

BIOFUNCTIONALIZATION OF TITANIUM ALLOYS: METHODS AND APPLICATIONS

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Abstract

Titanium alloys have long been esteemed for their exceptional mechanical properties and biocompatibility, making them a cornerstone material in various biomedical applications. However, to harness their full potential in implantology, orthopedics, and dentistry, biofunctionalization plays a pivotal role. This article provides a comprehensive exploration of the techniques and applications involved in biofunctionalizing titanium alloys.

Keywords: *Titanium Alloys, Surface Modification, Surface Treatment Techniques, Anodization, Thermal Spraying, Laser Surface Modification*

Introduction

In the materials engineering domain, titanium alloys serve as evidence of the inventiveness of people and the advancement of science. These remarkable materials, born from the depths of aerospace and military research, have transcended their origins to become indispensable components in a multitude of industries, touching our lives in ways both seen and unseen [1-4].

Titanium, in its pure form, is a lustrous, silver-grey metal renowned for its exceptional properties. It boasts an enviable strength-to-weight ratio, rivalling even steel, while maintaining extraordinary resistance to corrosion, even in the harshest of environments. This unique combination of attributes has propelled titanium to the forefront of modern materials science [5, 6].

However, it is the alloying of titanium with other elements—such as aluminium, vanadium, and nickel—that truly unleashes its potential. The resulting titanium alloys inherit the metal's inherent strength and corrosion resistance while gaining tailored properties that make them ideal for specific applications [7, 8].

One of the key reasons for titanium's extensive use in medicine is its ability to withstand corrosion from bodily fluids, ensuring longevity and safety when implanted in the human body. Additionally, titanium does not elicit a significant immune response, reducing the risk of rejection and complications post-surgery [9-11].

The most common alloy used in medical applications is Ti-6Al-4V, a combination of titanium, aluminium, and vanadium. This particular alloy offers an excellent balance of strength, weight, and compatibility with human bone and tissue. The aluminium in the alloy increases its strength and stiffness, which is crucial for load-bearing implants such as hip and knee

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replacements. Vanadium, on the other hand, enhances the mechanical properties of the alloy, making it durable and resistant to fatigue [12, 13].

Moreover, the versatility of titanium allows for customization in various medical devices, meeting the specific needs of different surgical procedures and patient requirements. The development of surface treatments and coatings for titanium implants further improves their performance by enhancing osseointegration, the process by which bone grows around the implant, securing it firmly in place [14-17].

This article highlights several techniques for improving titanium alloy surfaces, demonstrating the material's enormous potential for use in medical applications. The many surface modification methods for titanium alloys used in medical applications—such as anodization, plasma spraying, hydroxyapatite coating, laser surface modification, cold gas dynamic spray, sol-gel coating, and electrochemical deposition—will be discussed in this article (Fig. 1) [18-24].

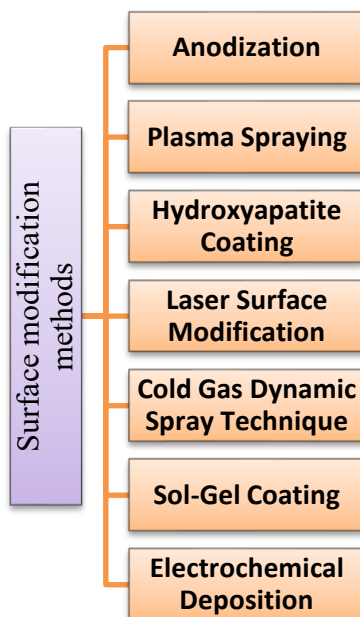


Fig. 1. Surface modification methods for titanium alloys used in medical applications

Anodization

Anodization significantly enhances the osseointegration and antibacterial properties of titanium alloys, promising to reduce implant failures and improve the longevity of orthopaedic devices.

The process of anodization for titanium alloys involves a sequence of well-defined steps, primarily focused on altering the surface properties of the titanium for enhanced performance, particularly in medical applications. The steps are composed of electrochemical treatment, oxide layer formation and porous structure formation [1, 2, 14].

