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Research Progress on the Application of Organosilane Coating on Medical Magnesium Alloy

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Abstract

The current pure protective silanization technology on the surface of magnesium alloy has made great development, but it still cannot meet the requirements. The thickness of the pure protective organosilane film is very thin, tens to hundreds of nanometers, and there are also small pores, so the barrier effect is limited, and its mechanical strength and wear resistance is also weak.The mechanical strength and wear resistance are also weak. This paper presents the research progress and related applications of organosilane coatings on biomedical magnesium alloys. Firstly, the effects of different organosilane coatings on the corrosion resistance and biocompatibility of biomedical magnesium alloys are reviewed, and different doping modification methods such as doping of organosilane films with barrier and corrosion inhibitor are introduced. The doping can improve the thickness and denseness of the composite silane film layer, improve the organization of the film structure to some extent, and enhance its corrosion protection performance. In addition, the applications and progress of organosilane coatings in the field of orthopedic and cardiovascular stents are reviewed. It is expected to be a reference for similar research in the future.

Keywords

Medical Magnesium Alloy; Organosilane; Corrosion Resistance; Biocompatibility.

1. Introduction

In the last decade, magnesium and magnesium alloys, due to their degradability and good biocompatibility, in the field of medical devices, especially in orthopedics [1] and in the field of vascular scaffolds [2], the applications are developing rapidly and are considered as new generation of revolutionary biomaterials, and a large number of studies have demonstrated their feasibility and safety as biodegradable medical devices and their feasibility and safety. Compared with traditional metallic The greatest advantage of magnesium alloy is its degradability compared to traditional metal implant devices, however However, the rapid degradation rate and the unevenness of degradation (pitting) However, the rapid degradation rate and uneven degradation (pitting) have severely limited its clinical application.

Organosilanes are bifunctional molecules with the general structure (R0O)3Si-R-X where R is an alkyl chain, R0 can be Cl, F, methyl or ethyl, and X is a functional group[8], such as a thiol, amine, carboxylic acid, alcohol, or alkyl group. The alkoxysilane portion of the molecule is capable of bonding to various mineral or metal surfaces through complex hydrolysis/condensation reactions in which silicon-o-metal bonds are ultimately formed [13]. Organosilane coatings can be divided into sol-gel and solid coatings, sol-gel coatings are considered a promising alternative to chromium plating, but due to the presence of microporosity and cracks, these coatings allow aggressive species to interact with the surface, organoalkoxysilane precursors can solve these problems [14].

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2. Effect of Organosilane Coating on Corrosion Resistance

Organosilanes have good corrosion protection properties[17]. Environmentally friendly and non-toxic organo-inorganic silica-based chemicals (i.e., "trialkoxysilanes" or "silanes") are replacing chromates traditionally used in metal corrosion protection[3]. Silanes are popular in the industries of corrosion protection and adhesion enhancement. However, there are few reports on the use of organosilane modification for medical magnesium alloys[10].

Dingchuan Xue [3] et al. investigated the use of a water-based silane, bis[triethoxysilyl]ethane (BTSE, $(OC_2H_5)_3Si(CH_2)_2Si(OC_2H_5)_3$). The results of the study showed that it was allowed to combine with a water-dispersible epoxy resin BTSE [28] to form a water-based epoxy-modified BTSE silane coating for the surface coating corrosion protection of Mg-4Y alloy, which was observed by corrosion probes, and according to various electrochemical tests, the epoxy-modified BTSE silane coating could effectively improve the corrosion environment of Mg-4Y alloy in and the corrosion resistance at the initial stage of injection, and the corrosion rate in the in vivo environment of dead rats was much smaller than that in the in vitro environment.Zucchi et al [12] found that long-chain silanes have better anti-corrosion properties than short-chain silanes.Montemor et al [13] found that rare earth salts and carbon nanotubes could improve the corrosion performance of silane films on magnesium alloys.

