REVISTAMATÉRIA V.28 N.1
ISSN 1517-7076 articles e20220257, 2023

Comparative assessment of TiN thin films created by plasma deposition technique on the surface features of NiCr alloys for dental applications

Nicole da Costa Cerqueira[1], Naasson Matheus Pereira Balica[1], Wênio Fhará Alencar Borges[2], Gabriel Melo Reis de Sousa[1], Denise Pupim[3], Polyana Alves Radi[4], Rubens Maribondo do Nascimento[5], António Ramos Silva[6], Lucas Filipe Martins da Silva[7], Thércio Henrique de Carvalho Costa[8], Heurison de Sousa e Silva[1], Lívio César Cunha Nunes[1], Rômulo Ribeiro Magalhães de Sousa[1], Rafaela Luiz Pereira Santos[1]

[1]Universidade Federal do Piauí, Centro de Tecnologia, Programa de Pós-Graduação em Ciência e Engenharia dos Materiais. Avenida Universitária, s/n, Ininga, 64049-550, Teresina, PI, Brasil.

[2]Instituto Federal do Maranhão. Rodovia MA-381 KM 0, s/n, Bairro Diogo, 65725-000, Pedreiras, MA, Brasil.

[3]Universidade de São Paulo, Faculdade de Odontologia de Ribeirão Preto. Avenida do Café, Subsetor Oeste,11 (N-11), 14040-904, Ribeirão Preto, SP, Brasil.

[4]Universidade Federal de São Paulo, Programa de Pós-Graduação em Engenharia e Ciência de Materiais. Rua Talim, n° 330, 12231-280, São José dos Campos, SP, Brasil.

[5]Universidade Federal do Rio Grande do Norte, Departamento de Engenharia de Materiais. Campus Universitário, Lagoa Nova, 59078-970, Natal, RN, Brasil.

[6]Universidade do Porto, Faculdade de Engenharia, Instituto de Ciência e Inovação em Engenharia Mecânica e Engenharia Industrial. Rua Dr. Roberto Frias 400, 4200-465, Porto, Portugal.

[7]Universidade do Porto, Faculdade de Engenharia, Departamento de Engenharia Mecânica. Rua Dr. Roberto Frias, s/n, 4200-465, Porto, Portugal.

[8]Universidade Federal do Rio Grande do Norte, Centro de Tecnologia, Departamento de Engenharia Mecânica. Campus Universitário, 59078-970 Lagoa Nova, Natal, RN, Brasil.

e-mail: ncerqueiracosta12@gmail.com, matheusbalica@hotmail.com, wenio.borges@ifma.edu.br, gabrielmelors@outlook.com, denisepupim@gmail.com, polyana.radi@unifesp.br, rubens.maribondo@ufrn.br, ars@fe.up.pt, lucas@fe.up.pt, thercioc@edu.ufrn.br, heurison@ufpi.edu.br, livionunes@ufpi.edu.br, romulorms@gmail.com, rafaelasantos@ufpi.edu.br

ABSTRACT

Introduction: Surface treatment is an important technique to increase adhesion between implants and bones, improving its mechanical characteristics and consequently the patient's comfort. **Objectives:** Ni-Cr alloys were the object of study in this work, with the purpose of analyzing and evaluating the effect of thin films deposition of titanium nitride via plasma, on its surface and comparing with cathodic cage (CC) and hollow cathode (HC) methods, for dental applications. **Methods:** Eighteen samples were prepared and the experiment was conducted in two steps: the pre-sputtering (1h, 350 °C, gases: Ar and H) and sputtering (4h, 450 °C, gases: Ar, Ni, and H). To characterize and compare the samples with those of reference, the Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), Vickers Microhardness and wettability tests were used. **Results:** The results presented by SEM showed that during the surface treatment using CC, voids were formed, and using HC, the samples showed a more homogenous behavior. In microhardness tests, using a 25gf load, it was possible to observe that the HC method allowed an increase of 87% when compared to the reference and treated samples. **Significance:** Lastly, it can be concluded that both methods are suitable for Ni-Cr alloy surface treatment, and the HC technique, a method already used by dental professionals, presents better results due to the formation of a thicker film layer.

Keywords: Ni-Cr alloys; Cathodic cage; Hollow cathode; Oral application.

1. INTRODUCTION

Nowadays, biomaterials have been widely used in medical field. Based on biological properties and the application area, some of the desired characteristics include among others, biocompatibility, cytotoxicity, hemocompatibility, allergenicity, cell proliferation and adhesion stimulation, and osseointegration [1–3]. Besides, it is also relevant to consider its physical properties, such as surface energy, surface morphology, roughness, porosity, and permeability [4–6], and its mechanical properties like hardness, ductility, high resistance to corrosion, fracture

Corresponding Author: Naasson Matheus Pereira Balica Received on 09/10/2022 Accepted on 24/01/2023

DOI: https://doi.org/10.1590/1517-7076-RMAT-2022-0257

resistance, toughness [7–10], as well as the chemical properties, like composition, stability, density, and the mechanism of degradation in the organism [11, 12].

These biological, physical, mechanical and chemical properties are essential in such kind of materials in order to increase, replace or support organs, tissues and, body parts. To make one diseased part functional, a combination of aspects in medicine, biology, chemistry, and materials science and engineering [13] results in biomaterials that can be used, e.g., in dental procedures, as a coating material on tooth implant devices [14].

Metallic materials are the most used as biomaterials due to its properties, since when compared to ceramic and polymeric materials, they offer the greatest tensile strength, fatigue strength, and highest toughness [15]. Additionally, metallic biomaterials are applied in several body parts as implants replacing shoulders, knees, hips, and elbows, as well as in structures used by orthodontics [16]. In this specific case, when it comes to oral environments, dental implants are susceptible to microbial contamination, causing the formation of a biofilm that facilitates the occurrence of infections [17]; and, there are changes in the potential of Hydrogen (pH) of saliva due to food intake and can vary between acidic, basic and neutral [18]. To overcome these problems, the most used metals are the cobalt-chromium (Co-Cr) and nickel-chromium (Ni-Cr) alloys, pure commercial titanium (CP-Ti), and titanium-based alloys, such as Ti6Al-4V, Ti-Nb-Zr and Ti-Nb-Ta-Mo [19], due its excellent resistance to corrosion, good mechanical resistance, besides not causing any damages, such as liberation of cytotoxic elements [20].

Introduced for the first time in dental prosthesis laboratories in the 1980s, Ni-Cr alloys were used as replacement materials to the precious alloys – since gold was the material generally used, because they have a greater elastic module and lower cost [21]. This material has Ni (70 to 90%wt.) and Cr (13 to 20%wt.), achieving stability through the addition of other elements, such as iron, aluminum, molybdenum, beryllium, silicon, and copper.

However, such alloys have an allergic factor to be considered, which can cause inflammation and the need to remove the prosthesis. Approximately, 10 to 15% of humans suffer from hypersensitivity due to metals contact [22]. Besides, when exposed to pH changes in saliva, they become subject to corrosion, with higher corrosion/ion release rates when exposed to acidic pHs [23]. The resistance to corrosion decreases as the pH decreases, and in the most acidic saliva, corrosion rates are higher due to the higher nickel dissolution rate [24], causing a greater manifestation of its allergenic properties.

Using techniques to modify or treat biomaterials surfaces favor the improvement of biocompatibility, osseointegration, by accelerating the healing process and cell adhesion and decreasing the probability of allergic reactions due to the contact with living skin or ions release (improvement of corrosion resistance) [25]. Among the main modification techniques, the following stand out: deposition of bioactive molecules, deposition of organic, metallic or oxide thin films [26].

