

Research Progress on Surface Treatments of Biodegradable Mg Alloys: A Review

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Cite This: *ACS Omega* 2020, 5, 941–947



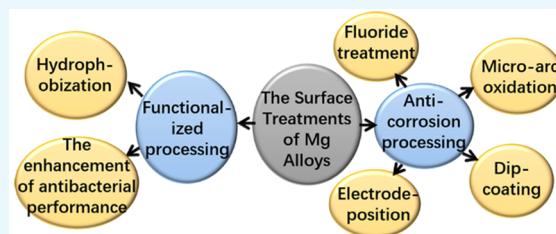
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ABSTRACT: Mg alloys have attracted extensive attention in the biomedical fields owing to their great biocompatibility, suitable mechanical properties, and biodegradability, etc. However, the fast degradation rate restricts the application of Mg alloys. Thus, the surface treatment of Mg alloys is considered as one of the most effective ways to enhance the corrosion resistance of Mg alloys. Nevertheless, simple processing to improve the corrosion resistance can no longer meet the growing biofunctional clinical requirements. Therefore, functionalized processing has become one of the key development directions for surface treatment in the future, such as functionalized Mg alloys with antibacterial property and hydrophobicity. There are few papers that review the functionalized processing of surface treatment. This review summarized and compared the major advances of the surface treatment (anticorrosion processing and functionalized processing) of Mg alloys. Then, some potential research suggestions are proposed, which may provide a reference for the development of Mg alloys.



1. INTRODUCTION

Nowadays, Mg alloys have attracted extensive attention especially in the biomedical fields due to their desirable biocompatibility, mechanical properties, and biodegradability.^{1,2} As a biomedical metal, Mg alloys have a density and elastic modulus similar to natural bone, which can effectively decrease the stress shielding effect. Moreover, secondary surgery can normally be avoided because of the biodegradability of Mg alloys used as implants such as a bone screw. However, Mg has active chemical properties and poor corrosion resistance in an aqueous environment, especially with a chloride ion. The over fast corrosion rate resulted in the serious degradation of mechanical properties of Mg alloys, while the bone heals, which may cause fractures again. At the same time, accumulated hydrogen which was the byproduct of Mg degradation may form an air cavity around implants, and this was disadvantageous for the healing of bone and tissue. Therefore, improving the corrosion resistance of Mg alloys is the primary goal.

Surface treatment, an effective way to enhance anticorrosion properties of Mg alloys, is to form a protective layer on Mg alloys, which can hinder the direct contact between Mg alloys and the physiological environment and thus control the over fast degradation of Mg alloys.³ Four typical methods of anticorrosion processing in surface treatments are fluoride treatment, microarc oxidation (MAO), dip-coating, and electrodeposition. It is a consensus that improving the corrosion resistance of Mg alloys is the fundamental purpose for surface treatment. However, with the application of Mg alloy in practice, new requirements for surface treatment are

consistently being put forward, like making the surface of Mg alloys functionalized. Hydrophobization is one of the functionalized processes in surface treatments.⁴ In addition, the coating with antibacterial property is given a lot of attention, which is meaningful for the healing of patients.⁵ The functionalized processing could be one of the key development directions of surface treatment in the future. However, there were few papers to review the functionalized processing of surface treatment. In this paper, the latest studies about the surface treatments (anticorrosion processing and functionalized processing) of Mg alloys were reviewed, and the development direction was briefly predicted.

2. ANTICORROSION PROCESSING

2.1. Fluoride Treatment. Fluoride treatment is a type of simple and effective chemical treatment, which can form a fluorine-containing coating on the surface of Mg alloys by reacting Mg alloys with hydrofluoric acid solution. The fluoride content in the coating was impacted by HF concentrations, reaction time, temperature, etc. Fluoride treatment can improve the corrosion resistance of Mg alloys, reduce their hemolysis rate, and improve their antiplatelet adhesion. However, it should be noted that the Mg alloy with