R. Grothe et al [16] studied the corrosion delamination of epoxy films on organosilane modified ZnMgAl alloy coated steel using a scanning Kelvin probe bubble. The results of the study showed that the organosilane film adhered surfaces consisted mainly of aluminum and magnesium oxides and surface carbonates. Due to the presence of nanopores, the ultrathin adhesion-promoting film is unlikely to act as an effective barrier film. However, γ-APS ultrathin films are effective in suppressing cathodic delamination under superimposed mechanical loading. γ-APS films form high cross-link density through siloxane bonding [22], while acid-base interactions with surface metal oxides occur through hydrogen bonds formed by silanols and amino groups. In addition, the amino group can form covalent bonds with the epoxy binder. This results in a stronger wet adhesion of the interface. The tight coupling of the adhesive to the oxide surface hinders the transport of corrosive ions along the interface, thus inhibiting corrosion at the adhesive/metal interface.

Vinodh K. Korrapati et al [10] investigated the double-layer coating of Mg-Az31 alloy for temporary and long-term corrosion protection. The results of the study showed that the double-layer coatings containing ODPA have better stability in corrosive media, while the impedance modulus of the natural oxides in alkanoic acid coatings decreased significantly. The results show that the double-layer coatings have temporary or long-term corrosion protection depending on their adhesion properties to metal oxides.

External conditions also have an effect on the corrosion protection properties of organosilanes [21].A.F. Scott et al [13] investigated the effect of coating bath chemistry on the deposition of 3-mercaptopropyltrimethoxysilane films on magnesium alloys. The results of the study showed that the most homogeneous MPTS coatings [26] were obtained from a pH 4 coating bath at which equilibrium was reached between the availability of minimal silanol (Si-OH) groups. Pre-hydrolysis of the coating bath is necessary to promote the condensation of MPTS with the surface of magnesium alloys, which is important for the production of MPTS films on magnesium alloys with optimal adhesion and corrosion resistance.Amos Doepkea [1] et al. studied the effect of corrosion of organosilane coated Mg4Y alloys in sodium chloride solution by impedance spectroscopy and pH variation. The results of the study showed that the pH of SECMg4Y samples was lower than that of uncoated Mg4Y. The pH samples were lower during the passivation phase compared to the uncoated samples. The low pH of the S50 sample solution indicated that the S50 coating reduced the corrosion of Mg4Y. The changes during corrosion of the S100 coated samples indicated a failure to protect the metal. pH changes were correlated with OCP, but the changes in OCP caused by pH were relatively small.

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3. Effect of Organosilane Coating on Biocompatibility

The modification of organosilanes can also increase their adhesion to the alloy and improve biocompatibility [9].Xiaoxi Yang et al [4] investigated the effect of mixed organosilane coatings with different RGD surface densities on the adhesion and proliferation of human osteosarcoma Saos-2 cells to MgAZ31. The results showed that organosilane coatings with three different MPTS/TEOS ratios were successfully and uniformly deposited on MgAZ31 at optimal organosilane concentrations and deposition times [25]. All three coating types showed reduced degradation rates compared to bare substrates. Furthermore, cell adhesion assays showed that the presence of immobilized RGD peptides increased the adhesion of Saos-2 cells on MgAZ31 substrates compared to bare or silylated biomaterials [23]. However, there was no significant difference in the relationship between cell adhesion and RGD surface density [24]. Surfaces with optimized RGD surface density and magnesium ion release rate could improve the biocompatibility of magnesium substrates. The importance of developing surface modification strategies for biodegradable magnesium alloys to control the degradation rate and cell/surface interactions to optimize the biocompatibility of these materials is indicated.

