



Estudo do efeito do jateamento em superfícies de tântalo

Dissertação de Mestrado em Reabilitação Oral

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Estudo do efeito do jateamento em superfícies de tântalo

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Study of air polishing effect on tantalum surfaces

Master's Dissertation in Oral Rehabilitation

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RESUMO

INTRODUÇÃO: A aplicabilidade dos implantes dentários tem sido amplamente reconhecida na reabilitação de pacientes parcial ou totalmente desdentados. O seu sucesso clínico depende de um fenómeno inevitável denominado osseointegração. Tem havido, por isso, uma necessidade crescente de desenvolver novos biomateriais que favoreçam naturalmente esse processo biológico através das suas propriedades biomecânicas e bioativas. O tântalo tem sido considerado um material promissor nas áreas médica e dentária. Além das suas atrativas propriedades mecânicas, permite a execução de processos de modificação de superfície, como a anodização, que confere maior rugosidade e porosidade. Essas modificações na nano-topografia e na composição química podem favorecer a adesão das células ósseas, promovendo a atividade osteogénica, evitando condições desfavoráveis ao processo de osseointegração, como a peri-implantite. Atualmente, existem várias opções de tratamento para o controle da peri-implantite, onde se inclui o jateamento, que tem sido considerado uma ferramenta valiosa no desbridamento mecânico do biofilme supra e infra-gengival em dentes e implantes. Este estudo *in vitro* visa avaliar o efeito do jateamento em superfícies de tântalo puro e modificado, de acordo com diferentes parâmetros.

MATERIAL E MÉTODOS: De acordo com a presença e tipo de técnica de modificação de superfície, 81 espécimens de tântalo previamente limpos (20 mm x 20 mm x 0,5 mm de espessura) foram divididos em 3 grandes grupos: grupo 1 - tântalo puro; 2 - tântalo com Anodização (PEO / MAO); 3 - tântalo com Anodização (PEO / MAO) e deposição de nanopartículas de Zn por Magnetron Sputtering. Cada um desses grupos (puro e funcionalizado) foi subdividido em 9 subgrupos, correspondendo às seguintes condições experimentais: procedimento de polimento a ar (com ou sem); pós de polimento de ar (Air-Flow® Plus e Air-Flow® Perio - EMS®, Electro Medical Systems, Nyon, Suíça); distância de jateamento (2 mm e 5 mm) e duração do jateamento (5 se 10 s). Por fim, foram selecionadas as seguintes técnicas de caracterização de superfície: SEM-EDS, XRD, AFM e Teste da Gota Sésil.

RESULTADOS: Através da análise SEM-EDS, nenhuma alteração foi evidenciada com o jateamento em superfícies de Ta puro. Em relação às superfícies funcionalizadas, o pó de bicarbonato de sódio alterou a topografia, tornando as superfícies mais rugosas, enquanto o eritritol-clorexidina não produziu efeitos significativos a esse nível. Ambos os pós diminuíram a quantidade dos elementos químicos Ca e P nas superfícies modificadas.. O procedimento abrasivo reduziu a quantidade de nanopartículas de Zn, principalmente quando o pó de bicarbonato de sódio foi aplicado. Dentre todos os parâmetros de jateamento, a combinação de 2 mm e 10 s foi a mais agressiva para as superfícies de Ta. Através da análise de XRD foi observada a presença de óxido de tântalo cristalino e hidroxiapatita, enquanto a AFM evidenciou alterações na rugosidade de diferentes superfícies de Ta.

CONCLUSÃO: Ambos os pós induzem modificações químicas e morfológicas nas superfícies de Ta. No entanto, o pó à base de eritritol-clorexidina revelou menor abrasividade. Mais investigações científicas são necessárias para coletar mais dados sobre o papel biológico do procedimento de polimento de ar na prevenção de condições desfavoráveis em superfícies de Ta.

PALAVRAS – CHAVE: jateamento, implantes dentários, peri-implantite, tântalo, modificações de superfície, anodização, caracterização de superfície

ABSTRACT

INTRODUCTION: The applicability of dental implants has been widely recognized in the rehabilitation of partially or fully edentulous patients. Its clinical success depends on an unavoidable phenomenon called osseointegration. Therefore, there has been a growing need to develop new biomaterials that naturally favor this biological process through its biomechanical and bioactive properties. Tantalum has been considered a promising material in the medical and dental fields. Besides its attractive mechanical properties, it allows the execution of surface modification processes, such as anodization, which gives greater roughness and porosity formation on its surface. These modifications in the nano-topography and chemical composition may favor bone cells' adhesion, promoting the osteogenic activity, thus preventing unfavorable conditions to the osseointegration process, such as peri-implantitis. There are currently several treatment options to control peri-implantitis, including the air polishing procedure, which has been considered a valuable tool in the mechanical debridement of supra and infra gingival biofilm in teeth and implants. This *in vitro* study aims to evaluate the air polishing effect on pure and modified tantalum surfaces, according to different air polishing parameters.

MATERIAL AND METHODS: According to the presence and type of surface modification technique, 81 previously cleaned tantalum specimens (20 mm x 20 mm x 0,5 mm thickness) were divided into 3 major groups: group 1 – pure tantalum; 2 – tantalum with Anodization (PEO/MAO); 3 – tantalum with Anodization (PEO/MAO) and deposition of Zn nanoparticles by Magnetron Sputtering. Each of these groups (pure and functionalized) were subdivided into 9 subgroups, corresponding to the following experimental conditions: air polishing procedure (with or without); air polishing powders (Air-Flow[®] Plus and Air-Flow[®] Perio – EMS[®], Electro Medical Systems, Nyon, Switzerland); air polishing distance (2 mm and 5 mm), and air polishing duration (5 s and 10 s). Finally, the following surface characterization techniques were selected: SEM-EDS, XRD, AFM, and Sessil Drop Technique.

RESULTS: Through the SEM-EDS analysis, no changes were evidenced with air polishing on pure Ta surfaces. Regarding the functionalized surfaces, the sodium-bicarbonate powder changed the topography, turning the surfaces into more rugged,

whereas the erythritol-chlorhexidine did not produce significant effects at this level. Both powders decreased the amount of the chemical elements Ca and P in the modified surfaces. The air abrasive procedure reduced the Zn nanoparticles' amount, especially when the sodium-bicarbonate powder was applied. Among all the air polishing parameters, the combination of 2 mm and 10 s was the more aggressive to Ta surfaces. Through the XRD analysis, the presence of crystalline tantalum oxide and hydroxyapatite were noticed, whereas AFM evidenced changes in the roughness of different Ta surfaces.

CONCLUSION: Both powders can induce chemical and morphological modifications on Ta surfaces. However, the erythritol-chlorhexidine-based powder had revealed a lower abrasiveness. Further scientific investigations are necessary to collect more data about the air polishing procedure's biological role in preventing unfavorable conditions on Ta surfaces.

KEYWORDS: air polishing, dental implants, peri-implantitis, tantalum, surface modifications, anodization, surface characterization

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À minha família,
o meu espelho de resiliência,
a minha pedra basilar,
a razão da minha ambição
que me faz acreditar
em ser mais e melhor,
e nunca desista de sonhar!

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**“A dreamer is a winner who
never gives up”**

~ Nelson Mandela ~

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ABBREVIATIONS

Ta = tantalum

Ta₂O₅ = tantalum oxide

cp-Ti = commercial pure titanium

MSCs = mesenchymal stem cells

CaP = calcium phosphate

Ca = calcium

P = phosphorus

Zn = zinc

O²⁻ = oxide ion

OH⁻ = hydroxide ion

H₂SO₄ = sulfuric acid

H₃PO₄ = phosphoric acid

HF = hydrofluoric acid

PEO = plasma electrolytic oxidation

MAO = micro arch oxidation

EFAD = electric field assisted dissolution

NPs = nanoparticles

SEM = Scanning Electron Microscopy

EDS = Energy Dispersive Spectroscopy

XRD = X-Ray Diffraction

AFM / SFM = Atomic Force Microscopy / Scanning Force Microscopy

Au = gold

Pd = palladium

Aca = calcium acetate

β -GP = β -glycerophosphate

HAp = Hydroxyapatite

bcc = body-centered cubic

Rms = root mean square

Ra = roughness average

Rmax = maximum roughness

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I. INTRODUCTION

“Study of air polishing effect on tantalum surfaces.”

In recent decades, the applicability of osseointegrated dental implants has been widely recognized for its clinical success and the possibility of intraosseous retention of oral prosthetic rehabilitations, whether in cases of single or multiple tooth loss (Gaviria *et al.*, 2014).

Introduced by Brånemark PI (1981), titanium is a material generally accepted as a component of dental implants, allowing the osseointegration process, *i.e.*, the establishment of direct contact between the alveolar bone tissue and the implant. This phenomenon, which is unavoidable in modern implantology, allows a high success and longevity rate, both in the intraosseous component and in the prosthetic structure in which the dental crown is placed (Jorge *et al.*, 2013).

However, the growing need to optimize bioactive and biomechanical properties has led to the development of new biomaterials, including tantalum (Ta). This material is a silver-colored, ductile, metallic solid with a high melting point (about 3800 °C), found in low concentration in the earth's crust, and applied as a refractory material in structures with a high thermal and chemical stimulus. Currently, in addition to the military, aerospace, naval and automotive industries, it has several applications in the medical and dental fields, namely in plates for repairing cranial fractures, bone fixation screws, and surgical implants, including dental ones (Sousa *et al.*, 2013).

Among the various surface modification processes, the anodization of tantalum stands out by giving greater roughness and porosity formation on the metal surface. These modifications in nano-topography may favor the adhesion of bone cells, accelerating the process of calcium phosphate deposition and, thus, promoting the osteogenic activity, as well as possibly modulating the adhesion of cytokines, such as interleukins (Moreira *et al.*, 2017; Almeida Alves *et al.*, 2016; Fialho and Carvalho, 2019; Fialho *et al.*, 2020).

The constant search for new biomaterials in modern implantology also arises due to the need to treat unfavorable conditions that interfere with the osseointegration process, such as peri-implantitis. There are currently several techniques, devices, and materials available to the dental clinician to control peri-implantitis, but sometimes their treatment does not prove as effective as expected. Within these control possibilities, in terms of

therapeutic approaches, air polishing seems to be a valuable tool in the mechanical debridement of supra and infra gingival biofilm, both in teeth and implants. (Hägi *et al.* 2015; Schwarz *et al.* 2015)

However, presently we still do not have scientific evidence on the effects of air polishing on tantalum surfaces, particularly regarding the impact of abrasiveness after applying different air polishing powders, specifically designed to treat peri-implantitis. In this way, it becomes relevant to study the effects of this therapeutic approach on this type of rehabilitating material. Eventually, it may benefit the dental clinical practice.

II. STATE OF ART

“Study of air polishing effect on tantalum surfaces”

1. ORAL REHABILITATION WITH DENTAL IMPLANTS

Teeth are essential sensory organs with several functions in different aspects of everyday life, such as chewing, speaking, and smiling, which make their role crucial to individuals' quality of life (Steele *et al.*, 2004). This can be directly affected across all ages when severe oral health problems, such as periodontal disease, caries, and dental trauma, lead to the inevitable tooth loss (Silva-Junior *et al.*, 2017).

Nowadays, many dental treatment choices are available to the clinician to save or either replace missing teeth. In cases where all requirements are present and when conservative treatments are no longer an option, dental implants are mostly recommended for oral rehabilitation of partially or fully edentulous patients (Buser, Sennerby and De Bruyn, 2016)

There are four substantial contributions to the foundations of implant dentistry: the development of many of the principles and surgical techniques used today, by E.J. Greenfield in 1913; the introduction of the first biocompatible material (Vitallium), by Alvin Strock in 1939; the use of titanium in dental implants as a biocompatible material with proved long-term success, by Per-Ingvar Brånemark in 1969, and the introduction of a roughened implant surface (one-piece implant with a titanium-plasma sprayed surface), by André Schroeder, in 1976 (Rudy *et al.*, 2008).

1.1. OSSEOINTEGRATION PROCESS

Brånemark, a Swedish orthopedic surgeon, used titanium in the 1950s to study blood flow in rabbit's tibiae and discovered that titanium components could bond irreversibly to the bone. This phenomenon was named "osseointegration". In 1981, Brånemark and his team published a 15-year follow-up study of their successful treatment cases with endosseous implants (Brånemark *et al.*, 1981). Since then, their work launched the use of titanium root-form dental implants to replace missing teeth, with promising

results and high success rates, as well as a new era of research on materials and shapes for dental implants.

Some authors, as Zarb and Koka (2012), have proposed another definition of osseointegration in recent years. They defined it as “a time-dependent healing process whereby clinically asymptomatic rigid fixation of alloplastic materials is achieved and maintained in bone during functional loading”. In terms of dental clinical practice, osseointegration is the biological anchorage of an implant into the alveolar bone. It is a complex process that takes several weeks to reach its final stage (Alghamdi, 2018). The first stage, called primary stability, begins immediately after implant insertion surgery and is ideally characterized by rigidity of fixation and the absence of micro-drive. Due to the injury caused in the bone jaw by implant insertion, blood cells, non-collagenous proteins, and bone growth factors are set free. They are activated at the implant's neighborhood to initiate bone repair. In the first month after surgery, a new vessel and primitive bone formation occur, through revascularization and remineralization processes, both on the implant's surface (contact osteogenesis) and on the surrounding bone areas (distant osteogenesis) – surface modeling. Over time, primary interlock decreases, as well as implant stability, at the benefit of a biological anchorage. This happens in the last stage of osseointegration and is characterized by bone remodeling. The primitive bone is replaced by mature bone, promoting a biological bonding at the interface between bone tissue and implant surface. After this stage, the bone-implant complex is perfectly adapted to support functional masticatory loads, which happens using an artificial dental crown (Kieswetter *et al.*, 1996; Davies, 2003; Parithimarkalaignan and Padmanabhan, 2013; Wang *et al.*, 2015) (Figure 1).

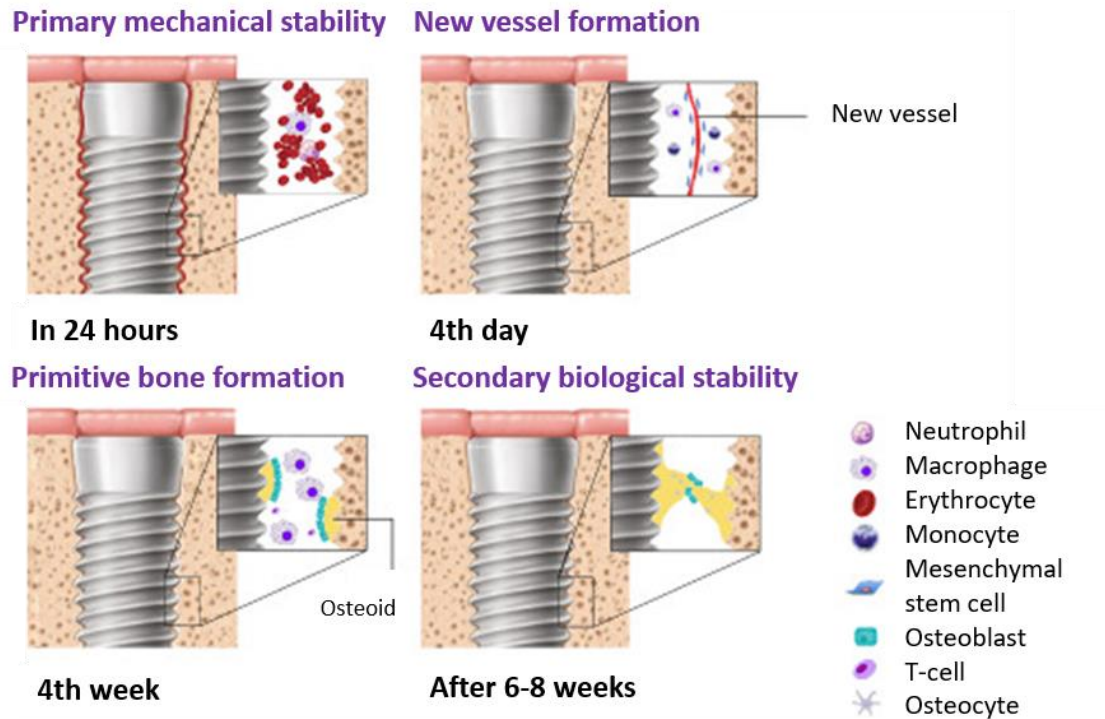


Figure 1 - Osseointegration as a complex chain of events. Search: Adapted without permission from Wang *et al.* (2015).

Several factors can directly affect bone formation and maintenance at the implant surface level, affecting the direct contact between bone and implant. Primary fixation and the absence of micro-movement after implant placement are crucial for long-term osseointegration achievement. Implant material, shape, design, and surface properties (roughness, hydrophilicity, surface energy) also have a remarkable influence in osseointegration, leading to the possibility of osteoconductive elements incorporation nano-topographic surface changes. The functional load is also vital because if it is not well planned in terms of timing and intensity, it can cause fibrous tissue formation around the implant. There are other factors to consider about osseointegration, such as patient's age, pre-existing health conditions, bone quality/quantity (volume, density, thickness), clinician's experience, and surgical technique issues. These factors can expose the implant bed to a more contaminated environment (Li and Mai, 2017).

There is no doubt that successful osseointegration is the basis for loading and long-term clinical success of functional endosseous dental implants. In this respect, Alberktson and colleagues (1986) have made an assessment of the long-term efficacy of

many dental implants used at that time and have proposed fundamental criteria to evaluate its success, such as: clinical immobility of the individual implant; when there is no evidence of peri-implant radiolucency at the radiographic evaluation; the mean vertical bone loss is less than 0,2 mm annually after the first year of loading; there is no persistent pain, discomfort, infection or other problems attributable to the implant and, finally, when there is at least 85% rate of success after the 5th year, as well as 80% after 10th year loading service.

One of the biggest challenges in implant dentistry, besides the long-term osseointegration, is to achieve and maintain the tight junction of healthy gingiva with the coronal portion of dental implants. This attachment of the soft tissue acts to provide a protective seal, preventing the development of bacterial colonization and future problematic conditions such as peri-implant mucositis or peri-implantitis (Lavenus *et al.*, 2012). As previously mentioned, several factors are considered fundamental for successful osseointegration. Among them stands out the implant biomaterial, which must satisfy specific requirements to provide long-term success to this approach.

1.2. BIOMATERIALS IN IMPLANT DENTISTRY

As any other biomaterial, endosseous dental implants are designed to stay inside the human body, in contact with living cells, and with chemically aggressive body fluids, such as saliva (Vogler, 1998). Besides an excellent corrosion resistance, implants must have biocompatibility with the host, which results in the ability to adapt with surrounding tissues and, as little as possible, undesirable local or systemic effects on the patient's health. In addition, the biomaterial must be bioinert, i.e., producing no response by the immune system (allergic reactions) and bioactive, forming a strong chemical bond between bone tissue and implant, thus enhancing the osseointegration process (Cristea, Ghiuță and Munteanu, 2015).

Furthermore, dental implants are submitted continuously to complex physiological loads, which occurs through masticatory movements, leading to wear and

fatigue phenomena (Barry *et al.*, 2015). In this context, the ideal implant should have physical and chemical properties that influence the clinical outcome and the prognosis of implant therapy, such as: adequate surface energy and wettability (hydrophilic surface); good fracture strength; sufficient toughness, corrosion, wear and fracture resistance, as well as microstructure and design favorable properties (Smith, 1993; Hermawan, Ramdan and Djuansjah, 2011; Narayan, 2012).

Over the years, several kinds of biomaterials have been used for manufacturing dental implants, ranging from metals, ceramics, carbons, polymers, and combinations of these. Polymers were soon discarded, having very little application in the dental implant industry due to its low fracture resistance, high softness, and flexibility (Gaviria *et al.*, 2014). Concerning ceramics, aluminum oxide (Al_2O_3), which is no longer commercially available (Andreiotelli *et al.* 2009), calcium phosphates, and, more recently, zirconia oxide (ZrO_2) have been used as implant biomaterials (Mihov and Katerska, 2010). Despite its aesthetic, biocompatible, and bioinert properties, one of the most significant drawbacks of choosing zirconia dental implants is low-temperature degradation, also known as aging. This can potentially interfere with the material's mechanical properties when degraded, reducing its strength, density, and toughness (Sanon *et al.*, 2013). In addition, zirconia tends to be far stiffer than bone (Young's modulus of elasticity of 160–240 GPa versus 15–30 GPa), raising doubts about its mechanical compatibility (Griggs, 2017). Another major limitation of choosing zirconia is its lack of bioactivity, which does not favor the osseointegration process (Schünemann *et al.*, 2019). Yet, there haven't been many clinical studies into these products' long-term success, making them not an excellent implant biomaterial (Hashim *et al.*, 2016; Cionca, Müller and Mombelli, 2015).

The excellent biocompatibility, corrosion resistance, strength, and low density of titanium for implant applications, made this metallic biomaterial widely used and recognized in the past decades as the “gold-standard”. In this sense, high survival rates were reported in two systematic reviews after a 5-year follow-up for titanium implants supporting single crowns (97%) (Jung *et al.*, 2012) or bridges (93%) (Pjetursson *et al.* 2012). These implants can be manufactured both from commercially pure titanium (cp-Ti) or alloys, such as titanium–aluminum–vanadium (Ti–6Al–4V), which it has better

physical and mechanical properties in comparison to cp-Ti (Pieralli *et al.*, 2017; Jorge *et al.*, 2013). When titanium and its alloys are exposed to air, there is a reaction with the oxygen that forms an oxide layer – TiO₂, which enhances the biological response and the resistance to corrosion (Alves, Cavaleiro and Carvalho, 2016), as well as the bone, soft tissue and proteins apposition in the metallic surface (Triplett *et al.*, 2003; Jorge *et al.*, 2013).

1.3. IMPLANT FAILURE

As mentioned before, biomaterials must be durable and usable from a prosthodontic point of view. Most importantly, they have to be biocompatible with the host's tissues, thus nontoxic and non-allergic to local or systemic patients' health. Despite the successful outcomes with titanium in implant therapy, biological and technical complications still occur in some patients who develop signs and symptoms of implant failure, before or after prosthetic rehabilitation (Chaturvedi, 2013). (Figure 2).



Figure 2 – Soft and hard tissue recession around dental implants leading to poor aesthetics, inflammation/infection (peri-implantitis) and, ultimately, implant loosening. Adapted without permission from Lindhe and Lang (2015).

The allergic reactions induced by titanium have been, in some cases, an unwelcome clinical finding, as reported by Egusa *et al.* (2008), as well as the development of peri-implantitis and subsequently poor aesthetics due to soft–hard tissue margin recession. In the study by Sánchez-Siles and colleagues (2015), besides other parameters,

peri-implant bone loss and the presence of peri-implantitis were evaluated in 400 patients who received implant-based prosthetic restorations using 1244 implants. They reported peri-implantitis in a total of 120 dental implants, which makes an approximate rate of 9.6% of implant failure.

In recent years, scientific evidence points to several limitations for biomedical applications of the commercially pure titanium (cp-Ti) and its alloys, such as Ti-6Al-4V, an alpha-beta titanium alloy that contains alpha stabilizer aluminum – Al – and beta stabilizer vanadium – V (Elias *et al.*, 2015; Zhang and Chen, 2019). These limitations are mainly due to the lower mechanical and wear resistance and the possibility of release of ions and/or metallic particles from the implant surface, i.e., vanadium and aluminum, which affect the surrounding living cells/tissues (Gepreel and Niinomi, 2013). The accumulation of wear toxic particles can be associated with several common effects like local fibrosis and/or necrosis; increased activation and production of macrophages and inflammatory cytokines; increased number of osteoblasts and fibroblasts, which may interfere with the function of the osteoclasts, and, ultimately, leading to the loss of alveolar bone and, consequently, loss of the previous osseointegrated implant (Bitar and Parvizi, 2015; Veronesi *et al.*, 2017)

Another major drawback of titanium dental implants is its low bioactivity, demonstrated by the slow osseointegration process. This allows the entrance of multiple microorganisms, as well as bacteria colonization into the peri-implant space, leading to the late infection of the adjacent tissues, bone resorption, and, consequently, a decreased mechanical anchorage of the implant – peri-implantitis process – which commonly ends in poor aesthetics, due to soft and hard tissue recession and implant loosening (Chaturvedi, 2013; Lindhe and Lang, 2015; Alves, Cavaleiro and Carvalho, 2016; Fialho and Carvalho, 2019;).

Therefore, endosseous dental implants' unequivocal success drives the need for continuing refinements in implant designs and biomaterials to achieve osteoinductive properties. The use of bioactive biomaterials, allied to surface modification techniques, will enhance the osseous growth, hence the long-term success of osseointegrated implants (Davies, 2003).

2. SURFACE MODIFICATION TECHNIQUES

In the past two decades, various surface modification approaches have been proposed and studied to improve implant osseointegration. It enhances interaction with biological fluids and accelerates peri-implant bone regeneration. The deposition of bioactive surface coatings onto the implant allows the delivery of drugs or bioactive factors to the surrounding alveolar bone. In this way, the increase of osteoblast differentiation and mineralization will be possible, promoting implant osseointegration (Alghamdi, 2018) (Figure 3)

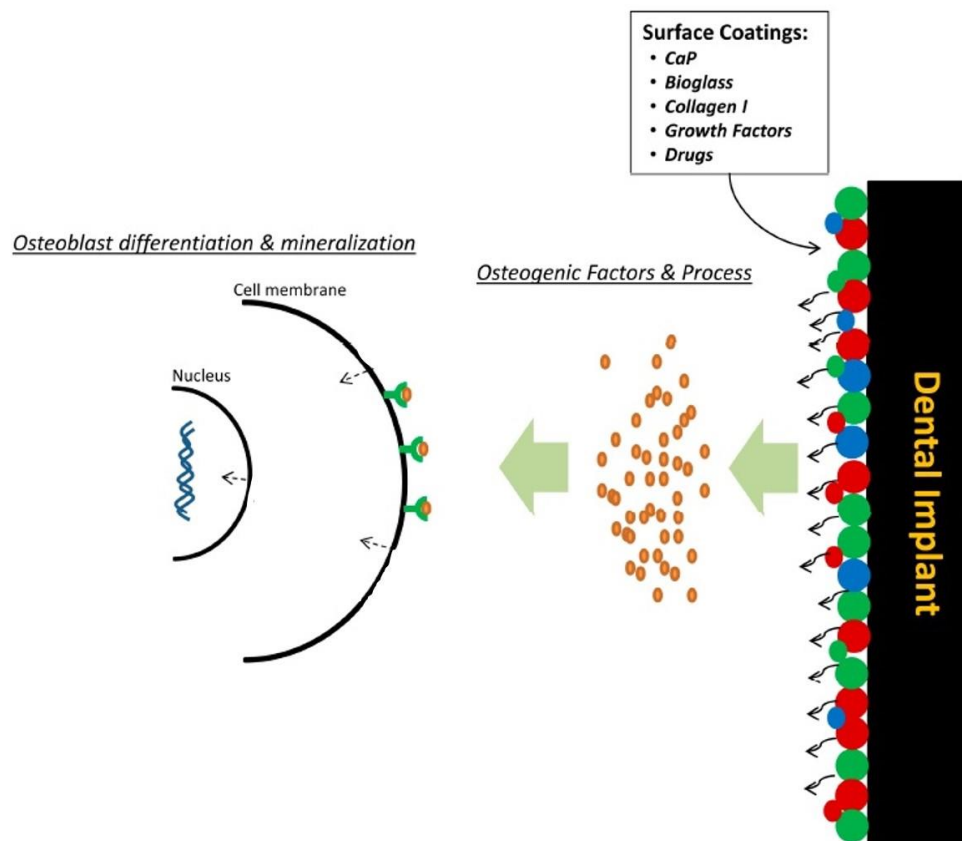


Figure 3 - Biological benefits of surface coatings on dental implants. Adapted without permission from Alghamdi (2018).

Although the selection of the rehabilitating material is essential, its surface characteristics are, in the same way, decisive. In this sense, to further stimulate a good

response from the host tissue, where the dental implant is placed, the surface must be functionalized. This can occur in two ways: modification of topography and changing the surface chemical composition (Simka *et al.*, 2013; Liu *et al.*, 2015; Wu *et al.*, 2015). One of the objectives of this experimental work is the modification

One of the objectives of this experimental work is the modification of tantalum surfaces to be porous and enriched with osteoconductive elements so that they can exponentiate osseointegration. Topography and chemical surface modification will be described next.

- **Topography modification**

The bone tissue has been described as a highly porous solid surface on the micrometer scale (Mour *et al.*, 2010). When a dental implant surface has a similar structure to the bone (porous structure), a greater connection between bone and implant is achieved (Liu *et al.*, 2015;). Therefore, there is a need for surface modification at the topography level, which increases the contact area with adjacent tissues, as well as the mechanical retention, adhesion, proliferation, and differentiation of osteoblasts, thus accelerating the osseointegration process (Zhang and Webster, 2009; Minagar *et al.*, 2012).

