



Active Corrosion Protection of Mg–Al Layered Double Hydroxide for Magnesium Alloys: A Short Review

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Abstract: Layered double hydroxides (LDHs) have been successfully applied in surface protection and functionalization of metal materials owing to their special structure, composition, controllability, anion exchange, and other excellent properties. Herein, this review focused on the most common LDH preparation methods on magnesium alloys in the past 10 years by summarizing about 70 research papers. At the same time, based on the corrosion protection mechanism of LDH materials, the performance of LDH films and LDH as filler on metal substrates was briefly introduced. The surface of LDH materials were chemically modified to enhance their compatibility with solvents, and their corrosion resistance function was developed as an additive. Finally, LDH-based composite coatings on Mg alloys by surface pretreatment and chemical modification were discussed.

Keywords: layered double hydroxides; magnesium alloy; corrosion protection; composite coating

1. Introduction

Magnesium (Mg) and its alloys, known as the lightest metal structural materials, are widely applied in the computer, electronics, automotive, and aerospace industries due to their advantages (including their low specific gravity, high specific strength and stiffness, processing, and recycling) [1-3]. The overall weight of a car is reduced by 10% and the fuel is economized by about 20%–30% with no significant design changes through using magnesium alloys [4]. In addition, the elastic modulus of magnesium alloys is similar to that of the human skeleton, which can relieve external stress and represent the major component of artificial skeletons. Therefore, as a medical material, magnesium alloys are ideal materials for cartilage repair and metal implantation [5,6]. Although magnesium alloys have many excellent properties, their inferior corrosion resistance due to the low standard potential (-2.36 V) limits their further development and extensive applications [7]. Hence, research on corrosion resistance of magnesium alloys is an important topic for their wide application. In the past few decades, plenty of approaches have been used to combat the corrosion of Mg alloys including alloying, improved heat treatment process, and advanced surface treatment technology. Among them, surface treatment technology is the most extensive and effective method, including chemical conversion coatings, polymer coatings, micro-arc oxidation (MAO), layer-by-layer film, and LDH coatings.

In recent years, LDHs have gained a key position not only due to environmentally friendly and low cost but more importantly due to their the high anionic exchange capability [8]. As a result, intercalated materials have shown broad application prospects as corrosion resistant coatings.

LDH is a type of hydrotalcite-like materials, composed of two or more metallic elements, with a layered structure of hydroxide [9]. The first studies of hydrotalcite com-



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). pounds can be traced back to 1842, a natural deposit from Norway was discovered by Hochstetter [10]. However, it was not until Manasse (1915) and Frondel (1941) that the structure of hydrotalcite was understood. In 1942, Feitknecht first proposed the idea of a double-layer structure and synthesized LDH by mixing a metal salt solution with an alkali metal hydroxide LDH [11]. LDHs consist of positive-charged laminae of mixed metal ion $M^{3+}/(M^{2+}+M^{3+})$ hydroxide layers, anions with water molecules among the layers. As depicted in Figure 1, the general crystal structure of LDH films is $[M^{2+}_{1-x} M^{3+}_x (OH)_2]^{x+}(A^{m-})_{x/m} \cdot nH_2O$, where M^{2+} refers to metal cations (e.g., Mg^{2+} , Zn^{2+} , Cu^{2+} , Ni^{2+}), M^{3+} means trivalent cationic (e.g., Al^{3+} , Fe^{3+} , Cr^{3+}), x is the mole ratio of $M^{3+}/(M^{2+}+M^{3+})$ and A^{m-} is an anion with m⁻ valence [12]; Whereas, layers of hydroxide are studded with water molecules during the synthesis [13]. Basically, the crystal structure, bonding strength and anion exchange capacity of LDH depend on the size and charge of the metal cation, the charge of the anion, and the relative amount of crystal water [14].



Figure 1. Schematic illustration of LDH structure and chemical component.

LDHs have potential applications in catalysis, functional materials, environmental protection, and biomedicine fields due to their unique memory effect and interlayer anion exchange capacity [15]. Recently, it has been widely used as prepared LDH coatings on alloys due to broad resource of raw material, simple synthesis methods, and synthesis in large quantities, especially on magnesium alloys [16].

The development of LDH can be traced back to recent research. In early 1997, Buchheit et al. [17] developed a number of LDH coatings; in their work, a hydrotalcite protective coating was created and contributed greatly to the progress of in-situ growth methods. Previous works have proven that LDH-based materials could serve as potential adsorbents and catalysts for the purification of dye waste water due to their special anionic exchange capability. Basu et al. [18] reviewed the production progress of LDH materials and based elastomer composites. In recent years, adjusting the composition of LDH to obtain ideal properties, which leading to various application in various industries. Given this, various LDHs and their coatings are prepared on Mg alloy surface to improve their corrosion resistance. In different types of LDH materials, a double compound consisting of Mg–Al LDH and carbonate as interlayer anions has been widely used in various fields.

