


Communication

Influence of Annealing Temperature on Corrosion Resistance of TiO₂ Nanotubes Grown on Ti–30Ta Alloy

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Abstract: With little success, researchers have been searching for alloys with elements such as tantalum to improve the long-term life of implants. The Ti–30Ta alloy presents an elastic modulus $E = 69$ GPa that is close to that of bone ($E = 17$ – 25 GPa) than Ti cp ($E = 105$ GPa). In addition, nanostructure surface modification influences cell behavior and antimicrobial activity. So, this study investigates the corrosion behavior of surface modification by TiO₂ nanotube grown on Ti–30Ta alloy after anodization process in the electrolyte glycerol + NH₄F 0.25% at 30 V, for nine hours without annealing and annealed in 450 °C, 530 °C and 600 °C (5 °C/min). The electrochemical behavior was evaluated by three electrodes cell. The counter-electrode of graphite, reference-electrode of saturated calomel electrode and working-electrode at electrolyte of 0.15 M NaCl + 0.03 M NaF, with pH = 6 for 8000 s. The scanned region ranged from -0.8 V to values up to 3.5 V with a sweep rate 0.166 mV/s. Potentiodynamic polarization curves were obtained with a potentiostat. The sample was characterized by scanning electron microscopy (SEM) imaging, X-ray diffraction analysis (XRD) and wettability with a contact angle goniometer. We conclude from the obtained results that all treatment surfaces are hydrophilic ($<90^\circ$). The surface covered with TiO₂ nanotube crystallinity showed anatase phase after annealing at 450 °C, 530 °C and 600 °C; the exceptions were the anodized-without-annealing treatment and without-surface-modification alloys. The electrochemical behavior of the five groups investigated showed similar high resistance to corrosion solution under all conditions.

Keywords: Ti–30Ta alloy; TiO₂ nanotube; corrosion resistance; annealing temperature

1. Introduction

Among metallic biomaterials, titanium are the most popular as structural materials in the biomedical field due to their excellent mechanical and chemical properties, their good corrosion resistance and biocompatibility. The field of the application is wide, including hip joints, bone plates,

screws, dental implants, stents and applications which are mainly used in implants that replace hard tissue [1–4].

However, researchers have been searching for alloys composed by elements such tantalum to improve the long-term life of the implant. Other improvements may apply in medical field by modifying Ti alloys such as weight reduction, corrosion resistance and good fracture resistance. The addition of 30% of tantalum changes the elastic modulus to $E = 69$ GPa, being nearer to the bone ($E = 17$ – 25 GPa) than Ti commercially pure ($E = 105$ GPa) [5–10]. The elastic modulus is an important featuring for any hard implant. Once implanted in the body, different elastic modulus between metallic implant and the material adjacent bone leads to stress shielding phenomenon, causing lesions to the tissue. The studied alloy features $E = 69$ GPa. Being its elastic modulus nearer to the bone by comparing Ti cp. It is the main reason to development alloys with elastic modulus lower than 100 GPa [5–10].

Materials with an elastic modulus lower than 100 GPa are still presenting failures on long-term clinical application by bio-inert surface that cannot bind directly to living bone at the early stage after implantation into human body. Hence, in order to improve cellular response, the studies have modified the surface on nanoscale topography [11–15].

Our previous studies have investigated the nanostructure influence on cell behavior and antimicrobial activity on Ti–30Ta alloy. The biologic properties of Ti–30Ta alloy can be selectively improved by using simple anodization process associated with surface annealing process [7,9,16–19].

Corrosion stands for deterioration of the metals due to their reaction with surrounding corrosive elements. Corrosion damages can drive to metallic implant failure causing not just perjury in terms of economic, but also pain, productive work decrease and social effects [20–25]. Zhou investigated Ti–30Ta alloy surfaces and conclude that the alloy presents better corrosion behavior than Ti cp in the same test solution [6]. However, there is still a gap on corrosion research of the Ti–Ta alloys surface modification. It is essential the acknowledgment of how annealing temperature influences on corrosion behavior for biomedical application.

Hence, this study investigates the corrosion behavior of TiO₂ nanotubes grown on Ti–30Ta alloy after anodization process in an electrolyte contained glycerol + NH₄F 0.25% at 30 V, for 9 h without annealing and annealed in three different temperatures: 450 °C, 530 °C and 600 °C with a ramping rate of 5 °C/min.