4. Effect of Oganosilane Cating on Oher Properties

The composite organosilanes have good hydrophobicity [19]. Matthew A. Hood et al. [5] investigated the hydrophobicity of silicon nanocapsules prepared from organosilanes, and their results showed that the hydrophobicity of the nanocapsules is related to their ability to resist corrosive aqueous environments, thereby delaying the degradation of the silica network. degradation, preventing the breakage of the nanocapsules. Jiafeng Liang et al. [20] studied the anticorrosion of three-layer hydrophobic graphene oxide-decorated organosilane composite coatings. The results showed that the bonding force between organosilane and graphene oxide flakes was significantly enhanced, and the composite coating showed good performance. anti-corrosion and hydrophobic properties.

Organosilanes have good adsorption properties [9]. Ozi Adi Saputra et al. [6] studied the adsorption of ramazole bright blue R by amino-functional organosilanes in aqueous solution, and the results showed that amino-functional organosilanes have good potential for synthesizing adsorbents.

5. Experimental Test Method for Organosilane Coating Performance

A. Rauter et al [15] used in situ IR and Raman spectroscopy as a tool to study the corrosion protection process of (3-ethylpropyl) trimethoxysilyl sol-gel coatings.Yingbo Dong et al [11] successfully formed MTMS passivation films with good antioxidant properties on the surface of pyrite in an aqueous environment by orthogonal and single-factor experimental methods, which can reduce the AMD production process of H+ release and effectively reduce the cost of organosilane use.Natalia Gladkikh et al [18] estimated the adsorption of organosilanes on aluminum surface by varying the frequency of quartz resonator after introducing the solution and calculating the change of mass.Xin Jin et al [7] followed up by FT-IR, XPS and CHNS elemental analysis of amino organosilanes functionalization and loading. The adsorption rate and adsorption capacity were significantly enhanced after functionalization, and the Cr(VI) residual concentration was below the WHO limit.M. Barletta et al [2] ensured good adhesion of the coating to the substrate by adhesion tests, and the surface hardness of the coating was tested by pencil tests.

6. Application of Organosilane Coating on Medical Magnesium Alloy

Organosilanes can also be used as adhesion promoters. Adhesion on magnesium alloys is an issue with organic coatings. Proper pretreatment may be necessary and organocoating is usually the last step of the process[12]. Organosilanes are commonly used as adhesion promoters between inorganic substrates and organic coatings[13].

Organosilanes can also be used as conversion coatings, epoxy/organic coatings, anodic oxidation and plasma electrolytic oxidation coatings [10].SA-modified surfaces reduce the difficulty of removing external polymer coatings after long-term use and maintain good alloy properties. On the other hand, the coatings can be used for long-term protection depending on the adhesion of the alkanoate to the pretreatment layer. Thereafter, approaching semi-finished TRC alloys by double coating between casting and rolling processes can preserve the material [30] and assist in transportation and warehouse necessities[10]. Studies of SA layers for temporary protection and as a pre-layered base for further strategies are mainly due to their growth thickness. Studies have demonstrated that the growth pattern of organosilanes (HDTMS) is in the form of cluster deposition [29], while organophosphorus (ODPA, PFDPA) is homogeneous.

7. Conclusion

Mg alloy has better biocompatibility compared to the traditional metal chromium, so it is used as the latest medical metal material.Mg and its alloys are beneficial as biocompatible materials to construct biodegradable implants for corrosion, but the rapid degradation rate of magnesium alloy in the early stage of implantation is a problem. So the modification of medical magnesium alloys by organosilane coating basically solved the above problems, but there are still many problems that need to be solved. On the existing research results, organosilane coating in medical magnesium alloy can also be studied from the following aspects.

1) for medical magnesium alloy implanted in different parts of the human body, organosilane coating should take different material ratios and production processes to meet the special clinical needs.

2) Now the application cost of organosilane coating on medical magnesium alloy is relatively high, so that it is not conducive to put into the market and produce economic value, so we should try to reduce the cost under the premise of ensuring the functionality.

3) single organosilane coating is difficult to adapt to the complex environment in the human body, the composite coating has better biocompatibility, biodegradability, non-toxicity, adsorption, adhesion, hydrophobicity, so the study of two or more components of the composite coating will be the future development trend.

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