

# Influence of Surface Modification on the Corrosion Resistance of Titanium Alloys in Marine Environments

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## Introduction

Titanium alloys are widely used in marine environments due to their exceptional combination of high strength, low density, and outstanding corrosion resistance. However, despite the inherent protection provided by their passive oxide layer, titanium alloys are still susceptible to localized corrosion phenomena such as pitting, crevice corrosion, and galvanic corrosion, particularly in chloride-rich seawater. To improve the corrosion resistance of titanium alloys in harsh marine conditions, a variety of surface modification techniques have been developed. This article explores the impact of different surface modification strategies, including anodization, plasma electrolytic oxidation, laser surface treatment, and coatings, on the corrosion behavior of titanium alloys. The mechanisms by which these surface modifications enhance corrosion resistance are reviewed, alongside their effects on the microstructure, mechanical properties, and long-term durability of titanium alloys. Additionally, the challenges and future directions for the development of corrosion-resistant titanium alloys for marine applications are discussed.

Titanium alloys, known for their superior mechanical properties and inherent resistance to corrosion, are widely used in marine environments, where exposure to seawater and harsh conditions often accelerates material degradation. The ability of titanium alloys to form a stable and protective oxide layer on their surface provides natural corrosion resistance. However, in seawater environments, particularly in the presence of chloride ions, the integrity of the passive oxide layer can be compromised, leading to localized corrosion such as pitting, crevice corrosion, and stress corrosion cracking. This limitation hinders the application of titanium alloys in critical marine structures such as ship hulls, offshore platforms, and underwater vehicles.

Surface modification techniques have emerged as effective means to further enhance the corrosion resistance of titanium alloys in aggressive marine environments. By altering the surface properties and microstructure of the alloy, these techniques can improve the uniformity, thickness, and stability of the oxide layer, thus reducing susceptibility to corrosion. This review aims to evaluate the influence of various surface modification methods on the corrosion behavior of titanium alloys in marine environments and to identify potential challenges and future research needs. Titanium alloys are generally resistant to corrosion due to the formation of a passive oxide layer, which acts as a protective barrier between the metal and the surrounding environment. However, in the marine environment, titanium alloys may still experience different forms of localized corrosion, primarily caused by the presence of chloride ions in seawater. This occurs when the passive oxide film is locally broken down, usually at sites where chloride ions accumulate. The breakdown

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of the oxide film leads to the formation of small pits that can penetrate deeper into the material [1-3]. In confined spaces such as joints or under deposits, oxygen depletion can cause the local breakdown of the oxide layer, leading to corrosion within these crevices.

## Description

When titanium alloys come into contact with more anodic materials, such as steel or aluminum, the electrochemical potential difference between the materials can accelerate corrosion at the interface. A combination of tensile stress and a corrosive environment can lead to the initiation and propagation of cracks in titanium alloys, which is exacerbated by the presence of chloride ions. While the natural oxide layer generally protects titanium alloys, the performance of this layer can be compromised in certain marine environments, necessitating the development of surface modification strategies. Surface modification techniques are designed to enhance the corrosion resistance of titanium alloys by improving the protective oxide layer or by applying additional coatings. The most common surface modification methods include anodization, plasma electrolytic oxidation, laser treatment, and coating technologies. Anodization is an electrochemical treatment that enhances the thickness and quality of the natural oxide layer on titanium alloys. The process involves immersing the titanium alloy in an electrolyte bath and applying a controlled voltage, resulting in the formation of a thicker, more uniform oxide film.

Anodization increases the thickness of the titanium oxide layer, which improves its resistance to both mechanical wear and corrosive attack. The oxide layer formed during anodization is generally dense and uniform, preventing the penetration of corrosive ions such as chlorides. Anodized titanium alloys show significantly improved corrosion resistance, especially in aggressive environments like seawater, where the thicker oxide layer helps resist pitting and crevice corrosion. Anodization also provides aesthetic benefits, as the process can produce a variety of colors on the surface of the alloy due to interference effects in the oxide layer.

