

Review

Advances in coatings on biodegradable magnesium alloys

Zheng-Zheng Yin^a, Wei-Chen Qi^b, Rong-Chang Zeng^{a,e,*}, Xiao-Bo Chen^c, Chang-Dong Gu^d,
Shao-Kang Guan^e, Yu-Feng Zheng^f

^aCorrosion Laboratory for Light Metals, College of Materials Science and Engineering, Shandong University of Science and Technology, Qingdao 266590, China

^bDepartment of Orthopaedics and Traumatology, Li KaShing Faculty of Medicine, The University of Hong Kong, Hong Kong 999077, China

^cSchool of Engineering, RMIT University, Carlton, VIC 3053, Australia

^dSchool of Materials Science and Engineering, State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027, China

^eSchool of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450002, China

^fState Key Laboratory for Turbulence and Complex Systems and Department of Materials Science and Engineering, College of Engineering, Peking University, Beijing 100871, China

Received 26 February 2019; received in revised form 14 September 2019; accepted 16 September 2019

Available online 14 February 2020

Abstract

The clinic applications of bioabsorbable magnesium (Mg) and its alloys have been significantly restricted owing to their poor corrosion resistance. Besides elemental alloying, surface modification and functionality is a major approach to increasing corrosion resistance for magnesium alloys. This article reviews the cutting-edge advances and progress of biodegradable surface coatings upon Mg alloys over the last decades, aims to build up a knowledge framework of surface modification on biodegradable Mg alloys. A considerable number of conversion, deposition, mechanical and functional coatings and their preparation methods are discussed. The emphasis has been placed on the composition of chemical conversion and deposited coatings to overcome the disadvantages of adhesion, corrosion resistance and biocompatibility of a single coating for biomedical materials. The issues have been addressed on the integration of the structural and functional factors of the composite coatings.

© 2020 Published by Elsevier B.V. on behalf of Chongqing University.

This is an open access article under the CC BY-NC-ND license. (<http://creativecommons.org/licenses/by-nc-nd/4.0/>)

Peer review under responsibility of Chongqing University

Keywords: Magnesium alloy; Biomaterial; Corrosion resistance; Coating; Biodegradability.

1. Introduction

Magnesium (Mg) and its alloys, exhibiting low density, high specific strength and superior hydrogen storage capacity and biocompatibility [1–6], are promising light-weight metals for transportation, 3C, aerospace, hydrogen storage and biomedical [7–12]. One of the bottle necks for the extensive applications for Mg alloys, however, is the low corrosion resistance [13–16] and rapid degradation rate [17–19]. Mg is susceptible to corrosion in chlorine-containing solutions, i.e.,

human body fluids [20–22]. Therefore, the faster degradation rate for Mg alloys causes following problems:

- (1) Excess hydrogen evolution occurs as cavities near the wound parts after implantation treatment [2]. Fortunately, the evolved hydrogen bubbles will disappear after several weeks, and are not a major concern in clinical cases [23,24].
- (2) The local alkalization around the surface of Mg-based implants, resulting from the degradation of Mg, leads to the high hemolysis of red blood cells [25]. Maximum pH value reaching up to an extremely alkaline microenvironments is harmful to living organisms [2].
- (3) With increasing $[Mg^{2+}]$, osmotic pressure of the human body fluid will be elevated. Therefore, maintaining the

* Corresponding author at: Corrosion Laboratory for Light Metals, College of Materials Science and Engineering, Shandong University of Science and Technology, Qingdao 266590, China.

E-mail address: rczeng@foxmail.com (R.-C. Zeng).

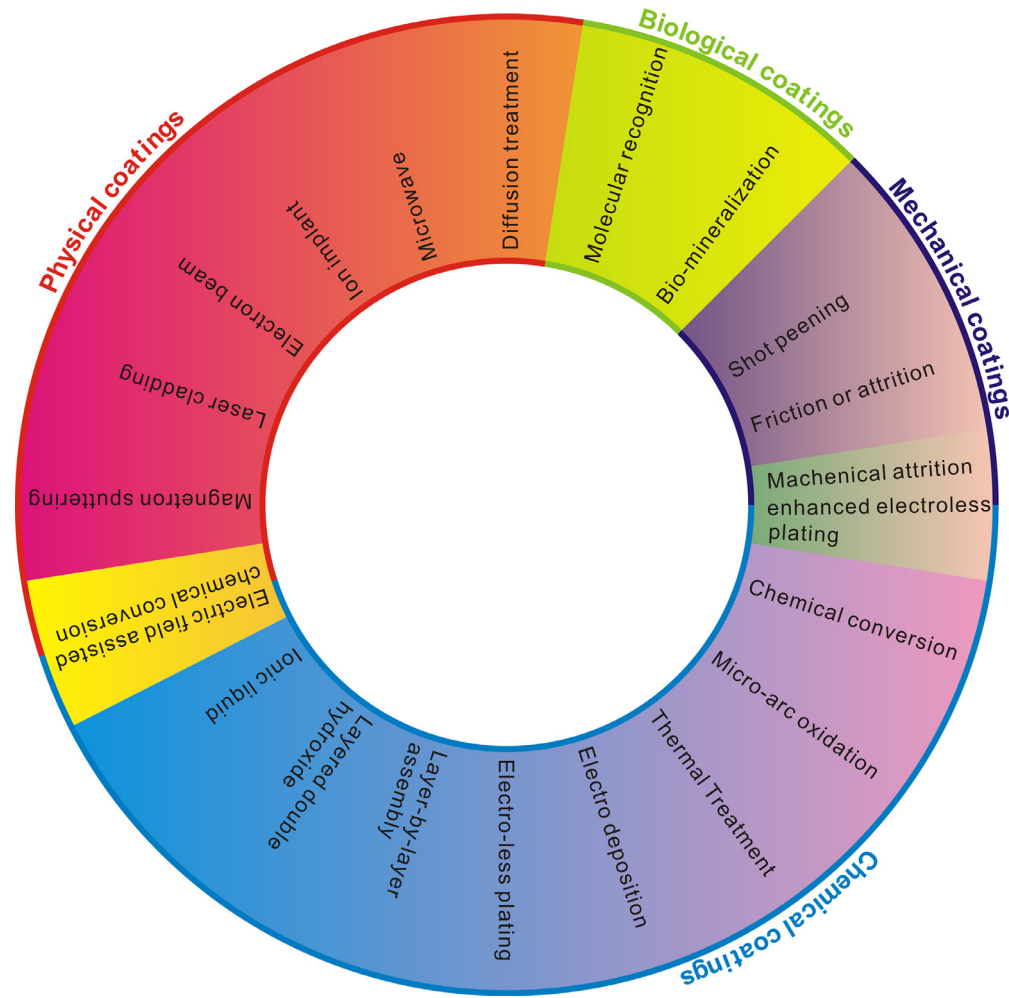


Fig. 1. Scheme of coatings for biodegradable Mg alloys.

local ionic concentration below a certain limit value is of great significance [25]. In general, extracts containing $[Mg^{2+}]$ over the range of 150–300 $\mu g/mL$ is associated with low cell viability ($< 80\%$) [26,27].

- (4) The structural imperfections of Mg alloys give rise to a rapid reduction in the mechanical strength of the implants with long-term *in vivo* degradation [28], which results in mechanical pre-failure.

The history on the development of degradable Mg alloys could trace back to 1878 by physician Edward C. Huse who used Mg wires as ligature to manage bleeding vessels [23]. Though subcutaneous gas bubbles were created by a high corrosion rate of Mg wires, it was rarely reported that the patients felt pain or suffered infections during the postoperative follow-ups [23]. Over the last two decades, Witte et al. [24,29] has made pioneering investigations on *in vivo* and *in vitro* degradation of Mg alloys. Later, alloying and post-processing for enhanced corrosion resistance draw much attentions [3,9,30,31]. Recently, a considerable number of studies have reported the progress of surface modification on

biomedical Mg alloys [10,32,33], regarding the improvement in corrosion resistance [16] and multi-functions of bioadaptation [34], bioactivity and biodegradability [35] along with biocompatibility [36]. This review aims to highlight the cutting-edge development and scientific issues of coatings on Mg alloys over the last decade from methodological, structural and functional perspectives.

2. Classification of coatings

Coatings can be prepared on Mg alloys by means of mechanical, physical, chemical and biological or biomimetic methods. The scheme and details of coatings are shown in Fig. 1.

- (1) Mechanical coatings can be made by shot peening [37] and friction or attrition [38,39].
- (2) Physical coatings are fabricated by magnetron sputtering [40], laser cladding [41], electron beam [42], and ion implant technologies [43].

- (3) Chemical coatings are obtained by chemical conversion, electro-deposition [44,45], sol-gel [46], electro-less plating [47], micro-arc oxidation (MAO) [48] or plasma electrolyte oxidation (PEO) [49], layer-by-layer assembly [50] and ionic liquid [51].
- (4) Biological methods involve bio-mineralization and molecular recognition.

In addition, surface coatings can be classified into two generic categories: chemical conversion and deposited coatings according to the coating formation mechanisms [18]. Based on their chemical nature and atomic structure, surface coatings for Mg alloys can be classified into metallic, ceramic and polymeric coatings.

- (1) Aluminum (Al) [52], titanium (Ti) [40], nickel (Ni) [53] and tantalum (Ta) [54,55] are the main components of metallic coatings. Noticeably, some of them are toxic elements and unsuitable for biomedical application from a biosafety perspective. Al is neurotoxic and leads to the pathogenesis of Alzheimer's disease due to its accumulation in nervous system [56]. Ni is an allergic element to skin. The release of Ni^{2+} ions is responsible for the cause of allergic contact dermatitis [57]. The major disadvantage of metallic coating is that severe galvanic corrosion will occur once the water molecules penetrate into the interface of metallic coating/the substrate due to the big difference in initial open circuit potentials (OCPs).
- (2) Ceramic and inorganic coatings are composed of oxides (e.g., TiO_2 [58], ZrO_2 [59,60], SiO_2 , CeO_2 [61] and Al_2O_3 [62]), phosphates (Ca-P salts) [44,63] and silicates [64], layered double hydroxide (LDH) [65,66] and montmorillonite [67].
- (3) Organic and polymeric coatings involve DNA [68], dopamine [69], tannic acid [70], PLA [71] or PLGA [72,73], chitosan [74,75], and so on. Moreover, there are a number of composite or hybrid coatings that are combinations of two or more distinct coatings on Mg alloys.

Surface coatings can be cathodic and anodic, according to the free open potential or OCP relative to their substrates. In most cases, the surface coatings on Mg alloys are cathodic coatings, i.e., metallic and MAO coatings. There are fewer coatings which are anodic for Mg alloys, for instance, pure Mg film on AZ91 alloy [76], LiC_6 coating on pure Mg [77] and chitosan/MAO coating on Mg–Li–Ca alloy [74]. These anodic coatings can be defined as self-degradation coating or self-sacrificing coatings [74,76], which can preferentially degrade to its substrate. As a result, the mechanical property and integrity of the alloy substrate can remain completely before the outer coating diminishes.

Furthermore, there are different kinds of coatings for biomedical Mg alloys on the basis of functions (Fig. 2). The examples include bio-functionalized coatings (i.e., drug-loading and anti-bacterial coatings) [78–80], super-

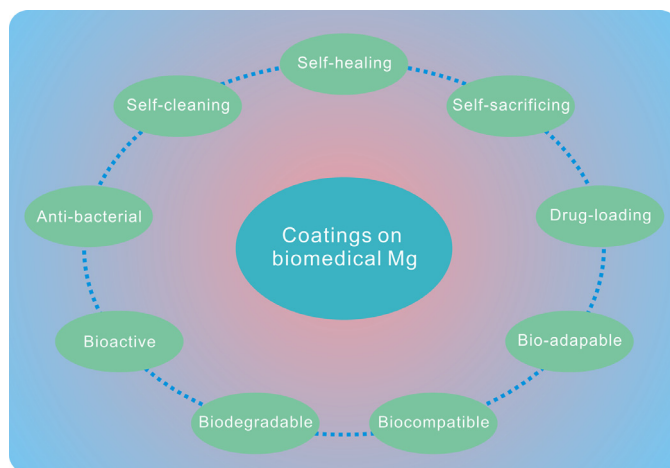


Fig. 2. Functions of coatings on Mg alloys.

hydrophobic coatings or self-cleaning coatings, self-healing or self-repairing coatings [81], self-sacrificing coatings. Of these, self-cleaning, self-healing coatings are categorized into smart coatings. Biologic coatings contain bioactive, biodegradable, biocompatible and bioadaptable coatings. So-called concept of bioadaptability emphasizes both the materials characteristics and biological aspects within a certain micro-environment and molecular mechanism [82].

Additionally, coating preparation techniques based on different energy sources can be further subdivided into electric energy (i.e., MAO, electrolytic deposition (ED) [83] and layer-by-layer (LBL) assembling) [84–86], chemical energy (i.e., chemical conversion and sol-gel) [87], and thermal, magnetic and mechanical energy (i.e., physical vapor deposition, friction, and peening) (Fig. 3).

Surface coatings on Mg alloys can be prepared in various acidic, alkaline and organic additives (i.e., EDTA) solutions. Examples include fluoride and $\text{Mg}(\text{OH})_2$ coatings [88,89] prepared in HF, NaOH and NaHCO_3 solutions as well as ionic liquid (IL) [90].

2.1. Conversion coatings

Conversion coatings are defined as in-situ coatings that are formed through chemical reactions between Mg substrate and coating solution. Conversion coatings arise in a complex interaction of metal dissolution and precipitation, usually carried out in aqueous solutions. The native metallic substrate surface is converted during chemical or electrochemical processes into a layer of oxide or other salts [91], so the adhesion between the substrate and the coatings is pretty good. That is the primary distinction between conversion coating and deposited coating. The morphology and properties of conversion coating are related to the substrate alloy. It is necessary to proceed a series of surface activation as pretreatment [92]. It should be noticed that the composition of conversion coating is rigidly restricted in insoluble Mg salt by thermodynamics and kinetics, which prefers to be an interlayer between a functional coating and its substrate rather than an outermost coating per se [93].

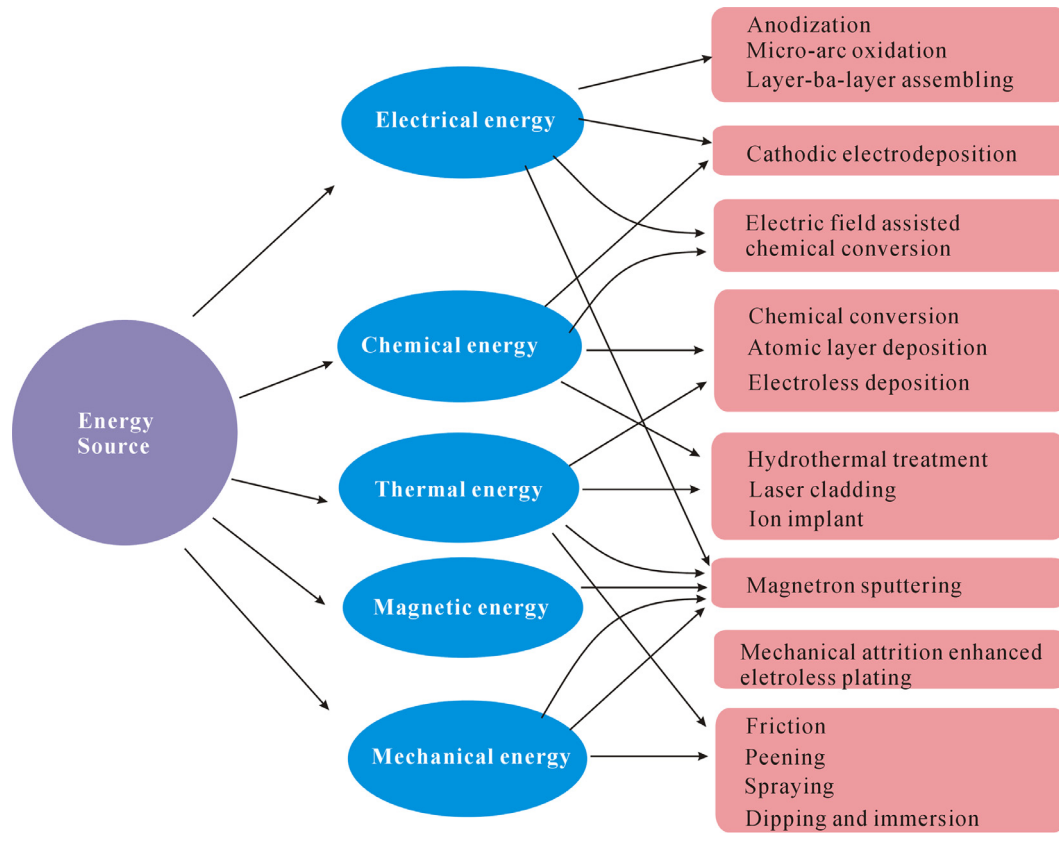


Fig. 3. Classifications and interconnections of surface coating methods on biomedical Mg alloys.

2.1.1. Chemical conversion coatings

Chemical conversion coatings are generated through interactions of chemical dissolution and precipitation, the coating bath usually includes fluoride, phosphate, carbonate and chromate [18]. Chemical conversion coatings, with the advantages of simplicity to be operated and low cost, can be widely used in biomedical fields. Although providing striking corrosion protection to Mg alloys, chromate-based coatings have been banned due to the concerns over environment and toxicity to human body. Therefore, the focus has been predominately concentrated on fluoride [94], phosphate conversion coatings [95,96] and MAO coating, etc. for biomedical applications. Usually, supersaturated solution is used to produce the sediments for preparing coatings in the case of changing pH of solution. MEDUSA is a necessary software to measure the forms of ions in solutions at different pH values. Fig. 4 shows (a) predominance area diagram for different Ca–P phases (i.e., dicalcium phosphate dihydrate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, DCPD), HA and $\text{Ca}(\text{OH})_2$) in presence of 10 mM PO_4^{3-} and (b) solubility of 17 mM Ca^{2+} and 10 mM PO_4^{3-} substances calculated using MEDUSA for preparing Ca–P coating

Fig. 5 lists several phosphate-based conversion coatings, which are usually the phosphates of Ca, Zn, Mg, Mn, Sr and Ce. Some are the Ca, Ce, Sr, K and F-doped phosphates. The detailed processing parameters can be seen in Table 1. Unfortunately, most conversion coatings exhibit riverbed-like

morphologies on their surfaces, which restricts the resistance of coatings. Thus, it's necessary to further modify the coating.

Phosphate conversion coating: Over recent years, phosphate conversion coatings (Table 1) such as zinc phosphate [97], calcium phosphate [98] have been reported as a feasible alternative to chromate coating as biomedical coating since they are insoluble in water and have high temperature resistance, chemical stability and excellent biocompatibility. The morphology and composition of those layers highly depends on the processing temperature, pH value and composition of the conversion baths [87]. Plenty of methods have been used for getting a better Mg-based biomedical devices. For instance, aiding by external magnetic field, it is readily to produce uniform and smooth phosphate conversion coating [99].