Compared to the bone structure, Ta has a higher density (16.86 g/cm^3), making it too rigid for biomedical applications. To overcome this limitation, porous Ta structures had been explored, inducing a significant decrease in the elasticity modulus (from 186 GPa to 1.3-10 GPa) and, thus, improving its acceptance by the human body. Bearing in mind that bone elasticity's modulus is around 0.1-18 GPa, porous Ta is considered very similar to this tissue, making it a desirable solution to the biomedical field (Liu *et al.*, 2015).

- **Chemical composition modification**

Several biochemical deposition techniques have been explored in the last decades (Junker *et al.*, 2009; Jonge *et al.*, 2008). Among them, there is the incorporation of osteoconductive elements, such as calcium phosphate (CaP). This is a very recurrent

practice and has received significant attention due to: their chemical similarity to the natural bone, allowing to form a chemical bond with the bone and in a faster way; it induces a favorable biological response in the body, and the fact that coatings can be applied along the implant surfaces by different industrial processing methods (Junker *et al.*, 2009; Wang *et al.*, 2015).

Surfaces enriched with Ca are promising in terms of dental implants since they promote an increase in osseointegration and reduce rehabilitation time. Recent scientific literature (Ribeiro *et al.*, 2015) showed that the incorporation of Ca in oxidized surfaces increases the viability of fibroblasts (responsible for the formation of connective tissue), their metabolic activity, as well as the adhesion of osteoblasts (accountable for bone mineralization) to those surfaces.

To obtain a porous surface with incorporated osteoconductive elements, it is necessary to resort to techniques that produce a physical and chemical modification in the material's surface, such as electropolishing, chemical attack, or anodization (Alves, 2013).

The anodizing process, together with the deposition of nanoparticles by magnetron sputtering, are some of the techniques previously mentioned that were used in this study and, therefore, are discussed in more detail below.

2.1. ANODIZATION

Anodization, or anodic oxidation, is a simple and industrially inexpensive process studied in the last decade due to its ability to increase the natural oxide layer's thickness on metal parts' surface. This electrochemical process can increase corrosion and wear resistance, serving cosmetic, decorative, biomedical, and/or other industrial purposes (Lee and Park, 2014; Uslu *et al.*, 2020).

In the anodization process, there is an application of a potential difference between the anode, which is the metal to be anodized (in this case, tantalum), and the cathode,

which is typically an inert material (i.e., platinum, carbon, graphite). Consequently, there will be the oxidation of the anode and the cathode reduction, which coincides in an electrolytic medium (Nageh *et al.*, 2008; Uslu *et al.*, 2020).

Basically, due to the potential difference applied, an electric field is formed, allowing the migration of oxide ions (O^{2-}) generated at the electrolyte/anode interface within the metal attached to the anode. This process, illustrated in Figure 4, leads to forming an oxide surface layer, which can be compact or porous (Nageh *et al.*, 2008; Momeni *et al.*, 2016).

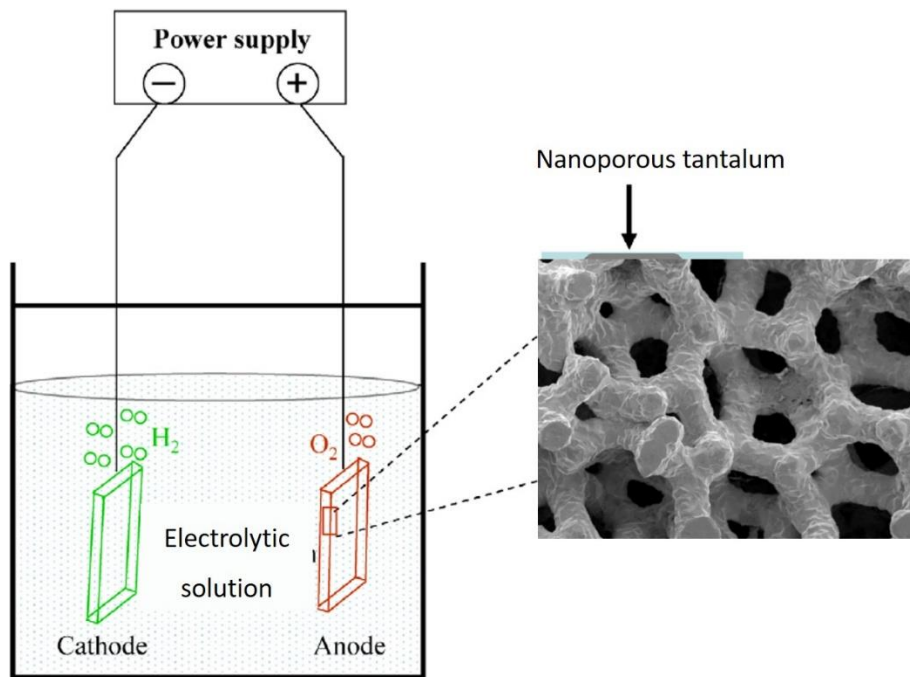


Figure 4 – Schematics of anodization of a tantalum setup, where the final product is a nanoporous tantalum surface. Adapted without permission from Neupane *et al.* (2009) and Maccauro *et al.* (2009).

In scientific literature, several studies are focusing on the anodization process. Wang *et al.* (2014) reported changes in the oxide layer properties, thus producing nanostructured surfaces, when parameters such as anodization potential, electrolyte concentration, duration, temperature, pH, among other electrochemical parameters, varied.

With respect to the anodization potential, this electrochemical process can be potentiostatic by applying continuous potential and galvanostatic by applying a direct current (the potential is variable). In the potentiostatic mode, the anodic oxide formation can be directly controlled by the previously mentioned anodizing parameters (Casado *et al.*, 2019; Wang *et al.*, 2014).

The electrolytic solution, where anodization occurs, influences all the process, once its composition can be responsible by anodization's efficiency and speed. The electrolyte must be conductive to occur formation of the oxide, caused by the migration of O^{2-} and OH^- ions. For this purpose, the selection of strong acids as sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), and hydrofluoric acid (HF) (Minagar *et al.*, 2012; Wang *et al.*, 2014) it is usual.

The formation of pores in the anodization process can occur by two different methods: electric field assisted dissolution (EFAD) or by plasma electrolytic oxidation (PEO), also known as micro arch oxidation (MAO) (Wang *et al.*, 2015). These two techniques will be described in more detail below.

2.1.1. ELECTRIC FIELD ASSISTED DISSOLUTION (EFAD)

EFAD is a simple, cost-effective technique that is used for micro and nano-structuring of metal surfaces. When anodization begins, a compact anodic oxide layer is formed on the metal surface. EFAD allows the selective dissolution of the anodic surface and stings on the lower compact metal layer to start to appear. The continuous dissolution of the anodic oxide transforms nanoporous into nanotubes. During this process, metal ions drift into a glass matrix under the application of some parameters, such as: moderately to elevated temperature (from 200 °C to 500 °C); an applied electric field; a potential ranging from 300 V to 1200 V, and an acidic electrolyte (Sancho-Parramon *et al.*, 2007; Janicki *et al.*, 2018; Okorn *et al.*, 2019).

2.1.2. MICRO-ARCH OXIDATION / PLASMA ELECTROLYTIC OXIDATION (MAO / PEO)

MAO, also known as PEO, is a similar process to anodization, defined as a high potential anodic oxidation process assisted by plasma. As mentioned, higher voltages are applied in the electrochemical setup, resulting in a more intense electrical field. Although they occur in a more reduced number, sparks are more intense, resulting in a more crystalline/ceramic type surface (Wang *et al.*, 2015).

In this process, the formation of pores happens as a result of the use of high potentials, which causes the break of the oxide and the collapse of the anodic surface, thus forming a surface with disordered micropores (micrometer order) (Liu *et al.*, 2015; Wu *et al.*, 2015). Each oxide has its collapse limit. In Ta's case, this potential is approximately 150 V. It seems that the electrolyte selected does not reveal such a fundamental role in this process since it is only responsible for the passage of current and the transport of ions. Therefore, it is possible to resort to any type of electrolyte (Wang *et al.*, 2015).

In comparison to EFAD, MAO / PEO process has several advantages, making it well succeed in Ta surface modification. As mentioned before, pores' formation does not depend on the electrolyte used, being possible to use any type of it. Therefore, the incorporation of osteoconductive elements in the electrolytic solution is possible and facilitated. In the study of Wang *et al.* (2016), tantalum oxide coatings were formed on pure tantalum by micro-arc oxidation (MAO) in electrolytic solutions of calcium acetate β -glycerophosphate disodium. These authors investigated the effect of the applied potential and revealed an increased Ca and P concentration in the sample when the potential was increased. According to this study, the higher voltage is also responsible for increasing the electrolyte temperature and for the increased thickness of the formed anodic layer.

2.2. ZN-ZNO NANOPARTICLES DEPOSITION BY MAGNETRON SPUTTERING

Magnetron sputtering is a high-rate vacuum coating technique that falls under the category of physical vapor deposition (PVD) and can be used to prepare a variety of types of materials, including metals, alloys, and other materials, with a thickness up to millimeter, using a specially formed magnetic field applied to a diode sputtering target. Some of the many advantages of magnetron sputtering are the simple equipment required (low-cost technique); the possibility of high deposition rates; the control of the production of metal nanoparticles (NPs) in size, shape, and distribution; the ability to produce homogeneous and extensive surface coverage, and NPs strong adhesion (Tudose *et al.*, 2019; Uhm *et al.*, 2013).

The primary mechanism of the magnetron sputtering coating process, shown in Figure 5, consists of a target or a metal precursor (correspondent to the desired material to be deposited) bombarded with high-energy ions of inert gases, such as argon or helium. The forceful collision of these energetic ions with the target ejects target metal atoms into space. These metal atoms are then deposited on the substrate material, forming a metallic film (Hassan, 2018; Tudose *et al.*, 2019).

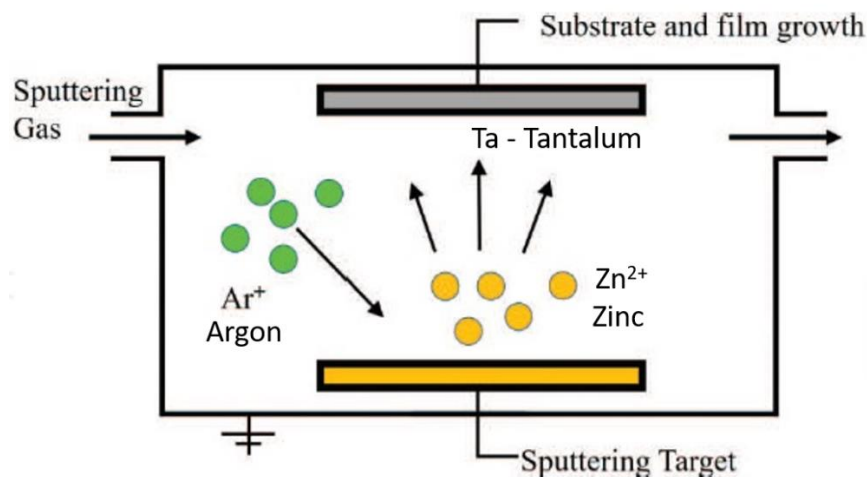


Figure 5 - Magnetron Sputtering process diagram with the representation of zinc nanoparticles deposition on tantalum. Adapted without permission from Shi (2018).

The adhesion of different kinds of bacteria to an implant's surface has been reported as a problematic condition for this rehabilitative approach's long-term success. Therefore, some antibacterial surfaces have been developed to directly prevent bacterial adhesion, so that they could kill all bacteria (bactericidal), remove dead bacteria (bacteria-release), and/or be resistant to the bacterial attachment (bacteria-resistant) (Hasan, Crawford and Ivanova, 2013). One of the chemical elements incorporated in these types of surfaces is zinc (Zn), under the form of zinc oxide nanoparticles (ZnO). These kinds of NPs have been considered antibacterial agents once they can cause bacteria's death through several biological mechanisms (Pasquet *et al.*, 2014; Agarwal *et al.*, 2018).

In this sense, nanoporous tantalum surfaces can receive Zn or ZnO nanoparticles by different surface treatments, such as anodization and magnetron sputtering. In the last one, the release of argon ions (Ar^+) against a pure zinc target (Zn) removes zinc atoms (Zn^{2+}) from it, which immediately oxidize (zinc passivation), thus forming a deposition of zinc oxide NPs (ZnO) into the substrate (Dave *et al.*, 2016).

As mentioned previously, there is a growing need to optimize bioactive and biomechanical properties of biomaterials and devices. Besides the use of surface modification techniques, there has been an interest in developing new promising materials, such as tantalum (Ta). This bioactive metal is actually considered an attractive candidate in the biomedical and tissue engineering fields, with multiple applications (Chen *et al.*, 2017).

3. SURFACE CHARACTERIZATION TECHNIQUES

Surface properties are essential for the performance of components used in biomedical devices, having a unique role in its biocompatibility, corrosion resistance, wear, or fracture resistance. As mentioned before, surface modification techniques are important to accomplish the desired performance of a biomaterial. Additionally, with equal importance, surface characterization techniques are applied later to surface modification ones, being required to obtain more detailed information about physical morphology, chemical properties, and the expected behavior of the biomaterial.

The next sections provide a brief review of the surface characterization techniques selected for this *in vitro* study. The essential information given by each method is schematized in the following figure – Figure 6.

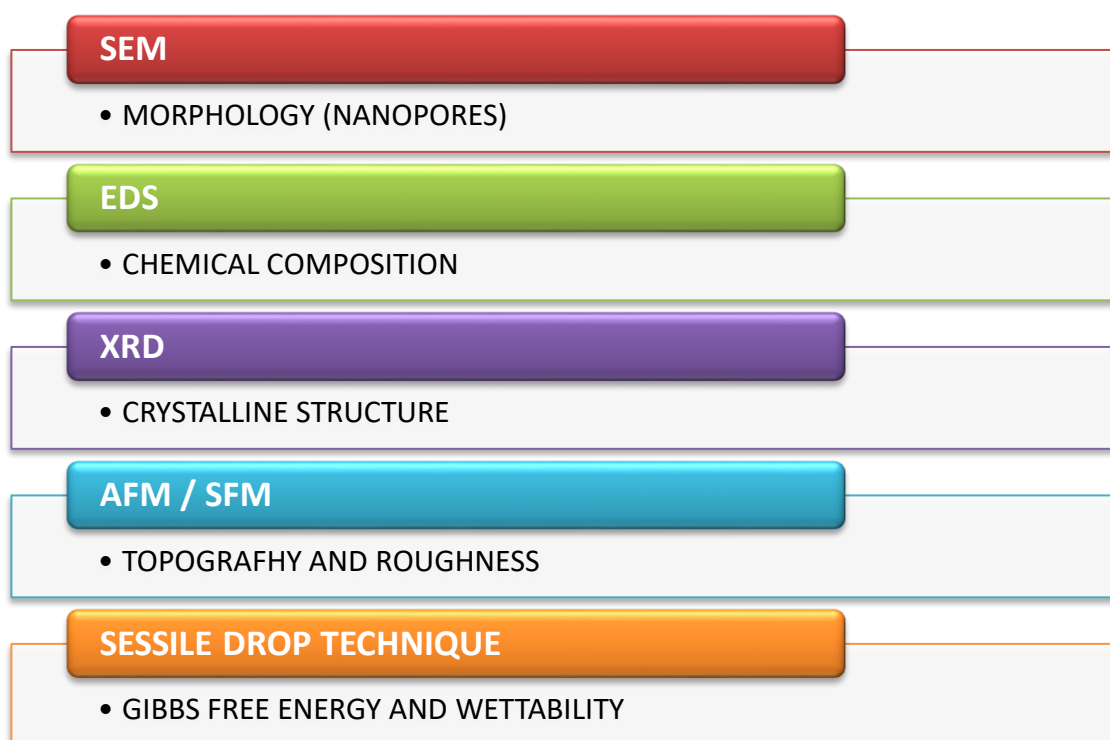


Figure 6 - Scheme with the summarized purpose of the selected surface characterization techniques for this *in vitro* study.

3.1. SEM/EDS - SCANNING ELECTRON MICROSCOPY (SEM) WITH ENERGY DISPERSIVE SPECTROSCOPY (EDS)

3.1.1. SEM

Scanning electron microscopy (SEM) is a method for high-resolution imaging of surfaces by scanning the surface with a focused beam of electrons under vacuum conditions. The electrons interact with atoms in the sample, producing various signals that contain information about the surface morphology and composition of the sample (Narayan, 2012).

3.1.2. EDS

Energy-dispersive X-ray spectroscopy (EDS) is a chemical microanalysis technique used in conjunction with SEM. It relies on detecting some source of X-rays emitted from the sample during the bombardment by an electron beam to characterize the elemental composition of the sample. Qualitative and quantitative chemical analysis information can be obtained with this technique so that the chemical composition and the quantity of each element present in the sample can be explored (Narayan, 2012).

3.2. X-RAY DIFFRACTION (XRD)

X-ray diffraction (XRD) is a powerful non-destructive technique that provides detailed information about the crystallographic structure, chemical composition, and materials' physical properties. XRD works by irradiating a crystalline material with incident X-rays, occurring its diffraction, and then measuring the intensities and scattering angles (diffraction angles) of the X-rays that leave the material. As well as crystalline phase identification, XRD also yields information on how the actual structure deviates from the ideal one, owing to internal stresses and defects (Bunaciu *et al.*, 2015).

3.3. ATOMIC FORCE MICROSCOPY (AFM) OR SCANNING FORCE MICROSCOPY (SFM)

Atomic force microscopy (AFM) is a form of scanning probe microscopy (SPM) used to map the topography and study the properties of one material on a nanoscale. In this technique, a sharp probing tip (<10 nm), supported on a flexible cantilever, is scanned across the sample at a very short distance to obtain information about the sample's surface. This information results from the tip's action, which can touch or not the sample, and gives rise to either attractive or repulsive forces. Those forces reveal the sample's physical topography and roughness and allow measurements of its physical, magnetic, or chemical properties. In this context, the AFM technique is rapidly emerging as a gold standard technique to collect more detailed information about surface and interface properties (Narayan, 2012; Kyeyune, 2017; Marrese, Gaurino and Ambrosio, 2017).

3.4. SESSILE DROP TECHNIQUE

The sessile drop technique is a method used to characterize solid surface energies, where a droplet of liquid, with known surface energy, is placed over a solid sample. To calculate the solid surface energy, some parameters are used, such as the shape of the drop, which is controlled by surface tension; the surface energy of the probe liquid, being required the use of different liquids, and specifically the contact angle (θ) between the solid surface and the interface. The sessile drop method is a geometric method for the determination of the static contact angle. Through this measurement is possible to determine the surface's wettability by oil and water, just being necessary a smooth, homogeneous surface. (Tiab, 2012; Wei and Zhang, 2012; Rudawska, 2019;).

This technique allows the evaluation of the wettability and Gibbs free energy of a surface. Wettability (Figure 7) consists in the degree to which a liquid will maintain contact with a solid surface and is considered a vital surface property of biomaterials, once it can influence the protein adsorption/desorption and induce cell attachment (van Oss, 1997). A material is considered hydrophilic when it has a contact angle less than

90 °, and a hydrophobic material has a contact angle greater than 90 °, thus considering 90 ° the hydrophilicity limit (Murmur *et al.*, 2017). In its turn, the Gibbs free energy of the surface is related to the number of free bonds on the material's surface.

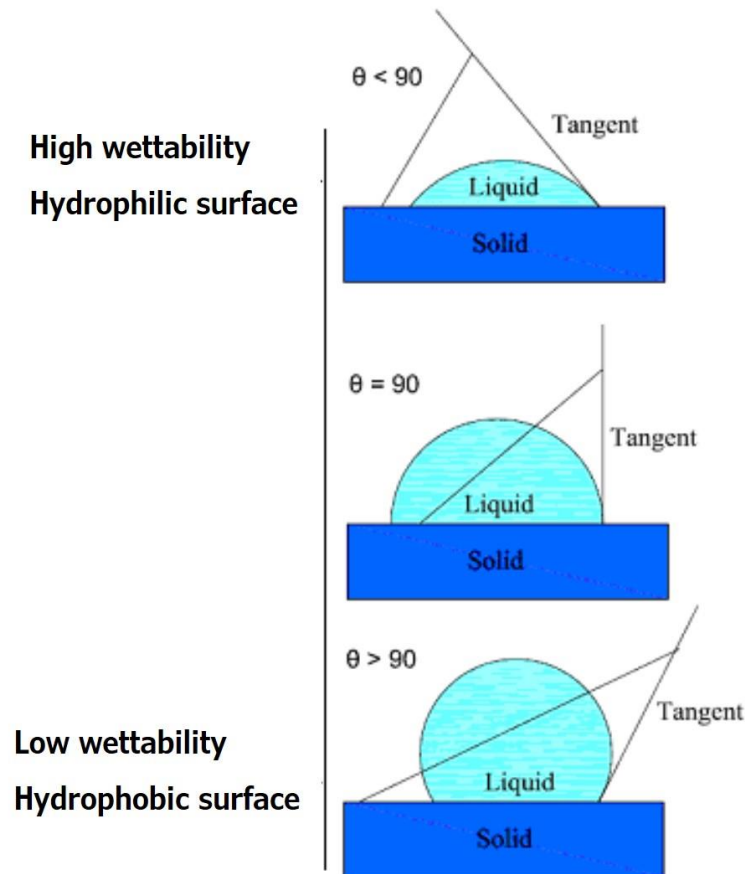


Figure 7 - Diagram of wettability and correspondent contact angles. Adapted without permission from Fathi-Azarbayjani, Jouyban and Chan, 2009.

It is known that as greater is the wettability and Gibbs free energy, the greater is the interaction of the surface with the surrounding environment, which, in the case of dental implants, favors the osseointegration process (Rupp *et al.*, 2014). Concerning tantalum surfaces, these characteristics will help to predict how the implant, or other biomedical devices, will interact with the bone and body fluids.

4. TANTALUM

4.1. CHARACTERISTICS

Tantalum (Ta) is a rare blue-grey metal with unique properties that have been in clinical use since the late 1930s. The overall excellent results that present granted a significant contribution to modern medicine, allowing millions of people to live longer and healthier

In 1802, the Swedish chemist and mineralogist Anders Gustaf Ekeberg (1767-1813) officially discovered and named tantalum (previously known as *tantalium*), in an allusion to the Greek mythology. Ekeberg referred to *Tantalus*, one of Zeus's sons and a villain, who was eternally tantalized and condemned by the gods to starve and be in endless thirst, yet surrounded by fruit and water (Friend, 1951). In this sense, Ekeberg wrote, "This metal I call *tantalum* (...) partly in allusion to its incapacity, when immersed in acid, to absorb and be saturated" (Greenwood and Earnshaw, 1997). Tantalum was only isolated in 1820 by Jöns Berzelius (Narayan, 2012). The first pure samples were obtained by the German scientist Werner von Bolton in 1903 (Maccauro *et al.*, 2009).

As already referred, tantalum is a rare element with the atomic number 73 in the Periodic Table, with a greyish-silver color, lustrous, very hard, and heavy. Today, this transition metal is found in the crust of the earth together with niobium. It is primarily obtained from the minerals columbite [(Fe, Mn, Mg)(Nb, Ta)₂O₆], tantalite [(Fe, Mn)(Nb, Ta)₂O₆], and euxenite [(Y, Ca, Ce, La, Er, U, Th)(Nb, Ta, Ti)₂O₆] (Maccauro *et al.*, 2009). According to *Minerals Commodity Summaries*, published by the United States Geological Survey (2015), Rwanda is the world's largest tantalum producer, accounting for over one-third of the mineral traded on the international market (Figure 8 and Figure 9).



Figure 8 – Tantalum samples. Adapted without permission from The Editors of Encyclopaedia Britannica (2018).

atomic number	73	180.948	atomic weight
symbol	Ta		acid-base properties of higher-valence oxides
electron configuration	[Xe]4f ¹⁴ 5d ³ 6s ²		crystal structure
name	tantalum		physical state at 20 °C (68 °F)

 Transition metals	 Solid
 Body-centred cubic	 Weakly acidic

Figure 9 - Tantalum representation in the Periodic Table. Adapted without permission from The Editors of Encyclopaedia Britannica (2018).

Tantalum exists in two crystalline phases: Alpha-Tantalum (α -Ta), which is a stable, body-centered-cubic structure, and Beta-Tantalum (β -Ta), which has a metastable tetragonal orientation. The properties of each phase are very different. The α -phase, which is almost entirely found in bulk tantalum, is responsible for its stability and good mechanical, thermal, and chemical properties, such as hardness, high density, good ductility, a high melting temperature (melting point of 3017 °C), and chemical resistance

to different corrosive environments. In its turn, the β -phase has a higher resistivity (170-210 $\mu\Omega\text{cm}$, against 15-60 $\mu\Omega\text{cm}$ of α -Ta), is more brittle, and is thermally unstable at temperatures above 750°C. As a result, it readily transforms into the α -form at 750 °C-1000 °C (Lee *et al.*, 2004; Sudarshan and Stiglich, 2006; Myers *et al.*, 2012).

As mentioned before, in allusion to Ekeberg's words, tantalum is highly acid-resistant. In fact, at temperatures less than 150 °C, tantalum is reactive only with concentrated hydrofluoric acid and other acids containing free fluoride ions (Considine, 1974). Tantalum has an excellent resistance to chemical attack by almost all organic and inorganic acids, aqueous salt solutions, organic solvents, and various combinations of these agents. The high affinity for oxygen and, in particular, the chemical stability of its passive oxide (Ta_2O_5), found in an impermeable surface coating, are the main reasons for its acid-resistance (Holleman, Wiberg and Wiberg, 2007).

Overall, besides the optimal chemical and mechanical properties, such as excellent corrosion and wear resistance, tantalum is a metal whose elastic modulus, high frictional properties, and biocompatibility make it an ideal structure to promote adequate bone regeneration. Besides, its inert (does not react with body fluids) and bioactive behavior *in vivo* makes this material desirable for biomedical and tissue engineering applications (Chen *et al.*, 2017; Zeng *et al.*, 2017). In this sense, Stiehler and colleagues (2008) reported in their study a significantly higher mesenchymal stem cells (MSCs) proliferation in tantalum, comparing with titanium and chromium surfaces. In the end, they concluded that Ta surfaces are a biocompatible material and a useful alternative for Ti surfaces in bone implants.

4.2. TANTALUM OXIDE AND NANOPOROUS TANTALUM OXIDE

Tantalum has a high chemical affinity with oxygen, easily forming a self-passivation layer on it, allowing an unparalleled corrosion resistance, including in a highly acidic environment. Due to this affinity, tantalum can exhibit several oxidation

states and, consequently, form several oxides. The most common oxide is a dense, non-porous oxide coating called tantalum pentoxide (Ta_2O_5), which can reveal an excellent chemical and thermodynamic stability, a high dielectric constant (useful as capacitors components), high reflection index (valid in the camera lenses glass) and high energy surface (allows strong chemical bonds). The oxide layer formed makes tantalum unique because it becomes resistant and inert to body fluids. In addition, bioactive behavior is increased through bone-like apatite production, thus enhancing cell adhesion of soft and hard tissues. In this way, tantalum pentoxide (Ta_2O_5) efficiently promotes osseointegration, being currently recognized as one of the essential compounds considering biomedical applications, focusing on modern Implantology. (Cardonne *et al.*, 1993; Kato *et al.*, 2000; Maccauro *et al.*, 2009; Sousa, Silva and Guerra, 2013; Cristea, Ghiuță and Munteanu, 2015).

Implants with tantalum oxidized coatings, such as titanium implants with surface modification, are considered by several authors as an innovation for Implantology, once osteoblasts can interact *in vivo* with the oxide layer, thus forming a strong chemical bond (bioactivity) and, consequently, avoid bacteria adhesion/colonization (Minagar *et al.*, 2012; Wang *et al.*, 2014).

On the other hand, more recently, it has been given relevance to a nanoporous tantalum pentoxide (Ta_2O_5) that combines two fundamental characteristics to achieve a high potential for osseointegration. In this type of tantalum, the presence of a mechanical interlocking due to surface topography (pores) favors bone formation through the pores. In its turn, the surface chemistry allows the biochemical bonding between bone and implant (Uslu *et al.*, 2020). Nanoporous tantalum oxide surfaces can be easily fabricated by a low-cost electrochemical process called anodization (Kim *et al.*, 2008; Macak *et al.*, 2007). Recently, Uslu *et al.* (2020) published the first evidence regarding nanoporous tantalum surfaces obtained after anodization, suggesting this surface as a promising solution for biomaterial applications.

