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ASTM F67 TITANIUM ANODIZING TO IMPROVE OSSEOINTEGRATION FOR DENTAL IMPLANTS

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Abstract. *Titanium alloys are widely applied in medicine and dentistry due to their biocompatibility, which favors dental or surgical implants fixation in bone tissues. These implants are usually manufactured by machining and undergo surface processing to generate an adequate texture on the surface of the piece. This textured surface is necessary to promote cell adhesion on the surface of the implants and improve the bioquality of the implant. The present work aims to investigate the effect of the anodizing treatment on the surface of ASTM F67 titanium grade 4 samples, promoting the formation of preferential corrosion pits for osseointegration improvement. An aqueous electrolyte composed by 10% oxalic acid was adopted in the electrochemical experiments, where direct and alternate current were applied from 20 to 100 volts during 10s, 1min or 5min at room temperature. The surfaces of the samples were observed and their roughness parameters were determined using a digital roughness meter. The results indicated variation in both color and the formation of microcavities in the surface with increasing electric potential, more evident in direct current treatments. Interaction between electric potential and anodizing time was considered quite complex and significant to surface texture of the samples. In the performed tests carried out, average roughness (Ra) 0.5 – 2.2 μm, very promising results to improving the process of adhesion of the biomaterial to the human bone.*

Keywords: *ASTM F67 titanium, anodizing, surface roughness, osseointegration.*

1. INTRODUCTION

Over time, studies have been carried out to analyze different types of modified topographies of the surface of dental implants manufactured in titanium grade 4 ASTM F67. These modifications have had an effect over decades, where the appropriate change in surface roughness can provide better results in terms of anchorage strength and mechanical locking in the early stages of osseointegration of dental implants (Wennerberg e Albrektsson, 2000).

Mechanical methods are typically imprecise and difficult to control and can also introduce contaminant particles to the implant surface (Kim et at., 2013).

There are several ways to modify the surface of implants and one of the ways found in the literature is through the anodizing process. The colors obtained in the anodizing process originate from the constructive interference of light reflected on the air/external oxide interfaces and on the internal oxide/metal interfaces (Wyszecki e Styles, 1982) e (Massau, 1983). There is a great frequency of use of anodizing on titanium due to the process collaborating with the improvement of biocompatibility and resistance to corrosion. (Yan et at., 2002) studied the effect of anodizing voltage on the chromatics (aesthetic appearance) of titanium. As a result, processes using direct current (DC) have been applied with the aim of producing surface layers of oxide with thicknesses that depend on the applied potential and the duration of the anodizing process (Izmir e Ercan, 2019), (Wadhwani et at., 2018) e (Manjaiah e Laubscher, 2017). Long-term anodizing tests can dramatically change the morphology and roughness of the anodic film on titanium-based substrates. An increase in anodizing voltage leads to increased layer thickness, increased roughness and changes in the phase composition of the surface. An increase in oxide layer thickness coincides with an increase in surface roughness (Manjaiah e Laubscher, 2017).

The main objective of this article is to analyze the changes that occurred on the surface of titanium grade 4 ASTM F67 samples after the anodizing process with the application of different values of continuous and alternating electrical current up to 5 minutes, observing the effects on surface roughness of the samples.

2. MATERIALS AND METHODS

2.1 Samples for anodizing

Samples for anodizing were prepared from scraps of grade 4 ASTM F67 titanium bars, with a nominal diameter of 4.76mm and whose chemical composition is shown in Table 1. From these bars, 30 pieces were machined for anodizing measuring 50mm in length with 4.00mm in diameter.

Table 1: ASTM F67 grade 4 chemical composition (% weight)

C – 0,0100%	Ti – 99,4671%	H – 0,0029%
N – 0,0100%	Fe – 0,1700%	O – 0,3400%

2.2 Anodizing of ASTM F67 G4 Titanium Samples and Roughness Analysis

For the electrochemical treatment, the samples were cleaned with a biodegradable degreasing solution, based on D'Limonene at 10% (v/v) with deionized water, at 60ºC for 30 minutes in ultrasound. After that, the samples passed through a solution of HNO_3 at 30% (v/v) diluted with deionized water at 60ºC in ultrasound to remove small burrs contained in the material, followed by rinsing and drying for 1 hour. For the anodization of the samples, an aqueous solution of oxalic acid (P.A. – A.C.S. Synth) at 10% (v/v) diluted in deionized water was prepared using a magnetic stirrer.