Between these deposition processes, the one that uses titanium nitrite (Ti-N) stands out as an excellent choice for coating substrates within dentistry once it's a ceramic material with a high melting point [27], favoring its use to increase thermal, tribological, mechanic, and anticorrosive properties of the coated substrate, including specially, the improvement of biocompatibility. Regarding the plasma deposition process using TiN in the form of thin films, the best option is to use advanced techniques such as Cathodic Cage Plasma Deposition (CCPD) [28] or Cathode Cage (CC) method and hollow cathode (HC) method, which consists in inserting Ti-N atoms on the surface of the substrate, firing high-energy ions on the surface of the target, causing atoms decomposition in this surface and incorporating to the substrate [29].

Given the above, this research aims to evaluate the effect of deposition of titanium thin films via plasma on the surface characteristics of NiCr alloys and compare the cathode cage and hollow cathode methods for dental applications. The samples were characterized and compared with the references samples via Scanning Electron Microscopy (SEM), Vickers microhardness, X-Ray Diffraction (XRD) and wetability tests.

2. MATERIALS AND METHODS

2.1. Preparation of the coatings

A Ni-Cr alloy (VeraBondII®, AalbaDent, Inc.), with a chemical composition by wt.%: of Ni 75.6%, Cr 11.5%, Mo 3.5%, Si 3.5%, Nb 4.3%, and Al 2.2%, was used to prepare disk-shaped samples, with 13 mm in diameter and 2 mm in thickness. Wax patterns were prepared and embedded in an investment material (Sculer-Dental, Ulm, Germany). Lastly, it was casted by lost wax technique using conventional flame fusion technique with conventional injection of the alloy by centrifuge (Electric centrifuge SL, EDG, São Carlos, Brazil). After casting and cooling of the rings, a hammer was used to remove the adhered coating, as shown in Figure 1.

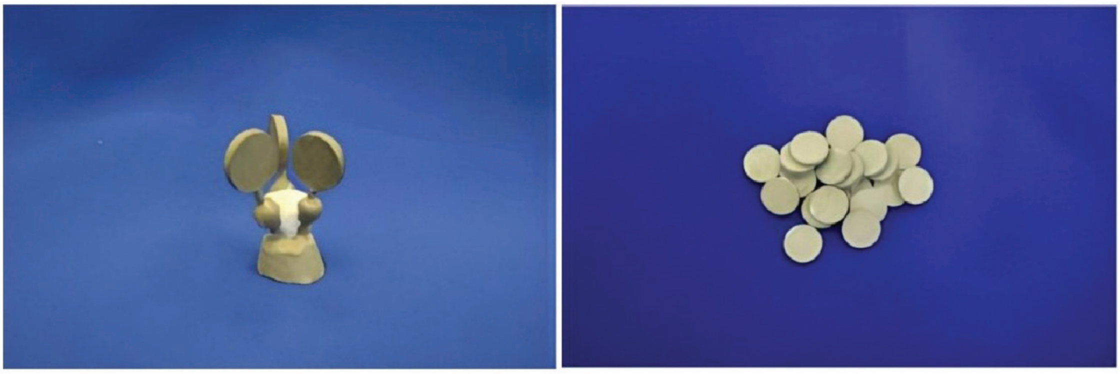

Figure 1: Unincluded specimens (left) and with the feed channels removed (right) [30].

In the final stage of the sample's preparation, a polishing was performed on the face that would be tested and sandpaper with 240, 400, 600, 1000, 1200 and 2000 grit was used in a polisher (PFL model, Fortel Ind. e Com. Ltda, São Paulo, Brazil). In this polishing, a cloth disc soaked in a lubricating solution and diamond suspension paste (Strues, Glasgow, UK) was used in granulations of 1 and 3 µm.

The samples were submitted to the presence of solutions that reproduced conditions like the ones found in oral cavity: pH 3 (acidic), pH 6.5 (neutral), pH 9 (basic), according to the methodology presented in [30]. Then, these specimens were named as: R3.0; R6.5; and R9.0 (reference samples), HC3.0; HC6.5; HC9.0 (hollow cathode samples), and CC3.0; CC6.5 e CC9.0 (cathodic cage samples), in a total of eighteen samples, two of each one.

In order to perform the surface treatment, the samples were cleaned and this step was divided into four stages. In the first one, samples were cleaned with hydrated ethyl alcohol 70° INPM for five minutes in a SONI-TECH ultrasound device (Soni-top 403 model, 40 kHz and 100 W). Already in the second stage, after 5 minutes, the parts were removed from the device and dried with the aid of a simply dryer. From that stage onwards, the samples were handled with the help of forceps. Then, in the third stage, after drying, the samples were placed in an acidic solution of HNO_3 + 3.25 mL HF + 125 mL H_2O, to remove impurities that could remain on the material surface. Lastly, in the fourth stage, in a Becker, the samples were placed again in the ultrasound device for five minutes. This procedure was also performed for cleaning other components, such as the cathodic cage, hollow cathode, and the sample holder.

To apply the plasma deposition techniques, a system was used for the deposition of TiN thin films, and it consists of a reactor (vacuum chamber), with a set of electronic sensors, a gas supply system, and a voltage source as peripherals. The samples were placed on a ceramic (insulator) substrate, surrounded by a cage, in which a cathodic potential was applied, and thus termed as a cathodic cage; so, they remained in a floating potential, to be treated with a post-discharge, Figure 2. There was an increase in the efficiency of the technique due to the presence of the holes in the cathodic cage walls, where occurs the hollow cathode effect.

In the procedure, it was used a titanium cathode cage with the following dimensions of 90 mm in diameter, 45 mm in height and 2 mm in thickness. This cage had holes with 8 mm in diameter and with 5 mm of distance between the centers of adjacent holes. Moreover, it was used a hollow titanium cathode with dimensions of 48 mm in diameter, 20 mm in height and 2 mm in thickness.

The arrangement containing the hollow cathode sample/cathodic cage was set on the reactor's sample holder, and each sample was placed on an aluminum disk with 30 mm diameter and 3 mm of thickness. Using this arrangement, the environment was kept isolated, preventing the plasma from reaching the sample surface directly. On the other hand, plasma reached on the cage's and the cathode's surface, which were both polarized.

After cleaning the samples, the next step was to apply a pre-treatment, named pre-sputtering. This process consists of exposing the cage and the samples to an atmosphere, where hydrogen (H_2) and argon (Ar) gases are added (H_2 = 50%; Ar = 50%), in order to remove the remaining oxides from its surfaces. The lack of this procedure may compromise part of the subsequent step. Pre-sputtering only starts when the temperature reaches 350 °C, and then, it is kept for an hour. The next step, after the pre-sputtering, it was modified the release of hydrogen and argon gases in the flowmeter in order to add nitrogen gas in the system (H_2 = 50%; Ar = 25%; N_2 = 25%). Current of the reactor system was gradually increased until reaching the desired temperature of 400 °C, which was maintained for a period of four hours.