At present, surface modification is still the most appropriate strategy to overcome the rapid corrosion of magnesium alloys and improve their performance, especially by adjusting the composition of LDH to obtain better performances. This review focus on describing the recent progress of common methods for preparing Mg–Al LDH coatings on magnesium alloys. In this work, the main fabrication methods are summarized, such as coprecipitation, in-situ growth, hydrothermal synthesis, urea hydrolysis, steam coating, electrochemical

deposition, rotating coating, and anion exchange reaction. Then the properties of LDH film and its application on metal substrate are introduced from the anticorrosion mechanism of LDH material. The surface chemical modification of LDH material was further analyzed to improve its compatibility with solvent, and the corrosion resistance of LDH material was developed. Finally, we will put forward the current limitations and future development direction from the perspective of application, and make a conclusion.

2. Synthesis of LDH

2.1. Co-Precipitation

Co-precipitation (CPT) means that under the protection of nitrogen, two or more kinds of soluble salt with the layered structure of metal ions are uniformly mixed, and the corresponding solid particles are obtained through precipitation reaction at an appropriate pH [18]. The CPT approach is one of the most attractive technique for preparing LDH intercalation materials. Due to the limitation of different pH values, it is difficult for metal ions such as Co, Mn, and Cr to achieve the purpose of co-precipitation under the conditions of pH values needed for urea decomposition. Therefore, the co-precipitation method is the only suitable for the preparation of LDH intercalation materials of Mg, Al, Zn, and other metals. The combination of CPT and hydrothermal reaction can form LDH coatings of different systems, no matter what the chemical composition of the substrate, the laminates, and the types of anions among the layers are different [19].

Zhang et al. [20] synthetised Mg–Al LDH coating on AZ31 alloy surface through the co-precipitation method and hydrothermal method. The LDH coatings showed extremely lower corrosion current density, which can be regarded as a candidate material for nonchromium chemical conversion coating of Mg–Al alloys. As showed in Figure 2, LDH layers are well combined with each other, and no defects are found at the interface. The whole Mg–Al LDH coatings were observed to be smooth and compact, which improves the adhesion of the substrate material and coating. Wu et al. [21] prepared Mg–Al LDH coatings with porous organic surface layer by integrating the co-precipitation technique and hydro-thermal synthesis method for the expanded application of Mg alloys. This work shows that appropriate addition of polyglutamic acid (PGA) can prolong the corrosion time of the composite coating when the pH reaches the minimum value, thus the corrosion resistance of AZ31 alloy were improved by the composite coating on the furface.



Figure 2. (**a**–**c**) The SEM images of the LDH coating on Mg alloy with different magnification; (**d**) the cross-sectional SEM images (crystallization with 48 h). Reprinted with permission from [20]; Copyright 2014 Elsevier.

widely used in the preparation of LDH powder due to its time consuming and poor adhesion between substrate and coating, which is not suitable for the preparation of coating on metal substrate [23].

2.2. In-Situ Growth Methods

The in-situ growth method refers to the selection of a special surface treatment of the metal plate, which directly participates in the reaction and provides metal cationic on the metal substrate to form a film technology. It is considered to be the most promising method due to good adhesion between LDH films and substrate formed by chemical bonds [24]. At present, there are five methods for in-situ growth synthesis of LDH films on Mg alloys.

2.2.1. One-Step In-Situ Growth Method

The one-step in-situ growth technique has been regarded as a promising method which can straight synthetize LDH films on the substrate and greatly improve the mechanical properties and adhesion of coating to the substrate. Yang et al. [25] determined that Mg–Al LDH films were first phosphorylated on cellulose microspheres (CMs) and then prepared by in-situ nano-growth. This finding offers a new approach that can not only improve the production and crystallinity of Mg–Al LDH but also improve the load of Mg–Al LDH and the porous structure of CMs, so that Mg–Al LDH @CMs are suited for superhydrophobic treatment. Th et al. [26] studied an inhibitor (2-mercapto benzo thiazole, MBT) combined with Mg–Al LDH coatings (Mg–Al LDH/MBT) on AZ31 alloy substrate at comparatively low temperature (95 °C) and environmental pressure by one-step in-situ growth technique. Then, the corrosion protection of the composite coating was evaluated by various testing method. As shown in Figure 3, the corrosion current density of LDH/MBT composite coatings are very low, and even there is no corrosion behavior exposed to NaCl solution or salt spray environment for 15 days, which proves its good corrosion resistance.



Figure 3. Digital images of (**a**) blank; (**b**) MBT; (**c**) Mg–Al LDHs; and (**d**) Mg–Al LDHs/MBT films synthetize with various reaction times at 95 °C and 1 barometric pressure. Reprinted with permission from [26]; Copyright 2021 Elsevier.

At present, Mg–Al LDH coatings produced through one-step in-situ growth technique on Mg alloys can solve the adverse effects brought by hydro-thermal method under higher temperatures and higher pressures in the past. However, it is worth noting that this process is merely applicable to Mg–Al alloys.