4.3. APPLICATIONS

In 1905, metallic tantalum became commercially used as a filament for electric lamps due to its high melting point (3017 °C), thus replacing fragile carbon filaments. Its use lasted for about six years, when then tungsten, which has an even higher melting point, started to be used (Friend, 1951; Weeks, 1933).

Since its introduction, tantalum has been widespread in several areas, whether in its pure form, its oxide, or combined with other materials (alloys), presenting an ample variety of applications. Currently, elemental tantalum is vital for electronics industries in the manufacture of precision electronic components. The use of this metal in capacitors has contributed to the miniaturization of electronic circuits. The exceptional stability and reliability in a wide range of temperatures and frequencies allows tantalum capacitors to provide high capacitance in a small volume, making it particularly important to produce smartphones, video game systems, computers, and an extensive range of other consumer electronic devices. The military, aerospace, automotive, oil, and gas exploration industries also benefit from recognized, high-performance tantalum capacitors. This refractory metal is also used to create high-power resistors, which is another electronic component commonly used in heavy-duty equipment across various industries and sectors. Outside of electronics, tantalum is combined with steel and other metals to produce different alloys that are strong and ductile, with high melting points. These superalloys are used to produce components for jet/airplane engines, nuclear reactors, and missile parts. In addition, the chemical inertness of tantalum makes it a valuable element to the fabrication of laboratory equipment for chemical processes (Sousa *et al.*, 2013; Narayan, 2012; Maccauro *et al.*, 2009; Cardonne *et al.*, 1995) (Figure 10).

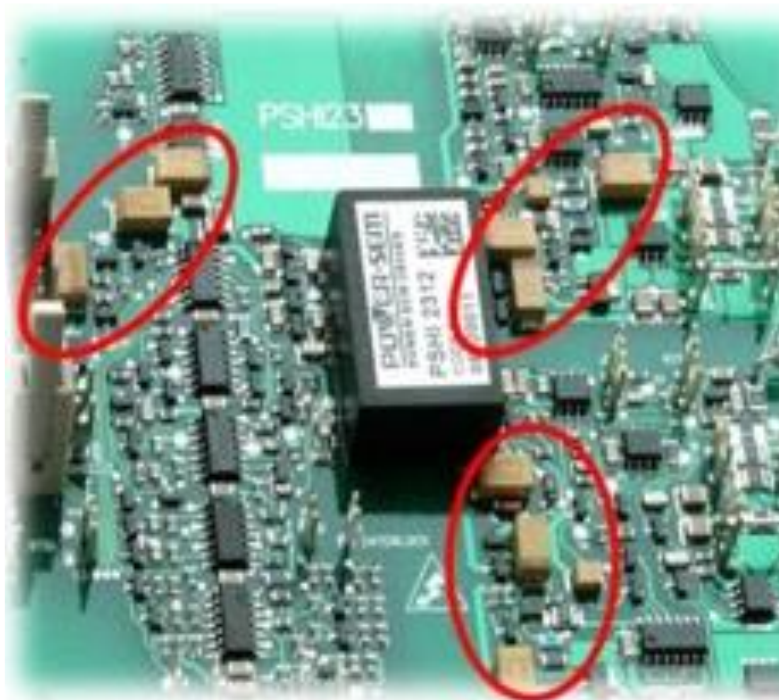


Figure 10 - Electrical circuit board with tantalum capacitors colored by yellow. Adapted without permission from Niu, Chen and Xu (2017).

Regarding the biomedical applications, since the first half of the 20th-century tantalum has been quite desirable, especially in the surgical field, as a result of its corrosion resistance, which is combined with its ductile capacity and the relative simplicity of manufacture into elaborated shapes (Sousa *et al.*, 2013).

In 1940, Burke was one of the first authors to introduce tantalum as a biomaterial, namely as a component of surgical sutures, reporting no reaction produced by tantalum wire in soft tissues. In addition, inflammatory changes were not found either in the bone or in other tissue when tantalum plates had been implanted in dogs and rabbits' bones (Burke, 1940).

Considering the modern medical applications, tantalum is used in nearly every aspect of medical electronics, both in extracorporeal and implantable devices such as insulin pumps, cardiac pacemakers, cardioverter defibrillators (ICDs), cochlear implants, or nerve stimulators. Specifically, the good mechanical properties (fracture toughness and workability), biocompatibility, and inertness make this metal safe and an interesting choice to be used in several medical fields, including surgical procedures and surgical

equipment. In this sense, tantalum has been successfully applied in the next areas and practices: surgical sutures (for both monofilament and multifilament suture wire) (Burke, 1940); neurological surgery (nerve regeneration) (Almansoori *et al.*, 2020); plastic and reconstructive surgery (repair of abdominal hernias and other soft tissue defects) (Shankaran *et al.*, 2010); vascular surgery (connecting clips, intraarterial and biliary stents - due to its biocompatibility and ductility) (Strecker *et al.*, 2007; Ferro *et al.*, 1995); orthopedics and dentistry (cranial plates, artificial joints, screws and pins to fix broken bones, prosthesis, endosseous implants), among other biomedical applications (Sousa *et al.*, 2013; Black, 1994; Niinomi, Nakai and Hieda, 2012; Levine *et al.*, 2006) (Figure 11).



Figure 11 - Tantalum cranial plates/screws, artificial joint, and tantalum sheet. Adapted without permission from T.I.C (2018) (<https://www.tanb.org/index>)

Tantalum can also be used as an X-ray marker during stent insertion surgery because of its low magnetic susceptibility and excellent radiopacity. This type of marker is used to track objects within the body, making them highly visible in X-ray analysis. (Hermawan, Ramdan and Djuansjah, 2011). Aronson and colleagues (1985), who evaluated the biocompatibility of two types of radiopaque tantalum markers (pin and spherical markers), found no adverse macroscopic reactions by X-ray exam. They have confirmed the bioinertness of tantalum, as well as its suitability for use as skeletal and soft tissue radiographic markers (Aronson, Jonsson and Alberius, 1985) (Figure 12).



Figure 12 - Radiographic image of tantalum markers inside the dotted yellow circle. Adapted without permission from Park *et al.* (2019).

Although the advantages stated, solid Ta's biomedical applications have been limited because of its high mechanical strength and density. To overcome this difficulty and improve the in vivo bioactive tantalum properties, porous tantalum was developed after the deposition of elemental tantalum onto a reticulated carbon-fiber skeleton (Bobyne *et al.*, 1999). This process is known as chemical vapor deposition/infiltration. Porous tantalum, currently marketed as Trabecular Metal (Zimmer Holdings), consists of a three-dimensional honeycomb interconnected structure with similar characteristics to the spongy human bone, designed for bone and blood vessel ingrowth. The average pore size is 430 μm , and the porosity is higher than other common metals (75% to 80%). The elastic modulus of porous tantalum (3 to 25 GPa) is between human cancellous bone (3.78 GPa) and cortical bone (14.64 GPa). It can also promote growth and bonding with bone and cartilage, ligaments, tendons, and other soft tissues, both in vitro and in vivo conditions. When all of the mentioned is combined with the possibility of creating multiple specifications and shapes, this material becomes especially suitable for dental and orthopedic (knee, hip) implants, as well as tissue filling and bone graft substitutes in the human body. An example of this is its use as a reconstructive material after tumor

resection or as a scaffold for bone growth in spine surgery (Bobyne *et al.*, 1999; Levine *et al.*, 2006; Narayan, 2012). (Figure 13 and Figure 14).

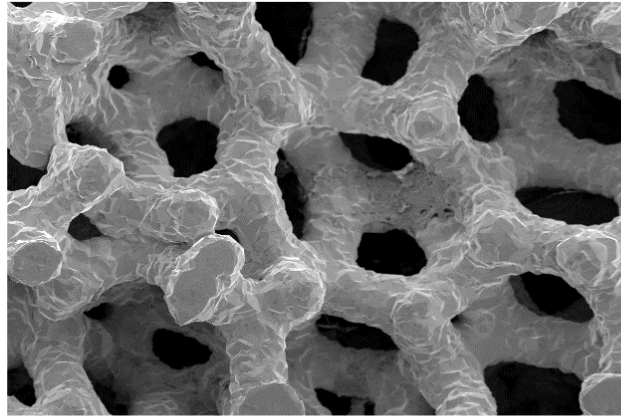


Figure 13 - Porous tantalum sample analyzed with scanning electron microscopy. Adapted without permission from Maccauro *et al.* (2009).



Figure 14 - Multiple orthopedic applications of porous tantalum for medical devices. Adapted without permission from Bombač (2007).

4.3.1. POROUS TANTALUM IN DENTISTRY

Thanks to its good mechanical properties, good corrosion/wear resistance, biocompatibility, superior bioactivity, and high osseointegration efficiency, tantalum has also been recognized as a promising material in the field of dental implantology, thus reducing implant rehabilitation time (Liu *et al.*, 2015). In the last years, porous tantalum surface coatings, among other surface modification methods, have been applied to titanium dental implants to increase the interaction between bone and implant (Vandamme *et al.*, 2008). This highly permeable surface of interconnected regular pores was specially designed for bone and blood vessel ingrowth, which happens into small healing chambers. In this sense, the unrestricted flow of blood and nutrients can directly reach a dental implant's interior, favoring cellular adhesion, viability, proliferation, and extracellular matrix formation, thus enhancing the osseointegration process. This phenomenon is the basis for the clinical success of a candidate biomaterial for dental purposes (Maccauro *et al.*, 2009; Arriba *et al.*, 2018; Narayan, 2012; Zeng *et al.*, 2017).

Despite its low modulus of elasticity and highly porous structure (which apparently can reduce mechanical resistance), its high frictional characteristics can withstand physiologic loads, continuously promoting new bone formation around the peri-implant area (Mohandas *et al.*, 2014).

In this context, a pilot study of a dental implant system with a midsection covered by porous tantalum was used instead of a standard titanium alloy (Kim *et al.*, 2013). Although the authors had observed a significant growth in and around the porous sections, they did not find a difference in long-term stability between traditional titanium alloy and porous tantalum.

Despite the excellent biological and mechanical properties evidenced across the literature (compared with titanium alloys), the higher cost of manufacturing tantalum and the difficulty of processing a bulk form (porous) dental implant have limited its wide application and acceptance in the market. More recently, some technological advances allowed the successful production and commercialization of Porous Tantalum Trabecular Metal (PTTM) (Trabecular Metal™, Zimmer®) – Figure 15 – which can be present in

dental implants, as a coating (tantalum oxide), or in a bulk structure (porous) (Balla *et al.* 2010; Mohandas *et al.*, 2014; Cristea, Ghiuță and Munteanu, 2015).

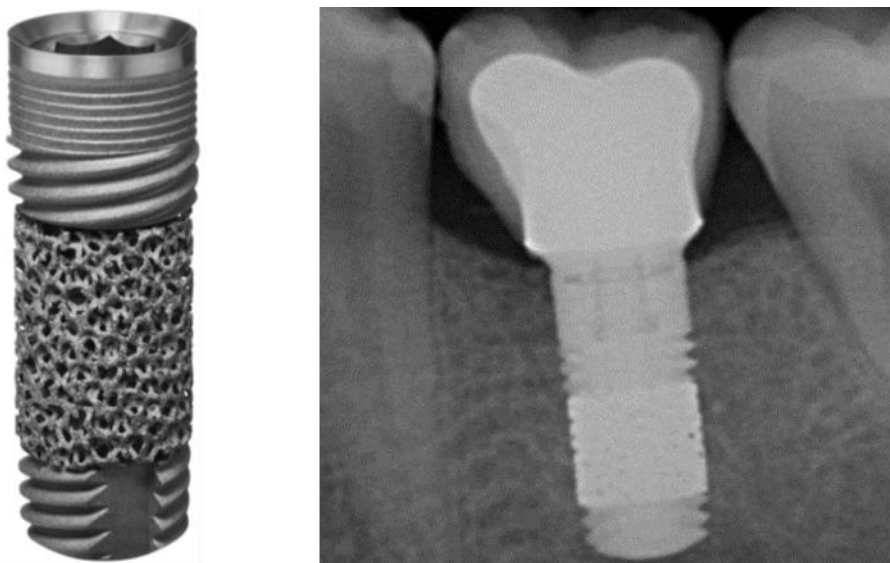


Figure 15 - Porous Tantalum Trabecular Metal (PTTM) dental implant. (Trabecular Metal™, Zimmer®)
Adapted without permission from Schlee and van der Schoor (2013).

Another advantage of porous tantalum in dentistry is its excellent radiopacity, due to its high atomic number, as it allows to distinguish rehabilitation inserted elements from the surrounding dental structures (Chan *et al.*, 1999). Besides being radiopaque, this homogenous heavy metal does not undergo hydrolysis. It does not degrade easily in the aggressive oral environment, making it highly attractive for regenerative and restorative dental solutions (Mohandas *et al.*, 2014).

5. PERI-IMPLANTITIS

Nowadays, oral rehabilitation is gaining more relevance in society due to aesthetic and functional patterns that motivate a specialized dentist's search. In modern Implantology, dental implants are an effective, safe, and widely used treatment option, with high success rates in replacing edentulous spaces. However, despite these high rates of success and survival of dental implants, complications such as peri-implantitis may occur (Smeets *et al.*, 2014; Moharrami *et al.*, 2019).

Consequently, peri-implantitis prevention and treatment strategies had gradually achieved more importance in contemporary oral rehabilitation with implants. (Smeets *et al.*, 2014) There are several techniques, devices, and materials that dentists can use for its control, but sometimes they are ineffective (Hägi *et al.*, 2015; Schwarz *et al.*, 2015).

5.1. DEFINITION

Peri-implantitis is defined as an irreversible inflammatory lesion in the hard and soft tissues surrounding the dental implant, causing a progressive loss of bone support, thus conditioning its osseointegration. Consequently, there is a higher risk for implant failure and unsuccessful implant therapy (Lindhe and Meyle, 2008; Smeets *et al.*, 2014; Mahalo, Wu, and Wang, 2016; Schwarz *et al.*, 2018). This condition is considered one of the leading causes of the late failure of osseointegrated dental implants. However, other relevant hypotheses support the presence of early bone loss, such as surgical trauma, occlusal overload, and bacterial infection (Silva *et al.*, 2008).

The criteria for defining success in oral implantology are still controversial; however, reaching and maintaining implant osseointegration is crucial. According to success ratings previously reported, it was believed that the loss of 2 mm of bone during the first year after implant insertion was within the normal range and was a good outcome (Albrektsson *et al.*, 1986; Misch *et al.*, 2008). Other authors reported that a bone 2000 represented good results. However, more recent studies have found a bone loss of less

than 1 mm after one year in function, redefining the success concept (Borges *et al.*, 2018). loss of 1.5 mm (Papaspnyridakos, 2011) or between 1.5 mm to 2 mm (Tarnow, Cho and Wallace,

According to Schwarz *et al.* (2018), peri-implantitis can occur, with bone loss beginning after implant placement, as indicated by radiographic controls. When there are signs and clinical symptoms, such as pain, suppuration, mobility, and increased depth of peri-implant pockets is considered an implant failure. Therefore, an alternative treatment solution must be thought out (Misch *et al.*, 2008; Levin, 2008).

Peri-implant soft tissues (peri-implant mucosa) have some similarities with the gingiva around the natural tooth; however, such as connective tissue composition, collagen fibers orientation, and vascularization, the differences are evident (Lindhe and Lang, 2015). The peri-implant mucosa is formed by a well-keratinized epithelium, sulcular and junctional epithelium, as well as associated connective tissue. The mean peri-implant biological width (including the sulcus depth) may often exceed 3 mm. Unlike the perpendicular collagen fibers found around the natural tooth, there are two groups of collagen fibers along the implant-bone surface without direct insertion: one has a circular orientation, and the other a parallel direction to the long axis of the implant (Wang, Zhang, and Miron, 2016) (Figure 16).

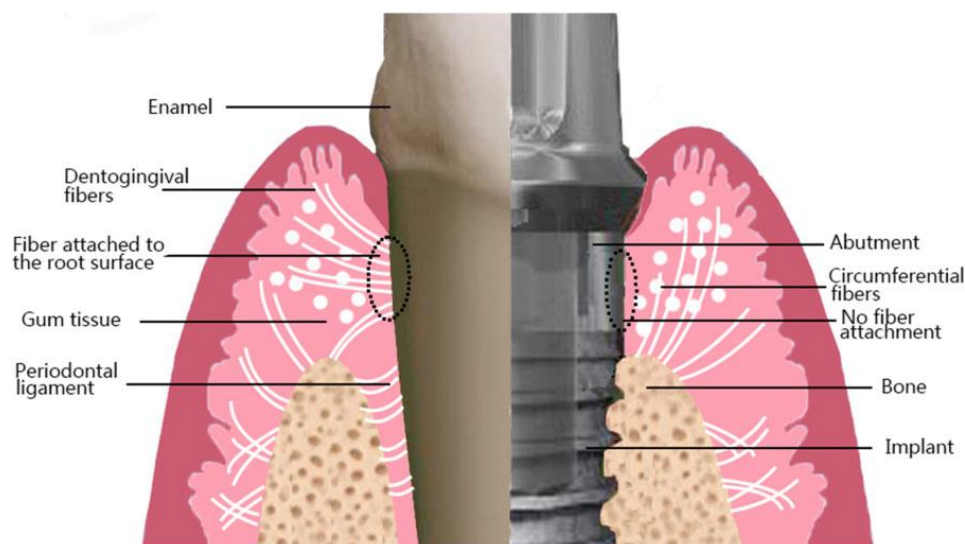


Figure 16- Comparison of the soft tissue's connection to the dental implant and the natural tooth (adapted without permission from Wang, Zhang and Miron, 2016).

Compared to periodontal tissue, the peri-implant mucosa has a greater inflammatory response in the presence of bacterial colonization. This exacerbated response is associated with the absence of periodontal ligament (functional ankylosis) and reduced blood vessels and fibroblasts. These fundamental differences, along with parallel collagen fibers, allow several bacteria to enter into the epithelial layer and subsequent connective tissue. Therefore, in peri-implantitis, the lesion in the tissues around the implant is considerably larger than periodontitis lesions and extends to the bone more quickly and aggressively. It is also possible to find many osteoclasts (Ikeda *et al.*, 2002; Lang and Berglundh, 2011; Derks *et al.*, 2016).

5.2. MICROBIOLOGY AND PREVALENCE

According to Dalago *et al.* (2019), bacterial infection is considered the most critical implant failure factor. *Staphylococcus aureus* appears to play a crucial role in the development of peri-implantitis, especially on titanium surfaces, for which this type of bacteria has a high affinity (Dalago *et al.*, 2019). In addition to *S. aureus*, the microbiota species around the peri-implantitis sites also include *Porphyromonas gingivalis*,

Aggregatibacter actinomycetemcomitans, *Tannerella forsythia*, *Treponema denticola*, *Campylobacter rectus*, *Prevotella nigrescens*, and *Prevotella intermedia*. These species are responsible for increasing the pocket depth and, consequently, alveolar bone loss (Hultin *et al.*, 2002).

In recent research, the summary estimates for peri-implant mucositis frequency were 46,83% of participants and 29,48% of implants, while those of peri-implantitis were 19,83% of participants and 9.25% of implants (Lee *et al.*, 2017). These results align with those reported by Derks and Tomasi (2015) and Atieh *et al.* (2013). Therefore, the mentioned estimates are possible to represent the general prevalence of peri-implant diseases in the actual clinical setting (Lee *et al.*, 2017).

Not all implants inserted are in the mouth in healthy conditions. Many are considered in some studies as “survived”, but they live under a state of peri-implant mucositis, peri-implantitis, and severe bone loss, leaving them at imminent risk of loss (Schwarz *et al.*, 2018; Heitz-Mayfield and Salvi, 2018; Berglundh *et al.*, 2018).

Although titanium and its alloys are widely used as materials for dental implants, they are not entirely fault-free. In this respect, Sánchez-Siles *et al.* have been reported that approximately 14% of inserted implants go through a state of peri-implantitis (Sánchez-Siles *et al.*, 2015).

5.3. ETIOLOGICAL FACTORS

Prior knowledge of the patient's condition and medical history allows the clinician to anticipate treatment results with implants, defining a higher or lower risk for clinical unsuccess. (Chrcanovic, Albrektsson and Wennerberg, 2015).

As risk factors for the development of the disease associated with the patient stand out tobacco consuming (Chrcanovic, Albrektsson and Wennerberg, 2015), presence of previous periodontitis, and/or loss of one or more dental implants (Stacchi *et al.*, 2016), poor oral hygiene (Serino and Strom, 2009), absence of maintenance dental appointments

(Smeets *et al.*, 2014), as well as some systemic diseases and health conditions (Renvert *et al.*, 2014; Figuero *et al.*, 2000; Smeets *et al.*, 2014).

There are, however, other factors that may not be directly associated with the patient and his clinical history, such as the following iatrogenic causes: inflammation caused by inadequate occlusal forces (due to poor design of the prosthetic element) (Rungsiyakull *et al.*, 2011); the residual cement in the peri-implant sulcus, in cemented implant-supported prostheses (Qian, Wennerberg and Albrektsson, 2012); the type of abutment selected for the definitive prosthetic rehabilitation (Galindo-Moreno *et al.*, 2014) and the time of placement of the prosthetic solution (Borges *et al.*, 2018). In this way, it seems that peri-implant pathology's appearance and progression can be justified or even enhanced in some treatments with dental implants.

5.4. DIAGNOSIS

Regarding peri-implantitis diagnosis, as previously mentioned, its presence can be observed through the progressive bone loss, the increase in the depth of the peri-implant pockets, suppuration, and pain. Clinical signs are detected with peri-implant soft tissue probing, while bone loss is radiographically identified (Misch *et al.*, 2008; Levin, 2008; Schwarz *et al.*, 2018; Lang *et al.*, 2011)

Peri-implantitis begins with mucositis, a clinical condition characterized by a reversible, bacterial-induced inflammatory process in the peri-implant soft tissue. Erythema, edema, bleeding on probing, and, still, absence of bone loss are common clinical signs of mucositis. Peri-implantitis develops from this inflammatory stage, and it is established when it already involves a bone loss after at least one year of the implant in function (Muthukuru *et al.*, 2012; Figuero *et al.*, 2014; Smeets *et al.*, 2014; Lindhe and Meyle, 2008).

5.5. TREATMENT

The primary treatment of peri-implantitis involves controlling the existent bacterial plaque, with a view to its reduction, either by improving the quality of oral hygiene, either by removing dental calculus and bacterial biofilm well as by eliminating cement residues in the peri-implant sulcus of cemented crowns. Scheduling regular check-ups and controlling factors that influence the host's response, such as tobacco consumption, are essential measures to the initial peri-implantitis treatment. (Mahalo, Wu, and Wang, 2016).

Although there is no universal and well-defined protocol for treating peri-implantitis, there are beneficial procedures when the disease appears. In this sense, several protocols with proven clinical efficacy have been documented, including surgical (regenerative, resective, or combined techniques) and non-surgical approaches (Roccuzzo and Layton, 2018).

5.5.1. SURGICAL APPROACH

The surgical approach, often considered the most effective choice, can be combined with other techniques and represents the affected area's debridement, with the inflammatory tissue removal, followed by mechanical and chemical decontamination of the implant's exposed surface. This procedure involves performing an open flap, positioned apically, osteoplasty, and smoothing the contaminated implant surface. Although it is considered a predictable therapeutic solution, it remains an invasive, traumatic, and limiting technique in aesthetic areas because of the excellent access and visibility of the affected area. These reasons have led to the search and development of new solutions, including non-surgical techniques (Englezos *et al.*, 2018; Buchter *et al.*, 2004).

5.5.2. NON-SURGICAL APPROACH

The non-surgical approach is referred to the control of the bacterial plaque and the debridement of the implant and abutment surface. This happens through its supra and sub-gingival scraping, without using a surgical flap (Ehizele and Akhionbare, 2013; Figuero *et al.*, 2014; Tanwar, Hungund and Dodani, 2016). However, the effectiveness of this submucosal cleaning is compromised by the difficulty of decontaminating the implant surface, due to limited access/visibility and to the roughness and grooves in the implant surface (Englezos *et al.*, 2018).

In this sense, scientific evidence showed that non-surgical mechanical debridement could be associated with other adjuvant techniques, such as the use of chlorhexidine, antimicrobial photodynamic therapy, Er: YAG laser or sodium bicarbonate air polishing jet, to improve clinical parameters, precluding the progression of peri-implantitis (Muthukuru *et al.*, 2012; Ramanauskaite *et al.*, 2018). Adding local or systemic administration of antibiotics is possible to reduce bleeding and probing depth, however, it fails to resolve inflammatory lesions when there is bone loss (Salvi *et al.*, 2007; Renvert, Roos-Jansaker, and Claffey, 2008).

Non-metal curettes (carbon-fiber, Teflon or plastic) and ultrasonic devices with polyether-etherketone-coated tips (PEEK) are, in most cases, used as auxiliary instruments in the mechanical decontamination and have as the primary goal to remove the peri-implant calculus and biofilm, without, however, changing the implant surface (Wang, Zhang, and Miron, 2016; Porras *et al.*, 2002). These procedures are usually combined with polishing the implant surface and its prosthetic components. For this purpose, a brush with polishing paste is used and an air polishing device, with different commercial powders. (Figuero *et al.*, 2014).

5.5.2.1. AIR POLISHING TECHNIQUE

The traditional mechanical method for polishing teeth, using a handpiece and rubber cup with prophylaxis paste, has been superseded by the air polishing technique,

which is more efficient at removing extrinsic stain and plaque biofilm by erosion (Graumann, Sensat, and Stoltenberg, 2013). Air polishing is accomplished by using an air spray loaded with abrasive powder particles and water, which is propelled through a handpiece nozzle directed against the tooth or implant surface, thereby removing stain and dental plaque by erosion (Graumann, Sensat, and Stoltenberg, 2013; Wang, Zhang and Miron, 2016; Sahm *et al.*, 2011)

Among others, one of the most important advantages provided by air polishing provides is the effective removal of bacteria and plaque formation inhibition, which undoubtedly makes it the best treatment option for patients with dental implants (Graumann, Sensat, and Stoltenberg, 2013). This technique was introduced to perform the supra and submucosal biofilm management, both in natural teeth and in dental implants, using repeated abrasive powder substances (Müller *et al.*, 2014; Hägi *et al.*, 2015; Schwarz, Becker and Renvert, 2015). Some of them have been applied to titanium surfaces, in *in vitro* studies, where the authors reported a higher success rate in removing the biofilm when compared to the use of other mechanical techniques, such as plastic curettes, ultrasonic tips, or Er: YAG laser (Schwarz *et al.*, 2005; Schwarz *et al.*, 2006; Schwarz *et al.*, 2009; Ronay *et al.*, 2017).

Several air polishing powders are available on the market with different properties and chemical compositions, which can have variable effects on the implants' surface. Sodium bicarbonate-based powders (NaHCO_3), with a particle size of up to 250 μm , were the first to be used in air polishing technology (Petersilka, 2000), making it useful in plaque removal, however too much abrasive to the implant surface (promotes changes in its topography, increasing bacterial adhesion). Later developments in air polishing powders include amino acid glycine, calcium sodium phosphosilicate, calcium carbonate, aluminum trihydroxide, and, more recently, erythritol-chlorhexidine powder (Schwarz *et al.*, 2009; Tastepe *et al.*, 2013; Drago *et al.*, 2014).

While sodium-bicarbonate (NaHCO_3) proved unsuitable for debriding implant surfaces, the low-abrasive amino-acid glycine powder has been described as having equal effectiveness in biofilm removal but being less abrasive when applied in dental implants (Schwarz *et al.*, 2009; Salermo *et al.*, 2010; Cochis *et al.*, 2013). This powder has been

shown to have a particle size of 63 µm or less, close to 4 times smaller than the particles in NaHCO₃ (Petersilka, 2000; Pelka *et al.*, 2010), producing no damage to hard or soft tissues and, most importantly, to the implant surface (Cochis *et al.*, 2013).

Drago and colleagues formulated a new low-abrasive powder with comparable particle size and physical properties to glycine powder, combining erythritol and chlorhexidine. They have reported a stronger *in vitro* antimicrobial and antibiofilm effects on bacteria (*S. aureus*, *Bacteroides fragilis*, and *Candida albicans*) than the previous gold-standard glycine powder (Hägi *et al.* 2015; Drago *et al.*, 2014).

Erythritol is a non-toxic, biocompatible, thoroughly water-soluble, and chemically neutral polyol (alcohol) having its use widespread as a food additive and artificial sweetener (Hägi *et al.* 2015; Munro *et al.*, 1998). Additionally, it has favorable chemical characteristics that allow the binding of antiseptic substances, both *in vivo* and *in vitro*, enhancing its anti-cariogenic activity (Mäkinen *et al.*, 2005), as well as its antimicrobial potential, especially against *Porphyromonas gingivalis* (Hashino *et al.*, 2013).

