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Investigating pre-treatment and post-treatment methods for magnesium alloys to improve corrosion resistance properties

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Abstract

Magnesium alloys possess excellent biological and mechanical properties, making them attractive materials for biomedical applications. However, their high susceptibility to corrosion has limited their widespread use in clinical settings. To overcome this challenge, various pre-treatment and post-treatment methods have been developed to improve the corrosion resistance of magnesium alloys. This article provides a comprehensive review of surface treatment techniques, including conversion coatings, Plasma Electrolytic Oxidation (PEO), and Chemical Vapor Deposition (CVD). Additionally, recent advancements in the development of polymeric, organic, and inorganic materials used in post-treatment methods for magnesium alloys are discussed.

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Introduction

Magnesium and its alloys are among the lightest metals, with a density of 1.74 g/cm^3, and have found immense application in industries such as automotive and aerospace [1,2]. In recent years, there has been growing interest in using these materials for orthopedic applications due to their favorable characteristics, such as biocompatibility, biodegradability, non-toxicity, and similar Young's modulus and density to natural bone [3-9]. The use of magnesium and its alloys in biomedical applications is limited by their low corrosion resistance, with a potential of -2.34 V vs. NHE, which presents a significant obstacle [10,11]. As a result, a variety of methods have been devised to regulate the corrosion of magnesium and its alloys [12,13]. This paper presents an overview of different techniques for surface treatment and post-treatment of biomedical coatings on magnesium implants, as well as materials utilized in these methods. The impact of these approaches on the corrosion characteristics of magnesium alloys is also examined based on existing research.

Pre-treatment methods

Conversion coatings

Phosphate conversion coating: It is frequently necessary to apply a surface treatment called phosphate conversion coating to improve the corrosion resistance and biocompatibility of magnesium implants. Phosphate conversion coating is a process that creates a thin layer of magnesium phosphate on the surface of a magnesium implant by causing a chemical reaction between the magnesium substrate and a solution containing phosphate [14]. Calcium phosphate is a widely occurring type of phosphate that can exist in various forms such as Calcium phosphate dihydrate - brushite (DCP), Anhydrous Calcium Phosphate - Monetite (ADCP), Octacalcium Phosphate (OCP), Tricalcium Phosphate - whitlockite (TCP) and Hydroxyapatite (HA). The application of calcium phosphate onto the surface of magnesium can be achieved through various techniques including biomimetic, sol-gel, and Electrodeposition (ED) methods [15]. Calcium phosphate coatings have been shown to reduce corrosion in magnesium implants through a number of mechanisms. First, the coating acts as a barrier that slows down the diffusion of corrosive species from the surrounding environment to the magnesium substrate. Second, the coating can release calcium and phosphate ions into the surrounding area, which can react with any corrosive species that do manage to penetrate the coating, neutralizing them and preventing further corrosion. Additionally, the release of calcium and phosphate ions can stimulate bone growth and promote osseointegration of the implant, further improving its biocompatibility and reducing the likelihood of implant failure due to corrosion [16].

Cerium conversion coating: Cerium conversion coating is a surface treatment technique that can be used to improve the corrosion resistance and biocompatibility of magnesium implants. The process involves the formation of a thin layer of cerium oxide on the surface of the magnesium implant, which acts as a barrier to enhance corrosion resistance and improve the biocompatibility of the implant. The cerium conversion coating process typically involves immersing the magnesium implant in a solution containing cerium ions and other additives. The solution is then heated to a specific temperature to induce the formation of a uniform layer of trivalent and tetravalent cerium oxides on the surface of the implant. The process is also environmentally friendly since it does not use toxic materials or produce hazardous waste [17]. Cerium conversion coating can improve the biocompatibility of magnesium implants by promoting cell adhesion and proliferation on the implant surface [18].