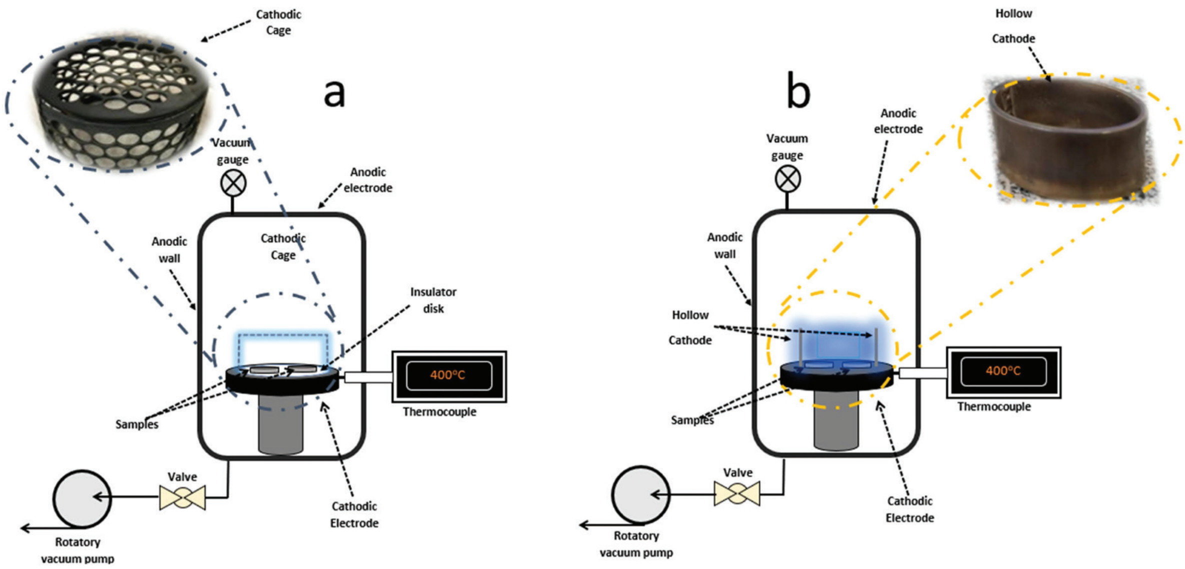

Figure 2: Schematic diagram of cathode cage and hollow cathode plasma deposition system.

2.2. Characterization

The Scanning Electron Microscope (SEM), (Quanta Feg-250 model, Thermo Fisher Scientific Company), with acceleration voltage from 1 to 30 KV was used to qualitatively evaluate the morphologies of the deposited coatings.

The X-Ray Diffraction analyzes to determine the phases present in the layers with deposition and base material were performed in a Rigaku X-Ray diffractometer, Ultima IV model, Cu-Kα radiation ($\lambda = 1.5406$ Å), operating at a voltage of 40.0 kV and 30.0 mA of current, sweep angle (2θ) from 10° to 90° with an angular step of 0.02° and a speed of 10°/min.

The Vickers microhardness tests were carried out in a microdurometer (ISH-TDV 1000 model, INSIZE). In these tests, it was used a pyramidal penetrator with a 136° angle between the opposite faces and gradual load (25gf ≅ 0.24N). Five indentation measurements were taken from the center to the edges from nine of eighteen samples, and it was considered the average values obtained for each sample.

The film's surface wettability was based on the sessile drop method, from which a 16 µL drop of ultrapure water was gently deposited on the surface, and the angle formed between the drop and the surface was determined by image analysis using a software (CAM 2008, KSV Instruments). Moreover, the contact angle was reported using an average of twenty measurements in each sample.

3. RESULTS

In the present work, eighteen Ni-Cr alloy samples, composed of Ni 75.6 wt.%, Cr 11.5 wt.%, Mo 3.5 wt.%, Si 3.5 wt.%, Nb 4.3 wt.%, and Al 2.2 wt.%, were used to reproduce conditions similar to the ones found in oral cavity, with pH 3 (acidic), pH 6.5 (neutral), pH 9 (basic), and named as: R3.0; R6.5; and R9.0 (reference samples), HC3.0; HC6.5; HC9.0 (hollow cathode samples), and CC3.0; CC6.5 e CC9.0 (cathodic cage samples), in a total of eighteen samples.

3.1. Scanning electronic microscopy

Figures 3 to 6 show the micrographs, after treatment, obtained for reference, hollow cathode, and cathodic cage samples, respectively. The microstructural characterization of the surface to the studied samples was analyzed by the support of images presented in [31].

The acidic and neutral (R3.0 and R6.5) reference samples went through a bigger corrosion process than the sample (R9.0) with pH 9.0 (basic), as one can see additionally in Figure 4. Such results corroborate the study carried out by [23], where they show that there was a strong influence of the pH level of artificial saliva on the corrosion behavior of the commercial Ni-Cr-Mo alloy: nickel (60–82%), chromium (11–25%) and molybdenum (0–14%).

Deposition of TiN thin films caused the presence of voids on the surface of samples treated in a cathodic cage, Figure 5. This inconvenient can be explained by assuming that voids in films can be transformed by the

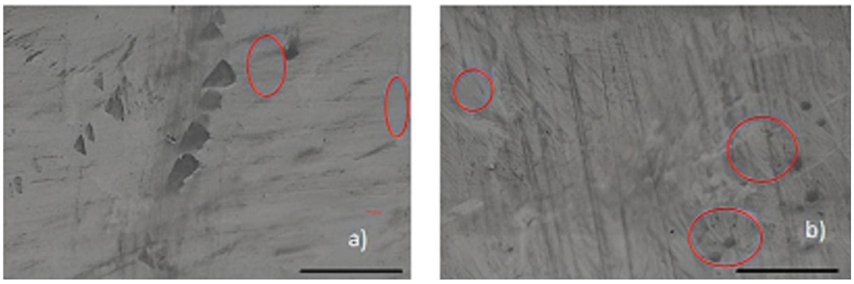

Figure 3: SEM images of the reference specimens: a) R3.0 and b) R6.5 (5000×, scale bar = 20 μm).

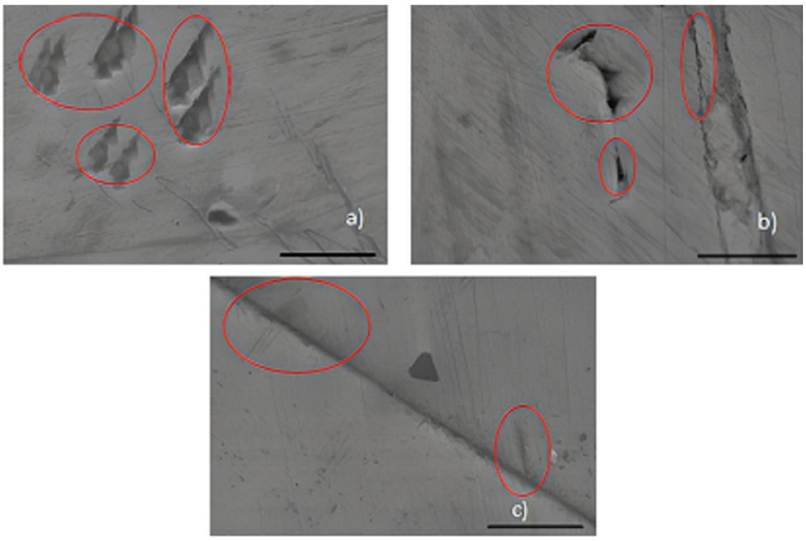

Figure 4: SEM images of the reference specimens: a) R3.0, b) R6.5 and c) R9.0 (20000×, scale bar = 5 μm).