In the present work, an air polishing device was used from the swiss company EMS[®] (Electro Medical Systems, Nyon, Switzerland). Two air polishing powders from the same company were selected: Air Flow[®] Plus (AFP) and Air Flow[®] Classic (AFC), which can be distinguished not only by their chemical composition but also by their particle size. According to the manufacturer, the AFP is a minimally invasive erythritol-chlorhexidine-based powder (99,7% erythritol, 0.3% chlorhexidine, and amorphous silica) with a granule-metric size of 14 µm, produced to easily reach the sulcus area, interdental spaces, as well as the peri-implant mucosa. In addition to biofilm and stains, this powder can remove calculus supra and sub-gingivally (up to 4 mm), both in teeth and in implants/implant abutments. In its turn, AFC is a sodium-bicarbonate-based powder (NaHCO₃), with a more alkaline pH than AFP and a particle size of 40 µm. It is more abrasive to the surfaces where the air polishing is performed. For this reason, EMS recommends its use only on teeth (elimination of early calculus and stains), making it unsuitable for debriding implant surfaces and in peri-implantitis treatment/prevention (Electro Medical Systems [APA], n.d.).

The comparison between these two kinds of powders and their clinical recommendations from EMS® is stated in Figure 17.



Name		PLUS	CLASSIC
			COMFORT
Ref		DV-082	DV-048
Flavor		NEUTRAL	LEMON MINT CHERRY NEUTRAL
Composition		ERYTHRITOL	SODIUM BICARBONATE
Particle size		~14µm	~40µm
pH		~7	~8.1
Teeth	Stains and early calculus	✓	✓
	Enamel	✓	✓
	Enamel white spots	✓	✗
	Pits and fissures	✓	✗
	Dentine	✓	✗
Soft tissues	Gingiva	✓	✗
	Tongue and palate	✓	✗
Restorations	Hybrid composite	✓	✗
	Glass ionomer	✓	✗
Implants	...and peri-implant tissues	✓	✗
Orthodontics	Brackets and appliances	✓	✗

Figure 17 - Comparison between Air Flow Plus® and Air Flow Classic®, Adapted without permission from EMS, n.d. (<https://www.ems-dental.com/en>).

6. AIMS OF THE STUDY

The knowledge of air polishing effects on tantalum may preview its behavior, which is essential when considering it as a biomaterial/biomedical device in the human organism (such as dental implants, prosthetic components, and others). Therefore, this study has been established as the main aim to determine the effect of the air polishing procedure on different tantalum surfaces, in terms of chemical and topographic changes.

Additionally, the following specific aims were preconized for this *in vitro* research:

- 1) Obtain modified tantalum surfaces to be porous and enriched with osteoconductive elements so that the evaluation of the air polishing effects can be performed;
- 2) Introduce X-Ray Diffraction as a valid technique to the characterization of air polished Ta surfaces;
- 3) Establish a comparative analysis between the effects of two air polishing powders, with different levels of abrasiveness, on Ta surfaces;
- 4) Categorize the selected air polishing parameters in desirable or non-desirable, according to the changes they produce on Ta surfaces;
- 5) Develop a differentiated air polishing protocol for both pure tantalum and nanostructured tantalum oxide surfaces, improving their life as rehabilitating materials, thus overcoming adverse conditions, such as mucositis and peri-implantitis.

III. MATERIALS AND METHODS

“Study of air polishing effect on tantalum surfaces.”

1. CHARACTERIZATION OF THE STUDY

In this *in vitro* study, Ta samples were cleaned and divided into three groups: one of pure Ta and the remaining two of modified Ta. Two surface modification processes were selected and later applied: anodization and magnetron sputtering. Pure and functionalized Ta samples were then subdivided into other groups according to the exposition or not to the air polishing procedure, and other specific parameters described ahead. Finally, all the samples were evaluated by surface characterization techniques to assess the overall impact of the air-abrasive method on Ta surfaces.

The representation of these experimental steps is shown in Figure 18.

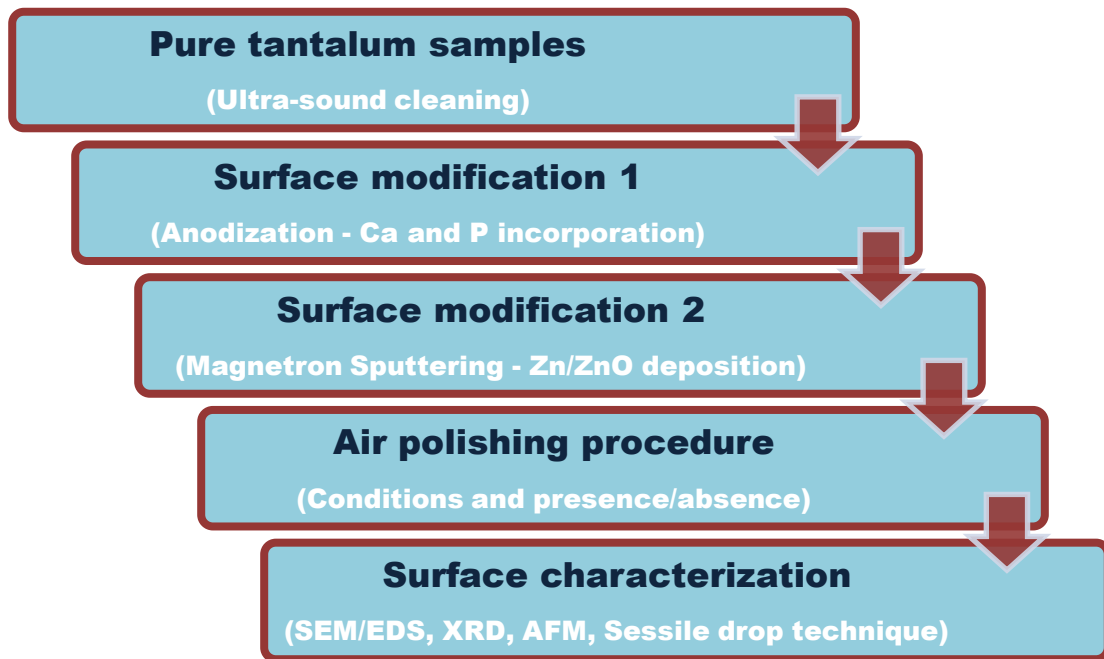


Figure 18 - Schematic representation of the experimental procedure steps.

2. EXPERIMENTAL PROCEDURE

For the development of the experimental procedure, Ta samples were distributed by groups, taking into account the combination of the next parameters selected for this *in vitro* study: presence and type of surface modification (without – Pure Ta; with – PEO/MAO, and Magnetron Sputtering); air polishing (with or without); air polishing powders (Air-Flow® Plus and Air-Flow® Perio – EMS®, Electro Medical Systems, Nyon, Switzerland); air polishing distance (2 millimeters and 5 millimeters), and air polishing duration (5 seconds and 10 seconds) (Table 1).

Table 1 - Distribution of Ta samples according to parameters selected for this study.

	GROUP	SURFACE MODIFIC.	AIR POLISHING	POWDER	DISTANCE (mm)	DURATION (s)
PURE Ta	1	Pure Ta	Without	CONTROL		
	2	Pure Ta	With	Air Fl. Plus	2	5
	3	Pure Ta	With	Air Fl. Plus	2	10
	4	Pure Ta	With	Air Fl. Plus	5	5
	5	Pure Ta	With	Air Fl. Plus	5	10
	6	Pure Ta	With	Air Fl. Classic	2	5
	7	Pure Ta	With	Air Fl. Classic	2	10
	8	Pure Ta	With	Air Fl. Classic	5	5
	9	Pure Ta	With	Air Fl. Classic	5	10
TaCaP – A1	10	A1	Without	CONTROL		
	11	A1	With	Air Fl. Plus	2	5
	12	A1	With	Air Fl. Plus	2	10
	13	A1	With	Air Fl. Plus	5	5
	14	A1	With	Air Fl. Plus	5	10
	15	A1	With	Air Fl. Classic	2	5
	16	A1	With	Air Fl. Classic	2	10
	17	A1	With	Air Fl. Classic	5	5
	18	A1	With	Air Fl. Classic	5	10
TaCaP-Zn – A2	19	A2	Without	CONTROL		
	20	A2	With	Air Fl. Plus	2	5
	21	A2	With	Air Fl. Plus	2	10
	22	A2	With	Air Fl. Plus	5	5
	23	A2	With	Air Fl. Plus	5	10
	24	A2	With	Air Fl. Classic	2	5
	25	A2	With	Air Fl. Classic	2	10
	26	A2	With	Air Fl. Classic	5	5
	27	A2	With	Air Fl. Classic	5	10

There was a total of 81 Ta samples divided by 3 major groups, according to the presence and type of surface modification: 27 samples of pure Ta (without surface modification); 27 samples of TaCaP – A1 (PEO/MAO with Ca, P incorporation), and 27 samples of TaCaP-Zn – A2 (PEO/MAO with Ca, P incorporation and Zn nanoparticles deposition by Magnetron Sputtering).

The 3 major groups were subdivided into 9 sub-groups each, performing 27 groups with, in its turn, 3 samples each. These 3 samples were meant to cover the air polishing procedure necessities, being later destined to the execution of the surface characterization techniques.

Among the 27 groups, 3 groups were designated as control groups (numbers 1, 10, and 19), where the air polishing procedure was not performed.

2.1. CLEANING AND DEGREASING

The experimental procedure started with the preparation of Ta samples. One tantalum sheet (T1-9000-D70, LOT004646, Testbourne Ltd, UK), with 99,95% purity, was previously cut into strips – Figure 19a). Each strip was first measured and then cut into squares of 20 mm x 20 mm x 0.5 mm thick, reaching 90 squares/samples – Figure 19b). Each of the squares was subjected to a polishing disc's action for eliminating sharp edges – Figure 19c). Then, its cleaning and degreasing were performed (to remove possible impurities) in an ultrasound bath consisting of five minutes in ethanol, followed by five minutes in deionized water (Figure 19).



Figure 19 - Procedures for Ta samples' preparation: a) Measurement of 20 mm x 20 mm x 0,5 mm squares in a Ta sheet previously cut; b) Individualization/cutting of Ta squares/samples; c) Polishing Ta squares/samples.

2.2. PEO / MAO

Plasma Electrolytic Oxidation was the anodization selected technique in this experimental procedure. As mentioned before, in this technique, pores' formation does not depend on the electrolyte used, being possible to use other types, including non-acidic electrolytes. Therefore, in this case, a calcium acetate (Aca) and β -glycerophosphate (β -GP) solution was prepared for incorporation of the osteoconductive elements Ca and P. In this sense, 11.08 g of Aca (Biochem, Chemopharma) and 7.36 g of β -GP (β -glycerol phosphate disodium salt pentahydrate $\geq 98.0\%$, Sigma) were mixed in an Erlenmeyer, with the addition of water to a volume of 200 mL. The electrolyte rested in a magnetic stirrer some hours before use, while an immersed stir bar was spinning very quickly.

The anodization process started with the placement of the first cleaned and dried Ta sample in the electrochemical cell (made by polypropylene), touching an O-ring positioned in a hole in the front of the cell – Figure 20a) and b). Over the sample was placed a cover, screwed to the cell by four screws, with a hole on the top, designed to have a copper tip serving the electrode connection – the anode – Figure 20 c).

In its turn, with a distance of 3 cm from the anode, the cathode was installed in the cover of the cell reservoir, which contained an orifice with a graphite (carbon) tip (electrode connection) in direct contact with 50 mL of an electrolyte solution, so that the

future anodized Ta surface could be covered. Immersed in the electrolyte was placed, once again, a stir bar – Figure 20 d). Then, the electrochemical cell was placed over a magnetic stirrer to optimize the ion exchange between the electrolyte and the sample and, thereby, forming the oxide layer along the surface of the sample. Both electrodes, red and green, were connected to the cathode and the anode, respectively – Figure 20 e). The anodization system was constituted by the electrochemical cell, a DC power supply, and a multimeter to register the current intensity in more detail – Figure 20 f). The anodization process occurred for 30 minutes, at room temperature, in potentiostatic mode, which means the potential was 200 V constant, unlike the current, that was variable, with a maximum limit fixed at 2.5 Amp.

A total of 54 samples of tantalum oxide nanostructured were produced with this step – PEO / MAO.

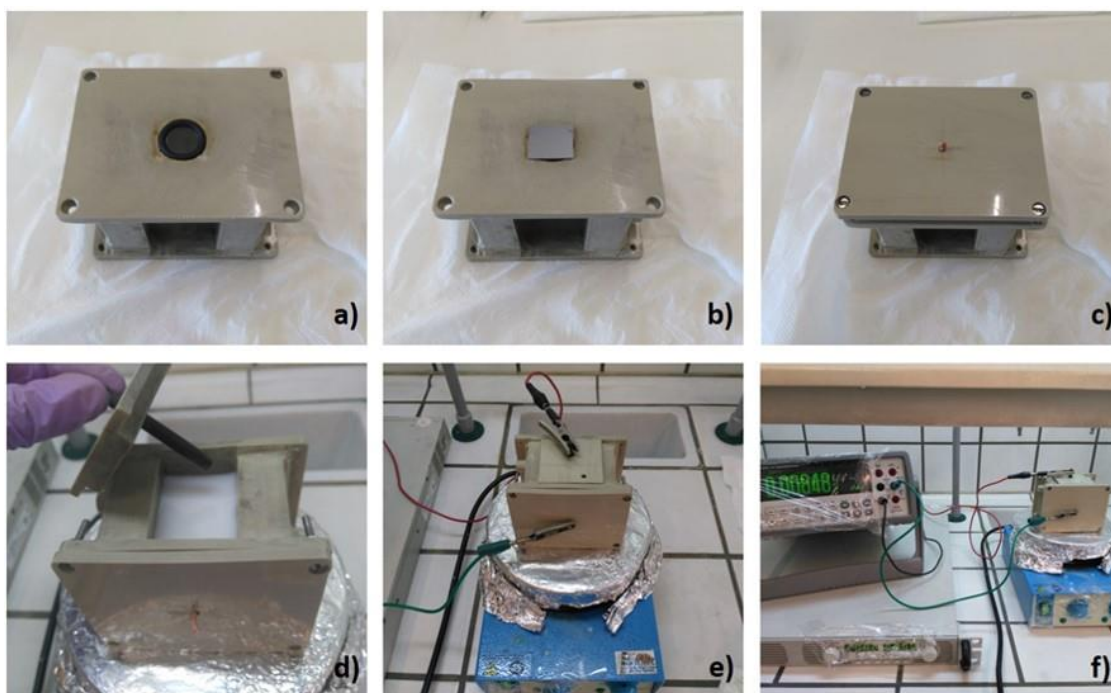


Figure 20 - Anodization system used: a) Electrochemical cell with O-Ring; b) Ta sample placed over the O-Ring; c) Cell cover with four screws and a copper tip – anode; d) Cell reservoir filled with electrolyte solution; e) Connection established between the electrodes and the anode (red) and cathode (green); f) Multimeter, DC power, electrochemical cell and magnetic stirrer in function.

2.3. MAGNETRON SPUTTERING – Zn/ZnO NANOPARTICLES DEPOSITION

From the 54 specimens obtained in the last technique, 27 samples were selected to perform magnetron sputtering, with the purpose of Zn/ZnO nanoparticles deposition.

An unbalanced dual magnetron sputtering chamber with closed field configuration was used. High purity Zn target (99.9 %, Testbourne Ltd) was connected to a DC-pulsed power supply (200 kHz, 1536 ns) for performing nanoparticles deposition. The substrate holder was placed at the center of the chamber (7 cm apart from the magnetrons), and 10^{-4} Pa was held as base pressure. The deposition chamber is equipped with two different vacuum pumps. The primary vacuum (atmospheric pressure to 1 Pa) was performed with a rotary vane pump (AEG AM 100LS4), while the secondary one (1 Pa to 10^{-4} Pa) was done by a turbomolecular pump (Alcatel PTM 5400). A full range pressure sensor (Pfeiffer Vacuum) was used to monitor every step in the deposition process. To guarantee a high vacuum quick recovery at the deposition chamber, a pre-chamber was used to perform the primary vacuum in uncoated samples. The holding time at the pre-chamber of substrates was approximately 20 minutes every time. After achieving 1 Pa at the pre-chamber, the substrates were put at the deposition chamber up to reach the aforementioned base pressure value. Zinc nanoparticles were prepared in an Ar atmosphere (80 sccm flow) at non-reactive mode. The substrate holder with uncoated Ta samples before being placed inside the chamber is represented in Figure 21.



Figure 21 - Substrate holder with attached samples of nanostructured tantalum oxide.

2.4. AIR POLISHING SYSTEM

2.4.1. EMS DEVICE: AIR FLOW[®] PROPHYLAXIS SYSTEM

In this work, an air polishing device was used from the swiss company EMS[®] (Electro Medical Systems, Nyon, Switzerland). This EMS device includes an Airflow Handpiece, a Perioflow Handpiece, a Piezon LED Handpiece, two chambers for Plus powder and Classic powder, respectively, one water recipient, and a wireless boost pedal. Each powder chamber is pressurized and depressurized within seconds by the pressurization system, which has an integrated magnetic connection.

The Air Flow[®] Prophylaxis System (Figure 22) – was kindly provided by EMS (Electro Medical Systems, Nyon, Switzerland) to perform the air polishing protocol to Ta surfaces, with the minimum pressure of the powder-water jet allowed by this device. For this purpose, were used the Air Flow handpiece, the wireless pedal to start the air jet, water, and two powders: Air Flow[®] Classic (40 µm particle size) and Air Flow[®] Plus (14 µm particle size).

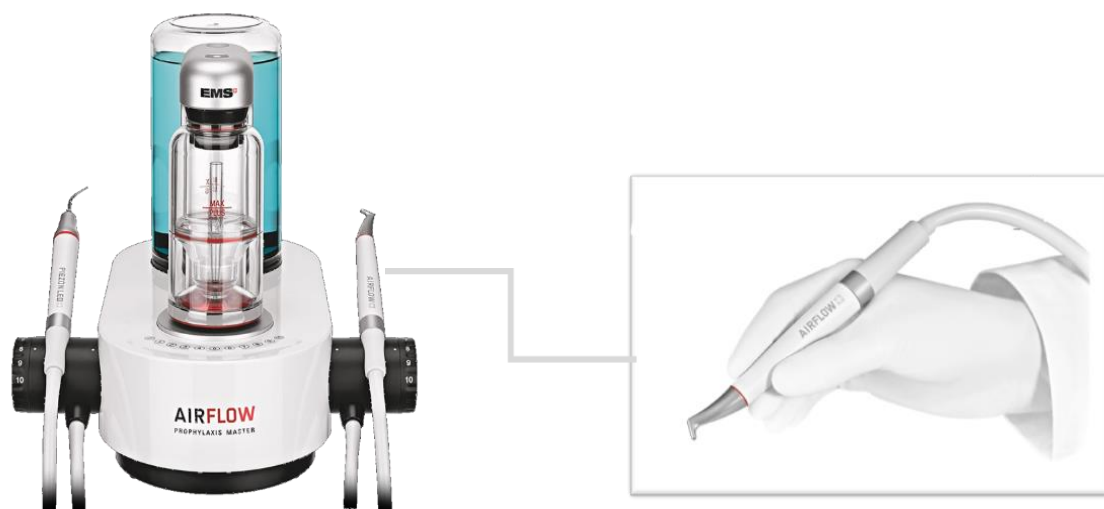


Figure 22 - Air Flow Prophylaxis System and Air Flow handpiece used in the experimental procedure. Adapted without permission n from EMS, n.d. (<https://www.ems-dental.com/en>).

2.4.2. AIR POLISHING PROTOTYPE – CONSTRUCTION, SCANNING AND DIGITAL MEASURES

According to EMS recommendations, the Air Flow[®] technique has to be performed with the Air Flow handpiece directed to the tooth / implant / prosthetic material surface at 3 to 5 mm distance and with an angulation of 30° to 60° (Figure 23). In this study, the chosen distances to the Ta samples' air polishing were 2 mm and 5 mm, with an angulation between the recommended 30° to 60°.

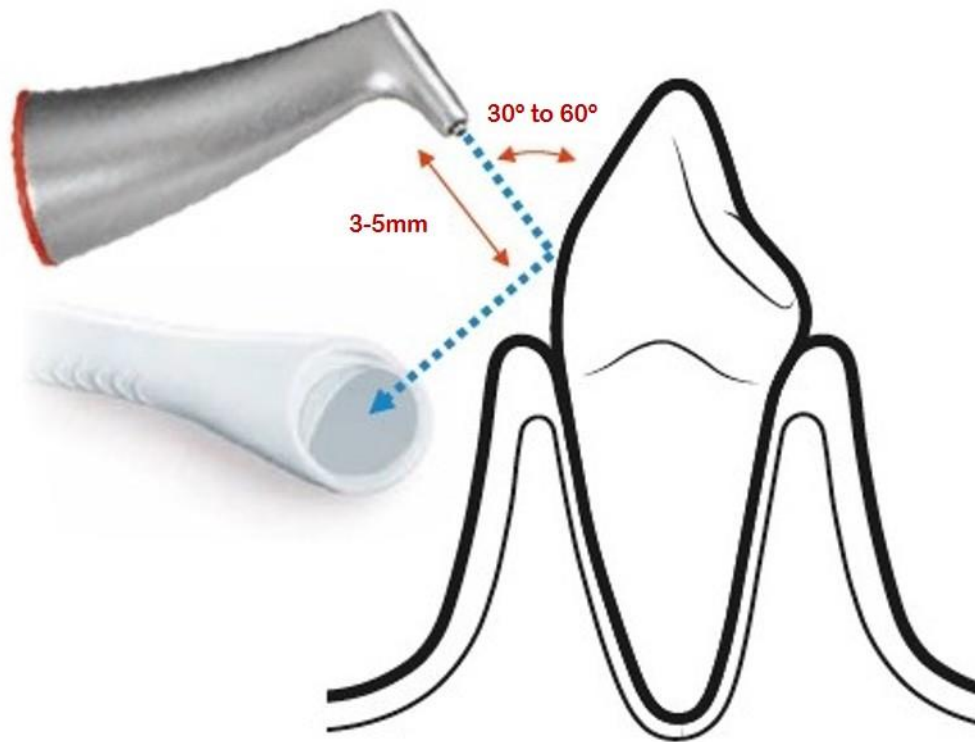


Figure 23 - EMS Air Flow® polishing procedure recommendations. Adapted without permission from EMS, n.d. (<https://www.ems-dental.com/en>).

The air polishing prototype designed for this experiment began to be constructed with the help of an adjustable metallic holder. It was adapted to the Air Flow handpiece using a silicone putty (Hydrorise, Zhermack®). The use of this material provided a stable position of the handpiece, which was “locked” in the metallic holder. In addition, it also

allowed achieving an approximated angulation of 45° between the active tip and the ground, which can be seen in Figure 24.

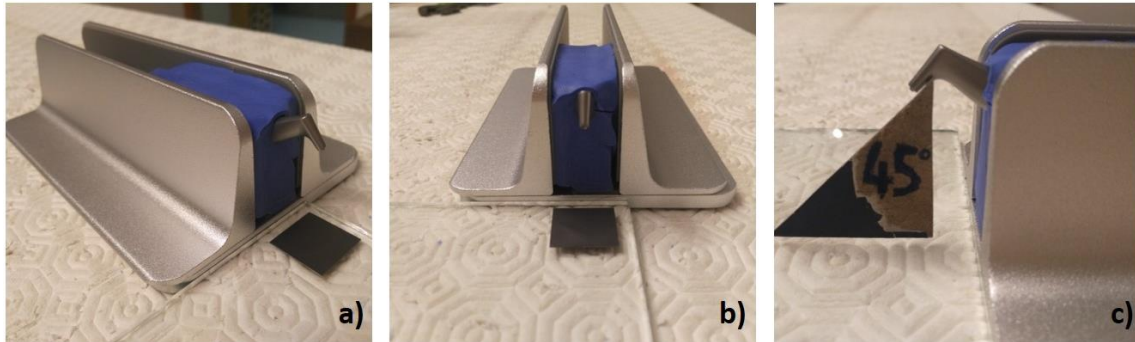


Figure 24 - Air polishing prototype and Ta uncleaned sample. a) Lateral view; b) Frontal view; c) Representation of an estimated angulation of 45° .

One of this study's main concerns was to ensure that the prototype would execute Ta samples' air polishing under the specifications required. Otherwise, all the experimental procedure would be compromised. In this sense, a high accurate metrology solution was kindly provided by FARO® Technologies to make a 3D scanning of the prototype (Figure 25) and assess all the key parameters of air polishing (distances and angles).

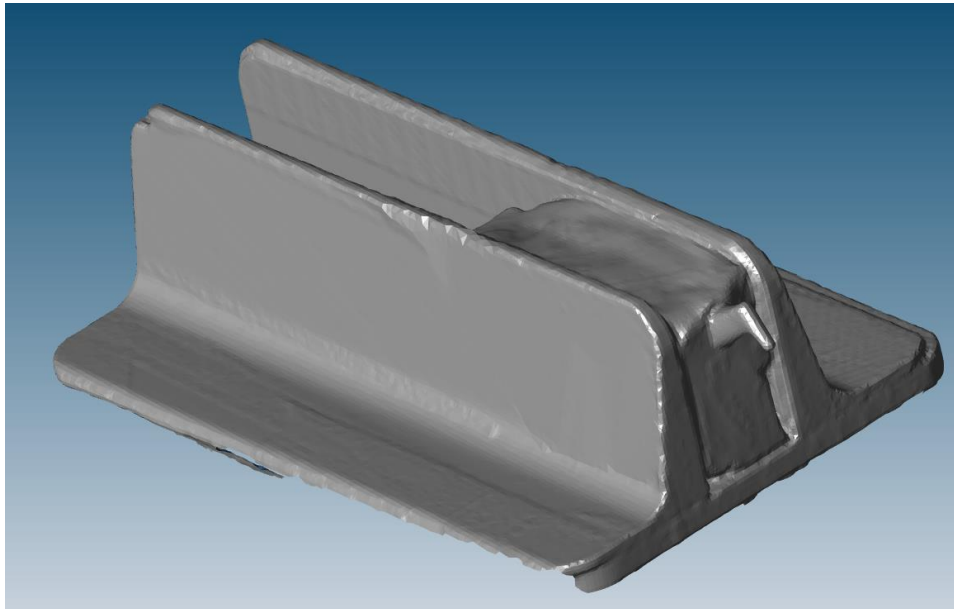


Figure 25 - 3D scanning of the air polishing prototype (courtesy of FARO® Technologies).

The metrology solution, represented in Figure 26, was composed of a Gage Arm and Prizm LLP (Laser Line Probe) on the hardware side, while, on the software side, was used the CAM2 product. Before collecting the data required for the analysis, the prototype was attached to a marble table to ensure it would not move during the process. Then, a Point Cloud was taken from the prototype, and the plane of the table was calculated.



Figure 26 - Representation of the Metrology FARO solution used in this study. Gage Arm and Prizm LLP, CAM2, with the sample/prototype being attached to a marble table (courtesy of FARO® Technologies).

Using the Point Cloud, a cone was extracted from the handpiece tip (“Device Tip Extracted Cone”), as well as the cone vector, which was used to calculate the angle of projection over the plane table (“Device Tip Angle”). A perpendicular plane to the cone vector was then calculated and placed at the tip of the handpiece (“Device Tip Perpendicular Plane”). Finally, two more planes (both parallel to “Device Tip Perpendicular Plane”) were constructed with, respectively, 2 mm and 5 mm distance from the handpiece tip. Therefore, it was possible to measure the vertical distance that existed between the table plane and the mentioned planes of 2 mm and 5 mm (Figure 27).

