva solution. The potentiodynamic polarization test also revealed a lower passive current density in the passive range compared to the untreated Ti alloy. They concluded that the formation of a nanoporous TiO_2 layer by anodization has successfully improved the corrosion performance of Ti−6Al−4V alloy.

6. FURTHER RESEARCH POTENTIAL AND OPPORTUNITIES

6.1 Nanocrystalline Titanium

Titanium and its alloys with a nanocrystalline structure exhibit improved mechanical properties and corrosion resistance. Currently, there is no commercially applicable process for producing nanocrystalline titanium. One effective method for producing titanium with a nanocrystalline structure is Equal Channel Angular Pressing (ECAP) because it maintains the dimensions of the

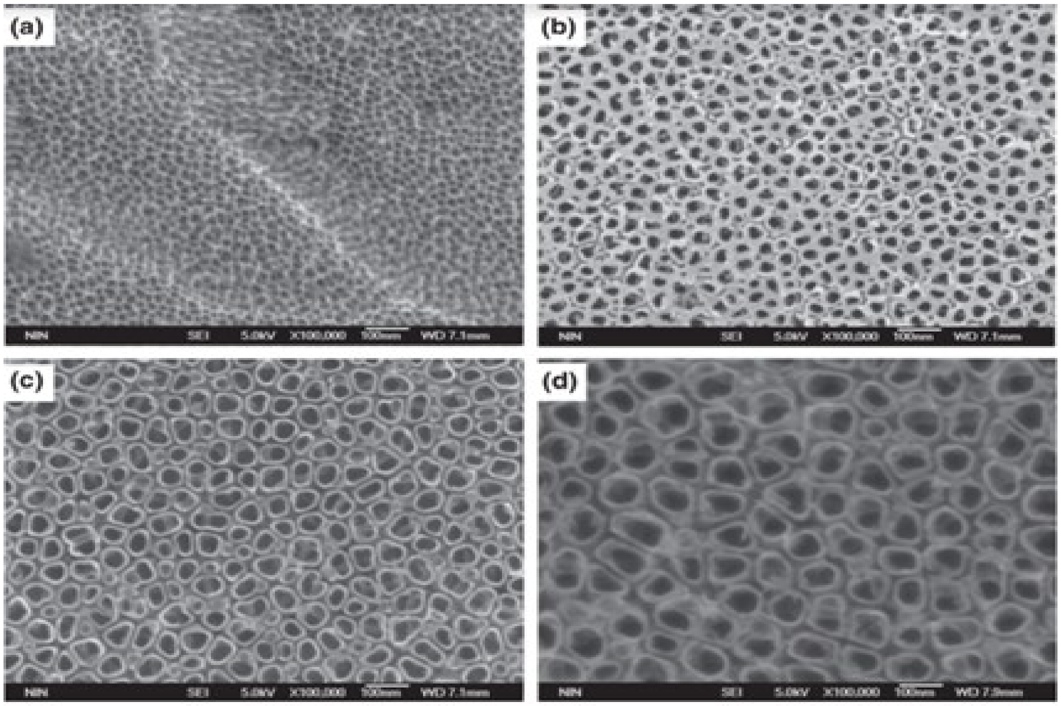

Figure 3. Surface Morphologies of TiO_2 Nanotubular Layer Formed on Ti by Anodizing Process in 0.5 wt.% HF at: (a) 5 V, (b) 10 V, (c) 15 V, and (d) 20 V (Liu et al., 2011)

Table 3. Reported Studies Related to the Relationship of TiO_2 Nanotubes Diameters to Immune Cell Depletion

Immune Cell	Nanotube Diameter (nm)	Remarks	Reference
Macrophage IC-21	40-50 and 60-70	A nanotube with a diameter of 60-70 nm reduces the density of macrophage	(Rajyalakshmi et al., 2011)
Whole blood lysate (leukocytes, platelets, and erythrocytes)	170	Nanotubular with a diameter of 170 nm reduces short-term and long-term activity in monocytes, macrophages, and neutrophils	(Smith et al., 2013)
Human monocytes	30 and 80	The number of cells attached is less to the nanotubular with a diameter of 30 nm	(Ma et al., 2014)
Macrophage raw 264.7	78	Nanotubular with a diameter of 78 exerts a suppressive effect on MAPK (mitogen-activated protein kinase)	(Neacsu et al., 2015)

processed material. However, the ECAP process has a limitation as it can only process high-ductility materials. Processing CP Ti at room temperature is challenging due to its lower ductility compared to other metals (Balasubramanian et al., 2021). However, extrusion and drawing can process materials with lower-ductility at room temperature, but cannot maintain the dimensions of the material (Balasubramanian et al., 2021). Therefore, further research could potentially combine the advantages of the ECAP process with other processes to produce nanocrystalline CP Ti at room temperature while maintaining its dimensions.