Electrochemical treatment

The anodization process commences with the submersion of the titanium alloy in an electrolytic solution to facilitate electrochemical reactions, followed by the application of an electrical current between the titanium alloy anode and a suitable metal cathode, such as stainless steel, to initiate the anodization.

Oxide layer formation

As the electrical current passes through the electrolyte during anodization, it triggers a reaction on the titanium surface, resulting in the formation of a titanium dioxide (TiO₂) oxide layer, the characteristics of which—such as thickness and composition—can be meticulously controlled by adjusting the voltage, current density, electrolyte composition, and treatment duration to meet specific application requirements.

Porous structure formation

During the anodization process, the formation of a porous structure within the oxide layer, with pore sizes ranging from nanometres to micrometres, is not only a remarkable outcome but also highly beneficial for medical applications such as implants, where this porosity enhances bone growth and integration, and can be custom-tailored in size and distribution by adjusting the process parameters to suit specific medical needs.

The anodization of titanium alloys offers significant benefits for medical applications: it improves biocompatibility, aiding in better integration with bone and tissues for implants; enhances corrosion resistance, crucial for the body's corrosive fluids; allows surface functionalization for drug loading and healing promotion; and improves osseointegration, essential for load-bearing implants. These advancements are particularly beneficial in dental implants for jawbone integration, orthopaedic implants like joint replacements requiring strong bone bonding, and cardiovascular devices where corrosion resistance is vital [19].

A specific study focused on the anodization of a medical-grade Ti-6Al-7Nb alloy, where the anodization at 450V led to the formation of an amorphous phase and made the surface strongly hydrophilic. It was noted that the layer formed at 350V showed more promise for functionalizing Ti-6Al-7Nb alloy surfaces. In contrast, the layer formed at 350 V appears to be more suitable for the functionalization of Ti-6Al-7Nb alloy surfaces, suggesting that lower voltage conditions may be more favourable for achieving the desired combination of durability, adhesion, and functional properties. This study [25] indicates the importance of carefully controlling the PEO process parameters to optimize the surface characteristics of Ti-6Al-7Nb alloys for specific applications.

Plasma Spraying

This process involves the use of a high-energy plasma jet to melt and project particles of a coating material onto the surface of a titanium alloy. This is particularly beneficial for orthopaedic implants, as it facilitates bone growth and implant integration.

In the plasma spraying process, a high-energy plasma jet of ionized gas, typically argon or nitrogen, is first created by passing it through an electric arc. This jet is then used to melt coating materials, usually in powder form, which are fed into the plasma stream. As these molten particles are propelled towards the titanium alloy, they strike its surface and rapidly cool, forming a solid, adherent layer that enhances the properties of the titanium substrate [3, 13, 20].

Plasma spraying offers numerous benefits for titanium alloys, particularly in the medical field: it enhances surface properties like wear and corrosion resistance, crucial for the longevity of medical implants. The process is highly customizable, allowing for a variety of coating materials to suit specific needs. Particularly valuable is its ability to improve osseointegration through coatings like hydroxyapatite, promoting better bone growth and implant stability. This translates to increased implant longevity and performance. Additionally, the versatility of plasma spraying makes it suitable for a range of medical applications, including orthopedic and dental implants.

The study of Smith T. [26] highlights the complex interplay between coating quality, substrate properties, and bonding strength in the context of implant fatigue performance. While plasma-sprayed coatings have the potential to enhance implant durability, the presence of defects and the nature of bonding interfaces play crucial roles in determining the overall performance of

coated implants. Further research may be needed to optimize the coating process and bonding to improve the fatigue resistance of titanium alloy implants.

Hydroxyapatite Coating

Applying a layer of hydroxyapatite, a naturally occurring mineral in bones, on titanium implants improves their biocompatibility and bone bonding. This method is especially effective for dental implants and bone screws.

