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REVIEW

# Advances in Medical Magnesium Alloy Surface Modification for Corrosion Resistance Improvement

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**Abstract:** Since the magnesium and magnesium alloys have good load transmission, exceptional biosafety, unique biodegradability, etc, they have significant application possibilities in the field of medical implantation. Furthermore, excellent corrosion resistance is one of the paramount prerequisites for magnesium and magnesium alloys as medical implants. However, magnesium alloys exhibit poor corrosion resistance, leading to rapid degradation in physiological environments due to high corrosion rates. This premature degradation, before completing their intended service life, compromises their structural integrity, severely limiting their clinical applications. Surface modification treatment of magnesium alloy to improve corrosion resistance has become a research hotspot of medical magnesium alloy. This study primarily focused on the research advancements in the corrosion resistance enhancement of medical magnesium alloys. The developmental trajectory and characteristics of medical magnesium alloys were outlined. Additionally, surface modification techniques such as micro-arc oxidation and ion implantation, as well as microstructure and properties of magnesium alloy surfaces after surface modification were reviewed. The formation mechanisms of various coatings were discussed, and their structures and properties were analyzed. The impact of coatings on the degradation rate of magnesium alloys was elucidated, aiming to identify key issues and potential solutions in the implementation and application of surface modification for medical magnesium alloys. Recommendations were also provided, presenting the research directions for surface modification of medical magnesium alloys.

**Key words:** magnesium alloys; surface modification; degradation ratio; corrosion resistance

Traditional biologically inert medical metal implantable materials, represented by stainless steel, titanium-based alloys, cobalt-based alloys, etc, have been widely used in clinical practice due to their advantages of high strength, good toughness, high stability and relatively low cost. However, these traditional implantable biomedical metal materials are too stable to be degraded independently, which need to be removed by secondary surgery after the patient's recovery, causing secondary damage to the patient's body and increasing the medical cost<sup>[1]</sup>.

Since the 21st century, usage of degradable metals in implantable devices for clinical applications has become a

research hotspot for medical metal materials. Magnesium and magnesium alloys are the most representative degradable metals. As an essential trace nutrient for the human body, magnesium exhibits a relatively low standard electrode potential ( $-2.37$  V), making it particularly prone to corrosion reactions with  $\text{Cl}^-$ , thereby promoting its complete degradation<sup>[2]</sup>. It activates various enzymes, stabilizes the structure of DNA and RNA, and plays a crucial role in nerve, muscle, bone and heart function. Additionally, excess magnesium, if not absorbed by the body, can be excreted through urine without causing toxicity<sup>[3]</sup>. Among all metals used in bone tissue engineering, magnesium and magnesium alloys possess

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similar densities and elastic moduli to natural bone, effectively reducing stress shielding effects, exhibiting good load transfer properties, thus promoting new bone growth and significantly enhancing osteoblast activity<sup>[4]</sup>.

However, magnesium is very chemically reactive and susceptible to corrosion in the physiologic environment. Since osteogenesis takes at least 12 weeks, most magnesium alloy implants have already been degraded and lost their mechanical integrity during this period, which severely limits their clinical application in orthopedic load-bearing sites. To make matters worse, a large amount of  $H_2$  produced during magnesium degradation rapidly swells the implant area, causing loosening between the implanted metal and the bone tissue<sup>[5-7]</sup>. The released hydrogen bubbles accumulate in air pockets near the implanted material and delay the healing process, even leading to tissue necrosis. The ratio of degradation of magnesium alloys in the human body is accelerated when the pH of the surrounding environment is below 11.5. With the increase in  $Mg^{2+}$  produced by the degradation of magnesium alloys, the osmotic pressure of the human body increases, leading to localized alkalization around the surface of magnesium alloy implant materials, which is detrimental to cell survival<sup>[8-9]</sup>. Therefore, enhancing the corrosion resistance of magnesium alloys to prevent excessive degradation in physiological environments has emerged as a crucial challenge to address for their clinical application.

Compared with enhancing the corrosion resistance of the medical magnesium alloy matrix, improving the surface corrosion resistance of medical magnesium alloys through surface modification techniques is widely recognized as the preferred approach, making it a current research hotspot in the field of medical magnesium alloys<sup>[10]</sup>. Based on the characteristics of medical magnesium alloys, the principle of surface modification technique and the surface microstructure and properties of modified medical magnesium alloys, we summarized the influence law of surface modification on the degradation ratio of medical magnesium alloys, and discussed the key problems and modification mechanisms of surface modification for medical magnesium alloys. The development prospect of surface modification of medical magnesium alloy was also reviewed to provide information and reference for researchers.

## 1 Surface Modification of Medical Magnesium Alloys

Material alloying, deformation processing, amorphization and surface modification are the main ways to improve the corrosion resistance of magnesium alloy. Although both alloying and deformation processing can significantly improve the corrosion resistance of magnesium alloy, it is insufficient to meet the actual requirements of implanted materials. Surface modification of magnesium alloys is simpler than changing the natural structure and composition. Surface modification improves the corrosion resistance of the magnesium alloy surface and slows down its degradation

behavior while maintaining good ontological properties of the material, as well as adjusting its surface hardness, which confers advantages such as antimicrobial properties, promotion of bone growth and better biocompatibility<sup>[11]</sup>. Surface coating is a common surface modification methods for medical magnesium alloys, including chemical conversion coatings, micro-arc oxidation (MAO) coatings, degradable polymer coatings, etc. These coatings aim to significantly enhance corrosion resistance by isolating corrosive media from magnesium alloys. Other surface modifications mainly involve selective laser melting, magnetron sputtering, friction stir processing (FSP), etc. These techniques aim to alter the microstructure of magnesium alloy surfaces, thereby changing corrosion mechanisms and achieving significant improvements in corrosion resistance. Table 1 summarizes the advantages and disadvantages of common surface modification methods for medical magnesium alloys.

### 1.1 Preparation of surface coating on medical magnesium alloys

#### 1.1.1 Chemical conversion coating

Chemical conversion coating involves immersing magnesium alloy in a plating solution by chemical methods, which often contains fluoride, phosphate, carbonate, chromate, etc, and the alloy surface reacts with the plating solution to generate a dense insoluble coating, which in turn protects the substrate<sup>[12-13]</sup>. Common chemical conversion coatings include hydrothermal treatment coatings, rare earth conversion coatings, fluorine conversion coatings and phosphorus conversion coatings. Currently, phosphate conversion coatings and fluoride conversion coatings can effectively enhance the corrosion resistance of magnesium alloys, while carbonate coatings only provide initial protection for magnesium alloys. However, as the reaction progresses, the coating is gradually detached, leading to a decrease in corrosion resistance.

Hydrothermal treatment is to generate a dense  $Mg(OH)_2$  protective film on the surface of magnesium alloys, i.e.,  $Mg^{2+}$  is dissolved from the magnesium alloys themselves in a relatively high-temperature and high-pressure reaction environment with aqueous solution as the medium. Song et al<sup>[14]</sup> successfully prepared a corrosion-resistant coating on the highly reactive magnesium-lithium alloy surface using deionized water as a precursor liquid through a hydrothermal method. The results indicate that the coating comprises a dual-layer structure consisting of  $Mg(OH)_2$  and  $LiOH$ . In Fig. 1, the accumulation structure of the coating can be observed, enhancing hydrophobicity while preventing the contact between the magnesium alloy and the corrosive medium, and thereby improving the corrosion resistance of the magnesium alloy. Zhu et al<sup>[15]</sup> also found that the thickness of the coating prepared by hydrothermal method increases with the increase in hydrothermal temperature and duration. Since the formed  $Mg(OH)_2$  layer is easily damaged by  $Cl^-$  in the human body, Peng et al<sup>[16]</sup> introduced  $Mg-Al$  layered double hydroxide (LDH) into hydrothermally treated  $Mg(OH)_2$  coatings, and utilized the interlayer anion exchange of  $Mg-Al$  LDH to

**Table 1** Advantages and disadvantages of common surface modification methods for medical magnesium alloys

| Surface modification method | Type                     | Advantage  | Disadvantage   |
|-----------------------------|--------------------------|--|--|
| Chemical conversion coating | Hydrothermal treatment   | Obtain coatings directly, eco-friendly and economically without the need for high temperatures | Observation of coating growth is not intuitive, and it is difficult to protect magnesium alloys for a long time              |
|                             | Fluorine treatment       | Coating is dense and exhibits high adhesion strength with the substrate                        | Strong corrosiveness of hydrofluoric acid poses safety hazards   |
|                             | Ca-P                     | Excellent biocompatibility, safe and non-toxic   | Presence of porous structure may reduce corrosion resistance, and there is still room for improvement in adhesion capability |
| MAO coating                 | -                        | High binding strength and controllable phase composition                                       | Microcracks and micropores   |
| Polymer coating             | -                        | Insulation, easy to modify and good biocompatibility   | Clear interface and easy detachment in the human environment   |
| Ion implantation            | -                        | High bonding strength and uniform distribution of coating surface elements                     | Galvanic corrosion may occur, and long-term accumulation of ions in the human body may be harmful                            |
| Other surface modification  | Laser surface melting    | No need to introduce additional alloying elements and no risk of poor coating bonding ability  | Discontinuous melting can form pores and irregular surfaces  |
|                             | Magnetron sputtering     | Low cost, high sedimentation rate and environmentally friendly                                 | Complex equipment and material size affect sputtering efficiency   |
|                             | Friction stir processing | Uniform surface structure and high bonding strength  | Not suitable for complex shaped workpieces   |

