

CHAPTER 9

Smart coatings on magnesium alloys in transportation industries

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9.1 Introduction

Magnesium (Mg) was recognized as an element in 1755 and isolated by Davy in 1808. It was prepared in a coherent form by Bussy in 1831. Magnesium is the eighth most abundant element in the Earth's crust and can be found in large deposits in the forms of magnesite, dolomite, and other minerals [1]. It is produced either through the metallothermic reduction of magnesium oxide with silicon or by electrolysis of magnesium chloride melts from seawater. Each cubic meter of seawater contains approximately 1.3 kg (0.3%) magnesium [2,3]. Mg is a light, silvery-white, and fairly tough metal. It tarnishes slightly in air and finely divided

magnesium readily ignites upon heating in air and burns with a dazzling white flame [1]. Currently magnesium has drawn great attention as an important material for constructing modern vehicles either for civilian or military purposes. Sustainable energy saving and reducing carbon dioxide (CO₂) emissions from transportation is among the most important considerations for all manufacturers and scientists working in transportation industries [4]. The automotive industry is one of the most advanced industries as transportation is vital for daily life and for economic development. Research in metal or metal alloys and coating technology is important to achieve an improved transportation system. There is increasing interest in light-weight construction in order to achieve a reasonable reduction in average fuel consumption. For this requirement, magnesium with its good strength-to-weight ratio is one of the candidate materials to realize light-weight construction, but it competes with various other materials [5]. Magnesium is considered to be a good choice of material in the areas of defence and aerospace engineering for aircraft and missile components, aircraft engine mounts, control hinges, fuel tanks, and wings. In the automotive sector, magnesium is used for wheels, housings, transmission cases, engine blocks, steering wheels and columns, and seat frames [6]. Despite these advantages of magnesium, it is extremely susceptible to different types of corrosion, especially galvanic corrosion. There are two ways to protect Mg from galvanic corrosion: (1) by minimizing the chemical potential difference between the magnesium or magnesium alloys and the dissimilar materials, and (2) by maximizing the circuit resistance by coating the magnesium part to protect the surface of magnesium and its alloys. This is specifically beneficial in cases where the part is in contact with other metal parts, which could cause galvanic corrosion. Some examples of protective coatings are fluoride anodizing, chemical treatments, electrolytic anodizing, sealing with epoxy resins, standard paint finishes, vitreous enamelling, electroplating, and cold spray [7].

Fuel economy and air pollution are crucial factors when selecting a vehicle and can be achieved by using alternate fuels, power-train enhancements, aerodynamic modifications, and weight-reduction methodologies. Among these, weight reduction of a vehicle by alternative materials is the simplest and most cost-effective strategy, which is why magnesium and its alloys have attracted much consideration as a powerful weight-saving option for aerospace and automotive industries [6].

9.2 Importance and applications of magnesium

Generally speaking, magnesium is an element of paramount importance for several aspects including plant and animal nutrition, flashlight photography, flares, and pyrotechnics, including incendiary bombs. Magnesium improves the mechanical, fabrication, and welding characteristics of aluminum when used as an alloying agent. Furthermore, magnesium is used as a reducing agent in the production of pure uranium and other metals from their salts. Dead-burned magnesite is employed for refractory purposes such as bricks and liners in furnaces and converters. Calcined magnesia is also used for water treatment and in the manufacture of rubber, paper, and others. It is also used in the automotive industry, particularly for light-weight vehicles [5,8,9].

Magnesium has a hexagonal closed-packed crystalline structure and, thus, magnesium and its alloys are difficult to deform at room temperature, which restricts their ability to deform at lower temperatures. Magnesium has a moderately low-melting temperature making it easier to melt for casting. Additionally, it is relatively unstable chemically and extremely susceptible to corrosion in aqueous media [7]. Magnesium and its alloys are characterized by their high strength-to-weight ratio making them ideal candidates for diverse engineering applications that require heavy-duty, but light-weight, materials [10]. Among other structural metals, magnesium is the lightest one with a density of 1.7 g/cm³ as given in Table 9.1 [7,11,12].

