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Preparation and Characterization of TiO_2-SiO_2 Bioceramic Coating on Ti Alloy via Electrochemical Anodization and Its Effect on Corrosion Resistance

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ABSTRACT

Purpose: The present study was carried out to study the effect of changing the anodization process parameters and investigate the corrosion resistance of the ceramic coating that will be formed on the CP-Ti by anodization method. **Materials and Methods:** CP-Ti samples of (10mm×10mm×2mm) were used for fabrication of bioceramic coating through anodization process with different parameters using potassium silicate as an electrolyte solution. The samples were characterized using XRD, AT-FTIR. The surface roughness was measured using ESEM and the surface topography was evaluated by SEM. Tafel polarization measurement and electrochemical impedance spectroscopy were used to detect the change in the corrosion resistance after anodization. **Results**: XRD revealed that the anodized coated samples showed well defined peaks at 2θ of Ti and TiO_2 and shallow peaks of SiO_2. AT-FTIR showed stretching bands of titania and silica. Regarding the surface roughness results, the anodized coated samples at the optimum conditions had the lowest Ra values while the uncoated (control) group had the highest Ra value. On comparing the results of the surface morphology, the best evenly distributed ceramic coat was formed at the optimum conditions where (the applied voltage =50v, the electrolyte concentration =3% and process duration=60min). The corrosion resistance of the anodized coated samples at the optimum conditions was markedly increased more than that of the uncoated CP-Ti samples. **Conclusions:** The optimum conditions of the anodization process to get a uniform anodized coating can be achieved when; the applied voltage is 50v, the electrolyte concentration is 3% and the process duration in 60min. Moreover, formation of a bioceramic coating has been shown to be a useful method for improving the corrosion resistance.

KEYWORDS

Anodization;
CP-Ti implant; Corrosion Resistance;
Surface Morphology

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INTRODUCTION

For long time ago, dentists have been working to restore missing teeth with suitable materials. Dental implants are like screws that act as replacements for the anchorage of the missing natural tooth and becoming familiar in the recent day dental procedures [1]. Not only the Ti-CP but also some alloys like binary and tertiary Ti alloys were in use. Regarding the recent reviews, it was concluded that most of the binary Ti alloys with alloying <20% elements of Zr, In, Ag, Cu, Au, Pd, Nb, Mn, Cr, Mo, Sn and Co have good impact as implant materials, as they have good mechanical properties [2]. Ti is commonly used as an implant material for its good biological acceptance, ablity of bonding with osteoblasts and its acceptable biocompatibility. The spontaneous passive layer formed on the surface is almost reliable and can isolate the bulk Ti material from its environment. Therefore, it could resist the corrosion. Unfortunately, this oxide layer is very tiny and can be destroyed. Hence, various efforts have been done to preserve TiO coating [3].

In an effort to improve corrosion resistance of the dental implant, the chemical structure and morphology of the implant surface need to be changed. Implant surface treatments have the opportunity of enhancing cell aposition, cell growth, and bone formation which markedly improve the osseogenesis process[4].There are different methods for modifying surface roughness or applying osteoconductive layers on titanium implants as titanium plasma-spraying, grit-blasting, acid-etching, anodization or calcium phosphate coatings, and their subsequent surface morphology and characteristics have proven clinical efficiency (>95% over 5 years) [5].

From all these forementioned methods, anodization is of higher quality and sheep method which can provide controlled nanostructures on Ti surface. As many researches have shown that the osteoblasts are habituated to a nano-scale environment more than to a micro-scale environment. The other methods are of more cost and may not provide both a thicker layer and acceptable cell adsorption [6, 7].It was claimed that anodic oxidation is a new technique in the biomedical field, a suitable method for making porous bioceramic films on surfaces of titanium. Moreover, it was stated that the benefits of these coating films is the higher cell adhesion, as the film formation includes oxidation the substructure [8, 9].

Scientists have tested ceramic oxides like Ti, Si, Nb, r mixed oxides and they have found that the oxides when formed on the metallic implant surface, provide an encouraging response to HA growth in vitro, osteoblast adhesion and proliferation in vivo and they also increased the wear and corrosion impedance of the dental implant[10]. Ti nano structures have a great importance in the medical field due to their special properties, expressed in the high repasivation rate, equivalent mechanical properties, increased surface area, and enhanced cell proliferation, adhesion and mineralization. However there is a deficiency in researches that could give exact knowledge about the main parameters and experimental variables needed to produce this such optimized structure [11].

