REVIEW

Research Progress of Superhydrophobic Polymer Composite Coatings for Mg Magnesium Alloys

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ABSTRACT
Magnesium (Mg) alloy is the lightest metal material found because of its excellent physical and mechanical properties, specific strength, biocompatibility and biomechanical compatibility, therefore, it has very promising development prospects in aerospace, automobile manufacturing, and biodegradable materials. However, due to the relatively chemical properties of magnesium alloys, poor corrosion resistance, fast degradation rate, and poor wear resistance, they have been greatly restricted in practical applications. Therefore, anti-corrosion measures of magnesium alloys are particularly important. The manufacture of hydrophobic surfaces is a very effective method of anti-corrosion. The surface of super-hydrophobic polymer composites (i.e., thin coatings) is constructed on the surface of magnesium alloy materials to enhance their corrosion resistance and wear resistance, and the effect of its antiseptic measures is very impressive.

1. Introduction
Magnesium (Mg) alloy has attracted worldwide attention due to its excellent mechanical properties, high specific strength and specific stiffness, low density, good electromagnetic shielding, and excellent biocompatibility\(^1\)\(^-\)\(^3\), which has become the most remarkable green environmental protection engineering material in the 21st century. In recent years, it has been favored in aerospace, automobile manufacturing, industrial materials, biodegradable materials and medical materials, and has achieved excellent research results. However, the poor wear resistance & corrosion resistance and fast degradation rate of magnesium alloys\(^4\)\(^5\), make magnesium alloys greatly hindered in practical applications. This rapid and uncontrollable rate of corrosion or degradation significantly reduces the mechanical strength of the magnesium alloy, causes the material to fail prematurely, and the service life cannot reach the expected effect. In biodegradable materials, magnesium alloy releases a large amount of hydrogen due to corrosion, which poses a great threat to the health of patients implanted with materials\(^6\). Therefore, measures to control the corrosion rate or degradation rate of magnesium alloys are particularly important. A protective coating is applied on the surface of the magnesium alloy as a physical barrier to reduce or block the contact between the magnesium alloy and the external corrosive medium, thereby achieving the purpose of protecting the magnesium alloy. Because the super-hydrophobic composite material has the advantages of self-cleaning, drag reduction, good thermal stability, etc., and makes the magnesium alloy anti-corrosion effect more obvious, and the service life is extended, regardless of corrosion resistance, wear resistance, adhesion and

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mechanical properties. Therefore, in recent years, superhydrophobic polymer composites have received much attention in the corrosion control of magnesium alloys. This paper mainly introduces the different preparation methods, corrosion resistance and thermal stability of superhydrophobic surfaces, reviews the superhydrophobic polymer composite coatings in recent years, and prospects the development direction of magnesium alloy superhydrophobic composites.

2. Preparation Method of Super-Hydrophobic Surface

At present, the most widely used method for magnesium alloy corrosion control is to prepare superhydrophobic surfaces on the base material to achieve the purpose of corrosion control. There are two common methods for preparing superhydrophobic surfaces [7]: the first is to construct micro-nano rough structures on low surface energy materials with a certain hydrophobicity. The second is mainly to modify the surface of micro-nanostructures with substances with low surface energy. The surface of the magnesium alloy base material is hydrophilic, so it is necessary to build a micro-nano structure on the surface, and then modify it with a substance with low surface energy. Common micro-nano structure surface treatment technologies include: chemical etching, hydrothermal method, electrochemical deposition, oxidation method, sol-gel method and vapor deposition. Currently, the surface modification technology using low surface energy materials has been very mature. The main low surface energy materials are: fluoride [8], organ silicide [9], long-chain alkanes [10] and other substances.

2.1 Chemical Etching Method

The chemical etching method is mainly a chemical reaction between the etching solution and the pre-etched material to form a micro-nano structure on the surface of the material, thereby increasing roughness and enhancing the hydrophobic effect. Liu [11] et al. Chemically etched magnesium alloys in silver nitrate solutions of different concentrations for a short period of time, and finally the surface of the magnesium alloy formed crater-shaped and petal-shaped binary micro-nano structures hydrophobic surfaces. A super-hydrophobic surface is obtained by a surface modification treatment with a low surface energy organ silicide. The contact angle is 138.4 °, and the rolling angle is 2 °. Its super-hydrophobic surface has good corrosion resistance. Wang [12] et al. Treated the treated magnesium alloy in a salt spray box for 120 min, and then used a low surface energy 1wt.% Fluor silane to perform surface hydrophobic modification to reduce the surface energy. The obtained super-hydrophobic surface generated a micro-nano structure similar to a petal structure. The surface morphology is shown in Figure 1 with a contact angle of 152.65 ° and a roll angle of 5 °. After testing, superhydrophobic surfaces have very good mechanical properties and corrosion resistance.