2.2.2. Two-Step In-Situ Growth Method

The two-step in-situ growth method consists of two parts: pre-treatment to embed ions into the LDH coatings, and post-treatment to maintain alignment by adding NaOH solution. Anjumet et al. [27] successfully prepared Mg–Al LDH coatings embedded with 8 hydroxy quinoline (8HQ) on AZ31 by two-step in-situ growth technique and studied the effect of 8HQ concentration on morphology and corrosion resistance. The results reveal that the LDH film possessed the function of ion exchange and chelation formation, and the 8HQ inserted into the layer has stronger corrosion resistance, which can better protect the metal from corrosion. Chen et al. [28] first made uses of the magnesium containing only alpha phase and magnesium alloys (with or without aluminum). After the sample was treated with NaOH solution, the initial precursor film was obtained and soaked at 80 °C for 1.5 h to obtain the final Mg–Al LDH coatings. It was concluded that the two-step in-situ growth approach is also suitable for other Mg alloys whether or not they contain Al elements, so long as the process parameters are properly adjusted. Therefore, the corrosion resistance of most Mg alloys can be improved by the two-step in-situ growth method.

According to the above statement, the in-situ growth method can obtain dense coating under the condition of controlling pH value, but the process is complicated. In this technique, the substrate is immersed in a solution of metal salts, the alkalis of the solution are added to control the pH value, and the metal substrate effectively becomes the metal source of the reaction, on which the film grows sacrifices part of the substrate [29]. Therefore, this method is only suitable for preparing LDH films directly on the metal matrix, but not for preparing LDH powder/particles.

2.2.3. Hydrothermal Treatment

Hydrothermal treatment method refers to the LDH obtained by mixing metal oxides or metal hydroxides with an alkaline solution in a high-pressure reactor for a period of time under certain temperature and pressure conditions. Yttrium-doped Mg–Al–Y LDH films reported by Yao et al. [30] revealed that Y ions perfectly inserted into the Mg–Al LDH by substitution, which not only enhance the corrosion resistance of the coating, but also makes the coating having the ability of self-repair. A new approach for composite coating on Mg alloy was designed by Li et al. [31]. As shown in Figure 4, the closed porosity of LDH layer and the absorption capacity of chloride ion limit the penetration of corrosive Cl⁻, and provide effective anti-corrosion protection for oxide film coating. Liao et al. [32] prepared Mg–Al–CO₃ LDH through hydrothermal synthesis using MgO and Al₂O₃. It was found that LDH with good crystallinity could be obtained at 100 °C. With the increase of temperature, the composition of brucite and bauxite in the reaction product increased gradually.

LDH is typically prepared by placing two mixed oxides in an autoclave with deionized water (DI) at 140 °C for several days [33]. Consequently, the main advantages of hydrothermal synthesis are a completely crystalline structure, obviously layered structure, and uniform grain size distribution of LDH [34]. However, it is worth noting that this method is suitable for use at high temperatures.



Figure 4. The schematic presentation of LDH structure, the anionic exchange with inhibitor ion, and their triggered release for corrosion protection. Adapted with permission from [34]; Copyright 2020 Elsevier.

2.2.4. Urea Hydrolysis

Urea is a kind of base with high solubility in water; it is easy to control the hydrolysis rate. It can generate ammonium hydroxide by hydrolysis in water, while CO_3^{2-} generated by hydrolysis can be used as interlayer anion for the synthesis of LDH in alkaline environment [35]. By controlling the hydrothermal conditions, Hibino et al. [36] synthesized Mg-Al LDH on Mg alloy using urea hydrolysis reaction. The advantage of this method is that the synthesized LDH has a high crystallization and large volume. However, when the Mg/Al ratio of the product in the initial solution with high concentration of metal ions reaches about two, the by-product will be produced, which means that there are the hydrated magnesium hydroxide phases. Zeng et al. [37] used the urea hydrolysis method to grow nano-sized LDH conversion films in-situ on AZ31 alloy. As shown in Figure 5, the dissolved Mg²⁺ in the precursor membrane is composed of MgCO₃ and $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ based on the mechanism of membrane formation. Secondly, the precursor is converted to crystallized Mg(OH)₂ under alkaline conditions. In the end, a more stable LDH structure with Al^{3+} in place of Mg^{2+} in $Mg(OH)_2$ was obtained. It was found that the nanostructure and ion exchange capacity of LDH can dramatically improve the corrosion protection of the AZ31 alloy.



Figure 5. Schematic diagram of Mg–Al LDH film. Adapted with permission from [37]; Copyright 20215 Elsevier.

Thus, a lot of similar findings display that urea hydrolysis can get good crystallization, bulky LDH films and product, but tended to produce by-products, and M²⁺ or M³⁺ could be consumed during the by-product formation process, leaving the number of LDHs following formation lower than usual [38].