A rectifier source (WG V) was used to supply direct electric current (DC) and to produce alternating current (AC) a variable autotransformer (JNG TDGC2 – 0.5KVA) was used. Digital multimeters (HIKARI HM – 1001) were used to measure voltage and current during treatment. Figure 1 shows the assembled experimental setup. Anodizing was carried out in an acrylic electrochemical cell, in which the samples were partially immersed in the electrolyte and continuous and alternating voltage was applied with nominal values of 20, 40, 60, 80 and 100 volts DC or AC for different times (10s, 1min and 5min). After the treatments, the samples were photographed with a digital camera with a resolution of 12 megapixels to observe the colors obtained from the oxide films on the titanium surface.

For the roughness test, a Mitutoyo Roughness Meter model SJ-210 was used, where 45 specimens were analyzed with 3 measurements for each sample, analyzing the average roughness (Ra) comparing the roughness variation between them. comparing the roughness variation between them. A cut-off of 4mm was defined on the roughness meter as standard for these tests. The results of this test were statistically analyzed by 2-way ANOVA, comparing the roughness variations between the samples.

3. RESULTS AND DISCUSSION

3.1 Coloring of Titanium Oxide Films

The samples, when subjected to the application of direct and alternating current, caused changes in the appearance of the surface of the samples. The observation of the anodized surfaces showed the formation of films with different colors in samples of commercially pure titanium ASTM F67 G4, resulting from the application of different direct and alternating current voltages. Figures 2, 3 and 4 illustrate the typical aspect of the surfaces obtained with anodizing after 10 seconds, 1 minute and 5 minutes respectively.

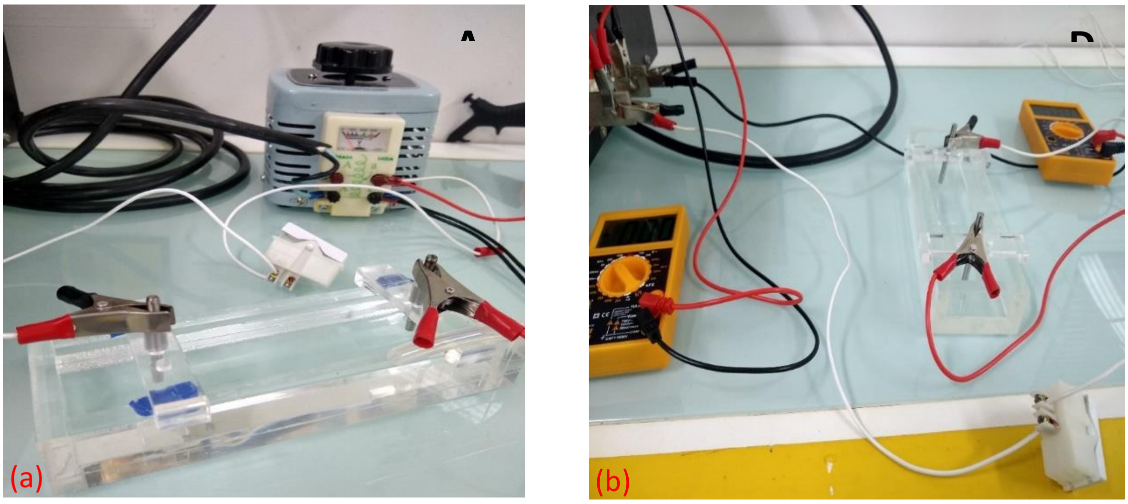

Figure 1: Samples assembled in the electrochemical tank used in the tests, where an autotransformer was used to adjust the alternating voltage in (a) and a rectifier source used to adjust the direct current voltages can be seen in (b).

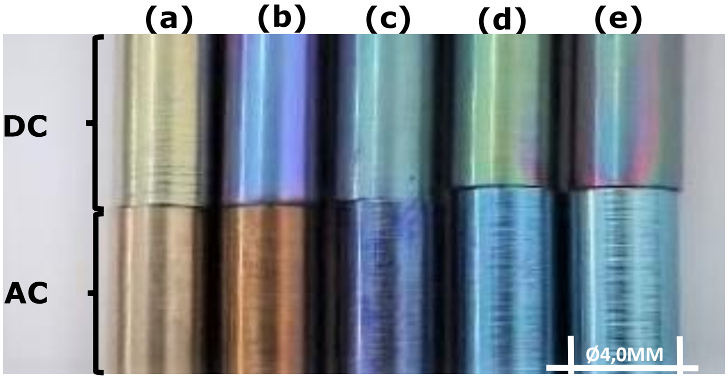

Figure 2 – Typical sample's surface after anodizing with continuous or alternating voltage for 10 seconds. (a) 20V, (b) 40V, (c) 60V, (d) 80V and (e) 100V.