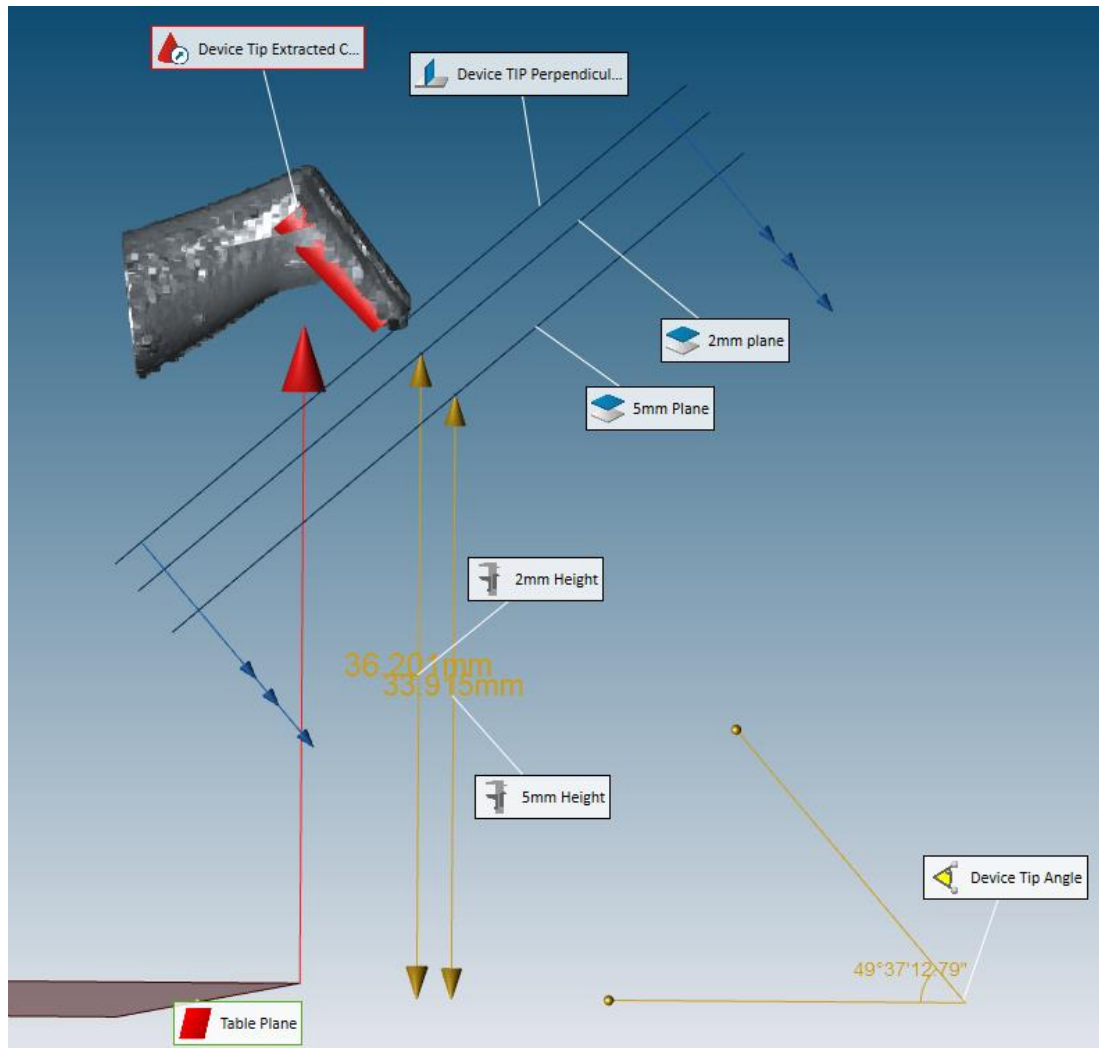


Figure 27 - Digital measurements of the angle and the distance between the extracted cone form Air Flow Handpiece and marble table plane (courtesy of FARO® Technologies).

From this metrology software analysis, it was deduced that the prototype tip was at 49° , regarding the table's plane. In addition to the angle, this software analysis was also a precious help in establishing the height from the table at which Ta samples should be, *i.e.*, 36 mm (36.201mm) and approximately 34 mm (33.915 mm), so that they could stand at 2 mm and 5 mm distance from the Air Flow tip, respectively.

2.4.3. AIR POLISHING IN VITRO PROCEDURE

Regarding the air polishing parameters (surface modification, type of powder, and distance), Ta samples were divided by groups of 6 and attached with double surface adhesive patches (placed on the non-anodized surface) to glass plates (100 mm x 150 mm) (Figure 28 a). Two kinds of glass plates were used, differing in their thickness (0,1 mm and 0,3 mm), so that the two distances of 2 mm and 5 mm could be kept. The glass plates were placed over waterproofed support, whose position remained unchanged throughout the process. Half of the glass plate, meaning three Ta samples, were air polished for 5 seconds and the other half (remaining three samples) for 10 seconds (Figure 28 b). The pressure of the powder-water jet was the minimum allowed by the instrument.

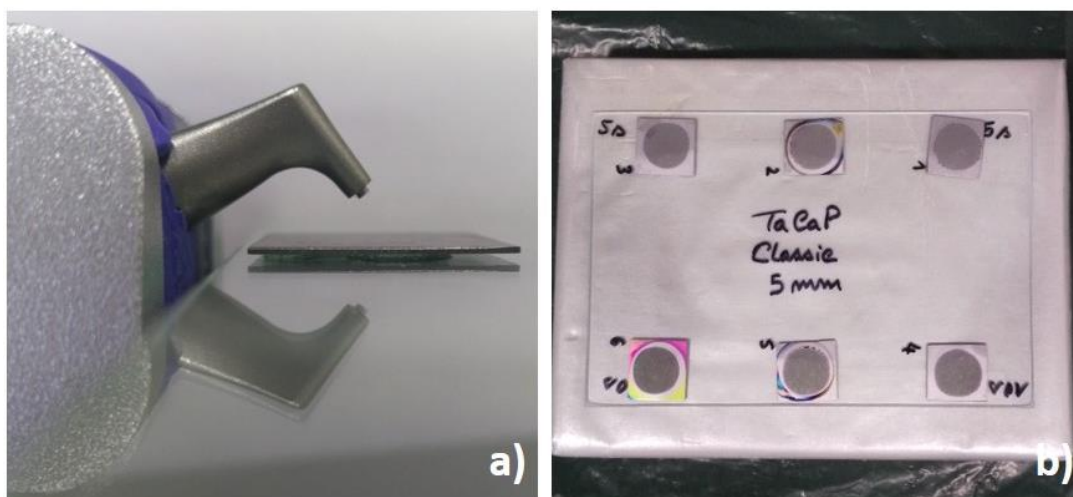


Figure 28 - a) Ta sample attached to the glass plate; b) Glass plate with 6 TaCaP samples, which will be air polished by Air Flow Classic, at 5 mm of distance, during 5 s (three samples) and 10 s (the other three samples).

Before the air polishing procedure gets started, the prototype was tested in real conditions so that the distances could be once again confirmed. For this purpose, a small triangle was made of millimetric paper and placed next to the handpiece tip to simulate the distances and the angulation of 49°. The pre-air polishing validation of 2 mm and 5 mm to the Ta surfaces is represented in Figure 29 a) and Figure 29 b).

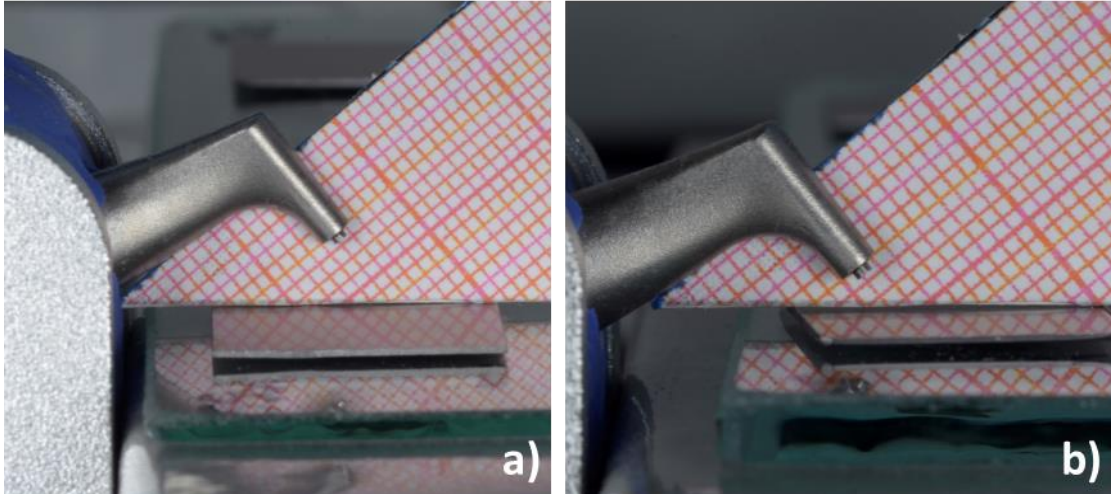


Figure 29 - Air polishing prototype for validate the distance of the handpiece tip to the Ta surface, respectively of 5 mm (a) and 2 mm (b).

The air polishing was executed (Figure 30 a) in 12 glass plates, with a total amount of 72 Ta samples: 24 of pure Ta; 24 of TaCaP (nanostructured Ta oxide), and 24 of TaCaP-Zn (nanostructured Ta oxide with Zn nanoparticles). During the process, another glass plate was used as an isolation method for the rest of the samples to avoid contamination due to the excessive amount of water and powder residues (Figure 30 b). After the air polishing procedure, Ta samples were stored in individual boxes without being cleaned with deionized water or other methods to preserve the integrity of the chemical elements incorporated into the modified surfaces.

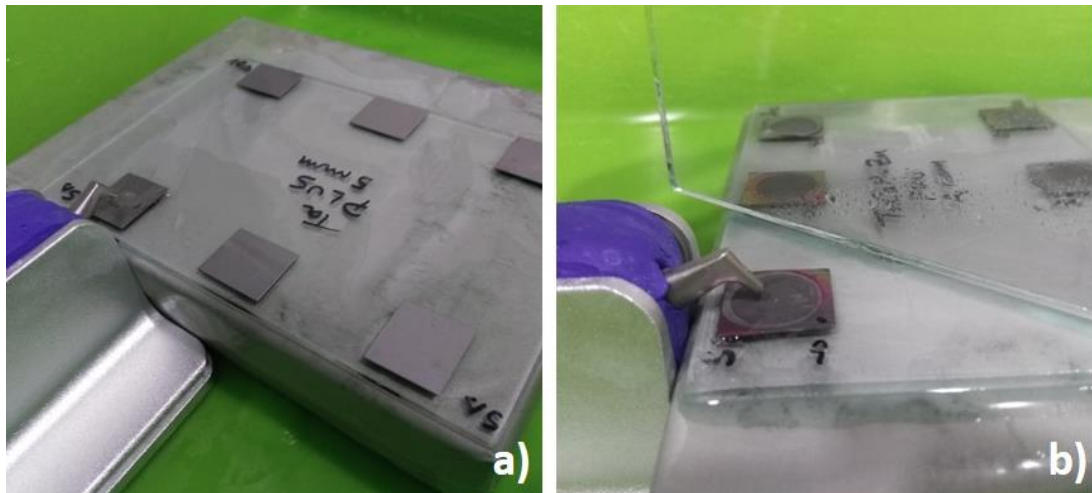


Figure 30 - a) Position adopted for the air polishing; b) The isolation method performed with another glass plate to avoid contamination.

2.5.SURFACE CHARACTERIZATION TECHNIQUES

To evaluate and compare the effect of air polishing, different surface characterization techniques were selected, such as Scanning Electron Microscopy (SEM); Energy Dispersive X-Ray Spectroscopy (EDS); X-Ray Diffraction (XRD); Atomic Force Microscopy (AFM) / Scanning Force Microscopy (SFM) and Sessile Drop Technique.

2.5.1. SEM/EDS - SCANNING ELECTRON MICROSCOPY (SEM) WITH ENERGY DISPERSIVE SPECTROSCOPY (EDS)

SEM/EDS was one of the elected techniques to evaluate the surface morphology and the chemical composition obtained due to the surface modification and air polishing procedure.

The morphological and chemical analyses of Ta samples were performed at the Materials Characterization Services Laboratory of the University of Minho (SEMAT-UM), Campus de Azurém, using the NanoSEM - FEI Nova 200 (FEG / SEM) equipment. Before the morphological analysis, the samples were coated with a thin film of Au / Pd (80/20% by weight) 10nm thick. For the morphological analysis, the scanning electron microscopy (SEM) technique was used, using a secondary electron detector with 10 KeV energy, at a working distance between 5 and 7 mm. For each sample, two groups of images were taken by SEM, referring to the magnifications of 2000x (50µm) and 5000x (20µm). For the chemical analysis, the energy dispersion spectroscopy (EDS) technique was used, using 15 KeV energy, at a working distance of approximately 6.5 mm.

Air polishing powders alone were also submitted to the morphological and chemical analyses by SEM/EDS. Morphological analyses were realized in an Ultra-high resolution Field Emission Gun Scanning Electron Microscopy (FEG-SEM), NOVA 200 Nano SEM, FEI Company. To obtain the topographic images, a secondary electron detector at an acceleration voltage of 10kV was used. Before the SEM analyses, samples were covered with a very thin film (25 nm) of Au-Pd (80-20 weight %); in a high-

resolution sputter coater, 208HR Cressington Company, coupled to an MTM-20 Cressington High-Resolution Thickness Controller. Chemical analyses were performed with the Energy Dispersive Spectroscopy (EDS) technique, using an EDAX Si(Li) detector at an acceleration voltage of 15 kV.

2.5.2. X-RAY DIFFRACTION (XRD)

In this work, XRD was used in six Ta samples (numbers 1, 10, 11, 12, 13, and 14) in low asymmetric mode. The XRD analysis in Ta samples was performed at the SEMAT-UM Laboratory at the University of Minho, Campus de Azurém, using the Bruker D8 Discover equipment (40 kV, 40 mA). The radiation used was copper $K\alpha_{1,2}$ ($\lambda = 1.54056 \text{ \AA}$), with a grazing angle geometry of 1° . The 2θ range analyzed was between $10^\circ - 80^\circ$, with a step size of $0.04^\circ / \text{s}$ and time per step of 1 s. (Figure 31)

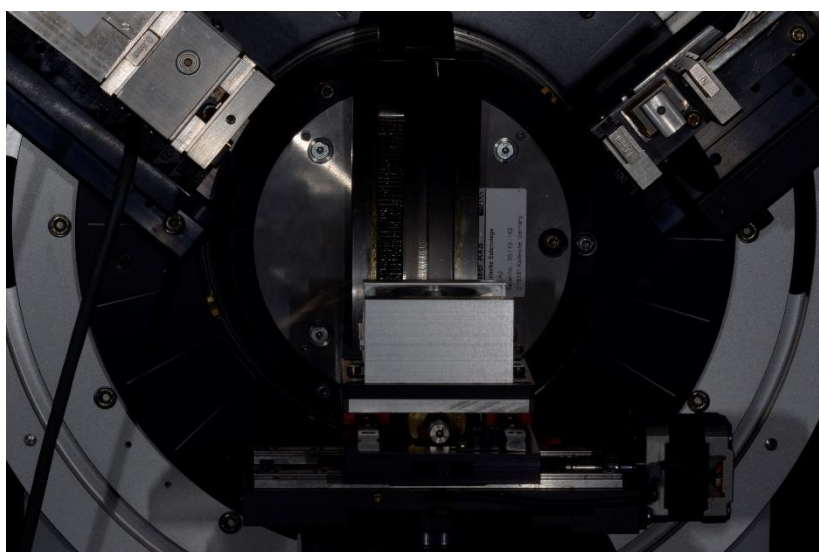


Figure 31 - Diffractometer (Bruker D8 Discover) used in Semat - UM for the XRD analysis.

2.5.3. ATOMIC FORCE MICROSCOPY (AFM) OR SCANNING FORCE MICROSCOPY (SFM)

This characterization technique was carried out at the 3B's research group using the Icon Dimension microscope with ScanAsyst by Bruker. The images were obtained in Tapping mode, with Bruker NCHV-A tips, with at least three measurements per sample.

2.5.4. SESSILE DROP TECHNIQUE

This technique was selected to calculate the contact angles, the values of surface tensions, and the value of Gibbs free energy from the Ta surfaces. These calculations were planned to be repeated nine times for each sample to have a statistical validation of the results, using three different liquids (ultrapure water, glycerol, and α -bromonaphthalene). The measurement of contact angles was performed using the OCA 15 Plus goniometer, Dataphysics, from the Biological Engineering Centre, at a temperature of 22°C, in statically mode, and starting with a drop of 2 μ l of ultrapure water (Figure 32).

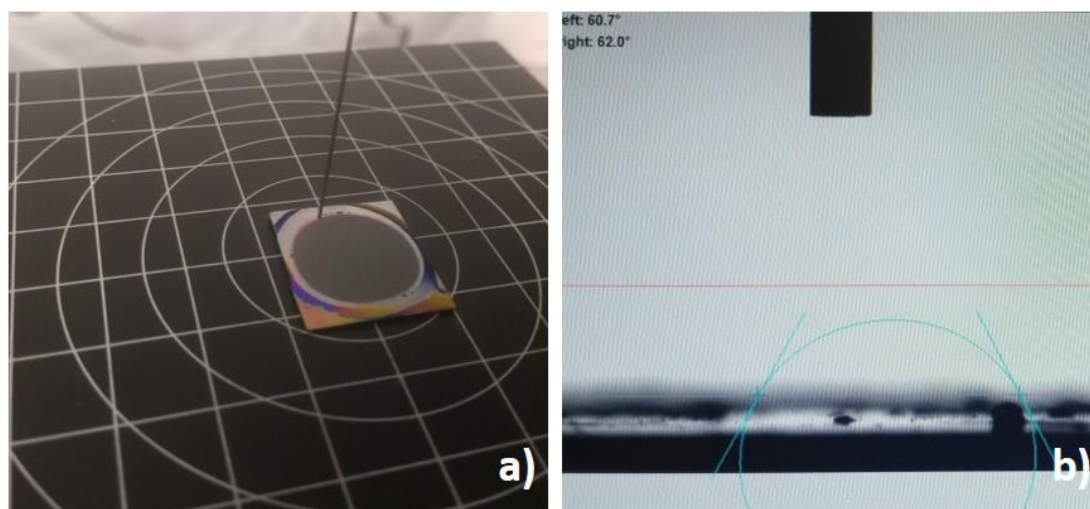


Figure 32 - Sessile Drop Technique: a) using an anodized Ta sample; b) Software image moments before the drop release.

IV. RESULTS

“Study of air polishing effect on tantalum surfaces.”

In this chapter, the results will be contextualized according to the surface characterization techniques mentioned in the previous sections. In this way, the analysis of results will begin with the SEM-EDS technique, followed by XRD, AFM, and, finally, the Sessile Drop Technique.

After being air polished, Ta samples' final appearance is demonstrated in Figure 33, where the powder residues can be seen in the form of white stains and granules.



Figure 33 - Final aspect of Ta samples (TaCaP-Zn) after being air polished (AFP).

1. SURFACE CHARACTERIZATION TECHNIQUES

1.1. SEM / EDS

SEM / EDS results will be presented according to the applied surface modification technique: first, it will be shown Pure Ta results, followed by TaCaP – A1 (anodization) and, finally, by TaCaP-Zn (sputtering).

In this section, SEM-EDS results will be presented according to surface modification techniques. There will be a representative SEM micrograph and EDS corresponding to one sample of each group. To facilitate the qualitative and comparative analysis, SEM micrographs were divided into sets of 4, regarding the type of air polishing powder (AFP and AFC), the distance (mm), and duration (s). In each set was included a 5th micrograph referring to the control group (without air polishing). The samples were analyzed according to two magnifications – 2000x (50μ) and 5000x (20μ). In this chapter, the micrographs of 5000x will be presented below. EDS results were included in each SEM micrograph corner, containing the chemical elements present and the respective atomic percent (At. %).

Before introducing the Ta samples' SEM-EDS results, it will be presented the SEM-EDS results of the Air Flow[®] Plus (AFP) and Air Flow[®] Classic (AFC) analysis. The next figures (Figure 34a and Figure 34b) represent SEM micrographs (1000x magnification) of the mentioned powders, where some particles' size could be measured.

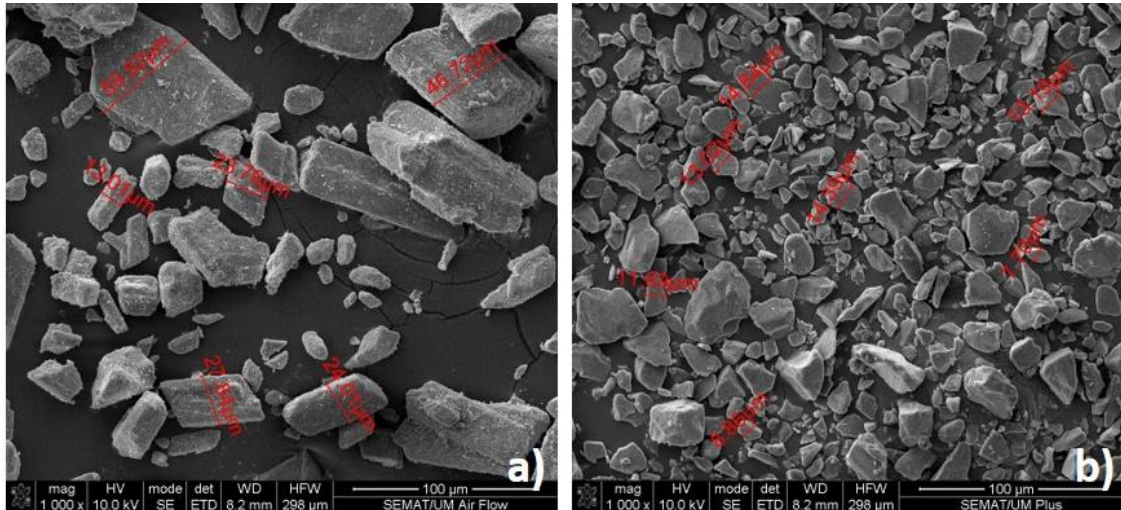


Figure 34 - SEM micrographs at 1000x magnification: a) Air Flow® Classic particles; b) Air Flow® Plus particles.

From the analysis of the measures performed to some representative powder particles, it is possible to notice a size ranging between 13,01 - 59,52 μm for AFC, with an average size of 32 μm , whereas the AFP have a size ranging between 7,70 - 13,84 μm , with an average size of 12 μm .

The next table (Table 2) represents the EDS results of the air polishing powders analysis that confirmed the presence of Carbon (C), Oxygen (O), and Silicon (Si) in both powders. Besides, it was found Sodium (Na) in AFC.

Table 2 - EDS results of air polishing powders.

EMS AIR POLISHING POWDERS					
AIR FLOW® CLASSIC (AFC)			AIR FLOW® PLUS (AFP)		
AVERAGE PARTICLE SIZE	ELEMENT	At. %	ELEMENT	At. %	AVERAGE PARTICLE SIZE
32 μm	C	24.32	C	74.76	12 μm
	O	55.07	O	24.99	
	Na	19.80	Si	0.25	
	Si	0.81			

1.1.1. PURE Ta

Table 3 represents the division of pure Ta samples by nine groups (1 to 9), according to the air polishing parameters applied,

Table 3 - Distribution of pure Ta samples according to the air polishing parameters.

	GROUP	SURFACE MODIFIC	AIR POLISHING	POWDER	DISTANCE (mm)	DURATION (s)
PURE Ta	1	Pure Ta	Without	CONTROL		
	2	Pure Ta	With	Air Fl. Plus	2	5
	3	Pure Ta	With	Air Fl. Plus	2	10
	4	Pure Ta	With	Air Fl. Plus	5	5
	5	Pure Ta	With	Air Fl. Plus	5	10
	6	Pure Ta	With	Air Fl. Classic	2	5
	7	Pure Ta	With	Air Fl. Classic	2	10
	8	Pure Ta	With	Air Fl. Classic	5	5
	9	Pure Ta	With	Air Fl. Classic	5	10

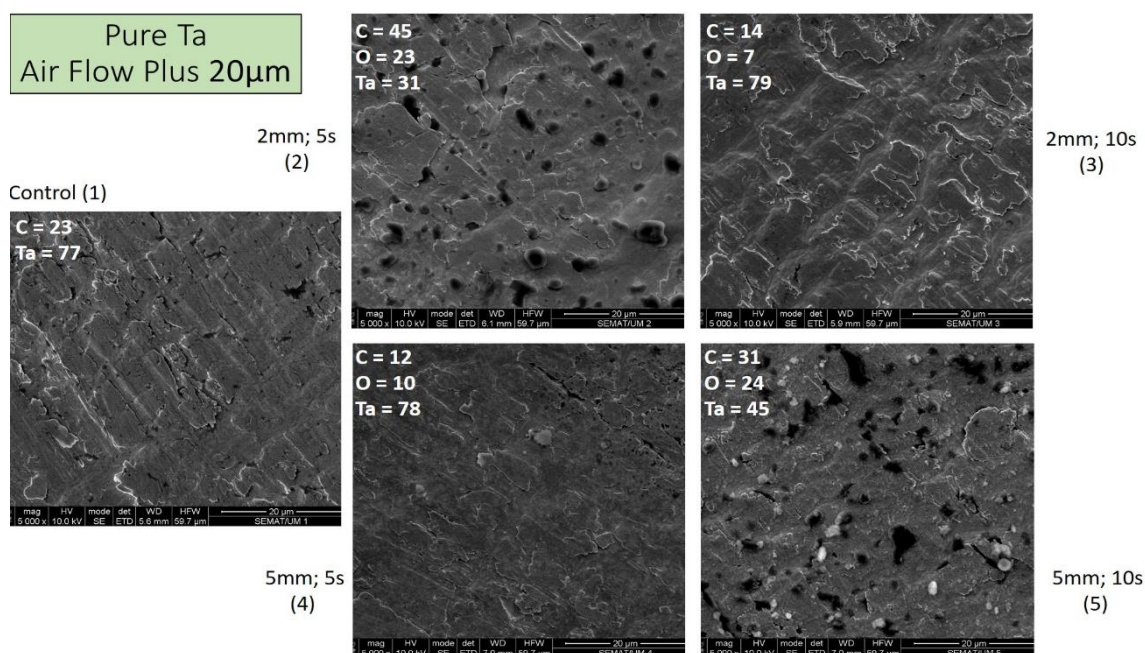
1.1.1.1. AIR FLOW[®] PLUS

Figure 35 - SEM micrographs and EDS results of samples number 1-5 – Air Flow Plus.

Comparing to the control sample, air polishing does not appear to have produced significant changes in the integrity of pure Ta. The ovoid stains present in the sample (2) and (5) resemble granules of powder accumulated on the surface (Figure 35**Error!** **Reference source not found.**).

After 5 seconds of air polishing, it seems that with a shorter distance (2 mm), greater are the powder residues present on the surface, namely in the sample (2). In samples where the distance is 5 mm, the excess of powder is more significant when air polishing was carried out for more seconds – sample (5).

In terms of chemical composition, the air polishing brought the incorporation of Oxygen (O) in all samples and a slight increase of At. % of Ta in the presence of a short distance and an increased duration – sample (3), as well as in the presence of an increased distance and short time – sample (4). Comparatively to the control sample, in (2) and (5) samples, Carbon increased, and Ta decreased.

1.1.1.2. AIR FLOW[®] CLASSIC

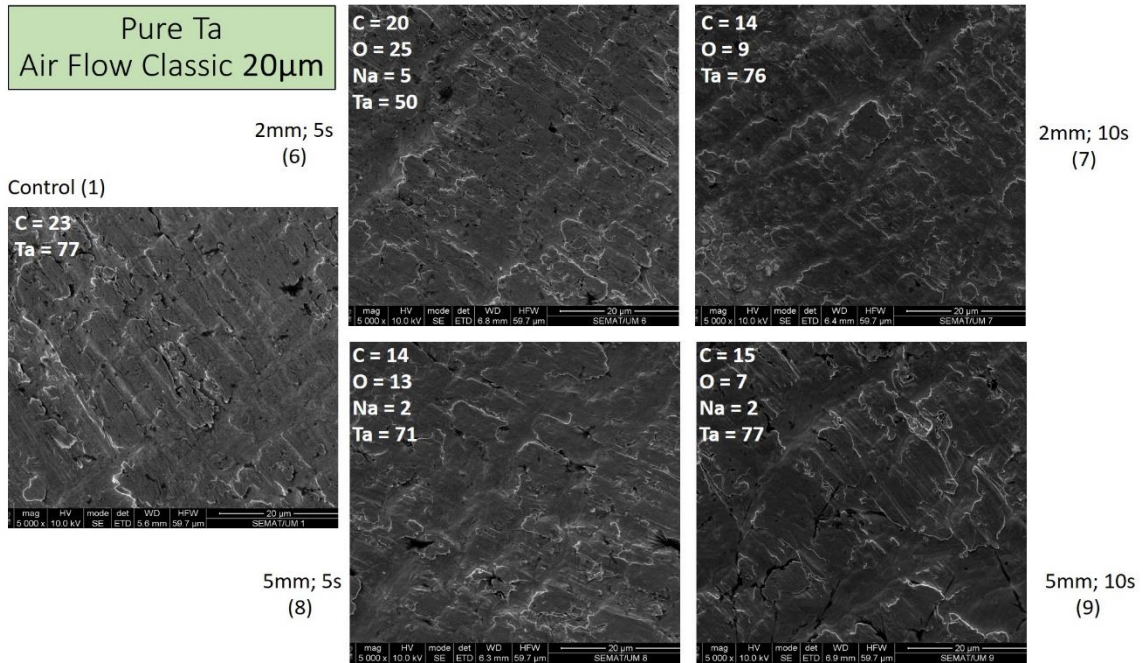


Figure 36 - SEM micrographs and EDS results of samples number 1 and 6-9 – Air Flow Classic.