![Figure 1. SEM images of super-hydrophobic surface prepared by chemical etching at different magnifications](image)

2.2 Hydrothermal Method

In the hydrothermal method, the reactants are placed in an autoclave aqueous solution, and the hydrothermal reaction is performed under high temperature and high-pressure conditions. The advantage of this method is that it can well control the crystal form and has good dispersibility. Zhang [13] et al. Used hydrothermal treatment and then awakened the surface with hydrophobic modification by stearic acid to finally produce a superhydrophobic surface with a surface shape similar to a petal structure with a static contact angle of 157.6 °. And the prepared super-hydrophobic coating significantly improves the corrosion resistance of the magnesium alloy. Zheng [14] et al. used a simple one-step hydrothermal method to prepare a hydrophobic coating on the surface of a magnesium alloy, and surface modified with stearic acid. The resulting surface has a superhydrophobic function and a contact angle of about 146 °. Corrosion behavior of the prepared magnesium alloy sample in a 3.5 wt% NaCl solution was compared with the untreated sample, and a great improvement in corrosion resistance was found.

2.3 Electrochemical Deposition Method

The electrochemical deposition method refers to a technology of forming a coating layer by an oxidation-reduction reaction occurring on an electrode through the migration of positive and negative ions in an electrolyte solution under the action of an external electric field. Liu [15] et al.
formed a cauliflower-like clustered micro-nanostructured superhydrophobic surface on a magnesium alloy by a nickel plating process, and then modified it with stearic acid. The contact angle of the prepared super-hydrophobic surface is as high as 160.8 ± 1 °, and the rolling angle is 1.8 ± 1 °, showing good long-term stability. Excellent corrosion resistance and self-cleaning function on the surface in 3.5% NaCl solution. Zhang [16] et al. Used electrochemical deposition to form super-hydrophobic surfaces in the form of gold clusters on the surface of magnesium alloys. The surface morphology is shown in Figure 2. In electrochemical deposition, polyelectrolyte multilayers were used as pre-made substrates to adjust the morphology of gold clusters. Only the surface covered with dendritic gold clusters showed super-hydrophobicity and the contact angle was greater than 150 °.

Figure 2. SEM photo of dendritic gold clusters on superhydrophobic surface [16]

2.4 Oxidation Method

The oxidation method mainly includes micro-arc oxidation and anodization. Anodizing refers to the electrochemical oxidation of metals or alloys. The process of forming an oxide film on the metal (anode) under the corresponding electrolyte and specific process conditions due to the applied current. Micro-arc oxidation is also called plasma electrolytic oxidation. Through the combination of electrolyte and corresponding electrical parameters, on the surface of metals such as aluminum, magnesium, titanium and their alloys, a film layer mainly composed of a base metal oxide is grown in situ by relying on the transient high temperature and high pressure generated by arc discharge. The film has very good adhesion to the base material. Zhang [17] et al. Successfully prepared a superhydrophobic coating based on calcium stearate by direct current and pulse electrodeposition on an anodized magnesium oxide alloy, and its static contact angle was about 158 °. The corrosion resistance of the coating matrix in simulated body fluids was also investigated. The results show that the coatings prepared under different deposition methods and working cycles show different corrosion resistance. A coating with a 50% duty cycle in pulse mode provides optimal corrosion protection for the substrate. Cui [18] et al. Used micro-arc oxidation to treat the surface of magnesium alloys to obtain micron-sized porous structures, and hydrophobically modified them with low surface energy materials to finally obtain super-hydrophobic surfaces with a contact angle of 151.5 °. With the extension of the micro-arc oxidation processing time, the surface structure (see Figure 3) appears to be closed. After 11 days in a 3.5 wt.% NaCl solution, only the edge portions were pitted. The results show that the surface has good long-term corrosion resistance.