Calcium phosphate (Ca–P) coatings possess excellent biocompatibility, osteoconductivity, and non-toxicity. Hence, lots of studies have focused on Ca–P coatings for biomedical application in bone substitution and orthopedic. The Ca and P elements can form a hydroxyapatite (HA) layer, which is the main composition of nature bone. But the most difficult part is to adjust the phase and increase the content because the Ca–P coatings are often mainly amorphous and have little HA content. According to the thermodynamic calculations of chemical reactions [96], HA is only formed over a particular range of Ca/P ratio in neutral and sub-alkaline conditions. On one hand, the formation of Ca–P coating would be

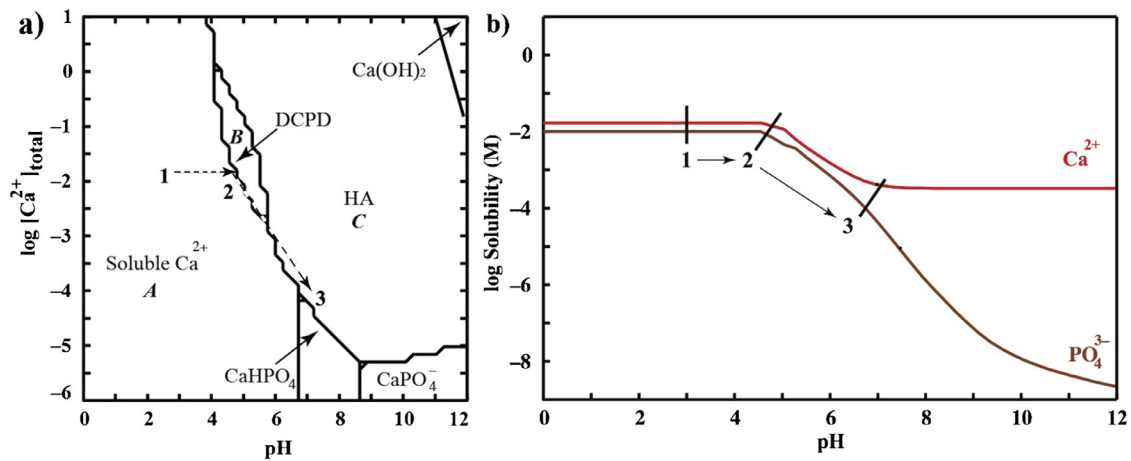


Fig. 4. (a) Predominance area diagram for different Ca-P phases in presence of 10 mM PO_4^{3-} and (b) solubility of 17 mM Ca^{2+} and 10 mM PO_4^{3-} substances calculated using MEDUSA [96].

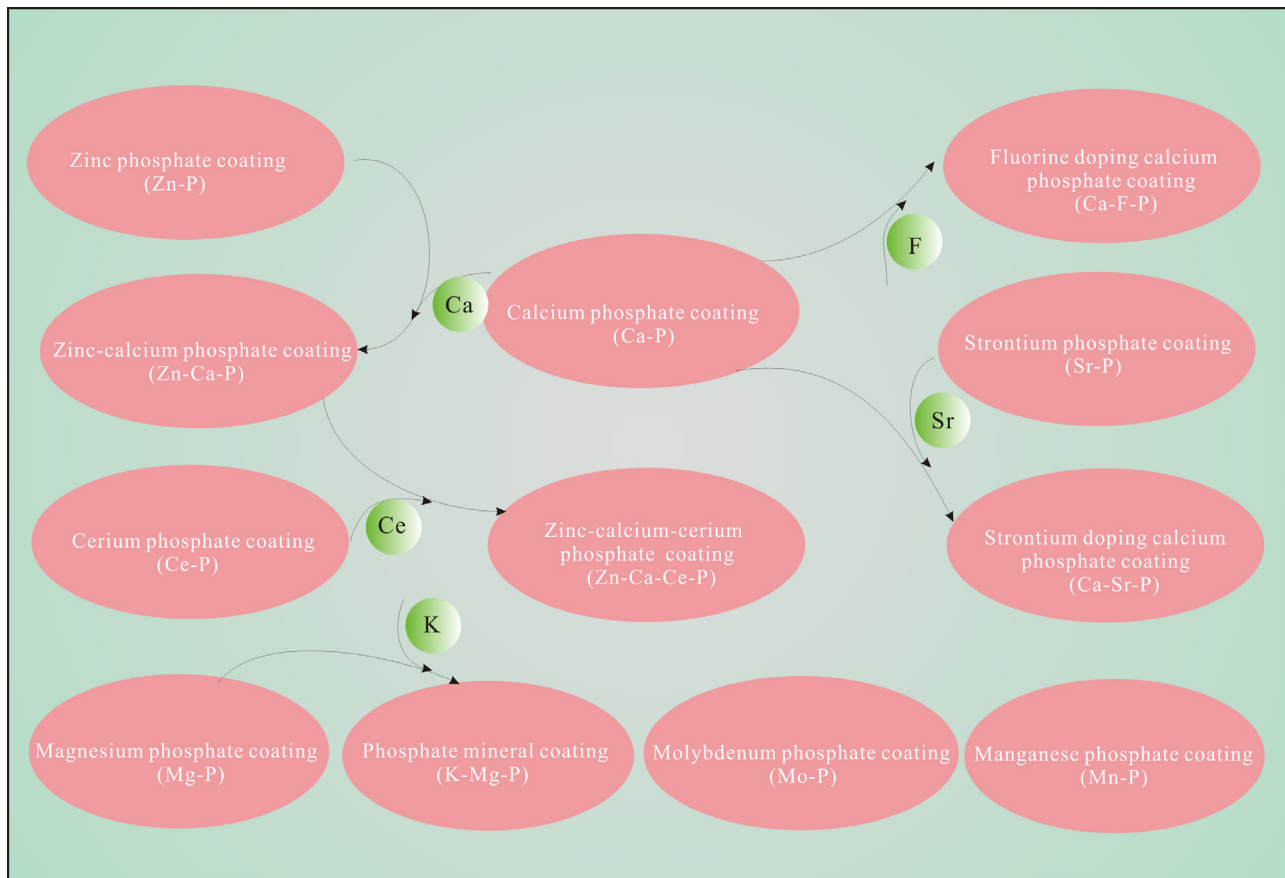


Fig. 5. Phosphate based conversion coatings on Mg alloys.

$Ca_3(PO_4)_2$ if the Ca^{2+} concentration is high (specify the limit pls) [100,101]; on the other hand, excessive PO_4^{3-} brings the tendency to precipitate $CaHPO_4 \cdot H_2O$. However, the existence of Mg^{2+} deteriorates the indeterminacy of Ca/P ratio, because Mg^{2+} ions would be more favorable to combine with PO_4^{3-} than Ca^{2+} and the products could be Mg_2PO_4OH [100], $Mg_3(PO_4)_2$ [102] or their mixture, depending on pH and Mg/P ratio of the baths [96].

Wang et al. [103] deposited a Ca-P coating, containing $Mg(H_2PO_4)_2$, $Ca(H_2PO_4)_2$, and $Ca_3(PO_4)_2$ and $Mg_3(PO_4)_2$ to mitigate the high degradation rate of Mg alloy AZ31B in simulated body fluid (SBF). The surface morphology, EDS result, and the cross section of the Ca-P coating were shown in Fig. 6. Regular petal-like crystals composed of small long block structure were formed on the surface with a thickness of approximately 20 μm . The corrosion current density of the

Table 1
Parameters of phosphate conversion coatings on Mg alloys [106].

Coatings	Composition	pH value	Temp., °C	Duration, min	Refs.
Mn-P	30 g/L $\text{Mn}(\text{NO}_3)_2$ 40 g/L NaH_2PO_4	2.0	60–85	30–40	[107]
Mn-P	0.1 M $\text{Mn}(\text{NO}_3)_2$ 0.06 M $\text{NH}_4\text{H}_2\text{PO}_4$	3.0 (HNO_3)	65	2	[95]
Ca-P	7 mL/L H_3PO_4 7.92 g/L $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ 1.55 g/L $\text{Zn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ 1.5 g/L NaNO_3 3.6 g/L NaNO_2	—	—	6	[108]
Ca-P	0.1 M $\text{Ca}(\text{NO}_3)_2$ 0.06 M $\text{NH}_4\text{H}_2\text{PO}_4$	3.0 (HNO_3)	65	2	[95]
Ca-P	25 g/L $\text{Ca}(\text{NO}_3)_2$ 25 g/L $\text{NH}_4\text{H}_2\text{PO}_4$	3.0	40	5	[109]
Ce-P	5 g/L $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ 1 g/L citric acid Na_3PO_4		Room temp.	120	[110]
Sr-P	0.1 M $\text{Sr}(\text{NO}_3)_2$ 0.06 M $\text{NH}_4\text{H}_2\text{PO}_4$	3.0 (HNO_3)	65	2	[95]
Mg-P	0.24 M H_3PO_4 0.1 M $\text{Mg}(\text{OH})_2$				[111]
Zn-P	0.24 M H_3PO_4 0.08 M ZnO 0.028 M NaF 0.042 M NaNO_2 0.021 M NaNO_3	3.2	45		[111]
Zn-P	10.0 g/L NaH_2PO_4 6.0 g/L $\text{Zn}(\text{NO}_3)_2$	2.5	50	20	[112]
Zn-Ca-P	10.0 g/L Na_2HPO_4 4.0 g/L NaNO_2 6.0 g/L $\text{Zn}(\text{NO}_3)_2$ 2.0 g/L NaF	2.5 (H_3PO_4)	50	10–20	[112]
Zn-Ca-Ce-P	10.0 g/L Na_2HPO_4 4.0 g/L NaNO_2 6.0 g/L $\text{Zn}(\text{NO}_3)_2$ 2.0 g/L NaF 1.0 g/L $\text{Ce}(\text{NO}_3)_3$	2.5 (H_3PO_4)	50	20	[113]

Ca-P coating decreased two orders of magnitude in comparison to its substrate. The hemolytic rate of AZ31B with and without coating increased at the early stage of immersion and reduced to an acceptable lower level with the immersion time in SBF. A slight decrease in the loading capacity of the Ca-P coated AZ31B occurred during the immersion and the loading capacity was reduced to 85% after 120 days' immersion in SBF. Even so, it's hard to tell which component plays the primary role in the corrosion resistance progress.

Liu et al. [104] produced a Ca-P coating on micro-arc oxidized (MAO) Mg to seal the porous structure by immersing in Ca-P solution. The results showed that the upper coating consists of HA and dicalcium phosphate dihydrate (DCPD). Flake-like and spherical-shaped morphologies were observed on the substrate surfaces at different temperatures which proved temperature had a great influence on the structure of coatings. The hydrogen evolution volume of MAO and soaked MAO was about 17.75 and 1.11 mL/cm² in 300 h of immersion in SBF. After immersing in SBF, bone-like apatite was formed on the coated sample. After Ca-P treatment coatings reached around 42 μm in thickness after 4 weeks of

immersion in SBF. The corrosion performance of the coating improved and exhibited self-adjustment.

Zeng et al. [97] designed a Ca-doped zinc phosphate (Zn-Ca-P) coating on Mg alloy AZ31, which displayed a flower-like morphology rather than the dry-riverbed-like morphology of the neat Zn-P coating. Further investigation [105] showed morphology of the Zn-Ca-P coating was related to the microstructure (grain size and secondary phases) and chemical composition of the substrates (i.e., extruded plate AZ31, pipe AZ31 and pipe AM30). The heterogeneous microstructure with relatively large secondary phase AlMn particles may trigger the formation of deep corrosion pits, which was ascribed to the micro-galvanic corrosion between the AlMn particles and surrounding α-Mg matrix. Hereby, the size, shape and orientation of the AlMn particles may have a critical impact on the quality of the Zn-Ca-P coating. It was likely that corrosion of the α-Mg matrix adjacent to an erect AlMnSi particle produced a deeper and occluded pit. On the contrary, a horizontal particle may generate an open, flat or shallow pit. As such, phosphate nucleus can readily deposit onto the side wall surface of the shallow pits rather than the deep pits.

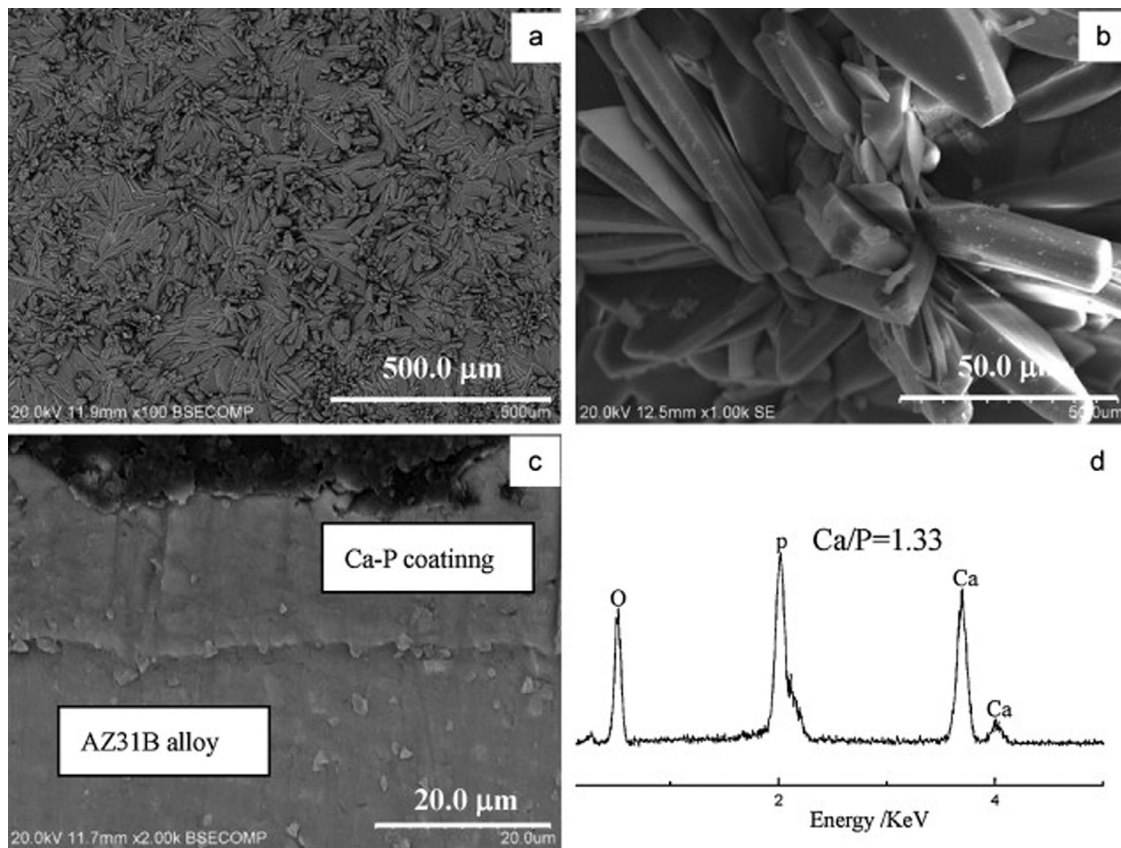


Fig. 6. Surface and cross section morphologies of Ca-P coated AZ31B Mg alloy sample (a) surface; (b) high magnification of (a); (c) cross section; (d) EDS analysis on surface [103].

As a result, a coarse grain coating formed on the surface of AM30.

Zhao et al. [99] synthesized a Mn-P conversion coating on Mg alloy AZ91D under magnetic field. Results indicated that the superposition of magnetic field can promote the generation of small hydrogen gas bubbles and accelerate the desorption from the surface during the phosphate conversion coating process. As a result, Mg^{2+} cations are dispersed comparatively uniformly, regardless of the microstructure of the alloy. A uniform and smooth phosphate conversion coating can be prepared by immersion in the treatment solution when magnetic field was imposed perpendicular to Mg alloy substrate in contrast to parallel to the specimen.

It is noteworthy that the biocompatibility of Mn-P, Ce-P and Zn-Ca-Ce-P coatings has not been demonstrated yet. However, Ca-P, Sr-P and Zn-Ca-P coatings possess excellent biocompatibility [95,108,114].

Fluoride conversion coating: Fluoride conversion coatings seem to be an effective way for the applications of Mg alloys as the biomaterials [115,116]. Conventionally, fluoride conversion coating is conducted in hydrofluoric acid (HF) solutions through the chemical reactions with Mg alloys. Fluorine in bones can mediate the metabolism of Ca and P, and benefit bone strength. Magnesium fluoride (MgF_2), as the main component of the fluoride conversion coatings, is insoluble in

water and easily deposited on Mg alloy surface. MgF_2 film, with good corrosion resistance, improved cell response and biocompatibility, has been utilized on biomedical Mg alloys [117,118]. The character and protective efficiency of the created coating depend on the preparation conditions, mainly on the HF concentration. Witte et al. [119] claimed that MgF_2 coating can mitigate *in vivo* corrosion rate of LAE442 alloy. Although the substrate was protected to some extent, MgF_2 layer degraded completely after 4 weeks of implantation. However, fluoride content in the neighboring bone did not increase during the initial 6 weeks of implantation. Localized pitting corrosion occurred but no subcutaneous gas cavities were observed in MgF_2 coated Mg implants. So to say, although fluoride conversion coating can provide protection in the early stages of implantation, it has a long way to go for the long-term application due to the fact of very thin coating. Simultaneously, the release of F^- during the degradation of Mg implant and its toxicity for implanted tissue are not clear because excess fluoride will have negative effect not only for bone in body.

Fintová et al. [120] prepared fluoride conversion coatings though unconventionally way by dipping of AZ61 specimens into Na $[BF_4]$ molten salt with various treatment time under 430 °C and 450 °C, followed by a boiling process in distilled water to remove the residual salts and the outer layer. The

2- μm thick coating had a double layer structure: a thick inner MgF_2 layer and a thin outer NaMgF_3 layer [120]. The corrosion current density, i_{corr} of the coatings decreased with the extension of treatment time except for 2 h at 450 °C, which indicated an improved corrosion resistance in SBF solution. The i_{corr} of the untreated substrate were about four orders of magnitude lower than the sample treated for 12 h at 450 °C. Although some defects are seen on the coating surface, these defects do not reach the substrate. The coatings are smoother than conventional conversion coatings which make it a better choice for fluoride treatment of Mg alloy. It is noted that the biocompatibility of the coating remains unclear.

To further promote the corrosion resistance of conversion coatings, Liu et al. [117] created a uniform and thin MgF_2 /polydopamine (PDA) coating on Mg-Zn-Y-Nd alloy via a simple two-step immersion method. Mg alloy immersed in HF solution, followed by the treatment in dopamine and tris-hydrochloric acid (tris-HCl) solution. The coating contains two layers: an upper layer of PDA and an inner layer of MgF_2 with an average thickness of about 100 nm. After PDA treatment the contact angle increased from $15.64^\circ \pm 0.33^\circ$ to $28.01^\circ \pm 2.98^\circ$. The HF-PDA-treatment contributes to higher free corrosion potential, E_{corr} and lower i_{corr} by two orders of magnitude than the bare Mg-Zn-Y-Nd alloy after an immersion in (DMEM+40 g/L BSA) solution for 1 h.