In this set of micrographs (Figure 36), when the air-polished samples are compared to the control (1), the surface topography appears to be very similar to each other, no matter the distance or the air polishing duration. It is not visible the accumulation of powder residues over the surfaces.

As for EDS results, the only sample with no incorporation of Na by air polishing was number (7). Regarding the amount of Ta, a more pronounced decrease in the sample (6) is evident, where the air polishing was performed at a shorter distance and with a shorter duration. Here, conversely to Ta, the Na incorporation was increased.

1.1.2. TaCaP – A1

In Table 4 is represented the division of nanostructured oxide tantalum samples, with Ca and P (TaCaP), by nine groups (10 to 18), according to the air polishing parameters applied.

Table 4 - Distribution of TaCaP samples according to the air polishing parameters.

	GROUP	SURFACE MODIFIC.	AIR POLISHING	POWDER	DISTANCE (mm)	DURATION (s)
TaCaP – A1	10	A1	Without	CONTROL		
	11	A1	With	Air Fl. Plus	2	5
	12	A1	With	Air Fl. Plus	2	10
	13	A1	With	Air Fl. Plus	5	5
	14	A1	With	Air Fl. Plus	5	10
	15	A1	With	Air Fl. Classic	2	5
	16	A1	With	Air Fl. Classic	2	10
	17	A1	With	Air Fl. Classic	5	5
	18	A1	With	Air Fl. Classic	5	10

1.1.2.1. AIR FLOW[®] PLUS

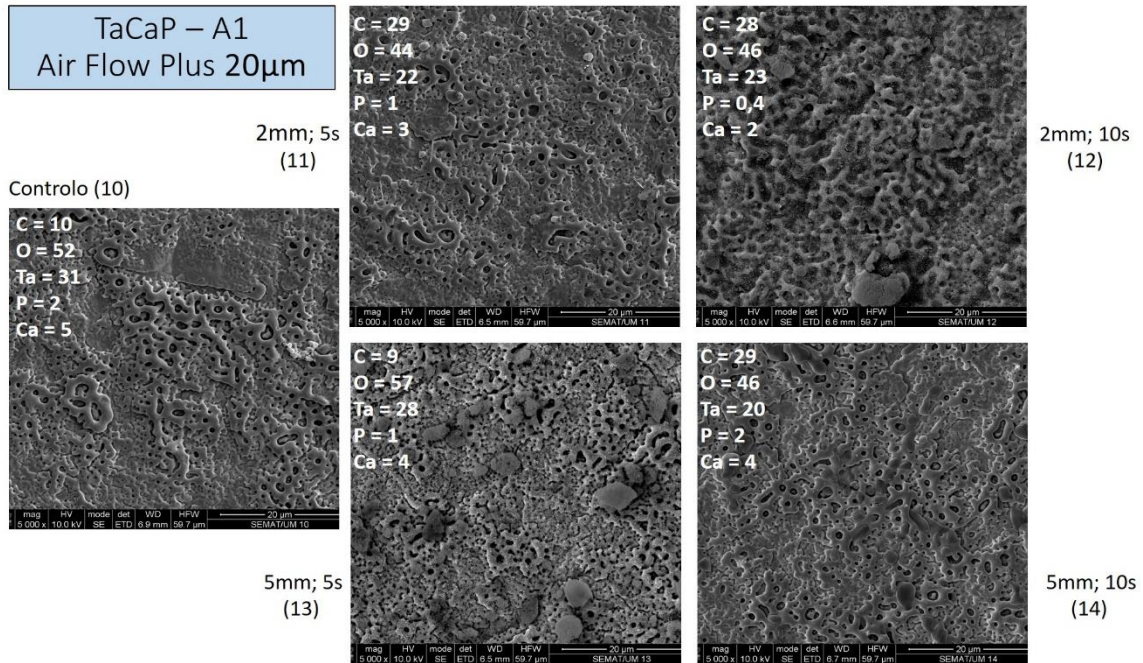


Figure 37 - SEM micrographs and EDS results of samples number 10-14 – Air Flow Plus.

These are samples of nanostructured oxide tantalum (Figure 37), which means that topographic and chemical changes have been made.

In the control group (10), pores and holes are visible, apparently arranged in layers, under an unorganized disposition, and with different sizes. These structures make up a highly textured surface. At first glance, the air polishing does not appear to affect the tested surfaces, since none of the samples, (11) to (14), show differences in the size and number of pores.

As with pure tantalum surfaces, ovoid granules corresponding to excess air polishing powder appear to be present, particularly when distance increases (5 mm), in a short duration (5 s) – (13). If the time increases (10 s) with the same distance (5 mm) – (14), there are fewer residues present.

Regarding EDS results, all the samples present in their chemical composition the elements Ca and P, incorporated by anodization. A lower At. % of Ta, P, and Ca is also

evident in the samples submitted to air polishing. This is particularly evident for the osteoconductive elements in the sample (12), where the air polishing distance is minimum, and the time is maximum.

1.1.2.1. AIR FLOW[®] CLASSIC

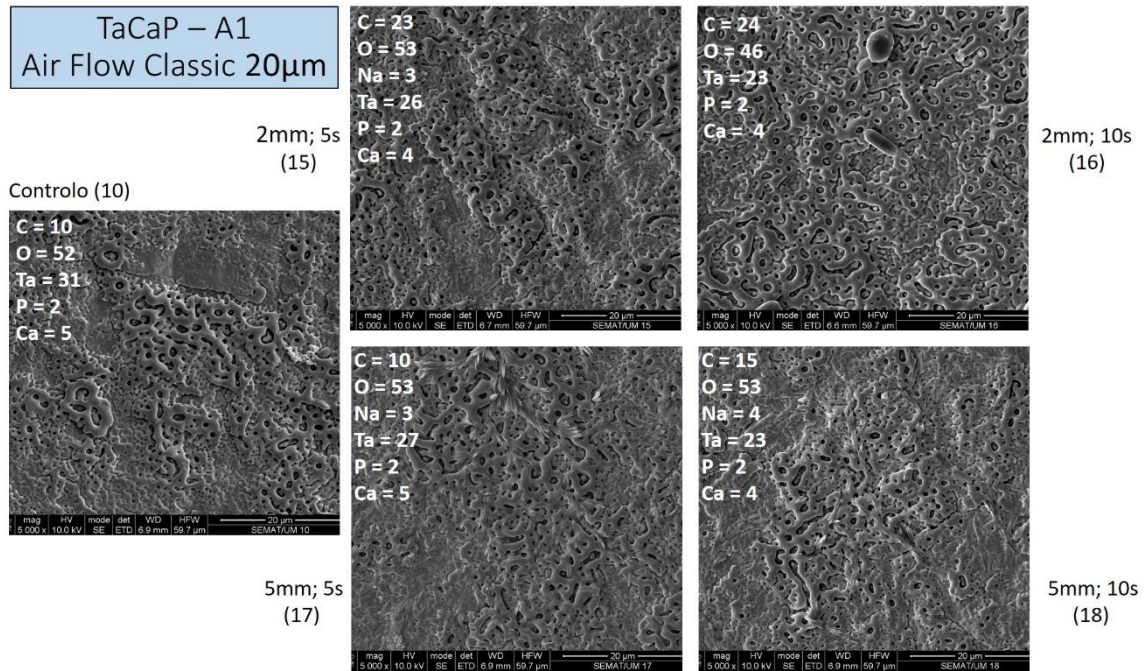


Figure 38 - SEM micrographs and EDS results of samples number 10, and 15-18 – Air Flow Classic.

In this set of micrographs (**Error! Reference source not found.**), the air-polished samples have a topography similar to the control (10) and to each other. The air polishing parameters, time and distance, do not seem to impose observable changes in the nanostructure of the samples, except in sample (16) (where the air polishing was performed in a short distance (2 mm), during 10 s), which seems to be more textured, and have more powder residues.

Na is clearly and only visible after air polishing. However, similarly to the correspondent sample of pure Ta, when the air polishing duration is increased (10 s), maintaining a short distance of 2 mm (16), Na is not present. About the osteoconductive elements (Ca and P), it seems that its atomic rate is lower when both

distance (5 mm) and duration (10 s) are increased – sample (18). Comparatively to the control sample, tested samples have Ta lower values.

1.1.3. TACAP-ZN – A2

Table 5 represents the division of nanostructured oxide tantalum samples, with Ca, P, and Zn (TaCaP-Zn), by nine groups (19 to 27), according to the air polishing parameters applied.

Table 5 - Distribution of TaCaP-Zn samples according to the air polishing parameters.

	GROUP	SURFACE MODIFIC.	AIR POLISHING	POWDER	DISTANCE (mm)	DURATION (s)
TaCaP-Zn – A2	19	A2	Without	CONTROL		
	20	A2	With	Air Fl. Plus	2	5
	21	A2	With	Air Fl. Plus	2	10
	22	A2	With	Air Fl. Plus	5	5
	23	A2	With	Air Fl. Plus	5	10
	24	A2	With	Air Fl. Classic	2	5
	25	A2	With	Air Fl. Classic	2	10
	26	A2	With	Air Fl. Classic	5	5
	27	A2	With	Air Fl. Classic	5	10

1.1.3.1. AIR FLOW[®] PLUS

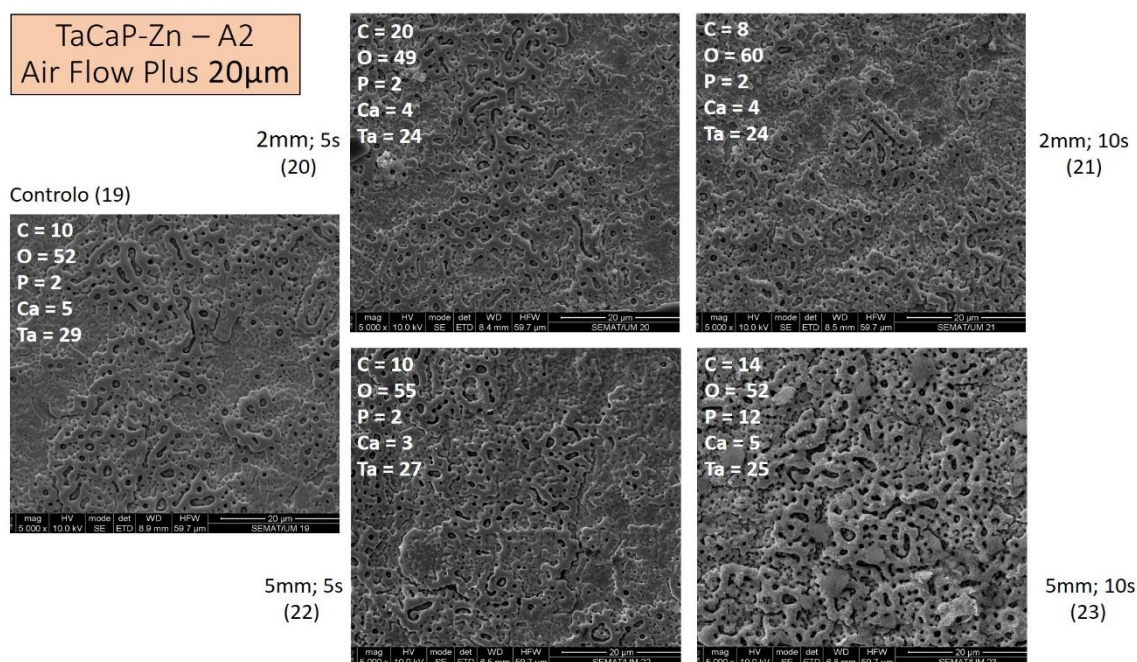


Figure 39 - SEM micrographs and EDS results of samples number 19-23 – Air Flow Plus.

Compared to the control group (Figure 39), the polished samples do not show remarkable changes in the tantalum nanostructure, either in terms of size or number of nanopores, except for the sample air polished for a longer time at a greater distance (23). This sample stands out between the rest of the others, presenting a pronounced pore network, which appears to be composed of multiple layers, thus not having a surface as homogeneous as the rest.

There is another surface change introduced by the air polishing procedure: the presence of stains, colored by white in these types of images, which seems to be in a more significant number when the air polishing is performed in 10 s – (21) and (23). Once again, this occurs with more prominence in the sample (23).

Regarding EDS results, the presence of Zn was not found in any sample, including the control. Like Ta, the elements Ca and P have a smaller At. % after polishing. Except for the sample (20), for O, and sample (21), for C, it is evident an increase of these elements' At.%, after the air-abrasive procedure.

1.1.3.2. AIR FLOW[®] CLASSIC

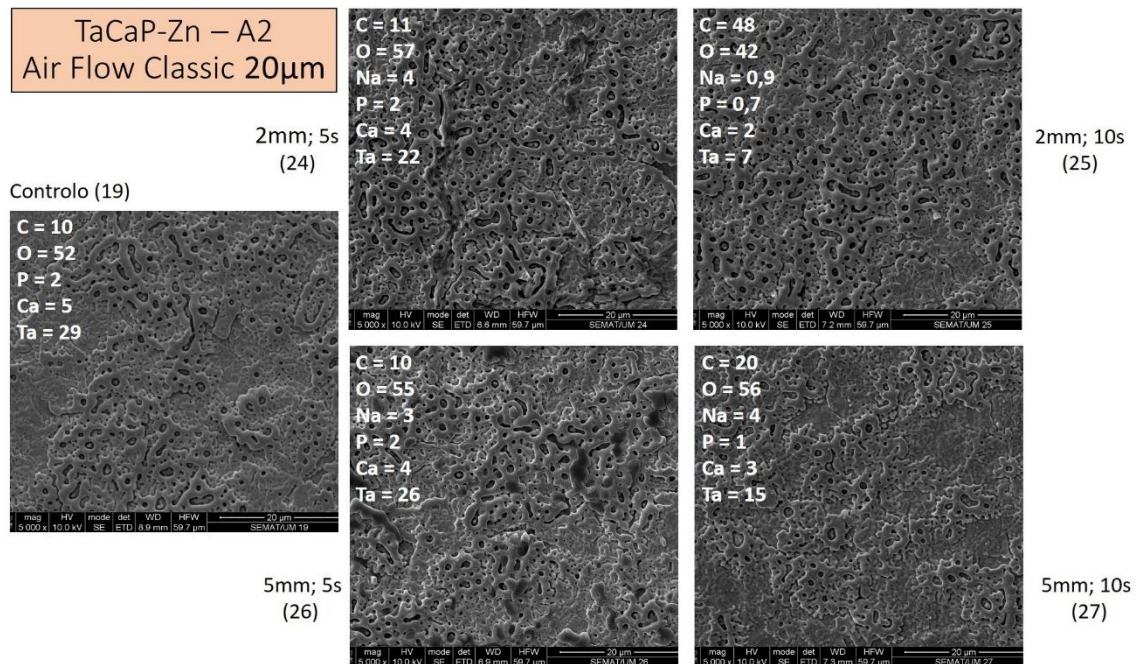


Figure 40 - SEM micrographs and EDS results of samples number 19 and 24-27 – Air Flow Classic.

In this set of micrographs (**Error! Reference source not found.**), some surface differences are visible between the control and tested samples. Although nanostructured, the control sample's surface is more discreet and apparently less textured than the rest. The number of pores appears to be smaller, and the surface more homogeneous. Sample (27) seems to be the most similar to the control.

Similar to the air polishing with AFP, some white stains are also visible here, although in a significantly smaller amount. This finding seems to be present, once again, with more significant evidence in the sample (27)

From the EDS analysis, it is easy to see Na's presence in the air-polished samples, which certainly have been incorporated by the AFC. Another change in the chemical composition stands out for sample (26), where the At. % values are quite different than the rest of the samples and control. This occurs by a pronounced decrease in Ta, Ca, and P values, with a visible increase in the C element.

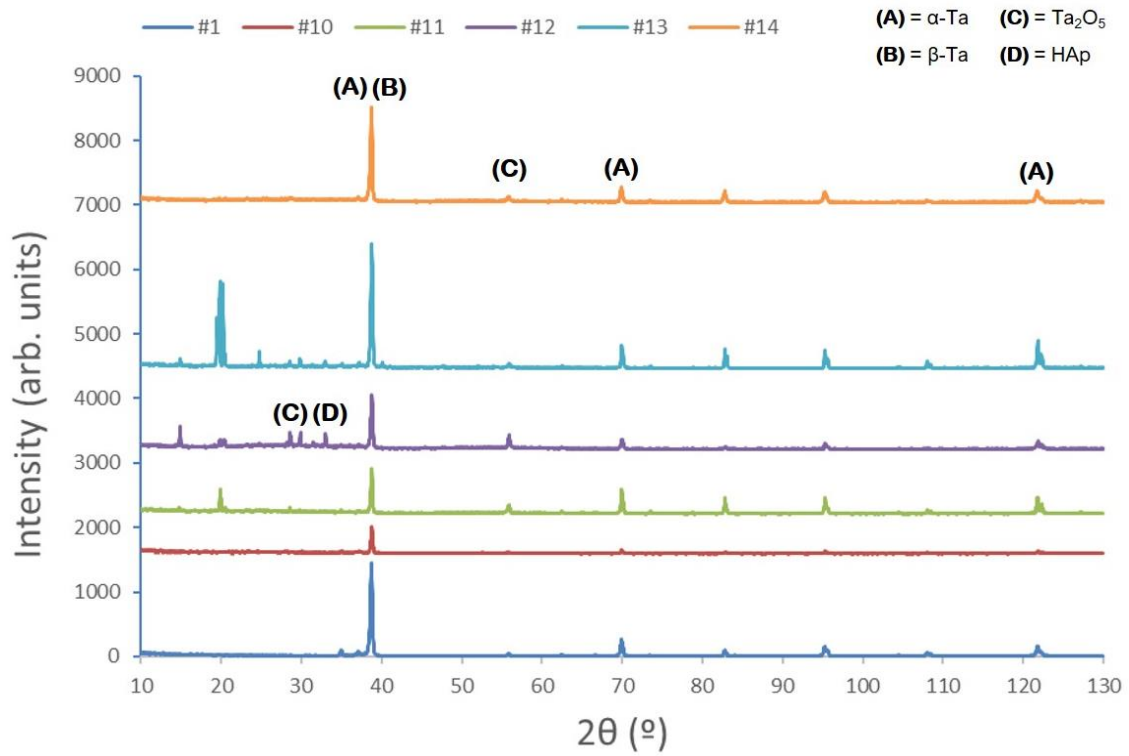
1.2. XRD

In order to study the crystalline structure, and the phases present in the Ta samples, an XRD analysis was performed. For this purpose, six Ta samples – number (1), (10), (11), (12), (13), and (14) – were selected. Among them, there are two control samples – (1) and (2) – where the air polishing procedure was not executed, with two types of surfaces – pure Ta and TaCaP – Table 6.

Table 6 - Representation of the selected Ta samples for XRD analysis, according to air polishing parameters. The colored geometric forms next to the sample's number refer to the corresponding XRD diffractogram described ahead (Graphic 1).

	SAMPLE	SURFACE MODIFIC.	AIR POLISHING	POWDER	DISTANCE (mm)	DURATION (s)
Ta	#1 	PURE	Without	CONTROL		
	#10 	A1	Without	CONTROL		
TaCaP – A1	#11 	A1	With	Air Fl. Plus	2	5
	#12 	A1	With	Air Fl. Plus	2	10
	#13 	A1	With	Air Fl. Plus	5	5
	#14 	A1	With	Air Fl. Plus	5	10

The diffractograms obtained from XRD analysis are shown in Graphic 1.



Graphic 1 - XRD diffractograms of Ta samples number #1, #10, #11, #12, #13, and #14.

After comparing the spectra with ICDD charts, it is possible to verify that in all samples, the main crystalline phases identified could be α -Ta: body-centered cubic (bcc) (ICDD No. 00-004- 0788) – (A) – and β -Ta: tetragonal (ICDD No. 00-025-1280) – (B). A higher peak of approximately $2\theta = 40$ represents these phases; however, they cannot distinguish from each other.

Diffraction peaks corresponding to tantalum oxide (Ta_2O_5) – (C) – (ICDD No. 01-070-9177) are also visible, with particular prominence in sample #12. This sample also seems to contain Hydroxyapatite – HAp (ICDD No. 00-055-0592) in the hexagonal crystalline phase.

In samples #11, #12, and #13, particularly in #13, it is visible a peak correspondent to $2\theta = 20$. However, it was not found a match for a chemical element/substance in the ICDD charts.

1.3. AFM

To access the Ta surfaces' physical topography and roughness and get additional data regarding the effect of the air-abrasive procedure, the AFM technique was performed. Similar to the XRD, the Ta samples #1, #10, #11, #12, #13, and #14 were selected for analysis. The next figures display the AFM images for the mentioned Ta surfaces (Figure 41, Figure 42, Figure 43, Figure 44, Figure 45, and Figure 46).

Sample #1:

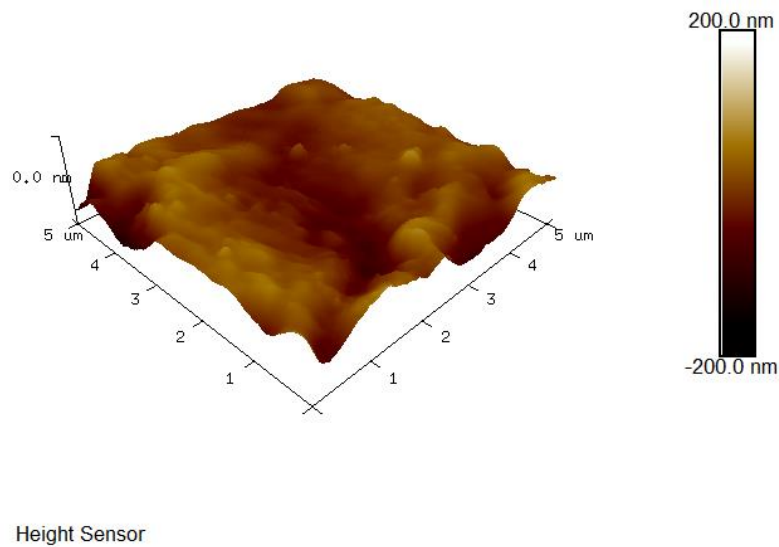
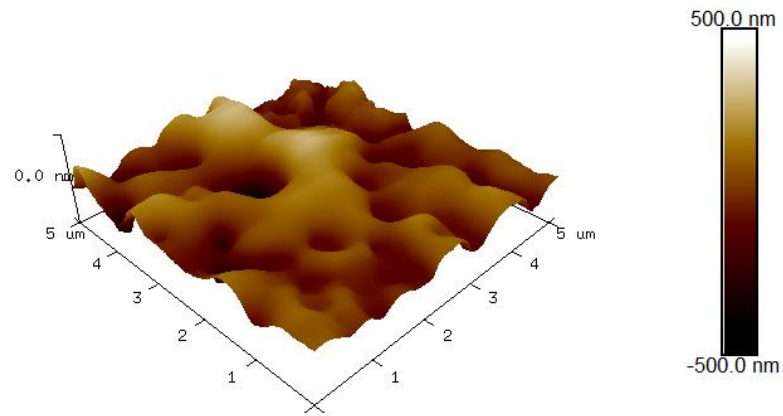


Figure 41 - Representative AFM image of tantalum surface #1.

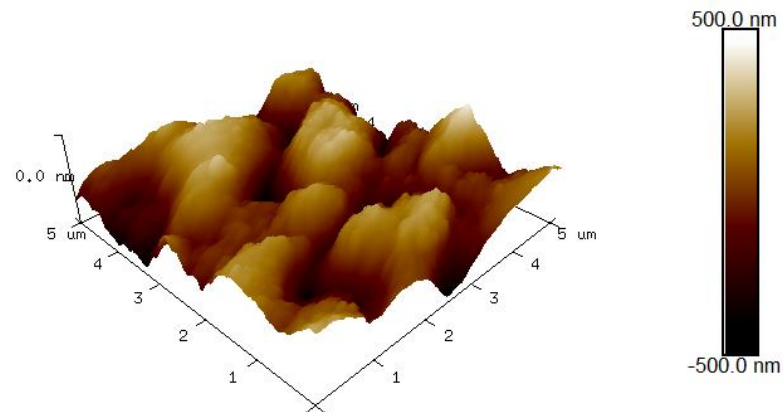
Sample #10:



Height Sensor

Figure 42 - Representative AFM image of tantalum surface #10.

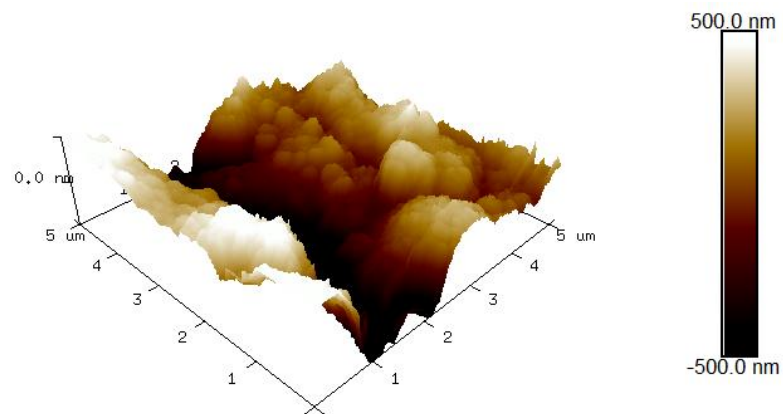
Sample #11:



Height Sensor

Figure 43 - Representative AFM image of tantalum surface #11.

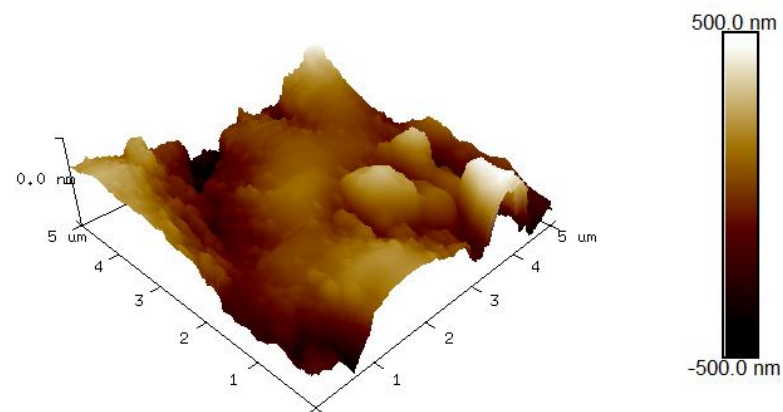
Sample #12:



Height Sensor

Figure 44 - Representative AFM image of tantalum surface #12.

Sample #13:



Height Sensor

Figure 45 - Representative AFM image of tantalum surface #13.

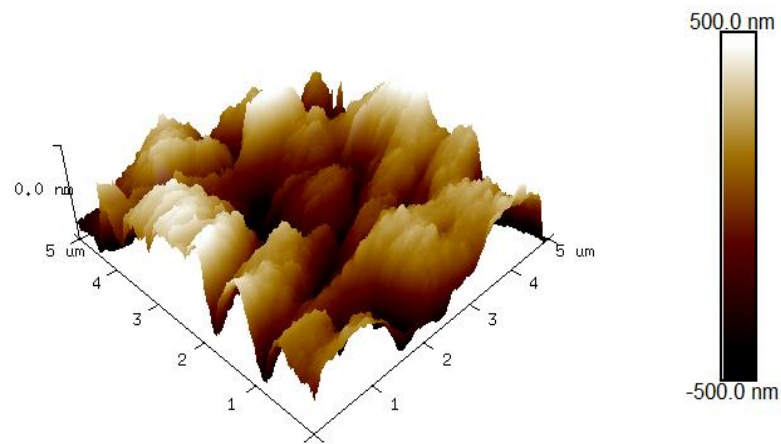
Samples #14:

Figure 46 – Representative AFM image of tantalum surface #14.

The next table (Table 7) represents the mean calculated values (nm), after three surface measurements', of Rms (root mean square), Ra (roughness average), and Rmax (maximum roughness), according to the surface modification and working parameters.

Table 7 – Rms, Ra, and Rmax values for the studied samples (n = 6) obtained by AFM.

	SAMPLE	SURFACE MODIFIC.	AIR POLISHING distance (mm) / time (s)	Rms (root mean square - nm)	Ra (roughness average - nm)	Rmax (maximum roughness - nm)
Ta	#1 ◆	PURE	Without	48 nm	38 nm	581 nm
TaCaP – A1	#10 ◆	A1	Without	130 nm	101 nm	773 nm
	#11 ◆	A1	2 / 5	153 nm	124 nm	946 nm
	#12 ◆	A1	2 / 10	154 nm	119 nm	1146 nm
	#13 ◆	A1	5 / 5	278 nm	218 nm	1795 nm
	#14 ◆	A1	5 / 10	229 nm	187 nm	1536 nm

From the analysis of Table 7, it can be noticed that the results corroborate what was possible to conclude by observing the AFM images. Therefore, the following outcomes can be suggested:

- 1) The PEO/MAO procedure increased the surfaces' roughness;
- 2) The air polishing procedure increased the roughness in the anodized surfaces;
- 3) The most significant values regarding Ta surface's roughness – Rms, Ra, and Rmax – were recorded on samples #13 and #14, with greater prominence in #13, which was submitted to PEO, and air polishing at 5 mm, for 5 seconds.
- 4) In its turn, the recorded values between sample #11 and #12 are relatively similar to each other.