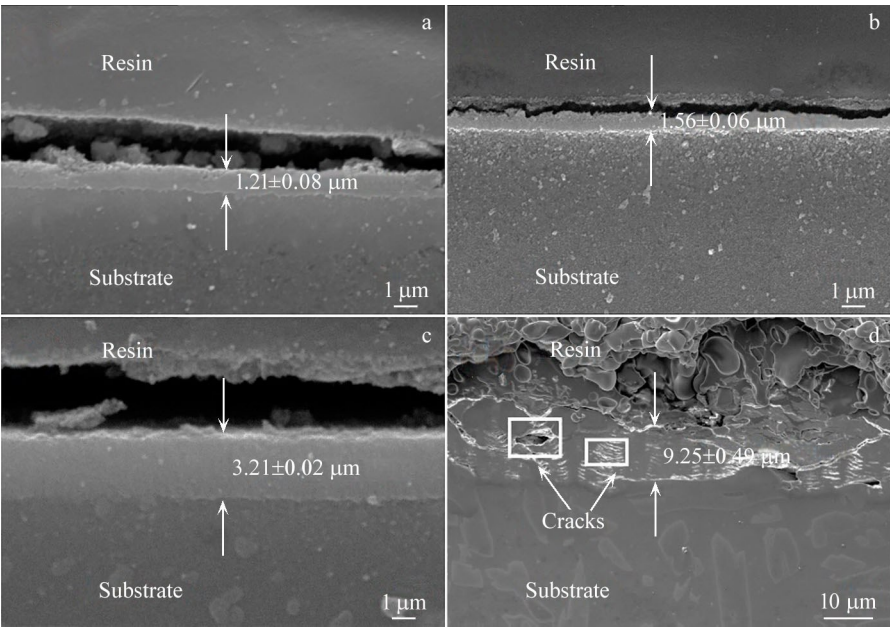


Fig.1 Cross-sectional morphologies of the coating samples prepared at 120 °C (a), 130 °C (b), 140 °C (c), and 150 °C (d)<sup>[14]</sup>

reduce the concentration of Cl<sup>-</sup> in the coatings, which made coatings possess superior anti-corrosion property than pure Mg(OH)<sub>2</sub> coating both in vivo and out-of-vivo.

The coating prepared by hydrothermal treatment is firmly bonded to the substrate, and the thickness of the coating can be regulated by controlling the hydrothermal time, which in turn controls the degradation ratio. During hydrothermal treat-

ment, water is employed as the sole or primary reagent, making it not only environmentally friendly but also comparatively stable. Extensive research indicates that this method is one of the most promising approaches for enhancing the corrosion resistance of magnesium alloys<sup>[17]</sup>. The drawback of this method is that the coating is susceptible to damage from Cl<sup>-</sup> in the human environment, making long-term protection of

the substrate difficult. Additionally, the coating is thin and cannot serve as the outermost layer. Composite coatings are expected to solve this problem.

Fluorine treatment involves immersing magnesium alloys in hydrofluoric acid, by which dense, homogeneous and biocompatible  $\text{MgF}_2$  protective layer can be generated on the surface of the magnesium alloys, thus retarding the corrosion of the substrate. At the same time, elemental fluorine is also an essential trace element for the human body, which exists in bones, teeth and tissues such as spleen and kidney. The appropriate amount of fluorine helps the formation of human bones, and  $\text{F}^-$  can resist corrosion and promote bone formation<sup>[18]</sup>. Panemangalore et al<sup>[19]</sup> investigated the degradation of fluoride-coated Mg-Zn-Er alloys in simulated body fluid (SBF) and found that fluoride coatings can effectively protect the substrate by creating a corrosion barrier and effectively impeding  $\text{Cl}^-$  penetration. Zhang et al<sup>[20]</sup> used fluorination treatment to prepare micro- and nano-structured  $\text{CaF}_2$  coatings on the surface of AZ31 magnesium alloy and modified the coating with stearic acid (SA) to obtain a superhydrophobic surface. It was found that the  $\text{CaF}_2$  layer with lamellar crystals was masked after SA modification, but the spherical structure could still be observed. Meanwhile, during the SA treatment, SA would penetrate the  $\text{CaF}_2$  layer instead of the  $\text{MgF}_2$  layer, so the modified fluoride coating consisted of an inner  $\text{MgF}_2$  layer and an outer SA/ $\text{CaF}_2$  layer. In addition, it was tested and found that none of the three coatings was toxic to cells, and the cell adhesion of the  $\text{CaF}_2$  layer and the SA/ $\text{CaF}_2$  layer could be improved. Huang et al<sup>[21]</sup> prepared calcium-deficient hydroxyapatite (CDHA)/ $\text{MgF}_2$  double coatings on the surface of high-purity magnesium (HP Mg) rods using fluorination and hydrothermal treatment to repair femoral ankle defects in rabbits. Micro-CT observations revealed that the degradation ratio of the CDHA/ $\text{MgF}_2$  double coatings at postoperative 4, 8 and 12 weeks was 0.4%, 1.8% and 2.8%, respectively, which were comparable to the degradation ratio of HP Mg and  $\text{MgF}_2$ ,

demonstrating good corrosion resistance (Fig.2).

The results showed that there was a large number of new bones with tighter adhesion between the CDHA/ $\text{MgF}_2$  double coating and the surrounding bone tissue (Fig.3). The  $\text{Mg}^{2+}$  in the serum of rabbits after implantation was always within the normal range, and the liver and kidney functions were not abnormal. The coatings obtained by fluorination treatment have a dense structure and high bonding strength with the substrate. Furthermore, Fintová et al<sup>[22]</sup> immersed AZ61 magnesium alloy in  $\text{NaBF}_4$  molten salt at different temperatures to prepare fluoride conversion coatings followed by boiling in



Fig.2 Growth of reconstructed femoral condyles with different coatings at postoperative 4, 8 and 12 weeks<sup>[21]</sup>

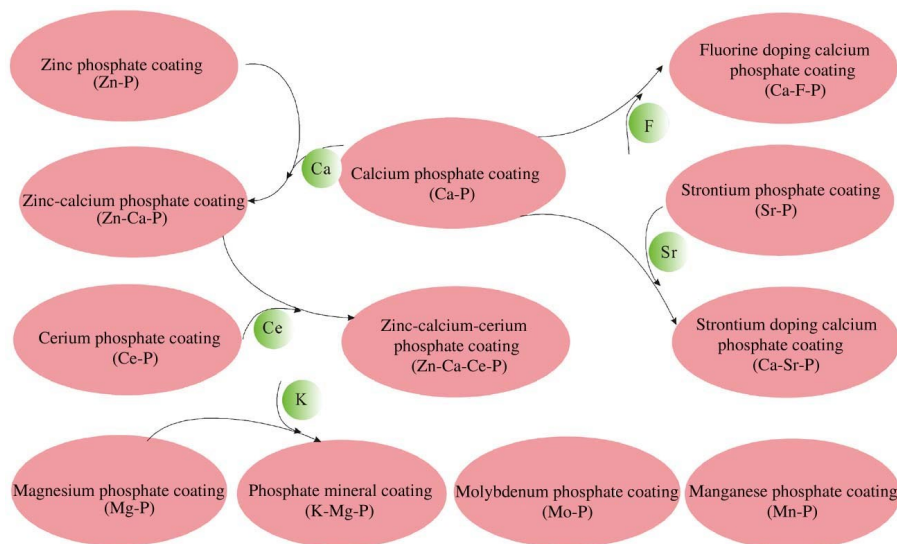


Fig.3 Phosphate conversion coatings for magnesium alloys<sup>[26]</sup>

distilled water, yielding a thick inner layer of Mg-F ( $\text{MgF}_2$ ) and a thin outer layer of Na-Mg-F ( $\text{NaMgF}_3$ ). The results indicate that the treatment duration has a certain influence on corrosion resistance. With prolonging treatment duration, the corrosion current density of the coating gradually decreases, indicating an improvement in the corrosion resistance of coatings in SBF. Therefore, fluoride ion conversion coatings represent an effective approach for enhancing the corrosion resistance of magnesium alloys. However, hydrofluoric acid has a certain corrosiveness, which leads to a safety hazard during the test. In addition, the impurity ions in the solution will affect the formation of the coating. Some coatings obtained by chemical conversion treatment introduce toxic elements, which can lead to a reduction in the biocompatibility of magnesium alloys. For example,  $\text{Cr}^{6+}$  introduced by chromate is toxic and thus not suitable for coating anymore. In recent years, the rare earth conversion films without chromates have attracted much attention due to their convenient process parameters and significantly improved corrosion resistance for magnesium and magnesium alloys in a short period of time<sup>[23]</sup>. However, the initial nucleation point of rare earth ions during the molding process is often at the inclusions or cracks of the metal matrix, so the formed conversion film is not uniform in thickness and has microporosity. Moreover, it needs to be further verified whether excess rare earth elements in the rare earth conversion films has any effect on cell biocompatibility. In addition, scholars have found a biomimetic solution method, by mimicking the formation of inorganic minerals in living organisms, to generate a kind of phosphate (Ca-P) coating on the surface of the substrate. The Ca-P coating is similar to the inorganic composition of human bone tissue, which improves the corrosion resistance of magnesium alloy and at the same time has good biocompatibility and bone induction

ability<sup>[24-25]</sup>. Fig. 3 lists several common phosphate coatings, typically consisting of phosphates of Ca, Zn, Mg, Mn, Sr and Ce<sup>[26]</sup>. To narrow the focus, this study primarily reviewed calcium phosphate coatings. Wang et al<sup>[27]</sup> deposited a Ca-P coating in SBF to enhance the corrosion resistance of AZ31B magnesium alloy. As shown in Fig. 4, the main components of the coating include  $\text{Mg}(\text{H}_2\text{PO}_4)_2$ ,  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ ,  $\text{Ca}_3(\text{PO}_4)_2$  and  $\text{Mg}_3(\text{PO}_4)_2$ , with a thickness of approximately 20  $\mu\text{m}$ . Compared with the substrate, the corrosion current density of Ca-P coating decreases by two orders of magnitude with prolonging corrosion time. Guo et al<sup>[28]</sup> employed a chemical conversion method to fabricate Ca-P coating with micro-nano fibrous porous structure on the surface of magnesium alloy. The results indicate that the coating is primarily composed of Ca, P, C, O and trace amount of Mg. The content of Ca in the coating increases as temperatures rises, and the composition gradually changes from DCPD phase to hydroxyapatite (HA). Additionally, after immersion in SBF, compared to coatings obtained at 30, 40 and 80  $^{\circ}\text{C}$ , coatings obtained at 60  $^{\circ}\text{C}$  show almost no significant variation in the rate of hydrogen evolution throughout the entire immersion process, suggesting the most dense structure and superior corrosion resistance. Zhao et al<sup>[29]</sup> also found that magnetic fields have a certain influence on the formation of the coating. During the formation process of phosphate coatings, the superposition of magnetic field can promote the generation of hydrogen gas bubbles, accelerate surface detachment, disperse  $\text{Mg}^{2+}$  evenly, and ultimately form a uniform and smooth phosphate coating on the surface of the magnesium alloy. In conclusion, employing the biomimetic solution method to fabricate Ca-P coatings on magnesium alloy surfaces can effectively enhance the corrosion resistance of magnesium alloys. Additionally, Luo et al<sup>[30]</sup> have also demonstrated that electrolytes containing phosphates can promote the formation of porous