Magnesium has good ductility and better noise and vibration dampening characteristics than aluminum and excellent castability [13,14]. Alloying magnesium with aluminum, manganese, zinc, thorium, zirconium, or rare-earth metals increases its strength-to-weight ratio making these alloys important materials for applications where weight reduction is important, and where it is imperative to reduce inertial forces. Because of this property, denser materials, not only steels, cast iron, and copper based

Table 9.1 Physical properties of magnesium (Mg), aluminum (Al), and iron (Fe) metals.

Property	Mg	Al	Fe
Density at 20°C (g/cm ³)	1.74	2.70	7.86
Tensile strength (MPa)	240 (for AZ91D)	320 (for A380)	350
Melting point (°C)	650	660	1.536

alloys, but even aluminum alloys, are currently replaced by magnesium-based alloys [15,16]. The requirement to reduce the weight of vehicle components because of legislation against excessive emission has incited renewed interest in magnesium and its alloys [11,17].

Pure magnesium is rarely used in the manufacturing of aerospace and automotive parts [7], but its alloys with aluminum, zinc, cerium, silver, thorium, yttrium, and zirconium are the most commercially applied in transportation industries such as automotive and aerospace due to their excellent mechanical properties, including low density, high-specific strength, good weldability, and ease of castability [4,5,18]. Their significant role in the automotive industry and hence in transportation is due to their light-weight characteristic that serves a great reduction in vehicle weight and CO₂ emission, as well as fuel cost [19,21].

9.3 The future need for light-weight vehicles

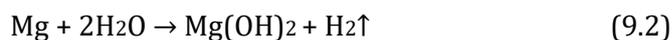
Broadly speaking iron, aluminum, and magnesium are the main metallic materials utilized for engineering applications, constructional purposes, and in the infrastructure of most industries due to their outstanding mechanical strength [22] and their availability in Earth's crust where their abundances (in mg/kg) are 5.63×10^4 , 8.23×10^4 , and 2.33×10^4 , respectively [1]. Concerning the automotive industry is one of the most fuel-consuming industries, which adds up to the final cost. This calls for the adoption of light-weight vehicles that makes many candidate metals such as aluminum and steel are down the list to magnesium and its alloys [5]. Pollution is a nightmare for any industrial country that wants to achieve optimal standards for a green environment, which is particularly the case for their transportation sectors. Pollution from vehicles is largely related to gas emissions from fuel consumption, which leads to serious health problems, mainly respiratory, due to hazardous gases such as carbon monoxide and carbon dioxide [23]. Apart from these health-related problems, the excessive emissions of CO₂ have a significant catastrophic impact on climate change leading to global warming due to its greenhouse effect [24,27].

Light-weight vehicles do not only have the benefit of saving energy [5], but also have the advantage of pollution control because the reduction in net vehicle weight gives rise to a reduction in the combusted fuel and, thus, CO₂ emissions can be controlled. Sustainable energy saving and reducing CO₂ emissions from transportation by the development of

advanced technologies for high-performance, light-metal-alloy materials for fuel-efficient vehicles is an important topic for manufacturers and scientists working in the transportation industry. Improving the mechanical properties, formability, and corrosion resistance of magnesium alloys have received much attention [4]. Therefore, magnesium and its alloys play a significant role in the aerospace and automotive industries in fulfilling the light-vehicle requirement [28].

9.4 Drawbacks of magnesium alloys

Despite the advantages of magnesium and its alloys, they have some drawbacks due to their high reactivity toward oxygen and water and, hence, their facile deterioration due to the formation of a porous film on the surface that does not offer protection [4]. Pure magnesium is unreliable as it is highly volatile at increased temperatures and highly corrosive in wet environments [7]. Magnesium is a highly reactive metal and, thus, it is not normally found in the metallic state in nature. Instead, it is usually in the form of oxide, carbonate, or silicate often in combination with calcium. Due to its reactivity, the production of magnesium requires large amounts of energy, and, therefore, is an expensive metal. There are two mechanisms describing the reactivity of magnesium. First, magnesium can react with oxygen to form oxides and the presence of water or moisture (even at ambient temperatures) may lead to an increased risk of fire due to the evolution of hydrogen accompanying its general corrosion process [Eqs. (9.1) and (9.2)]:



The second mechanism is attributed to the galvanic action, where Mg can form active galvanic couples acting as corroding anodes with other metallic components in its proximity [11,29]. The major step for improving the corrosion resistance of magnesium alloys is the introduction of high-purity alloys [12]. Alloying can further improve the general corrosion behavior, but it does not change galvanic corrosion problems if magnesium is in contact with another metal and an electrolyte. Therefore, general and galvanic corrosion problems can only be solved effectively by proper coating systems [5,11].

9.5 Corrosion protection of metals

Multiple ways can be used to protect metallic structures from corrosion and prevent their eventual decay, including corrosion inhibition [23,30], cathodic protection [31], sacrificial anodes [31,32], and metal coating [32]. To improve the corrosion resistance of magnesium and its alloys as well as to fulfill decorative requirements, coating systems are generally used in the automotive industry, especially for viewed parts which are in contact with the external environment. Combinations of conversion coatings as primer and sealing top coats (paint, lacquer, e-coat, etc.) are state-of-the-art for corrosion protection of magnesium. Chemical conversion coatings are just a few micrometers thick and, thus, they only offer limited protection; however, they are an excellent primer for a subsequent organic coating. The best results were obtained by chromating, but because of the health risk associated with chromate, such use is strictly limited. Alternatives for chromating are conversion coatings such as those based on phosphate, permanganate, or fluorozirconate. Proper coating should also protect against oxidation that leads to corrosion [32]. However, the cost and weight of these coatings and their general ineffectiveness for lighter alloys, along with some concern for their environmental impact, make them less than ideal for many aerospace applications [33]. An ideal anticorrosion inhibitor coating is meant to exert its effect through physical and functional roles, but the latter could be lost easily upon its damage [34]. Coating damage can occur due to mechanical, physical, chemical, thermal, and biological factors. Mechanical damage can occur to the protective coating layer leading to electrochemical corrosion upon metallic surface exposure due to cuts or scratches. Physical damage can lead to microcracks without metal loss. Chemical damage can lead to no metal loss in the presence of microdamage in a similar mechanism of physical damage [31]. Thermal damage occurs in cases of increased metal surface temperature leading to thermal shock stress of the metal and damage from thermal expansion and instability [35]. Biological damage occurs mainly in the human body due to altered metabolic and immunologic reactions within the body. These types of damage makes the coating lose its efficacy in corrosion protection [31].

9.6 Smart coatings

A smart coating is defined as one that can change its properties as a response to an environmental stimulus such as pH change, mechanical

friction, wetting, heat, attack by aggressive ions, and redox activity [36]. Typically, a smart coating consists of a matrix of a traditional coating material involving smart micro or nanoscale containers having the ability to radically protract the life of structures and to add additional functionalities to the coated systems. Nanotechnology has recently added to the wide panel of available smart coating systems [33,3739]. Recently, computational chemistry simulates smart coating by designing and selecting specific and functional coating units [40]. Smart-overlay coating is supposed to be a functional gradient coating system that protects against elevated temperature conditions by a coating technology that combines spraying technologies and chemical vapor deposition [41].

9.6.1 Characteristics of smart coatings

In 2007, Alam et al. reported their research on corrosion indicators or sensors that are color-sensitive to different pH media [42]. The same color-sensitive coating mechanism was later shown by Di Credico et al. using UV-absorbing microcapsules that encapsulate UV-responsive photochromic dye that responds to areas of damaged metal surface allowing for a self-healing mechanism [43]. When such a smart coating is damaged or scratched, the containers are stimulated or triggered to release the active agents (corrosion inhibitors) to provide an extended lifetime to the underlying metal [34]. However, more studies should be done to optimize the coating's conditions because "smart" coating technology is industrially unattractive when multiple steps (around 8–12 steps) must be used to prepare the coatings as well as the raw materials being quite expensive. Moreover, the presence of a tank or reservoir containing "liquid" inhibitors in the coating may negatively affect the adhesion performance and wear and abrasion resistances of the coatings over the metallic substrates. The healing efficiency of such coatings at low temperature (near 0 °C) is unknown as the inhibitors inside the reservoirs might freeze. The overall coating quality is also unclear at high temperatures (> 40°C) where swelling and microcracks due to partial inhibitor evaporation may occur [4,13].