Hydroxyapatite (HA) coating for titanium alloys is a critical process in biomedical applications, especially for implants. Hydroxyapatite is a naturally occurring mineral form of calcium phosphate, similar to the composition of human bone, which makes it highly biocompatible. The process involves applying a layer of hydroxyapatite onto the surface of titanium alloys to improve their integration with bone tissue [14, 21].

Hydroxyapatite, a compound akin to the mineral component of bones and teeth, is prepared in powder form for coating titanium alloys. It is applied using techniques such as plasma spraying, sputtering, or electrochemical deposition, ensuring a uniform and strongly adherent layer on the titanium surface. Once applied, this HA coating forms a crucial bond with the titanium, significantly enhancing the implant's stability and effectiveness.

This process offers several advantages like:

Critical for Medical Implants: The role of hydroxyapatite (HA) in dental and orthopaedic implants, like bone screws, is essential for successful medical outcomes.

Enhancing Compatibility with Bone Tissue: Titanium alloys, favoured for their robustness and light weight in orthopaedic and dental implants, gain improved bone integration through HA coatings, a substance mimicking bone's natural minerals.

Promoting Bone Cell Growth: The osteoconductive nature of HA coatings on titanium alloys fosters the growth and attachment of osteoblasts, enhancing bone development around the implant and ensuring a durable bond with the adjacent bone.

Coating Application Techniques: Employing plasma spraying, a method where HA powder is superheated and applied to titanium surfaces, results in a porous coating conducive to bone growth. Alternatives like sputtering and electrochemical deposition are also utilized for specific coating attributes.

Addressing Longevity and Wear Issues: The ongoing challenge in HA coatings is combating their potential weakening over time, a factor critical to the implant's stability and effectiveness. Research is focused on enhancing these coatings' durability and resilience.

Positive Clinical Impact: The application of HA-coated titanium implants has been linked to improved bone healing rates and higher implant success, particularly beneficial in scenarios of compromised bone quality [27].

Singh and collab. [27] presents a critical review of the plasma spray deposition of hydroxyapatite (HA)-based coatings on titanium-based alloys. It includes a bibliometric analysis revealing significant contributions in the area of HA coatings on titanium alloys using plasma spray techniques. This study underscores the evolving landscape of HA coatings for orthopedic applications, highlighting the importance of integrating alloying elements to enhance performance and suitability for bio-implants. The bibliometric analysis provides a valuable overview of the research trends, key contributors, and influential works in this domain, offering insights into the direction and impact of this critical field in biomedical engineering.

Laser Surface Modification

Using lasers to modify the surface texture of titanium can enhance its wear resistance and promote better cell attachment and proliferation. This is advantageous for joint replacement implants, where both durability and tissue integration are critical.

Despite their advantages, titanium alloys can benefit from enhanced surface properties like increased wear resistance, reduced friction, and improved surface hardness. This is where LSM comes into play.

LSM involves using high-intensity laser beams to alter the surface properties of titanium alloys. The process can be used to achieve various outcomes, such as hardening, texturing, or coating the surface of the alloy.

Advantages of LSM offers precise control over the modification process, allowing for targeted improvements in properties without affecting the bulk material. It's also a relatively quick and environmentally friendly process.

An article with this method [28] contains information on the development of laser surface engineering of titanium alloys over the past thirty years. It describes the production of a modified layer up to 1 mm in depth, which is thicker than what alternative techniques offer. The main tool used in this process has been continuous-wave CO₂ lasers for both surface cladding and alloying.

Cold Gas Dynamic Spray Technique

Cold Gas Dynamic Spray, also known as Cold Spray, is a unique coating technology used for various materials, including titanium alloys. The process involves the deposition of powdered materials to create a coating or to fabricate a freestanding part.

In this method, powdered materials are deposited on the titanium surface at high velocities. It enhances the surface's mechanical properties and biocompatibility, making it suitable for various biomedical applications.

Cold Spray uses a high-speed gas jet to accelerate powder particles towards a substrate. Unlike traditional thermal spray techniques, it does not involve significant heating of the powder; hence it's termed 'cold'. For this method, Air, nitrogen, or helium are commonly used, with helium providing higher particle velocities due to its lower density and higher sound speed.