Phytic acid conversion coating: Phytic acid ($\text{C}_6\text{H}_{18}\text{O}_{24}\text{P}_6$, PA), as a hexaphosphoric acid ester of inositol, can chelate Ca, Mg, and Zn to form stable metal-phytic complexes such that a coating is deposited on the surface, and thus the corrosion resistance of Mg alloys is improved. Zhang et al. [121] fabricated a crack self-healing PA conversion coating by dipping Mg alloy AZ31 samples into PA solution, followed by a heat-treatment at a temperature of 150, 300 and 400 °C in air for 1 h. PA conversion coating is composed of C, O, Zn, Mg, Al and P elements and presents a bulk feature with plenty of distributed mesh-like cracks. It was interesting to find that the width of cracks on the conversion coatings gradually narrowed after the heat-treating. Meanwhile, the surface structure seemed more and more compact, regardless of the coating thickness decreased from 4.82 μm to 1.04 μm . The tensile adhesion strength became much stronger (from 20.4 ± 3.1 MPa to 37.9 ± 1.5 MPa) between the conversion coating and its substrate. This scenario was ascribed to the change in coatings from amorphous magnesium phytate into crystalline $\text{Mg}_2\text{P}_2\text{O}_7$ at heat-treated temperature of 300 °C. The findings demonstrated that the compact coatings were more effective to improve the protection of the substrate.

Also, a cracked surface was observed by Liu et al. [122] on a PA/ Ca^{2+} conversion coating through LBL method on Mg-Sr alloy. The defects such as cracks and pits occurred in the PA film can decrease the corrosion resistance and biocompatibility. These problems can be solved by adjusting the pH value of PA, and followed by chelating the PA coating with Ca^{2+} . The Ca^{2+} -modified PA film promoted the expression of alkaline phosphatase activity markedly in comparison to the bare Mg-Sr alloy.

2.1.2. Ionic liquid conversion coating

Ionic liquids (ILs) refer to room-temperature molten organic salts that are composed entirely of ions [123]. The salts are characterized by weak interactions, owing to the combination of a large cation and a charge-delocalized anion. Numerous ILs have been categorized as biocompatible or green chemicals. Mg and its alloys can remain stable for a long time without being corroded in specific ILs owing to no free H^+ or other metal cations, which provides favorable conditions for the control of film formation on active metals [124]. Forsyth's group explored "IL films" based on the reaction of ILs with pure Mg [125], which initiated the potential application of ILs in film/coating formation on Mg alloys. Various ILs conversion films have been proposed before [90,126–128]. In particular, P-containing coatings (i.e., phosphonate derivatives) had been investigated as novel chemicals in corrosion protection of Mg alloys due to their biocompatibility. M. Forsyth's group proposed a surface treatment of the AZ31 Mg alloy in biocompatible phosphate-based ionic liquids to mitigate its degradation in human body [129]. The cytotoxicity and corrosion resistance of the IL films were evaluated and it was found the corrosion resistance highly depended on treatment times. When a potential bias of -200 mV was applied on the ZE41 Mg alloy during exposure to the IL of trihexyl(tetradecyl)phosphonium diphenylphosphate, a more uniform IL film would be formed [127]. It was suggested that ILs based on the protic ammonium-phosphate and the trihexyltetradecylphosphonium cation coupled with organophosphate, organophosphinate, or $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ anions could react with Mg alloy on the surface to form an effective corrosion-protective film [125,130]. Elsentriecy et al. [51] demonstrated corrosion resistance was substantially enhanced through an aprotic ammonium-phosphate IL treatment at 300 °C (IL_300C) compared to the treatment at room temperature. The IL_300C conversion coating, possibly consisting of metal oxides, metal phosphates, and carbonaceous compounds, exhibited a two-layer structure with 70–80 nm thickness and strong passivation behavior in a 1 wt.% NaCl solution saturated with $\text{Mg}(\text{OH})_2$.

Deep eutectic solvents (DESs) are a new type of environmentally green ILs based on eutectic mixtures of choline chloride (ChCl) with a hydrogen bond donor species [131]. Unlike the conventional ILs, DESs are easy to prepare in a pure state and non-reactive with water. Many of them are biodegradable and the toxicological properties of the components are well characterized [131]. Recently, Gu's group [132] explored the formation of chemical conversion coatings on Mg alloys with DESs. A novel ionothermal method was proposed to fabricate a corrosion-resistant film by the interaction of the ChCl-urea mixture-based DES with the AZ31B Mg alloy at 160 °C. The reaction between the DES and Mg alloy surface formed the desired conversion coating composed of MgH_2 and MgCO_3 , which replaced a hazardous process. Moreover, upon further reaction with stearic acid/ethanol, the conversion film was found to be superhydrophobic. The electrochemical polarization measurements indicated that the DESs-conversion films could

improve the corrosion resistance of the Mg alloys [132]. The same group also applied an electric field to stimulate the decomposition of DES, facilitating the reaction of DES/Mg alloy interface [124]. Interestingly, conversion films with various nanostructures were formed on the Mg alloy substrates by the proposed anodic treatment in DESs. It was found that a higher anodic current density produces a better corrosion resistant conversion film. Superhydrophobic and slippery surfaces can be also achieved on the as-prepared conversion films to further improve the corrosion resistance [124]. In the DES-based media, smart conversion coatings with dual function of superhydrophobicity and self-healing can be also fabricated on the AZ31B Mg alloy [133]. It would be promising that more effective coatings or films might be produced on Mg alloys by adopting different external fields at the IL/substrate interface.

2.1.3. Biomimetic and biomineralization coating

Biomineralization is a process by which living organisms produce minerals such as Ca-P compounds, including HA, to harden or stiffen existing tissues [134]. Ca-P-based coatings on Mg alloys feature excellent biocompatibility, osteoconductivity and non-toxicity in *in vivo* environments. Scientists have employed various organic molecules i.e., ethylenediaminetetraacetic acid (EDTA) [135], dopamine [136] and arginine-glycine-aspartic acid-cysteine (RGDC) peptide [134] to promote mineralization of Ca-P coatings on Mg alloys. These organic molecules have a common function that is the so called molecular recognition. Namely, a specific interaction arises between two or more molecules via noncovalent bonding such as metal coordination, hydrogen bonding, van der Waals forces and π - π interactions together with electrostatic effects [137]. For example, HA coating can be successfully fabricated on AZ31 by hydrothermal treatment with $C_{10}H_{16}N_2O_8$ (EDTA, from the added EDTA-Ca) acted as chelating agent [135]. The HA coating with plate-shaped grains was accumulated on the surface of Mg alloys and some of the grains were stacked to form a flower-like structure. In accordance with the result of immersion tests, the electrochemical corrosion tests in Hank's balanced salt solution (HBSS) with i_{corr} values for AZ31 and HA coating were equal to 1.84×10^{-5} and 1.77×10^{-6} A/cm², respectively. But the biological properties of the coating were absence.

Cui et al. [138] prepared a dicalcium phosphate (DCP) coating on Mg alloy AZ31 with the aid of EDTA-2Na. The carboxyl groups in EDTA could identify Ca^{2+} ions in SBF solution; simultaneously, Ca^{2+} ions combined with the PO_4^{3-} ions. As a result, Ca-P coatings with a higher Ca/P ratio could be obtained. Similarly, the principle of molecular recognition was utilized by Fan et al. [88] and Li et al. [89], who developed a compact $Mg(OH)_2$ coating on AZ31 and anodized AZ31 substrate with the assistance of EDTA-2Na. The obtained $Mg(OH)_2$ layer exhibited higher compactness and corrosion resistance. The denser biomimetic coating with the help of organic chelate agents plays a central role in contribution to the corrosion resistance of Mg alloys. The subsequent

section can give the answer to the good biocompatibility of $Mg(OH)_2$ coating.

2.1.4. Alkali-heat treated conversion coating

Alkali-heat treated is an essential step of Mg and Mg alloy for removing oil and other impurities. As for coatings, it usually acts as pre-treatment for better corrosion resistance and the middle layer for strengthening the adhesion between the substrate and the outer layer. Alkali-heat treatments were carried out through immersing the substrate alloys in a super saturated $NaHCO_3$ - $MgCO_3$ solution with an initial pH of 9.3 for 24 h, followed by a heat-treatment at 500 °C for 10 h [139]. The coating shows high corrosion resistance in SBF. Simultaneously it displays no cytotoxicity by cell growth in preliminary cytotoxicity study with no signs of morphological changes on cells or inhibitory effect. Kunjukunju et al. [140] prepared LbL assembled coatings by alkali-heat pre-treatment which not only improved the corrosion resistance but also enhanced binding force between LbL layer and the substrate. The advantages of the alkali-heat treated conversion coating are their good corrosion resistance and biocompatibility. But the shortcomings are that the coatings are very thin and cannot act as the topcoat, usually be the primer.

2.1.5. MAO coating

MAO, also referred to plasma electrolytic oxidation (PEO), is a high voltage plasma-assisted anodic oxidation process, and a potential process derived from conventional anodizing to form ceramic-like coatings, extensively employed for the surface modification of Mg alloys [33,141].

Typically, the quality and chemistry of MAO coatings are determined by the electrolyte and alloy properties and also by the processing parameters such as pulse frequency [142], reaction time and potential [33]. As electrical discharges arise due to electric currents locally breaking through the growing layer, the characteristic craters are produced on the coating surface [18]. Such porous coatings provide considerable corrosion resistance to the substrate which can also play as an interlayer for improving binding force of a composite coating [71].

Corrosion behavior of MAO/HA-coated Mg-Zn-Ca alloy under constant compressive stress close to that of human tibia was investigated under *in vitro* condition [143]. Results indicated that the applied stress could change the degradation mode of coated samples and accelerate corrosion rate, causing peeling-off locations on the coating.

As mentioned above, besides the restricted chemical compositions and high energy consumption, the numerous micropores or high porosity is main disadvantage for MAO coatings to achieve long-term protection or multifunctional surfaces [141]. The porous MAO coating may provide the path of the solution and caustic ions passes into, contact and react with the substrate. Sealing are necessary approaches to the improvement in the physical barrier role of MAO coatings for Mg alloys. The common pore-sealing methods include in-situ sealing or self-sealing [48] and ex-situ sealing such as

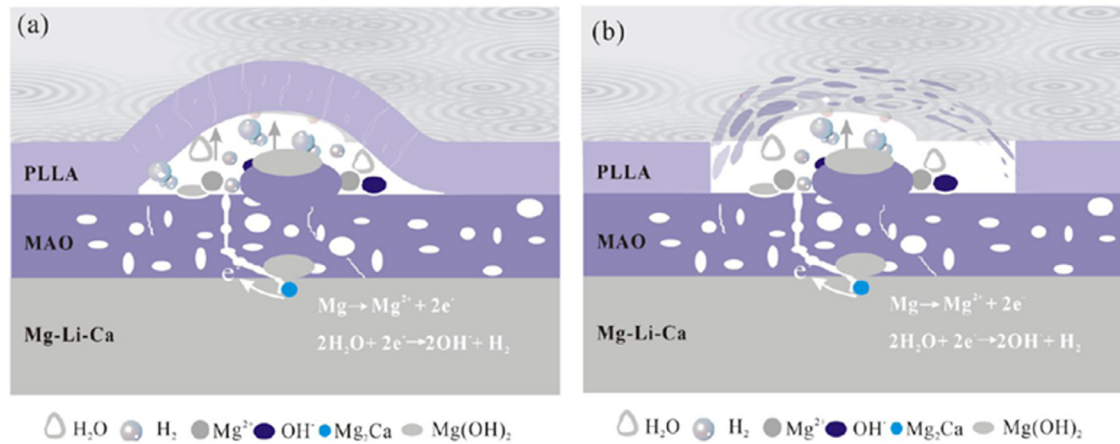


Fig. 7. Schematic illustrations of the degradation mechanism of porous MAO/PLLA composite coatings on Mg-Li-Ca alloys in HBSS: (a) swelling of PLLA and corrosion of the substrate at the initial stage, and (b) blistering and final peeling-off of PLLA under the pressure of hydrogen gas and corrosion products [147].

silicate and phosphate [144], sol-gel [46] and alkaline treatments [145] and additional polymeric coating [81] as well.

Li et al. [146] attempted to obtain a compact MAO coating via in-situ sealing of carbon sphere. The introduction of carbon sphere in the electrolyte leads to an increase in coating thickness, hardness and corrosion and wear resistance due to the formation of SiC.

Alkaline treatment is the post-treatment of MAO coating performed by immersing the coated samples in an alkaline solution [145]. As a result, the formation of Mg(OH)₂ and (Mg₂SiO₄)₂(Mg(OH)₂)₃ leads to the sealing of the small pores. The decrease in the medium and large pores size and the pore-density is due to the converting of the MgO film into Mg(OH)₂.

Polymer coating is a preferential choice for the topcoat. The pores in MAO coating can interlock with polymer for enhanced bonding strength. Thus, numerous MAO/polymer composite coatings have been developed. Yu et al. [74] employed chitosan on MAO coating. Wei et al. [72] obtained a PEO/PLLA composite coating on Mg alloy AZ31 by means of sealing PEO with PLLA. After PLLA treatment, the porous surface is completely covered. The results from *in vitro* tests indicate significant reduction in degradation kinetics, a low hemolysis ratio of 0.80%, and good adhesion and proliferation of MC3T3-E1 cells on the composite coating. Zeng et al. [147] fabricated MAO/PLA composite coatings on Mg-Li-Ca-(Y) alloys. Results disclose that the MAO coatings could only protect the substrate at the initial limited immersion stage; whilst in the subsequent immersion, an acceleration in corrosion rate occurs due to the presence of pores and micro-cracks in the coating, which offer pathways for the permeable ingress of corrosive components onto the surface of substrate. The difference in free corrosion potentials between MAO coating and its substrate gives rise to galvanic corrosion. In addition, the top layer of PLLA on the MAO coating is subject to swelling and subsequent delamination or peeling off under the pressure of hydrogen gas and corrosion products (Fig. 7).

Table 2 presents some examples about the corrosion resistance of MAO coatings on Mg alloys. The values of i_{corr} and E_{corr} differ in every research group due to different substrates, electrolytes and immersion periods. However, the reduction in i_{corr} , regardless of MAO or MAO-composite coatings, is over a range of 1–6 orders of magnitude than the substrates.

MAO coating is not only biodegradable but also biocompatible, indicating that it is promising coating for orthopaedic surgery. It has been reported that MAO coating on Mg-Ca alloy exhibits beneficial effects on corrosion resistance and MG63 cell adhesion, proliferation and differentiation [91]. Currently, research focus has shifted to the improvement of MAO coating on corrosion resistance, biocompatibility and cyto-compatibility [92]. Ren et al. [156] claimed that porous Si-containing MAO coating on pure Mg not only enhanced corrosion resistance but also sustained antibacterial function, which was attributed to the direct exposure of bacteria to the released Mg²⁺ ions as a result of corrosion of the underlying substrate through the existing channels in MAO coatings.

Nevertheless, the influence of the microstructure (especially, the intermetallic compounds) in substrate alloy on the formation of MAO coating cannot be ignored. Our previous study [157] shows that the presence of the second phase Mg₂Ca in Mg-Li-Ca alloy results in the defects of MAO coating, which deteriorates the quality of MAO coating. Basically, three types of the imperfections are found in MAO coating. They are open micro-pores on the surface, isolated pores in the middle and through-cracks from the surface to the substrate [158]. These pores can exchange with each other. E.g., open pores and isolated pores can be changed into through-cracks and open pores, respectively, with the degradation. As a result, two degradation mechanisms exist for the MAO coating on Mg alloy [158]. One is chemical dissolution, caused by open pores, in which no electrons join the chemical reactions. The other is electrochemical corrosion, produced by through-cracks, through which the ingress of water molecules into the interface of coating/substrate leads to preferential dissolution of Mg matrix and release of electrons. Spontaneously, they

Table 2

Electrochemical parameters of MAO and its composite coatings on Mg alloys.

Substrates	Coating	Solution	E_{corr} (V/SCE)			i_{corr} ($\mu\text{A}/\text{cm}^2$)*			Refs
			Substrate	MAO	Composite	Substrate	MAO	Composite	
AZ31	MAO	SBF	−1.31	−1.12	/	106.00	1.44	/	[148]
AZ31	MAO	SBF	−1.64	−1.52	/	214.00	2.73	/	[149]
AZ31B	MAO	3.5% NaCl	−1.50	−1.32	/	46.03	0.000780	/	[150]
Pure Mg	MAO	SBF	−1.85	−1.69	/	13.50	0.173	/	[151]
ZK60	nMAO+EPD	SBF	-1.63 ± 0.05	1.42 ± 0.03	1.29 ± 0.02	660 ± 59	12.8 ± 1.2	0.438 ± 0.031	[152]
Mg-4Zn-0.6Zr-0.4Sr	MAO+PLGA	SBF	−1.66	−1.57	−1.54	195.00	1.87	0.139	[153]
AZ31B	MAO+HA	SBF	−1.59	−1.73	−1.51	132.00	10.6	0.387	[154]
AZ31B	MAO+ sol-gel	SBF	/	/	/	3750	650	0.00125	[155]

* The electrochemical data listed are the best among the samples with different test parameters.

are caught by water molecules to form hydrogen gas and hydroxide ions.

The major advantages for MAO coating are improved corrosion and wear resistance, biocompatibility and biodegradability and so on. The porous surface morphology plays dual role. On one hand, the pores have a positive impact on top-coat for adhesion strength and cell adhesion for the implants. On the other hand, the pores play a negative role such as the origin of fatigue cracks and the paths for the ingress of aggressive medium.

2.1.6. Hydrothermal coating

Hydrothermal coating is developed by applying a liquidus synthetic technique to put the precursor into an autoclave under high pressure at suitable temperature. The advantage is the promotion in crystallization, easy to operate and low cost.

The example for hydrothermal coating is layered double hydroxide (LDH). It is a class of anionic clays with a highly tunable brucite structure [159]. The general formula of LDH can be represented as $\text{M}^{2+}_{1-x}\text{Mg}^{3+}_x(\text{OH})_2\text{A}^{n-}_x/n\cdot m\text{H}_2\text{O}$, where M^{2+} and M^{3+} are di- and tri-valent metal cations, respectively; x is defined as the molar ratio of $\text{M}^{3+}/(\text{M}^{2+} + \text{M}^{3+})$ and generally has a value ranging from 0.2 to 0.33; A^{n-} are the interlayer anions, i.e., NO_3^{3-} , Cl^- , PO_4^{3-} , MO_4^{2-} and CO_3^{2-} [65,160]. The typical structure of LDH is shown in Fig. 8 [161].

The crystal structure parameters of LDH, bond strength and anion exchange capacity were determined by size, charge and ratio of metal cations, charge and orientation of anions. In the synthesis process, cations occupy the octahedral holes in the brucite ($\text{Mg}(\text{OH})_2$)-like layer and gradually release from this intercalated structure [65,162,163]. The anions in the double layer structure are replaced by the anions in the environment and further bind with metal ions to form precipitation on the coating surface. The concentration of aggressive anions, such as chloride ions in the environment, decreases as the ion-exchange emerges in the coating; thus protective effect on the substrate is achieved.

A molybdate intercalated hydrotalcite coating with a lamellar structure was synthesized by a combination of the co-precipitation and hydrothermal processes [164]. The experiments demonstrated that such an interlocking plate-like coat-

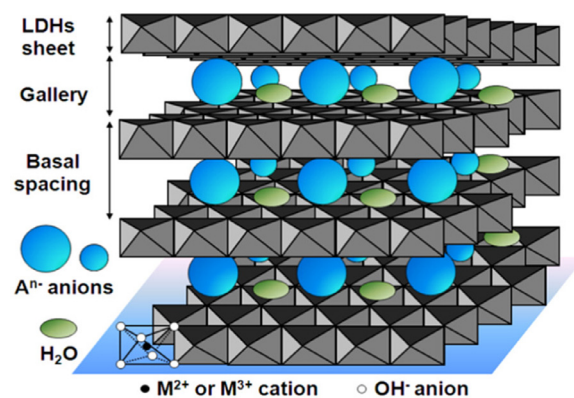


Fig. 8. Schematic representation of the LDH [161].

ing has ion-exchangeable and self-healing ability, which can respond to the stimuli from the environment as “smart” coating. Zeng et al. [165] synthesized a Zn-Al-LDH coating consisted of uniform and compact hexagonal nano-plates by co-precipitation and hydrothermal treatment on Mg alloy AZ31; and then a porous poly(lactic acid) (PLA) coating was applied to seal the Zn-Al-LDH coating using vacuum freeze-drying. The composite coating possesses excellent corrosion resistance, which is ascribed to its barrier function, ion-exchange and self-healing ability. Zhang et al. [166–168] prepared different LDH coatings by various methods. Self-healing ability was also achieved on PA/LDH/Mg(OH)₂ coating [168].

