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REVIEW ARTICLE

Anodizing of ASTM F67 grade 4 titanium under continuous and alternating stresses for surface modification of implants in dentistry

Anodizado de titanio ASTM F67 grado 4 bajo tensiones continuas y alternas para la modificación de la superficie de implantes en odontologia

Anodização de titânio ASTM F67 grau 4 em tensões contínua e alternada para modificação da superfície dos implantes na odontologia

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Abstract

Titanium alloys are widely used in medicine and dentistry due to their biocompatibility, which favors the fixation of dental or surgical implants in bone tissue. These implants are usually manufactured by machining and undergo surface processing to generate an appropriate texture on the surface of the part. This textured surface is necessary to promote cell adhesion on the surface of the implants and improve their osseointegration. This study aimed to investigate the effect of anodizing treatment on the surface of ASTM F67 Grade 4 titanium samples, promoting the formation of preferential microcavities to improve osseointegration. This is a bibliographic research and the descriptors used were: “Titanium”, “ASTM F67”, “anodization”, “osseointegration” available in the BVS and SciELO databases, with articles in Portuguese and English, between 2015 and 2025. The results indicated variation in both color and increased roughness and formation of microcavities on the surface with varying the electrical voltage, more evident in treatments with alternating voltages. The tests performed obtained average roughness between 0.5 µm and -1.5 µm, and the formation of microcavities in the alternating voltage samples. The potentiodynamic polarization test showed a corrosion potential (Ecorr) of -470.2, suggesting very promising results for improving the adhesion process of the biomaterial to human bone.

Descriptors: Titanium; ASTM F67; Anodizing; Corrosion; Osseointegration.

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Resumén

Las aleaciones de titanio son ampliamente utilizadas en medicina y odontología debido a su biocompatibilidad, lo que favorece la fijación de implantes dentales o quirúrgicos en el tejido óseo. Estos implantes suelen fabricarse mediante mecanizado y se someten a un tratamiento superficial para generar una textura adecuada en la superficie de la pieza. Esta superficie texturizada es necesaria para promover la adhesión celular en la superficie de los implantes y mejorar su osteointegración. El objetivo de este estudio fue investigar el efecto del tratamiento de anodizado en la superficie de muestras de titanio ASTM F67 Grado 4, promoviendo la formación de microcavidades preferenciales para mejorar la osteointegración. Se trata de una investigación bibliográfica y los descriptores utilizados fueron: "Titanio", "ASTM F67", "anodización", "osteointegración" disponibles en las bases de datos BVS y SciELO, con artículos en portugués e inglés, entre 2015 y 2025. Los resultados indicaron variación tanto en el color como aumento de la rugosidad y formación de microcavidades en la superficie al variar el voltaje eléctrico, más evidente en tratamientos con voltajes alternos. En los ensayos realizados se obtuvieron rugosidades promedio entre 0,5 µm – 1,5 µm y formación de microcavidades en las muestras de tensión alterna. La prueba de polarización potenciodinámica mostró un potencial de corrosión (Ecorr) de -470,2, lo que sugiere resultados muy prometedores para mejorar el proceso de adhesión del biomaterial al hueso humano.

Descriptores: Titanio; ASTM F67; Anodizado; Corrosión; Osteointegración.

Resumo

As ligas de titânio são amplamente aplicadas na medicina e odontologia devido à sua biocompatibilidade, que favorece a fixação de implantes dentários ou cirúrgicos nos tecidos ósseos. Esses implantes geralmente são fabricados por usinagem e passam por um processamento superficial para gerar uma textura adequada na superfície da peça. Essa superfície texturizada é necessária para promover a adesão celular na superfície dos implantes e melhorar sua osseointegração. Objetivou-se investigar o efeito do tratamento de anodização na superfície de amostras de titânio ASTM F67 Grau 4, promovendo a formação de microcavidades preferenciais para melhoria da osseointegração. Trata-se de uma pesquisa bibliográfica e os descritores utilizados foram: "Títânio", "ASTM F67", "anodização", "osseointegração" disponível nas bases BVS e SciELO, com artigos em português e inglês, entre 2015 e 2025. Os resultados indicaram variação tanto na cor quanto no aumento da rugosidade e formação de microcavidades na superfície variando a tensão elétrica, mais evidentes nos tratamentos com tensões alternadas. Nos testes realizados foram obtidas rugosidades médias entre 0,5 µm –1,5µm e formação de microcavidades nas amostras de tensão alternada. O ensaio de polarização potenciodinânica apresentou um potencial de corrosão (Ecorr) de -470.2, sugerindo resultados muito promissores para melhorar o processo de adesão do biomaterial ao osso humano.