2.2.5. Steam Coating

Steam coating is a method of preparing magnesium alloy anticorrosive coating without chemical steam using ultra-pure water as steam source. Ishizaki et al. [39] reported that protective Mg–Al LDH was produced on magnesium alloys through chemical-steam

coating, which is a simple, environmentally friendly, and inexpensive method. As shown in Figure 6, XRD analysis shows that Mg–Al LDH films have been successfully prepared. Corrosion experiments also show that the film has a good effect of protecting the substrate. Ishizaki et al. [40] obtained Mg(OH)₂ and Mg–Al LDH on Mg–Al alloy at 160 °C with 3–9 h exploiting aluminum nitrate (Al(NO₃)₃·9H₂O) aqueous solution as the vapor source by steam coating method.



Figure 6. (a) XRD patterns of the sample with various treatment, SEM graphics of the film coated AZ31 (b) before and (c) after immersion. Reprinted with permission from [39]; Copyright 2013 Royal Society of Chemistry.

The advantage of steam coating in contrast to other methods is that it can directly grow the film on the matrix material, and the adhesion between the two is good. Meanwhile, the corrosion protection of the composite film can be enhanced by increasing the Al content in the composite film. However, the main disadvantage of steam coating is that it limits the types of LDH cationic and the extremely high temperature required for the reaction [41].

2.3. Electrochemical Deposition

Electrochemical deposition can be seen as a valid method to produce LDH films, which has the advantages of high purity, fast deposition speed, and simple equipment. Wu et al. [42] produced Mg–Al LDH coatings on AZ31 magnesium alloy by electrochemical deposition. In particular, on behalf of dealing with LDH macropores, Al₂O₃ nanoparticles were grown on the coating by electrochemical deposition. The Mg–Al LDH film with nitrate is homogeneous and tight, thinner than that of Li-Al LDH film, but there are some small defects and cracks. Potentiodynamic polarization and EIS measurements demonstrated that the corrosion proctetion of LDH-coated magnesium alloy is better than that of magnesium alloy without coatings in 3.5 wt.% NaCl solutions. However, the electrochemical deposition method is more expensive and complicated than the above methods [43].

2.4. Spinning Coating

Spinning coating is another way of preparing regenerative smooth film, and the advantages of this method are that it is environment-friendly, provides excellent adhesion between film and substrate, uniform film formation, and achieves good micro-concave and convex structure on the surface. LDH films with good corrosion protection and bonding can be prepared through a simple process. Zhang et al. [44] combined LDH films on AZ31 Mg alloy through rotating coating method using aqueous solution as the vapor source. The obtained film surface is uniform, and the electrochemical polarization curve of the film after

coating for 7 h shows very low corrosion current density, which is much lower than that of AZ31 magnesium alloy without coating. The fantastic anticorrosive performance of LDH films on Mg alloys is obtained through spinning coating technology, since the infiltration of erosive ions is limited and therefore the corrosion of matrix is inhibited. Nevertheless, this method is not suitable for the substrates with complicated shape, and the protective action is also reduced due to the thin coatings [45].

2.5. Anion-Exchange

The anion-exchange method derives from the intracellular anion exchange feature of LDH, which not only maintains the original lamellar structure of LDH, but also selects the type of intracellular anions. Kim et al. [46] used anion exchange method to insert diacrylic acid and pvinyl benzoic acid into the LDH interlayer, and realized the polymerization of organic molecules in the LDH interlayer. The corrosion inhibition anions can be delivered slowly, and the corrosive media also can be adsorbed, owing to the LDHs produced by this method, so that the matrix is double-protected. Therefore, Cl⁻ or NO₃⁻ intercalation LDH is often used as the precursor to obtain some special composition of LDH materials through ion exchange reaction. Chen et al. [47] prepared Mg–Al LDH on AZ31 magnesium alloy and studied the corrosion mechanism of Mg–Al–CO₃²⁻ LDH. As showed in Figure 7, it can be seen that the surface of the matrix is completely overlapped with tight and falculate lamina, the coating is dense, smooth, and has almost no micro-cracks. Nevertheless, this method is demanding and the degree of crystallinity of the LDH is smaller than that of before-mentioned methods [48].



Figure 7. Images of the LDH film: (**a**) optical miscrostructure; SEM images with low magnification (**b**), and (**c**) high magnification. Reprinted with permission from [47].; Copyright 2012 Elsevier.

To sum up, although significant progress has been made in the preparation of Mg–Al LDH films on AZ31 Mg alloy surfaces, two major challenges remain to be considered when combining the advantages and disadvantages of each method. The first is how to make the size and specific surface area of LDH film adjustable. The second is that it is necessary to improve the service life of metal materials in large quantities, reduce the damage of corrosion products to products, and increase the application of corrosion protection in various engineering fields.

3. The Anti-Corrosion Mechanisms

For the past few years, LDH films are regarded as the next potential generation coating for magnesium alloys due to their stable lamellar structure and adjustable international anions, which can not only provide protection for the metal matrix but also absorb corrosive ions. The corrosion properties and corrosion resistance mechanism of LDH materials were investigate intensively [49].