As for the biocompatibility of LDH coating on Mg alloys, Li et al. [69] prepared a LDH/PDA composite coating with surface heparinization on AZ31 Mg alloys. The findings designate that the LDH/PDA coating with heparinization can be a candidate for the coating on biodegradable Mg alloys with significantly enhanced corrosion resistance, endothelialization and hemocompatibility.

2.2. Deposited coating

Deposited coatings are defined as ex-situ coatings whose substrates do not participate in the formation of coatings. The constituents of deposited coatings are flexible [169]. The bind-

ing force between the substrate and its coating is guaranteed by intermolecular forces (such as electrostatic force, hydrogen bond, etc.) and mechanical force [170]. Deposited coatings are generally regarded as the outmost layer or functional layer because of its feeble adhesion with substrate and not suitable for the intermediate layer [171].

Most of them are organic materials or polymer coatings (i.e., PLLA). This type of coating can provide both enhanced corrosion resistance and functions, especially for biomedical application. The major drawback for polymer coating is the bonding strength between the coating and the underlying layer or substrate, is not good enough as expected. The problem of peeling-off under the stress (hydrogen bubbling) and corrosion needs to be solved. Therefore, the future focus may be concentrated on the improvement of barrier effect and binding force for a full-life corrosion resistant service [18].

2.2.1. Co-precipitation

Co-precipitation (CPT) designates simultaneous precipitation of more than one substance normally dissolved in solution. For example, CPT is an applicable method for preparing LDH coatings with features such as precisely controlled chemical composition, low cost and high reaction activity. In general, the combination of CPT and hydrothermal process can readily produce various LDH coatings. Zeng et al. [163,164] prepared molybdate intercalated hydrotalcite (HT-MoO_4^{2-} -LDH) and Mg-Al-LDH coatings on Mg alloy AZ31 using the combination of CPT and hydrothermal process. The advantages of LDHs coatings exhibit interlocking plate-like nanostructure, ion-exchangeable and self-healing ability as well as good corrosion resistance. However, the disadvantages of LDH coatings are the difficult preparation processes with a strict temperature and time conditions.

2.2.2. Physical vapor deposition

Physical vapor deposition (PVD) is an alternative technology to confront the high chemical reactivity and low electrode potential of Mg [172]. According to Wu et al. [173], a metallic-inorganic composite coating was prepared by PVD to reduce the electrochemical *in vitro* activity. An Al or Ti interlayer was deposited on the surface of Mg alloy AZ31 to improve the adhesion between AlO_xN_y ceramic coating and substrate. The AlO_xN_y ceramic coating significantly improved the bio-corrosion resistance of the magnesium alloy. The Al interlayer could impede corrosion effectively with a deficiency of smaller enhancement in the surface mechanical properties of the AlO_xN_y coating compared with the Ti layer. Unfortunately, there is a risk for its application; if surface coating is locally damaged, galvanic corrosion will occur and consequently, the corrosion of the underlying Mg alloys speed up [174]. Another issue is the neurotoxicity of Al, as mentioned above.

Graphene oxide (GO), analogy to graphene, consisting of monomolecular sheets, can be applied as coating material, due to its unique surface properties, ease of chemical functionalization, and good biocompatibility. GO films are optically transparent and impermeable, comprising millions of

randomly stacked flakes and leaving nano-sized capillaries between them. Bakhsheshi-Rad [175] obtained a novel nano-silica (SiO_2)/GO composite coating on Mg–1Ca–6Zn alloy using PVD followed by dip coating. The nano- SiO_2 interlayer, deposited via radio frequency (RF) magnetron sputtering (MS), designates a dense columnar microstructure with a thickness of $1\mu\text{m}$; whilst the outer dip coating of GO has a sheet-like morphology with a thickness of approximate $30\mu\text{m}$. The nano- SiO_2 /GO coating reveals enhanced *in vitro* corrosion resistance and antibacterial ability.

Magnetron sputtering: In generic sputtering process, a target (or cathode) plate is bombarded by energetic ions, which are generated in a glow discharge plasma in front of the target. The bombardment process generates sputtering of the target atoms, which may then deposit on the substrate as a thin film. In addition, secondary electrons are emitted from the target surface as a result of the ion bombardment. A magnetic field is configured parallel to the target surface so that secondary electron motion is constrained to the vicinity of the target [176]. The advantage of MS lies on the formation of uniform coating and good adhesion between the yielded coatings to the substrate.

MS has become optional process for the deposition of corrosion-resistant (i.e., metallic and polymeric) coatings on Mg alloys. As mentioned above, Al, Ti and Al/Ti film have been deposited on Mg alloys via MS. Wu et al. [177] deposited fluorocarbon polymeric film on pure Mg by means of MS. The coating was transparent with a thickness of about 120nm after deposition for 30min . EDS showed the presence of C and F after depositing and the water contact angle increased from 61.5° to 107.3° , indicated that formation of hydrophobic fluorocarbon-based coating on Mg alloy. The corrosion potential positively shifted from -1.625 to -1.576V and the corrosion current density significantly decreased from $2.14 \times 10^{-5}\text{A}/\text{cm}^2$ to $2.80 \times 10^{-8}\text{A}/\text{cm}^2$. However, the coatings had random defects, which might cause the pre-failure of coatings.

Microwave assisted deposition: Microwave assisted deposition can occur over a short time and accelerate the coating deposition kinetics under microwave irradiation, with notable features such as manipulation of thickness and uniformity of the coatings along with irregular contour. Ren et al. [178] fabricated a calcium-deficient HA coating on Mg alloy AZ31 through microwave irradiation of Ca-P solutions with various Ca/P ratios. The obtained coating resulted in an enhancement of corrosion resistance and biological response. Yu et al. [179] developed a strontium (Sr)-doped HA (Sr-HA) coating on AZ31 via microwave assisted deposition. The Sr-HA coating possesses a double-layer structure with excellent mineralization ability and long-term protection in corrosive environments.

2.2.3. Atomic layer deposition

Atomic layer deposition (ALD), a recently developed surface covering technique, regarded as a kind of chemical vapor deposition is being used in various fields such as semiconductor [180], biomedicine [60] and corrosion protection

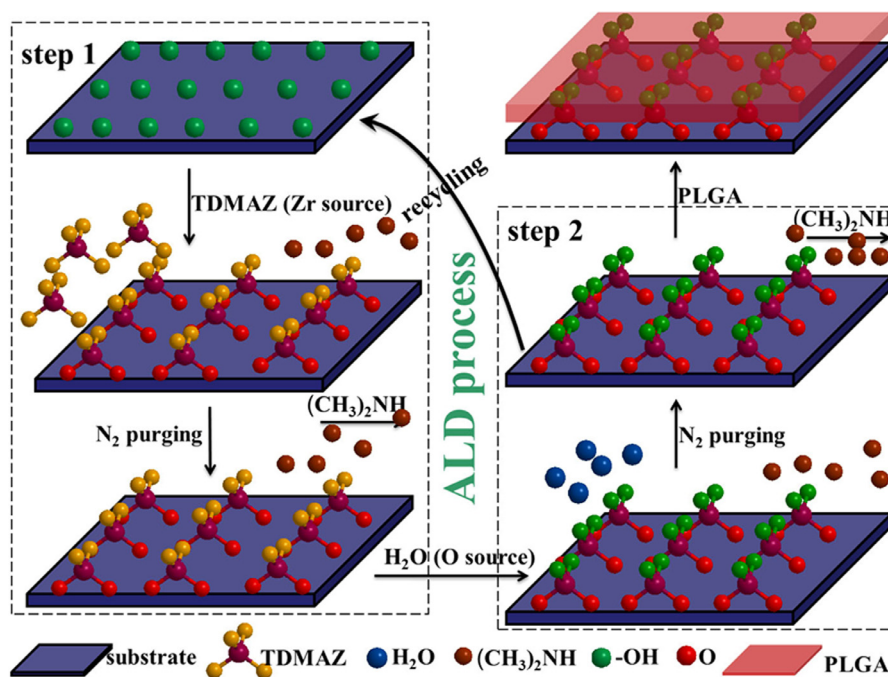


Fig. 9. Schematic illustration of formation mechanism of ZrO_2 coating deposited through ALD and the followed PLGA covering [181].

[181]. The ALD deposits atoms layer by layer utilizing special self-limitation characteristics which can meet the needs for atomic layer control and conformal deposition [182]. Films made by ALD have excellent reproducibility, simplicity, and conformality and accurate thickness control as well [183,184]. What's more, without surface defects during and after growth, the films tend to be very continuous and pinhole-free [182]. Therefore, they can effectively improve the corrosion resistance of Mg alloys [185]. ALD technique has great advantages over traditional methods such as porous MAO coatings and cracked chemical conversion coatings.

Basically, the ALD coating and its corrosion resistance can be regulated by changing the number of cycles of the ALD processes. Liu et al. [181] prepared ZrO_2 nanofilm on Mg substrate by ALD and subsequently adhered to a PLGA layer through a spin-coating process to further improve the corrosion resistance. ZrO_2 cycles from 25 to 100 lead to two or three orders of magnitude increase in corrosion resistance of coatings. The E_{corr} of the untreated, ZrO_2 (25 cycles), and PLGA/ ZrO_2 (25 cycles) were -1.557 , -1.523 , and -1.518 V, respectively. During the immersion period from 72 to 96 h, hydrogen evolution rate followed in the decreasing order: PLGA/ ZrO_2 (25 cycles) > ZrO_2 (25 cycles) > Untreated > ZrO_2 (100 cycles) > PLGA/ ZrO_2 (100 cycles). In addition, nano-scratch tests showed that the hybrid coating had good bonding strength with the substrate. The schematic illustration of formation mechanism of ZrO_2 ALD and PLGA coating is shown in Fig. 9.

Yang et al. [60] deposited ZrO_2 nano-film on Mg–Sr alloy for enhanced corrosion resistance and biocompatibility. The ZrO_2 film can not only enhance the corrosion resistance of Mg–Sr alloy but also benefits for the growth of cells and tis-

ues *in vitro* studies. Unfortunately, this method is relatively high time-consuming, especially for increasing the cycle number. Nevertheless, the ceramic coatings like Al_2O_3 , TiO_2 and ZrO_2 might be the possibility of degradation and accelerated attack on the substrate resulted from galvanic corrosion between the coating and its substrate.

2.2.4. Electrolytic deposition

Electrolytic deposition (ED) mainly concerns the deposition of inorganic phases on bare or pre-coated surface of metallic substrate by an electric field [85]. The composition of Ca-P coating can be delicately controlled via the regulation of Ca/P ratio and current mode in the ED process [186].

In general, the inorganic products exhibit flake-like [187] or bundle-like [188] morphology. When the Ca/P ratio is set at 1.67 with a pulse potential (duty cycle of 0.2), the formation of coating is unitary HA [189,190]. Meanwhile, alkali-heat pretreatment could transform dicalcium phosphate dehydrate (DCPD, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) precipitates into HA [188]. Theoretical analyses [191] illustrate that the precipitation of HA, octacalcium phosphate and DCPD are all possible when pH is higher than 6 at 80°C . High pH value is favorable for the formation of HA.

Currently, various interlayers were introduced to improve the adhesion between ED coating and its substrate. Alabbasi et al. [192] applied a two-step process to prepared dual layer inorganic coating on Mg. A layer of silicate-based coating was formed on the base metal using PEO method, and then a second layer of Ca-P was formed on the PEO coating using ED preparation.

ED also can be applied to other composite coatings. A γ -glutamic acid-g-amino-4-methylcoumarin (γ -PGA-g-AMC)

coating with encapsulation of vitamin was prepared on the surface of Mg–Ca alloy [193], which can controllably release bioactive agents or drugs and endow Mg implants with excellent functionality. Wu et al. [194] electrochemically deposited $\text{Mg}(\text{OH})_2/\text{GO}$ composite coating on AZ91D alloy at constant potential. The $\text{Mg}(\text{OH})_2/\text{GO}$ hybrid coating exhibits more uniform and dense structure than $\text{Mg}(\text{OH})_2$ film. Hence, it enhances the corrosion resistance of $\text{Mg}(\text{OH})_2$ coating by more than one order of magnitude.

2.2.5. Dipping and immersion

Dipping and immersion are both extensively applied coating methods for desired corrosion resistance and functionality through regulating composition of the deposited layers [171]. In recent years, organic biopolymer coatings on Mg alloy substrates have received wider attention than inorganic coatings through dipping preparation [18].

Organic coating: Organic coatings feature corrosion protection, bioactivity, and drug-loading together with biodegradability. Due to the versatility of polymers, chemical composition and structure, the coatings can be fabricated with a number of chemical and physical properties and functions. In addition, polymeric coatings are able to deliver drugs by assembling these polymers into functional materials. These coatings include polymer-derived active coatings [195] and polymer-derived antibacterial coatings [196]. There are several typical organic coatings, i.e., silane, dopamine and stearic acid (SA) besides PLA and chitosan, on biomedical Mg alloys.

Silanes are a series of silicon substitutes for carbon alkanes, which consisting of multiple silicon atoms linked to each other as the main chain and hydrogen atoms or other chemical elements linked with the main chain. This chemical structure furnishes silanes with very reactive and moderate biological activity. Thus, the silane coating could be a feasible technical route to improve the biological performance of Mg alloys [135,197]. A triethoxy(octyl) silane coating was prepared by electric deposition to improve the corrosion resistance and biocompatibility of AZ31B alloy [198]. It demonstrated significant performance on cell viability, hemolysis and platelet adhesion. The first step involves treating the NaOH-activated Mg with bis(triethoxysilyl)ethane (BTSE) to immobilize a layer of densely cross-linked silane coating with good corrosion resistance. The second step is to impart amine functionality to the surface by treating the modified Mg with 3-amino-propyltrimethoxysilane. Heparin was covalently conjugated onto the silane treated AZ31 to render the coating haemocompatible, as demonstrated by reduced platelet adhesion on the heparinized surface [199]. Compared to bare AZ31 Mg alloy, Mg-B (1h)-A (0.5h)-Heparin exhibits both improved corrosion resistance and reduced platelet adhesion. The development of a surface modification strategy that can simultaneously control corrosion resistance and inhibit platelet adhesion will inevitably have major significance for improving the blood compatibility of biodegradable metallic implants.

The fluoroalkylsilane (FAS)-modified hierarchical hydroxide zinc carbonate (HZC) film was fabricated on AZ31

Mg alloy via dipping method [197]. This FAS/HZC film exhibited a significantly hydrophobic property for substrate and improved the corrosion resistance of the AZ31 alloy. Cui et al. [81] deposited a micro-arc oxidation (MAO)/polymethyltrimethoxysilane (PMTMS) hybrid coating via MAO processing. It was subsequently sealed with alkaline treatment and PMTMS (Fig. 10). The MAO coating has a porous morphology with some cracks (Fig. 10b). Compared with the partial coverage of alkaline treatment (Fig. 10d), the coating of PMTMS (Fig. 10f) reveals a compact and smooth surface with circular self-condensation silane spheres. The results indicate that the alkaline treatment is beneficial for the silane treatment. The MAO coating was efficiently sealed by the PMTMS film. The E_{corr} of the substrate, MAO and MAO/PMTMS coating is positively shifted from -1.51 V/SCE to -1.46 V/SCE and to -1.41 V/SCE . The i_{corr} of the substrate, MAO and MAO/PMTMS coated samples is 1.37×10^{-5} , 2.40×10^{-7} , $2.86 \times 10^{-8} \text{ A/cm}^2$, respectively. The findings demonstrate that the corrosion resistance of the AZ31 alloy is significantly enhanced by the MAO/PMTMS coating due to its self-healing function.

Dopamine (DA, contracted from 3, 4-dihydroxyphenethylamine) is a hormone which is made naturally in the body. Namely, it is an organic chemical of the catecholamine and phenethylamine families that plays several important roles in the brain and body. A dopamine molecule consists of a catechol structure (a benzene ring with two hydroxyl side groups) with one amine group attached via an ethyl chain. Chen et al. [200] produced a TiO_2 /polydopamine (PDA) composite coating on pure Mg. Firstly, the PDA layer was covalently immobilized on Mg, and subsequently the TiO_2 was deposited by liquid phase deposition on it. The hybrid TiO_2 /PDA coated Mg shows much smaller corrosion current density as well as a remarkably lower degradation rate *in vitro* (up to 21 days) in phosphate buffered saline compared to direct TiO_2 coated and untreated Mg. The result relates to the organic PDA layer which inhibits the electric pathway of galvanic corrosion cell between the TiO_2 coating and Mg so as to suppress the corrosion of Mg. Herein, the PDA acted as an anchoring layer to the Mg substrate, template for the TiO_2 deposition, and barrier layer isolating the electric pathway for electron motion.

SA is an environmentally-friendly saturated fatty acid with an 18-carbon chain and has the International Union of Pure and Applied Chemistry (IUPAC) name octadecanoic acid (chemical formula, $\text{C}_{17}\text{H}_{35}\text{CO}_2\text{H}$) with a low surface energy. SA was used on the top of $\text{Mg}(\text{OH})_2$ [201] and MAO coatings with Mg alloy [202]. All studies indicated SA-modified surface can provide a long-term corrosion protection for the Mg alloy owing to the formation of superhydrophobic surface.