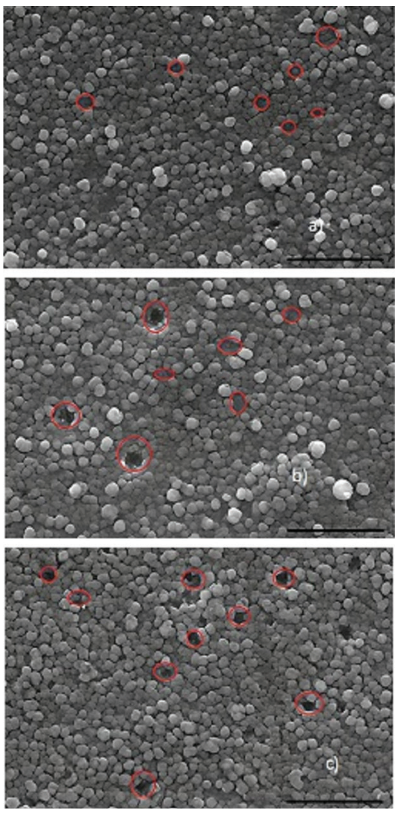

Figure 5: SEM images of the reference specimens: a) R3.0, b) R6.5 and c) R9.0 (20000×, scale bar = 5 μm).

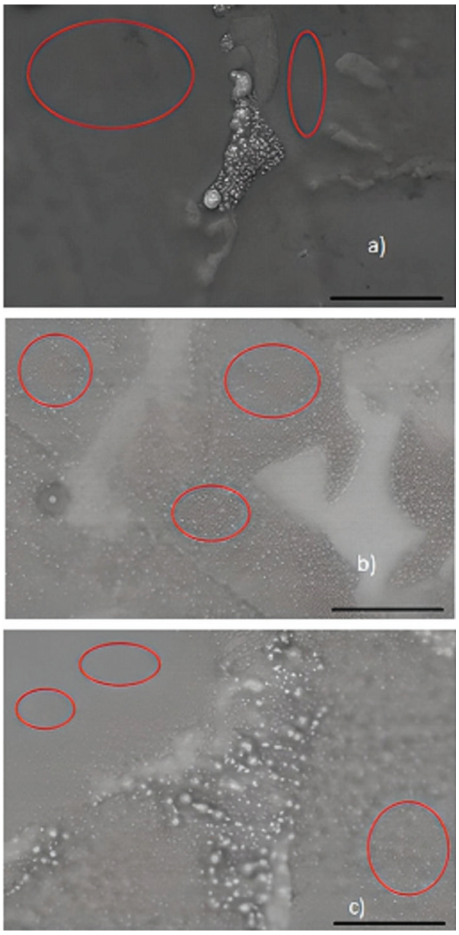

Figure 6: SEM images of the hallow cathodic specimens: a) HC3.0, b) HC6.5 and c) HC9.0 (5000×, scale bar = 20 μm).

release of particles due to the development of stresses, which depend on the conditions applied during the surface treatment [32]. Such statement, it is endorsed by the study conducted by [33], who analyzed TiN deposition in cobalt-chromium samples. The authors concluded that topographic defects are related to the process of coating thin film deposition and such locations, with the presence of holes and pores may act as corrosion sites.

In addition, the results found in this work can be endorsed by studies conducted by [34], where they deposited thin films of titanium carbonitride and titanium nitride in cobalt-chromium alloys, another alloy widely used for dental prostheses. After deposition, samples were immersed in an acidic solution and subsequently the corrosion process was analyzed.

3.2. X-Ray diffraction

The graphs generated from X-Ray Diffraction for NiCr samples with and without TiN plasma deposition for the three pH conditions (3; 6.5 and 9) are shown below in Figure 7.

According to the diffractogram, Figure 7, for the samples treated with titanium cathodic cage and hollow cathode, it is possible to identify the NiCr phases, which is the base material of the alloy, as well as the TiN and Ti_2N phases. The presence of the titanium nitride phase comes from the titanium cathode cage after reacting with nitrogen gas in a plasma environment and being deposited on the sample surface [35].

3.3. Vickers microhardness

Materials used for dental prostheses are directly exposed to pH changes that occur within the oral cavity that can shift several properties, such as in microhardness, which has a direct influence on the longevity of the biomaterial [36]. In addition, the prosthesis is exposed to mechanical wear within the masticatory cycle, which occurs when two surfaces come into contact, causing the loss of surface material [37]. Table 1 presents the data obtained from the microhardness characterization for the reference samples (R as well as in the samples treated in CC and HC).

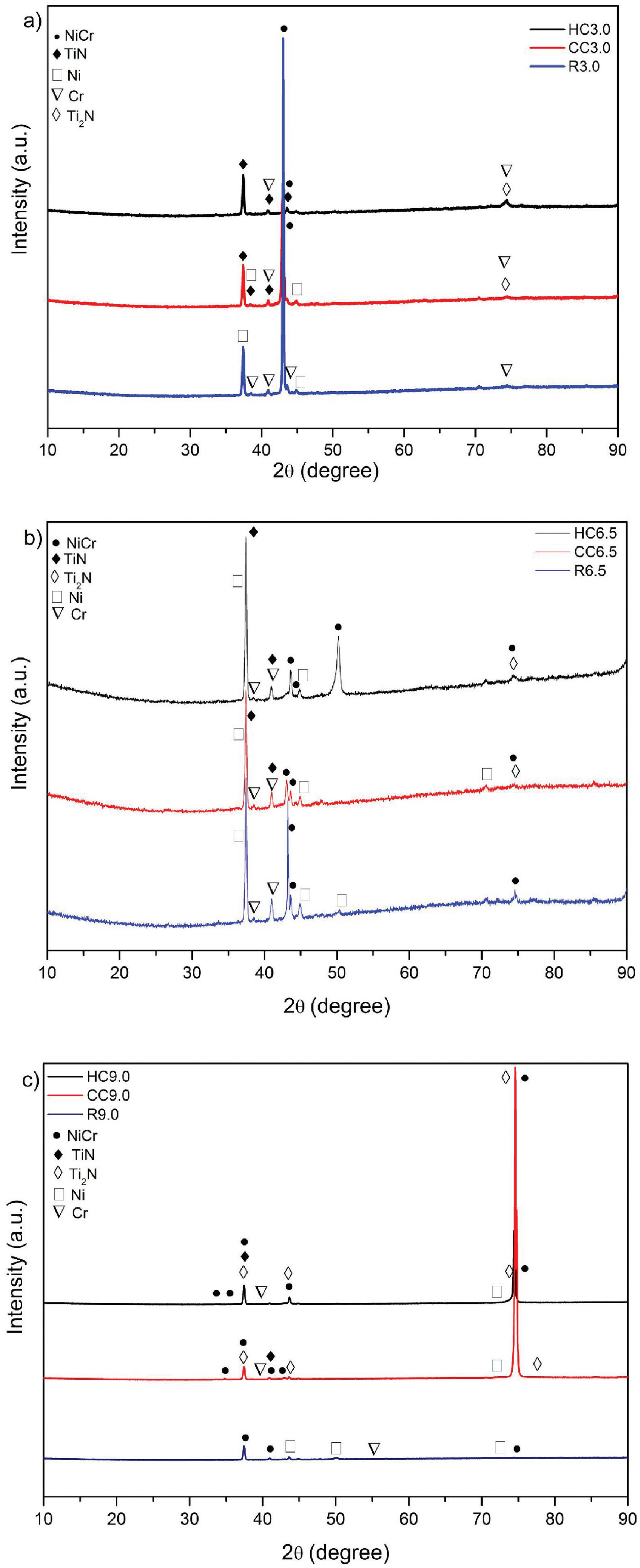

Figure 7: Diffractogram of NiCr alloy samples for conditions of pH 3.0 (a), pH 6.5 (b), pH 9 (c), for samples without treatment and with plasma treatments with cathodic cage (CC) and hollow cathode (HC).

Table 1: Vickers microhardness (in gF).

SAMPLE	R3.0	R6.5	R9.0	CC3.0	CC6.5	CC9.0	HC3.0	HC6.5	HC9.0
AVERAGE	523.64	565.14	526.16	496.71	537.00	581.99	883.61	966.32	982.34

Table 2: Wettability.