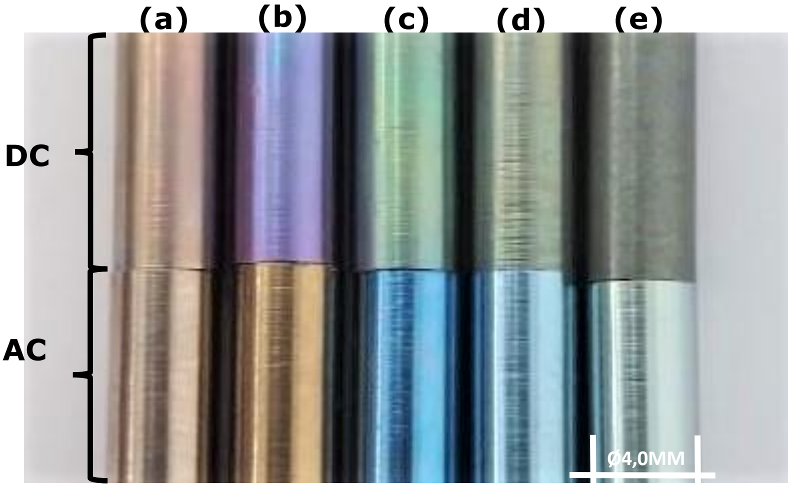

Figure 3: Typical sample's surface after anodizing with continuous or alternating voltage for 1 minute. (a) 20V, (b) 40V, (c) 60V, (d) 80V and (e) 100V.

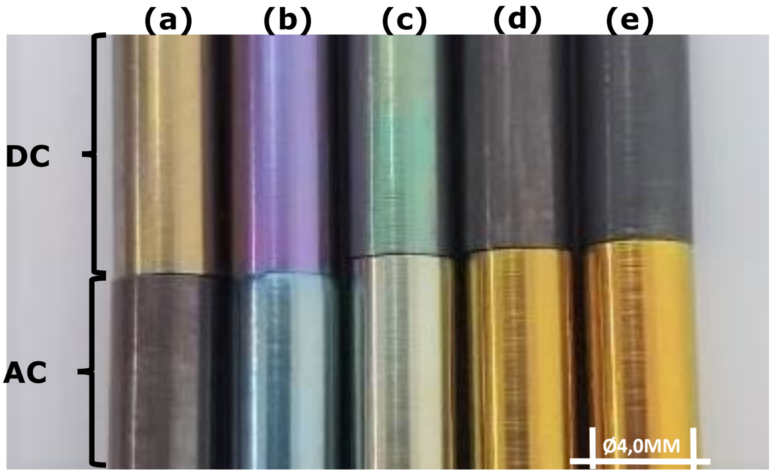

Figure 4: Typical sample's surface after anodizing with continuous or alternating voltage for 5 minutes. (a) 20V, (b) 40V, (c) 60V, (d) 80V and (e) 100V.

Observing the samples, it was noted that the surface color changes with the treatment time and with the type of voltage applied during anodizing. For example, anodizing at 80 volts for 10 seconds produced a greenish surface on direct current and a bluish surface on alternating current. In the case of anodization in the time of 5 minutes, at 100 volts in direct current the surface presented a dark gray color and in alternating current the surface color presented a golden coloration. This coloration is associated with the formation of an oxidized layer on the titanium pieces, which refracts light at different wavelengths depending on the thickness of the layer (Delplancke et al., 1982). The formation of the oxide layer is influenced by the composition of the electrolyte and by the electrolytic parameters, as (Manjaiah and Laubscher, 2017) observed different colors in pieces of pure titanium anodized in direct current voltages and also mentions that the colors produced are not pigments or dyes. Interference colors are produced by a thin and transparent layer on a reflective surface and that this layer has the ability to reflect, refract and transmit light, causing the white light that falls on the layer to be partially reflected and partially transmitted.

3.2 Roughness of Samples

Table 2 presents the average roughness Ra measurements obtained after the anodizing treatments with direct current application. Statistical analysis (ANOVA) showed that there are no significant differences in the roughness used in each test. Such behavior may be associated with changes in electrical contact with the direct current source and/or variations in the level/quantity of electrolyte used in each test.