3.1. Interlayer Anion Exchange Mechanism

LDHs are the best nanotube for corrosion inhibitor due to their stable layered structure, high efficiency, low cost, and simple operation. Adding only minor trace quantities of chemical substances to the corrosive medium through physical or chemistry reaction, which can slow down the speed of metal corrosion and keep the physical, the chemical properties of the metal unchanged. Interlamellar anion exchangeability is an important property of LDH, and its interlamellar anions can swap with various anions for obtaining materials with different functions [50].

Owing to the anion-exchange ability between LDH layers, it is an effective way for intercalating corrosion inhibitor into the protective layer with lamellar structure to obtain high corrosion protection of the substrate. Chen et al. [51] prepared corrosion inhibitor on AZ31 Mg alloy inserting aspartic acid (ASP) into Mg-Al LDH by one-step hydrothermal method. Resulting from the maximum porosity coverage rate and the lamellar nanostructure, Mg-Al-ASP LDH has a good corrosion inhibition performance and a higher specific surface area to insert invasive anionic species such as Cl⁻. Hence, it is an effective anticorrosive and environmentally friendly conversion coating for light metals and alloys. Zhang et al. [52] prepared nitrate-containing LDH in situ on Mg alloys with low Al content without introducing additional trivalent metal salts by using an anode film composed of Mg–Al mixed oxide (MgAl₂O₄ spinel) as an internal source. Then, vanadate inhibitor anions were inserted into the interlayer channel of LDH through anion exchange process. It can be seen that VO_3^- is beneficial to the protection of anode film and LDH NO_3^- under corrosion conditions due to the value of icorr = 5.1×10^{-7} A cm⁻² also higher than that of LDH VO3⁻. Although different corrosion inhibitor anions are inserted into LDH films according to the principle of anion exchange, only part of the anions show a high affinity for the lamellar structure. In order to prepare more stable LDH films with lamellar structure, Miyata obtained from the experiment that the anion exchange order in LDH intercalation is: $CO_3^{2-} > SO_4^{2-} > OH^- > F^- > Cl^- > Br^- > NO_3^-$. High-priced anions are easy to be exchanged into LDH materials, while low-priced anions are easy to be exchanged out. Therefore, in order to synthesize some special LDH materials, chloride ion or nitrate ion intercalation is often used, and LDH is obtained through ion exchange reaction as the precursor [53]. LDHs can be used as an effective component to inhibit the corrosion reaction of corrosive ions entering its interlayer, meanwhile LDH interlayer exchange corrosion inhibitor can also protect the matrix metal material from local corrosion.

In summary, LDH protects metal groups by physical barrier, anion exchange mechanism and surface modification. In other words, LDHs generally use physical barriers on the surface of the metal matrix to block the aggressive anions, so as to reduce the interaction between the substrate and the aggressive ions. In addition, LDH can also exchange and intercalate anions with electrolytes, and improve the protection of metal matrix by surface modification with organic solvents.

3.2. Composite Synergistic Corrosion Resistance Mechanisms

In recent years, water-borne epoxy resins have been considered as effective adhesives, coatings and compound substrates due to their good adhesion, stable chemical properties and good corrosion resistance. However, in the process of high temperature curing, waterborne epoxy resins can generate numerous micro-pores, which will allow the external corrosive media to penetrate into the protective matrix material, which severely restrict the wider application of waterborne epoxy resin [54]. Hayatdawoudi et al. [55] dispersed

scale inhibitor-intercalated LDH nanocontainers in a zinc-rich epoxy resin (ZRE) film. The effect of LDH nanocontainers on the protective properties of ZRE films was also studied. It was noticed that adding LDH nanocontainer into ZRE film can catch corrosive Cl⁻ and liberate appropriate substances, so the carbon steel matrix has a stronger corrosion inhibition performance. Secondly, due to the two-dimensional layered structure of LDH, their structure can block some holes in the coating, so as to effectively restrain permeation of corrosive ions in the film and improve the corrosion resistance of the matrix material. The ZRE intercalated LDH nanocontainers exhibit a blocking effect, sacrificing cathodic protection and intelligent inhibition in the curve area of the epoxy zinc-rich coating and reducing the local corrosion of zinc particles.

Graphene can effectively restrain oxygen and water molecules from diffusing into the surface of metal-based materials owing to the particular layered structure. The synergistic effect of adding other nano-materials and LDH interlayer inhibitor ions into graphite composites can enhance the corrosion protection of LDH films. Chen et al. [56] deposited graphene-modified LDH nanocephalic films on the surface of Mg alloy using a two-step method, and then studied the structure, morphology and composition of LDH/Graphene films. Experimental results showed that the modified Graphene layer can seal the pores of the nest-like LDH films, making LDH films have hydrophobicity (CA 127.8°) and enhance corrosion resistance, which can enhance the corrosion protection of the metal matrix. The synergistic action of the impermeable inert Graphene layer and the LDH substrate films loaded with active inhibitors give better anticorrosion performance of the composite films.