Plasma electrolytic oxidation is a surface treatment process that generates a thick, ceramic-like oxide layer on titanium alloys by applying a high voltage in an electrolyte bath. Unlike conventional anodization, PEO produces a more complex oxide structure that includes both TiO<sub>2</sub> and other oxides such as TiO and Ti<sub>2</sub>O<sub>3</sub>. PEO involves the generation of high-energy discharges on the alloy surface, leading to the formation of a porous, high-adhesion oxide layer. The oxide is typically thicker and denser than the anodized film, offering superior wear resistance and stability in harsh environments. The PEO-modified surface provides excellent protection against corrosion in marine environments, particularly in the presence of chloride ions. The thick, durable oxide layer significantly reduces the risk of pitting and crevice corrosion, and the ceramic-like properties of the coating provide additional resistance to mechanical wear and abrasion.

Laser surface treatment uses high-power lasers to locally modify the surface of titanium alloys. The laser treatment melts the surface layer, and upon rapid cooling, a refined microstructure and a more stable oxide layer are formed. Laser treatment induces localized heating, causing the alloy's surface to melt and form a new oxide layer. The rapid cooling process results in a fine microstructure with enhanced mechanical properties, while the modified oxide layer provides improved corrosion resistance. Laser-treated titanium

alloys exhibit enhanced resistance to localized corrosion, including pitting and crevice corrosion. The process helps refine the microstructure and create a more homogeneous surface, improving the integrity of the oxide layer and making it more resistant to breakdown in chloride-rich marine environments.

Coatings provide an additional layer of protection against corrosion by physically isolating the titanium alloy from the surrounding environment. Common coatings include metallic coatings (such as TiN, TiC, and Al coatings) and polymer-based coatings (such as epoxy resins and fluoropolymer coatings). Coatings can be applied through various techniques, such as chemical vapor deposition, physical vapor deposition (PVD), electroplating, or spray coating [4,5]. The coatings act as a physical barrier to corrosive agents, preventing direct contact between the titanium alloy and the seawater. Coated titanium alloys generally exhibit enhanced corrosion resistance, especially in terms of protection against pitting and galvanic corrosion. However, the long-term effectiveness of coatings depends on factors such as adhesion strength, wear resistance, and the stability of the coating in seawater. Coatings like TiN and TiC also provide added benefits in terms of wear resistance.

The effectiveness of surface modifications in enhancing the corrosion resistance of titanium alloys in marine environments depends on several factors, including the type of surface modification, the alloy composition, and the specific marine conditions. Several studies have demonstrated that surface modifications such as anodization, PEO, and laser treatments significantly enhance the resistance of titanium alloys to localized corrosion in seawater. Both anodization and PEO result in the formation of thicker, more durable oxide layers that offer improved protection against corrosion in chloride-rich marine environments. PEO-treated titanium alloys, in particular, exhibit superior wear resistance and can withstand higher temperatures, making them ideal for applications exposed to mechanical wear and harsh environmental conditions.

Laser surface treatment refines the microstructure of titanium alloys and enhances the uniformity of the oxide layer, which significantly reduces the susceptibility to localized corrosion. This treatment is especially beneficial for applications requiring high wear resistance in addition to corrosion protection. Coatings provide a reliable and effective means of protecting titanium alloys from corrosion in marine environments. However, the long-term stability of coatings is a concern, particularly under conditions of mechanical wear or thermal cycling. The choice of coating material and application technique plays a crucial role in determining the durability and effectiveness of the coating. The long-term performance of modified titanium alloys in marine environments requires further investigation. The stability of oxide layers and coatings over extended periods, particularly in dynamic conditions such as fluctuating temperatures and seawater flow, needs to be evaluated. Some surface modification techniques, such as PEO and laser treatment, can be expensive and may not be easily scalable for large-scale production. Developing cost-effective methods for surface modification is crucial for their widespread adoption in marine applications. Certain surface modification processes, such as the use of toxic chemicals in anodization or coating applications, may have environmental implications. Future research should focus on developing more sustainable and environmentally friendly methods for surface modification.

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## Conclusion

Surface modification techniques significantly enhance the corrosion resistance of titanium alloys in marine environments. Methods such as anodization, plasma electrolytic oxidation, laser surface treatment, and coatings can effectively mitigate localized corrosion, pitting, and crevice corrosion, making titanium alloys more reliable for use in harsh marine conditions. While these techniques offer considerable improvements, challenges related to long-term durability, cost, and environmental impact remain. Future research should focus on optimizing these surface modification methods and exploring new approaches to improve the performance of titanium alloys in marine environments.

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None.

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## Conflict of Interest

None.

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