6.2 TiO_2 Nanotubes

Titanium dental implants with TiO_2 nanotubes offer several advantages and show greater potential for dental implant applications than conventional titanium with TiO_2. One of the most attractive properties is their superior corrosion resistance. However, there are still many unanswered questions, and several gaps need to be addressed. While TiO_2 nanotubes could generally enhance immunity compared to conventional oxide layers, studies have shown that a specific diameter of TiO_2 nanotubes shows can have a negative effect on immunity (Gulati et al., 2018). Table 3 lists the impact of TiO_2 nanotube dimensions on immune cells as reported in several studies. Nevertheless, the correlation between the diameter of TiO_2 nanotubes and immune cell depletion persists.

Nano topography can affect immunity, including the mechanotransduction effect (Gulati et al., 2018). Mechanotransduction is a biological phenomenon in which the mechanical stress imposed on immune cells is translated into chemical signals, resulting in an adaptive response (Rajyalakshmi et al., 2011). However, the mechanotransduction effect of nanotubular TiO_2 in dental implant applications remains a challenge, and only a few studies have explained the mechanism (Gulati et al., 2018).

TiO_2 nanotubes have a tubular shape that can be used as a place or container for drugs or proteins that aid in the postoperative healing process (Gulati et al., 2018). Additionally, nanotubular TiO_2 can contain multiple types of drugs or proteins simultaneously (Gulati et al., 2018). One such drug is anti-inflammatory medication, which helps to alleviate pain following dental implant surgery. The process of loading and releasing this drug from nanotubular TiO_2 can be controlled. However, the rate of drug release has not been determined yet (Gulati et al., 2018).

Research on immunomodulation (modification of immune response) in dental implants is primarily conducted in vitro, through cell or tissue culture in the laboratory. Long-term in vivo studies in living organisms are necessary to bridge the gap between these two types of studies (Gulati et al., 2018). While short-term in vivo studies have confirmed the good biocompatibility and non-toxicity of nanotubular TiO_2, these studies have not included mechanical loading (Gulati et al., 2018). Therefore, further research opportunities concerning the long-term in vivo testing of TiO_2 nanotubular applications under mechanical loading are still open for investigation.

7. CONCLUDING REMARKS

Numerous efforts have been made to improve titanium and its alloys to meet the requirements for ideal dental implants. One notable challenge is their susceptibility to corrosion over prolonged exposure to saliva. The modification of titanium dental implant materials and their alloys through surface treatment has shown positive results in reducing corrosion current density values and increasing corrosion potential values. The increase in grain boundaries and the change in orientation of the titanium plane to close-packed structures significantly improve the corrosion resistance of ultrafine-grained and nanocrystalline CP Ti and Ti alloys. Increasing the thickness of the TiO_2 oxide layer, which consists of the inner and outer layers, and the formation of phosphate deposits on the outer layer of TiO_2 has been shown to enhance the corrosion resistance of TiO_2 nanotubes. However, fabricating ultrafine-grained and nanocrystalline CP Ti and Ti alloys remains a challenge. The ECAP method, which is an effective fabrication method, has a significant limitation in processing low ductility CP Ti at room temperature. Therefore, further research should focus on modifying ECAP or exploring alternative processing technologies to produce ultrafine-grained and nanocrystalline CP Ti and Ti alloys at room temperature. Additionally, TiO_2 nanotubes show promising potential for dental implant applications due to their superior corrosion resistance. However, it is important to note that certain diameters of TiO_2 nanotubes may have a negative effect on immunity. The relationship between the diameters of TiO_2 nanotubes and immune cell depletion is appealing for further analysis.

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