SAMPLE	R3.0	R6.5	R9.0	CC3.0	CC6.5	CC9.0	HC3.0	HC6.5	HC9.0
CONTACT ANGLE	98.56°	99.40°	102.28°	0°	0°	0°	40.47°	45.36°	25.96°
STANDARD DEVIATION	0.65	0.87	0.46	–	–	–	0.45	0.57	0.46

Samples with pH 9.0 showed the highest microhardness values. The results presented for the pH of 9.0, corroborate with the studies of [20], both for the reference and for hollow cathode samples. The research in question did not analyze the alloy behavior for acidic and neutral pH and under cathodic cage procedure. Ion bombardment in plasma deposition process, which is identified as one of the most relevant parameters and its variation can dramatically alter the structure, thickness, and properties of the film [38].

3.4. Wettability

It is assumed that when the contact angle (θ) is less than 90°, the surface is hydrophilic and, in the case of $\theta > 90°$, it is hydrophobic [39]. In addition to the hydrophobic and hydrophilic surface, the superhydrophobic surface ($\theta > 150°$) and the superhydrophilic surface ($\theta < 10°$, close to 0°) are cited in the study conducted by [40]. Metal implants generally have a high surface energy (low wettability) due to their smooth surfaces, creating a poor environment for cell adhesion. If the surface has been modified to introduce roughness, the biocompatibility of the implant can be altered [41]. Therefore, Table 2 shows the data obtained for the R, CC and HC specimens.

Hydrophilic surfaces exhibit less adsorption of proteins present in the surrounding environment and less interaction with cells (i.e., adhesion and activation) and bacteria compared to hydrophobic surfaces [42]. It is considered that proteins tend to bind to hydrophobic surfaces and cells normally adhere selectively to the hydrophilic regions of the biomaterial, considering that cell behavior depends on the type of cell present in the surrounding environment [43]. Hydrophilicity can provide superior fixation and growth of osteoblasts and, therefore, better bioactivity and biocompatibility, compared to smooth counterparts. One study conducted by [44] confirms this statement when analyzing the behavior of a titanium dental implant in a clinical trial for 12 months. The authors also reiterated that the synergistic effect of increased surface roughness and hydrophilicity can induce a microenvironment that reduces curing time.

Another process that occurs under the hydrophilic surface is the adhesion and activation of thrombocytes (platelets), and subsequent formation of a blood clot. The activated platelets interact with the implant surface, then cross into the extracellular environment. Through this mechanism, the healing process begins, a reduction in the innate immune response causing a non-inflammatory environment, and as consequence, bone regeneration [45].

Within the application considered in this research, it is necessary that in the healing phase, the interaction of the implant-living tissue occurs since adhesion of certain proteins and osteoblastic cells help in this process [46], therefore, the samples with treatment surface considered hydrophilic (hollow cathode) and superhydrophilic (cathodic cage) would be those that would present a better performance when comparing the initial samples.

Considering the pH of the samples, it was stated in [40] and [46] that this variable is fundamental for the regulation of cell adhesion. The study conducted by [47] shows that under the most acidic conditions (pH = 2), there was a greater cell adhesion and of certain biomolecules, including lipopolysaccharides, a component of the cell walls of Gram-negative bacteria, which favors the occurrence of inflammation. The authors also state that as the pH becomes less acidic, this adhesion tends to decrease (analyzed pHs: 4 and 7). With a smaller standard deviation between the measurements, it is possible to infer a certain uniformity in the contact angle measurements, a consequence of a homogeneity of the surface roughness [48].

4. DISCUSSION

In this study, the main goal was to evaluate the thin films created on substrate surfaces by the CPPD technique for dental applications. Figures 3 to 6 show SEM micrographs after treatment, obtained for reference, hollow cathode, and cathodic cage samples, respectively. The microstructural characterization of the surface to the studied samples was analyzed by the support of images presented in [31].

Analyzing micrographs in Figure 3 (after treatment, obtained for reference, hollow cathode, and cathodic cage samples, respectively), it could be seen that the worn surface of these samples shows several scratches with larger and deeper grooves in detriment of an intense process of corrosion, with the probability of surface thinning [49]. The scaly nature of the surface is characteristic of the studied alloy after the corrosion process in acidic environment [50]. A lamellar constituent can be seen in the interdendritic space, as shown in Figure 1, and such dendritic microstructure is a characteristic of this type of alloy, after its exposure to acidic environments [51].

In Figure 4, results in relation to corrosion process for the acid sample (R3.0) and neutral sample (R6.5) were bigger than basic sample (R9.0). This was reported in a similar way by authors in [23], in which they showed that there was a strong influence of the pH level of artificial saliva on the corrosion behavior of the commercial Ni-Cr-Mo alloy. The acidic artificial saliva presented a significant degrading effect over corrosion and perform of the commercial Ni-Cr-Mo alloy. The measured corrosion, in this study, varies as a function of pH in the order of pH = 3 > pH = 5 > pH = 9 > pH = 7.

Figure 5 showed the presence of voids on the surface of the treated sample by using cathodic cage. The micrographs of samples coated both in hollow cathode (HC) and in cathodic cage (CC) revealed the presence of a lower quantity of scratches and grooves, when compared to uncoated substrates [52]. In addition, because the thickness of the film is greater than in samples treated in HC than in cathodic cage CC, the surface of the material is more homogeneous [44]. Through the analysis of electron microscopy images, in the samples before and after, it became clear that the uncoated substrate (R), was more affected by corrosion than the coated surfaces (HC and CC). In this sense, it can be highlighted that the sample HC9.0, Figure 6, showed better microstructural behavior due to its uniformity.

According to the XRD analysis of Figure 7, it was possible to identify the phases of the Ni and Cr elements in isolation. For the untreated samples, it was possible to identify the NiCr phases, as well as in an isolated way for these elements, but without the presence of the phases of the elements that constitute the titanium cage or the hollow cathode. Peak analyzes showed two phases of titanium nitride, cubic TiN (Fm/3m) and tetragonal Ti_2N (P42/mnm) [53, 54].

For samples treated for pH3 and pH6.5, the predominant phase was cubic TiN, Figure 7a and b, while for samples treated for pH9, Figure 7c, the phase that stands out the most was tetragonal Ti_2N, but also presenting the cubic phase with lower intensity for the same substance. Regarding the technique used, it was observed that for the samples treated via cathodic cage and with pH9, a Ti_2N peak was identified with great intensity in relation to the other peaks of the other treated samples, reinforcing that this condition of hydrogenionic potential is the one that was more suitable for plasma deposition, reinforcing its mechanical and anti-corrosion properties.

Using the Vickers microhardness, it was noted that the samples submitted to acidic (CC3.0 and HC3.0) and neutral (CC6.5 and HC6.5) pHs, in both methods, presented lower microhardness. Regarding samples with acidic pH (3.0), the numbers were 496.71 gF in CC and 883.61 gF in HC, which compared to other methods and pHs, was lower, indicating that the pH influences directly on the samples surface behavior, inducing more intense surface corrosion. This conclusion was corroborated by the study conducted by [55], when they mention that the pH of the environment can induce intraoral corrosion of dental biomaterials, thus compromising its mechanical properties. In addition, the degree of corrosion may depend on the composition and acidity of the oral cavity [56].

Samples with pH 9.0 showed the highest microhardness values and corroborate with the studies of [20], both for the reference and for hollow cathode samples. When considering the thickness of the coating, it had a direct influence on the increase of samples microhardness [28].