Descritores: Titânio; ASTM F67; Anodização; Corrosão; Osseointegração.

Introduction

Over time, several studies have been conducted to analyze different types of modifications to the surface topography of dental implants manufactured in ASTM F67 Grade 4 titanium. These modifications have been shown to have a significant impact on the early stages of osseointegration, providing improved anchorage strength and mechanical locking (Wennerberg; Albrektsson, 2000). However, traditional mechanical methods can be complex and introduce contaminating particles into the implant surface; one of the promising approaches to modify the surface of implants is the anodizing process[1-3].

Anodizing results in the formation of titanium oxide layers with varying colors, which originate from the constructive interference of reflected light between the air/external oxide and internal oxide/metal interfaces. Much research has been conducted on the use of anodizing on titanium to improve biocompatibility and corrosion resistance. For example, the effect of anodizing voltage on the chromaticity (aesthetic appearance) of titanium. As a result, processes using direct voltage (DC) and alternating voltage (AC) have been applied to produce surface oxide layers with thicknesses dependent on the applied potential and the duration of the anodizing process. However, it is important to note that long-term anodizing tests can drastically alter the morphology and roughness of the anodic film on titanium substrates. An increase in anodizing voltage results in an increase in the thickness of the oxide layer, increased roughness, and changes in the phase composition of the surface. This increase in the thickness of the oxide layer coincides with an increase in surface roughness. These changes in titanium morphology have led to research into the growth of microcavities, which provide a suitable structure for bone integration and can be used to store drugs such as antibiotics, anti-inflammatories, and growth inhibitors[4-6].

In this specific study, titanium oxide films and microcavities were created on the surface of ASTM F67 Grade 4 titanium using an electrochemical process in oxalic acid solution, varying the electrical voltages. The subsequent characterization of these modifications aims to improve the performance of the materials in osseointegration, especially

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in dental implant applications. The objective of this work was to analyze the effects of anodic oxidation on ASTM F67 Grade 4 titanium samples by applying different values of continuous and alternating voltages in treatments lasting up to 30 minutes, observing the creation of microcavities on the surface of the samples.

Methodology

This work was developed as a bibliographic review of the literature, with a qualitative approach, to compile and analyze the available scientific evidence on the corrosion processes in ASTM F67 titanium implants, the anodizing techniques, and their relationship with osseointegration. Bibliographic research was conducted using the Virtual Health Library (BVS) and Scientific Electronic Library Online (SciELO) databases as main sources.

To search for articles, the following descriptors were used in Portuguese and English: "Titânio" or "Titanium", "ASTM F67", "Anodização" or "Anodization", and "Osseointegração" or "Osseointegration". The research did not use complex Boolean operators, maintaining a simplified search strategy. Only articles published between 2015 and 2025, available in Portuguese and English, with free access to the full text, were considered.

The criteria for including studies in the review were based on the availability of the full text, relevance to the central theme of the research, and publication in peer-reviewed journals. Studies that were not directly related to ASTM F67 titanium, studies outside the established period, and articles without access to the full content were excluded.

The selection process of the materials occurred in three main stages. Initially, a preliminary screening was carried out by reading the titles and abstracts of the identified articles. Then, the pre-selected works were subjected to a more careful evaluation through full reading, verifying their adequacy to the established criteria. Finally, the articles considered relevant had their data extracted and organized for qualitative analysis.