9.6.2 Advantages of smart coatings

Smart coatings are capable of changing their properties when they are subjected to environmental stimuli. Selective response to external stimuli in the local environment is a goal in order to reach high-tech smart coating. Ongoing research in this field concerns selecting the most reliable

foundation species for smart coating products, such as the case of using zeolite pigment in smart coatings [44]. In addition, these coatings can heal their damage by themselves without external interventions. When the coating layer is cracked, the containers are broken or melted to release the functional agent to form a protective layer on the metal surface. The size of the microcontainers has to be sufficient, for example, tens of micrometers, to promote fast release when the containers are mechanically damaged, therefore, limiting their application since thick coatings are needed to encompass these containers. To tackle this technical issue, smaller containers were developed for thinner coatings, such as coatings via the solgel technique [34]. However, one of the disadvantages of coatings is their easy degradability upon exposure to external environmental stimuli such as UV radiation. This can be overcome by the incorporation of an active species capable of corrosion protection by an inhibitory mechanism [45]. The best coatings for corrosion protection provide not only a barrier against harsh environment conditions, but also the controlled release of a corrosion inhibitor as demanded by coating damage and the presence of a corrosive environment resulting in a self-healing capability [33].

9.7 Smart coating designs

These coatings are smart enough in the sense of their ability of self-healing when metallic cracks occur [4,22,46,48]. They have their own setup starting point for the healing process without the need for an intervention by an external human factor [39,46,49,50]. But this industry is also focusing on smart coatings that are environment friendly to minimize the emission of greenhouse gases [11]. A typical smart coating is composed of an appropriately sized reservoir filled with active healing ingredients [18,45]. Coating is a pretreatment method aimed at upgrading the metal to improve its functionality by preserving its main metallic bulk from notorious environmental stressful stimuli like high oxidation [42]. Smart coating composition varies, but to avoid environmental hazards there is a tendency toward the use of nonheavy metals, such as camphor sulfonate doped polyaniline and poly(methyl methacrylate). Coating deposition on a metallic surface can be either electrochemical or chemical [51]. Monitoring a “thermally sprayed” smart coating can be achieved by the introduction of built-in sensors [52]. Another type of smart coating contains a driving nonconductive layer (drives substrate cracks toward the sensing layer) and a sensing conductive layer (its resistance to the substrate

crack would determine crack length) [53]. Corrosion inhibitors can be incorporated into the coat matrix via direct doping or encapsulation into specific micro- or nanoscale containers.

9.7.1 Direct doping of inhibitors into coatings

There are several methods for loading corrosion inhibitors into a coating matrix that are based on direct mixing with the coating material or the use of a container or encapsulation [54]. The first procedure (see Fig. 9.1A) is followed to feed the metal with corrosion inhibitors to protect its surface against deterioration. However, drawbacks include early inhibitor leakage with the undesired interaction between the metallic matrix and inhibitor leading to coating disruption [22].