A previous study incorporated the SiO_2 with titania nanotubes and they found that they are efficient in apatite nucleation while soaked in simulating body fluid. Also, it was claimed that Si is essential in bone formation with Ca and P [12].Many scientists claimed that Si-containing bio-ceramics can help in the formation of apatite crystals. Therefore, it is very effective to add Si into the oxide film [12, 13]. Convenient anodization parameters such as applied voltages, electrolyte concentration and different temperatures can equilibrate the growth and dissosiation of the micro-nano surface structure[14].

It was reported that the thickness of TiO_2 formed layer is mainly dependent on the voltage applied, which results to the believe that the TiO_2 layer has a high electrical resistivity. The morphological

structure can be handled by changing the factors of the process, which are the voltage applied, electrolyte type, and duration of the process [15]. It is known that HA form and grow on anatase phase of TiO_2 relatively more than on rutile one. Therefore, heat treatment of TiO_2 nanotubes at 350 °C is required for changing the amorphous to crystalline structure with anatase phase [16].It was also found that anatase crystallites formed inside the tube walls and changed totally to rutile at about 600 °C in dry environments and 570 °C in humid argon [17].

Another study evaluated the surface modifications of titanium implants. The surface topography was examined using SEM. They demonstrated that the main differences in the surface properties were mainly depending on the type of surface treatment utilized. They concluded that anodization process for Ti-Unite implants provides microporous surface (pore size: 0.5-3.0microm), moreover, it changes the surface chemistry due to incorporating the ions of the used electrolyte [18].

The corrosion resistance of Ti alloy was determined. Anodization process for surface alteration was used. The surface topography, chemical structure and the formed phases of the CP-Ti and surface treated Ti–6Al–4V alloy were inspected using (SEM), (EDX), (XPS) and X-ray diffraction (XRD). They found that the anodization process produced porous coating. The bioactivity study in (SBF) solution and with human bone marrow stromal cells (MSCs) revealed that after anodizing at 140 V and after alkali treatment the Ti–6Al–4V alloy shows osteoinductive behavior. The corrosion resistance evaluation showed that application of the anodizing process of the Ti–6Al–4V alloy apparently increased its corrosion resistance in Ringer solution [19].

MATERIALS AND METHODS

CP-Ti foil (Sigma Aldrich-USA), Etching solution (mixture of $HF+NHO_{3+}H_2O$), Ethanol, Potassium Silicate (Loba Chemie-India), Ringers' solution (ADWIA-Egypt) were used in the present study.

Samples' preparation:

The CP-Ti foil was cut into samples of (1cm 1cm 0.2cm) using wire cut machine. The samples were polished before starting the anodization process by sand paper disks up to 1200 grit. After that, the samples were etched for 30 seconds using $HF+NHO_{3+}H_2O$ with the ratio of 1:4:5 then, washed using deionized water and ethanol alternatively for five minutes and dried with air dryer.

Sample's grouping:

Regarding to the anodization process, three parameters were studied; (applied voltage, electrolyte concentration and process duration). A total of (90) samples were prepared for the laboratory study. Each parameter was divided into three groups so that the total number of the groups was nine groups in addition to a control group (n=9).

Formation of bioceramic coating:

The anodization process was done exploiting two-electrode joined with a direct current power provider. CP-Ti was used as anode having the surface area of $1cm^2$ and platinim basket was used as cathode in a temperature controlled set up. To investigate the effect of changing the anodization parameters on the properties of anodic coating, the process was done in different i) applied voltage (40 v – 60 v) ii) concentration of K_2SiO_3 (2% - 4%) and process duration (30 min – 90min). Following anodic oxidation, the samples were washed with deionized water and annealing was done to get crystallized phases (oxygen crystallization) at 350 °C for 5 hours.

Characterization of the formed coat:

The surface chemistry of the formed ceramic coat was investigated using AT-FTIR (400 Perkin Elmer infrared spectrometer), the new formed phases on the CP-Ti surface was confirmed using XRD (PHILIPS-binary scan), surface roughness was detected by ESEM (Quanta 200- company FEI - Netherlands) and surface morphology was examined by SEM Quanta 250 FEG-Netherlands).