1.4. SESSILE DROP TECHNIQUE

The sessile drop technique was performed in two Ta samples, using only pure water. The complete analysis could not be performed for all samples with any of the three liquids.

V. DISCUSSION

“Study of air polishing effect on tantalum surfaces.”

No scientific publications have been found in the literature research reporting *in vitro* studies of air polishing procedures in tantalum surfaces, making this a pilot project in the area. Considering the properties of Ta previously described, which make this material very promising in Oral Rehabilitation, it was chosen to study the effect of the air polishing on this metal. Therefore, this investigation's starting point was well defined: to evaluate the impact of the air-abrasive procedure on tantalum surfaces. In this sense, it can be possible to predict these surfaces' future behavior concerning the risk of peri-implantitis, once integrated into a dental implant or prosthetic/regenerative component.

As it is a pilot project and innovative in the approached theme, the discussion of this work will be done mainly by comparing the results obtained in the *in vitro* studies of air polishing on pure titanium surfaces/discs. Regarding the air polishing in biofunctionalized titanium surfaces, no published data was found in the literature research. The number of tested specimens reported in the studies selected after the literature research was very variable, although it did not reach the number of tantalum samples decided for this study (81).

It is expected that it can be established a direct relationship between the application of the different air polishing conditions, such as distance, duration or type of powder used, and the possible observable modifications in the air polished surfaces.

Two distances were chosen (2 and 5 mm). The recommended by the manufacturer is 5 mm. However, it was decided to test a shorter distance, placing the jet closer to Ta's surface. In this way, it was intended to evaluate the possible surface degradation through the presence of morphological modifications and the detachment of the nanoparticles of P, Ca, and Zn, previously incorporated by the surface modification techniques.

Tantalum is typically not bioactive and, thereby, is unable to directly bond to surrounding bone (Levine *et al.*, 2006; Wang, Wang and Han, 2013). To enhance the bonding of tantalum to the bone, bioactive coatings must be developed.

In this study, the surface modification techniques applied to tantalum were crucial to the production of nanostructured tantalum oxide. In this sense, Plasma Electrolytic Oxidation (PEO) helped to change the surface topography, producing nanopores, and, at

the same time, allowed the incorporation of osteoconductive elements – Ca and P. Similar to PEO, the Magnetron Sputtering technique revealed the possibility of changing the chemical composition, by deposition of Zn coatings into the nanostructured Ta.

Next will be presented the detailed discussion of the obtained results according to the surface characterization technique applied – SEM/EDS, XRD, AFM, and Sessil Drop Technique. This chapter will then end with the comparison between the outcomes of this *in vitro* study, i.e., the effects of the two air polishing powders, with the current literature.

1. SURFACE CHARACTERIZATION TECHNIQUES

1.1. SEM / EDS

In the case of this study, EDS is useful in detecting Ca and P incorporation into the pure Ta, as well as ZnO/Zn by magnetron sputtering. It can also reveal if the air polishing powders selected are additive to the surfaces in terms of the chemical composition. Some samples had to be covered by a conductive coating, like gold (Au) and palladium (Pd), to meet one of the requirements for this analysis's success: the presence of electrical conductivity.

The present study tested and compared two powders for air polishing from EMS (Electro Medical Systems, Nyon, Switzerland): a sodium bicarbonate powder – Air Flow[®] Classic (AFC) – and a low abrasive erythritol-chlorhexidine-based powder – Air Flow[®] Plus (AFP) – which was recently introduced in the market for subgingival air polishing. According to the manufacturer, AFP is much less abrasive than AFC, having a particle size of 14 µm, against 40 µm of AFC (Electro Medical Systems [APA], n.d.).

The statements mentioned above were verified by SEM/EDS analysis of the powders. With SEM results, it was possible to confirm the difference between the size of the two kinds of powder particles: 32 µm for AFC and 12 µm for AFP. These findings are consistent with the obtained by Hägi *et al.* (2015). They also confirmed by SEM the smaller particles for erythritol (AFP) in comparison to glycine powder, which, by EMS definition, is smaller than sodium bicarbonate (AFC) (Electro Medical Systems [APA], n.d.).

However, larger-than-expected particles were found in the AFC (59,52 µm), which did not happen with AFP. Depending on the quantity, this can increase the AFC's degree of abrasiveness, thus influencing its effect on the surface.

Regarding EDS results, as expected in a sodium-bicarbonate-based powder, the Na element was revealed in AFC powder.

The effect of the two air-abrasive powders applied to different Ta surfaces will be discussed below. To facilitate the reading and understanding of this part of the Discussion chapter, the same content organization presented in the Results chapter will be next included (SEM micrographs and corresponding results, written in a different color, between “”).

1.1.1. PURE TA

1.1.1.1. AIR FLOW[®] PLUS

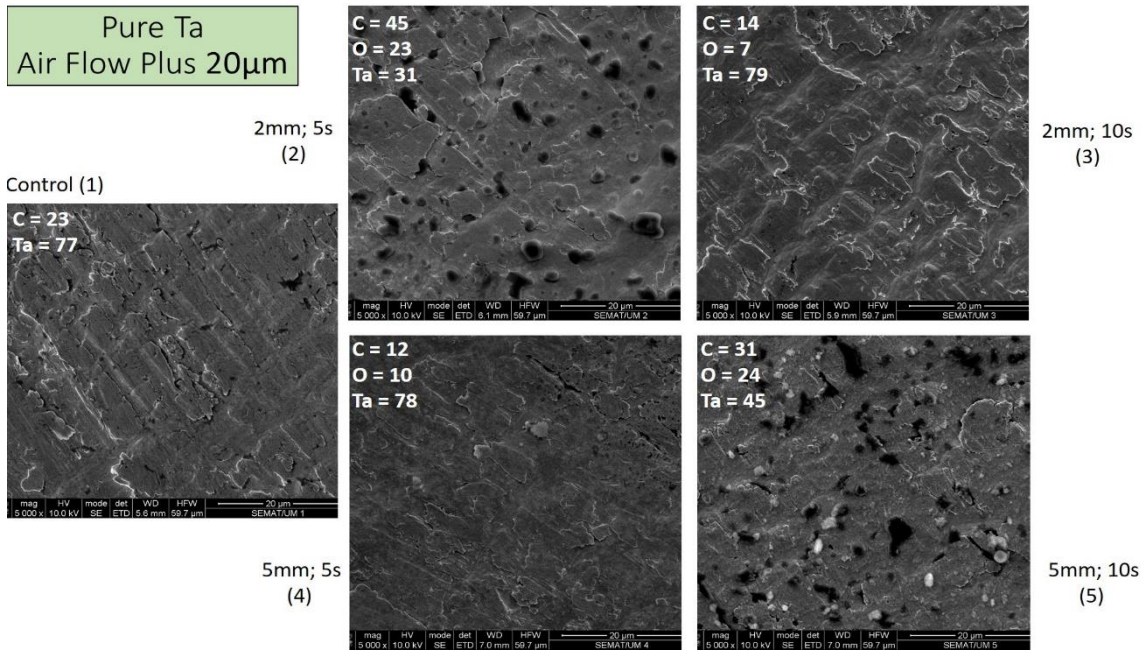


Figure 47 - SEM micrographs and EDS results of samples number 1-5 – Air Flow Plus.

“Comparing to the control sample, air polishing does not appear to have produced significant changes in the integrity of pure Ta. The ovoid stains present in the sample (2) and (5) resemble granules of powder accumulated on the surface.

After 5 seconds of air polishing, it seems that with a shorter distance (2 mm), greater are the powder residues present on the surface, namely in the sample (2). In samples where the distance is 5 mm, the excess of powder is more significant when air polishing was carried out for more seconds – sample (5).”

The qualitative analysis between the control and the tested surfaces did not reveal visible effects induced by the air polishing with erythritol-chlorhexidine. This supports that erythritol-chlorhexidine powder particles are not enough to produce damages on these surfaces, confirming its low-abrasive character.

Powder residues were found in two samples: (2) and (5). In sample (2), this can be explained by the fact that the shorter the distance between the handpiece and the sample (2 mm), the greater the jet's intensity, so a more significant number of particles will be retained on the surface for 5 seconds of polishing. This did not happen in sample (3) (2 mm; 10 s) because, eventually, the duration allowed the particles to disperse with the accumulation of water from the jet. In sample (4), the absence of residues can be due to the insufficient time for its aggregation and, also, to the greater distance. As for sample (5) (5 mm; 10 s), the powder residues can be explained by a longer air polishing time, which allowed for its accumulation. They did not disperse as easily as in sample (3), possibly due to the lower jet intensity, caused by the greater distance (5 mm).

“In terms of chemical composition, the air polishing brought the incorporation of Oxygen (O) in all samples and a slight increase of At. % of Ta in the presence of a short distance and an increased duration – sample (3), as well as in the presence of an increased distance and short time – sample (4). Comparatively to the control sample, in (2) and (5) samples, Carbon increased, and Ta decreased.”

The Oxygen element incorporated after the air polishing is present in the air-water jet that characterizes this procedure. Beyond O, the increase of C in the samples (2) and (5) is also due to the air-abrasive process, namely the air polishing powder residues. These element's incorporation in the surfaces changes the Ta balance, explaining its decrease.

1.1.1.2. AIR FLOW® CLASSIC

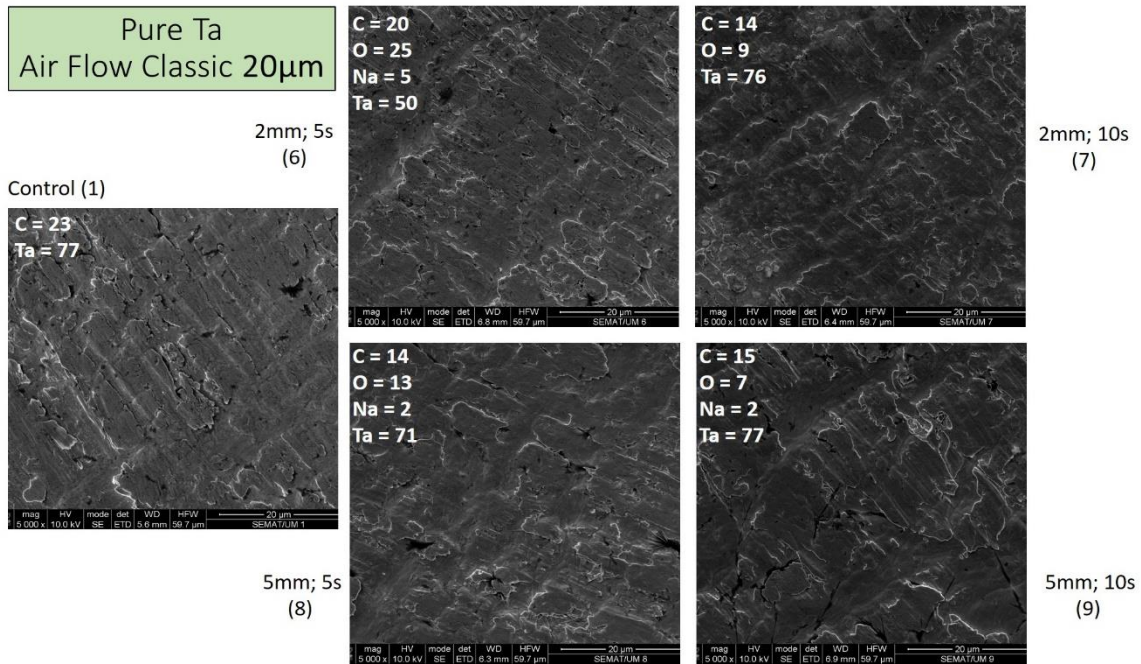


Figure 48 - SEM micrographs and EDS results of samples number 1 and 6-9 – Air Flow Classic.

“(...) when the air-polished samples are compared to the control (1), the surface topography appears to be very similar to each other, no matter the distance or the air polishing duration. It is not visible the accumulation of powder residues over the surfaces.”

As for EDS results, the only sample with no incorporation of Na by air polishing was number (7). Regarding the amount of Ta, a more pronounced decrease in the sample (6) is evident, where the air polishing was performed at a shorter distance and with a shorter duration. Here, conversely to Ta, the Na incorporation was increased.

Some degree of abrasiveness in pure Ta would be expected, mainly caused by sodium bicarbonate particles at a shorter distance than the recommended. However, no changes in the surface morphology were verified. This fact can be supported by some properties that characterize tantalum, such as its good resistance to wear and its hardness (Maccauro *et al.*, 2009).

“As for EDS results, the only sample with no incorporation of Na by air polishing was number (7). Regarding the amount of Ta, a more pronounced decrease in the sample (6) is evident, where the air polishing was performed at a shorter distance and with a shorter duration. Here, conversely to Ta, the Na incorporation was increased.”

Although the effect of sodium-bicarbonate powder has not been noticed in the surface topography, in the chemical composition it is evidenced by the presence of Na. The only exception is in the sample (7), where 10 seconds of air polishing may be too long and, therefore, instead of incorporating it removes Na from the surface. Besides, after 10 seconds of continuous air polishing, there is an excess of water, removing the powder's chemical elements.

In sample (6), there seems to have been an increase in the incorporation of O, C, and Na from the air polishing procedure/powder, since it was produced with greater intensity (shorter distance and shorter duration). On the contrary, the Ta has decreased because of the increase in the rest of the elements. Therefore, it can be assumed that in the presence of a short distance, and for a short time, Na's incorporation in these surfaces is more efficient without changing the surfaces' topography.

Although it is a minimum amount, according to some authors, air polishing sodium-bicarbonate may induce an excess of Na in the body, which can be problematic in some patients, especially in those who have a sodium-restricted diet, hypertension, respiratory illness, infectious disease, and renal insufficiency (Graumann, Sensat and Stoltenberg, 2013). Some patients also relate discomfort with the salty taste of bicarbonate when AFC is performed (Biazussi *et al.*, 2019).

1.1.2. TACAP – A1

1.1.2.1. AIR FLOW[®] PLUS

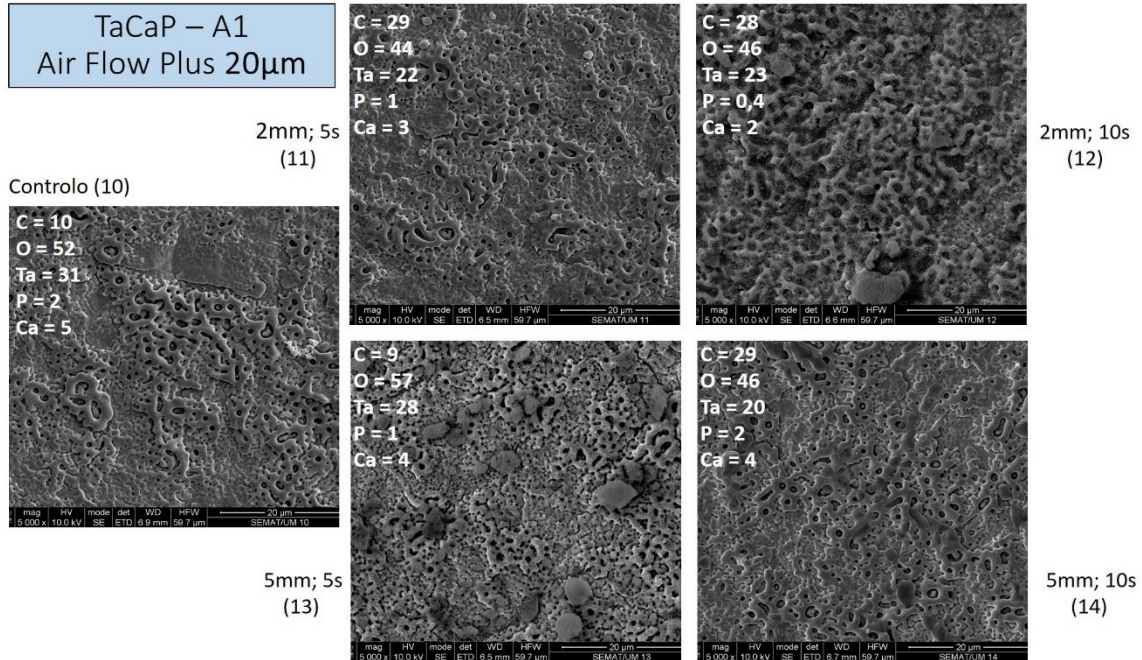


Figure 49 - SEM micrographs and EDS results of samples number 10-14 – Air Flow Plus.

“In the control group (10), pores and holes are visible, apparently arranged in layers, under an unorganized disposition, and with different sizes. These structures make up a highly textured surface. At first glance, the air polishing does not appear to affect the tested surfaces, since none of the samples, (11) to (14), show differences in the size and number of pores.

As with pure tantalum surfaces, ovoid granules corresponding to excess air polishing powder appear to be present, particularly when distance increases (5 mm), in a short duration (5 s) – (13). If the time increases (10 s) with the same distance (5 mm) – (14) there are far fewer residues present.”

Despite the better biological properties exhibited by tantalum, the nanoscale modifications can still improve cells' interactions with these surfaces compared to the currently used implant materials (Uslu *et al.*, 2020).

Comparing the control samples of pure Ta – (1) and TaCaP – (10), the effects of the first surface modification technique applied – A1 – are clearly visible. Conversely to pure tantalum, these samples present a nanostructure characterized by unevenly distributed micropores with varying sizes, apparently disposed by layers. This is characteristically produced by the spark discharge of the PEO/MAO process. These results are in line with those obtained by Zhao *et al.* (2017), who reported crater-like discharge channels in the coating tantalum surfaces. According to the authors, these channels were caused by the exit of gas bubbles and molten oxide from the surface during the PEO/MAO process, some being superimposed. Due to the proximity of the discharges' location, some channels ended to connect, forming a large discharge channel, thus increasing the surface roughness.

Sowa *et al.* (2017) described a series of plasma and thermochemical reactions that occur in PEO/MAO and, although they chose to work under galvanostatic conditions, the authors of this study obtained coatings relatively thick, disposed of by porous layers. In addition, these layers presented a rugged appearance due to the high voltage applied and could also be enriched with electrolyte components.

Once again, the AFP powder has demonstrated a low abrasive potential to the porous oxide nanostructure, not affecting its morphology. The differences between the number of powder granules between samples (13) and (14) are possible due to air polishing duration. When the air-abrasive jet is applied for 10 seconds, there is an increase in the amount of water, which can reduce these residues' accumulation.

“Regarding EDS results, all the samples present in their chemical composition the elements Ca and P, incorporated by anodization. A lower At. % of Ta, P, and Ca is also evident in the samples submitted to air polishing. This is particularly evident for the osteoconductive elements in the sample (12), where the air polishing distance is minimum, and the time is maximum.”

As mentioned in previous sections, PEO/MAO technique allows physicochemical changes in the submitted surfaces by producing an anodic oxide layer and, at the same time, by the incorporation of chemical elements within the nanopores. In this case, EDS

reveals the presence of Ca and P in all the samples, with atomic ratio ≈ 2 , not so far from HAp ratio (1.67), which is consistent with the electrolytic solution used: calcium acetate (Aca) and β -glycerophosphate (β -GP) solution. Zhao *et al.* (2017) achieved similar results. In their study, coatings containing Ca and P were successfully fabricated on pure Ta via PEO/MAO, using a similar electrolyte to the one used in this work (Aca – β -GP).

The lower At. % of Ta, P, and Ca in the air-polished samples can be explained by the increase of C and O, with origin in the air polishing powder. In its turn, it seems that the air polishing procedure can make a selective remotion of P or, at least, masks it. Therefore, the Ca amount increases. This finding is consistent with those reported by Fialho, where it is visible a decrease of P in depth (Fialho and Carvalho, 2019).

Although the AFP is a low-abrasive powder, its effects might be noticed by a slight decrease in the amount of the osteoconductive elements incorporated before and in the level of Ta. Nevertheless, the air polishing procedure did not remove chemical elements, regardless of the distance and the duration applied, thus maintaining the bioactive profile of these types of surfaces.

1.1.2.2. AIR FLOW[®] CLASSIC

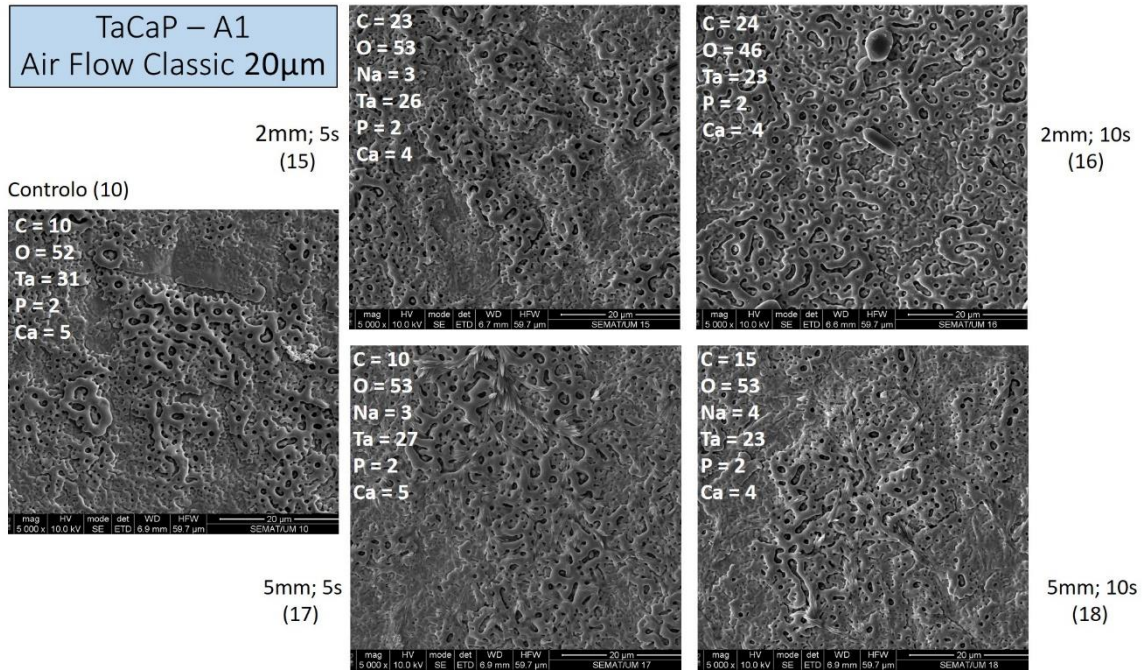


Figure 50 - SEM micrographs and EDS results of samples number 10, and 15-18 – Air Flow Classic.

“(...) the air-polished samples have a topography similar to the control (10) and to each other. The air polishing parameters, time and distance, do not seem to impose observable changes in the nanostructure of the samples, except in sample (16) (where the air polishing was performed in a short distance (2 mm), during 10 s), which seems to be more textured, and have more powder residues.”

After comparing the type of surface of control and the tested samples, the potential abrasiveness of AFC powder, which has a superior particle granulometry, is not significantly denounced, apart from the sample (16). Here, the shorter distance and the longer duration in which the air polishing was performed seem to cause a more intense air-abrasive procedure, leading to a more rugged surface. This fact can also contribute to more powder particles being trapped on the textured surface. As has been already speculated for pure Ta, this metal's physical properties can make it a material resistant to the effects of air polishing, even in its most abrasive version.

“Na is clearly and only visible after air polishing. However, similarly to the correspondent sample of pure Ta, when the air polishing duration is increased (10 s), maintaining a short distance of 2 mm (16), Na is not present. About the osteoconductive elements (Ca and P), it seems that its atomic rate is lower when both distance (5 mm) and duration (10 s) are increased – sample (18). Comparatively to the control sample, tested samples have Ta lower values.”

Compared to AFC's performance in pure Ta samples, the results are very similar in the nanostructured tantalum oxide. As expected, apart from the sample (16), Na is incorporated in the tested samples due to AFC's chemical composition. The absence of Na in the sample (16) is, once again, speculated by its dispersal due to the significant amount of water during 10 seconds of air polishing and, perhaps, due to the larger size of AFC's particles. A pattern begins to show when AFC is applied over a shorter distance and for a prolonged time since, like what happened in the sample of pure Ta, this powder ends up removing Na instead of incorporating it.

Once the AFC is more abrasive, it slightly decreased Ca rates. However, it did not remove from the nanoporous surface. The incorporation of Ca by anodization is, typically, obtained in greater depth in Ta structures than P. This last element usually stands in a more superficial position than Ca. If Ca decreases, it confirms this air polishing powder's effect on these surfaces, revealing it as more abrasive, thus not so desirable for the surface's osteoconductive potential. Ta also reduced due to the remaining element's incorporation, changing the chemical balance. About the lower rates of Ca, it can be due to the longer time of air polishing, which, in some way, slightly removed the incorporated elements from the nanoporous.

1.1.3. TACAP-ZN – A2

1.1.3.1. AIR FLOW[®] PLUS

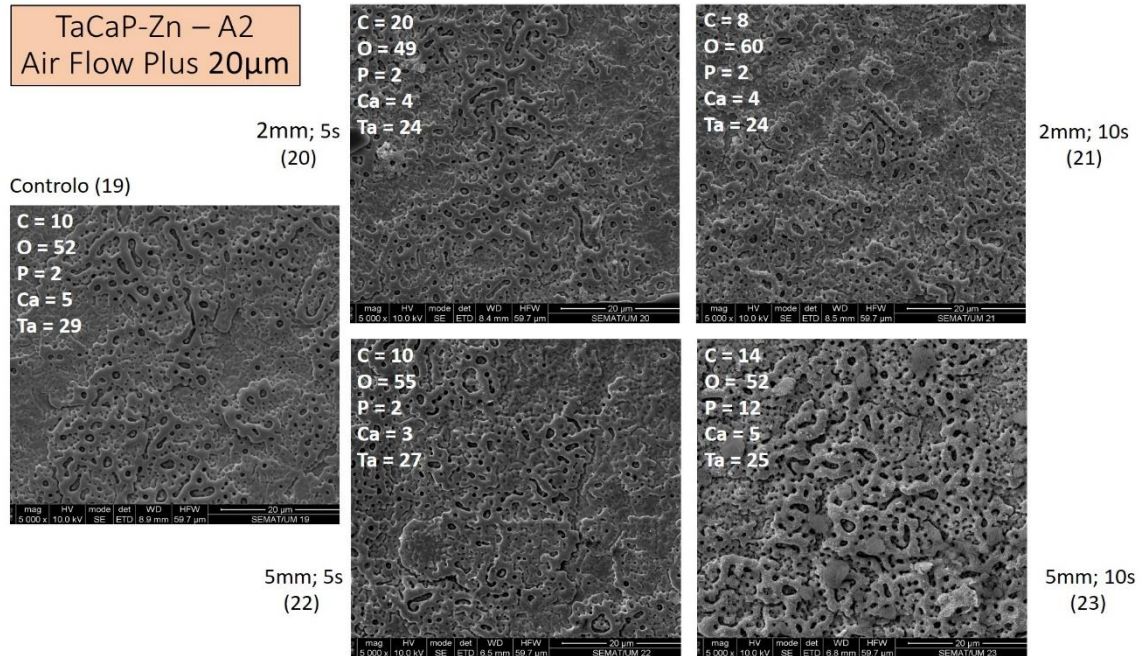


Figure 51 - SEM micrographs and EDS results of samples number 19-23 – Air Flow Plus.

“Compared to the control group (Figure 38), the polished samples do not show remarkable changes in the tantalum nanostructure, either in terms of size or number of nanopores, except for the sample air polished for a longer time at a greater distance (23). This sample stands out between the rest of the others, presenting a pronounced pore network, which appears to be composed of multiple layers, thus not having a surface as homogeneous as the rest.”

The main difference between the TaCaP-Zn surfaces (A2) and the previous TaCaP (A1), both produced via PEO/MAO, is the application of an additional surface modification technique in the first ones – Magnetron Sputtering – which represents the deposition of Zn nanoparticles, thus altering the chemical composition of the surface. In this sense, it is not expectable to have significant surface modifications in the morphology. Sample (23) stands out due to a more rugged appearance. However, this

might not have been caused by the air-abrasive procedure, once it is a low-abrasive air polishing powder.

“There is another surface change introduced by the air polishing procedure: the presence of stains, colored by white in these types of images, which seems to be in a more significant number when the air polishing is performed in 10 s – (21) and (23). Once again, this occurs with more prominence in the sample (23).”