In the Cold Gas Dynamic Spray technique, particle acceleration is achieved as particles are propelled by a supersonic gas jet through a de Laval nozzle, attaining high velocities essential for effective bonding, while upon substrate impact, these particles experience plastic deformation and adhere to the substrate, thereby forming a dense and uniform coating [20].

The Cold Gas Dynamic Spray technique offers significant advantages for titanium alloys, including low oxidation due to its operation at relatively low temperatures, thus minimizing oxidation and maintaining the alloy's integrity; preservation of microstructure, as the low-heat input maintains the original microstructure of the titanium alloy; and enhanced properties, with coatings that improve wear resistance, corrosion resistance, and enable the restoration of dimensions or the repair of damaged parts.

The Cold Gas Dynamic Spray technique finds diverse applications in titanium alloys, such as in the aerospace industry for the repair and manufacturing of components where titanium's strength is crucial, in medical implants where coatings are applied to enhance biocompatibility and wear resistance, and in the automotive industry for producing lightweight yet high-strength coatings on various components.

The Cold Gas Dynamic Spray process faces several challenges and limitations, including the need for precise control of particle velocity and temperature to ensure effective bonding, the high cost of equipment setup, particularly when using helium as the accelerating gas, and limitations in the maximum thickness of the coating that can be achieved due to residual stresses.

Phuong Vo et al. [29] describes the cold spray process as a layer-by-layer buildup of material through successive high-speed impacts of solid-state, micron-sized particles onto a substrate or workpiece. In the final observations, opinions are presented on the present state and potential future evolution of the technology.

Sol-Gel Coating

Sol-gel coating is a versatile and widely used technique for applying thin films to various substrates, including titanium alloys. This method is particularly valued for its ability to produce high-quality, uniform coatings with controlled thickness and composition.

The process begins with the formation of a 'sol', which is a colloidal suspension of solid particles in a liquid. This is typically done by mixing metal alkoxides and water in a solvent. The sol undergoes gelation, a process where it transforms from a liquid to a gel-like substance, through hydrolysis and polycondensation reactions.

The application of specialized coatings to titanium alloys offers several advantages: it notably enhances their corrosion resistance, which is essential in harsh environmental conditions, significantly improves the hardness and wear resistance of the alloys, and provides versatility in composition, allowing the inclusion of various dopants to tailor the properties of the coating for specific applications.

The application of coatings on titanium alloys, while offering significant benefits, also presents challenges and limitations: there is a tendency for the coatings to crack or peel if not applied or cured properly; achieving a uniform thickness and the desired properties of the coating is a complex process that demands precise control over various parameters; and the use of certain sol-gel precursors and solvents raises environmental and health concerns, necessitating cautious handling and proper disposal.

The future of coatings, particularly for titanium alloys, looks promising with several advancements on the horizon: there is a growing trend towards developing customizable sol-gel coatings tailored to meet the specific requirements of advanced engineering applications; there is potential in integrating sol-gel coatings with additive manufacturing techniques, paving the way for innovative material fabrication methods; and the development of smart coatings, capable of responding to environmental stimuli, is an exciting area of research, opening up new possibilities in material science and engineering [17, 30].

A study described by Jaafar A. [30], optimized the sol-gel process to prepare hydroxyapatite, which was then used to deposit a hydroxyapatite layer on Ti6Al4V. The focus was on promoting osseointegration and biocompatibility of metallic implants, despite certain limitations that affect implant longevity.

Electrochemical Deposition

This process can be used to deposit bioactive substances or create a texture on the titanium surface, enhancing cell interaction and integration with body tissues.

Basic principle of electrochemical deposition involves the use of an electric current to reduce dissolved metal cations so that they form a coherent metal coating on an electrode. The process typically occurs in a specially formulated electrolyte solution containing ions of the metal to be deposited.