9.7.2 Encapsulation of inhibitors into micro- or nanoscale containers

Due to the negative effects of direct mixing of a polymer coating and a corrosion inhibitor (e.g., inhibitor deactivation, osmotic blistering, and uncontrollable spontaneous leaching within the polymer coating), further steps can be taken to hinder these negative effects, including loading a corrosion inhibitor into nanoscale containers (Fig. 9.1B) [54]. Nanocontainers are nanochambers or nanoreservoirs [45] that modulate the release of corrosion inhibitors upon triggering stimuli in the local environment [30]. The release rate of the inhibitor encapsulated into their containers is low and depends mainly on the molecular diffusion from the pores of these containers into the environment. For this reason, the smart coat will be more practical and responsive to environmental change if

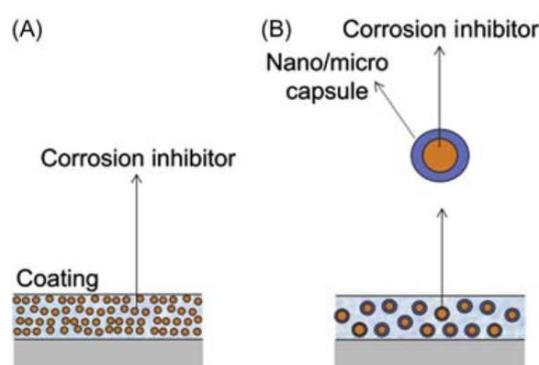


Figure 9.1 Some types of self-healing coatings: (A) mixed coating, and (B) capsule-loading coating [54].

these containers are degradable in water when corrosion mainly takes place in aqueous environments [34]. The fabrication of an active coating proceeds via multiple steps: (1) smart container fabrication, (2) inhibitor loading, (3) dispersing containers in the coating matrix, and (4) applying a coating on the metal surface [22,34]. The extremely tiny size of microcapsulations ranging from 1 μm to several hundred micrometers allow the encapsulation of controlled amounts of active substances that, in return, enhance efficacy through protecting the contained material from alterations in the local environment. Microcapsules are typically 1 μm , while nanocapsules are in the nanometer range allowing a large surface area that permits a wide range of functional activities, such as adsorption or desorption, chemical reactions, and light scattering. It is worth mentioning that microcapsules can be classified into three basic categories, namely monocored, polycored, and matrix types. Monocored microcapsules have a single hollow chamber within the capsule, polycore microcapsules have a number of differently sized chambers within the shell, and matrix type microparticles have active ingredients integrated within the matrix of the shell material. However, the morphology of the internal structure of a microparticle depends largely on the selected shell materials and the microencapsulation methods that are employed [55]. Two main mechanisms are involved in the synthesis of microcapsulated structure, that is, chemical and nonchemical [55]. Li and Calle [47] described the average size of an ideal microcapsule as 5–100 μm , typically ~ 20 μm with a narrow size distribution, and size control can be obtained through adjusting the emulsion formula and the microcapsule forming conditions. In addition, adjusting the emulsion formula and polymerization reaction time can help adjust the microcapsule pH sensitivity. Micro- or nanocapsules in smart coating ideally contain active ingredients that can be referred to by different names according to their mechanism of action in controlling the localized corrosion sites following their release due to the micro or nanocapsule rupture, that is, as healing agents (terminate the corrosion process early), corrosion sensors (sense local environmental changes like pH or oxidative process at the corrosion site by the transformation of the active ingredient upon interaction with the corrosive environment leading to the emission of a color or fluorescence that can be easily observed), or corrosion indicators (release dyes at corrosion site) [22,33,47,53,56]. There is a diverse range of micro- or nanocapsules, including organic polymers, inorganic clays, mesoporous silica nanoparticles, and polyelectrolyte multilayers [22].

9.7.2.1 Organic polymeric coatings

Organic coatings have been intensively used for enhancing corrosion resistance in addition to abrasion and wear properties of magnesium alloys for biomedical and industrial applications [57]. Organic coating can be applied using several approaches, including painting, powder coating, electrophoretic coating, and solgel coating. Table 9.2 lists the comparisons between these approaches [58].