2. Materials and Methods

2.1. Alloy Processing

The Ti–30Ta alloy was obtained from a titanium (Ti) and tantalum (Ta) pure metals in a high purity argon atmosphere. The ingot was homogenized in a vacuum at 1000 °C for 24 h. Then, the alloy was cold-worked by a rotary swaging process and solubilized at 950 °C for 2 h followed by water-cooling. The bars were cut into discs of 10 mm in diameter and 3 mm in thickness [10,26].

2.2. Nanotubes Growth

The nanotubes of TiO₂ were obtained on the Ti substrate by anodization process in an electrolyte contained glycerol and NH₄F 0.25% using a dual electrode system with platinum (counter electrode) and Ti–30Ta alloy (working electrode) fixed a 15 mm of distance. Then, applied 30 V at room temperature. The as-grown TiO₂ nanotubes were then annealed in a furnace at different temperatures: 450 °C, 530 °C and 600 °C with a ramping rate of 5 °C/min, for 9 h [18,27].

Hence, the samples were divided into 5 groups: 1—Ti–30Ta alloy without surface modification, 2—anodized without (w/o) annealing-nanotubes of TiO₂ without annealing, 3—450 °C-nanotubes of TiO₂ annealed at 450 °C, 4—530 °C-nanotubes of TiO₂ annealed at 530 °C annealed and 5—600 °C-nanotubes of TiO₂ annealed at 600 °C.

2.3. Electrochemical Behavior

The electrochemical behavior of five groups: 1—Ti–30Ta alloy without surface modification, 2—anodized without (w/o) annealing-nanotubes of TiO₂ without annealing, 3—450 °C-nanotubes of TiO₂ annealed at 450 °C, 4—530 °C-nanotubes of TiO₂ annealed at 530 °C annealed and 5—600 °C-nanotubes of TiO₂ annealed at 600 °C was evaluated through corrosion resistance tests. The characterization was performed by three electrodes cell. The counter-electrode of graphite, reference-electrode of saturated calomel electrode and worked-electrode, with 1 cm² exposed, samples of the 4 conditions. The electrochemical measures were performed by having as electrolyte a solution of 0.15-M NaCl + 0.03-M NaF, with pH = 6 for 8000 s. The scanned region from −0.8 V until values close 3.5 V with sweep rate 0.166 mV/s. In addition, the potentiodynamic polarization curves were obtained with a potentiostat EG&G PAR 283 (PerkinElmer Instruments Inc., Guaratinguetá, Brazil) [28,29].

2.4. Sample Characterization

The surface topography was characterized by scanning electron microscopy (SEM) imaging (JEOL JSM 6100, Carl Zeiss, Guaratinguetá, Brazil). All substrates were coated with 15 nm layer of gold prior to imaging. The crystallinity of the samples was investigated by X-ray diffraction analysis (XRD), using X' Pert Philips PMD (Philips, São Carlos, Brazil) with Panalytical X'Celerator detector (using a CuK α radiation, λ = 1.5418 Å, Philips, São Carlos, Brazil). The wettability of the substrate surfaces was investigated using sessile drop method (2 mL) with a contact angle goniometer (Kruss DSA 10, Kruss, Guaratinguetá, Brazil), equipped with video capture. The resulting images at the water–substrate interface were fit by the circle fitting profile.

3. Results and Discussion

Mechanical properties and surface are important criteria to choosing biomaterial for metal implants. Ti–30Ta alloy shows elastic modulus nearer to bone (E = 69 GPa) when comparing to Ti Cp (E = 105 GPa). The not commercial Ti–30Ta alloy smooth surface corrosion behavior was investigated and presented high corrosion resistance [6]. This work presents five condition named 5 Groups: 1—Ti–30Ta alloy without surface modification, 2—anodized w/o annealing-nanotubes of TiO₂ without annealing, 3—450 °C-nanotubes of TiO₂ annealed at 450 °C, 4—530 °C-nanotubes of TiO₂ annealed at 530 °C annealed and 5—600 °C-nanotubes of TiO₂ annealed at 600 °C. In addition, the chemical surface modification was performed to active an attractive surface to cell. The layers of nanotubes are studied in surface modifications because of their chemical stability and structural properties that mimic the human bone. The morphologies of SEM micrographs of Ti–30Ta alloy surface after anodization process in 0.25% NH₄F + glycerol at 30 V for 9 h and the annealing process was performed at (a) anodized w/o annealing, (b) 450 °C, (c) 530 °C and (d) 600 °C (5 °C/min) for 1 h are shown in Figure 1.