Received: October 14, 2019

Accepted: December 31, 2019

Published: January 9, 2020



Table 1. Parameters for Coating Prepared by Dip-Coating and the Thickness of the Coating

ref	substrate	coating material	solution concentration	solution temperature	dipping time (s)	dipping number	withdrawal speed	drying, curing, or cross-linking	coating thickness (μm)
14	AZ31B, AZ91D	hybrid silica sol	120 g/L (silica)				30 cm/min	curing for 30 min at 180 °C	
15	AZ31	poly(lactide coglycolide) (PLGA)	2% w/v				80 mm/min		<1.61
16	Mg-32 wt % Ca	polycaprolactone (PCL)	2.5 wt %		30			drying at room temperature (RT)	70–80
17	pure Mg	PCL	5% w/v		5	1 time 10 times 50 times	10 mm/ 60 s	drying at RT for 24 h	2.88 \pm 0.91 4.33 \pm 0.40 13.31 \pm 0.36
18	Mg-4Zn-0.2Ca alloy	PCL	1%, 2.5% and 5% (w/v)	30 °C	10		3 mm/s	drying in cold air for 5 min	
19	Mg3Gd	chitosan	0.01 mg/mL					drying for 30 min at 60 °C	2.07 \pm 0.50
20	AZ31	poly(L-lactic acid) (PLA)	8 wt %	RT			1 mm/s	drying at RT for at least 1 week	
21	Mg rods	polyurethane (PU)	20 wt %	RT	30		1000 $\mu\text{m/s}$	first, hang-drying at RT for 2 h; then, drying at 50 °C for 48 h	9.5 \pm 0.54
22	AZ91	gelatin (GEL)	10% (w/v)	50 °C				gelation for 1 h by chemical cross-linking	about 40
23	AZ60	PLA	10% (w/v)			3 times	220 $\mu\text{m/s}$	drying at RT	
24	AZ91D	PLA	4% (w/v)		30		20 mm/min	drying at RT	

fluorine-containing coating has some toxicity to the cells. The release of a high concentration of F^- in the coating was not conducive to the growth of cells.⁶

Furthermore, Li et al.⁷ found that the Mg alloy with fluorine-containing coating slowly degraded layer by layer. However, the result was different from the study of Barajas et al.,⁸ where SEM images of the cross-sectional of fluoride-treated AZ31 after 28 days of immersion displayed that the corrosion of MgF_2 coating was not uniform, and fluoride coating peeled off. Wang et al.⁹ also found that the cracks and localized corrosion were observed on the surface of Mg alloys treated with alkali-fluoride treatment after 20 days of immersion. The difference of three studies may be due to the presence of the second phase in Mg alloys, which results in the defect (irregularly distributed pores) of the fluoride coating and the local stress concentration on the surface of Mg alloys.

Besides enhancing the corrosion resistance of Mg alloys, Lin et al.¹⁰ reported that fluoride treatment can maintain the surface features of Mg alloy microstructure. The Mg alloy which was processed by ultrasonic etching in advance displayed a bowl-like nest structure, and this structure remained after fluoride treatment. Hence, fluoride treatment is a good choice for surface treatment of Mg alloys with special morphology, like the papillary-like pits or bowl-like nest structure.

2.2. Microarc Oxidation. Microarc oxidation is ordinarily used to form bioceramic coatings such as MgO coating. The Mg alloy matrix is oxidized under high voltage in the electrolyte, and then a protective ceramic layer is formed in situ on the surface of Mg alloys. The protective layer fabricated by MAO has a high bonding strength with the substrate. Due to the complex reaction process, the MAO coating result is affected by various factors, such as voltage, duty cycle, MAO time, current density, and so on. MAO coating can effectively improve the corrosion resistance of Mg alloys, but the coating contains a large number of pores and cracks.¹¹ The further improvement of corrosion resistance is

limited by the pores in the MAO coating. The solution penetrates into the Mg alloy matrix through the pores of the MAO coating, which will decrease the protective effect of the coating. Therefore, researchers generally post-treat the as-deposited MAO coating through other methods to solve this problem. The hydrothermal treatment⁶ and sol-gel method¹² are the common post-treatment methods. In addition to sealing the pores, there is a viewpoint that the semisealing pores formed by the post-treatment of MAO coating pores can be utilized as a medicine loader or to enhance the bonding strength of multiple coatings.