Organic coatings in their pure or composite forms can assist in controlling corrosion [22,59]. These types of coatings can exert noncolor or color response based on the coating design. Color-sensitive polymers are considered smart in providing a visual based response upon an ongoing corrosion process [60,61]. Following a lesion in the metal surface, the self-defence effect, usually called the self-healing effect, comes into effect where the released “healing agent” is the main player. The agent is incorporated into the microcapsule polymeric coatings and will be released by crack propagation or another triggering mechanism from its reservoir [60]. This is a crucial step in treating corrosion injury on the metal surface. On the other hand, polymer coatings can help in decontaminating surfaces from harmful materials and, thus, contribute to environment protection such as the case of cleansing Chernobyl after the nuclear disaster in 1986 [62]. Uhlmann et al. [63] described the use of binary polymer brushes that are engrafted on the substrate surface for physicochemical surface variations monitoring to elaborate appropriate adaptive surface responding properties. Interestingly, polymeric smart coatings have gained a key role in monitoring certain biological reactions within the human body, such as the host’s reaction against an implantable glucose biosensor, in which case the polymer coating of the sensor is designed [64].

Table 9.2 Main differences between techniques followed to apply organic coatings [58].

Technique	Advantages	Disadvantages
Paintings Powder coating Electrophoretic coating Solgel	<ul style="list-style-type: none"> • Flexibility • Utilizing no solvents • Being ecofriendly • Simplicity and little restriction • Low processing temperature 	<ul style="list-style-type: none"> • Using organic solvents • Containing multistep • High processing temperature • High energy consumption • Requiring complicated electrical control • Long-time processing flow

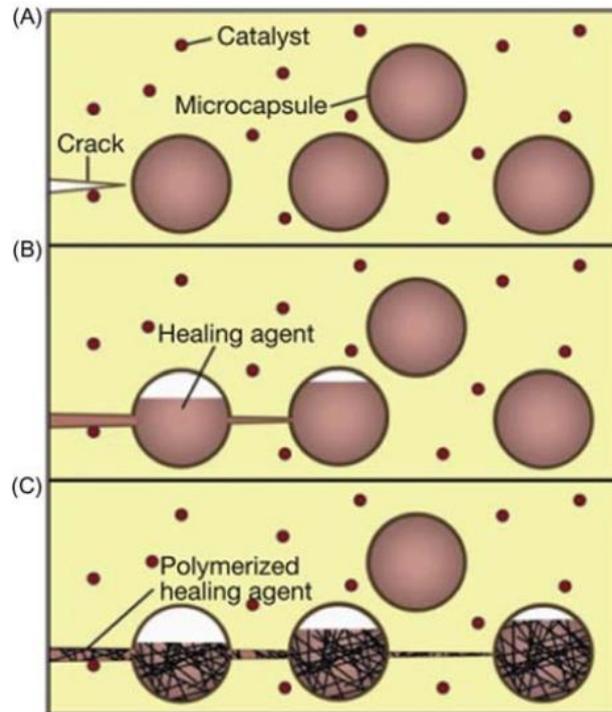


Figure 9.2 Stages of autonomic self-healing ability of polymer composites. (A) Cracks formation in the matrix, (B) microcapsules rupture releasing the healing agent, and (C) bonding the crack faces closed [65].

White et al. at the University of Illinois [65] reported on their pioneering work on a structural polymeric material with the ability to autonomically heal cracks. The material incorporates a microencapsulated healing agent that can be released upon crack intrusion. Polymerization of the healing agent is then triggered by contact with an embedded catalyst, thereby bonding the crack faces. Fig. 9.2 shows the stages of the autonomic self-healing process: (1) cracks form in the matrix wherever damage occurs (Fig. 9.2A); (2) the cracks rupture the microcapsules, releasing the healing agent into the crack plane through capillary action (Fig. 9.2B); and (3) the healing agent contacts the catalyst, triggering polymerization that closes the crack faces through bonding (Fig. 9.2C).

9.7.2.2 Inorganic clays

The mechanism of function for inorganic clays is dependent on their coating structure. This can be hollow type that works like polymeric nanocontainers encapsulating active corrosion inhibitors, or ion-exchange

minerals that are capable of releasing inhibitor species or sequestering aggressive ions encountered in a corrosive environment, like chloride ions [22,66]. Layered double hydroxides (LDH) or other anion- and cation-exchangers, (e.g., natural clays, zeolites, and bentonites) can be utilized to store inorganic corrosion inhibitors and, hence, are released via an ion exchange mechanism [67]. This regime involves the combination of organic and inorganic entities at the nanometer level that forms the basis for preparing multifunctional intelligent materials that provide specific functions as a response to different types of stimuli [68]. Inorganic porous particles are used as carriers for low-molecular weight active agents (e.g., healing compounds, corrosion inhibitors, antibiotics, etc.) [48].