Figure 1a shows the anodized w/o annealing with nanotubes unorganized covered all surface of the alloy of Ti–30Ta after anodization process. The TiO₂ layer presents nanotubes of average diameter about 80 to 100 nm. The effect the annealing temperature on the morphology of TiO₂ nanotubes can be evaluated on Figure 1b–d. When the temperature was increased the diameter of the nanotube decreased. Likewise, the top of the nanotube seems to be covered of oxide at annealing temperature at 450 °C, 530 °C and 600 °C. The software ImageJ was used to determine the diameter h of the TiO₂ nanotubes [30–33].

The crystallinity of the amorphous layer and nanotubular structure was investigated by X-ray diffraction. In Figure 2, the spectra obtained after anodizing in electrolyte glycerol +0.25% NH₄F at 30 V for 9 h. The first spectrum show the Ti–30Ta alloy surface with titanium element. That anodized w/o annealing surface, and annealing at 450 °C, 530 °C and 600 °C showed anatase phase with the highest peaked around 25°. Tsurkan, 2020 found similar results when investigated the crystallinity of nanotubular topography on titanium [34,35]. The anatase phase is a desirable surface due to provides an improvement in the cellular response that is ideal for biomedical applications [20,34,36–38].

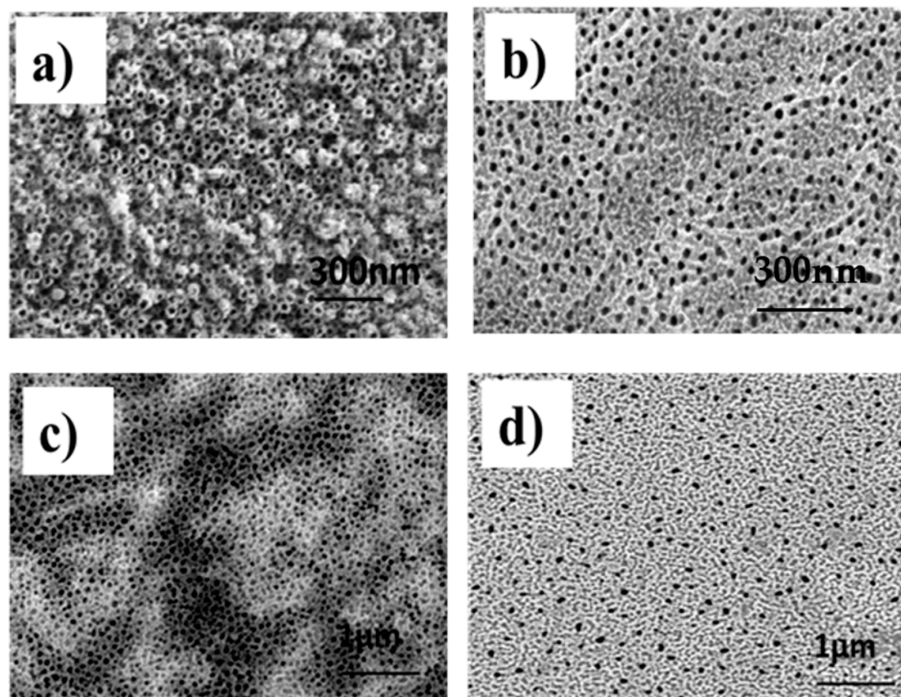


Figure 1. SEM images of Ti-30Ta alloy surface after nanotubes of TiO_2 growth in 0.25% NH_4F + glycerol at 30 V for 9 h. (a) Group 2—anodized w/o annealing, (b) group 3—450 °C-nanotubes of TiO_2 annealed at 450 °C, (c) group 4—530 °C-nanotubes of TiO_2 annealed at 530 °C annealed and (d) group 5—600 °C-nanotubes of TiO_2 annealed at 600 °C.