Zhang et al. [203] prepared an HA/SA composite coating using the combination of ED and dipping method. It was found that the HA/SA coating was porous, which may provide abundant sites for the growth of osseous tissue. Gupta et al. [204] obtained a chemical conversion coating with a PA solution. They further improved it by soaking in SA

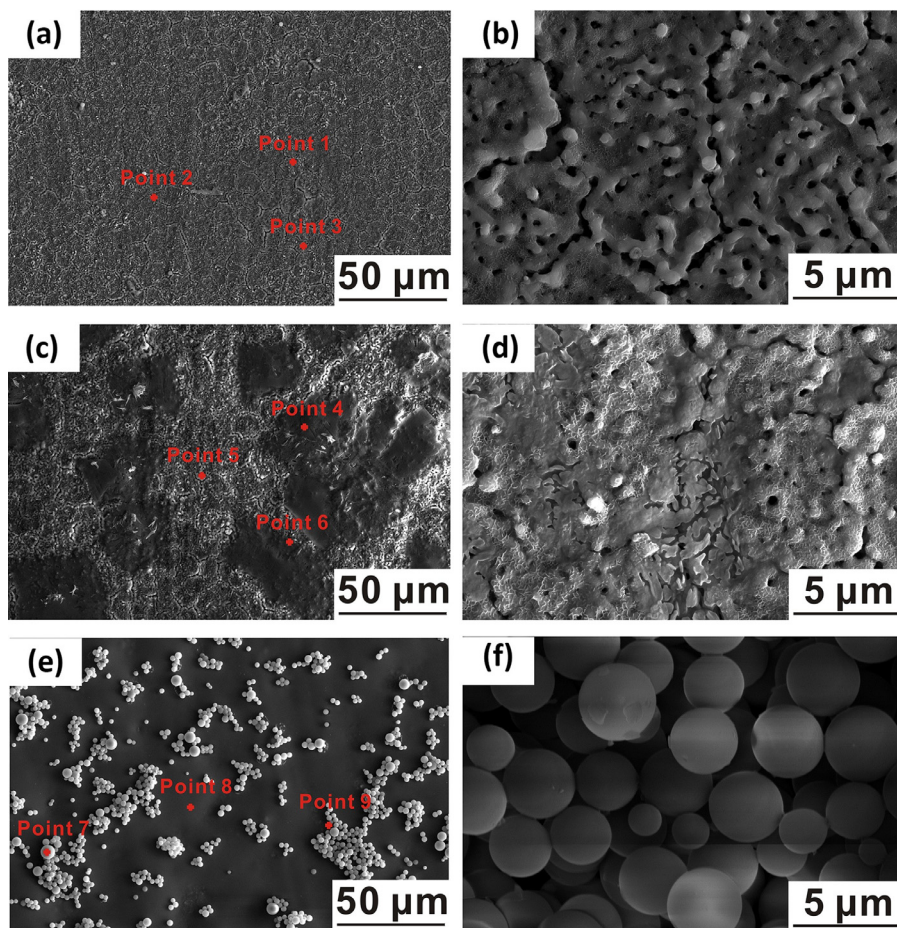


Fig. 10. FE-SEM micrographs of the (a and b) MAO coating, (c and d) the NaOH-treated MAO coating, and (e and f) the MAO/PMTMS coating [81].

solution to provide effective corrosion protection for Mg samples.

Preparation methods for organic coatings: LbL assembling is a versatile, simple method based on the alternating exposure of a charged substrate to solutions of positively and negatively charged polyelectrolytes on the basis of the electrostatic attraction between the opposite charges [205,206]. In spite of little even detrimental for corrosion resistance in the long run, the film with different deposition cycles and types of polyelectrolytes realizes multi-functionalization (biomedicine etc.) [207,208]. For instance, Schmidt et al. [209] fabricated a nanoscale thin films by LbL using negatively charged Prussian Blue nanoparticles and positively charged gentamicin, demonstrating an systematic electro-activated drug release property. LbL assembling films by polyelectrolytes can protect the substrate to some degree. Cui et al. [68] assembled DNA coatings on Mg alloy by LbL method lead to one order of magnitude decrease in corrosion current density.

Ostrowski et al. [210] employed LbL to fabricate a silane/poly(allylamine hydrochloride)/poly(sodium 4-styrenesulfonate) multilayer coating on alkaline-treated Mg alloy. The composite coating revealed good corrosion protection for degradable Mg alloys. Fan et al. [211] prepared a self-healing coating which contained a cerium conversion layer

as primary layer, then followed by a graphene oxide (GO) layer and a branched poly(ethylene imine) (PEI)/poly(acrylic acid) (PAA) multilayer. Here GO was a corrosion inhibitor and PEI/PAA multilayers offer the self-healing ability for the coating systems. The results showed that GO acted as the barrier layer by hindering the penetration of aggressive electrolyte. Kunjukunju et al. [212] reported the biocompatible organic natural polymer-based coatings on the AZ31 alloy prepared by LbL. They first obtained alkaline- and fluoride-pretreated AZ31 substrates. Then the multi-layered coatings of alginate and poly-L-lysine on the substrates were fabricated using LbL technique under physiological conditions. The coatings were surface functionalized by chemical cross-linking and fibronectin immobilization. The modification in surface properties exerts a beneficial influence on cellular activity. The alginate and poly-L-lysine multi-layered coatings did not alter the degradation kinetics of the substrates but improved their surface bioactivity.

The major disadvantage of LbL assembled coatings relates to the processing acidic solutions, which may attack the Mg substrates, to some extent. Thus, it is better for the Mg substrates to experience a pretreatment and make them possess good corrosion resistance. In addition, the LbL method is a little complicated; and the coating is very thin, regardless of

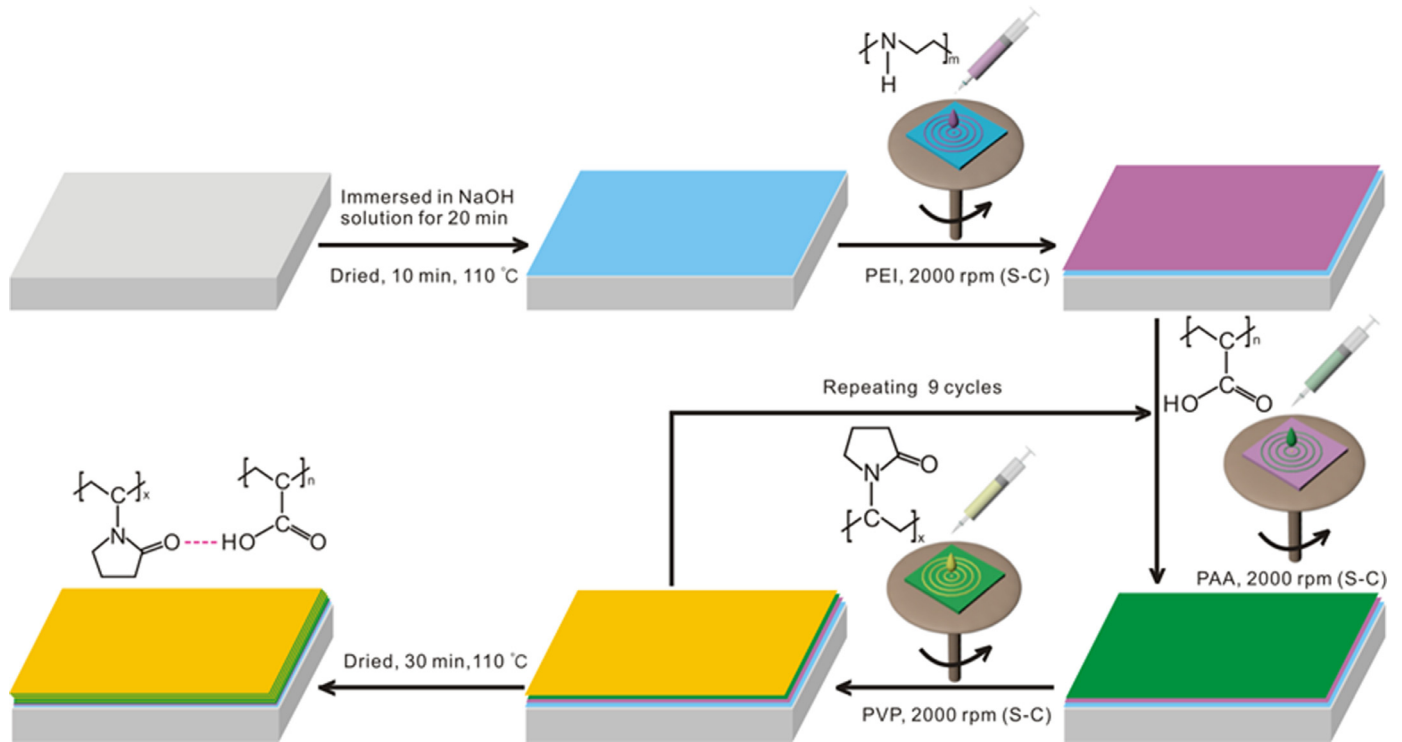


Fig. 11. Schematic representation of the spinning technique used for the coating production [86].

the functionality. Hence, complicated or hybrid coatings with LbL, i.e., dipping and spinning, have been developed on Mg alloys.

Dipping or spinning coating is widely used for producing thin polymer films with a homogeneous thickness. The majority of spin assembly is performed by either casting the solution onto a spinning substrate [213] or casting the solution onto a stationary substrate that is then spun [214,215]. For fabricating a biodegradable esophageal stent, Yuan et al. [216] coated polycaprolactone (PCL) and poly(trimethylene carbonate) (PTMC) on Mg alloy stents by means of the combination of dipping and spinning method. The hybrid coating demonstrated good flexibility, elasticity and an ability to prolong the service life of the stent. It can also maintain mechanical capacity and nontoxicity in the long term.

A composite coating was fabricated using MAO coating on Mg–Zn–Ca alloy and dip-coating in chitosan solution to improve its biodegradation resistance in SBF [75]. Another example for PCL coated porous Mg scaffold designates that PCL coating significantly enhances the compressive strength and degradation resistance of Mg scaffolds [217].

There are still insuperable defects for organic biopolymer coating in long-term degradation [218]. On one hand, polymer would absorb water and swell at its first step of degradation. This process generates an internal stress which leads to the peeling off or delamination of the organic layer from the substrate. On the other hand, the water permeable rate of polymer is much higher than its absorbent rate. The accumulation of hydrogen and corrosion products result from Mg corrosion also triggers the peeling-off of the organic layer [71].

A spin coating method has been used to prepare PLA coating on the Ca-P-coated alloy. This composite coating has a better performance such as biocompatibility in long-term test [219]. Alabbasi et al. [220] performed a silicate-based MAO coating on pure Mg using a pulsed constant current method, then the PLA was coated using a two-step spin coating method as sealing process to delay the localized degradation in body fluid for better in-service mechanical integrity. Therefore, the composite coating could be a feasible means to improve the binding force of organic biopolymer coating.

Zhao et al. [86] fabricated a polyvinylpyrrolidone (PVP)/polyacrylic acid (PAA) composite coating with a multilayer structure on AZ31 alloy by LbL-assembling and spin-casting method (Fig. 11). A (PVP/PAA)₁₀ hybrid coating on Mg alloy has a defect-free, dense and uniform morphology and exhibits excellent corrosion resistance and adhesion strength.

Different adsorption mechanisms resulted in significant difference between the dipping and the spinning methods. In the dipping method, electrostatic interaction leads to the adsorption and rearrangement of polyelectrolytes on the substrate. In the spinning process, nevertheless, air shear force and the centrifugal force forces the polyelectrolytes to be absorbed and rearranged in a short time and the water molecules to be removed rapidly. As a result, the corrosion resistance and adhesive bonding can be enhanced.

Sol-gel method is a practical process to synthesize mesoporous bioactive glass (MBG) coating on the surface of biodegradable Mg [221]. In a typical synthesis, silicon-based ester, phosphorus ester, polyol and calcium salt were dissolved

in ethanol solution in a certain Si/Ca/P ratio; then Mg substrates were dried and dipped into this MBG sol, and finally aged, repeated and heat treated. Another example is the deposition of a titanium sol–gel layer on the MAO film on Mg–Li alloy [222]. The long run immersion testing showed that the composite coating, with higher compactness and fewer defects, exhibits a corrosion-resistant property superior to the MAO film alone.

2.3. Mechanical coatings

Mechanical coatings refer to the deformed surface and subsurface emerged by a severe plastic deformation processing. As a result, a layer of refined structure, different from the original surface, is obtained without introducing any substances, such as deposited minerals and attached organics. The mechanical processing improves the physical properties and corrosion resistance of Mg alloys by refining grains, improving the hardness, and optimizing the distribution of second phases or intermetallic compounds [223]. Normally, chemical reactions are not involved in the procedure. Friction stir processing (FSP) and shot peening (SP) are introduced here for improving the practical properties of medical Mg alloys. Compared with the traditional chemical coatings, the mechanical layer has better binding force with the substrate. In addition, post processing of chemical coatings on the surface of mechanical layer can be considered to further realize various functions.

2.3.1. FSP

FSP has a marked effect on the physical and chemical properties of Mg alloy surface. The FSP for microstructural modification is based on the basic principles of friction stir welding (FSW), which has been originally developed for the joint of aluminum alloys [224]. FSW is considered to be the most significant development in green metal joining, especially for Mg and Al alloys due to its energy efficiency, environment friendliness, and versatility [225]. In the FSP procedure, a non-consumable rotating tool with a specially designed pin and shoulder (Fig. 12a) is inserted into the material [226]. Friction-induced high-temperature plastic deformation severely occurs onto the material near the tool. Partially-overlapped multi-pass FSP is used to enlarge the processed surface region of the alloy, where the tool traverses along a predetermined route to cover the material over the target region (Fig. 12b).

Intense plastic deformation can be introduced into the base material without additional heating by FSP. Therefore it has been proved to be an effective technique for producing uniform structure, adjusting surface composites [227,228], modifying the microstructure of Mg-based alloys and improving the corrosion-resistant properties to some degree [226].

Cao et al. [227] investigated microstructure evolution and its effect on the mechanical properties of Mg–Nd–Y alloy during normal friction stir processing (NFSP) and submerged friction stir processing (SFSP). After NFSP and SFSP, α -Mg dendrites were greatly refined with an average grain size

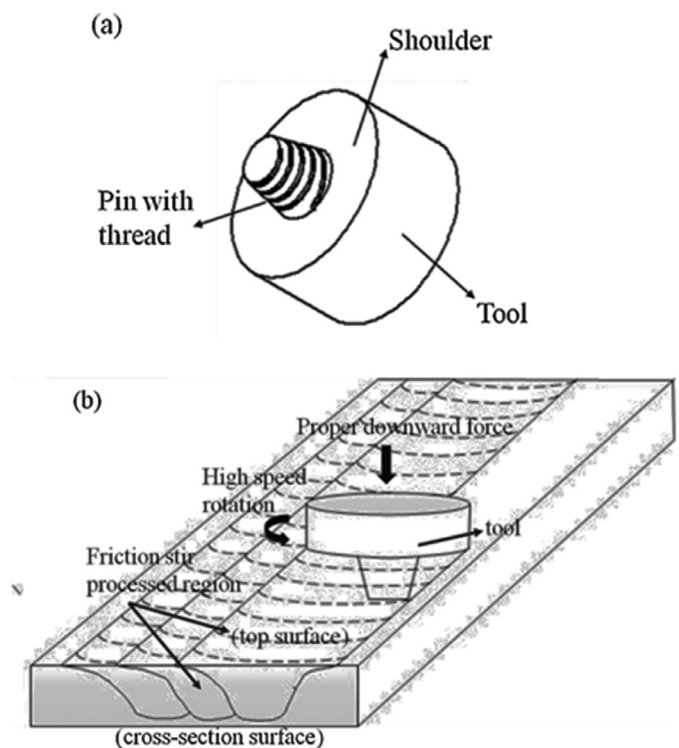


Fig. 12. Schematic drawings of FSP technique: (a) FSP tool, (b) FSP procedure [226].

Table 3

Results of tensile tests of the samples obtained by different treatment methods [227].

Processing mode	UTS, MPa	YS, MPa	EL, %
Untreated	178 ± 3.5	172 ± 3	3.4 ± 0.5
NSFP treated	291 ± 4.6	270 ± 5	7.5 ± 0.5
SFSP treated	297 ± 6.9	281 ± 3.9	20.3 ± 1.8

of 2.7 μm and 1.9 μm , respectively. Another net-shaped intermetallic compound Mg_{12}Nd was smashed into small particles and the SFSP specimen had more homogeneous microstructure than that of the NSFP. Ultimate tensile strength (UTS), yield strength (YS) and elongation to failure (EL) have been improved significantly and the results are list in Table 3.

Zhu et al. [229] employed FSP on biodegradable Mg–Zn–Y–Nd alloy. The result indicates that the microstructure of the FSPed Mg alloy is characterized by homogeneously equiaxed refined grains with a size of approximately 5 μm and the dispersively distributed intermetallic compound particles in a nano scale due to the dynamic recrystallization.

Liu et al. [226] studied the corrosion resistance of AZ91 Mg alloy through refinement and homogenization of surface microstructure through FSP. They found the formation of a compact and continuous β phase layer on the FSPed surface owing to the segregation of fine β phase effectively enhances the stability and passivity of corrosion product film. The E_{corr} of as-cast AZ91, the

cross-sectional and top surface of the FSPed samples is positively enhanced from -1.3 ± 0.03 V/SCE to -1.17 ± 0.05 V/SCE and to -1.16 ± 0.03 V/SCE. And the i_{corr} of the corresponding samples decreases from 6.76 ± 0.65 $\mu\text{A}/\text{cm}^2$ to 3.01 ± 0.07 $\mu\text{A}/\text{cm}^2$ and to 2.05 ± 0.13 $\mu\text{A}/\text{cm}^2$. For as-cast sample, the hydrogen evolution volume increases more rapidly than the FSPed samples. The hydrogen evolution volume of the top surface and cross-section surface is almost three-fold higher than that of the FSPed samples after one-week immersion. That is to say, FSP process is beneficial for the enhancement in corrosion resistance but not remarkable for this work.

FSP is a post treatment; while laser cladding (LC), with localized heating input from the high-energy laser beam, leads to a small thermal deformation and heat affected zone. The microstructure of the surface may be refined and homogenized together with increasing mechanical properties such as micro-hardness, wear and corrosion resistance [230,231]. But LC coatings, sometimes, could be rough, cracked and porous. FSP is an effective method to modify the LC coating. Laser cladding (LC) and FSP hybrid method was adopted to modify Al-Si coatings on AZ31B by Liu et al. [228]. The OCP of AZ31B, LC, and LC+FSP is 1.563, 1.272, and 1.085 V/SCE, respectively. The maximum OCP of the LC-FSP specimen is 0.478 V/SCE, much higher than that of the bare AZ31B specimen. A large number of intermetallic compounds β ($\text{Al}_{12}\text{Mg}_{17}$) and Mg_2Si with a continuous network in the Al-Si coatings is the mainly reasons for the improvement of corrosion resistance. So, it is feasible to further improve the comprehensive properties of Mg alloys by combining surface treatment such as FSP and LC and coating preparation process.

2.3.2. SP

SP is a powerful mechanical treatment to modify surface and enhance the fatigue performance of structural metallic materials such as steel, aluminum, titanium and magnesium alloys [232–235]. The improvement in fatigue life stems from a combination of work hardening of the surface and an increased dislocation density, and the introduction of a near-surface compressive residual stress [236]. A plastically deformed zone formed by SP processes have extended and refined grain structure [237].

Effect of SP on enhancing the fatigue performance is one of the most popular direction of research [236,238,239]. Zhang and Lindemann [239] studied the influence of SP on fatigue properties of the high-strength wrought Mg alloy AZ80. The result was the fatigue strength increased about 60% from 100 to 160 MPa at the optimum condition. Simultaneously, the limited deformability of the hexagonal crystal structure makes the Mg alloy sensitive to SP. Jamalain et al. [240] conducted a study on the effect of the severe shot peening (SSP) parameters on the microstructural variation and plastic deformation of AZ31. The optimum parameters of SSP lead to a thicker fine-structured layer in the material surface. Higher pressure or shot mass intensity results in finer grains at the surface while an increase in shot size only controls the thickness of

the layer. The SSP with optimized parameters gives rise to an increased YS and UTS, but a loss of ductility. As the average grain size of the treated and untreated samples reduces from $44 \mu\text{m}$ to $3.42 \mu\text{m}$, the micro-hardness increases from 50 HV to 92 HV.