When the samples were treated in a CC, the film layer formed was considered too thin, therefore, the microhardness exhibited in samples treated in CC were an average between the hardness of the film and the base metal (substrate). However, for the HC deposition, plasma confinement occurs, allowing the sample temperature to become higher than that used for the treatment. Therefore, a greater film thickness was obtained when compared to deposition by CC, with the microhardness obtained referring to the deposited thin film.

By the wettability test, doing the treatment with the HC technique, it was observed that it can be categorized as hydrophilic due to the reduction in the contact angle. For the HC9.0 sample, this decrease was more noticeable when compared to the reference sample, obtaining a reduction of 74.62% in the contact angle. One can infer that the smaller the contact angle, the more hydrophilic the surface can be considered [57]. Some authors [58] consider that the reduction in the contact angle was due to the growth rate of the formed titanium nitride layer.

Relating to the results obtained in this last test, the statement is valid only for samples treated in HC, since the lowest contact angle obtained was in the sample HC9.0. When analyzing the reference samples (R), however, the sample R9.0 presents the opposite behavior, having the largest contact angle, being characterized, therefore, as the sample with the greatest hydrophobicity.

5. CONCLUSION

In this work, using the Cathode Cage (CC) and hollow cathode (HC) deposition methods on NiCr alloy samples, used in dental applications, it was possible to evaluate the quality of the TiN thin films formed on its surface. Based on this research, it can be concluded that:

1. SEM micrographs showed that the reference samples, exposed to the acidic (R3.0) and neutral (R6.5) pHs underwent a corrosion process, forming grooves on the sample surface.
2. When comparing the two methods, HC and CC, the samples treated via HC obtained a more uniform structure and with less voids, as for the CC technique, one can observe the presence of voids formed during the deposition of thin films, demonstrating that this deposition method is less effective when compared to the other studied.
3. XRD analysis showed that there was formation of TiN and Ti_2N phases in the films deposited on the surface of NiCr samples, which corroborates which an increase in mechanical and anticorrosive properties. In addition to the cubic and tetragonal phases of titanium nitride, the films formed by the CC and HC methods show the phases of the elements Ni, Cr and NiCr, which come from the base material (substrate).
4. The thickness of the film formed in CC is less than that formed in a HC. Therefore, the measurement obtained average data between the microhardness of the substrate and the film. For the samples treated via hollow cathode, the highest levels of microhardness were found, so that the one with a basic pH (HC9) was the one that presented the highest microhardness among all the evaluated samples. The uniformity in the films deposited via hollow cathode indicated by the SEM reinforces the results found through the microhardness, which indicates that the cathodic cage method was less effective, mainly with regard to samples with acidic or neutral pH.
5. Through the analysis of wettability and surface tension, it was found that the NiCr samples after treatment with HC method began to show hydrophilic surface characteristics, whereas with CC method they became superhydrophylic. Due to these conditions acquired after the depositions, there was an increase in the potential for osseointeraction and biocompatibility of the samples, in addition to the inhibition of inflammatory processes related to superficial adhesions related to the evaluated material.

Thus, from the results obtained in this research, one can affirm that both methods are suitable for the surface treatment of NiCr alloys. However, these results also confirm that the HC technique, a method already used by professionals in the dental field, presents better results to the detriment of the formation of a thicker layer of film, providing greater microhardness and surface uniformity, thus ensuring good adhesion to living tissue.

6. ACKNOWLEDGMENTS

The authors thanks to CAPES for their financial support of this work and the Laboratory of Plasma of UFPI (LABPLASMA/UFPI).

7. BIBLIOGRAPHY

[1] AMATO, S.F., EZZELL JUNIOR, R.M., *Regulatory affairs for biomaterials and medical devices*, Cambridge (UK), Woodhead Publishing, 2015.

[2] ULLAH, S., CHEN, X., "Fabrication, applications and challenges of natural biomaterials in tissue engineering", *Applied Materials Today*, v. 20, n. 1, pp. 100656–100677, Sep. 2020. doi: http://dx.doi.org/10.1016/j.apmt.2020.100656.

[3] LIU, Y., RATH, B., TINGART, M., *et al*., "Role of implants surface modification on osseointegration: a systematic review", *Journal of Biomedical Materials Research. Part A*, v. 108, n. 3, pp. 470–484, Aug. 2020. doi: http://dx.doi.org/10.1002/jbm.a.36829. PubMed PMID: 31664764.

[4] FAN, H., GUO, Z., "Bioinspired surfaces with wettability: biomolecule adhesion behaviors", *Biomaterials Science*, v. 8, n. 6, pp. 1502–1535, 2020. doi: http://dx.doi.org/10.1039/C9BM01729A. PubMed PMID: 31994566.

[5] AL-ZUBAIDI, S.M., MADFA, A.A., MUFADHAL, A.A., *et al*., "Improvements in clinical durability from functional biomimetic metallic dental implants", *Frontiers in Materials*, v. 7, n. 1, pp. 106, May. 2020. doi: http://dx.doi.org/10.3389/fmats.2020.00106.

[6] WANG, J., ZHANG, S., SUN, Z., *et al*., "Optimization of mechanical property, antibacterial property and corrosion resistance of Ti-Cu alloy for dental implant", *Journal of Materials Science and Technology*, v. 35, n. 10, pp. 2336–2344, Oct. 2019. doi: http://dx.doi.org/10.1016/j.jmst.2019.03.044.

[7] PANDEY, A., AWASTHI, A., SAXENA, K.K., "Metallic implants with properties and latest production techniques: a review", *Advances in Materials and Processing Technologies*, v. 6, n. 2, pp. 167–202, Mar. 2020. doi: http://dx.doi.org/10.1080/2374068X.2020.1731236.

[8] LI, J., JANSEN, J.A., WALBOOMERS, X.F., *et al*., "Mechanical aspects of dental implants and osseointegration: a narrative review", *Journal of the Mechanical Behavior of Biomedical Materials*, v. 103, n. 1, pp. 1103574, Mar. 2020.

[9] HUSSEIN, M., MOHAMMED, A., AL-AQEELI, N., "Wear characteristics of metallic biomaterials: a review", *Materials*, v. 8, n. 5, pp. 2749–2768, 2015. doi: http://dx.doi.org/10.3390/ma8052749.

[10] ROY, A.K., JONES III, D., WEBSTER, T.J., "Translational medicine and biomaterials: basics and relationship", In: Yang, L., Bhaduri, S.B., Webster, T.J. (eds), *Biomaterials in translational medicine: a biomaterials approach*, Academic Press, v. 15, n. 1, pp. 1–22, 2018.

[11] BAI, L., GONG, C., CHEN, X., *et al*., "Additive manufacturing of customized metallic orthopedic implants: materials, structures, and surface modifications", *Metals*, v. 9, n. 9, pp. 1004–1030, Sep. 2019. doi: http://dx.doi.org/10.3390/met9091004.

[12] STEWART, C., AKHAVAN, B., WISE, S.G., *et al*., "A review of biomimetic surface functionalization for bone-integrating orthopedic implants: mechanisms, current approaches, and future directions", *Progress in Materials Science*, v. 106, n. 1, pp. 100588–100600, Dec. 2019. doi: http://dx.doi.org/10.1016/j.pmatsci.2019.100588.

[13] KAPUSETTI, G., MORE, N., CHOPPADANDI, M.S., *Biomedical engineering and its applications in healthcare*, 1 ed., Sudip Paul, Springer, 2019.

[14] DE AVILA, E.D., VAN OIRSCHOT, B.A., VAN DEN BEUCKEN, J.J.P., "Biomaterial-based possibilities for managing peri-implantitis", *Journal of Periodontal Research*, v. 55, n. 2, pp. 165–173, Oct. 2020. doi: http://dx.doi.org/10.1111/jre.12707. PubMed PMID: 31638267.