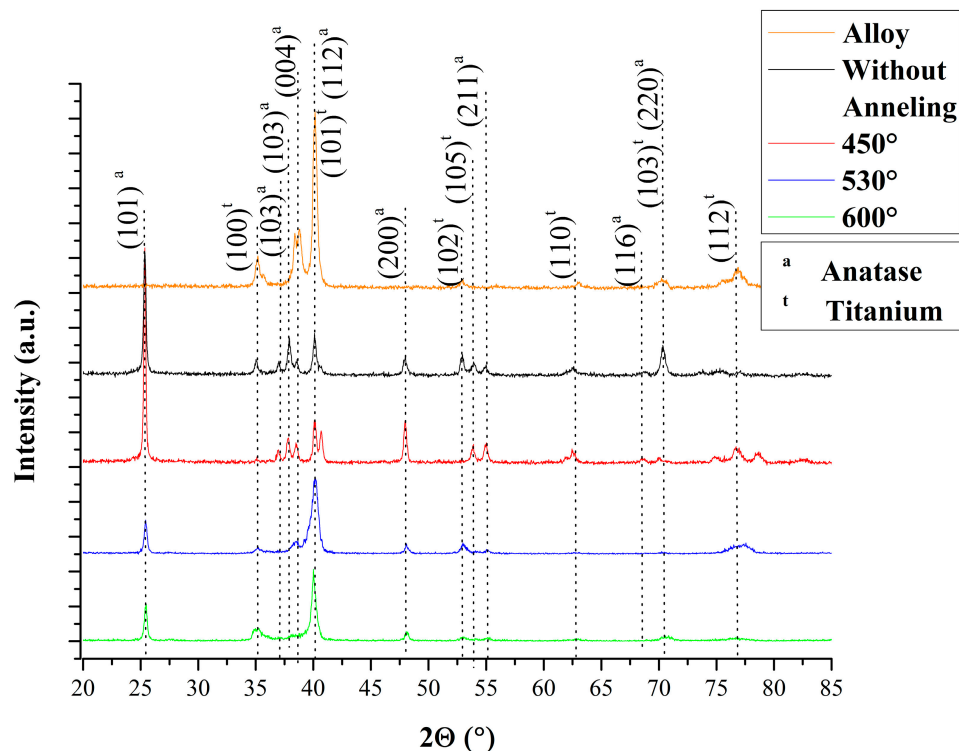


Figure 2. XRD of Ti-30Ta alloy surface before and after nanotubes of TiO_2 growth in 0.25% NH_4F + glycerol at 30 V for 9 h. Group 1—Ti-30Ta alloy without surface modification, Group 2—anodized without annealing, Group 3—450 °C-nanotubes of TiO_2 annealed at 450 °C, Group 4—530 °C-nanotubes of TiO_2 annealed at 530 °C annealed and group 5—600 °C-nanotubes of TiO_2 annealed at 600 °C.

The wettability of the surface is an important parameter to evaluating ideal biomaterial. Metallic biomaterial to biomedical application demands a hydrophilic surface due to cell behavior. The result shows all surfaces hydrophilic ($<90^\circ$), as seen in Figure 3. The nanostructured topography favors the surface to interaction with cells. Previous studies have shown the antimicrobial effect on the TiO₂ nanotubular surface [7,16,30,39].

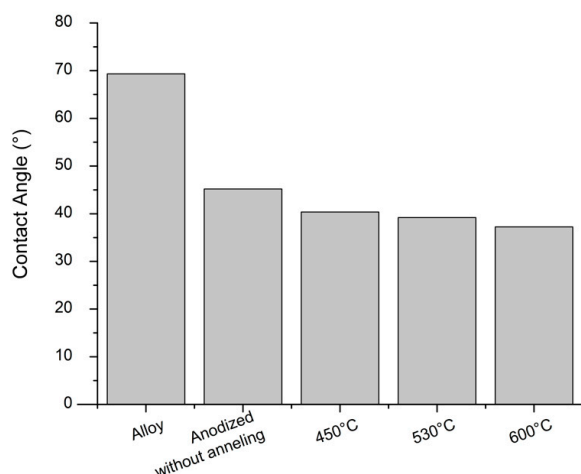


Figure 3. Contact angle of Ti-30Ta alloy before and after nanotubes of TiO₂ growth in 0.25% NH₄ F + glycerol at 30 V for 9 h. Group 1—Ti-30Ta alloy without surface modification, Group 2—anodized without annealing, Group 3—450 °C-nanotubes of TiO₂ annealed at 450 °C, Group 4—530 °C-nanotubes of TiO₂ annealed at 530 °C annealed and group 5—600 °C-nanotubes of TiO₂ annealed at 600 °C.