Also, the impact of SP on corrosion resistance and biocompatibility have been studied [237,241,242] beside fatigue performance. Bagherifard et al. [242] investigated the effects of nano features, developed by SSP, on mechanical, corrosion and cytocompatibility properties of Mg alloy AZ31. The E_{corr} of unpeened, conventional SP, severe SP, and repeened-severe SPed samples is -1542 ± 25 , -1503 ± 23 , -1479 ± 26 , and -1483 ± 27 mV, respectively; and the corresponding i_{corr} is 21 ± 2 , 325 ± 5 , 326 ± 4 , and 321 ± 6 $\mu\text{A cm}^{-2}$. This disadvantage could be attributed to the rough surface layer after SP with a high density of crystallographic lattice defects. The SSP treatment leads to an increased surface roughness (up to 150%), enhanced micro-hardness (up to 133%) and surface wettability (up to 20%), and compressive residual stresses in a deep surface layer (max compressive stress of -56 MPa). Cytocompatibility tests certify that SSP has no adverse effects on the growth of osteoblasts. Although the electrochemical properties of the samples were tested, there was no immersion test which could not fully reflect the corrosion resistance.

SP generates a rough layer with high density of crystallographic imperfections or dislocations, which are deteriorated to the corrosion resistance of Mg alloys. If the rough surface layer is removed without the entire nano-crystallized layer, the corrosion resistance might be improved. Chemical conversion film as an effective method, combined with SP, can dissolve the outer surface and the better internal structure can be retained.

2.4. Functional coatings

The ideal functional coatings on biodegradable Mg alloys for clinic applications may be self-degradable, bioactive or biocompatible, antibacterial and drug-loading coatings. In addition, corrosion resistance and controllability of corrosion rate are also critical standards. Much work had been done for one or multiple functional coatings.

2.4.1. Self-sacrificing or self-degradable coating

Since Mg alloy has very active chemical character, few methods can prevent its corrosion, such that a novel idea is proposed to enhance the corrosion resistance by self-sacrificial coating. Originally, self-sacrificial coating is a typical metal coating with a lower potential relative to the protected metal. One of the example of this kind of coating is Zn-coated steel or galvanized steel. Another type of composite coating is Zn, Al and Mg-loading polymer coating on steels. As a result, the electrons, released from the dissolution of Zn, Al and Mg, flow to that part of the protected metal or the substrate.

It is noted that the existing coatings on Mg alloys are almost nobler than their substrates. The ideal coatings have to be uniform, strongly adherent and pore-free for applications; otherwise, the pores or micro-cracks in the coatings offer a

path for the ingress of water onto the coating/Mg substrate interface to form micro-galvanic cells; thus, the substrate acts as a local anode, the degradation of it will be accelerated.

One of the challenges for the coating applications is that the presence of defects such as pinholes, pores and micro-cracks in the coating or developed during operation often result in the formation of galvanic cells between the coating and its substrate, leading to accelerated corrosion of Mg. An ideal and effective coating should be anodic relative to its substrate. That is, a sacrificial anode-based cathodic protection, active corrosion protection to minimize corrosion at defects (for example by releasing active inhibitors), and formation of a self-healing protective barrier layer on the substrate surface. Developing a protective coating which could fulfill the above requirements is extremely challenging.

Song et al. [77] suggested that Mg is too active to be protected by a sacrificial anode coating. It is extremely difficult to form a metallic sacrificial anode layer on Mg. The standard equilibrium potential of pure Mg is as negative as -2.644 V vs. SCE. Although active alkaline or alkali earth metallic elements such as Ca, Li, K and Na, may have potentials more negative than Mg, their self-dissolution/corrosion is too rapid [77]. They are too reactive to form a stable and durable coating on Mg. However, Yu et al. [76] fabricated pure Mg film with a thickness of $20\text{--}35\text{ }\mu\text{m}$ on an AZ91D sample by means of PVD. The sacrificial Mg film uniformly forms and cathodically protects the AZ91D substrate due to the fact that the mixed potential of the Mg coating/AZ91D couple was more anodic than the free corrosion potential of the substrate.

Interestingly, Song et al. [77] obtained lithiated C (LiC_6) and metaphosphate coatings with a complicated metallurgical powder process, exhibiting a sacrificial anode coating behavior on Mg in saturated $\text{Mg}(\text{OH})_2$. But these films are not continuously covered on the substrate, implying that they may not effectively protect Mg in a very corrosive environment. Although the self-sacrificial coatings have many drawbacks, they can effectively reduce the biodegradation rate and further slowdown the hydrogen evolution and alkalization of the surrounding.

Wang et al. [243] reported Ca-P self-sealing MAO coating on pure Mg from a solution of 0.8 g/L calcium hydroxide, 3.5 g/L sodium hexametaphosphate and 8 g/L potassium fluoride in distilled water. This coating mainly comprises MgO , Ca, P and F. Their polarization curves indicate that the MAO coating has a more negative potential than pure Mg. However, this phenomenon is ignored regarding the formation of anodic coating and reason.

2.4.2. Bioactive and biocompatible coating

Bioactive coating refers to the coating containing bioactive components for bone replacements and promoting early bone growth. Biocompatible coating means that the coating is nontoxic and harmless to tissues, i.e., must not cause adverse biological reactions. For example, Xu et al. [108] utilized a phosphating process to develop a Ca-P coating on $\text{Mg-1.2 wt.\%Mn-1.0 wt.\% Zn}$ alloy. It is characterized by a porous and net-like $\text{CaHPO}_4\cdot 2\text{H}_2\text{O}$ layer with traces of Mg^{2+} and

Zn^{2+} . The in-vitro cell tests disclosed significantly good adherence, high growth rate and proliferation for cells L929 on the Ca-P coated Mg alloy ($p < 0.05$). That is, the Ca-P coating significantly improved the cytocompatibility. Both routine pathological examination and immunohistochemical analysis demonstrated that the Ca-P coated Mg alloy was endowed with a significantly good surface bioactivity (a better cell response) and promoted early bone growth at the implant/bone interface. The Ca-P coating might be an effective approach to improved surface bioactivity of Mg alloy. Pan et al. [244] prepared calcium phosphate coating on Mg-Zn-Zr Mg alloy through micro-arc oxidation (MAO) technology with diverse phosphate source. Mouse acute systemic toxicity test was performed which demonstrated the excellent biocompatibility of the coatings.

2.4.3. Antibacterial coating

As mentioned before, the Mg alloy itself has antibacterial properties due to the increase of pH value during its degradation in the bacterial solution. It has significant meaning in clinical areas to restrain the infections associated with surgical implants [245]. On one hand, rapid degradation rate means the failure of the biomedical Mg facility which conflicts with our initial intention. A feasible route is to prepare coatings with antibacterial property. Bakhsheshi-Rad et al. [246] prepared nanostructured silver-doped zinc oxide (Ag-ZnO) coating on Mg-2Ca-0.5Mn-6Zn alloy by PVD along with the antimicrobial and other examinations. According to disc diffusion antibiotic sensitivity and colony forming units, with calculating *Escherichia coli* and *Staphylococcus aureus*, the results indicated that the Ag-ZnO coating considerably improves antimicrobial performance of the Mg alloy substrate. At the same time, the coating leads to reduced corrosion rate of the substrate. Yang et al. [247] introduced copper (Cu)-containing bioactive glass nanoparticles (Cu-BGNs) into polycaprolactone (PCL) coating aiming to improve the bioactivity, antibacterial property, and corrosion resistance of Mg alloys in physiological condition. Cyto-compatibility experiments were conducted by MG-63 cells which proved the increased viability and proliferation on Cu-BGN coatings compared to Mg substrates. Recently, Zou et al. [67] hydrothermally prepared a Zn-loaded montmorillonite (Zn-MMT) coating using Zn^{2+} ion intercalated sodium MMT upon Mg alloy AZ31 as bone repairing materials. This coating exhibits an improved corrosion resistance, cytocompatibility and higher suppression toward both *E. coli* and *S. aureus*. It is designated that Zn-MMT coating destroys bacterial membrane and leads to the leakage of cytoplasmic materials from the bacterial cells due to the slow but sustainable Zn^{2+} release.

2.4.4. Drug-loading

Drug-loading can be another applied direction for biomedical Mg alloys [79]. Li et al. [248] studied *in vitro* drug loading and release of enoxacin (Enox)-loaded poly(lactic-co-glycolic acid) (PLGA) coating on Mg scaffold. The loading and release efficiency were appraised by ratio of loaded vs. initial enoxacin amount and spectrophotometrically. The

loading efficiency of Enox-PLGA-Mg was ($52.2\% \pm 7.7\%$ to $56.9\% \pm 6.7\%$) about ten times higher than that of Enox-Mg ($4.0\% \pm 1.5\%$ to $5.8\% \pm 1.7\%$). At the same time, Enox-PLGA-Mg had slower and more sustained liberative performance. Shi et al. [195] prepared a rapamycin drug-loading PLGA coating on Mg–Nd–Zn–Zr based drug-eluting stents. The H_2 evolution from substrate degradation accelerated the drug release in the drug diffusion-controlled phase. Although physiochemical stability of the released rapamycin has partially been deteriorated by the degradation of Mg, the smooth muscle cell proliferation has better inhibition than drug-loaded on stainless steel. The preparation of drug-loading coatings can not only improve the corrosion resistance of Mg alloys, but also make Mg alloys have antimicrobial properties through the release of antibacterial agents [78]. The focus should on the regulation and the influence factors of drug release rate.

2.5. Composite coatings

Single coating cannot bear comprehensive requirements for corrosion resistance and multi-function due to its pinholes or porous structure. Conversion coatings are defined as in-situ coatings. The metallic substrate participates in the interfacial reactions with satisfactory adhesion, however, the compositions of coating are limited by dynamics of converted reactions and substrates. It can be regarded as an interlayer to improve the binding force between the outer layer and its substrate. Deposited coatings are defined as ex-situ coatings which the weak adhesion is based on electrostatic interaction or mechanical bond. However, the flexible and multiple compositions of the coating could confer favorable biological activity. It can be served as final layer to improve the functionality of the substrate. The composition of conversion coating and deposited coating is the research emphasis for Mg biomaterial, because this composite coating could overcome the shortcoming of limited corrosion resistance, poor binding adhesion and lacking bioactivity for the single coating. Nevertheless, the degradation behavior of composite coatings is more complicated. The variation in degradation rate is uncontrollable and susceptible. It should be further researched and verified under *in vitro* and *in vivo* conditions.

For realizing the multifunctional demands and conquering the drawbacks of one single coating, multilayer coating is applied. As a matter of fact, most of the methods can be classified into multilayer coatings on layer number. Such as the alkali pretreatment by NaOH forms the $Mg(OH)_2$ layer and acid pretreatment, e.g., HF and other pre-treatment for specific purposes are all multilayer coatings. Kunjukunju et al. [140] prepared and made comparison the LbL coatings with diverse pretreatment of NaOH and HF. Cytocompatibility studies using MC3T3-E1 osteoblasts demonstrated the fluoride-pretreated, cross-linked and fibronectin-immobilized LbL-coated substrates are more bioactive and less cytotoxic than the hydroxide pretreated. The bottom layer can provide corrosion resistance properties and the LbL coating can improve the biological properties for Mg alloys.

In conclusion, even if the biomedical Mg alloys and their coatings have many deficiencies, the advantages of them can not be neglected. With the continually work of researcher, shortcoming will be decreased even eliminated.

3. Summary and concluding remarks

The major challenge for biomedical applications is to prepare gradient, degradation-controllable and multifunctional coatings and interfaces between the coating and substrate. As for biodegradable Mg alloys, a controllable degradation velocity is also vital.

Degradation of Mg alloys depends on their alloying elements, chemical composition and microstructure. Usually, the secondary or intermetallic phases are nobler than α -Mg matrix. This could cause micro-galvanic cells between them. The presence of secondary or intermetallic phases may facilitate overall corrosion dependent on their distribution, size, and amount. Therefore, chemical conversion coatings, MAO coatings etc. have been utilized to improve the corrosion resistance of Mg alloys. There still exist huge challenges for the development of advanced coatings on biomedical Mg alloys. The previous studies reveal that the morphology, roughness, and corrosion resistance of the phosphate chemical conversion coating, MAO coating and ED coating, are affected by the intermetallic compounds (i.e., $Mg_{17}Al_{12}$, AlMnSi) of the substrate alloys.

- (1) Conversion coatings are defined as in-situ coatings which the metallic substrate participates in the interfacial reactions with a satisfactory adhesion. It can be regarded as an interlayer to improve the binding force between outer layer and the substrate.
- (2) Deposited coatings are defined as ex-situ coatings which the weak adhesion is based on electrostatic interaction or mechanical bond. The flexible and multiple compositions of the coatings could possess favorable biological activity. It can be served as final layer to improve the functionality of the substrate.
- (3) Mechanical coatings lead to refined grains and redistribution of the second phase of the surface, improvement in mechanical properties and corrosion resistance of Mg alloys due to severe plastic deformation in mechanical procedure.
- (4) The composition of conversion coating and deposited coating are the research emphasis of Mg biomaterials, because this composite coating could manage the conflict of binding force and bioactivity of single coating. However, the degradation behavior of composite coating is more complicated and the variation in degradation rate is uncontrollable and impressionable. It should be further researched and verified under *in vitro* and *in vivo* conditions.

There still are huge challenges for the development of advanced coatings on biomedical Mg alloys. The ideal coatings on biodegradable Mg alloys for clinic applications may

be corrosion-resistant, self-degradable, and biocompatible as well as drug-loading etc. But it's almost impossible to fabricate coatings with all properties mentioned before so far. Especially for achieving the effectiveness of controllable corrosion rate is quite difficult for degradable biomedical Mg alloys as implant materials.

Anodic gradient coatings might be the choice of Mg-based implants. The outer anodic coating preferentially degrades and its substrate alloy can be well-kept so that the integrity and mechanical properties can be maintained. While for the conventional cathodic coatings, the substrate will be the anodic, and preferentially be attacked. Thus, its strength will be lost.

Declaration of Competing Interest

The authors declared that they have no conflicts of interest to this work.

Acknowledgments

This research was financially supported by National Natural Science Foundation of China (51571134), SDUST Research Fund (2014TDJH104). The authors thank Yanbin Zhao for his effort of modifying Figs. 1 and 2.

References

- [1] M.P. Staiger, A.M. Pietak, J. Huadmai, G. Dias, *Biomaterials* 27 (2006) 1728–1734.
- [2] R.C. Zeng, W. Dietzel, F. Witte, N. Hort, C. Blawert, *Adv. Eng. Mater.* 10 (2008) B3–B14.
- [3] Y.F. Zheng, X.N. Gu, F. Witte, *Mater. Sci. Eng. R Rep.* 77 (2014) 1–34.
- [4] X.W. Liu, Y. Liu, B. Jin, Y. Lu, J. Lu, *J. Mater. Sci. Technol.* 33 (2017) 224–230.
- [5] A. Atrens, G.L. Song, F.Y. Cao, Z.M. Shi, P.K. Bowen, *J. Magnes. Alloy.* 1 (2013) 177–200.
- [6] Y. Chai, Y. Song, B. Jiang, J. Fu, Z. Jiang, Q. Yang, H. Sheng, G. Huang, D. Zhang, F. Pan, *J. Magnes. Alloy.* 7 (2019) 545–554.
- [7] S.X. Zhang, X.N. Zhang, C.L. Zhao, J.N. Li, Y. Song, C.Y. Xie, et al., *Acta Biomater.* 6 (2010) 626–640.
- [8] L.Y. Li, B. Liu, R.C. Zeng, S.Q. Li, F. Zhang, Y.H. Zou, H.G. Jiang, X.B. Chen, S.K. Guan, Q.Y. Liu, *Front. Mater. Sci.* 12 (2018) 184–197.
- [9] M.S. Song, R.C. Zeng, Y.F. Ding, R.W. Li, M. Easton, I. Cole, N. Birbilis, X.B. Chen, *J. Mater. Sci. Technol.* 35 (2019) 535–544.
- [10] L.Y. Li, L.Y. Cui, R.C. Zeng, S.Q. Li, X.B. Chen, Y.F. Zheng, K.M. Bobby, *Acta Biomater.* 79 (2018) 23–36.
- [11] A. Atrens, S. Johnston, Z.M. Shi, M.S. Dargusch, *Scr. Mater.* 154 (2018) 92–100.
- [12] Q. Luo, J. Li, B. Li, B. Liu, H. Shao, Q. Li, *J. Magnes. Alloy.* 7 (2019) 58–71.
- [13] G.L. Song, A. Atrens, *Adv. Eng. Mater.* 5 (2003) 837–858.
- [14] G.L. Song, A. Atrens, *Adv. Eng. Mater.* 1 (2010) 11–33.
- [15] Z.M. Shi, M. Liu, A. Atrens, *Corros. Sci.* 52 (2010) 579–588.
- [16] A. Atrens, G.L. Song, L. Ming, Z.M. Shi, F.Y. Cao, M.S. Dargusch, *Adv. Eng. Mater.* 17 (2015) 400–453.
- [17] Y. Xin, T. Hu, P.K. Chu, *Acta Biomater.* 7 (2011) 1452–1459.
- [18] H. Hornberger, S. Virtanen, A.R. Boccaccini, *Acta Biomater.* 8 (2012) 2442–2455.
- [19] Z.Y. Ding, L.Y. Cui, R.C. Zeng, Y.B. Zhao, S.K. Guan, D.K. Xu, C.G. Lin, *J. Mater. Sci. Technol.* 34 (2018) 1550–1557.
- [20] N.T. Kirkland, N. Birbilis, M.P. Staiger, *Acta Biomater.* 8 (2012) 925–936.
- [21] M. Esmaily, J.E. Svensson, S. Fajardo, N. Birbilis, G.S. Frankel, S. Virtanen, S. Virtanen, R. Arrabale, S. Thomas, L.G. Johansson, *Prog. Mater. Sci.* 89 (2017) 92–193.
- [22] Y. Wang, B.H. Ding, S.Y. Gao, X.B. Chen, R.C. Zeng, et al., *Mater. Sci. Eng. C* 105 (2019) 110042.
- [23] F. Witte, *Acta Biomater.* 6 (2010) 1680–1692.
- [24] F. Witte, V. Kaese, H. Haferkamp, E. Switzer, A. Meyer-Lindenberg, C.J. Wirth, H. Windhagen, *Biomaterials* 26 (2005) 3557–3563.
- [25] Z. Zhen, X.L. Liu, T. Huang, T.F. Xi, Y.F. Zheng, *Mater. Sci. Eng. C* 46 (2015) 202–206.
- [26] X.N. Gu, X.H. Xie, N. Li, Y.F. Zheng, L. Qin, *Acta Biomater.* 8 (2012) 2360–2374.
- [27] B.P. Zhang, Y.L. Hou, X.D. Wang, Y. Wang, L. Geng, *Mater. Sci. Eng. C* 31 (2011) 1667–1673.
- [28] J. Hofstetter, E. Martinelli, A.M. Weinberg, M. Becker, B. Mingler, P.J. Uggowitzer, J.F. Löffler, *Corros. Sci.* 91 (2015) 29–36.
- [29] F. Witte, J. Fischer, J. Nellesen, H.A. Crostack, V. Kaese, A. Pisch, F. Beckmann, H. Windhagen, *Biomaterials* 27 (2006) 1013–1018.
- [30] R.C. Zeng, L.Y. Cui, W. Ke, *Acta Metall. Sin.* 54 (2018) 1215–1235.
- [31] Y. Zhou, P. Fu, L. Peng, D. Wang, Y. Wang, B. Hu, M. Liu, A.K. Sachdev, W. Ding, *J. Magnes. Alloy.* 7 (2019) 113–123.
- [32] F. Witte, N. Hort, C. Vogt, S. Cohen, K.U. Kainer, R. Willumeit, F. Frank, *Curr. Opin. Solid State Mater. Sci.* 12 (2008) 63–72.
- [33] T.S.N. Sankara Narayanan, I.S. Park, M.H. Lee, *Prog. Mater. Sci.* 60 (2014) 1–71.
- [34] Y.J. Wang, *J. Mater. Sci. Technol.* 32 (2016) 799–800.
- [35] Z.J. Li, X. Gu, S.Q. Lou, Y.F. Zheng, *Biomaterials* 29 (2008) 1329–1344.
- [36] E. Willbold, X.N. Gu, D. Albert, K. Kalla, K. Bobe, et al., *Acta Biomater.* 11 (2015) 554–562.
- [37] M. Mhaede, F. Pastorek, B. Hadzima, *Mater. Sci. Eng. C* 39 (2014) 330–335.
- [38] Y.D. He, H.F. Fu, X.G. Li, W. Gao, *Scr. Mater.* 58 (2008) 504–507.
- [39] X. Xiong, Y. Yang, J. Li, M. Li, J. Peng, C. Wen, X. Peng, *J. Magnes. Alloy.* 7 (2019) 696–706.
- [40] R.C. Zeng, K. Jiang, S.Q. Li, F. Zhang, H.Z. Cui, E.H. Han, *Front. Mater. Sci.* 9 (2015) 66–76.
- [41] Y. Guo, Y.Q. Zhang, Z.Y. Li, S.Z. Wei, T. Zhang, L.Q. Yang, S.Y. Liu, *Surf. Coat. Technol.* 334 (2018) 471–478.
- [42] Y.L. Gao, C.S. Wang, H.J. Pang, H.B. Liu, M. Yao, *Surf. Coat. Technol.* 253 (2007) 4917–4922.
- [43] J. Liu, Y. Zheng, Y.Z. Bi, Y. Li, Y.F. Zheng, *Mater. Lett.* 205 (2017) 87–89.
- [44] H.X. Wang, S.K. Guan, Y.S. Wang, H.J. Liu, H.T. Wang, L.G. Wang, C.X. Ren, S.J. Zhu, K.S. Chen, *Colloids Surf. B* 88 (2011) 254–259.
- [45] Z.Q. Zhang, R.C. Zeng, W. Yan, C.G. Lin, L. Wang, Z.L. Wang, D.C. Chen, *J. Alloy. Compd.* 821 (2020) 153515.
- [46] J.H. Gao, X.Y. Shi, B. Yang, S.S. Hou, E.C. Meng, F.X. Guan, S.K. Guan, *J. Mater. Sci. Mater. Med.* 22 (2011) 1681–1687.
- [47] A.A. Zuleta, E. Correa, J.G. Castañón, F. Echeverría, A. Baron-Wiechec, P. Skeldon, G.E. Thompson, *Surf. Coat. Technol.* 321 (2017) 309–320.
- [48] K.H. Dong, Y.W. Song, D.Y. Shan, E.H. Han, *Corros. Sci.* 100 (2015) 275–283.
- [49] L. White, Y. Koo, S. Neralla, J. Sankar, Y. Yun, *Mater. Sci. Eng. B* 208 (2016) 39–46.
- [50] S.Y. Kim, Y.K. Kim, K.S. Kim, K.B. Lee, M.H. Lee, *Colloids Surf. B* 173 (2019) 437–446.
- [51] H.H. Elsentriecy, H. Luo, H.M. Meyer, L.L. Grado, J. Qu, *Electrochim. Acta* 123 (2014) 58–65.
- [52] H.Y. Yang, X.W. Guo, G.H. Wu, W.J. Ding, N. Birbilis, *Corros. Sci.* 53 (2011) 381–387.
- [53] C. Singh, S.K. Tiwari, R. Singh, *Corros. Sci.* 151 (2019) 1–19.
- [54] W.H. Jin, G.W. Wang, Z.J. Lin, H.K. Feng, W. Li, X. Peng, A.M. Qasim, P.K. Chu, *Corros. Sci.* 114 (2017) 45–56.
- [55] B. Singh, G. Singh, B.S. Sidhu, J. Compos. Mater. 53 (2019) 2661–2673.