The little stains found in the SEM micrographs can be explained by the presence of a coating of Zn nanoparticles from magnetron sputtering. In the sample (23), the air polishing conditions are considered less aggressive than in the sample (21), which means that the 5 mm distance removes less Zn nanoparticles in 10 seconds than 2 mm. Therefore, it is more desirable to air polish at a greater distance, even if the duration is prolonged, increasing the antibacterial effect of this type of surface.

“Regarding EDS results, the presence of Zn was not found in any sample, including the control. Like Ta, the elements Ca and P have a smaller At. % after polishing. Except for the sample (20), for O, and sample (21), for C, it is evident an increase of these elements' At.%, after the air-abrasive procedure.”

It seems that the air polishing procedure does not directly cause the absence of Zn once it is not present in the control sample. Although At. % Zinc is not included in the EDS results, it does not mean that the Zn particles are not part of the tantalum nanostructure. One hypothesis for this event is that the nanoparticles may be masked by the remaining chemical elements and/or because they are in very little quantity. Considering the increase in C and O in almost all the samples, this is due to the air polishing powder, which tends to mask the remaining chemical elements.

1.1.3.2. AIR FLOW[®] CLASSIC

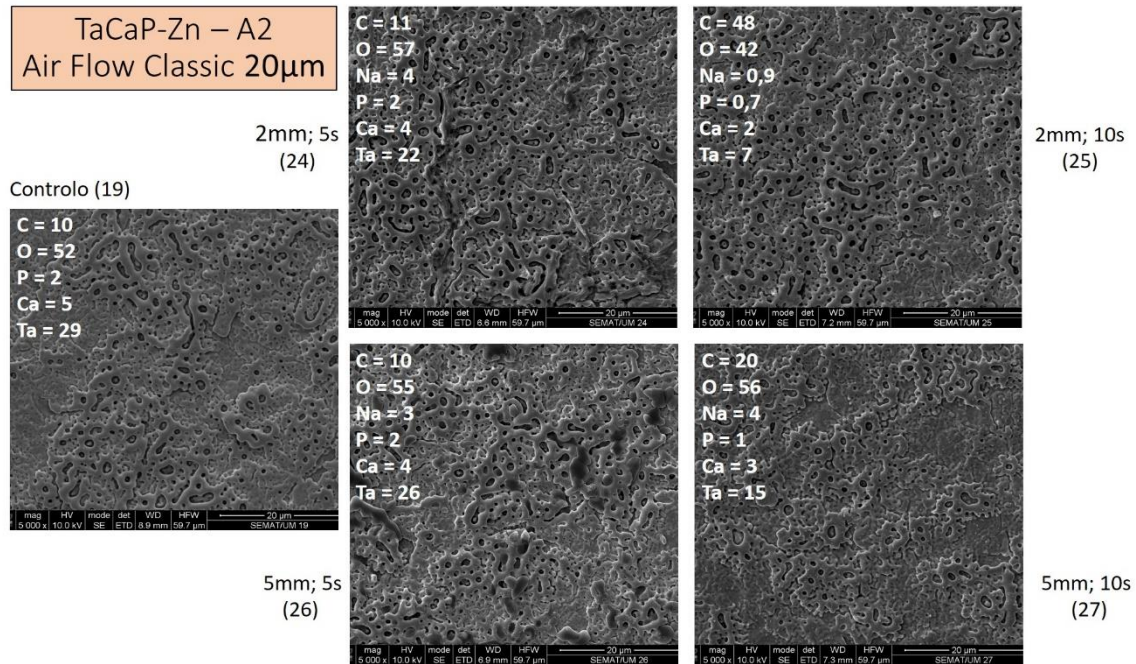


Figure 52 - SEM micrographs and EDS results of samples number 19 and 24-27 – Air Flow Classic.

“(...) some surface differences are visible between the control and the tested samples. Although nanostructured, the control sample's surface is more discreet and apparently less textured than the rest. The number of pores appears to be smaller, and the surface more homogeneous. Sample (27) seems to be the most similar to the control.”

In the control sample is evident a smoother surface, which confirms the effect of the deposited coating of Zn nanoparticles: turning the surfaces into more regular and uniform. Apparently, in terms of abrasiveness, AFC's impact seems to be more noticeable, transforming the tested surfaces into more textured and irregular. Although sample (27) has been air polished for a longer time (10 s), the greater distance (5 mm) may have decreased the jet intensity, not being enough to produce surface modification. This may explain the similarity of this sample with the control.

“Similar to the air polishing with AFP, some white stains are also visible here, although in a significantly smaller amount. This finding seems to be present, once again, with more significant evidence in the sample (27).”

As expected on a surface subjected to Zn deposition by magnetron sputtering, these nanoparticles are visible through the white stains found in the qualitative analysis of this set of SEM micrographs. They are noticeably fewer in number compared to those found in the samples air polished with AFP. The larger size of the AFC particles makes this powder more abrasive, causing an increased remotion of the Zn nanoparticles. In the sample (27), this removal is not so intense because the effect produced by a greater distance, although for a longer time, is not enough to promote a more effective removal. Despite the AFC's greater abrasiveness evidenced by the previously mentioned results, the air polishing procedure did not entirely remove the nanoparticles or the osteoconductive elements.

“From the EDS analysis, it is easy to see Na's presence in the air-polished samples, which certainly have been incorporated by the AFC. Another change in the chemical composition stands out for sample (26), where the At. % values are quite different than the rest of the samples and control. This occurs by a pronounced decrease in Ta, Ca, and P values, with a visible increase in C element.”

Similarly to what happened in the sample air-polished with AFP at 2 mm and with 10 s of duration, with AFC, there is also a decrease in the osteoconductive elements (Ca and P). It seems that these air polishing conditions – powder, distance, and time – are more aggressive to the tested surface, implying the remotion of Ca and P rather than its incorporation, thus inducing a more pronounced chemical surface modification.

It is evident that the minor is the powder granulometry, the little are the morphological surface modifications induced by the air-abrasive system.

1.2. XRD

In the literature research carried out, no articles were found that included the XRD technique to characterize air polished tantalum/titanium implant surfaces. Therefore, this *in vitro* study presents itself as a first attempt in establishing a relationship between the areas of Dentistry (Oral Rehabilitation field) and Materials' Science and Technology.

The XRD technique was used to assess the crystallinity of the Ta surfaces' elements to obtain more data that would confirm possible effects produced by the air-abrasive procedure.

After the qualitative analysis of the twenty-seven SEM images, six samples were selected, according to the topographic differences found in the surfaces. Compared with the first surface modification technique applied – anodization - it seems that the second one – magnetron sputtering with Zn – did not significantly alter the tested surface, which explains the selection of five samples belonging to the group TaCaP and a control sample of pure Ta.

It was expected to visualize crystalline and organized structures in the modified surfaces, such as Ta and Ta₂O₅, due to the anodic oxidation of Ta performed by PEO/MAO. Hydroxyapatite (HAp) is also an element expected to be found once Ta surfaces were enriched with Ca and P during the anodization process (TaCaP).

The PEO process was performed under potentiostatic conditions, where a 200V potential was kept constant. Although high temperatures are reached during the anodization process, the potential applied may not be enough to produce higher temperatures, so that could not be enough to crystalize the Ta₂O₅ and HAp.

In this sense, the appearance of the Ta₂O₅ phase is not widely detected since the PEO technique only modifies the sample superficially, forming an oxide layer and keeping the remaining structure (substrate) of the sample unchanged. Thus, as the XRD technique studies the samples in greater depth, the Ta₂O₅ layer that forms on the sample's surface is not detected on a large scale. Nevertheless, Ta₂O₅ can still exist in an amorphous

phase without being detected by XRD. As explained before, this is due to the low temperature reached during the PEO process.

Despite the explanations mentioned above, Ta₂O₅ and HAp seem to be present in sample #12 and, in a lower expression, in sample #13, which is consistent with the applied technique of anodization via PEO/MAO. These results are favorable to the bioactive behavior of this type of surface. The existence of crystalline tantalum oxide structures eventually promotes a greater ionic exchange between the biomaterial and the surrounding environment, thus promoting surface bioactivity (Zhao *et al.*, 2017; Kannan *et al.*, 2018).

The higher peak of approximately $2\theta = 40$ can represent both Ta phases, α -Ta, and β -Ta. However, they cannot distinguish from each other. The formation of the bcc α -Ta phase maybe can be excluded since recently it was demonstrated that the critical deposition temperature for preferential nucleation of the α -Ta phase on amorphous silicon is 600 K (Colin *et al.*, 2017). In this study, it is expected that the PEO technique does not reach such a high temperature.

Regarding the air polishing procedure, it seems that it might produce some effects on modified surfaces of Ta – samples #11, #12, #13, and #14. Except for sample #14, new peaks of $2\theta = 20$ have arisen after the air-abrasive jet, with more expression on sample #13, which refers to 5 mm and 5 s of air polishing. These new peaks may be attributed to the air abrasive powder (AFP), whose crystalline elements may have been possibly detected through this technique. A complete XRD analysis of this abrasive product should be performed. Therefore, it seems that the air-abrasive system allows the incorporation of chemical elements from the erythritol-chlorhexidine powder into the Ta nanoporous surfaces, revealing the combination of 5 mm, and 5 s as the most favorable conditions to this outcome. In this sense, if the erythritol-chlorhexidine can be more incorporated, it can be extrapolated that its antibacterial effect will increase, which is desired in treating and preventing unfavorable conditions such as peri-implantitis.

1.3. AFM

Recently, AFM analysis was introduced to provide qualitative and quantitative information on various dental materials (Spagnuolo *et al.*, 2012; D'Antò *et al.*, 2012). Since AFM is used to map the topography and study the properties of the material surface on a nanoscale, it was a valuable tool in reaching additional data about the morphological effects of air polishing on Ta surfaces.

As expected, the nanostructured Ta (sample #10) presented a higher surface roughness than pure Ta (sample #1), confirming the ability of PEO/MAO in changing Ta topography and increasing the surface area. In this way, cell adhesion can be facilitated on these surfaces, thus enhancing the bioactive potential of Ta. This result is in concordance with those reported by Uslu *et al.* (2020), who also performed an AFM analysis and noticed an increase in tantalum surface roughness after anodization. According to the same authors, the increase in roughness and sample surface area could be attributed to nanopores' formation on the anodized surfaces.

Additional studies were found in the literature, showing an increased surface roughness and surface area for other anodized metals, which were suggested to facilitate interactions with the cells in the peri-implant area (Kulkarni *et al.*, 2016; Srivas *et al.*, 2019).

In its turn, the air polishing procedure also increased the surfaces' roughness (samples #11 to #14), which was visible by the increase in the mean Ra and Rms values, compared to the control sample (#10). Di Salle *et al.* (2018) reported similar results in an *in vitro* study in titanium implants. Their AFM analysis showed an increase in the surface roughness after the air-polishing procedure, which was performed using the EMS[®] glycine powder - Air Flow Perio[®] (Electro Medical Systems, Nyon, Switzerland) - at a working distance of 5 mm, for 5 s (Di Salle *et al.*, 2018).

Bearing in mind that AFP is the least abrasive powder on the market, it is likely that the increase in the surface roughness of the air polished surfaces is mainly due to the incorporation of air-abrasive powder elements into the Ta samples.

The AFM results are aligned with those of XRD: sample #13 also stands out, this time by presenting the higher Ra and Rms values. As mentioned before, incorporating the air polishing powder into the Ta surfaces seems to be the main reason for a higher roughness. In this sample, the higher air polishing distance (5 mm) and duration (5 s) possibly allow the addition of chemical elements to the surface, instead of its remotion (as it seems to happen in the more aggressive combination of 2 mm and 10 s).

Among other factors, the increased implant surface roughness offers an advantage as the contact area with bone is enlarged. It is a determining factor for the protein adsorption and, subsequently, in cell attachment stimulation on the implant surface (Schneider *et al.*, 2003). Therefore, faster osseointegration and superior biomechanical resistance will be more easily achieved than implants whose surface is smoother (Wang, Zhang, and Miron, 2015). However, several authors had demonstrated an intimate relationship between the increased surface roughness and bacterial adhesion, biofilm growth, and plaque formation on dental and implant/prosthetic surfaces (Salermo *et al.*, 2010; Song, Koo and Ren, 2015; Passarelli *et al.*, 2020).

The literature research suggests that bacterial adhesion declines as surface roughness decreases. However, there is a lower limit to this relationship, at a roughness level called the “threshold Ra” (Di Salle *et al.*, 2018). Several studies reported that a Ra < 0.2 μm can be considered the threshold for obtaining a reduction of bacterial adhesion (Bollen *et al.*, 1996; Mei *et al.*, 2011). As mentioned before, in this study, the higher Ra value of 218 nm was registered for sample #13, which means an increased surface roughness. Bearing in mind the clinical advantages and disadvantages previously explained, this Ra value can have two interpretations: it can turn the Ta surface into more bioactive, promoting cell adhesion and the peri-implant osteogenic capability, or it can predict future bacterial adhesion into this surface, enhancing the risk of peri-implantitis. Although 218 nm (the same as 0,218 μm) is a high value, it is not far from the mentioned “threshold Ra” (< 0.2 μm), which means that the influence of surface roughness on bacterial adhesion and biofilm formation may not be that significant.

Additional and carefully designed *in vitro* and *in vivo* studies are required to clarify the influence of surface roughness in biofilm formation and the following process of peri-implant infection (peri-implantitis).

It would also be interesting to perform the AFM analysis in other Ta samples, which present different working parameters, including surface modification, air-abrasive powder, distance, and times. Overall, it seems to exist a clear relationship between the control of the air polishing parameters and their effects on the Ta surfaces' roughness. Therefore, it is possible to reach higher or lower roughnesses in different Ta surfaces.

1.4. SESSILE DROP TECHNIQUE

The analysis of all Ta samples could not be performed, either with water or with the other two liquids, due to the excess of air polishing powder residues, which accumulated on Ta samples' surfaces, making them highly rough and unstable for consistent measurements. Therefore, in the absence of a smooth and homogeneous surface, the drop of water did not remain static, and the contact angles could not be measured. There were not found in the current literature research articles with similar *in vitro* studies supporting the findings mentioned above, so it is assumed that this finding may be a novelty.

After the air polishing procedure was done, the samples were not rinsed with deionized water or cleaned with other methods, thus keeping the powder remnants on the surfaces. If the cleaning process were done, perhaps it would be possible to get a smoother surface, thus allowing the contact angle measurement. Nevertheless, it would be essential to ensure the previously incorporated NPs not to be lost, therefore securing these surfaces' bioactive potential.

2. COMPARATIVE ANALYSIS OF THE EFFECTS OF THE AIR POLISHING POWDERS AND CONDITIONS IN TANTALUM SURFACES

From this *in vitro* study, the next outcomes can be presented:

1 – The results are suggestive of the overall Ta's wear resistance when it is submitted to air polishing procedures with powders of different levels of abrasiveness. Therefore, Ta can be considered as a promising material for dental implants or prosthetic components, among other biomedical solutions;

2 – No changes in the surface's morphology of pure Ta were verified with erythritol-chlorhexidine, nor with sodium-bicarbonate air polishing;

3 – No changes in the surface's morphology of nanostructured (porous) Ta enriched with Ca and P (TaCaP), presented by SEM-EDS results, were verified with erythritol-chlorhexidine air polishing. However, it induces a slight decrease in the osteoconductive elements, which may affect the surface's bioactivity. In addition, XRD and AFM results showed an increase in the surface roughness after anodization and air polishing.

4 – Changes in the surface's morphology of nanostructured (porous) Ta enriched with Ca and P (TaCaP) were verified with sodium-bicarbonate air polishing, turning it into more rugged. This surface modification can eventually favor bacterial adhesion, thus increasing the risk of peri-implantitis in dental implants. Nevertheless, the effects of this powder are not significant to induce surface damage to biofunctionalized Ta surfaces. Sodium-bicarbonate also causes a slight decrease in the osteoconductive elements, which may affect the surface's bioactivity;

5 – Significant changes in the surface's morphology of nanostructured (porous) Ta enriched with Ca, P, and Zn (TaCaP-Zn) were verified with sodium-bicarbonate air polishing, revealing it to be more aggressive than erythritol-chlorhexidine. Both powders decrease Zn NPs, thus compromising this material's bactericidal effect;

6 – Besides conferring an antibacterial ability, the Zn NPs' coating deposition turned nanoporous Ta into more smooth surfaces. Therefore, biofilm aggregation can be more easily avoided, favoring peri-implantitis prevention but yet allowing cell adhesion for the osseointegration;

7 – In an overview, both powders seem to be secure to Ta surfaces. Although the erythritol-chlorhexidine-based powder is better positioned due to its lower abrasiveness, antibacterial effect, and more versatility concerning its applicability, it can produce changes at the surface roughness level.

8 – The air polishing with sodium-bicarbonate promotes Na incorporation, whereas the erythritol-chlorhexidine is possible to be incorporated into nanoporous surfaces, as XRD and AFM suggested. Further analysis of this air-abrasive powder is needed.

9 – None of the air polishing powders were sufficiently abrasive to remove all the NPs inserted by the surface modification techniques totally;

10 – When the air polishing is performed at a little distance (2 mm) for a long time (10 s), there is a tendency to remove chemical elements from the surface instead of incorporating them. This combination of air polishing parameters seems to be less desirable to the increase of the bioactivity and the osseointegration potential of Ta;

11 – Although there are produced some changes in the surface roughness with the erythritol powder, in an overview, it appears to be more desirable to air polish at a greater distance (5 mm), with 5 s (the recommended by EMS[®]), to secure Ta surfaces' bioactive and antibacterial purposes;

12 – Regarding the desirable air polishing parameters and conditions tested for Ta surfaces in this *in vitro* study, it would be recommended to:

- a) Air polish with low-abrasive powders, to secure the surfaces' and the integrity of the oral structures;

- b) Avoid the air polishing combination of a distance lower than 3 mm, and time longer than 5 s;
- c) Avoid air polishing porous surfaces with previous deposition of Zn NPs;
- d) When it is performed in the intra-oral medium, avoid subgingival air-polishing with AFC powder, as recommended by EMS®;

3. COMPARATIVE ANALYSIS TO AIR POLISHING STUDIES' ON TITANIUM AND ORAL TISSUES

As mentioned before, peri-implantitis occurs due to the accumulation of a biofilm around the implant soft tissues and on implant surfaces, causing an inflammatory response (Schwarz *et al.*, 2018). Successfully osseointegrated implants can fail if peri-implantitis is left untreated. Therefore, biofilm removal plays a central role in preventing periodontal and peri-implant diseases associated with microbial infections (Drago *et al.*, 2014).

Periodontal and peri-implant maintenance imply periodical prophylaxis. Air abrasion is one of the decontamination methods that have demonstrated promising results in treating peri-implant diseases once it facilitates the mechanical removal of bacterial biofilm (Biazussi *et al.*, 2019). However, it is compulsory to choose safe polishing devices, powders, and techniques for the implant abutment surface. Otherwise, topographic changes will be induced, causing surface damage, and biofilm adherence to this structure (Subramani *et al.*, 2009).

Air polishing devices can contribute to the development of surface defects. This *in vitro* study was performed by using EMS® device and the respective abrasives. However, there are in the market other air polishing devices with different settings and technical specifications. In the literature review was found an *in vitro* study by Pelka *et al.* (2010), reporting that the Prophyflex3® (KaVo, Biberach, Germany) produced significantly greater defects on flat root surfaces than the EMS® model ($p < 0.05$), regardless of the abrasive product used.

Regarding the morphological changes produced by air polishing powders in implant surfaces, there is limited evidence in the literature comparing the implant decontamination with low-abrasive powders, such as erythritol. Many studies compare air polishing effects with bicarbonate and glycine powders, both on teeth and implants. However, few specifically reached the effects of bicarbonate and erythritol on the surfaces of the implants.

Biazussi *et al.* (2019) evaluated the effect of glycine and sodium-bicarbonate powders on 15 titanium disks, using 4 mm distance, for 20 s. Their study demonstrated that air-polishing powders containing glycine had less of an effect on titanium surfaces' roughness than sodium bicarbonate. Therefore, sodium bicarbonate powder would be more damaging to prosthetic components' surface and result in higher roughness values than glycine powder after 20 seconds of air polishing. Although erythritol-chlorhexidine powder has the smallest particle size (average 14 μm), according to some authors, its level of abrasiveness is not significantly lower than glycine (Müller *et al.*, 2014; Hägi *et al.*, 2015).

Mensi *et al.* (2018) also used the EMS[®] AFC and AFP powders in their study. The air polishing procedure was performed on pure titanium disks for 30 s, keeping 5 mm of distance. Despite the longer duration of the air polishing process – 30 s (compared to the maximum time used in this study – 10 s), the reported results were similar to those obtained in pure Ta air polishing. None of the powders determined a significant surface alteration, being both considered as good options for air polishing at the implant surface.

Different authors have found contrasting results regarding the effects of sodium-bicarbonate powder on titanium surfaces. Some authors had demonstrated the absence of modifications on these surfaces' morphology after performing the air-abrasive procedure with sodium-bicarbonate (Augthun *et al.*, 1998; Mengel *et al.*, 1998), whereas other authors reported modifications on the morphology of implant surfaces, increasing biofilm adhesion (Schwartz *et al.*, 2009; Louropoulou *et al.*, 2012; Cochis *et al.*, 2013;)

Although sodium bicarbonate had been shown useful in biofilm removal from micro-structured titanium discs (Schwartz *et al.*, 2009), there was a demand for new low-

abrasive powder formulations, which had to be introduced. For this reason, less aggressive methods using erythritol-chlorhexidine, or the alternative glycine powder reported by other authors (Schwartz *et al.*, 2009; Cochis *et al.*, 2013; Schmidt *et al.*, 2017), had been studied. In this context, an efficient remotion of subgingival plaque without producing significant surface modifications was reported (Schmidt *et al.*, 2017). Moreover, the reduced pressure and the shorter time (5 s per site) have been shown to cause less damage to the implant surface, less trauma to biologic tissues, being generally more accepted by patients (Flemming *et al.*, 2012). These findings are consistent with those obtained in this study: the air polishing with AFP was performed on Ta surfaces at a working distance of 5 mm, without producing significative surface modifications.

According to Matsubara *et al.* (2019), small powder particles are more likely to reach areas in the rough implant surface, which are inaccessible by larger particles, and have a higher solubility potential. The major drawback of the larger, undissolved particles is the induction of surface abrasion (Wei *et al.*, 2017) and salt contamination (Menini *et al.*, 2015). In this work, despite not being found in a significant amount, powder remnants were evidenced in some tested samples. Although sodium bicarbonate had incorporated Na into the surfaces, the excessive amount of powder residues could not be attributed to a specific air polishing condition/parameter. However, according to Anselme and Biggerelle (2006), since the attachment and spreading of the cells depend on the surface chemistry and surface structure, the powder residues and releasing of the surface ions after the air abrasive process can lead to a decrease in fibroblast adhesion. If this occurs, the implant biocompatibility will also be compromised (Eisenbarth *et al.*, 1996).

Regarding the effects of the air polishing on oral tissues, although sodium-bicarbonate powder is considered to be effective in supragingival biofilm and stain removal (Graumann, Sensat and Stoltenberg, 2013), it may cause damage to the hard and soft tissues when used subgingivally (Bühler *et al.*, 2016; Cobb *et al.*, 2017). Some authors had demonstrated that the decreased air polishing distances induced deeper and larger tooth surface defects (Petersilka *et al.*, 2003; Tada *et al.*, 2012). Beyond the air polishing distances, there were also found results about the air polishing time in the literature review. In this sense, increasing treatment time strongly affected defect depth

and volume (Galloway and Pashley, 1987; Bester *et al.*, 1995; Petersilka *et al.*, 2003; Pelka *et al.*, 2010). Although these findings were contextualized in tooth surfaces, they are in line with those achieved in this *in vitro* study, once the combination of 2 mm and 10 s were the more aggressive conditions to Ta surfaces.

In a general view, air abrasion has been considered safe, particularly for the nonmodified surfaces (Moharrami *et al.*, 2019). In this study, the air abrasion was equally secure in pure Ta samples. Besides, the small-sized air abrasive particles (AFP) was found to be less damaging to Ta surfaces, which is consistent with Moharrami *et al.* (2019) results in titanium surfaces. For all the reasons mentioned before, the erythritol-chlorhexidine-based powder seems to be an excellent air polishing option, once it combines both the advantages of mechanical and chemical debridement (by incorporating chlorhexidine into its formulation), without inducing surface damage (Ng *et al.*, 2018).

This *in vitro* study had some limitations regarding the conditions in which the experimental procedure was performed. Most of the studies found in the literature point to maximum air polishing times higher than those used. Although SEM-EDS did not reveal significant effects on Ta's surfaces after 10 s of air polishing, the AFM analysis evidenced differences in the surface roughness. Even so, it would be interesting to test longer duration times.

Another limitation comes from the absence of a suction device during the experimental air-abrasive procedure. Indeed, in the presence of an aspiration cannula, as it happens in the case of intraoral polishing, there would not be as much accumulation of water and powder remnants on the surfaces. In this way, perhaps some chemical elements were not diminished in the samples air polished with 10 seconds, as well as it would be possible to carry out the test of the sessile drop to evaluate the contact angles.

VI. CONCLUSION

“Study of air polishing effect on tantalum surfaces.”

Although the selection of the rehabilitating material is essential, its surface properties are, in the same way, decisive. In the dental field, tantalum is a potential candidate for an implant or a prosthetic component. In the case of implants, changing the surface topography and its chemical composition, by the deposition of bioactive surface coatings, enhances the interaction with biological fluids and accelerates peri-implant bone regeneration.

In this *in vitro* study, porous Ta samples were produced, and the elements Ca, P, and Zn were successfully incorporated into its surfaces through the PEO/MAO and sputtering techniques. These PEO/MAO coatings endowed Ta with potential bioactivity, a fact that was confirmed by the EDS and XRD analysis.

Regarding the overall effects of the air-abrasive procedure on Ta surfaces, the results are suggestive of the wear resistance of this metal when it is submitted to the air polishing process with powders of different levels of abrasiveness. However, the sodium-bicarbonate powder's effect was noticed on the Ta modified surfaces, once it was more abrasive, thus not ideal for the air polishing procedure. Besides being less aggressive to the Ta surfaces, due to the small-sized particles, the erythritol-chlorhexidine powder has the advantage of having antimicrobial and antibiofilm activity, making it a preferable option. Additionally, it can be used in subgingival air-polishing, conversely to the sodium-bicarbonate powder.

The experimental procedure performed in this *in vitro* investigation allowed to establish relations between the type of surface, air polishing powder, time, and distance. Both powders seem to be safe to Ta surfaces, although they produced changes in its morphology and chemical composition. This study demonstrated that air polishing altered the roughness of Ta surfaces. The combination of a lower distance (2 mm) and a longer duration (10 s) was considered the most aggressive condition, being undesirable. In contrast, one of the desirable conditions was to air polish at a greater distance (5 mm), even if the duration is extended to more than the recommended (5 - 10 s). In addition, the air polishing procedure on porous surfaces with the incorporation of Zn NPs is contra-indicated.

To perform air polishing effectively, clinicians need to be informed about its indications and contraindications and be trained in its proper execution. To secure the implant/prosthetic surface's integrity, an appropriate selection of the air air-abrasive powders and devices is mandatory.

Further investigations are needed to evaluate the *in vitro* and *in vivo* effect of different combinations of air polishing parameters on tantalum surfaces. In this way, these surfaces' behavior will be more predictable when applied to a dental implant or other rehabilitating/prosthetic solution. In this sense, peri-implantitis prevention and treatment will be more intuitive and achievable in the modern era of Oral Rehabilitation. The relevance of the present results for clinical practice should be clinically investigated in an *in vivo* human study. Considering the limitations of this *in vitro* study, it may be necessary to obtain more robust scientific evidence to support the choice of a prophylactic protocol in the prevention and treatment of periodontitis and peri-implant diseases.

VII. FUTURE WORK

“Study of air polishing effect on tantalum surfaces.”

As this is a pilot project, it would be interesting in the context of an upcoming scientific investigation to evaluate the air polishing at a distance greater than 5 mm and duration longer than 10 seconds, comparing the results with those obtained in this work.

It would be interesting to include a control group in another prophylaxis protocol where the air polishing would be performed without powder, which means the samples would be submitted only to air and water jet.

An XRD analysis should be performed on both powders to see the influence of their chemical elements in the incorporation by the air-abrasive procedure. It would also be interesting to conduct an AFM analysis of the remain Ta samples prepared for this study so that it would be possible to establish more relations between the working parameters.

To overcome one of the limitations of the actual study, it would be desirable to design an investigation where the air polishing in Ta surfaces would be made with a suction cannula's help. In this sense, intra-oral conditions would be simulated, thus preventing the excess of water and powder residues over Ta surfaces.

It would also be interesting to analyze the effect of the air polished tantalum surfaces in osteoblast adhesion/proliferation and bacterial growth/inhibition to establish its bioactive and bacteriostatic potential.

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