The electrochemical reactions at the interface of a material depend on the electrode potential. The reactions are verified in the applied potential and the current generated in the electrochemical reactions developed (anodic and cathodic). The scan potential and generated current present the electrochemical behavior of a biomaterial. It generates the polarization. Potentiodynamic polarization is the technique for obtaining polarization curves also provides continuous scanning of the potential. The corrosion potential is called open circuit potential which is established when the material is immersed in the solution [21,25,40,41].

Table 1 exhibit the impedance modulus, corrosion current density and corrosion potential of the Ti-30Ta alloy, amorphous layer, annealed surface at 450 °C, 530 °C and 600 °C. Table 1 shows the values of impedance modulus, corrosion current density and corrosion potential for the studied materials. The lowest value of corrosion potential is obtained for the Ti30 Ta alloy without surface modification. This indicates a higher reactivity of the alloy in the presence of the 0.15 M NaCl + 0.03 M NaF electrolyte. There is an increase in the corrosion potential for TiO₂ nanotubes formed after anodizing and when it is subjected to annealing at 450 °C, 530 °C and 600 °C. This increase in the potential for corrosion is attributed to changes in the nature of the nanotube layer formed, as mentioned earlier in the X-ray diffraction analysis, which indicates the presence of the anatase phase, after heat treatment. The corrosion current density values obtained are very close and vary from 2.76×10^{-8} A/cm² to 5.8×10^{-8} A/cm². The small difference in this parameter does not allow ordering the different materials studied for corrosion resistance, but the extremely low values of current density indicate that they all have high resistance to corrosion. The lower impedance modulus values observed for annealed TiO₂ nanotubes reveal that, in general, this treatment decreases corrosion resistance, which can be attributed to the change in properties such as porosity and conductivity of the TiO₂ nanotube layer.

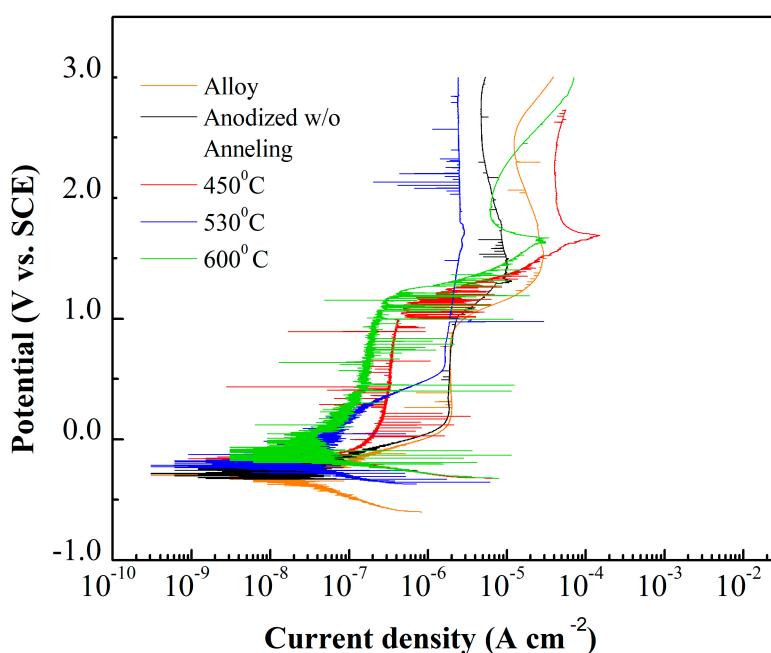
Figure 4 shows the potentiodynamic polarization curves obtained from Ti-Ta alloy before and after anodization process in 0.25% NH₄F + glycerol at 30 V for 9 h. Previous and post annealing process performed at, 450 °C, 530 °C and 600 °C (5 °C/min) for 1 h. The polarization measurement evaluates the stability and intensity for passive oxide film formation. All condition exhibited typical spontaneous passivation characteristics [15,42,43].

Table 1. Impedance modulus, corrosion current density and corrosion potential of the Ti–30Ta alloy, amorphous layer, annealed surface at 450 °C, 530 °C and 600 °C.