Plasma electrolytic oxidation (PEO)

Plasma Electrolytic Oxidation (PEO), also known as Micro Arc Oxidation (MAO), is a surface treatment technique that can be used to further improve the surface properties of magnesium implants. PEO involves immersing the magnesium implant in an electrolyte solution and applying a high voltage electrical pulse to the solution. This results in the formation of a plasma discharge on the surface of the implant, which causes the formation of a ceramic-like oxide layer. The PEO process can produce a highly porous oxide layer on the surface of the magnesium implant, which can enhance its biocompatibility and corrosion resistance. The porosity of the oxide layer can be controlled by adjusting the process parameters, such as the voltage, current, and electrolyte composition [19].

Due to their double-layered structure comprising an outer porous layer and an inner dense layer, PEO coatings can enhance the anti-corrosion properties of Mg alloys. The addition of metallic elements with antibacterial properties, such as Ag, Cu, and Zn, into the PEO electrolyte can further improve the antibacterial properties and corrosion resistance of Mg alloys. In addition to improving the biocompatibility and corrosion resistance of magnesium implants, PEO can also improve their mechanical properties, such aswear resistance. This makes PEO a particularly useful technique for producing magnesium implants for load-bearing applications [20].

Chemical vapor deposition (CVD)

Chemical Vapor Deposition (CVD) is a surface treatment technique that involves the deposition of a thin film of a material onto a substrate surface, such as a magnesium implant. The process is carried out in a vacuum chamber where a precursor gas is heated to high temperatures, causing it to break down and react with the surface of the substrate. CVD can be used to deposit a variety of materials onto magnesium implants. The range of coating thickness produced by CVD is usually between 1-100 µm, which can improve the resistance of the material against wear and corrosion. This technique has various advantages, including the ability to deposit refractory materials at temperatures below their melting points, achieving densities close to the theoretical limit, controlling the grain size and orientation, processing at atmospheric pressure, and obtaining good adhesion. Nonetheless, CVD method demands high deposition temperatures, which may lead to difficulties in maintaining the material's thermal stability. Efforts have been made in recent years to decrease the temperature required for CVD processes. These efforts have included the development of techniques such as atmospheric pressure chemical vapor deposition (APCVD), Low-Pressure Chemical Vapor Deposition (LPCVD), plasma-enhanced chemical vapor deposition (PECVD) or Plasma-Assisted Chemical Vapor Deposition (PACVD), and laser-enhanced chemical vapor deposition (LECVD). Additionally, hybrid processes that combine elements of both physical and CVD techniques have been developed [21].

Post-treatment methods

The application of a Hydroxyapatite (HA) coating is a common method for safeguarding Mg alloys, but the coating is often not sufficiently dense to offer durable protection against corrosion [22,23]. Researchers have dedicated significant efforts in recent years to investigating post-treatment techniques that can enhance the density of HA coatings, thereby improving their resistance to corrosion. Effective post-treatment of coatings on Mg alloys can significantly enhance their corrosion resistance by obstructing the penetration of corroding agents and preventing them from reaching the surface of the magnesium metal [24,25]. Used hydrothermal treatment on an AZ31 alloy in order to develop a HA/GO coating with graphene oxide as the outer layer and hydroxyapatite as the inner layer. The surface of the AZ31 alloy displayed a substantial number of cracks, which were considerably minimized following the application of the HA coating. Furthermore, when the AZ31 substrate was coated with HA/GO, scarcely any cracks were detected. The reduction in the number of cracks results in reduced liquid permeation in the coating, indicating an improved resistance to corrosion [24]. Carried out a research study to explore the possibility of using Adipic Acid (AA) to enhance the in-vitro bioactivity and anti-corrosion performance of hydroxyapatite coatings applied to AZ31 Mg alloy using post-treatment techniques. The results of their study demonstrated that applying post-treatment with AA led to the creation of a layer of adipic acid on the surface of hydroxyapatite crystals. The generated layer effectively impeded the spread of harmful ions to the interface of the substrate/coating, leading to an enhanced corrosion resistance of the coating. Adipic acid contains two -OH functional groups that support the creation of insoluble salts, like magnesium adipate and magnesium hydroxy adipate. These salts can fill up the pores of the coating and prevent the electrolyte from penetrating through it. The formation of magnesium adipate (Equation 1) and magnesium hydroxy adipate (Equation 2) during this process is shown in the following reactions:

$2C_6H_{10}O_4 + Mg \rightarrow Mg\ (C_6H_9O_4) + H_2$ ------------- (1)

$2C_6H_{10}O_4 + Mg\ (OH)_2 \rightarrow Mg\ (OH)\ (C_6H_7O_4) + H_2O$ -----(2)

Chitosan, a stable and non-toxic polymer, has been employed as a coating material for modifying the surface of metals due to its ability to chelate with metal ions, exceptional film-forming characteristics, and significant anti-corrosion properties [26,27]. Considering these properties, it is worthwhile to explore the potential of HA-chitosan coatings as anti-corrosion coatings for magnesium alloys [28]. Devised an environmentally friendly technique to improve the anti-corrosion properties of Mg alloys through chitosan-modified Hydroxyapatite (HA) coatings. They analyzed the impact of the chitosan concentration, immersion time, and pH of the post-treatment solution on the performance of the coating. The outcomes revealed that the AZ31 Mg alloy sample coated with HA-chitosan 0.1 wt% exhibited a compact morphology and a lower corrosion current density. This resulted in reduced degradation of Mg in Simulated Body Fluid (SBF) environments as compared to other samples. Chitosan was linked to the hydroxyapatite coating via chelation and hydrogen bonding, and the optimal immersion time was determined to be 3 minutes. In general, the treatment of the HA coating with chitosan had a beneficial impact on the coating's anti-corrosion performance while also being environmentally friendly. Polymer-based coatings have proven to be highly effective in creating barriers against corrosion on metal surfaces, but they may lose their protective properties over time [29]. To tackle this problem, one practical solution is to incorporate corrosion inhibitors to offer active corrosion protection. 8-hydroxyquinoline (8-HQ) is a sustainable and ecologically friendly corrosion inhibitor that has been found to impede the processes of anodic dissolution and cathodic hydrogen evolution, resulting in an improved anti-corrosion performance [30]. It has the ability to create complexes and chelate with Mg^{2+} ions, leading to the development of insoluble precipitates that obstruct active sites and prevent further substrate dissolution [31]. Furthermore, 8-HQ and its derivatives exhibit antibacterial properties, especially against Gram-negative pathogens, but their presence may increase the surface hydrophobicity [32]. Ahmadi et al [33]. conducted a research study on the production of triple polyvinyl alcohol (PVA) coatings that incorporated Hydroxyapatite (HA) and 8-hydroxyquinoline (8-HQ) using two different methods: Electrospinning and immersion. The outcomes indicated that the electrospun coating containing HA and 8-HQ exhibited remarkable anti-corrosion performance, with Rct values of 7891 and 12,680 ohm cm^2 in NaCl 3.5 wt. % and Simulated Body Fluid (SBF), respectively, in comparison to the same composition immersion samples with Rct values of 3231 and 3727 ohm cm2. The enhanced anti-corrosion performance was attributed to the release of HA and 8HQ from the coating.

Conclusion

Conversion coatings, Plasma Electrolytic Oxidation (PEO), and Chemical Vapor Deposition (CVD) have all shown promise for improving the biocompatibility and corrosion resistance of magnesium implants. Conversion coatings such as calcium phosphate and cerium conversion coatings have been shown to be relatively simple and cost-effective to produce, while PEO and CVD have the advantage of being able to control the coating thickness and composition. However, each technique has its own challenges, such as the potential toxicity of some of the chemicals used in conversion coatings, the need for careful control of the PEO process parameters, and the high deposition temperatures required for CVD. The post-treatment technique takes into account both organic and inorganic materials that are mainly biocompatible. These materials possess certain abilities such as facilitating bonding between the metallic substrate and the coating applied on magnesium alloys, as well as forming a uniform film or insoluble salts that can be deposited in the crevices of the coating. Overall, these techniques represent promising approaches for enhancing the properties and biocompatibility of magnesium implants, and they have the potential to improve patient outcomes in a variety of medical applications.

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