Results and Discussion

Passive alloys can suffer localized corrosion, mainly through crevices and pits, making them susceptible to manipulation. Crevice corrosion occurs in places where the electrolyte remains stagnant, forming a galvanic cell. This process is influenced by factors such as material geometry, presence of deposits, temperature, and concentration of chloride ions. The lack of oxygen inside the crevice prevents the passivation of the metal, accelerating metal dissolution and local acidification. This manifestation can be aggravated by bacterial colonization, leading to inflammation of the peri-implant tissue and bone loss[5-7].

Galvanic corrosion occurs when different metals come into contact in the same electrochemical medium, forming a galvanic pair. The metal with the lower potential acts as the anode, causing corrosive damage, while the other acts as the cathode. In the oral environment, this corrosion can occur between dental implants, metal restorations, and prostheses, and is intensified by the presence of fluoride, pH variations, and contact with nickel, cobalt, and chromium alloys. This can cause bone resorption, discomfort, and compromise the biocompatibility of the materials. Electrochemical methods are used to prevent galvanic corrosion and minimize its effects[7,8].

Authors[9,10] argue that uniform corrosion is characterized by a relatively homogeneous attack of the metal surface exposed to very aggressive media, such as strong reducing acids and high temperatures. Uniform corrosion represents an electrochemical manifestation of corrosion that manifests itself uniformly across the entire exposed surface of a material in contact with a corrosive medium. This process results in the formation of scales or deposits, causing a uniform loss of thickness. Uniform corrosion is considered one of the most controllable and visible forms, being relatively easy to protect. Pitting corrosion is a form of localized corrosion that occurs due to the presence of aggressive ions in the medium and begins in imperfections in the oxide film or inclusions of another metal in the oxide. As a result of the manufacturing process, in the formation of pitting corrosion, a passive protective film is formed on the surface of the titanium during corrosion. As a result, some aggressive ions penetrate and destroy the film, resulting in holes in the surface. Pitting corrosion of titanium rarely occurs at temperatures below 100°C, except in very aggressive media characterized by high temperature, high halide content, and reducing conditions, with low oxygen content, low pH, and presence[9].

Corrosion phenomena can begin when the electrode potential of titanium exceeds a certain critical value, known as the corrosion potential. The corrosion potential of titanium alloys in chloride solutions, i.e. the concentration of seawater, at room temperature, is several volts nobler than the spontaneous corrosion potential. Consequently, corrosion can only occur if the metal is polarized to the corrosion potential by an anodic current. The main factors influencing pitting corrosion are the applied potential, the temperature, the composition of the metal alloy, and unclear factors such as the variation of the current according to the pH values of the electrolytes[10].

To reduce vulnerability to corrosion, post-fabrication anodizing treatments are recommended for titanium alloys to increase the thickness of the passive film and corrosion resistance. Corrosion erosion occurs when the electrolyte exceeds a certain critical velocity that is characteristic for each material and medium. In the case of titanium in seawater, the critical velocity is 27 m/s. In addition to these more common forms of corrosion, titanium-based metallic materials can also suffer from stress corrosion cracking, corrosion fatigue, and hydrogen damage. Stress corrosion cracking in NaCl, at low potentials in an acidic HCl medium, which suggested that the formation and propagation of cracks are associated with the diffusion of atomic hydrogen and the formation of titanium hydride, which have non-protective characteristics, in addition to being fragile and being able to constitute the preferential path of cracks, the descending potentiostatic polarization curves (from -0.5 V) in a strongly acidic medium, present the curves corresponding to the hydrogen reduction reaction, at

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potentials where the formation of titanium hydride can simultaneously occur, in addition to producing conditions for crack propagation in the material[11].