[15] AL-MIN, M.D., RANI, A.M.A., ALIYU, A.A.A., *et al*., "Bio-ceramic coatings adhesion and roughness of biomaterials through PM-EDM: a comprehensive review", *Materials and Manufacturing Processes*, v. 35, n. 11, pp. 1157–1180, Jul. 2020. doi: http://dx.doi.org/10.1080/10426914.2020.1772483.

[16] AGNIHOTRI, R., GAUR, S., ALBIN, S., "Nanometals in dentistry: applications and toxicological implications: a systematic review", *Biological Trace Element Research*, v. 197, n. 1, pp. 70–88, Nov. 2020. doi: http://dx.doi.org/10.1007/s12011-019-01986-y. PubMed PMID: 31782063.

[17] LOKE, C., LEE, J., SANDER, S., *et al*., "Factors affecting intra-oral pH – a review", *Journal of Oral Rehabilitation*, v. 43, n. 10, pp. 778–785, Aug. 2016. doi: http://dx.doi.org/10.1111/joor.12429. PubMed PMID: 27573678.

[18] JAVADHESARI, S.M., ALIPOUR, S., AKBARPOUR, M.R., "Biocompatibility, osseointegration, antibacterial and mechanical properties of nanocrystalline Ti-Cu alloy as a new orthopedic material", *Colloids and Surfaces. B, Biointerfaces*, v. 189, n. 1, pp. 110889, May. 2020. doi: http://dx.doi.org/10.1016/j.colsurfb.2020.110889. PubMed PMID: 32114284.

[19] TURDEAN, G.L., CRACIUN, A., POPA, D., *et al*., "Study of electrochemical corrosion of biocompatible Co–Cr and Ni–Cr dental alloys in artificial saliva. Influence of pH of the solution", *Materials Chemistry and Physics*, v. 233, n. 1, pp. 390–398, May. 2019. doi: http://dx.doi.org/10.1016/j.matchemphys.2019.05.041.

[20] MANSOOR, N.S., FATTAH-ALHOSSEINI, A., SHISHEHIAN, A., *et al*., "Tribological properties of different types of coating materials deposited by cathodic arc-evaporation method on Ni-Cr dental alloy", *Materials Research Express*, v. 6, n. 5, pp. 056421–056433, Feb. 2019. doi: http://dx.doi.org/10.1088/2053-1591/ab07e8.

[21] SLOKAR, L., PRANJIC, J., CAREK, A., "Metallic materials for use in dentristry", *The Holistic Approach to Environment*, v. 7, n. 1, pp. 38–57, 2017.

[22] CHEN, Q., THOUAS, G.A., "Metallic implant biomaterials", *Materials Science and Engineering R Reports*, v. 87, n. 1, pp. 1–57, Jan. 2015.

[23] MOSLEHIFARD, E., MOSLEHIFARD, M., GHASEMZADEH, S., *et al*., "Corrosion behavior of a nickel-base dental casting alloy in artificial saliva studied by weight loss and polarization techniques", *Frontiers in Dentistry*, v. 1, n. 16, pp. 13–20, Jan. 2019. doi: http://dx.doi.org/10.18502/fid.v16i1.1104. PubMed PMID: 31608332.

[24] DAN, M.L., COSTEA, L.V., SAVENCU, C.E., *et al*., "Influence of pH on the corrosion behaviour of laser-processed Co-Cr dental alloys in artificial saliva", *IOP Conference Series. Materials Science and Engineering*, v. 416, n. 1, pp. 012036–012046, Sep. 2018. doi: http://dx.doi.org/10.1088/1757-899X/416/1/012036.

[25] BREME, H., BIEHL, V., REGER, N., *et al*., "Handbook of biomaterial properties", In: Murphy, W., Black, J., Hastings, G. (eds), *A metallic biomaterials: introduction*, 2 ed., chapter 1, New York, USA, Springer, 2016.

[26] REDDY, H., GULER, U., KUDYSHEV, Z., *et al*., "Temperature-dependent optical properties of plasmonic titanium nitride thin films", *ACS Photonics*, v. 4, n. 6, pp. 1413–1420, Apr. 2017. doi: http://dx.doi.org/10.1021/acsphotonics.7b00127.

[27] UWAIS, Z.A., HUSSEIN, M.A., SAMAD, M.A., *et al*., "Surface modification of metallic biomaterials for better tribological properties: a review", *Arabian Journal for Science and Engineering*, v. 42, n. 11, pp. 4493–4512, Jun. 2017. doi: http://dx.doi.org/10.1007/s13369-017-2624-x.

[28] ABREU, L.H.P., NAEEM, M., BORGES, W.F.A., *et al*., "Synthesis of TiN and TiO_2 thin films by cathodic cage plasma deposition: a brief review", *Journal of the Brazilian Society of Mechanical Sciences and Engineering*, v. 42, n. 9, pp. 496, Sep. 2020. doi: http://dx.doi.org/10.1007/s40430-020-02584-z.

[29] WU, W.Y., CHAN, M.Y., HSU, Y.H., *et al*., "Bioapplication of TiN thin films deposited using high power impulse magnetron sputtering", *Surface and Coatings Technology*, v. 362, n. 1, pp. 167–175, Mar. 2019. doi: http://dx.doi.org/10.1016/j.surfcoat.2019.01.106.

[30] PUPIM, D., "*Evaluation of changes in surface roughness and ion release from dental casting alloys after an experimental tribocorrosion process*", Tese de D.Sc., Ribeirão Preto University, USP, Ribeirão Preto (SP), Brasil, 2015.

[31] TONETTO, E.M., "Caracterização microestrutural de grãos de quartzo por microscopia eletrônica de varredura (MEV)", *Sínteses: Revista Eletrônica do Sim Tec*, v. 1, n. 7, pp. 1–2, 2019.

[32] WATHANYU, K., TUCHINDA, K., DAOPISET, S., *et al*., "Microstructure, hardness, adhesion and corrosion properties of Ti and TiN films on stainless steel 316L", *Key Engineering Materials*, v. 856, n. 1, pp. 66–75, Aug. 2020. doi: http://dx.doi.org/10.4028/www.scientific.net/KEM.856.66.

[33] HERBSTER, M., DORING, J., NOHAVA, J., *et al*., "Retrieval study of commercially available knee implant coatings TiN, TiNbN and ZrN on TiAl6V4 and CoCr28Mo6", *Journal of the Mechanical Behavior of Biomedical Materials*, v. 112, n. 1, pp. 104034–104049, Dec. 2020. doi: http://dx.doi.org/10.1016/j.jmbbm.2020.104034. PubMed PMID: 32871541.

[34] DINU, M., PANA, L., SCRIPCA, P., *et al*., "Improvement of CoCr alloy characteristics by Ti-based carbonitride coatings used in orthopedic applications", *Coatings*, v. 10, n. 5, pp. 495–512, May. 2020. doi: http://dx.doi.org/10.3390/coatings10050495.

[35] LIBÓRIO, M.S., PRAXEDES, G.B., LIMA, L.L.F., *et al*., "Surface modification of M2 steel by combination of cathodic cage plasma deposition and magnetron sputtered MoS2-TiN multilayer coatings", *Surface and Coatings Technology*, v. 384, pp. 125327, Feb. 2020. doi: http://dx.doi.org/10.1016/j.surfcoat.2019.125327.

[36] NERES, È.Y., MODA, M.D., CHIBA, E.K., *et al*., "Microhardness and roughness of infiltrated white spot lesions submitted to different challenges", *Operative Dentistry*, v. 42, n. 4, pp. 428–435, Jul. 2017. doi: http://dx.doi.org/10.2341/16-144-L. PubMed PMID: 28402735.