Figure 3. Surface morphology and contact angle of different micro-arc oxidation coatings [18]

2.5 Sol-Gel Method

The sol-gel method is to use a compound containing a highly chemically active component as a precursor, uniformly mix these materials in a liquid phase, and perform a chemical reaction of hydrolysis and condensation. A stable transparent sol system is formed in the solution. The sol slowly polymerizes between the aged colloidal particles to form a gel with a three-dimensional network structure. The gel network is filled with a solvent that loses fluidity and forms a gel. The gel is dried and sintered to prepare molecular and nano-substructure materials. Hu [19] et al. Successfully prepared tetraethoxysilane and methyltriethoxysilane as precursors by combining micro-arc oxidation (MAO) and sol-gel method on magnesium alloys. A MAO layer having a highly porous surface is formed as an intermediate layer to ensure excellent adhesion of the superhydrophobic silica film to the substrate.

Superhydrophobic surface is mainly composed of micro-nano structure and low surface energy modification. For magnesium alloy superhydrophobic polymer compos-
ite coatings, the micro-nano structure is mainly composed of inorganic nanoparticles, and the surface modification is mainly performed by substances with low surface energy. The polymer provides the connection between the nanoparticles and the metal substrate or the underlying coating, so that the coating and the metal substrate have stronger adhesion.

3. Superhydrophobic Polymer Composite

Polymer composite protective coatings are usually multilayer systems consisting of at least a primer and a topcoat \(^{[20]}\). The primer provides primary corrosion inhibition and adhesion, and the topcoat is responsible for environmental (such as UV, water, mechanical, microbial, etc.) resistance and different functions as well as some aesthetic requirements \(^{[20]}\). Polymer composites with super-hydrophobic function are materials that are macro- or micro-composite together through polymers and micro-nano particles with two or more components with different properties. The two main components are polymer-based coatings and micro-nano particles. Polymer-based coatings are mainly polymers with hydrophobic properties, which can enhance the adhesion between the polymer coating and the substrate, provide primary corrosion protection, and are one of the key components of anticorrosive coatings. The micro-nano structure of micro-nano particles can not only provide the roughness required for superhydrophobic, but also increase the wear resistance and mechanical properties of the coating. The modification of low surface energy substances can be performed by modifying nanoparticles or by modifying the entire composite coating.

3.1 Polymer

3.1.1 Polydimethylsiloxane (PMDS)

Polydimethylsiloxane (PMDS) is a kind of high-molecular organosilicon compound, which has a certain degree of hydrophobicity and is easy to be concentrated at the interface of air. Therefore, in superhydrophobic polymer composites, polydimethylsiloxane (PMDS) is one of the common polymers. Li et al. \(^{[21]}\) et al., made a strong superhydrophobic coating by spraying a fluorine-free suspension composed of epoxy resin (EP), polydimethylsiloxane (PDMS) and modified SiO2 on a substrate (Figure 4). The coating exhibits excellent superhydrophobicity with a contact angle of 159.5 ° and a sliding angle of 3.8 °. The prepared super-hydrophobic EP-PDMS @ SiO2 coating exhibits good mechanical durability and remains super-hydrophobic after exposure to harsh conditions.

3.1.2 Polylactic Acid (PLA)

Polylactic acid (PLA) is a non-toxic and non-stimulating synthetic polymer material of hydrophobic aliphatic polyesters. It has good transparency, biodegradability, biocompatibility and thermoplasticity. It is a recyclable resource, and is therefore widely used. Because the hydrophobic nature of polylactic acid itself can play an effective antibacterial role in medical applications, using polylactic acid as the main component of superhydrophobic composite materials in biodegradable materials can not only effectively antibacterial, and it also has a certain effect on controlling cell growth or inhibiting cell growth. The resulting superhydrophobic polymer composite coating also has good corrosion resistance. So far, polylactic acid (PLA) has been mainly used in magnesium and magnesium alloy biodegradable materials. Kannan et al. \(^{[27]}\) proposed to perform CaP conversion on MgAl alloy AZ91 by electrodeposition, and then impregnate to prepare CaP / PLA superhydrophobic composite coating with contact angle up to 153 °.

3.1.3 Polytetrafluoroethylene (PTFE)

Polytetrafluoroethylene (PTFE), commonly referred to as "non-stick coating" or "easy-to-clean material". It has the characteristics of acid and alkali resistance and resistance to various organic solvents, and is almost insoluble in all solvents. At the same time, polytetrafluoroethylene has the characteristics of high temperature resistance. It is currently known that no solid material can adhere to the surface. It is also a solid material with the smallest surface energy. Its surface energy friction coefficient is extremely low. Therefore, it has a considerable application potential in polymer composites with superhydrophobic functions.