Microarc oxidation (MAO) treatment can enhance the corrosion resistance. However, for biomedical application, the biocompatibility of MAO coating is far from enough, which should be further improved. Some bioactive material such as calcium phosphates can be introduced into the MAO coating. The surface microstructure is also a considerable method to enhance the bioactivity. Meanwhile, as a ceramic coating, the surface of the MAO coating is normally magnetic and electrically insulated. Magnetic or electric simulation is proved to be effective for the osteogenesis.¹³ Therefore, the electric conductor MAO coating could be a profound field.

2.3. Dip-Coating. Dip-coating is one of the most frequently used sol-gel methods, which mainly includes several procedures of dipping, extraction, cross-linking or curing, and drying. It is simple and easy to operate, but there are many factors for the coating, like solution concentration and withdrawal speed. Table 1 listed common parameters in the process of dip-coating and the thickness of the coating.^{14–24} These factors have a significant impact on the thickness, pore size, uniformity, and corrosion resistance of the coating.

Dip-coating is widely used to prepare organic coating, which is considered to have superior biological properties.¹⁹ To date, the most commonly prepared organic coatings are PCL, PLGA, PLA, and chitosan, etc. Despite the advantages of outstanding organic coating, their disadvantages limit their further application. Organic coatings have poor mechanical

Table 2. Hydrophobization and the Properties of the Substrate after Hydrophobization^a

substrate	treatment	hydrophobic coating	contact angle (deg)		E_{corr} (V)	I_{corr} (A/cm ²)	ref
			before	after			
Mg-5Sn-1Zn	MAO (400 V, 5 min) + chemical modification	stearic acid (SA)	37.1	122.5	-1.53	0.07×10^{-6}	39
Mg-4Li-1Ca	MAO + electrodeposition	zinc stearate	54.4 ± 0.8	153.5 ± 0.5	-1.65	7.68×10^{-8}	40
AZ61	electrochemical machining + chemical modification	fluoroalkylsilane (FAS)	30.9	165.2	-1.4221	9.68×10^{-8}	41
AZ31B	etching + electroplating + chemical modification	SA	68.5	153	-0.39377		42
Al-Mg	electrochemical etching + low surface energy modification	FAS	3 ± 0.8	160.4 ± 2.2	-0.52		43
AZ31	MAO + corrosion inhibitor + hydrophobic wax film technologies	hydrophobic wax	68.71 ± 0.6	106.89 ± 1.1	-1.412	5.764×10^{-9}	44
AZ31	anodized treatment + chemical modification	SA	13.3	150.6			45
		sodium laurate		153.7			
		myristic acid		152			
		PFDTMS		145.5			
Mg-9Al-1Zn	linear laser ablation + annealing treatment		33 ± 1	$158.8 \pm 2^\circ$	-1.556(± 0.005)	$(6.7 \pm 1.2) \times 10^{-6}$	46
Mg-Li	electroplating + SA modification	super hydrophilic Ni-Cu-SiC		156.0	-1.209	1.43×10^{-3}	47
AZ31	laser ablation + chemical etching + chemical modification	SA		>150			48

^aCorrosion potential (E_{corr}), corrosion current density (I_{corr}), and 1H,1H,2H,2H-perfluorodecyltrimethoxysilane (PFDTMS); corrosion solution was NaCl.

strength and thermal instability and easily fall off from the substrate.¹⁷ Therefore, it is urgent to solve the problem of poor adhesion of organic coatings prepared by dip-coating on the substrate. Moreover, there is much room for further improvement of the coating quality by optimizing the experimental parameters and freeze-drying.

Besides organic coating, dip-coating can also be used to prepare inorganic coating such as silica sol-gel, Al₂O₃, ZrO₂, and TiO₂ coating.^{12,14} The inorganic coating can effectively enhance the corrosion resistance of Mg alloys, and it possessed strong adhesive strength. However, due to the sintering or drying process at high temperature, many pores and microcracks formed on the surface of Mg alloys during the preparation of the inorganic coating by dip-coating. Although the pretreatment or UV-assisted treatment can slightly reduce the microcracks, the defect of inorganic coating was still a problem which needs further study.²⁵ Even so, dip-coating was widely applied because it is simple, fast, and preferably secure.