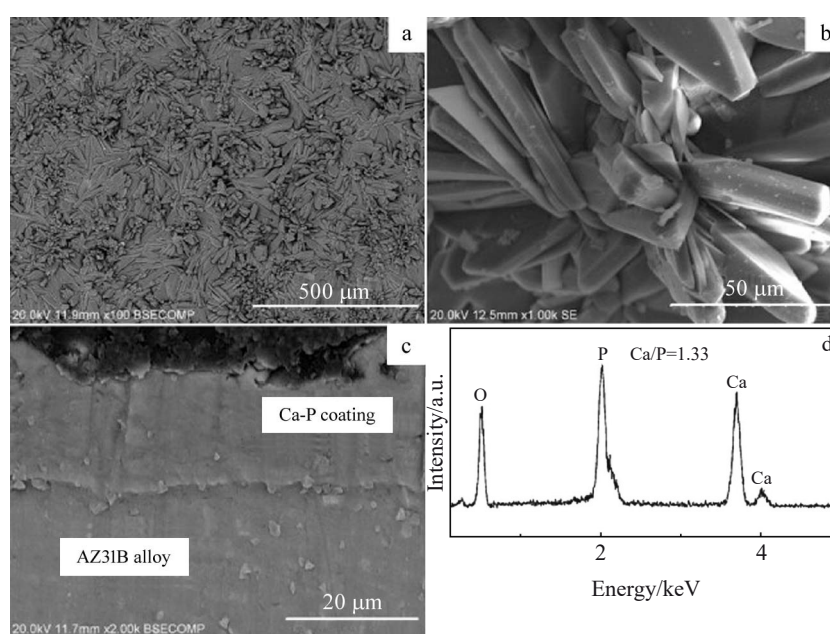


Fig.4 Surface (a–b) and cross-section (c) morphologies of Ca-P-coated AZ31B magnesium alloy samples; (d) EDS spectrum of surface<sup>[27]</sup>

structures in the MAO process, thereby increasing the growth rate of MAO coatings. However, the available material systems are limited, and further research should be conducted in the future.

In summary, it is found that a coating with good adhesion and difficult to dissolve can be formed on the surface of magnesium alloy by chemical conversion method, which can improve the corrosion resistance of magnesium alloy and improve the adhesion of subsequent coatings. This method is simple to operate and has a wide range of applications in the biomedical field. In the future, chemical conversion coatings should be combined with other surface modification techniques to prepare coatings with excellent corrosion resistance and good biocompatibility.

### 1.1.2 MAO coating

MAO, also known as plasma electrolytic oxidation (PEO), is developed on the basis of anodic oxidation. It introduces the Faraday working area of common anodic oxidation to the high-voltage discharge area, resulting in corona, spark discharge, micro-arc discharge and other phenomena on the metal surface of valves such as Mg, Al, Ti, Zr, Ta and Nb, which are placed in the treatment solution. In the thermochemical, plasma chemical and electrochemical joint action, micro-arc discharge produces instantaneous high temperature and high pressure (local temperature up to 2000 °C or above), which makes the anode oxide instantly melt and solidify on the metal surface, and thus the oxidized ceramic coatings ultimately form, achieving the strengthening of the surface properties of the material<sup>[31–32]</sup>. Tian et al<sup>[33]</sup> investigated the effect of fluorine-containing MAO coatings on the corrosion resistance of magnesium alloys. The results showed that the reaction of F<sup>-</sup> with magnesium generated a more stable phase MgF<sub>2</sub> than MgO, which improved the corrosion resistance of the coating. Wang et al<sup>[34]</sup> prepared TiO<sub>2</sub> ceramic coatings with hydrophobicity on the surface of AZ31 magnesium alloy using MAO technique. It was found that the TiO<sub>2</sub> ceramic coating was anatase crystalline and its corrosion potential was negatively shifted compared to that of the substrate and the corrosion current density was reduced by 7 orders of magnitude. In addition, the TiO<sub>2</sub> ceramic coating showed hydrophobicity with a surface contact angle of 112.4°. Jiao et al<sup>[35]</sup> prepared a ceramic coating on the surface of magnesium alloy by placing the magnesium alloy in phosphate solution in order to further improve the corrosion resistance of the MAO coating. The results showed that the MAO coating consisted of Mg, P and O without other harmful elements. Chen et al<sup>[36]</sup> successfully prepared MAO coatings containing nano-Y<sub>2</sub>O<sub>3</sub> by adding nano-Y<sub>2</sub>O<sub>3</sub> to the electrolyte. The main constituents of the coatings were found to be Ca<sub>8</sub>MgY(PO<sub>4</sub>)<sub>7</sub> and Y<sub>2</sub>O<sub>3</sub> particles. The results indicate that Ca<sub>8</sub>MgY(PO<sub>4</sub>)<sub>7</sub> plays a stabilizing role in the coating, while nano-Y<sub>2</sub>O<sub>3</sub> particles can plug micropores. Furthermore, the degradation rate of the coatings in Hank's solution decreased from 0.14 mm/a to 0.06 mm/a, resulting in a significant improvement in corrosion resistance.

Researchers have also investigated how electrical para-

meters (voltage, current, duty cycle and pulse frequency) and time affect the formation mechanism, film formation rules as well as the microstructure and properties of the resultant coatings in the MAO process<sup>[37]</sup>. Particularly, the operating voltage and current directly influence the thickness and morphology of the MAO coatings<sup>[38]</sup>. Yong et al<sup>[39]</sup> conducted an orthogonal experimental study on the influence of (NH<sub>4</sub>)<sub>2</sub>ZrF<sub>6</sub> concentration, voltage and treatment time on the corrosion resistance of ZK61M magnesium alloy. The results indicate that lower voltages result in lower discharge intensity, leading to the formation of smaller pores and thus better corrosion resistance of the coatings. Ur Rehman et al<sup>[40]</sup> suggested that longer processing time may lead to internal damage of the coating, thereby reducing its corrosion resistance. Currently, most studies focus on optimizing the magnitude of the current while relatively overlooking the influence of current patterns on the corrosion resistance of MAO coatings<sup>[41–42]</sup>. Previous coatings formed by a single power source exhibited poor quality and performance. Therefore, optimizing current patterns can help to reduce energy consumption and achieve high-performance MAO coatings<sup>[43–44]</sup>. Yuan et al<sup>[45]</sup> employed constant current/gradient current control methods to prepare MAO coatings on the surface of AZ31 magnesium alloy and investigated the impact of current output modes on the growth rate and microstructure of MAO coatings. As observed from Fig. 5, for the constant current mode (C5), with increasing the reaction time, the pore diameter increases from 6.27 μm to 10.52 μm. For the current ramp-up mode (G258), the pore diameter increases from 2.24 μm to 11.19 μm. The current ramp-down mode (G852) maintained pore diameter within 8–10 μm throughout the entire MAO process, resulting in smaller and denser pores due to some pores being sealed. Additionally, it can be observed that the corrosion current value of G852 was slightly lower than that of C5 and G258. In summary, G852 (forming denser coatings with lower porosity) can mitigate its corrosion rate to a certain extent. Yao et al<sup>[46]</sup> employed three different power supply modes for MAO treatment of AZ91D magnesium alloy, as illustrated in Table 2 and Fig. 6. By optimizing the power load parameters, it can be found that smaller voltage increments are favorable to form dense and uniform coatings. Additionally, voltage increments should be small at start and gradually increase, which is conducive to efficiency improvement and energy consumption reduction.

Through a large number of tests, it is found that MAO technique has the following advantages compared to other surface modification techniques. First of all, the coating is an oxide formed by instantaneous plasma oxidation on the surface of magnesium alloy, and the substrate and solute components react by high-temperature melting and solidification. The coating grows from the surface of the base magnesium alloy inwardly and outwardly in two directions, so the resulting coating is metallurgically bonded to the substrate with high bonding strength, and thus the corrosion resistance and abrasion resistance of the substrate are enhanced<sup>[47]</sup>. Secondly, the outer surface of the formed coating is rough and