Corrosion studies

The corrosion studies of the different CP-Ti samples surfaces' before and after anodization process were carried out using Electrochemical workstation- metrohm autolab (NOVA 1.11) by the use of ringer's solution. A three electrode biuld up was established for corrosion testing, where Platinum is used as counter electrode, Ag/AgCl was used as reference electrode and the anodized coated sample was the working electrode for both Tafel and impedance measurements. The surface area of working electrode was maintained at 0.38 cm^2. Tafel measurements were performed by applying potential in the range of +2 V to -2 V with a scan rate of 0.001 mV/s. The impedance measurements were done by using a sinusoidal wave of 10 mV to the working electrode at a frequency range of 0.1 MHz – 10 MHz.

Statistical analysis

The differences between Control group and the groups in each parameter were tested. ANOVA test was used to determine whether the differences are significant or not. As the differences were significant, the Post Hoc test (Tukey's method for multiple comparisons) was done to confirm that the variation returns to each group. The statistical analysis was done with IBM SPSS Statistics Version 20 for Windows.

RESULTS

Results of Anodization Process:

The color of the samples changed from the normal silvery white of the CP-Ti to different other colors by proceeding in the anodization parameters' variables. Regarding the applied voltage; the color changed to (yellow, brown, blue). Regarding the electrolyte concentration; the color changed to (orange, brown, pink). Regarding the process duration; the color changed to (fuchsia, brown, purple).

Surface characterization:

Results of XRD analysis:

Regarding the control group; Sharp and well defined peaks corresponded to Ti and TiO_2 phases were found. Regarding the anodization parameters (V, C and D): sharp and well defined peaks of corresponded to Ti and TiO_2 phases. A new peak of the SiO_2 phase was represented by a shallow peak (figures 1 and 2).

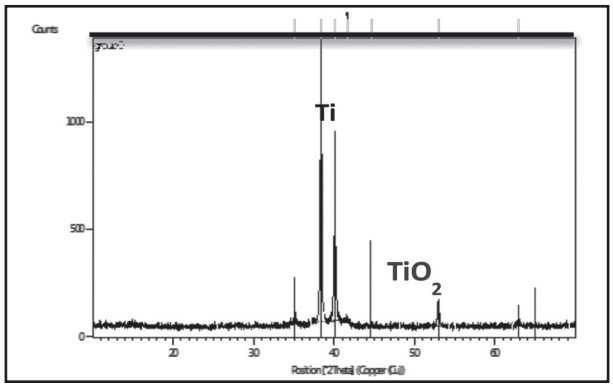

Figure (1) XRD patern of the control group

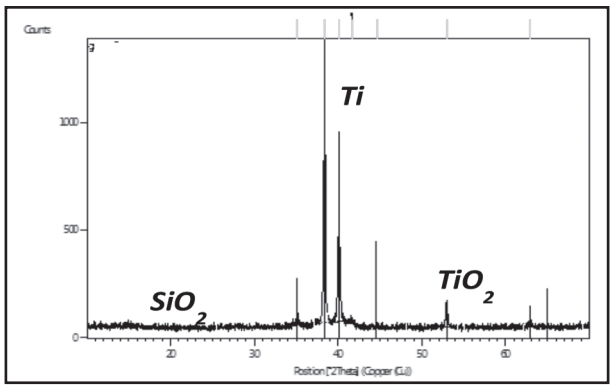

Figure (2): XRD patern of the anodized coated showing the Ti and TiO_2 peaks samples showing the Ti, TiO_2 and SiO_2 peaks

Crystal shape and Size of the Control group and the Anodized coated groups:

Table (1) shows the crystal size and shape of the formed phases. Ti phase was varying from hexagonal to cubic crystalline structure, TiO_2 phase was in the form of tetragonal crystalline structure

Table (1): *The crystal size and shape of the formed phases:*

Group / Crystal Size(nm)	Control	Applied voltage (V)			Electrolyte concentration (C)			Process duration (D)		
		V=40	V=50	V=60	C=2%	C=3%	C=4%	D=30m	D=60m	D=90m
CP-Ti Hexagonal & cubic	14-126 nm	27-76 nm	55- 380 nm	21-32 nm	39-2 nm	57- 380 nm	32-110 nm	32-95 nm	55- 370 nm	19-120 nm
TiO_2 Tetragonal	--------	22-42 nm	37- 312 nm	19-90 nm	20-38 nm	30- 323 nm	30-122 nm	22-30nm	36- 310 nm	19-78 nm
SiO_2 Rhombohedral	--------	29-37 nm	19-320 nm	7-20 nm	20-100 nm	19-320 nm	20-130 nm	11-15 nm	15-317 nm	19-70 nm

and the SiO_2 phase was in the form of rhombohedral crystalline structure. Regarding to the crystalline size; there was a change of the crystal size through the variables of all the anodization parameters in the same trend.