2.4. Electrodeposition. The electrodeposition is an electrochemical treatment method and is divided into direct electrodeposition and pulse electrodeposition.²⁶ During the electrodeposition, Mg alloys are used as the cathode of the electrolytic cell, and then the elements in electrolytes will deposit on Mg alloys through oxidation and reduction. As a result, a protective coating is formed on the surface of Mg alloys. Electrodeposition is frequently used to prepare Ca-P coating.²⁷ Hydroxyapatite (HA) is the most common Ca-P coating because it is the main component of bone tissue. Based on HA, Dehghanian et al.²⁸ found that the silicon-substituted hydroxyapatite behaved much better. The coating prepared by electrolyte with the addition of 0.005 mol/L of SiO₃²⁻ increased corrosion resistance by 7 times and had better cell proliferation performance. The electrodeposited coatings are compact and thin, but they are easily doped with an

unexpected element and then form new phases. It is also a good way to prepare the new deposited coating on Mg alloys by changing the composition of the electrolyte.

In addition to the electrolyte, electrodeposition is influenced by many factors, such as the voltage, time, and duty cycle. For instance, the surface roughness of the coating decreased with the increase of voltage, but the coating was more difficult to form; meanwhile, the increase of time can increase the thickness and hydrophobicity of the coating and reduced the corrosion current density.²⁹ The thickness and surface roughness of the coating reduced with a decrease of duty cycle, while the hydrophobicity increased.²⁶ Besides, pH values of electrolyte, temperature, and the pretreatment of the Mg alloy also had an influence on the formation of electrodeposited coating.^{30,31}

Except for the above four methods, there are many other anticorrosion processing methods, such as electrospinning and magnetron sputtering. However, the effect of a single anticorrosion processing method to promote the properties of the Mg alloy is limited. Therefore, combining two or more anticorrosion processing methods together to form the composite coating on the surface of Mg alloys has become a trend.³²

3. FUNCTIONALIZED PROCESSING

3.1. Enhancement of Antibacterial Performance. In general, the occurrence of fractures is always accompanied with inflammation or infection. Therefore, it is desirable to provide Mg alloys with antibacterial property. To our best knowledge, bacteria can be killed by the high pH environment caused by degradation of Mg and will not adhere to areas where the corrosion of Mg alloys is active.^{33,34} However, the antibacterial ability of Mg alloys is dramatically restricted in vivo due to the buffering effect of human fluid and the control in the corrosion of Mg.

To reduce the risk of inflammation and infection, Mg alloy loading with antibacterial drug is a common choice as implants.⁵ However, the use of antibiotics can induce drug resistance. Hence, a combination of coating with the elements possessing antibacterial ability was studied. Cu and Ag are common additive elements in the coating owing to the inhibitory effect on the proteins in bacterial biofilm.^{35,36} Moreover, Zou et al.³⁷ prepared a Zn-loaded montmorillonite coating to improve the antibacterial properties of AZ31. Besides the coating with antibacterial ions, Pei et al.³⁸ prepared a carboxymethyl chitosan coating loaded with heparin to make the surface of AZ31B functionalized, which exhibited excellent antibacterial and anticoagulant properties. Wang et al.²¹ utilized the functionalized PU to improve the antibacterial performance of Mg alloys. Overall, the coating containing ions with antibacterial behavior (Cu^{2+} , Ag^+ , etc.) had great antibacterial performance. However, the development of the antibacterial materials such as the functionalized chitosan and PU is still necessary because those can avoid the potential toxic side effect of heavy metal ions and provide more options for the applications of Mg alloys under different environments.

3.2. Hydrophobization. The introduction of hydrophobic property can reduce the contact area between Mg alloys and water. The general way to introduce the hydrophobic property is to form a hydrophobic surface on Mg alloys. Table 2 listed hydrophobization and the properties of substrate after hydrophobization in some literature.^{39–48} It can be found that chemical modification is a common way to prepare the hydrophobic coating. SA and FAS are the common materials in hydrophobic coating. Except for organics, inorganic coating and the organic–inorganic composite coating were studied to improve the corrosion resistance of Mg alloys.