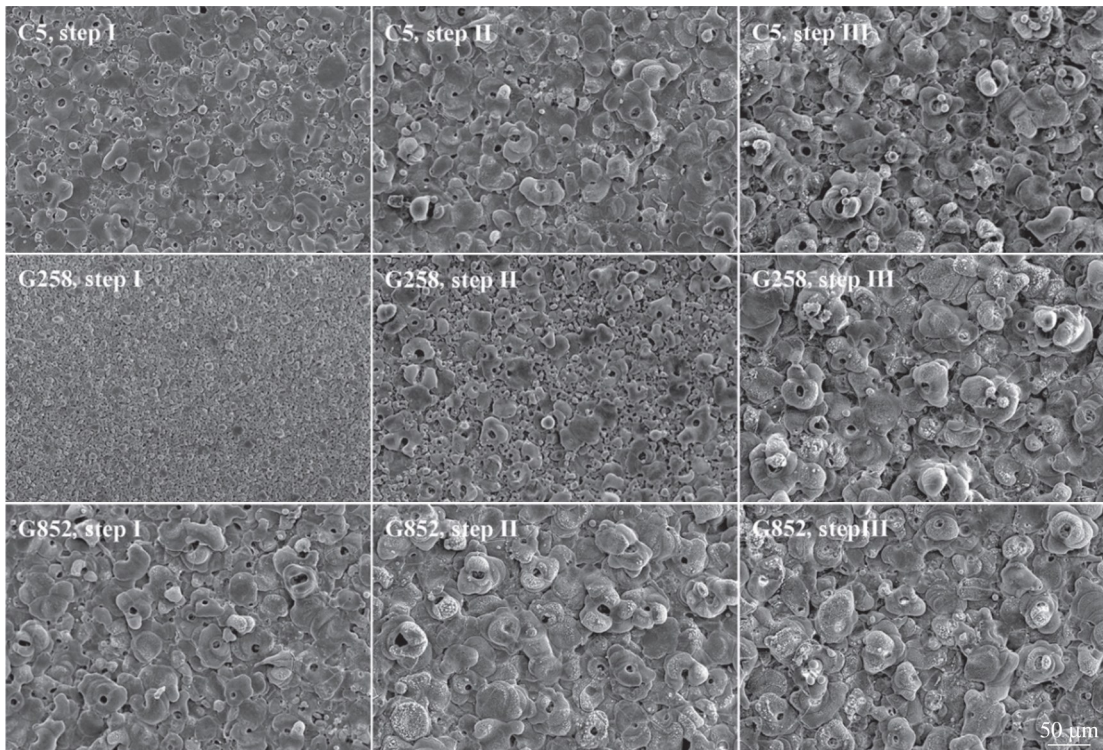


Fig.5 Scanning electron microscope (SEM) images of C5, G258 and G852 coatings at different steps<sup>[45]</sup>

Table 2 MAO treatment of AZ91D magnesium alloy by different power supply methods<sup>[46]</sup>

| Method                       | Advantage   | Disadvantage   |
|------------------------------|---|--|
| Direct current (DC)          | -   | It is easy to generate large discharge phenomenon and there are a mass of ablatives on the surface of MAO coatings |
| Bipolar current (BC)         | Suppressing large discharge phenomena                                       | Uneven coating and micro-cracks  |
| Discharge loop current (DLC) | Surface morphology of the coating is smoother, crack-free, and grows faster | -  |

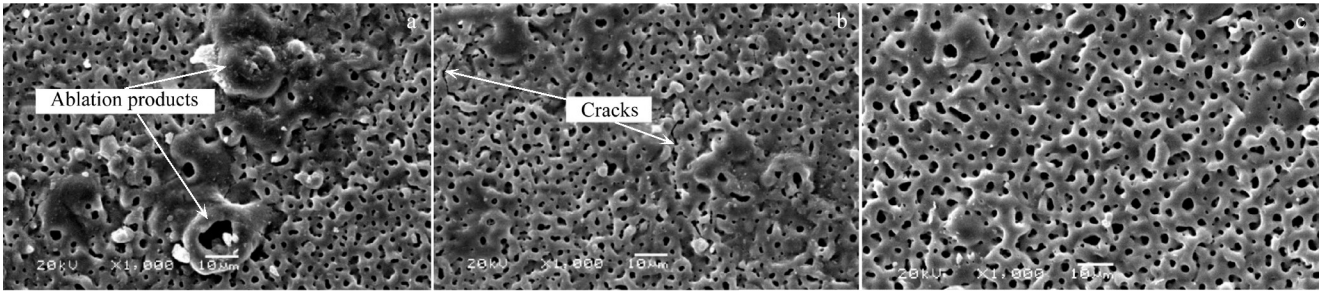


Fig.6 Surface morphologies of MAO AZ91D magnesium alloy under different power supply modes: (a) DC, (b) BC, and (c) DLC<sup>[46]</sup>

porous, which facilitates the attachment of osteoblasts. Finally, the method has a short processing flow and can regulate the phase composition of the coating, making it easy to obtain a uniform and highly thermally stable coating. The ceramic coatings generated by MAO have better corrosion and wear resistance than the coatings generated by anodizing. However, the MAO coating is not favorable for long-term corrosion resistance of the coating due to the presence of micropores and cracks on the surface. Moreover, it is prepared

by high voltage power supply with high energy consumption<sup>[47-48]</sup>. By preparing multistage composite coatings based on the existing MAO coatings for magnesium alloys, filling micropores and cracks while improving the biocompatibility of the coatings is an important research direction in the future.

1.1.3 Biodegradable polymer coating

Degradable organic polymer coatings can effectively enhance the corrosion resistance and biocompatibility of magnesium and its alloys, which can be obtained through

immersion or soaking processes. Currently utilized biodegradable polymer coatings mainly include polylactic acid and its copolymers, polydopamine, chitosan, collagen, etc. Moreover, polymer coatings exhibit special multifunctionality and can be applied in medical implants, as shown in Fig.7.

Poly-lactic acid (PLA), as a biodegradable polymer, possesses Young's modulus of approximately 3 GPa, ultimate tensile strength ranging from 50 MPa to 70 MPa, elongation-to-break of about 4%, and fracture toughness of approximately  $2.5 \text{ kJ/m}^2$ <sup>[49]</sup>. In the medical field, PLA finds widespread applications due to its non-toxicity, excellent biocompatibility and slow degradation rate. Sheng et al<sup>[50]</sup> discovered the potential of poly-L-lactic acid (PLLA) coatings in improving the corrosion resistance of the substrate material. Munoz et al<sup>[51]</sup> employed an immersion method to prepare PLA coatings on the surface of AZ31 magnesium alloy and studied their adhesion and degradation behavior. The results indicated that the maximum bonding strength between the PLA coating and AZ31 magnesium alloy was approximately 8.1 MPa, representing an enhancement of about 50% compared to that of PLA/PEO/AZ31 magnesium alloy. This enhancement is primarily attributed to water, which is one of

the factors influencing the bonding between metal and polymer. Electrochemical experiments demonstrated that PLA/PEO/AZ31 magnesium alloy exhibited the best corrosion resistance. In the experiments, PLA was rapidly deposited into the porous structure of the PEO coating, further enhancing the corrosion resistance of AZ31 magnesium alloy. Voicu et al<sup>[52]</sup> prepared PLA nanofiber coatings on the surface of AZ31 magnesium alloy using electrospinning technique. Electrochemical test results revealed that the PLA coating inhibited the evolution of hydrogen, thus improving the corrosion resistance of AZ31 magnesium alloy.

Recently, polydopamine (PDA) has been utilized as a multifunctional coating, and extensively applied in antibacterial coatings, wound dressings, tissue engineering and biomedical implants<sup>[53]</sup>. Inspired by mussels, PDA is a polymer composed of dopamine (DA)<sup>[54]</sup>, effectively inhibiting the migration of corrosive ions in solution. Therefore, this property of PDA is utilized to protect metals, metal oxides, polymers, ceramics, etc<sup>[55]</sup>. Qian et al<sup>[56]</sup> demonstrated that PDA coatings not only control the release of corrosion inhibitors but also act as chelating agents, protecting the substrate material from corrosion, as shown in Fig.8. Zhou et al<sup>[57]</sup> investigated the in-vitro and in-vivo degradation behavior of  $5\beta$ -TCP/Mg-3Zn scaffolds coated with a DA-gelatin complex. It was found that neat gelatin and PDA/gelatin organic coatings were formed on the surface of the scaffolds, and the degradation ratio of the alloy continuously decreases (from 119.734 mm/a to 85.002, 67.408, 32.419 mm/a in sequence). XRD analysis showed rapid degradation of the Mg-3Zn alloy, with a large amount of subcutaneous emphysema appearing at 1 week postoperatively, whereas the emphysema of the  $5\beta$ -TCP/Mg-3Zn coatings was small and disappeared at 4 weeks postoperatively. Carangelo et al<sup>[58]</sup> found that PDA, used as an intermediate layer, enhanced the adhesion between the metal substrate and the external organic coating and reduced the degradation ratio of the substrate. Jin et al<sup>[59]</sup> coupled ferulic acid (FA) with PDA/Mg-Zn-Y-Nd to prepare FA-PDA

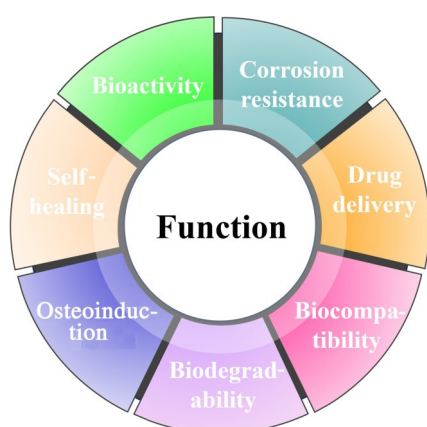


Fig.7 Various functions of polymer coatings

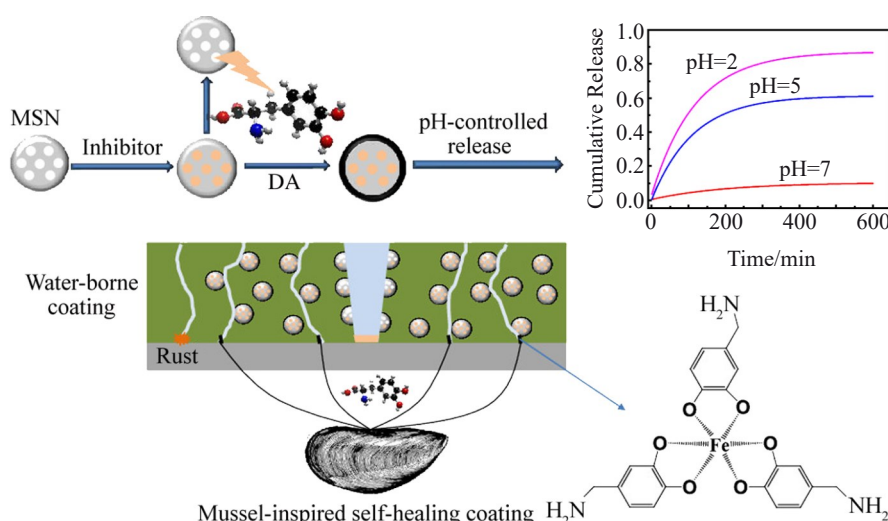


Fig.8 Self-healing mechanism of PDA coating<sup>[56]</sup>

coatings. The results showed that the FA-PDA coating could improve the corrosion resistance and blood compatibility of magnesium alloys. Inspired by mussel adhesive proteins, Meng et al.<sup>[60]</sup> fabricated zinc-loaded PDA (PDA/Zn<sup>2+</sup>) coatings on alkaline-heat treated magnesium alloy surfaces through the chelation between PDA and metal ions to enhance their corrosion resistance. On the one hand, as the concentration of Zn<sup>2+</sup> increased, the corrosion resistance of the coating was significantly improved. On the other hand, higher levels of Zn<sup>2+</sup> could react with hydroxyl groups to form stable and dense Zn(OH)<sub>2</sub> protective layers, further enhancing corrosion resistance. In recent years, self-healing coatings have been regarded as one of the most effective methods to protect metal materials from corrosion<sup>[61]</sup>. Self-healing coatings refer to those capable of repairing localized damage, such as corrosion or scratches, through external stimuli. Zhang et al.<sup>[62]</sup> employed a combination of electrodeposition and immersion methods to prepare nitrogen-doped carbon dots (N-CDS) and PDA composite coatings on magnesium alloy surfaces. The N-CDS coating, acting as a transition layer, was coupled with the magnesium alloy and PDA coating to protect the magnesium alloy and to enhance its corrosion resistance by forming a planar graphene structure. The results indicate that the corrosion resistance of the N-CDS coating is enhanced with