Values	Impedance Modulus ($\Omega \text{ cm}^2$)	Corrosion Current Density (A cm^{-2})	Corrosion Potential (V)
Alloy	3.81×10^6	2.84×10^{-8}	−0.299
Anodized w/o Annealing	5.66×10^5	5.80×10^{-8}	−0.288
450 °C	2.98×10^4	3.68×10^{-8}	−0.284
530 °C	3.98×10^5	4.90×10^{-8}	−0.221
600 °C	6.29×10^4	2.76×10^{-8}	−0.122

The open circuit potential (OCP) is the potential of working electrode relative to the reference electrode when no potential or current is being applied to the corrosion system. Therefore, OCP shows the tendency of metallic substrate to be subject in the electrochemical corrosion reactions. The electrolyte was 0.15 M NaCl + 0.03 M NaF, pH = 6, for 8000 s. OCP vs. time increases and reaches a stable value, consequently the investigated surface Ti–30Ta alloy, anodized without annealing, annealed at 450 °C, 530 °C and 600 °C had a noble behavior and it can resist to the electrolyte aggressive action, forming a protective film for the exposure time (Figure 5). The chemical surface analysis on the metallic substrates are useful to validate these conclusions that this material has great potential to biomedical application [23,30,43–45].

Then, in a complimentary analysis electrochemical impedance spectroscopy (EIS) evaluated the effect of annealing temperature on the capacitive response of the oxide film. Figure 6 shows representative Bode plots from 4 samples. All four conditions exhibited capacitive behavior over a wide range of frequencies. In the high frequency range, the spectra showed a flat portion due to the response of the electrolyte resistance. In the lower frequency the spectra revealed a linear slope which is indicative of the capacitive characteristics of a passive film. The impedance response, described by the equivalent circuit (EC) model can be used to describe the capacitive behavior of Ti–30Ta alloys before and after anodization process and also on three different temperature of annealing; 450 °C, 530 °C and 600 °C [24,45,46].

**Figure 4.** Polarization curves in 0.15 M NaCl + 0.03 M NaF solution at 25 °C, and −0.8 V–3.5 V potential range and sweep rate 0.166 mV/s.

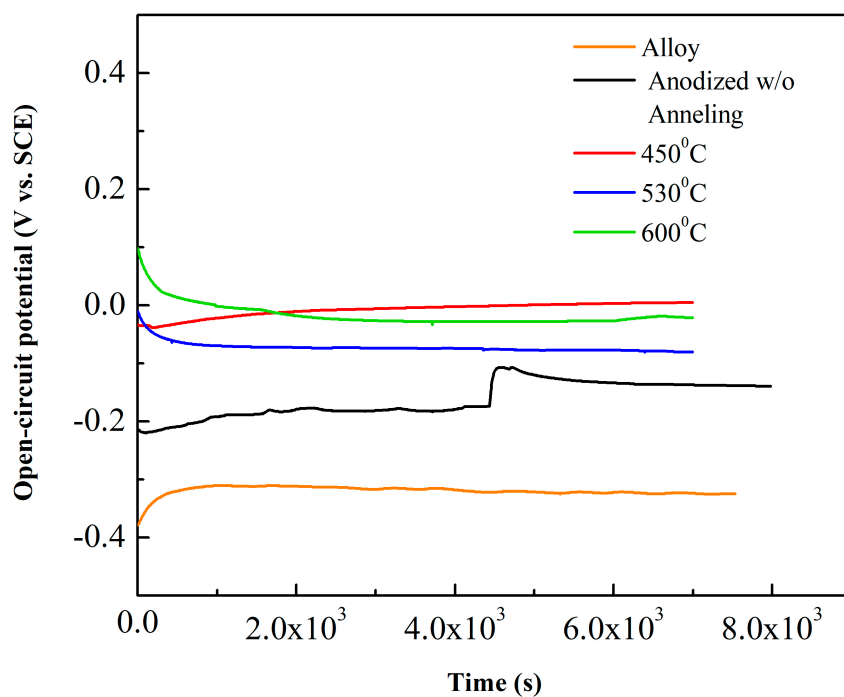


Figure 5. Open circuit potential curves in 0.15 M NaCl + 0.03 M NaF solution at 25 °C.