At present, organic coating is one of the most common and effective methods for metal protective coating. The corrosion inhibitor is directly mixed with the organic coating that allow the corrosive ions from the outside to invade into the metal matrix, and even cause the loss of corrosion inhibitor activity. Due to the particularity of the layered structure of LDH and its anion exchange performance, the direct contact between the inhibitor and the organic coating can be effectively avoided. Therefore, the addition of a corrosion inhibitor such as LDH into the organic coating can effectively increase the protection of the coating to the metal materials. Zhang et al. [57] prepared phytic acid (PA) composite coating with Ce salt sealing on Mg alloy surface by plasma electrolytic oxidation and hydrothermal synthesis. The corrosion protection and self-healing ability were studied by polarization curve, EIS, immersion test, and SVET. The Ecorr and icorr values for PEO were $-0.46 \text{ V}_{\text{SCE}}$ and 2.31 μ A·cm⁻², respectively. This is due to the synergistic effect of Ce and phosphate and the optimum anticorrosion performance of PA modified composite coating on magnesium alloy. Chen et al. [58] produced Mg-Al-PA LDH by embedding phytic acid (PA), an environmentally friendly corrosion inhibitor-intercalated acid into the synthesized Mg–Al–CO₃^{2–}LDH coatings to obtain the synergistic protection by metal chelating ability, Mg-Al-PA LDH has good stability and lasting protection effect on metal matrix. Nitrite is generally considered to be the most effective anodic inhibitor embedded in concrete, but its potential toxicity to humans and the environment limits its application in corrosion protection. To reduce these harmful effects, a novel multifunctional inhibitor of Mg-Al LDH loading with nitrite anions was produced through a calcination-rehydration in air. Mg–Al–NO₃ LDH effectively reduces the toxicity of nitrites compared to adding nitrites directly to concrete and hide nitrites in the structure, preventing their release into the environment from the concrete structure. After the concrete construction is finished, the effective nitrite can be discharged. In other words, nitrite can undergo anion exchange reaction and be released when the oxide permeates the concrete internal environment.

LDH materials have been widely used in organic coatings and concrete due to its good barrier property of two-dimensional layered structure. On the one hand, it can extend the diffusion path of corrosive media, and on the other hand it can fill the microholes in the coating, reducing the generation of defects. Nevertheless, as a class of inorganic clay compounds, LDHs will show hydrophilicity and the compatibility with organic solvents will be poor, which speed up the corrosion rate. Therefore, it is necessary to modify LDH appropriately to improve its compatibility with organic polymers.

4. LDH Modified Coating on Magnesium Alloy

LDHs grow directly on the metal substrate by forming chemical bonds through in situ growth technology, so that there is a strong adhesion between LDH films and the metal matrix. On the other hand, the use of in-situ growth results in the alignment of LDH perpendicular to the substrate, resulting in crystals with different crystal orientation. This orientation of the film is generally associated with crystallization defects and the formation of corrosion channels. Therefore, in order to maximize corrosion resistance life of LDH films, anion-exchange and surface modification are often used to obtain better corrosion resistance and super-hydrophobic properties.

4.1. Anticorrosive Intercalated Structure

The LDH films have good corrosion protection owing to its anion-exchange capacity and special layered structure, which decelerate the corrosion rate of Mg alloy [59]. Compared to the common coatings, LDHs nanosheets typically grow perpendicular to the surface of the substrate, and there are many pores between the layers, providing diffusion paths for anion exchange [60,61]. In addition, different anionic intercalation structure can confer different protective effects of LDH on magnesium alloys. Therefore, a discussion of the effects of different anionic intercalation structures on the corrosion resistance of LDH films will be presented in detail below.

Wu et al. [62] used in situ hydrothermal method to grow Mg–Al LDH on the surface of AZ31 alloy, followed by vanadate intercalation reactions to produce Mg–Al–V₂O₇^{4–} LDH coatings. Kameda et al. [63] studied Mg–Al LDH intercalated with CO_3^{2-} as a reusable adsorbent with anion exchange capacity, which has been used to remove HCl, SO₂, and NO_x. Table 1 illustrated the values of corrosion current density (i_{corr}) and corrosion potential (E_{corr}) of the samples in 3.5 wt.% NaCl solution.

Table 1. Corrosion potential (E_{corr}), corrosion current density (I_{corr}) of the samples in 3.5 wt.% NaCl solution.