increasing the particle size. Additionally, the N-CDS/PDA composite coating surface exhibited remarkable self-healing properties (Fig. 9), which is attributed to the diffusion and extension of PDA to the surroundings.

Chitosan (CS) is a natural polysaccharide derived from partial deacetylation of chitin, possessing excellent biological properties such as biodegradability, biocompatibility and non-toxicity<sup>[63]</sup>. Consequently, CS has wide applications in the medical field<sup>[64]</sup>. CS is a new non-toxic biodegradable biomaterial, which is produced in a strongly alkaline environment and has a structure similar to that of human bone. When CS was used as a surface coating on magnesium alloy, the overall degradation ratio of magnesium alloy was reduced. Common preparation methods for CS coatings include immersion coating, spin coating, chemical conversion, electrodeposition, etc<sup>[65]</sup>. Hong et al.<sup>[66]</sup> immobilized a synthesized poly-(ethylene glycol)-heparin (PEG-Hep) polymer onto the surface of magnesium alloy modified with CS by electrostatic action and investigated the corrosion resistance and biocompatibility of the modified magnesium alloy. The results showed that the positive charge of CS could absorb the negatively charged heparin to immobilize PEG-Hep on the surface of CS-Mg, thus protecting the matrix alloy to improve corrosion resistance. Kozina et al.<sup>[67]</sup> utilized spin coating to fabricate CS

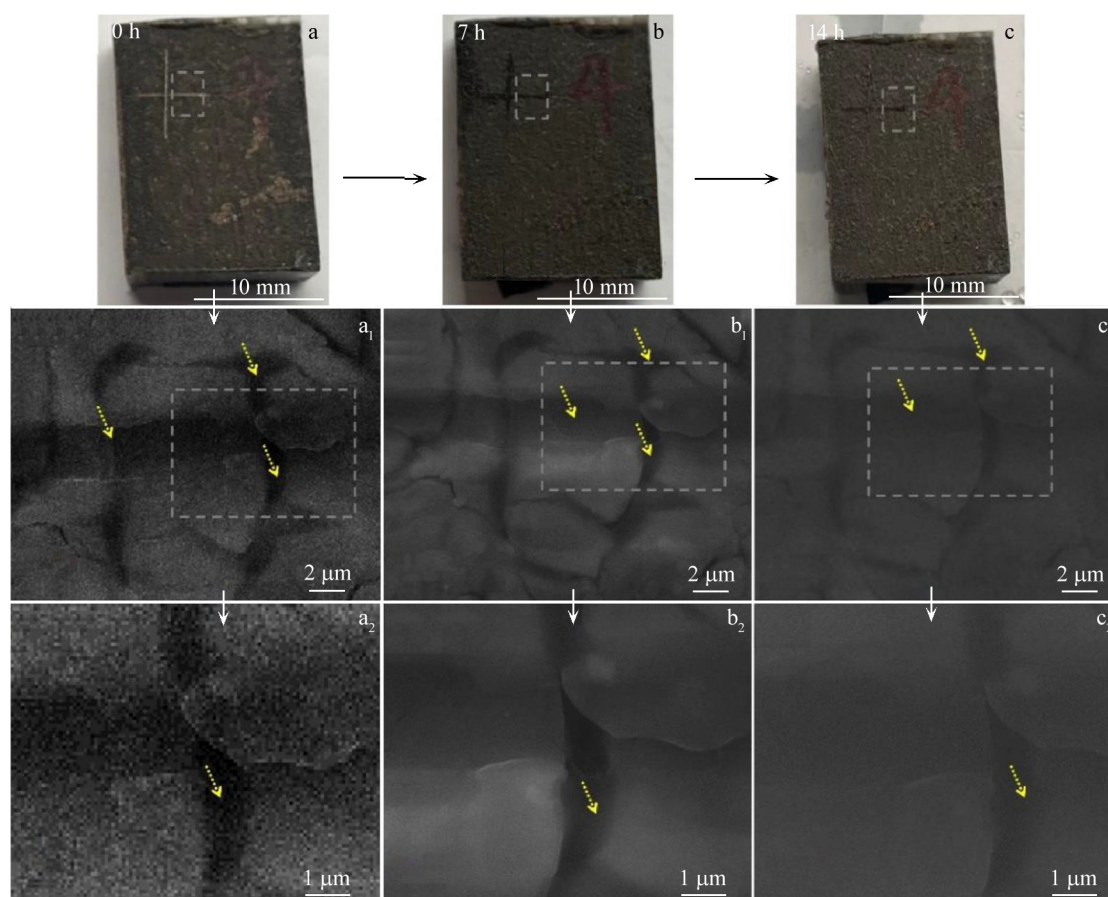


Fig.9 Surface morphologies of N-CDS-8/PDA composite coating after soaking in deionized water for different durations: (a, a<sub>1</sub>, a<sub>2</sub>) 0 h, (b, b<sub>1</sub>, b<sub>2</sub>) 7 h, and (c, c<sub>1</sub>, c<sub>2</sub>) 14 h (a<sub>1</sub>–c<sub>1</sub> are corresponding magnifications of the rectangular areas in a–c; a<sub>2</sub>–c<sub>2</sub> are corresponding magnifications of the rectangular areas in a<sub>1</sub>–c<sub>1</sub>)<sup>[62]</sup>

coatings on Mg20Zn magnesium alloy surfaces, and quantitatively analyzed the corrosion behavior of different coating structures (CS/WG and Ca-P/CS/WG) in Hank's solution. The results indicate that under the condition of single-layer coatings (Ca-P or CS/WG coatings), corrosion is more severe, possibly due to potential galvanic coupling between the coating and the metal. Galvanic coupling promotes corrosion, thereby reducing the corrosion resistance of the metal material. It is noteworthy that the corrosion rate of PDA/Mg20Zn magnesium alloy is 1.2 mm/a, while that of Mg20Zn magnesium alloy is 3.2 mm/a. CS is reported to degrade easily in biological media; thus, preparing CS composite coatings is beneficial for enhancing the long-term stability of the coatings in biological environments. Kalaiyarasan et al<sup>[68]</sup> aimed to further enhance the corrosion resistance of AZ31 magnesium alloy by preparing a CSSiO<sub>2</sub> composite coating on surface. The results indicate that the Mg(II)CHI complex formed on the intermetallic compound  $\beta$ -phase hinders ion movement, reduces the deposition rate on the metal surface, and consequently impedes cathodic reactions. CH-1, CH-2, CH-3 and CH-4 represent coatings prepared with different immersion durations. Among them, the CH-3 coating exhibited a uniform surface distribution (as shown in Fig. 10) and demonstrated excellent corrosion resistance. Witecka et al<sup>[69]</sup> investigated the corrosion resistance of magnesium alloys coated with CS and bioactive glass (BG) in Dulbecco's modified eagle medium (DMEM). The results indicate that BG particles can be uniformly embedded within the CS matrix. The composite coating is the most uniform when deposited at a voltage of 50 V for 60 s. After DMEM pre-treatment, the polarization resistance  $R_p$  of WE43 magnesium alloy significantly increases, suggesting an increased thickness of the surface coating and a notable enhancement in the corrosion resistance of the magnesium alloy. Bakhsheshi-Rad et al<sup>[70]</sup> investigated the corrosion resistance of PCL/CS/ZnO composite coatings on magnesium alloy surfaces. The results showed that the PCL/CS coating has a porous structure with thickness of approximately 40–50  $\mu\text{m}$ , which improves the corrosion resistance of the magnesium alloy by preventing corrosive ions from

contacting the substrate. CS coating acts as a corrosion-resistant layer, potentially reducing hydrogen gas release from medical implants in corrosive environments and thereby enhancing their corrosion resistance.

The good mechanical properties of magnesium alloys can make up the low strength of polymers, while polymer coatings can improve the corrosion resistance and biocompatibility of magnesium alloys. In addition, polymer coatings also function as drug-carrying and control platforms. When polymers are employed as coatings on magnesium alloy surfaces, they effectively mitigate direct contact between the magnesium alloy surface and corrosive media, thereby inhibiting hydrogen evolution. Simultaneously, polymer molecules possess a versatile chemical structure, allowing for the modulation of various performance attributes through alterations in monomeric composition or polymerization methods. This tunability makes the modification of polymer coatings relatively straightforward. Additionally, since polymer coatings are insulators, they do not undergo galvanic corrosion with the substrate material<sup>[71]</sup>. Hence, polymer coatings have certain advantages in improving the corrosion resistance of magnesium alloys. The degradation rate of polymer coatings is low, and the degradation products can be metabolized and eliminated from the human body<sup>[72]</sup>. However, the polymer coating is physically bonded to the substrate and there is a clear interface, which is prone to peeling off in the in-vivo environment.