The lowest average roughness (0.277µm) was observed when titanium was anodized at 40 volts for 10 seconds, while the highest average roughness (1.241µm) was produced with 100 volts after 5 minutes. Performing the variance analysis considering Factors A and B (voltage and time), it was possible to determine the effect of variables on anodizing, the result of which is shown in Table 3.

Table 2: Ra average roughness measurements after anodizing using DC voltage.

Tension V	Time [Min]	Ra [µm]			Statistical Analysis	
		CP			Average	$IC_{[0,05]}$
		1	2	3		
20	0,10	1,049	0,993	1,036	1,026	0,033
	1	0,522	0,534	0,470	0,509	0,038
	5	0,553	0,823	0,696	0,691	0,153
40	0,10	0,302	0,255	0,275	0,277	0,027
	1	0,617	0,570	0,648	0,612	0,044
	5	0,476	0,481	0,485	0,481	0,005
60	0,10	0,781	0,567	0,601	0,650	0,13
	1	0,696	0,673	0,654	0,674	0,024
	5	0,880	0,869	0,826	0,858	0,032
80	0,10	0,687	0,640	0,711	0,679	0,041
	1	1,146	1,095	1,047	1,096	0,056
	5	0,568	0,605	0,637	0,603	0,039
100	0,10	0,877	0,650	0,858	0,795	0,143
	1	0,708	0,507	0,579	0,598	0,115
	5	1,213	1,443	1,068	1,241	0,214

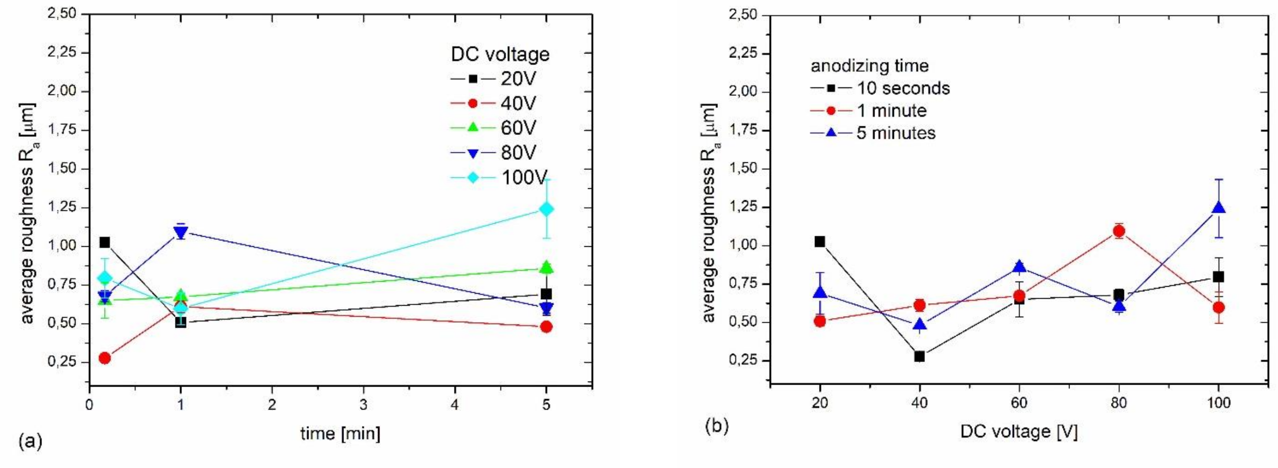

Figure 5: Variation of average roughness Ra with stress (a) and time (b) applied in the DC anodizing of titanium samples.

Table 3: Significance of roughness variation after DC anodizing - ANOVA (2 FACTORS).

	DF	Sum of Square	Mean Square	F Value	P Value
Factor A	2	0.07046	0.03523	5,0912 (2,30)	0.01248
Factor B	4	0.9022	0.2255	32.5934 (4,30)	1.586e-10
Interaction AB	8	1.665	0.2081	30.0767 (8,30)	2.756e-12
Error	30	0.2076	0.00692	--	--
Total	**44**	**28.453**	**0.06467**	--	--

Table 4 shows the average roughness Ra measurements obtained after anodizing treatments with the application of alternating current, whose correlation with voltage and time is shown in Figure 6. Applying statistical analysis (ANOVA) where it showed that there are significant differences in roughness between the 2 electrodes used in each test. Such behavior may be associated with changes in electrical contact with the alternating current source and/or variations in the level/quantity of electrolyte used in each test.