Results of Attenuated Reflectance Fourier Transform Infrared (AT-FTIR):

Frequencies of the absorption bands of AT-FTIR spectra of control and anodized samples with different anodization parameters (V, C, D) were recorded by diffused reflection from 4000 to 400 cm^{-1} (figures 3 and 4).

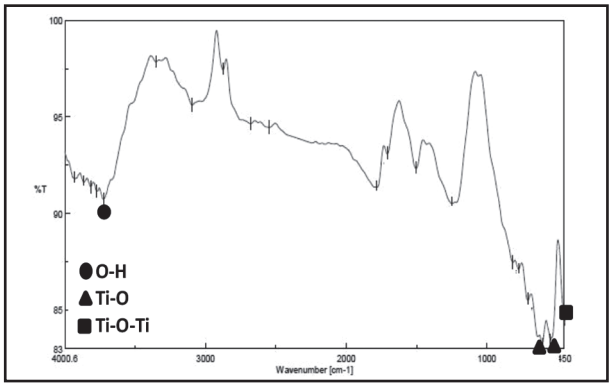

Figure (3): AT-FTIR spectrum of the control group showing the stretching bands of O-H, Ti-O, Ti-O-Ti

Surface Roughness Measurement (Ra):

Table (2) and Figure (5) show the mean and standard deviation (SD) of surface roughness (Ra) in nm of the control group and the anodized coated groups. Regarding the applied voltage parameter; the highest surface roughness was for group (V=60v) and the lowest surface roughness was for group (V=50v) in comparison with the control group. Regarding the electrolyte concentration; there was no statistically marked difference between the groups (C=2%, C=3%). Regarding the process duration; the highest surface roughness was for group (D=90min) while, the lowest value was for group (D=60min).

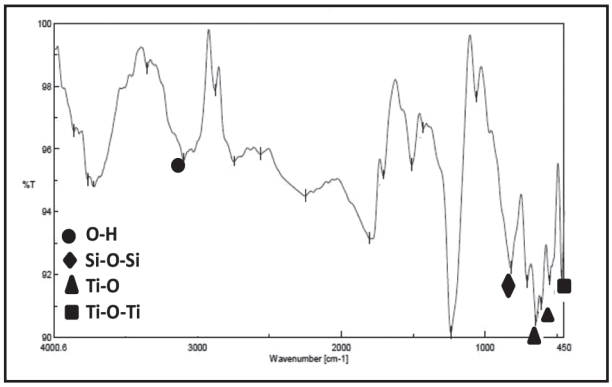

Figure (4): AT-FTIR spectrum of the anodized coated samples showing the stretching bands of O-H, Ti-O, Ti-O-Ti and SiO_2

Table (2): *The mean and standard deviation (SD) of surface Roughness (Ra) in nm of the control and the anodized coated groups:*

Group	Control	Voltage (V)			Concentration (C)			Duration (D)		
		V=40v	V=50v	V=60v	C=2%	C=3%	C=4%	D=30min	D=60min	D=90min
Mean	2.84 ^{e}	7.44 ^{b}	4.63 ^{d}	15.31 ^{a}	4.40 ^{d}	4.50 ^{d}	13.05 ^{a}	5.58 ^{c}	4.75 ^{d}	7.04 ^{b}
S.D	0.257	0.942	1.587	1.217	0.399	1.211	2.765	2.167	1.530	1.206
P- value	P ≤0.000*	P ≤0.000*			P ≤0.000*			P ≤0.000*		

**: Significant at P ≤0.05, Different letters in the same row are statistically significantly different according to Tukey's test*

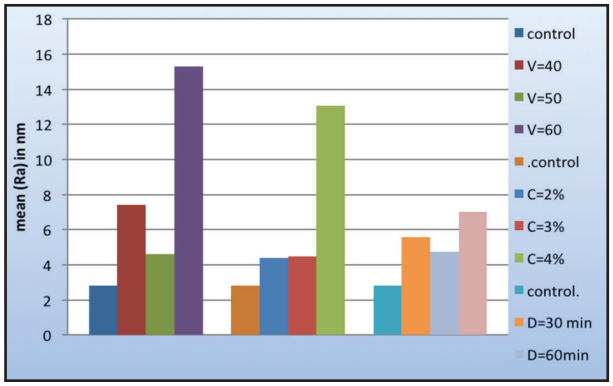

Figure (5): A bar chart representing the mean Ra values in (nm) of control group and the anodized coated groups with different anodization parameters.