The different behaviors of the metal when the surface is previously coated with oxide or devoid of the same overpotential, the surface becomes activated and the anodic current increases proportionally, although some hydrogen continues to be released. In the case of oxide-free metal, the metal initially dissolves, and after the hydrogen reaction is established and the cathodic current predominates. In the sector, studies on the concepts of osteoinduction and osteoconduction are common. These terms are frequently discussed, addressing issues such as high long-term osseointegration rates, which are around 95%. However, as the demand for improvements in the implant surface increases, these high rates may seem insufficient. The aim is to develop new surfaces for dental implants that improve success rates and promote faster and more effective osseointegration, especially in patients with compromised bone regeneration capacity, such as smokers, people with osteoporosis, or diabetes[11].

Osteoinduction is the process by which bone formation is stimulated, involving the activation of non-specialized cells that transform into bone-forming cells. Osteoconduction refers to the ability of a material to serve as a support for the growth of bone tissue. The effectiveness of the osteoconductive potential of a surface is influenced by its roughness, microtopography, nanotopography, and porosity. Both processes, osteoinduction and osteoconduction, play a crucial role in osseointegration, which is the direct connection, both structural and functional, between the newly formed bone and the biomaterial used in the implant. For this to occur effectively, surface treatments are applied to the implants, which, in addition to modifying the roughness, form edges/roughnesses with characteristics suitable for osseointegration[11,12].

Surface treatments are performed to alter the surface morphology, attract and allow connections with pre-osteogenic cells (cells essential for bone development and regeneration), including fibronectin, a glycoprotein that acts as a bridge between cells and the extracellular matrix, allowing cells to anchor themselves to surfaces. The aim is to obtain adequate surface properties to have the highest possible concentrations of proteins. Although the morphology and roughness of implants influence the differentiation of mesenchymal cells into osteoblasts, fibroblasts, or chondrocytes, not all the mechanisms involved are known. It is known that cell remodeling depends on continuous adaptation to functional loads and repair of damage resulting from overloads at the interface[12].

It has been proven that a rough surface generates compressive residual stress, and this residual stress improves the mechanical properties of the dental implant. These values are very similar to those obtained by other authors in sandblasted titanium implants; the surface roughness can vary by several hundred percentage points in different locations of the same implant. Therefore, an average value that supposedly represents the entire screw should be based on measurements from different locations, since it is known from studies of recovered samples that the important factors that influence osseointegration are biocompatible material, implant shape, implant surface, bone quality and quantity, surgical technique and loading conditions. Considering that the number of variables is large and to date the possible combinations and variations of these parameters have not been analyzed, there is no consensus among researchers as to the best surface, roughness, and even the shape of the implants[12-14].

In Implantology, there are a variety of techniques for treating the surface of commercial implants. The implants sold in Brazil with different treatments stand out, the models below and their morphologies are Acid etching: (a and b); Titanium oxide blasting: (c); Anodizing: (d). Many coatings on the surface of titanium have been tested, including plasma spraying, biomimetic coatings, gel oxidation, chemical vapor deposition, and anodic oxidation. Among these surface treatments, anodic oxidation has gained prominence due to its easy production, low production cost, and high bone cell acceptance rates[14-16].

Conclusion

The experimental results obtained indicated that the use of an oxalic acid-based electrolyte for anodization, either in direct or alternating voltage, was effective in forming surfaces of ASTM F67 Grade 4 titanium dental implants suitable for osseointegration. The use of oxalic acid in the electrolyte allows for a more sustainable and less aggressive surface treatment than conventional treatments. The variation in voltage and duration of the treatments resulted in the formation of oxidized layers with different colors and roughness. The interaction between voltage and anodization time was statistically significant in the roughness, and promising levels were obtained for promoting the surface texture necessary for osseointegration.

The application of alternating voltage in electrochemical treatments resulted in greater topographical changes on the surface of the samples, when compared to anodization performed with direct voltage. In the samples produced with alternating voltage, an intense formation of microcavities was observed, which was not observed when direct current was used. Potentiodynamic polarization studies in 3.5% NaCl solution showed that the surface generated with anodization with alternating current showed high levels of corrosion resistance, superior to ASTM F67 Grade 4 titanium without treatment. Therefore, it is considered that the most promising surface in this material is generated with anodization performed with an oxalic acid-based electrolyte, under alternating voltage of 30 volts for 30 minutes.

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