#### 1.1.4 Ion implantation coating

Ion implantation technique was firstly applied to magnesium alloy surface treatment in 1984. It is the process of ionizing the prepared elemental atoms into ions and sputtering high-energy ions at high speed under the action of vacuum and high-voltage electric field onto the surface of the alloy, in order to adjust the surface composition and achieve the structure modification, ultimately forming a highly stacked and dense metal injection layer on the upper surface of the alloy<sup>[73–75]</sup>.

Ion implantation technique has the following advantages: (1) good bonding between the substrate and the coating can be achieved; (2) the problem of thermodynamic solubility

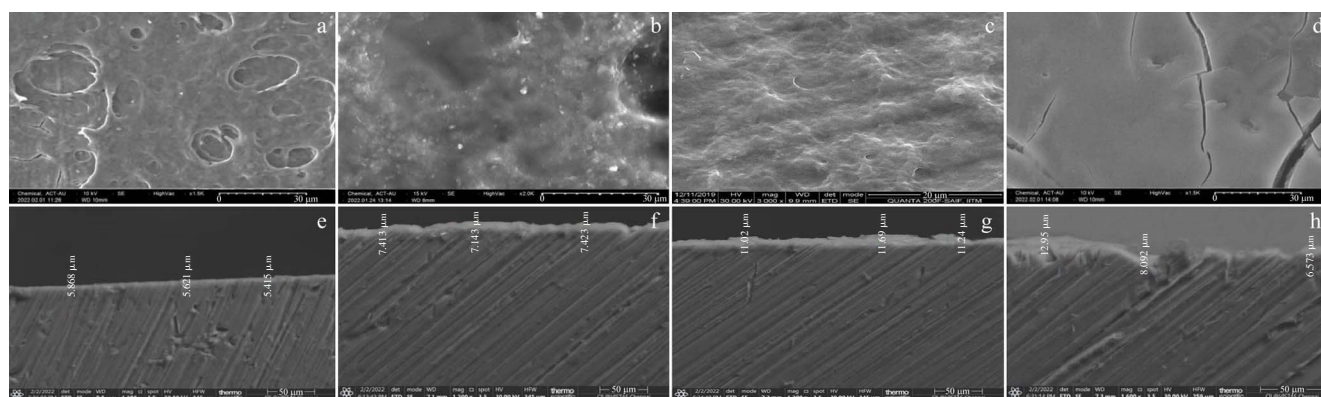


Fig.10 Surface (a–d) and cross-sectional (e–h) SEM images of CS conversion coatings on AZ31 magnesium alloy: (a, e) CH-1, (b, f) CH-2, (c, g) CH-3, and (d, h) CH-4<sup>[68]</sup>

between different metals is overcome; (3) the quality and quantity of the injected elements can be precisely measured and controlled to ensure that the injected elements can be uniformly distributed on the metal surface<sup>[76]</sup>. Although it is theoretically possible to inject any ions, the depth of injection is limited, which is generally between a few nanometers and a few hundred nanometers. Recently, metal ions such as Fe, Ce, Zn, Zr and Sr have been mainly studied, as well as non-metal ions such as C, O and N<sup>[77–79]</sup>.

Wang et al<sup>[80]</sup> injected Nd ions on the surface of Mg-Gd-Zn-Zr alloy and found that a mixed coating consisting of Nd<sub>2</sub>O<sub>3</sub>, Gd<sub>2</sub>O<sub>3</sub> and metallic Nd was produced on the alloy surface, as shown in Fig. 11a. The Nd<sub>2</sub>O<sub>3</sub> and Gd<sub>2</sub>O<sub>3</sub> were relatively stable in aqueous solution, which prevented further corrosion of the substrate material by Cl<sup>-</sup>, as shown in Fig. 11b. Fig. 11c–11f show the surface and cross-sectional morphologies of the corrosion product layer on the alloy surface before and after ion implantation. It is noteworthy that the thickness of the corrosion product layer decreases after ion implantation and the corrosion is more uniform.

Cheon et al<sup>[81]</sup> injected Ta ions into polyetherimide (PEI) coatings on the surface of WE43 magnesium alloy to obtain structurally uniform and corrosion-resistant Ta/PEI coatings. To assess the actual corrosion behavior of each stent, bare stents, PEI-coated stents and Ta/PEI-coated stents were placed separately inside silicone tubes with a diameter expansion rate of 171.4%. Accelerated corrosion was induced by artificial plasma solution flowing at a rate of 0–45 mL/min to simulate blood flow within human coronary arteries. Changes in stent shape and remaining volume were monitored via CT at fixed intervals. Bare stents exhibited severe corrosion, leading to fracture, with the remaining volume decreasing from 100% to

3% within 3 d. Stents coated with PEI and Ta/PEI maintained relatively intact structures during the 10 d dynamic corrosion test, without sudden fractures. After 10 d, their remaining volumes were still around 40%, five times higher than that of the bare stents. Jin et al<sup>[82]</sup> injected Hf<sup>3+</sup> into the surface of WE43 magnesium alloy to form a coating composed of Hf<sup>3+</sup> and MgO (HWE43). The backscatter electron (BSE) images showed that after 1 d of immersion in SBF, the surface of HWE43 alloy showed less corrosion area and fewer surface cracks (Fig. 12). The polarization curves of WE43 and HWE43 magnesium alloys indicated that the corrosion current density of HWE43 ( $40.0 \pm 1.2 \mu\text{A} \cdot \text{cm}^{-2}$ ) is significantly lower than that of WE43 ( $625.7 \pm 45.5 \mu\text{A} \cdot \text{cm}^{-2}$ ), demonstrating a notable enhancement in corrosion resistance due to Hf<sup>3+</sup> incorporation into the WE43 magnesium alloy. Li et al<sup>[83]</sup> injected N<sup>+</sup> at a dose of  $1 \times 10^{15}$  ions/cm<sup>2</sup> onto the surface of AZ31 magnesium alloy to reduce its degradation ratio in SBF. The samples, both with and without ion implantation, were immersed in Hank's solution for 3, 7, 15 and 30 d. As the immersion time was prolonged, numerous cracks and corrosion pits appeared on the surface of the non-implanted samples. As observed from Fig. 13, the corrosion resistance of the ion-implanted samples was significantly superior to that of the non-implanted ones. As a rare earth element with limited solubility, Nd contributes to corrosion resistance improvement. Therefore, adding a small amount of Nd can refine the microstructure of magnesium alloys, enhancing their mechanical properties and corrosion resistance<sup>[84]</sup>. It has also been reported that intermetallic compounds and surface layers containing neodymium oxide can suppress galvanic effects, thereby improving the corrosion resistance of magnesium alloys<sup>[85]</sup>. Jin et al<sup>[86]</sup> injected a small amount of neodymium ions into the rare earth

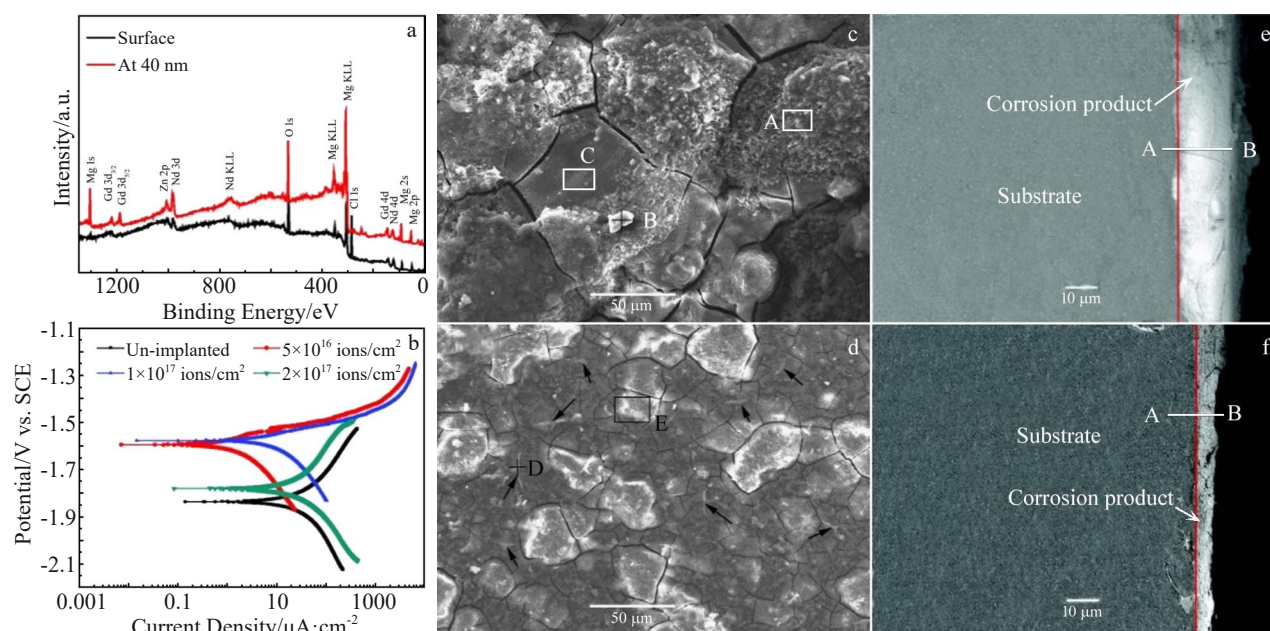


Fig. 11 XPS spectra of the alloy surface after ion injection at different depths (a); polarization curves of Mg-Gd-Zn-Zr alloy in SBF solution under different injection doses (b); morphologies of the surface (c–d) and cross-section (e–f) of the non-ion-injected (c, e) and ion-injected (d, f) alloys after corrosion resistance experiments<sup>[80]</sup>

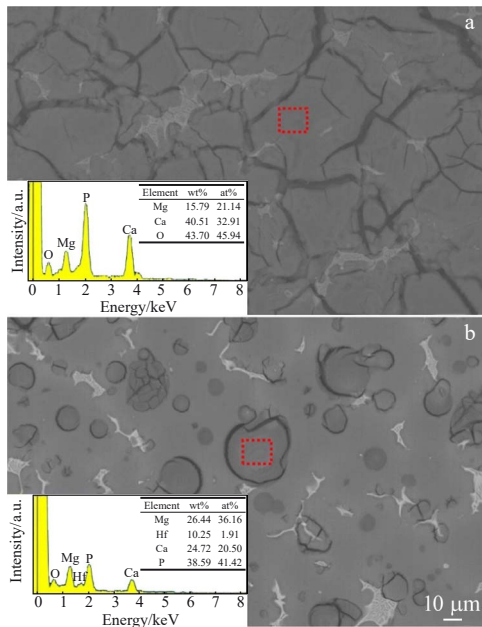


Fig.12 BSE images of surface and corresponding EDS results of WE43 (a) and HWE43 (b) after immersion in SBF for 1 d<sup>[82]</sup>

WE43 magnesium alloy to obtain a Nd/WE43 magnesium alloy with Nd<sup>3+</sup>-rich surface and significantly reduced corrosion ratio. After Nd ion implantation, the surface of the magnesium alloy contained a neodymium oxide layer with a thickness of only a few nanometers. This thin oxide layer impeded further reaction between the corrosive medium and the substrate, enhancing the corrosion resistance of the magnesium alloy.