According to the characteristics of polytetrafluoroethylene itself, Mashalayar et al. \(^{[30]}\), through plasma electrolytic oxidation (PEO), followed by a suspension of telomere solution of superdispersed polytetrafluoroethylene (SPTFE) and tetrafluoroethylene (TFE) Surface modification of medium-treated magnesium alloy. The electrochemical, tribological and wetting properties of the obtained composite protective coatings were studied. Compared to unprotected magnesium alloys and base
PEO coatings, the manufactured coatings reduce the corrosion current and wear density by orders of magnitude. This versatile coating has high corrosion resistance and a good coefficient of friction under dry abrasion conditions, thereby extending the area of application of magnesium alloys. According to the electrochemical impedance spectroscopy data and calculated parameters of equivalent circuit elements, the SPTFE treatment of PEO coating results in an increase in the thickness of the composite coating.

The protective performance of the composite coating obtained by the SPTFE treatment is four orders of magnitude higher than that of the initial coating formed by the PEO method. The corrosion current density and wear of the composite coating were reduced by three orders of magnitude. In addition, the coating obtained by impregnating PEO and SPTFE telomer dispersion has superhydrophobic properties, the contact angle is greater than 152°, and the wettability of water and other liquids is poor, which further enhances the corrosion resistance of the coating.

The polymer in the protective coating of the polymer composite material with super-hydrophobic function, in addition to having a certain degree of hydrophobicity itself, can also be used for the adhesion between the coating and the substrate.

3.2 Nanoparticles

Nanoparticles refer to particles with a particle size between 1-100nm (nanoparticles are also called ultrafine particles). It belongs to the category of colloidal particle size. They are located in the transition zone between atom clusters and macroscopic objects, between the microscopic system and the macroscopic system, and are a group composed of a small number of atoms or molecules. Therefore, they are neither a typical microscopic system nor a typical macroscopic system. The distinguishing feature of nano particles from the structure of macroscopic objects is that their surface area accounts for a large proportion, and the surface atoms have neither long procedures nor short procedures. It can be considered that the state of the atoms on the surface of the nanoparticle is closer to the gaseous state, and the atoms inside the particle may be in an orderly arrangement. Even so, due to the small particle size and large surface curvature, a high Gihbs pressure is generated inside, which can cause some deformation of the internal structure. This structural feature of nanoparticles makes it widely used in hydrophobic functional protective coatings.

3.2.1 Nano Silica

As an excellent structural and functional material, nano-silica shows excellent surface activity, high specific surface area, high temperature resistance, and non-toxic and pollution-free performance. Due to the high surface energy of silica, it is easy to agglomerate during use, and the nano-silica has poor compatibility with most polymer materials and cannot achieve the desired composite material properties. Surface modification of nano-silica not only effectively prevents agglomeration, but also improves the compatibility and dispersion stability of nano-silica and polymer materials. At the same time, the surface modification can also make the surface of nano-silica have special functional groups, and the binding force with the polymer is enhanced, so that the composite material has more special functions. For example: Wu et al. fabricated a composite material containing a diamond dodecahedron zeolite imidazolate skeleton (ZIF-8@SiO2) on an AZ31 magnesium alloy by chemical etching and dip coating methods to enhance stability and corrosion resistance. (Figure 5) Modify the hydrophobic Cetyltrimethoxysilane (HDTMS) on ZIF-8@SiO2 to improve its hydrophobicity. The results show that various liquids can stabilize and maintain contact angles above 150° on their surfaces. Hydrophobic modification is achieved in alkoxysilanes. Finally, the etched Mg alloy with a micron morphology was immersed in a hydrophobic ZIF-8@SiO2 n-hexane solution. The super-hydrophobic surface with a layered structure made of magnesium alloy not only has good water resistance, but also has excellent corrosion resistance, mechanical properties and chemical stability.