Topographical 3D Images of the control group and the anodized coated groups using ESEM:

In comparison with the control group (figure 6-a), the surface roughness of the anodized coated samples increased at the beginning of the process (figure 6-b), then, by preceding in the process the surface roughness decreased showing shallow valleys and slightly broad elevated projections (figure 6-c). Finally, the surface roughness increased once again revealing deep valleys with prominent sharpened and pointed peaks (Figure 6-d).

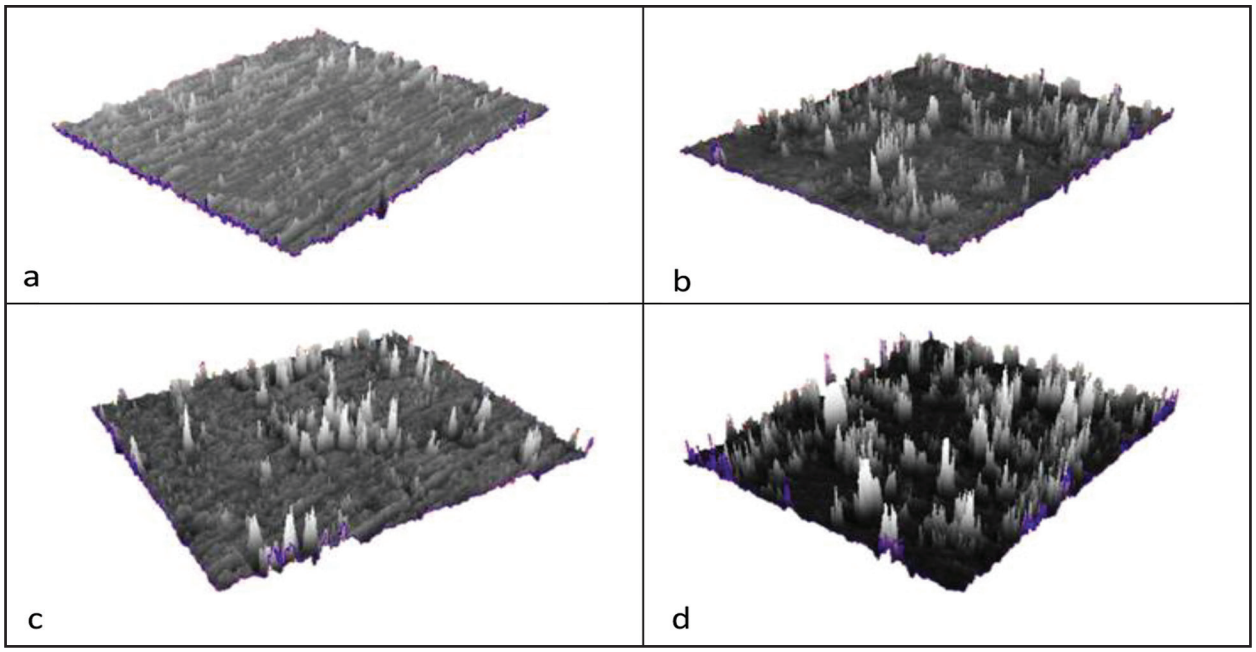

Figure (6): 3D Surface roughness of the control group and the anodized coated groups at different anodization parameters' variables

Surface morphology of the control group and the anodized coated groups using SEM:

A representative Scanning Electron Micrographs were selected for the investigated groups. Figure (7) shows the control group with normal appearance of the CP-Ti surface after polishing and the anodized coated samples where few crystals of SiO_2 were deposited on the sample surface and some islands of TiO_2 were formed (figure 7-b). By proceeding in the process where (V=50, C=3%, D=60) enlargement of the silica crystals took place and fusion of the titania islands were found to form a uniform layer with well distribution of its constituents (figure 7-c). Finally, at the highest variables cracks were developed and micro porosities were found in the formed coat (figure 7-d).