In summary, although the ion implantation technique can improve the corrosion resistance of magnesium alloys, it requires strict test conditions (vacuum, high voltage and high current density) and carries certain risks (injection of metallic elements may lead to galvanic coupling corrosion). In addition, it should be considered that the injected ions may accumulate in the human body for a long period of time whether they are harmful to the human body. Currently, single ion injection has limitations in improving material properties.

The injection of multiple functional ions can not only improve the mechanical properties and biocompatibility of alloy materials, but also improve the antimicrobial ability. With the development of ion implantation technique, simultaneous injection of multiple ions to obtain multifunctional magnesium alloy materials will be a new trend.

## 1.2 Other surface modifications

In addition to the surface modifications mentioned above, several methods can also significantly improve the corrosion resistance of magnesium alloys, such as laser surface melting (LSM), magnetron sputtering and FSP. These techniques induce surface deformation of magnesium alloys through physical means such as mechanical processing, resulting in microstructural and performance differences from those of the substrate. Moreover, they often do not involve chemical reactions<sup>[26]</sup>.

The LSM technique eliminates concerns of the introduction of additional alloying elements and interface bonding issues, so it has attracted much attention in improving the mechanical properties and corrosion resistance of magnesium alloys<sup>[87]</sup>. Rakesh et al<sup>[88]</sup> modified the surface of Mg-1Zn-2Dy alloy using LSM technique. The results showed that a high degree of homogenization and micron-scale grain refinement could be observed in the melting zone due to rapid heating and cooling cycles. The in vitro degradation experiments revealed that the in vitro degradation ratio of the samples with an energy density of 45 J/mm<sup>2</sup> was increased by 72% compared to that of the alloy in the as-cast state. Fajardo et al<sup>[89]</sup> investigated the corrosion resistance of AZ31 magnesium alloy under different energy density conditions (14 and 17 J/cm<sup>2</sup>) using LSM technique. Electrochemical impedance spectroscopy analysis indicated that laser melting treatment significantly enhanced the polarization resistance of AZ31 magnesium alloy and its corrosion resistance under open circuit and anodic polarization conditions, resulting in a passive region of approximately 100 mV. Ding et al<sup>[90]</sup> employed laser melting treatment to modify the surface of the eutectic Mg67Zn28Ca5 alloy and investigated its effect on the corrosion resistance. The results revealed that a melted layer with a thickness of approximately 508  $\mu$ m was formed on the

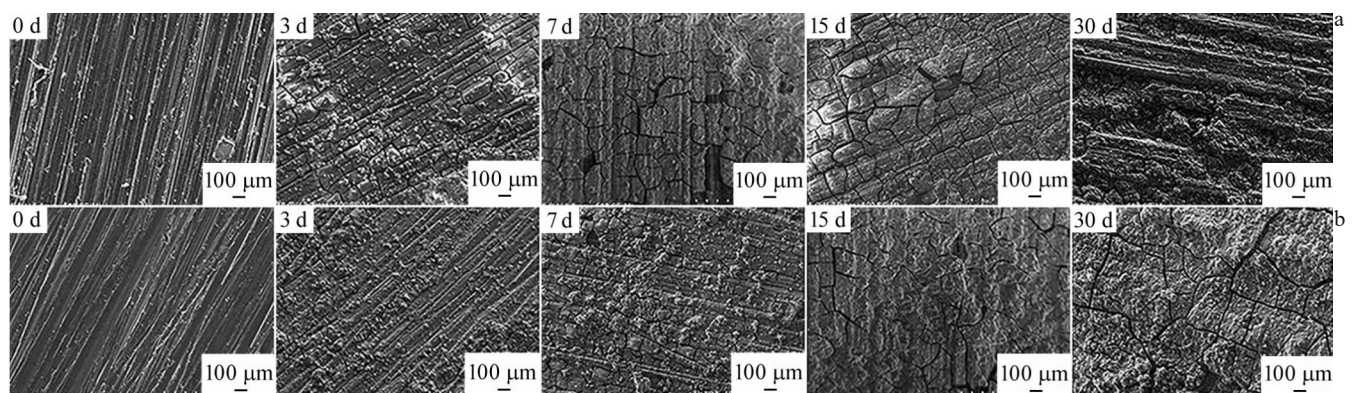


Fig.13 SEM images of corrosion morphology of the samples without ion implantation (a) and implanted at a dose of 10<sup>15</sup> ions/cm<sup>2</sup> (b) after immersion for different durations<sup>[83]</sup>

surface of the Mg67Zn28Ca5 alloy after laser melting treatment. Compared to the as-cast and solution-treated alloys, the corrosion potentials of the melted layer in SBF shifted positively by 76 and 60 mV, respectively, while the corrosion rates decreased by 82% and 78%, respectively. Laser melting treatment reduced galvanic corrosion, slowing down the corrosion of the  $\alpha$ -Mg matrix phase. Li et al<sup>[91]</sup> investigated the effect of LSM treatment on the corrosion resistance of MB26 and AZ80 magnesium alloys. The results revealed that after the melting treatment, the corrosion potentials of MB26 and AZ80 magnesium alloys increased by 122 and 60 mV, respectively, while the corrosion current densities decreased by 1.8 and 2.5 times, respectively. Moreover, after LSM treatment, the melted layer exhibited distinct microstructural differences from the substrate, and the variations in grain structure and phase morphology were identified as crucial factors influencing the corrosion resistance of magnesium alloys. Zhang et al<sup>[92]</sup> investigated the effect of the surface weave formed during LSM on the degradation behavior of magnesium alloys. The results indicated that LSM generated a uniformly distributed modified layer without the presence of pores or cracks. The melted zone was primarily composed of columnar  $\alpha$ -Mg phase grains, with an average thickness of 380  $\mu\text{m}$ . These findings collectively demonstrate the enhancement in mechanical properties and corrosion resistance of magnesium alloys. However, due to the fact that magnesium alloys are characterized by their active chemistry, high affinity for oxygen, low melting point (923 K) and high vapor pressure, their application and development by LSM technique have relatively lagged behind. In addition, the lack of mechanical pressure during LSM may reduce the solubility of certain elements during solidification, leading to discontinuous melting to form pores and irregular surfaces<sup>[93–94]</sup>.

Magnetron sputtering is a common physical vapor deposition method used to produce coatings consisting of various materials such as inorganic, organic and metallic compounds. It can also fabricate coatings with different structures, including single-layer and multi-layer. Coatings prepared by magnetron sputtering exhibit high density, excellent adhesion and a wide range of types, making them suitable for targeted protection solutions for magnesium alloys based on different application scenarios. Bitá et al<sup>[95]</sup> used magnetron sputtering to deposit highly crystalline hydroxyapatite (HA) and silica-rich glass coatings on the surface of a biodegradable Mg-0.8Ca alloy. The results indicated that both the HA and silica-rich glass coatings adhered well to the substrate with a dense morphology, uniformly filling surface defects and having thicknesses of 480 and 330 nm, respectively. Corrosion resistance testing in SBF revealed that the highly crystalline HA coating exhibited excellent corrosion resistance performance. Hou et al<sup>[96]</sup> successfully prepared an amorphous titanium dioxide coating with a thickness of about 400 nm on the surface of a magnesium-zinc alloy by magnetron sputtering. The results indicated that the coating surface was smooth and dense, with a distinct boundary between the substrate and the coating.

During the sputtering process, electrons collide with Ar atoms as they travel towards the substrate, causing ionization and the generation of  $\text{Ar}^+$  and new electrons. These new electrons move towards the substrate, while  $\text{Ar}^+$  is accelerated towards the cathode titanium dioxide ( $\text{TiO}_2$ ) target. High-energy bombardment of the target surface results in the ejection of neutral target molecules, i. e. titanium dioxide, which are progressively deposited onto the substrate, ultimately forming a nano-sized particle coating. Immersion tests and electrochemical experiments revealed severe corrosion and substantial deposition of corrosion by-products on the surface of the magnesium-zinc alloy samples lacking coatings. In contrast, the coated samples exhibited smoother surfaces with smaller and discontinuous corrosion by-products. Furthermore, samples coated with titanium dioxide demonstrated reduced corrosion current density of 49  $\mu\text{A}/\text{cm}^2$ , showcasing excellent corrosion resistance. Gao et al<sup>[97]</sup> utilized DC magnetron sputtering to deposit nanostructured Al coatings on the surface of AZ31 magnesium alloy, and investigated the influence of sputtering power on the corrosion resistance of the Al coatings. Compared to low-power sputtering, the Al coatings deposited at high power exhibited the best corrosion resistance. At excessively high sputtering power (150 W), although microcracks appeared on the coating surface, the coating thickness was greater, resulting in smaller and shallower microcracks on the coating surface that did not penetrate the entire coating. When the corrosive medium was accumulated at the microcracks, it effectively impeded the progression of the reaction, thereby significantly slowing down the corrosion rate. To enhance the corrosion resistance of AZ31 magnesium alloy, Ding et al<sup>[98]</sup> employed magnetron sputtering to deposit  $\text{Nb}_2\text{O}_5/\text{Nb}_2\text{O}_5\text{-Mg/Mg}$  multilayer coatings (named as M- $\text{Nb}_2\text{O}_5$ ) on its surface. Results revealed that the structure of the M- $\text{Nb}_2\text{O}_5$  multi-layer coatings was dense and uniform. In contrast, the single-layer  $\text{Nb}_2\text{O}_5$  coatings exhibited noticeable cracks (Fig. 14) and poorer adhesion due to significant internal stress and interfacial stress between the relatively thick single-layer ceramic coating and the metal substrate. Compared to the single-layer coatings, the adhesion of the multi-layer coatings increased by approximately 10.6 times, the corrosion current density decreased by an order of magnitude, and the anodic polarization curve notably shifted towards regions of lower current density. This also indicates a deceleration in the degradation rate of the magnesium alloy. In recent years, it has been found that the corrosion resistance of magnesium alloy surfaces can be effectively improved by magnetron sputtering technique combined with other auxiliary processes, and this method has become a hot spot of research<sup>[99]</sup>.