The lowest average roughness (0.574µm) was observed when titanium was anodized at 40 volts for 5 minutes, while the highest average roughness (2.224µm) was produced with 100 volts after 10 seconds. These values are in line with the typical roughness of dental implants. (Le Guéhennec et al., 2007) point out that the ideal surface of the dental implant should be covered with hemispherical cavities with a depth of up to 1.5µm. Performing the analysis of variance considering 2 factors (voltage and time) made it possible to determine the effect of the variables on anodizing, the result of which is shown in Table 3. It is verified that voltage (FactorA) and time (FactorB) present significant variations with α=5%, as well as the interaction between these factors. The contribution of each factor was estimated at 20.1% for voltage, 11.6% for time and 32.9% for voltage-time interaction, showing that the electrochemical treatment presents a very complex behavior. The comparison between the average voltages, made by Tukey's test, confirmed equality between the effects of applied alternating voltages except at 100 volts, suggesting that changes in roughness caused by the use of smaller voltages are negligible at a significance level of 5%. The roughness obtained after 10 seconds is significantly different from those obtained in longer times, but there is no difference comparing the results after 1 minute and 5 minutes.

Table 4: Ra average roughness measurements after anodizing at different voltages and times in alternating current.

Tension [V]	Time [min]	Ra [µm]						Statistical Analysis	
		CP01			CP02			Average	$IC_{[0,05]}$
		1	2	3	1	2	3		
20	0,10	0,639	0,739	0,673	0,688	0,623	0,579	0,657	0,023
	1	0,682	0,552	0,624	0,736	0,774	0,697	0,678	0,064
	5	0,768	0,853	0,879	1,373	1,180	1,203	1,043	0,193
40	0,10	0,863	1,090	1,078	0,728	0,675	0,597	0,839	0,167
	1	1,117	1,220	1,203	0,532	0,553	0,566	0,865	0,278
	5	0,521	0,376	0,339	0,770	0,613	0,824	0,574	0,16
60	0,10	0,830	0,788	0,765	0,583	0,889	0,730	0,764	0,084
	1	0,726	0,558	0,567	0,699	0,666	0,564	0,630	0,061
	5	0,869	0,724	0,668	0,584	0,664	0,637	0,691	0,079
80	0,10	0,938	0,845	0,745	1,196	0,983	0,776	0,914	0,133
	1	0,574	0,595	0,550	0,684	0,634	0,604	0,607	0,038
	5	0,580	0,663	0,583	0,793	0,590	0,584	0,632	0,068
100	0,10	2,896	3,535	3,039	1,207	1,291	1,373	2,224	0,836
	1	0,714	0,743	0,652	0,840	0,686	0,941	0,763	0,087
	5	1,162	0,920	1,029	0,598	0,592	0,756	0,843	0,187

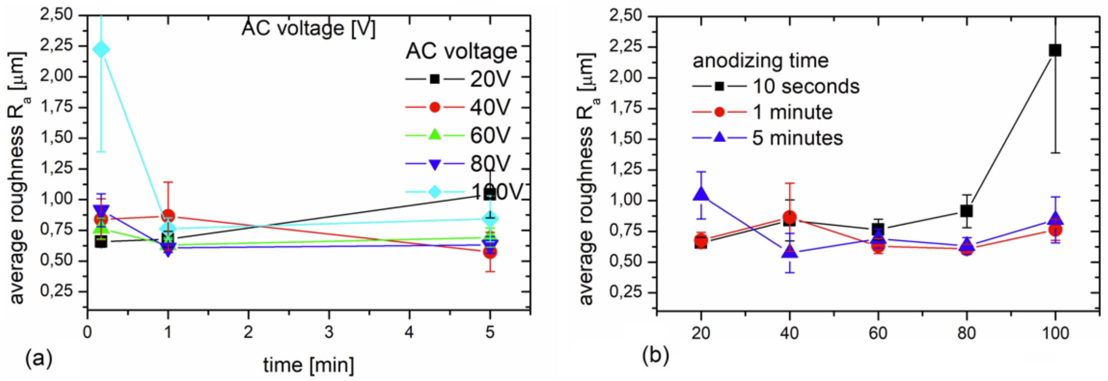

Figure 6: Variation of average roughness Ra with voltage (a) and time (b) applied in the AC anodizing of titanium samples.