![Figure 5. Hydrophobic process and experimental flow on ZIF-8@SiO2](image)

In addition, Zhang et al. prepared a micro-nano-structured polydimethylsiloxane and silicon dioxide (PDMS / SiO2) composite coating on the surface of a magnesium alloy with two different-sized SiO2 nanoparticles by a simple painting method. Floor. The effects of 40nm and 50-250nm SiO2 ratio on the wettability, wear resistance and corrosion resistance of composite coatings were studied. By using scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FT-IR), contact angle measuring instrument, sandpaper weight device and other tools, the morphology, composition, water contact angle, abrasion resistance and corrosion resistance of the composite coating were measured, and mechanical and thermal stability were
also obtained by finger wiping, scratch test and thermogravimetric analysis. The results show that the PDMS / SiO2 composite coatings prepared under optimized parameters are stable and superhydrophobic, and their contact angles can be maintained at a high level after 50 sanding cycles. (138-150 ° and 133-153 °). The composite coating shows good resistance to cuts and finger touch. And electrochemical experiments show that a strong coating can significantly improve the corrosion resistance of magnesium alloys.

3.2.2 Nano Zinc Oxide

Nano zinc oxide is a new type of multifunctional inorganic material. In recent years, nano zinc oxide has been widely used in textiles, coatings and other fields, especially in biomedicine. Like nano-silica, nano-zinc oxide can also improve the corrosion resistance and abrasion resistance of protective coatings to achieve the same effect. For example, Zhou [35] et al. proposed a new idea to imitate the process of weeding (see Figure 6). It solves the problems of low adhesion, weak abrasion resistance and poor corrosion resistance of general super-hydrophobic coatings. The ratio of epoxy resin to ZnO seeds is strictly controlled so that ZnO seeds are not completely coated. On this basis, a clustered ZnO coating composed of cross-index ZnO rods was prepared. After being modified with stearic acid, the coating showed superhydrophobicity, the contact angle was 163 °, and the coating showed excellent abrasion resistance and obvious robustness. The coating has excellent corrosion resistance due to the epoxy / ZnO seed and the barrier layer of clustered ZnO. At the same time, the clustered ZnO / epoxy resin coating prepared like the rooting of seeds has good robustness, which can adapt to various harsh environments, such as tape peeling, friction between objects, etc., expanding the application range of superhydrophobic coatings.

3.2.3 Nano Titanium Dioxide

Nano titanium dioxide has self-cleaning, anti-aging, chemical stability and thermal stability, so it is also widely used in anticorrosion control. Huang [37] et al. used atomic layer deposition (ALD) technology to prepare a layer of TiO2 nano-film with controlled thickness on the surface of AZ31 magnesium alloy (see Figure 7), which can adjust the corrosion behavior of AZ31 magnesium alloy. Compared with the untreated magnesium alloy, the corrosion current density (i_corr) of the magnesium alloy covered with TiO2 over 200 cycles can be reduced by 58%, and as the thickness of the nanofilm reaches 63 nm (400 cycles), the corrosion current density further decreases to 74%. Subsequently, the 3-aminopropyltriethoxysilane (APTES) cross-linked conversion layer was modified by the dipping method. A dense silane coating can be formed on the TiO2 nanofilm, which can seal the pinholes of the TiO2 nanofilm, and further adjust the substrate's corrosion barrier behavior. In a TiO2 / silane composite coating, the corrosion current density can be reduced by about two orders of magnitude. Making adjustable corrosion rates a reality can be attributed to the precise control of metal oxide nanofilm thickness and the additional protection of compact silane coatings.

In summary, nanoparticles can provide the rough structure required for superhydrophobic surfaces. The ability to attach to the surface of the coating through polymers also provides some abrasion and mechanical durability. In recent years, more and more researchers have added inorganic nanoparticles, such as nano-silica, nano-alumina, etc. to the coating in order to enhance the roughness of the coating and to protect the corrosion with self-healing. The coating provides space to store healing agents or inhibitors, and has great prospects in the research of smart materials.

4. Conclusion

This article reviews the preparation methods and structural composition of polymer composite coatings with superhydrophobic function for magnesium alloys. To achieve superhydrophobic effect, one is to increase the roughness, but to reduce the surface energy. Polymers provide the
adhesion between the coating and the substrate, and also increase the protection of the substrate to a certain extent. Nanoparticles can not only increase the roughness, but also reduce the surface energy of the coating after hydrophobic modification on the surface. In addition, the coating can also be directly hydrophobically modified. So far, the related research of magnesium alloy anticorrosion in the medical field is very promising, and the corrosion control of magnesium alloy is still a major difficulty in the application of magnesium alloy. At the same time, poor adhesion between the coating and the substrate, super mechanical properties, and poor abrasion resistance are all important issues that need to be resolved, and also indicate the direction of development for metal corrosion.

References

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