Corrosion studies

Tafel polarization technique:

The parameters obtained from the potentio-dynamic curves; (Tafel polarization) were displayed in (Table 4). The Tafel polarization curves showed that the resistance of anodized coated samples improved by proceeding in the anodization parameters; (applied voltage, electrolyte concentration and process time) which in turn leaded to marked decrease in the corrosion rate.

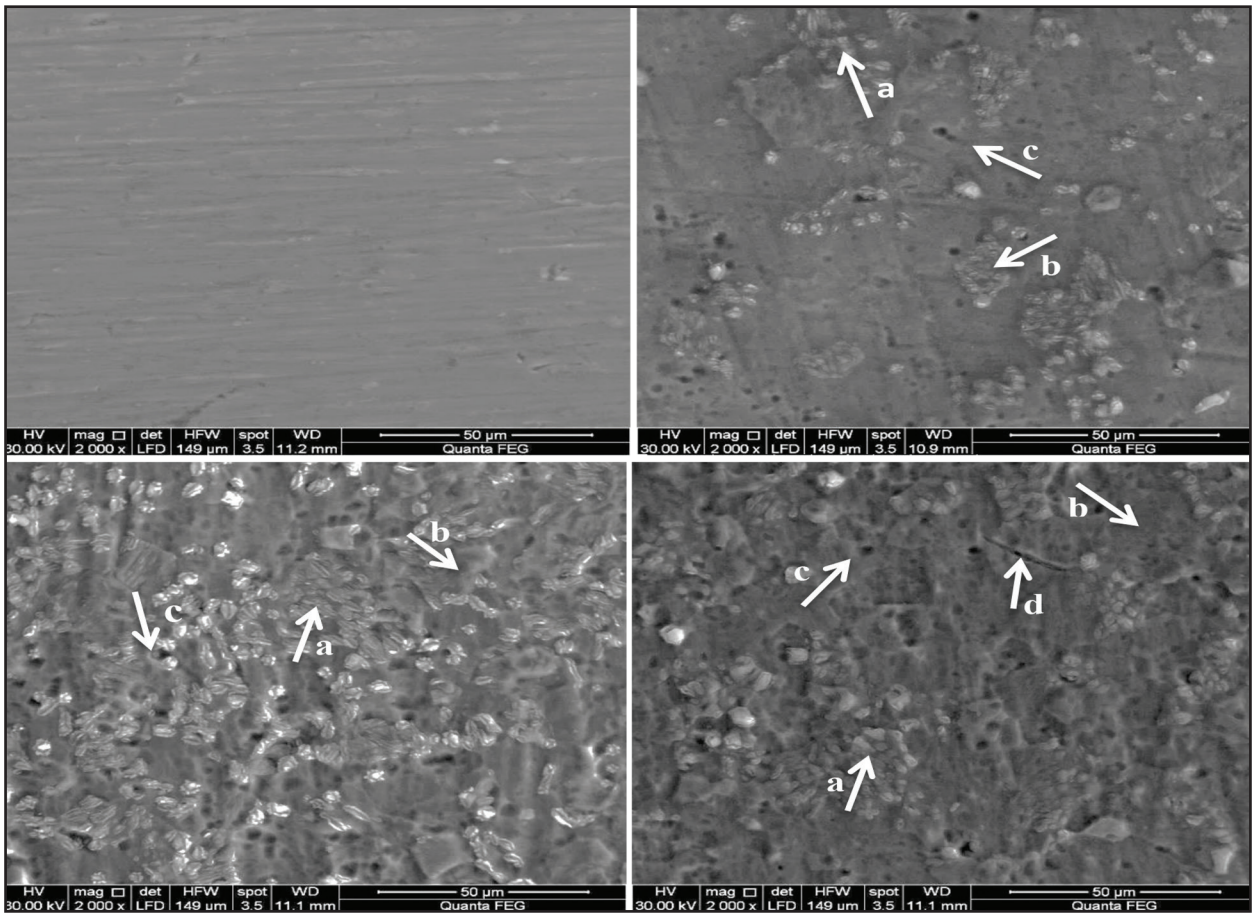

Figure (7): SE micrographs of the control group and the anodized coated groups where:The (a) arrow pointed to the silica crystals, the (b) arrow pointed to the titania islands, the (c) arrow pointed to the porosities, the (d) arrow pointed to the developed cracks.