FSP technique, derived from friction stir welding, was initially proposed by Mishra et al and successfully used to produce high-performance ultrafine-grained aluminum alloys<sup>[100]</sup>. FSP can induce intense plastic deformation without requiring additional heating. Consequently, it can alter the microstructure of magnesium alloys and, to some extent, enhance their corrosion resistance.

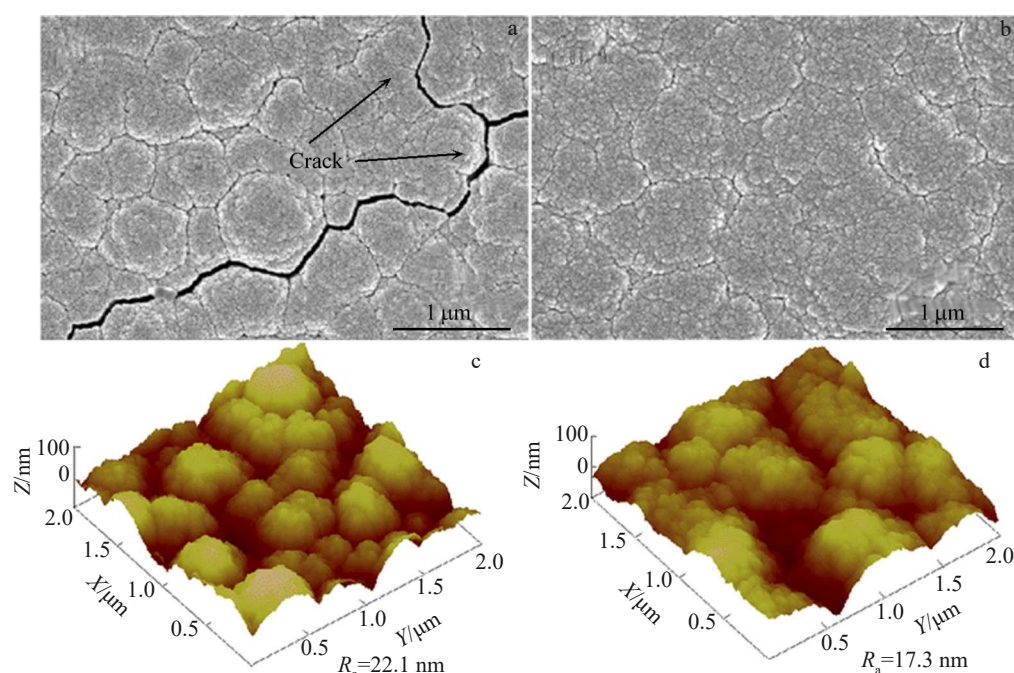


Fig.14 SEM (a–b) and three-dimensional atomic force microscope (c–d) images of coating samples: (a, c)  $\text{Nb}_2\text{O}_5$  and (b, d)  $\text{M-Nb}_2\text{O}_5$ <sup>[98]</sup>

Liu et al<sup>[101]</sup> used FSP to refine and to homogenize the surface organization of AZ91 magnesium alloy. At the same time, due to the polarization of the fine  $\beta$ -phase, a dense and continuous  $\beta$ -phase layer was formed on the surface of the magnesium alloy, which effectively improved the corrosion resistance of the base material. Vignesh et al<sup>[102]</sup> prepared surface composites of AZ91D magnesium alloy reinforced with nano-phase  $\text{SiO}_2$  using FSP. The results of corrosion tests showed that an adhesion layer of calcium hydroxyapatite and calcium-magnesium phosphate was formed in the SBF, which reduced the corrosion ratio of the composite. FSP machining of ZE41 magnesium alloy was conducted by Kiran et al<sup>[103]</sup>. The results showed that apatite in the SBF was more mineralized on the surface of ZE41 magnesium alloy after FSP, and compared with the untreated alloy, the post-FSP ZE41 Mg alloy had better corrosion resistance due to the deposition of more Ca/P mineral phases. Rokkala et al<sup>[104]</sup> utilized the FSP technique to process the surface of Mg-1Zn-2Dy (wt%) alloy. Due to the occurrence of dynamic recrystallization during the FSP process, the grain size in the stir zone decreased from 60  $\mu\text{m}$  to below 3  $\mu\text{m}$ . Electrochemical corrosion and mass loss tests were conducted in DMEM supplemented with 10% fetal bovine serum. The post-FSP magnesium alloy exhibited a lower degradation rate and uniform corrosion in the physiological solution, attributed to the generation of fine grains and a more uniform distribution of second-phase particles through FSP. Furthermore, after FSP, significant changes occurred at the grain boundaries, greatly enhancing passivation kinetics. The substantial increase in high-angle grain boundaries formed adhesive passive layers, leading to lower corrosion rates. Similar studies have also indicated that FSP can improve the corrosion resistance of magnesium alloys, attributed to grain refinement

and the generation of basal texture<sup>[105]</sup>. Liu et al<sup>[106]</sup> highlighted that FSP can enhance the corrosion resistance of magnesium alloys. This is attributed to the significant plastic deformation induced by FSP, which greatly refines the grain structure, leading to a change in the corrosion mode.

## 2 Summary and Prospect

Magnesium alloy has a broad application prospect in the field of medical implants because of its degradability, excellent biosafety and density close to that of natural human bone. However, the corrosion resistance of magnesium alloys is very poor, leading to too fast degradation in the human body, which seriously limits the clinical application of magnesium alloys. Recently, significant studies have been conducted on surface modification to solve the problem of fast degradation of magnesium alloys. For example, dense and insoluble coatings are prepared on magnesium alloy surfaces through chemical conversion methods, which effectively isolates the substrate from corrosive environments, thus protecting the substrate. Representative coatings include calcium phosphate coatings, fluorinated coatings, etc. Despite their high density, which is similar to that of MAO coatings, these coatings suffer from defects such as micropores and microcracks, significantly impacting the clinical application of medical magnesium alloys. In the future, composite coatings can be employed to fill these micro-defects while providing good adhesion for the inner layer and excellent biocompatibility for the outer layer, thus offering more comprehensive protection for magnesium alloys. Ideal surface-modified magnesium alloys need to possess good corrosion resistance, biocompatibility and drug-carrying properties. However, almost none of the surface-modified coatings on magnesium alloys can meet all these characteristics.

Furthermore, given that traditional coatings passively protect the substrate, damage to the coating integrity may lead to continuous degradation of the substrate in corrosive environments. Future research is poised to introduce an active corrosion protection mechanism, including the incorporation of corrosion inhibitors or the formation of stable corrosion product layers, endowing the coatings with self-healing properties, thereby further delaying the corrosion process.

Based on the current research status of surface modification for medical magnesium alloys, future research on surface modification of medical magnesium alloys may focus on the following aspects. (1) Due to the complex physiological environment of the human body, it is difficult for a single coating to simultaneously meet the multiple requirements for degradation ratio and biological properties of medical magnesium alloys. Composite coatings that can meet the requirements for comprehensive surface performance will be more popular. (2) In order to make medical magnesium alloys have better clinical application value, the composite coatings will be further studied in terms of bonding strength with magnesium alloy substrate, cohesive strength, degradation mechanism and biological properties. (3) Different service scenarios have different requirements for coating performance (e.g., thin-walled vascular scaffolds require coatings with pro-endothelialization and anti-thrombotic capabilities; bone repair and internal fixation implant materials require coatings with antimicrobial properties, bone induction and neo-osteoclastogenic capabilities). It is also very important to choose appropriate preparation process (low carbon, environmental friendly, energy efficient, low cost and conducive to industrialization on a large scale) that matches the comprehensive performance of excellent coatings.

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医用镁合金表面改性改善耐蚀性研究进展

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**摘 要:** 镁及镁合金具有优异的生物安全性、独特的生物可降解性和良好的载荷传递性等优点, 在医用植入领域应用前景广阔。良好的耐蚀性是镁及镁合金作为医用植入物重要的前提条件之一。然而, 镁合金耐蚀性差, 在生理环境中因过快腐蚀而迅速降解, 导致其尚未完成服役就失去了固定支撑作用, 严重限制了临床应用。对镁合金进行表面改性处理, 改善其表面耐蚀性和生物相容性, 已成为医用镁合金表面改性的研究热点。围绕改善医用镁合金表面耐蚀性研究进展, 介绍了医用镁合金的发展历程及特点, 并从微弧氧化和离子注入等表面改性技术的原理, 以及表面改性后镁合金表面微观结构和性能等方面进行综述。讨论了多种涂层的形成机制并分析其结构和性能, 阐述了涂层对镁合金降解速率的影响规律, 旨在明确医用镁合金表面改性在实施和应用过程中存在的关键问题及可能的解决途径, 并就医用镁合金表面改性的发展方向提出了建议。  
**关键词:** 镁合金; 表面改性; 降解速率; 耐腐蚀性

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