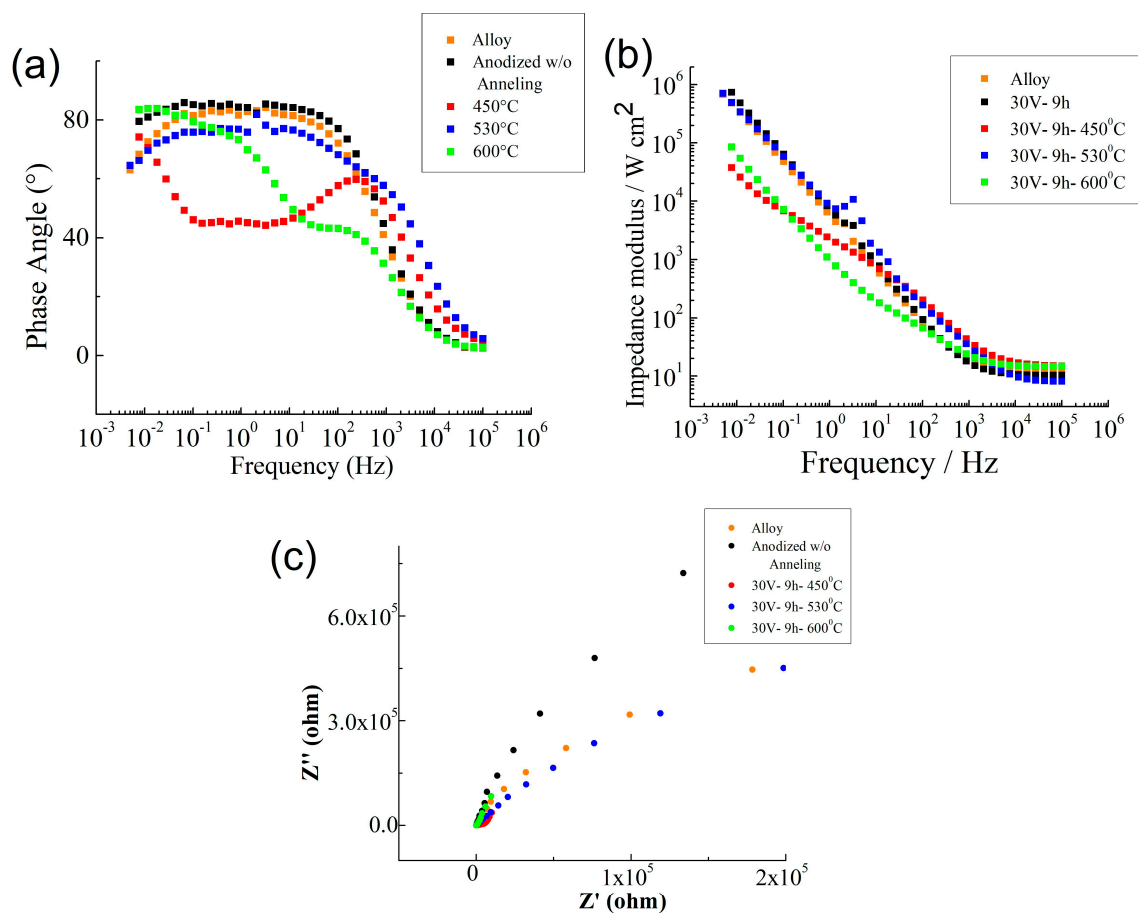


Figure 6. Impedance modulus (a), impedance angle (b) and Nyquist plots (c) in 0.15 M NaCl + 0.03 M NaF solution at 25 °C.

4. Conclusions

Researchers have been searching for alloys with elements like tantalum to improve the long-term life of implant and nanostructure surface modifications to improve cell interactions in the implant and the human body.

Hence, in this study the corrosion behavior of TiO₂ nanotube annealed at 450 °C, 530 °C and 600 °C for one hour was investigated.

The results obtained show TiO₂ nanotube growth on the Ti–30Ta alloy and all surfaces are hydrophilic (<90°). Crystals covered the surface with TiO₂ nanotubes showing anatase phase after annealed 450 °C, 530 °C and 600 °C in opposite of anodized without annealing and alloy without surface modification. The electrochemical behavior of the five groups investigated had good resistance to a corrosive solution of 0.15 M NaCl + 0.03 M NaF for 8000 s. In addition, all five groups presented the same corrosion features.

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Conflicts of Interest: The authors declare no conflict of interest.

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