As is well-known, different materials had different static contact angles, and the level of static contact angle directly reflects the degree of hydrophobicity of the material. Cui et al.⁴⁰ formed a superhydrophobic zinc stearate coating on the MAO-coated Mg-4Li-1Ca alloy by electrodeposition. The results showed that the contact angle of zinc stearate coating reached 153.5° , which was super hydrophobic. Xu et al.⁴¹ prepared a fluoroalkyl-silane coating on the AZ61 alloy. The contact angle of coating increased from 30.9° to 165.2° . Meanwhile, I_{corr} of the Mg alloy reduced by 3 orders of magnitude, while E_{corr} only increased from -1.5847 to -1.4221 V. Interestingly, the superhydrophilic coatings exhibited great anticorrosion properties as well as superhydrophobic coatings.⁴⁷ Besides materials, the microstructure of Mg alloys can also impact its hydrophobicity.⁴⁸ Therefore, both the microstructure and coating materials should be taken into consideration in order to control the hydrophobicity of Mg alloys.

Functionalized processing is developing rapidly with great potential in the future. Except for the properties mentioned above, the coatings with other properties have also been studied. For instance, Wang et al.⁴⁹ prepared the coating with great blood biocompatibility and the property of endothelialization. Wang et al.⁵⁰ manufactured the coating with good mineralization ability on the Mg–Zn–Zr–Sr alloy. Therefore, it is no doubt that the employment of functionalized processing promotes the applications of Mg alloys in different fields.

4. CONCLUSION

Surface treatment is an effective method to improve the performance (appropriate degradation rate) of Mg alloys. It is desired to form a protective layer on the surface of Mg alloys so that the corrosion resistance of Mg alloys can be improved. To date, surface treatments not only improve the corrosion resistance of the Mg alloy but also can make Mg alloys functionalized. According to this, surface treatments of Mg alloys can be divided into two parts: anticorrosion processing and functionalized processing. The anticorrosion processing mainly includes fluoride treatment, MAO, dip-coating, and electrodeposition, and those methods can effectively improve the corrosion resistance of Mg alloys. New properties (such as antibacterial and hydrophobic properties) will be achieved for Mg alloys through the functionalized processing.

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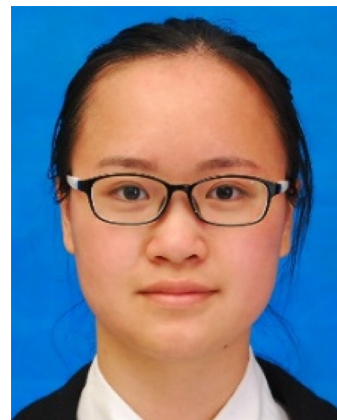
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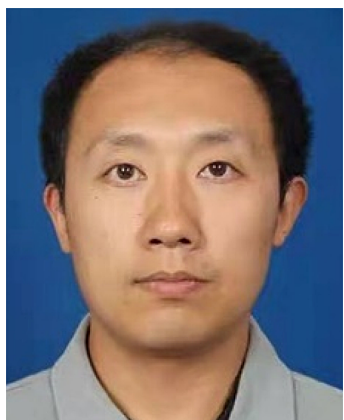
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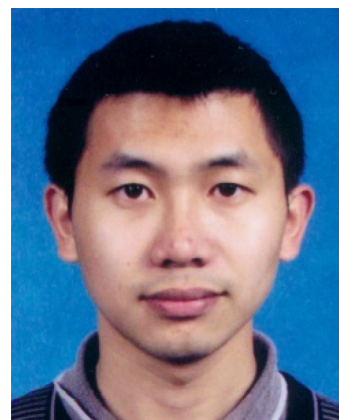
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■ ACKNOWLEDGMENTS

This work was supported by the project from the National Natural Science Foundation of China (No. 81500897), China Scholarship Council (No. 201408210385), and Foundation of the Education Department of Liaoning Province in China (No. QN2019035).

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