[37] LUCCHETTI, M.C., FRATTO, G., VALERIANI, F., *et al*., "Cobalt-chromium alloys in dentistry: an evaluation of metal ion release", *The Journal of Prosthetic Dentistry*, v. 114, n. 4, pp. 602–608, Oct. 2015. doi: http://dx.doi.org/10.1016/j.prosdent.2015.03.002. PubMed PMID: 25979449.

[38] RAMASESHAN, R., JOSE, F., RAJAGOPALAN, S., *et al*., "Preferentially oriented electron beam deposited TiN thin films using focused jet of nitrogen gas", *Surface Engineering*, v. 32, n. 11, pp. 834–839, Jun. 2016. doi: http://dx.doi.org/10.1080/02670844.2016.1159832.

[39] BANASZEK, K., KLIMEK, L., "Wettability and surface free energy of Ti (C, N) coatings on nickel-based casting prosthetic alloys", *Archives of Foundry Engineering*, v. 15, n. 3, pp. 11–16, 2015. doi: http://dx.doi.org/10.1515/afe-2015-0050.

[40] CUI, H., WANG, W., SHI, L., *et al*., "Superwettable surface engineering in controlling cell adhesion for emerging bioapplications", *Small Methods*, v. 4, n. 12, pp. 2000573–2000593, Dec. 2020. doi: http://dx.doi.org/10.1002/smtd.202000573.

[41] BOSE, S., ROBERTSON, S.F., BANDYOPADHYAY, A., "Surface modification of biomaterials and biomedical devices using additive manufacturing", *Acta Biomaterialia*, v. 66, pp. 6–22, Jan. 2018. doi: http://dx.doi.org/10.1016/j.actbio.2017.11.003. PubMed PMID: 29109027.

[42] KOVACH, K.M., CAPADONA, J.R., GUPTA, A.S., *et al*., "The effects of PEG-based surface modification of PDMS microchannels on long-term hemocompatibility", *Journal of Biomedical Materials Research. Part A*, v. 102, n. 12, pp. 4195–4206, Dec. 2014. doi: http://dx.doi.org/10.1002/jbm.a.35090. PubMed PMID: 24443272.

[43] SU, Y., LUO, C., ZHANG, Z., *et al*., "Bioinspired surface functionalization of metallic biomaterials", *Journal of the Mechanical Behavior of Biomedical Materials*, v. 77, n. 1, pp. 90–105, Jan. 2018. doi: http://dx.doi.org/10.1016/j.jmbbm.2017.08.035. PubMed PMID: 28898726.

[44] HUANG, M.S., CHEN, L.K., OU, K.L., *et al*., "Rapid osseointegration of titanium implant with innovative nanoporous surface modification", *Implant Dentistry*, v. 24, n. 4, pp. 441–447, Aug. 2015. doi: http://dx.doi.org/10.1097/ID.0000000000000258. PubMed PMID: 25946663.

[45] ALMAS, K., SMITH, S., KUTKUT, A., "What is the best micro and macro dental implant topography?", *Dental Clinics of North America*, v. 63, n. 3, pp. 447–460, Apr. 2019. doi: http://dx.doi.org/10.1016/j.cden.2019.02.010. PubMed PMID: 31097137.

[46] CHENG, H.C., CHANG, T.L., LIN, C.S., *et al*., "Wettability of laser-textured copper surface after a water-bath process", *AIP Advances*, v. 9, n. 12, pp. 125140–125148, Dec. 2019. doi: http://dx.doi.org/10.1063/1.5126173.

[47] HAN, A., TSOI, J.K.H., RODRIGUES, F.P., *et al*., "Bacterial adhesion mechanisms on dental implant surfaces and the influencing factors", *International Journal of Adhesion and Adhesives*, v. 69, n. 1, pp. 58–71, Sep. 2016. doi: http://dx.doi.org/10.1016/j.ijadhadh.2016.03.022.

[48] KUNG, C.H., SOW, P.K., ZAHIRI, B., *et al*., "Assessment and interpretation of surface wettability based on sessile droplet contact angle measurement: challenges and opportunities", *Advanced Materials Interfaces*, v. 6, n. 18, pp. 1900839–1900866, Aug. 2019. doi: http://dx.doi.org/10.1002/admi.201900839.

[49] ZHANG, S., YAN, F., YANG, Y., *et al*., "Effects of sputtering gas on microstructure and tribological properties of titanium nitride films", *Applied Surface Science*, v. 488, n. 1, pp. 61–69, Sep. 2019. doi: http://dx.doi.org/10.1016/j.apsusc.2019.05.148.

[50] EBRAHIMI, N., NOEL, J.J., RODRÍGUEZ, M.A., *et al*., "The self-sustaining propagation of crevice corrosion on the hybrid BC1 Ni–Cr–Mo alloy in hot saline solutions", *Corrosion Science*, v. 105, n. 1, pp. 58–67, Apr. 2016. doi: http://dx.doi.org/10.1016/j.corsci.2016.01.003.

[51] SILVA, L.H., LIMA, E., MIRANDA, R.B.P., *et al*., "Dental ceramics: a review of new materials and processing methods", *Brazilian Oral Research*, v. 31, n. 1, pp. 133–146, Aug. 2017. doi: http://dx.doi.org/10.1590/1807-3107bor-2017.vol31.0058. PubMed PMID: 28902238.

[52] GODWIN, G., JAISINGH, S.J., PRIYAN, M.S., *et al*., "Wear and corrosion behavior of Ti-based coating on biomedical implants.", *Surface Engineering*, v. 2, n. 1, pp. 1–10, 2020.

[53] FAROKHZADEH, K., QIAN, J., EDRISY, A., "Effect of SPD surface layer on plasma nitriding of Ti–6Al–4V alloy", *Materials Science and Engineering A*, v. 589, pp. 199–208, Jan. 2014. doi: http://dx.doi.org/10.1016/j.msea.2013.09.077.

[54] SILVA, H.S., MARCIANO, F.R., MENEZES, A.S., *et al*., "Morphological analysis of the TiN thin film deposited by CCPN technique", *Journal of Materials Research and Technology*, v. 9, n. 6, pp. 13955, Dec. 2020. doi: http://dx.doi.org/10.1016/j.jmrt.2020.09.080.

[55] MERCIECA, S., CONTI, M.C., BUHAGIAR, J., *et al*., "Assessment of corrosion resistance of cast cobalt- and nickel-chromium dental alloys in acidic environments", *Journal of Applied Biomaterials & Functional Materials*, v. 16, n. 1, pp. 47–54, Oct. 2017. doi: http://dx.doi.org/10.5301/jabfm.5000383. PubMed PMID: 29076515.

[56] ACEV, D.P., KATIC, V., TURCO, G., *et al*., "The coating of a NiTi alloy has a greater impact on the mechanical properties than the acidity of saliva", *Materiali in Tehnologije*, v. 52, n. 4, pp. 469–473, 2018. doi: http://dx.doi.org/10.17222/mit.2017.133.

[57] ZHOU, S., JIANG, L., DONG, Z., "Bioinspired surface with superwettability for controllable liquid dynamics", *Advanced Materials Interfaces*, v. 8, n. 2, pp. 2000824–2000839, Aug. 2021. doi: http://dx.doi.org/10.1002/admi.202000824.

[58] ALI, M.M., RAMAN, S.G.S., PATHAK, S.D., *et al*., "Influence of plasma nitriding on fretting wear behaviour of Ti–6Al–4V", *Tribology International*, v. 43, n. 1, pp. 152–160, Feb. 2010.