Sample	Electrolyte	E _{corr} (V/SCE)	I_{corr} (µAcm ⁻²)
CO3 · Mg−Al LDH	3.5 wt.% NaCl	-0.805	$1.13 imes 10^{-7}$
Cl·Mg–Al LDH	3.5 wt.% NaCl	-1.300	$2.52 imes10^{-7}$
NO3·Mg–Al LDH	3.5 wt.% NaCl	-1.357	$5.580 imes10^{-7}$
V ₂ O ₇ ·Mg–Al LDH	3.5 wt.% NaCl	-0.92	$1.30 imes 10^{-8}$

In general, a larger E_{corr} and a smaller i_{corr} can inhibit corrosion in terms of thermodynamics and kinetics conditions. As the table shows, the corrosion protection is successively in the same sodium chloride solution: $CO_3^{2-} > V_2O_7^{4-} > Cl^- > NO_3^-$. Among these coatings, it is noted that the i_{corr} of the MgAl– CO_3^{2-} LDH coatings is four orders of magnitude lower than that of the MgAl– NO_3^- LDH coatings, and zero to two orders of magnitude lower than that of other LDH coatings. It is worth noting that in some high temperature superconducting materials, thin films have stronger anion exchange ability to capture chloride ions in corrosion solution and enhance the corrosion protection of magnesium alloys. Therefore, the thickness and density of the coating are usually also key factors affecting the corrosion resistance, since they can limit the direct contact between the matrix and the corrosive medium.

Hence, based on the excellent anion exchange ability and special lamellar structure of LDH, this intercalation process is effective and time-saving in anticorrosion protection. From the perspective of the application of LDH films on Mg alloys, loading inorganic anions into LDH films is an optimal and effective method of corrosion protection, but if the inhibitor anions can be directly inserted into LDH, additional ion-exchange steps will be reduced.

4.2. Super-Hydrophobic Modification

Biologists have found that the lotus is a self-cleaning plant and have linked its selfcleaning mechanism to a microscopic morphology of its superhydrophobic surface. They found that the superhydrophobic properties of the lotus leaf surface are due to a certain roughness on the nanoscale surface [64]. Inspired by the 'lotus effect', scholars began to prepare artificial hydrophobic coating on metal surface to gain uneven surface materials with small surface energy, so as to achieve the purpose of the super hydrophobic.

Wang et al. [16] produced the corrosion inhibitors intercalated Mg–Al LDH films on magnesium alloys by in-situ growth method, and studied the effect of multi-component synergistic effects, such as molybdate intercalation and lauric acid low surface modification, on the corrosion protection of the films. This finding shows that the film modified by lauric acid has good hydrophobic protection (CA 148.6°). Electrochemical measurement displayed that the superhydrophobic LDH coatings significantly reduce the corrosion current density, which prove that the corrosion protection of Mg alloy can be improved due to the combination effect of molybdate and lauric acid. Wu et al. [65] synthesized Mg–Al LDH films on the AZ31 Mg alloy by modifying in-situ grown method with stearic acid (SA), sodium laurate (SL), myristic acid (MA)and Per Fluoro Decyl Tri Methoxy Silane (PFDTMS). The static contact angles measured are 150.6°, 153.7°, and 152° by the contact Angle tester as showed in Figure 8. The results indicated that the smallest corrosion current density, the most active corrosion potential and the highest impedance modulus were observed for superhydrophobic Mg–Al LDH-PFDTMS, which can significantly reduce the surface energy and enhance the corrosion protection of magnesium alloy.

Zhang et al. [66] prepared Mg–Al LDH by hydrothermal treatment on Al-rich Mg alloy. The interior is a lethal layer and the top is a uniform surface composed of magnesium aluminum bimetallic hydroxide micro-wafers, which has obtained excellent corrosion resistance in the brine solution. Besides, due to the natural super-hydrophobic phenomena such as the lotus leaf effect, trimming the direction of the top micro-sheet layer by variating the reaction temperature, time, and pH to obtain hydrophobic surface following the embellishment of silane fluoride. The super-hydrophobic surface exhibits good corrosion protection due to the appearance of trapped cyclone in the tissue, which provided an economic and environmental protection method for controlling of pre-corrosion products of Mg alloys.

Thus, it is concluded that the surface of the superhydrophobic film is not easy to infiltrate, which can prevent water molecules, Cl⁻ and other corrosive ions from getting to the surface of the matrix to better protect the metal from corrosion.

4.3. Biocompatible Coatings

In recent years, biocompatible materials are extensively needed owing to their special excellent abilities and the surface modification on magnesium alloys has attracted more and more attention in particularly due to their better biocompatibility. The biocompatible materials include two types. One is the original biocompatible materials, and the other is the materials that need to be shown biocompatibility through surface modification and other means.



Figure 8. Optical photographs of surface droplets and their corresponding static contact angles: (**a**,**b**) Mg–Al LDH; (**c**,**d**) SA; (**e**,**f**) SL; (**g**,**h**) MA; (**i**,**j**) PFSTMS. Reprinted with permission from [65]; Copyright 2015 Nature Research.