Table (3): *Corrosion resistance and Corrosion rate the control group and the anodized coated groups regarding different anodizaion Parameters (V, C, D):*

	Control	Applied voltage			Electrolyte concentration			Process duration		
		V=40	V=50	V= 60	C=2%	C=3%	C=4%	D=30min	D=60min	D=90min
Corrosion resisrance (kΩ)	127.570 Ω	=89.320 kΩ	461.380 kΩ	=171.070 kΩ	122.690 kΩ	=478.550 kΩ	=145.020 kΩ	=235.160 kΩ	=492.310 kΩ	=444.500 kΩ
Corrosion rate (mm/year)	0.10774	0.01341	0.00092	0.02366	0.04055	0.00108	0.00415	0.01124	0.00130	0.00491

Electrochemical Impedance Spectroscopy (EIS):

The equivalent circuit of the control group and the anodized coated group of the highest corrosion resistance and the lowest corrosion rate (optimum conditions; V=40v, C=3%, D=60min.) was demonstrated in (table 4) based on EIS fitted curves. Like in the Tafel data, EIS study also revealed that the selected anodized coated CP-Ti group had higher corrosion resistance compared to that of the control group.

Table (4): *The Corrosion Resistance, Electrical Double Layer Capacitance and Solution Resistance Regarding the Control Group and the Anodized Coated Group:*

Group / Parameter	Control group	Anodized coated group
Corrosion resistance (R_{ct})	112 KΩ	247.7 KΩ
Electrical double layer capacitance (C_{dl})	18.1µMho	11.5 µMho
Solution resistance (Rs)	142 Ω	205 Ω

DISCUSSION

Generally, the long-term service of dental implants is acceptable. However, the failure of dental implants still occurs in a small quantity of patients. There are few researches studying the failed Ti dental implants due to rusting and errosion and its effect on anchorage and biological aspects [23]. Patients remain a great challenge in dental implantology and prompt the need for bioactive surface modifications that accelerate osseointegration after implant insertion. In addition, the aim of designing new bioactive surface properties is to accelerate osseointegration for more convenient, early loading protocols. The main task of biomedical studies on surface alterations is to facilitate early osseointegration and to secure longevity of bone-to-implant contact without subsequent bone loss at the interface [24]. Therefore this work was conducted to modify the surface of the dental implant and evaluate the effect of this surface modification on improving its corrosion resistance.

In the current study; CP-Ti foil was used as it is considered as good biomedical *material*. Precision and longevity of these implants are guaranteed by the combined effect of high fatigue strength, good corrosion resistance, biocompatibility and free of toxic elements compared with other older materials [25]. Anodization process was selected as it is the most easy and inexpensive reliable method to fabricate (nano-micro) porous oxide layer without adding any foreign materials to the samples [26]. Moreover, TiO_2-SiO_2 bioceramic coating fabrication was selected in this study as a surface modification of the CP-Ti dental implant because it has synergestic action on biocompatibility and corrosion resistance, ideal combination of potential bioactivity on the surface with desirable mechanical properties and osteoblastic cell adhesion.

A mixture of ($HF+HNO_3+H_2O$) was used as an etching solution in the present study. The use of HF as etching solution might allow the formation of soluble TiF_4 species due to high reactivity of Ti to fluorine incorporated fluorides that are favorable to osseointegration of dental implants. NHO_3 make the etching solution more stable, allows the elimination of H_2 gas and accelerates the etching rate [27]. Cleaning after etching and before starting the electrochemical anodization process is essential because of the high chemical reactivity of titanium which can lead to its contamination or embrittleness, and can increase its susceptibility to stress corrosion [10].

Potasium silicate was used (as a silica source) as an electrolyte in the anodization process as it is known that the aqueous *silicate* solutions support precipitating and forming mixed silica nanoparticles. In addition, silica coating nanoparticles solve the problem of peri-implantitis as it has antibacterial effect and in turn it improves the osteointegration and bone formation. Furthermore, it was claimed that silica coating improves the corrosion resistance of the anodized Ti surface [28]. Oxygen crystallization of the anodized coated samples was done in the furnace to be sure that all the newly formed phases were of crystalline structure. Furnace or air cooling is preferred as oil or water quenching can promote non-uniform cooling, which can induce residual stresses [29].