- [56] X.N. Gu, S.S. Li, X.M. Li, Y.B. Fan, *Front. Mater. Sci.* 8 (2014) 200–218.
- [57] R.L. Nixon, C.L. Higgins, D. Maor, H.R. Bala, A. Lalji, K.E. Heim, *Contact Derm.* 79 (2018) 356–364.
- [58] R.C. Zeng, W. Dietzel, J. Chen, W.J. Huang, J. Wang, *Key Eng. Mater.* 373–374 (2008) 609–612.
- [59] Y.C. Xin, C.L. Liu, W.J. Zhang, K.F. Huo, G.Y. Tang, X.B. Tian, P.K. Chu, *J. Mater. Res.* 23 (2008) 312–319.
- [60] Q.Y. Yang, X.Liu W.Yuan, Y. Zheng, Z. Cui, X. Yang, *Acta Biomater.* 58 (2017) 515–526.
- [61] Y.B. Zhao, Z. Zhang, L.Q. Shi, F. Zhang, S.Q. Li, R.C. Zeng, *Mater. Lett.* 237 (2019) 14–18.
- [62] Y.C. Xin, C.L. Liu, W.J. Zhang, J. Jiang, G.Y. Tang, X.B. Tian, P.K. Chu, *J. Electrochem. Soc.* 155 (2008) C178–C182.
- [63] L. Bing, Z. Xian, G.Y. Xiao, Y.P. Lu, *Mater. Sci. Eng., C* 47 (2015) 97–104.
- [64] M. Razavi, M. Fathi, O. Savabi, S.E. Razavi, B. Hashemibeni, M. Yazdimamaghani, D. Vashae, L. Tayebi, Comparative study on the biodegradation and biocompatibility of silicate bioceramic coatings on biodegradable magnesium alloy as biodegradable biomaterial, in: *Proceedings of the APS Meeting APS Meeting Abstracts*, 2014.
- [65] L. Guo, W. Wu, Y.F. Zhou, F. Zhang, R.C. Zeng, J.M. Zeng, J.M. Zeng, *J. Mater. Sci. Technol.* 34 (2018) 1455–1466.
- [66] F. Peng, D.H. Wang, D.D. Zhang, B.C. Yan, H.L. Cao, Y.Q. Qiao, X.Y. Liu, *ACS Biomater. Sci. Eng.* 4 (2018) 4112–4121.
- [67] Y.H. Zou, J. Wang, L.Y. Cui, R.C. Zeng, et al., *Acta Biomater.* 98 (2019) 196–214.
- [68] L.Y. Cui, X.H. Fang, W. Cao, R.C. Zeng, S.Q. Li, X.B. Chen, et al., *Appl. Surf. Sci.* 457 (2018) 49–58.
- [69] H. Li, F. Peng, D.H. Wang, Y.Q. Qiao, D.M. Xu, X.Y. Liu, *Biomater. Sci.* 6 (2018) 1846–1858.
- [70] L.Y. Cui, H.P. Liu, K. Xue, W.L. Zhang, R.C. Zeng, S.Q. Li, et al., *J. Electrochem. Soc.* 165 (2018) C821–C829.
- [71] R.C. Zeng, W.C. Qi, Y.W. Song, Q.K. He, H.Z. Cui, E.H. Han, *Front. Mater. Sci.* 8 (2014) 343–353.
- [72] Z.L. Wei, P. Tian, X.Y. Liu, B.X. Zhou, J. Biomed. Mater. Res. Part B 103 (2015) 342–354.
- [73] R.C. Zeng, L.Y. Cui, K. Jiang, R. Liu, B.D. Zhao, Y.F. Zheng, *ACS Appl. Mater. Interfaces* 8 (2016) 10014–10028.
- [74] C. Yu, L.Y. Cui, Y.F. Zhou, Z.Z. Han, X.B. Chen, R.C. Zeng, et al., *Surf. Coat. Technol.* 344 (2018) 1–11.
- [75] K.F. Bai, Y. Zhang, Z.Y. Fu, C.L. Zhang, X. Z.Cui, E. Meng, J.H. Hu, *Mater. Lett.* 73 (2012) 59–61.
- [76] B.L. Yu, J.Y. Uan, *Scr. Mater.* 54 (2006) 1253–1257.
- [77] G.L. Song, N.J. Dudley, J. Li, R.L. Sacci, J.K. Thomson, *Corros. Sci.* 87 (2014) 11–14.
- [78] X.J. Ji, Q. Cheng, J. Wang, Y.B. Zhao, Z.Z. Han, F. Zhang, S.Q. Li, R.C. Zeng, Z.L. Wang, *Front. Mater. Sci.* 13 (2019) 87–98.
- [79] X.J. Ji, L. Gao, J.C. Liu, J. Wang, Q. Cheng, J.P. Li, S.Q. Li, K.Q. Zhi, R.C. Zeng, Z.L. Wang, *Colloids Surf. B* 179 (2019) 429–436.
- [80] Y.B. Zhao, X.Y. Chen, S.Q. Li, R.C. Zeng, F. Zhang, Z.L. Wang, S.K. Guan, *J. Colloid Interface Sci.* 547 (2019) 309–317.
- [81] L.Y. Cui, S.D. Gao, P.P. Li, R.C. Zeng, F. Zhang, S.Q. Li, E.H. Han, *Corros. Sci.* 118 (2017) 84–95.
- [82] Y.J. Wang, *J. Mater. Sci. Technol.* 32 (2016) 801–809.
- [83] T. Zheng, Y. Hu, F. Pan, Y. Zhang, A. Tang, *J. Magnes. Alloy.* 7 (2019) 193–202.
- [84] S.B. Guo, Y.Q. Zhang, R.F. Zhang, S.F. Zhang, H.H. Zhang, *Mater. Chem. Phys.* 141 (2013) 121–127.
- [85] C.Y. Zhang, R.C. Zeng, C.L. Liu, J.C. Gao, *Surf. Coat. Technol.* 204 (2010) 3636–3640.
- [86] Y.B. Zhao, H.P. Liu, C.Y. Li, Y. Chen, S.Q. Li, R.C. Zeng, Z.L. Wang, *Appl. Surf. Sci.* 434 (2018) 787–795.
- [87] R.C. Zeng, X.X. Sun, Y.W. Song, F. Zhang, S.Q. Li, H.Z. Cui, E.H. Han, *Nonferrous Met. Soc. China* 23 (2013) 3293–3299.
- [88] X.L. Fan, Y.F. Huo, C.Y. Li, M.B. Kannan, X.B. Chen, S.K. Guan, R.C. Zeng, Q.L. Ma, *Rare Met.* 38 (2019) 520–531.
- [89] C.Y. Li, X.L. Fan, R.C. Zeng, L.Y. Cui, et al., *J. Mater. Sci. Technol.* 35 (2019) 1088–1098.
- [90] M. Forsyth, W.C. Neil, P.C. Howlett, D.R. Macfarlane, B.R. Hinton, N. Rocher, et al., *ACS Appl. Mater. Interfaces* 1 (2009) 1045–1052.
- [91] X.N. Gu, N. Li, W.R. Zhou, Y.F. Zheng, X. Zhao, Q.Z. Cai, L.Q. Ruan, *Acta Biomater.* 7 (2011) 1880–1889.
- [92] L. Zhang, J.Q. Zhang, C.F. Chen, Y.H. Gu, *Corros. Sci.* 91 (2015) 7–28.
- [93] D. Sreekanth, N. Rameshbabu, *Mater. Lett.* 68 (2012) 439–442.
- [94] M.D. Pereda, C. Alonso, M. Gamero, J.A. Del Valle, *Mater. Sci. Eng. C* 31 (2011) 858–865.
- [95] X.B. Chen, D.R. Nisbet, R.W. Li, P.N. Smith, T.B. Abbott, M.A. Easton, D.H. Zhang, N. Biribilis, *Acta Biomater.* 10 (2014) 1463–1474.
- [96] X.B. Chen, H.Y. Yang, T.B. Abbott, M.A. Easton, N. Biribilis, *Surf. Eng.* 30 (2014) 871–879.
- [97] R.C. Zeng, Z.D. Lan, L.H. Kong, Y.D. Huang, H.Z. Cui, *Surf. Coat. Technol.* 205 (2011) 3347–3355.
- [98] X. B.Chen, N. Biribilis, T.B. Abbott, *Corros. Sci.* 55 (2012) 226–232.
- [99] M. Zhao, J.G. Li, G.P. He, H.L. Xie, Y.A. Fu, *Appl. Surf. Sci.* 282 (2013) 499–505.
- [100] A. Alabباسي, B.M. Kannan, R. Walter, M. Störmer, C. Blawert, *Mater. Lett.* 106 (2013) 18–21.
- [101] Y.K. Pan, C.Z. Chen, D.G. Wang, Z.Q. Lin, *Mater. Chem. Phys.* 141 (2013) 842–849.
- [102] Y.H. Gu, S. Bandothyay, C.F. Chen, C. Y.Ning, Y.J. Guo, *Mater. Des.* 46 (2013) 66–75.
- [103] Q. Wang, L.L. Tan, W. L.Xu, B.C. Zhang, K. Yang, *Mater. Sci. Eng. B* 176 (2011) 1718–1726.
- [104] G.Y. Liu, S. Tang, D. Li, J. Hu, *Corros. Sci.* 79 (2014) 206–214.
- [105] R.C. Zeng, F. Zhang, Z.D. Lan, H.Z. Cui, E.H. Han, *Corros. Sci.* 88 (2014) 452–459.
- [106] Z.Z. Yin, R.C. Zeng, L.Y. Cui, Y.H. Zou, S.Q. Li, F. Zhang, *J. Shandong Univ. Sci. Technol. Nat. Sci.* 2 (2017) 57–69.
- [107] W.Q. Zhou, D.Y. Shan, E.H. Han, W. Ke, *Corros. Sci.* 50 (2008) 329–337.
- [108] L.P. Xu, F. Pan, G.N. Yu, E.Zhang L.Yang, K. Yang, *Biomaterials* 30 (2009) 1512–1523.
- [109] Y.W. Song, D.Y. Shan, R.S. Chen, F. Zhang, E.H. Han, *Surf. Coat. Technol.* 203 (2009) 1107–1113.
- [110] C. Wang, S.L. Zhu, F. Jiang, F.H. Wang, *Corros. Sci.* 51 (2009) 2916–2923.
- [111] N.V. Phuong, S. Moon, *Mater. Lett.* 122 (2014) 341–344.
- [112] R.C. Zeng, Z.D. Lan, L.H. Kong, Y.D. Huang, H.Z. Cui, *Surf. Coat. Technol.* 205 (2011) 3347–3355.
- [113] R.C. Zeng, H.U. Yan, F. Zhang, Y.D. Huang, Z.L. Wang, S.Q. Li, E.H. Han, *Trans. Nonferrous Met. Soc. China* 26 (2016) 472–483.
- [114] Y.H. Zou, R.C. Zeng, Q.Z. Wang, L.J. Liu, Q.Q. Xu, C. Wang, Z.W. Liu, *Front. Mater. Sci.* 10 (2016) 281–289.
- [115] L. Mao, G.Y. Yuan, J. L.Niu, Y. Zong, W.J. Ding, *Mater. Sci. Eng. C* 33 (2013) 242–250.
- [116] T.T. Yan, L.L. Tan, B.C. Zhang, K. Yang, *J. Mater. Sci. Technol.* 30 (2014) 666–674.
- [117] X.L. Liu, Z. Zhen, J. Liu, T.F. Xi, Y.D. Zheng, S.K. Guan, Y.F. Zheng, Y. Cheng, *J. Mater. Sci. Technol.* 31 (2015) 733–743.
- [118] M. Thomann, C. Krause, N. Angrisani, D. Bormann, T. Hasel, H. Windhagen, A. Meyer-Lindenberg, *Mater. Res.* 93A (2010) 1609–1619.
- [119] F. Witte, J. Fischer, J. Nellesen, C. Vogt, J. Vogt, T. Donath, F. Beckmann, *Acta Biomater.* 6 (2010) 1792–1799.
- [120] S. Fintová, J. Drábiková, F. Pastorek, J. Tkacz, I. Kuběna, L. Trško, B. Hadzima, J. Minda, P. Doležal, J. Wasserbauer, P. Ptáček, *Surf. Coat. Technol.* 357 (2019) 638–650.
- [121] R.Y. Zhang, S. Cai, G.H. Xu, H. Zhao, Y. Li, X.X. Wang, K. Huang, M. G.Ren, X.D. Wu, *Appl. Surf. Sci.* 313 (2014) 896–904.
- [122] L. Liu, Q.Y. Yang, L. Huang, X.M. Liu, Y.Q. Liang, et al., *Appl. Surf. Sci.* 484 (2019) 511–523.
- [123] M. Armand, F. Endres, D.R. Macfarlane, H. Ohno, B. Scrosati, *Nat. Mater.* 8 (2009) 621–629.