PVA is one of the most widely used polymer materials at present, which is a biodegradable polymer with fine biocompatibility, stability and chemical resistance. Modified Mg-Al-CO₃ LDH with organic acid via co-precipitation method can promote the intercalation of LDH in the polymer matrix, which can obtain a suitable grade of dispersion [67]. In order to promote intercalation in LDH polymer matrix and improve the ideal dispersion, organic diacid was prepared from tetrabromophthalic anhydrides and L-aspartic acid in reflexed acetic acid with pyridine [68]. Under ultrasonic irradiation, the interlayer base spacing of lactate dehydrogenase was modified by organic diacid co-precipitation method, which effectively reduced the polymerization time and cohesion of nano-cla. The modification process is shown in the Figure 9, tensile strength and modulus of PVA/mLDH NCs are improved due to hydrogen bonding and the good dispersion of mLDH in the polymer matrix. Also, due to the biodegradability and biocompatibility of both chiral amino acid dicarboxylic acid and polyvinyl alcohol, hybrid organic–inorganic PVA/modified NCs are considered to be biodegradable, which can be applied in various fields.



Figure 9. The pure PVA and PVA/mLDH NCs images of (**a**) TG curve; (**b**) typical stress–strain diagrams. Reprinted with permission from [68]; Copyright 2017 Elsevier.

On behalf of further expanding the long-range protective effect of absorbable magnesium alloy, Wu et al. [21] prepared PGA sealed Mg–Al LDH coatings on AZ31 magnesium alloy by combining hydrothermal method and vacuum freeze drying method, which synthesized composite coating of LDH and PGA coatings. Electrochemical polarization, impedance spectroscopy and hydrogen evolution tests indicate that the composite coatings effectively provide corrosion protection for AZ31 alloy. In addition, the hybrid coating made mouse embryonic fibroblasts compatible, which improved cell adhesion, migration and proliferation. The composite coating acts as a physical barrier to seal the porous LDH coating, which enhances the corrosion protection of the film and provides long-term protection to the AZ31 substrate. PGA is a kind of synthetic peptide with good hydrophilicity and biodegradability. Zhang et al. [69] synthesized PGA and rose Bengal (RB) conjugate (PGA-RB), which improved the pharmacokinetics and anti-tumor efficacy. In addition, hydrophobic polycaprolactone (PCL) and PGA were used as raw materials to synthesize tissue-engineered menisci with good biomechanical and biodegradable properties. Therefore, Lai et al. [70] successfully applied PGA coating on Mg–Al LDH by hydrothermal treatment, and the results show that LDH has good corrosion resistance. The cell adhesion study of rat bone marrow stem cells also showed that PGA/LDH coatings can significantly enhance the cell compatibility of substrates, and it has a broad application prospect in orthopedic surgery. Kaseem et al. [71] proposed WO₃ nanoparticles to interact with LDH film through intermolecular hydrogen bond in AZ31 Mg to prepare LDH film by surface modification. This is a novel composite composed of albumin, WO_3 , and LDHs film, which can be used for intelligent corrosion protection of magnesium alloys, and it is also an effective strategy to improve the chemical stability of inorganic layers.

Surface modification is the most widely used method to improve the cellular compatibility and corrosion resistance of Mg alloys. Hence, many researchers only focus on enhancing the corrosion resistance of AZ31 Mg alloys by surface modification to obtain a cellular compatibility surface, ignoring the special requirements of different biomedical applications. Therefore, it is of great significance to develop sufficient bone-bonded magnesium alloy coatings for bone-related applications.

5. Summary and Perspectives

LDH materials have been widely used in the metal protection field due to the rapid development of LDH in anion exchange, preparation technology, modification methods, and corrosion mechanism. However, there are few studies on the mechanism of anion exchange between layers of LDH and the recombination mechanism of layered structure from the microscopic point of view. In this review, the synthesis methods of LDH coatings have been summarized. The corrosion resistance mechanism of LDH materials on magnesium alloy was briefly discussed. The surface of LDH materials were chemically modified to enhance the compatibility with solvent, and the corrosion resistance function was developed in the form of additives, which summarized the composite coating with special function.

In conclusion, LDH coatings have a good protective effect on magnesium alloy, but there are still problems to be further studied. In-situ growth is the most widely used method, but the degree and thickness of LDH coatings are sometimes inadequate. This indicates the importance of multiple synthesis methods for LDH coatings. The bonding force between LDH and substrate can be changed by changing the ratio of metal cationic and the corrosion resistance can be enhanced to prolong the working life of the film. In order to improve the corrosion resistance and other functional effects of Mg alloy, it is necessary to study the recombination mechanism of LDH interlamination structure, which can maximize the release of inhibitor ions and absorption of corrosion ions to obtain better corrosion resistance of materials. Chemical modification or incorporation of synergistic ions can enhance the compatibility between LDHs and organic polymers, thus increasing the compactness of the composite coating and improving the corrosion resistance of the coating.

With the research on the preparation of Mg–Al LDH coating system on Mg alloy surface to improve its corrosion resistance, it is particularly important to better grasp how to select the appropriate key parameters and synthesis process. As an LDH film has the main characteristics of positive anticorrosion function, it is necessary to find new regulatory parameters to realize the preparation of multifunctional LDH film withs controllable sizes and specific surface areas, and further improve the protective performance of composite film on Mg alloys. Therefore, Mg–Al LDH composite films prepared on the surface of Mg alloy have broad application prospects in Marine corrosion and protection applications.

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