Characterization of the ceramic coating was done using the samples without being grinded as only the formed phases on the surface of the samples were to be detected using (XRD). In the present study, (figures 1, 2) the presence of sharp and strong intense peaks of TiO_2 with tetragonal crystal structure, in addition to a weak and not well defined peak corresponds to silica in the form of rhombohedral crystals in all the anodized coated groups. This may be attributed to two reasons; the supper imposition of the titania peak over that of the silica peak and due to the small amount of the silica incorporated in the coat compared to that of titania.

Regarding Surface roughness; the surface roughness linearly decreased up to the optimum conditions (V=50, C=3%, D=60) then, increased again owing to the fact that the higher voltage afforded a higher chance for the ions which needed for anodic growth and it was possible to increase the presence of SiO_2 into the oxide coating hence, decreases the surface roughness. Moreover, increased presence and inward diffusion of the oxygen ions (O^{2-}) towards the Ti/oxide interface in the bath increased that interacted with the Ti^{4+} ions that are travelled out of the Ti surface. So, the oxide layer covered the whole surface of the sample. Furthermore, increased addition of SiO_2 into the oxide film leads to the stabilization of the coating. The fabrication rate of the coat is in direct relation with the thickness of the oxide layer produced per time. Therefore, when the process duration is increased, the interaction between the titanium electrode and oxide ions was taking place for a longer duration, which might increase the thickness of the anodized coating. This finding was supported by the results of the SEM that showed enlargement of the crystals to form islands making the surface more smooth (figure 7-c) [30, 31]. However, increasing the anodization parameter variables led to increase in surface roughness. This may be caused by the amount of heat liberated that couldn't be completely and effectively dissipated from the anodic titanium surface (although with the presence of the electrolytic cell in a water bath of controlled temperature) which as a consequence, increased the dissociation thereby strongly leading to the breakdown of the oxide coat. Also, with higher applied voltage, dissolution of the ions increased leading to production of more quantities of potassium ions to form potassium hydroxide, which in turn synergize the pH of the electrolyte which results in the dissolution of the coating (table 2, figure 6).

Regarding surface morphology; at the optimum conditions (V=50, C=3%, D=60), a smooth and uniform distributed oxide coat with normal

arrangement of dome like structure was formed. This may be due to the addition of SiO_2 which decreased the structural defects of the coating. With higher electrolyte concentration (C=4%) some micro cracks appeared on the formed film which might be the result of internal stress developing in the oxide film on the Ti surface due to the micro cracks developed and the volume expansion. However, the incorporation of SiO_2 into the oxide film is high at this condition due to the diffusion through the cracks and the porosity. The results of the SEM of this study were in accordance with that of another study which claimed that the cracks in the coatings might be caused by the production of O_2 bubbles during anodization [31] (figure 7).

Regarding Corrosion results;Tafel polarization results showed that the best corrosion resistance and the lowest corrosion rate was gained at the anodization parameters (V=50, C=3%, D=60). This may be due to the good quality of the formed coating obtained at the optimized conditions. As the imperfections are very little in the formed coat at optimum condition, the corrosive media can't diffuse through the formed coat easily. Therefore, the results proved that the corrosion resistance of the coat was depending on its morphology and the properties of the oxide film (table 3). Moreover, the electrochemical impedance results showed that the formed oxide layer on the samples' surface had a double effect on the corrosion process of Ti; it decreased the rate of charge transfer process and decreased the penetration across the surface layer [32]. This may be attributed to the fact that the presence of SiO_2 along with TiO_2 which formed a protective shield thus decreased the deterioration of the coating compounds owing to its impeding property. These results were in accordance with the work that done in a previous study which studied the effect of the similar parameters and concluded that the corrosion resistance was increased linearly as the parameters increased [33] (table 4).

CONCLUSIONS

Within the limitations of the current study the following could be concluded:

1. Anodic oxidation is an effective method for preparing bioactive titanium metal as an implant material.
2. The surface roughness could be tailor made by changing the parameters of the anodization process.
3. Applied voltage, electrolyte concentrations and process duration, clearly influenced the morphological and topographical features, as well as the chemical composition of the anodized coated layer.
4. The optimum conditions of the anodization process to get a uniform, dense and compact anodized coating can be achieved when; the applied voltage is 50v, the electrolyte concentration is 3% and the process duration in 60min.
5. Formation of a bioceramic coating has been shown to be a useful method for improving the corrosion resistance.

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