Table 5: Significance of roughness variation after AC anodizing - ANOVA (2 FACTORS).

	DF	Sum of Square	Mean Square	F Value	P Value
Factor A	2	2.4414	1.2207	12.2565 (2,75)	0.00002479
Factor B	4	4.2273	1.0568	10,6111 (4,75)	7,229e-7
Interaction AB	8	6.9311	0.8664	8.6989 (8,75)	2.541e-8
Error	75	7.4698	0.0996	--	--
Total	**89**	**21.0697**	**0.2367**	--	--

3.2 Roughness Comparison between Direct Current and Alternating Current

Analyzing the mean roughness values in tables 2 and 4, it was possible to statistically analyze (ANOVA) a greater and lesser variation in roughness between the demonstration in continuous and alternating voltages (DC/AC) as shown in figure 7. It was observed in the sample 100 volts for 0.10 seconds as application of alternating current a greater variation between voltages (0.7308µm). A smaller roughness variation was observed in the exception of 80 volts for 5 minutes (0.0004µm). (Schreckenbach et al., 1999) demonstrated several advantages of surface modification by anodizing and control of process parameters including the ability to fabricate porous TiO_2 layers through dielectric breakdown, the ability to alter crystalline structures and chemical composition, and the ability to improve resistance to corrosion.

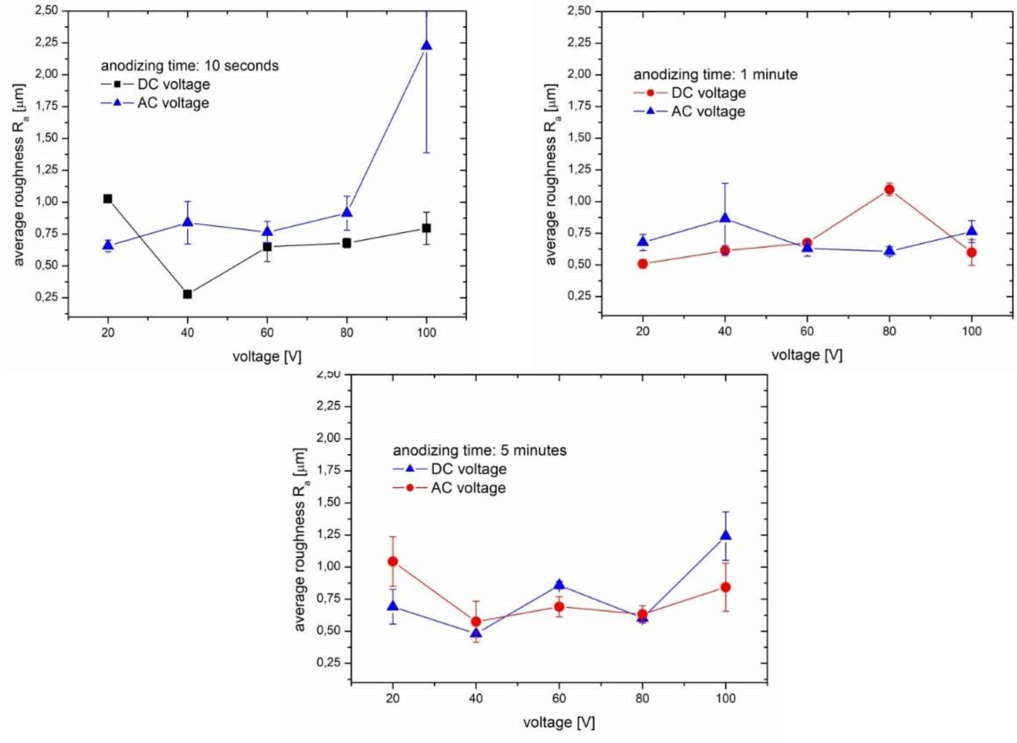

Figure 7: Variation of average roughness Ra between voltages (DC-AC) and time (b) applied in the anodizing of titanium samples.

4. CONCLUSIONS

The experimental results obtained allowed concluding that the use of an electrolyte based on oxalic acid for anodizing in direct or alternating current was effective in promoting surface modifications in titanium sample grade 4 ASTM F67. Variations in tension and duration of treatments led to the formation of oxidized layers with different colors and roughness, not being found a direct relationship between them. The interaction between voltage and anodizing time proved to be complex and statistically significant on roughness, which was found at promising levels to promote osseointegration of titanium as a dental implant.

5. ACKNOWLEDGEMENTS

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