In the electrochemical deposition process, the titanium alloy intended for coating acts as the cathode, and the anode is typically composed of the coating metal; upon the application of an electric current, metal ions in the solution are reduced and subsequently deposited onto the titanium alloy, forming a coherent and uniform coating.

Electrochemical deposition offers significant advantages for titanium alloys used in medical applications: it allows for the engineering of coatings that enhance the biocompatibility of titanium, a critical factor for medical implants; the process can significantly improve the corrosion resistance of titanium alloys, ensuring their durability in bodily environments; and it provides precise control over coating thickness and composition, enabling the customization of titanium alloys for specific medical applications.

Electrochemical deposition is particularly valuable in medical applications, such as in dental and orthopaedic implants where it is used for coating to enhance bone integration and reduce rejection rates; in the manufacturing of surgical instruments, where it provides a corrosion-resistant coating, thereby increasing the durability and safety of these tools; and in the production of drug-eluting stents, where it enables the creation of surfaces designed to release therapeutic agents over time, enhancing the efficacy of such medical devices.

This method several challenges and considerations: it necessitates meticulous control over various parameters, including current density, temperature, and pH, to maintain consistent coating quality; the strength of adhesion between the deposited layer and the titanium substrate is critical to ensure the longevity of medical implants; and the selection of materials for coatings must be judicious, ensuring they are biocompatible to avoid any adverse reactions within the human body.

An article illustrated that AgNPs (silver nanoparticles) [31] were deposited onto well-ordered TiO₂ nanotube surfaces on titanium using anodic oxidation and electrochemical deposition processes. This study showcases a specific application of electrochemical deposition in modifying titanium surfaces.

Conclusion

The variety of coating methods for titanium alloys, such as anodization, plasma spraying, hydroxyapatite coating, laser surface modification, cold gas dynamic spray, sol-gel coating, and electrochemical deposition, each come with their unique advantages, challenges, and limitations.

Anodization of titanium alloys enhances their corrosion resistance and wear properties and can improve aesthetics and coloration. However, the method is limited by the oxide layer's thickness, potential colour inconsistencies, and sensitivity to the specific composition of the titanium alloy.

Plasma spraying provides titanium alloys with a dense coating, making it suitable for high-temperature applications. The method's high operating temperatures, however, can alter the properties of the titanium substrate, and there may be issues with coating adhesion and porosity.

Hydroxyapatite coating on titanium alloys is ideal for medical applications due to its excellent biocompatibility and bone bonding properties. This method, however, faces challenges in ensuring strong adhesion of the coating to the titanium alloy and requires precise control over the process conditions.

Laser surface modification offers precise control over treated areas of titanium alloys and can significantly improve their surface hardness and wear resistance, which is beneficial in medical applications. The main limitations include the high cost of equipment, the need for specialized expertise, and the potential to alter the titanium alloy's microstructure.

The Cold Gas Dynamic Spray technique, used at low temperatures, preserves the microstructure of titanium alloys and is effective for repairs and dimensional restoration in medical devices. However, it faces challenges with particle bonding, high equipment costs, and limitations in the thickness of the coating that can be applied.

Sol-gel coating offers versatility in terms of achievable coatings on titanium alloys for medical applications and is effective even for complex geometries. It can be used at low temperatures but comes with challenges such as the risk of cracking or peeling, the need for precise process control, and environmental and health concerns related to some precursors and solvents.

Electrochemical deposition allows for custom, precisely controlled coatings on titanium alloys, enhancing their biocompatibility and corrosion resistance for medical use. The process, however, demands meticulous control and faces challenges in ensuring strong adhesion of the coating and the selection of biocompatible coating materials.

Each of these methods offers unique benefits for coating titanium alloys, ranging from enhanced wear and corrosion resistance to improved biocompatibility for medical applications.

However, they also come with specific challenges, such as process control, equipment cost, potential alterations in substrate properties, and environmental concerns. The choice of a particular method depends on the specific requirements of the application, balancing the advantages with the potential limitations. Continuous research and development in these technologies are essential to overcome existing challenges and to expand their applicability in various industries, especially in the rapidly evolving field of material science and engineering.

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