- [124] J.L. Zhang, C.D. Gu, Y. Wei, J.P. Tu, X.D. Ding, *Surf. Coat. Technol.* 344 (2018) 702–709.
- [125] N. Birbilis, P.C. Howlett, D.R. Macfarlane, M. Forsyth, *Surf. Coat. Technol.* 201 (2007) 4496–4504.
- [126] P. Huang, J.A. Latham, D.R. Macfarlane, P.C. Howlett, M. Forsyth, *Electrochim. Acta* 110 (2013) 501–510.
- [127] J. Efthimiadis, W.C. Neil, A. Bunter, P.C. Howlett, B.R. Hinton, D.R. MacFarlane, M. Forsyth, *ACS Appl. Mater. Interfaces* 2 (2010) 1317–1323.
- [128] P.C. Howlett, T. Khoo, G. Mooketsi, J. Efthimiadis, D.R. Macfarlane, M. Forsyth, *Electrochim. Acta* 55 (2010) 2377–2383.
- [129] Y.F. Zhang, S.S. Jamali, X.Liu, B.R.W. Hinton, S.E. Moulton, G.G. Wallace, M. Forsyth, *Surf. Coat. Technol.* 296 (2016) 192–202.
- [130] H.H. Elsentriecy, J. Qu, H.M. Luo, H.M.M. Iii, C. Ma, M.F. Chi, *Thin Solid Films* 568 (2014) 44–51.
- [131] E.L. Smith, A.P. Abbott, K.S. Ryder, *Chem. Rev.* 114 (2014) 11060–11082.
- [132] C.D. Gu, W. Yan, J.L. Zhang, J.P. Tu, *Corros. Sci.* 106 (2016) 108–116.
- [133] J.L. Zhang, C. D.Gu, Y.Y. Tong, W. Yan, J.P. Tu, *Adv. Mater. Interfaces* 3 (2016) 1500694.
- [134] L. Cao, L. Wang, L.Y. Fan, W.J. Xiao, B.P. Lin, Y.M. Xu, J. Liang, B.C. Cao, *Materials* 10 (2017) 358.
- [135] Y.B. Zhao, L.Q. Shi, L.Y. Cui, C.L. Zhang, S.Q. Li, R.C. Zeng, F. Zhang, Z.L. Wang, *Acta Metall. Sin.* 31 (2018) 180–188.
- [136] B.P. Lin, M. Zhong, C.D. Zheng, L. Cao, D. L. Wang, L. Wang, *Surf. Coat. Technol.* 281 (2015) 82–88.
- [137] S. Mann, B.R. Heywood, S. Rajam, V.J. Wade, *Molecular recognition in biomineralization*, in: S. Suga, H. Nakahara (Eds.), *Mechanisms and Phylogeny of Mineralization in Biological Systems*, Springer, Tokyo, 1991, pp. 47–55.
- [138] L.Y. Cui, G.B. Wei, R.C. Zeng, S.Q. Li, Y.H. Zou, E.H. Han, *Bioact. Mater.* 3 (2018) 245–249.
- [139] L.C. Li, J.C. Gao, Y. Wang, *Surf. Coat. Technol.* 185 (2004) 92–98.
- [140] S. Kunjukunju, A. Roy, M. Ramanathan, B. Lee, J.E. Candiello, P.N. Kumta, *Acta Biomater.* 9 (2013) 8690–8703.
- [141] X.P. Lu, M. Moledano, C. Blawert, E. Matykina, R. Arrabal, K. Kainer, M.L. Zheludkevich, *Surf. Coat. Technol.* 307 (2016) 1165–1182.
- [142] Y.H. Gu, C.F. Chen, S. Bandopadhyay, C.Y. Ning, Y.J. Zhang, Y.J. Guo, *Appl. Surf. Sci.* 258 (2012) 6116–6126.
- [143] B. Wang, J.H. Gao, L.G. Wang, S.J. Zhu, S.K. Guan, *Mater. Lett.* 70 (2012) 174–176.
- [144] U. Malayoglu, K.C. Tekin, S. Shrestha, *Surf. Coat. Technol.* 205 (2010) 1793–1798.
- [145] T.S.N.S. Narayanan, M.H. Lee, *RSC Adv.* 6 (2016) 16100–16114.
- [146] C.Y. Li, X.L. Feng, X.L. Fan, X.T. Yu, Z.Z. Yin, M. Bobby Kannan, X.B. Chen, *Adv. Eng. Mater.* (2019), doi:10.1002/adem.201900446.
- [147] R.C. Zeng, L.Y. Cui, K. Jiang, R. Liu, B.D. Zhao, Y.F. Zheng, *ACS Appl. Mater. Interfaces* 8 (2016) 10014–10028.
- [148] Y.H. Gu, S. Bandopadhyay, C.F. Chen, Y.J. Guo, C.Y. Ning, *J. Alloy. Compd.* 543 (2012) 109–117.
- [149] B. Salami, A. Afshar, A. Mazaheri, *J. Magnes. Alloy.* 2 (2014) 72–77.
- [150] V. Ezhilselvi, J. Nithin, J.N. Balaraju, S. Subramanian, *Surf. Coat. Technol.* 288 (2016) 221–229.
- [151] L.C. Zhao, C.X. Cui, Q.Z. Wang, S.J. Bu, *Corros. Sci.* 52 (2010) 2228–2234.
- [152] Y. Xiong, C. Lu, C. Wang, R.G. Song, *Appl. Surf. Sci.* 322 (2014) 230–235.
- [153] L.X. Chen, Y.Y. Sheng, H.Y. Zhou, Z.B. Li, X.J. Wang, W. Li, *Corros. Sci.* 148 (2019) 134–143.
- [154] W.T. Yu, R.X. Sun, Z.Q. Guo, Z.Y. Wang, Y. He, G.Y. Lu, G.Y. Chen, P.Y. Chen, K.Z. Chen, *Appl. Surf. Sci.* 464 (2019) 708–715.
- [155] X.H. Zheng, Q. Liu, H.J. Ma, S. Das, Y.H. Gu, L. Zhang, *Surf. Coat. Technol.* 347 (2018) 286–296.
- [156] L. Ren, X. Lin, L.L. Tan, K. Yang, *Mater. Lett.* 65 (2011) 3509–3511.
- [157] Z.Y. Ding, L.Y. Cui, X.B. Chen, R.C. Zeng, S.K. Guan, S.Q. Li, F. Zhang, Y.H. Zou, Q.Y. Liu, *J. Alloy. Compd.* 764 (2018) 250–260.
- [158] L.Y. Cui, R.C. Zeng, S.K. Guan, W.C. Qi, F. Zhang, S.Q. Li, E.H. Han, *J. Alloy. Compd.* 695 (2017) 2464–2476.
- [159] J. Tedim, A. Kuznetsova, A.N. Salak, F. Montemor, D. Snihirova, M. Pilz, M.L. Zheludkevich, M.G.S. Ferreira, *Corros. Sci.* 55 (2012) 1–4.
- [160] M.Q. Zhao, Q. Zhang, J.Q. Huang, F. Wei, *Adv. Funct. Mater.* 22 (2012) 675–694.
- [161] X. Bi, H. Zhang, L.G. Dou, *Pharmaceutics* 6 (2014) 298–332.
- [162] Q.S. Dong, Z.X. Ba, Y.Q. Jia, et al., *J. Magnes. Alloy.* 5 (2017) 320–325.
- [163] F. Zhang, Z.G. Liu, R.C. Zeng, S.Q. Li, H.Z. Cui, L. Song, E.H. Han, *Surf. Coat. Technol.* 258 (2014) 1152–1158.
- [164] R.C. Zeng, Z.G. Liu, F. Zhang, S.Q. Li, H.Z. Cui, E.H. Han, *J. Mater. Chem. A* 2 (2014) 13049–13057.
- [165] R.C. Zeng, X.T. Li, Z.G. Liu, F. Zhang, S.Q. Li, H.Z. Cui, *Front. Mater. Sci.* 9 (2015) 355–365.
- [166] G. Zhang, L. Wu, A.T. Tang, et al., *RSC Adv.* 8 (2018) 2248–2259.
- [167] G. Zhang, L. Wu, A. Tang, X.B. Chen, Y.L. Ma, Y. Long, P. Peng, X.X. Ding, H.L. Pan, F.S. Pan, *Appl. Surf. Sci.* 456 (2018) 419–429.
- [168] G. Zhang, L. Wu, A.T. Tang, et al., *Corros. Sci.* 139 (2018) 370–382.
- [169] S. Shadanbaz, G.J. Dias, *Acta Biomater.* 8 (2012) 20–30.
- [170] S.V. Dorozhkin, *Acta Biomater.* 10 (2014) 2919–2934.
- [171] G.S. Wu, J.M. Ibrahim, P.K. Chu, *Surf. Coat. Technol.* 233 (2013) 2–12.
- [172] R.C. Zeng, J. Chen, J. Kuang, J. Zhang, Y. Wang, *Rare Met.* 29 (2010) 193–197.
- [173] G.S. Wu, A. Shanaghi, Y. Zhao, X. Zhang, R.Z. Xu, Z. Wu, G.Y. Li, P.K. Chu, *Surf. Coat. Technol.* 206 (2012) 4892–4898.
- [174] C. Zhong, F. Liu, Y.T. Wu, J.J. Le, L. Liu, M.F. He, J. Zhu, W.B. Hu, *J. Alloy. Compd.* 520 (2012) 11–21.
- [175] H.R. Bakhsheshi-Rad, E. Hamzah, M. Kasiri-Asgarani, S.N. Saud, F. Yaghoubidoust, E. Akbari, *Vacuum* 131 (2016) 106–110.
- [176] P.J. Kelly, R.D. Arnell, *Vacuum* 56 (2000) 159–172.
- [177] H. Wu, A.M. Qasim, S. Xiao, Q. Huang, F. Zhang, Z.Z. Wu, R.K.Y. Fu, G.S. Wu, P.K. Chu, *Surf. Coat. Technol.* 352 (2018) 437–444.
- [178] Y.F. Ren, H. Zhou, M.Y. Nabyouni, S.B. Bhaduri, *Mater. Sci. Eng. C* 49 (2015) 364–372.
- [179] N. Yu, S. Cai, F.W. Wang, F.Y. Zhang, R. Ling, Y. Li, Y.Y. Jiang, G.H. Xu, *Ceram. Int.* 43 (2017) 2495–2503.
- [180] L.G. Wang, Z.Y. Cao, X. Qian, L. Zhu, D.P. Cui, A.D. Li, *ACS Appl. Mater. Interfaces* 9 (2017) 6634–6643.
- [181] X.M. Liu, Q.Y. Yang, Z.Y. Li, Y. Wei, Y.F. Zheng, Z.D. Cui, et al., *Appl. Surf. Sci.* 434 (2018) 1101–1111.
- [182] S.M. George, *Chem. Rev.* 110 (2010) 111–131.
- [183] M. Catherine, B. Mikhael, P. Nicola, *Adv. Mater.* 43 (2012) 1017–1032.
- [184] Y.Z. Zhu, X.M. Liu, K.W.K. Yeung, P.K. Chu, S.L. Wu, *Appl. Surf. Sci.* 400 (2017) 14–23.
- [185] Y. Li, H. Li, Q.Y. Xiong, X.M. Wu, J. Zhou, J.Z. Wu, W. Qin, *Nanoscale* 9 (2017) 8591–8599.
- [186] M.B. Kannan, *Mater. Lett.* 76 (2012) 109–112.
- [187] M.B. Kannan, O. Wallipa, *Mater. Sci. Eng. C* 33 (2013) 675–679.
- [188] M. Jamesh, S. Kumar, T.S. Narayanan, *J. Coat. Technol. Res.* 9 (2012) 495–502.
- [189] M. Saremi, S. H. Mohajernia, S. Hejazi, *Mater. Lett.* 129 (2014) 111–113.
- [190] M. Saremi, S. H. Mohajernia, S. Hejazi, *Adv. Mater. Res.* 829 (2014) 376–380.
- [191] H.X. Wang, S.J. Zhu, L.G. Wang, Y.S. Feng, X. Ma, S.K. Guan, *Appl. Surf. Sci.* 307 (2014) 92–100.
- [192] A. Alabbasi, M.B. Kannan, C. Blawert, *Mater. Lett.* 124 (2014) 188–191.
- [193] J.D. Sun, Y. Zhu, L. Meng, W. Wei, Y. Li, X.Y. Liu, Y.F. Zheng, *J. Mater. Chem. B* 3 (2015) 1667–1676.
- [194] F.X. Wu, J. Liang, W.X. Li, *J. Magnes. Alloy.* 3 (2015) 231–236.
- [195] Y.J. Shi, J. Pei, L. Zhang, B.K. Lee, Y. Yun, J. Zhang, Z.H. Li, S. Gu, K. Park, G.Y. Yuan, *Corros. Sci.* 123 (2017) 297–309.

- [196] B. Wang, L. Zhao, W. Zhu, L. Fang, F. Ren, Colloids Surf. B 157 (2017) 432–439.
- [197] R.C. Zeng, L.J. Liu, T.T. Pang, F. Zhang, W.W. Zhang, S.Q. Li, H.Z. Cui, E.H. Han, Acta Metall. Sin. 28 (2015) 373–380.
- [198] X.N. Gu, H.M. Guo, F. Wang, Y. Lu, W.T. Lin, J. Li, Y.F. Zheng, Y.B. Fan, Mater. Lett. 193 (2017) 266–269.
- [199] X. Liu, Z.L. Yue, T. Romeo, J. Weber, T. Scheuermann, S. Moulton, G. Wallace, Acta Biomater. 9 (2013) 8671–8677.
- [200] Y.Q. Chen, S. Zhao, M.Y. Chen, W.T. Zhang, J.L. Mao, Y.C. Zhao, M.F. Maitz, N. Huang, G.L. Wan, Corros. Sci. 96 (2015) 67–73.
- [201] F. Zhang, C.L. Zhang, L. Song, R.C. Zeng, S.Q. Li, H.Z. Cui, J. Mater. Sci. Technol. 31 (2015) 1139–1143.
- [202] C.L. Zhang, F. Zhang, L. Song, R.C. Zeng, S.Q. Li, E.H. Han, J. Alloy. Compd. 728 (2017) 815–826.
- [203] X.X. Zhang, Q. Li, L.Q. Li, P. Zhang, Z.W. Wang, F. Chen, Mater. Lett. 88 (2012) 76–78.
- [204] R.K. Gupta, K. Mensah-Darkwa, J. Sankar, D. Kumar, Trans. Nonferrous Met. Soc. China 23 (2013) 1237–1244.
- [205] V. Chiono, I. Carmagnola, P. Gentile, F. Boccafroschi, C. Tonda-Turo, M. Ballarini, Surf. Coat. Technol. 206 (2012) 2446–2453.
- [206] Y. Zhao, L.Q. Shi, X.J. Ji, J.C. Li, Z.Z. Han, S.Q. Li, R.C. Zeng, F. Zhang, Z.L. Wang, J. Colloid Interface Sci. 526 (2018) 43–50.
- [207] D.V. Andreeva, E.V. Skorb, D.G. Shchukin, ACS Appl. Mater. Interfaces 2 (2010) 1954–1962.
- [208] L.J. He, J.C. Hao, L. Dai, R.C. Zeng, S.Q. Li, Mater. Lett. 261 (2020) 127001.
- [209] D.J. Schmidt, J.S. Moskowitz, P.T. Hammond, Chem. Mater. Chem. Mater. 22 (2010) 6416–6425.
- [210] N. Ostrowski, B. Lee, N. Enick, B. Carlson, S. Kunjukunju, A. Roy, P.N. Kumta, Acta Biomater. 9 (2013) 8704–8713.
- [211] F. Fan, C.Y. Zhou, X. Wang, J. Szpunar, ACS Appl. Mater. Interfaces 7 (2015) 27271–27278.
- [212] S. Kunjukunju, A. Roy, M. Ramanathan, B. Lee, J.E. Candiello, P.N. Kumta, Acta Biomater. 9 (2013) 8690–8703.
- [213] P.A. Chiarelli, M.S. Johal, J.L. Casson, J.B. Roberts, J.M. Robinson, H.L. Wang, Adv. Mater. 13 (2001) 1167–1171.
- [214] J. Cho, K. Char, J.D. Hong, K.B. Lee, Adv. Mater. 13 (2001) 1076–1078.
- [215] J.J. Richardson, M. Björnalm, F. Caruso, Science 348 (2015) 2491.
- [216] T.T. Yuan, J. Yu, J. Cao, F. Gao, Y. Zhu, Y. Cheng, Materials 9 (2016) 384–394.
- [217] M. Yazdimamaghani, M. Razavi, D. Vashae, L. Tayebi, Mater. Lett. 132 (2014) 106–110.
- [218] A. Leroy, C. Pinese, C. Bony, X. Garric, D. Noel, B. Nottelet, Mater. Sci. Eng. C 33 (2013) 4133–4139.
- [219] M.B. Kannan, S. Liyanaarachchi, Mater. Chem. Phys. 142 (2013) 350–354.
- [220] A. Alabbasi, A. Mehjabeen, M.B. Kannan, Q. Ye, C. Blawert, Appl. Surf. Sci. 301 (2014) 463–467.
- [221] X.J. Wang, C. Wen, Appl. Surf. Sci. 303 (2014) 196–204.
- [222] Z.J. Li, X.Y. Jing, Y. Yuan, M.L. Zhang, Corros. Sci. 63 (2012) 358–366.
- [223] S.W. Xia, Y. Liu, D.M. Fu, B. Jin, J. Lu, J. Mater. Sci. Technol. 32 (2016) 1245–1252.
- [224] Z.Y. Ma, Metall. Mater. Trans. A 39 (2008) 642–658.
- [225] K. Singh, G. Singh, H. Singh, J. Magnes. Alloy 6 (2018) 399–416.
- [226] Q. Liu, Q.X. Ma, G.Q. Chen, X. Cao, S. Zhang, J.L. Pan, G. Zhang, Q.Y. Shi, Corros. Sci. 138 (2018) 284–296.
- [227] G.H. Cao, D.T. Zhang, Z. Wen, Q. Cheng, J. Alloy. Compd. 363 (2015) 12–19.
- [228] F.J. Liu, Y. Ji, Q.S. Meng, Z.S. Li, Vacuum 133 (2016) 31–37.
- [229] S.J. Zhu, J. Jin, J. Wang, Y.F. Sun, J. Chen, L.G. Wang, H. Fujii, S.K. Guan, Effect of friction stir processing on microstructures and corrosive properties in simulated body fluid of biological Mg-Zn-Y-Nd alloy, in: Proceedings of the 1st International Joint Symposium on Joining and Welding, Woodhead Publishing, 2013, pp. 411–415, doi:10.1533/978-1-78242-164-1.411.
- [230] Y.Y. Yang, H. Wu, Mater. Lett. 63 (2009) 19–21.
- [231] B.J. Zheng, X.M. Chen, J.S. Lian, Opt. Lasers Eng. 48 (2010) 526–532.
- [232] V. Pandey, J.K. Singh, K. Chattopadhyay, N.C.S. Srinivas, V. Singh, J. Alloy Compd. 727 (2017) 826–840.
- [233] M. Thomas, M. Jackson, Scr. Mater. 66 (2012) 1065–1068.
- [234] S.E. Khany, M.A. Moyeed, M.S. Siddiqui, G.M.S. Ahmed, M.M.A. Baig, Mater. Today 2 (2015) 3363–3370.
- [235] Y.K. Wei, Y.J. Li, Y. Zhang, X.T. Luo, C.J. Li, Corros. Sci. 138 (2018) 105–115.
- [236] N. Barry, S.V. Hainsworth, M.E. Fitzpatrick, Mater. Sci. Eng. A 507 (2009) 50–57.
- [237] H. Kovacı, Y.B. Bozkurt, A.F. Yetim, M. Aslan, A. Çelik, Surf. Coat. Technol. 360 (2019) 78–86.
- [238] E. Segurado, F.J. Belzunce, I.F. Pariente, Surf. Coat. Technol. 340 (2018) 25–35.
- [239] P. Zhang, J. Lindemann, Scr. Mater. 52 (2005) 485–490.
- [240] M. Jamalain, D.P. Field, Mater. Charact. 148 (2019) 9–16.
- [241] C.C. Liu, H. Zheng, X. Gu, B.L. Jiang, J. Liang, J. Alloy. Compd. 770 (2019) 500–506.
- [242] S. Bagherifard, D.J. Hickey, S. Fintová, F. Pastorek, I. Fernandez-Pariente, M. Bandini, T.J. Webster, M. Guaglianosa, Acta Biomater. 66 (2018) 93–108.
- [243] W.D. Wang, W. Peng, L. Chen, L.L. Tan, W.R. Li, L.G. Li, K. Yang, Regen. Biomater. 2 (2015) 107–118.
- [244] Y.K. Pan, C.Z. Chen, D.G. Wang, T.G. Zhao, Colloids Surf., B. 109 (2013) 1–9.
- [245] D.A. Robinson, R.W. Griffith, D. Shechtman, R.B. Evans, M.G. Conzemius, Acta Biomater. 6 (2010) 1869–1877.
- [246] H.R. Bakhsheshi-Rad, E. Hamzah, A.F. Ismail, M. Aziz, M. Kasiri-Asgarani, H. Ghayour, Mater. Corros. 68 (2017) 1228–1236.
- [247] Y. Yang, K. Zheng, R. Liang, A. Mainka, N. Taccardi, J.A. Roether, R. Detsch, W.H. Goldmann, S. Virtanen, A.R. Boccaccini, Biomed. Mater. 13 (2017) 015001.
- [248] Y. Li, X.Q. Liu, L. L. Tan, L. Ren, P. Wan, Y.Q. Hao, X.H. Qu, K. Yang, K.R. Dai, J. Mater. Sci. Technol. 32 (2016) 865–873.