9.7.2.3 Mesoporous silica nanoparticles

Mesoporous silica is a porous material that has been applied as a host for corrosion inhibitors due to their large-pore volume, high chemical and thermal stability, and easy functionalization [69]. These hollow structures are also known for their biocompatibility and large specific surface area, rendering them efficient as smart coatings [22]. Due to the interesting properties of mesoporous silica nanoparticles they have been extensively used in various applications, such as in the fields of biomedicine, catalysis, environmental protection, and optics [70]. These materials act as containers for small-molecule organic corrosion inhibitors, such as benzotriazole (BTA), and they can release the encapsulated inhibitor upon exposure to a stimulus in a harsh environment [71]. Mesoporous silica can act as containers for inorganic corrosion inhibitors as well. For example, Saremi and yeganeh [69] have used mesoporous silica as hosts for molybdate and then dispersed the formed powders into a polypyrrole matrix and used this formula as a coating against steel corrosion (Fig. 9.3).

9.7.2.4 Polyelectrolyte multilayers

Polyelectrolytes are usually assembled on the surface of nanoparticle inorganic substrates via a layer-by-layer (LbL) approach. This method involves the stepwise electrostatic assembly of oppositely charged species onto the substrate surface and allows the formation of a coating with multiple functionalities. The coating properties are affected by the number of deposition cycles and the type of polyelectrolytes used. The inhibitors will be released in a controllable way from the host structure when the polyelectrolyte molecules are stimulated by changes in pH resulting from the corrosion process [22], which is based on the permeability dependence of

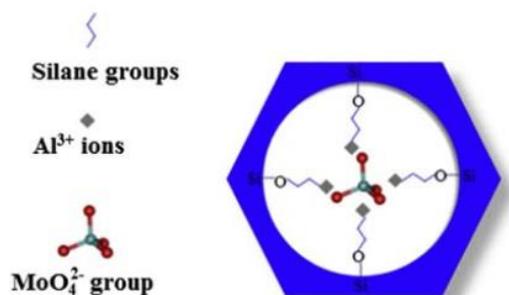


Figure 9.3 Molybdate corrosion inhibitor hosted in mesoporous silica nanocontainer [69].

polyelectrolyte shells on pH [45]. Due to the sensitivity of the polyelectrolyte multilayers to pH changes, they release corrosion inhibitors to the damaged area leading to its self-healing without external intervention. Moreover, polyelectrolytes that form the coating are relatively mobile and have the tendency to seal and eliminate the mechanical cracks of the coating [42]. Polyelectrolyte multilayers are able to retard the corrosion process in the defective area and provide effective local corrosion protection. The most probable mechanism is based on the local neutralization of the pH in the damaged area at the beginning of the corrosion process as proposed by Andreeva et al. (Fig. 9.4) [72].

In Fig. 9.4, $\text{R} - \text{HSO}_4^-$ is a strongly negative polyelectrolyte that has good adhesion properties to the metal surface without pronounced buffering ability, while weakly positive $\text{R} - \text{NH}_3^+$ contains neutral amine groups associated with negative groups of $\text{R} - \text{HSO}_4^-$ to generate ion pairs during LbL assembly. The positively charged amine groups are able to bind with the free hydroxide ions produced during the corrosion process in the corrosive area and, therefore, keep the pH value of the system constant and suppress corrosion processes. However, this method is limited to lab-scale and is far from industrialization due to the complex technologies involved [22].

9.8 Smart coatings for magnesium and its alloys

A number of smart coatings that have been reported in the literature for magnesium and its alloys in various corrosive media has to be reviewed in order to shed some light on the potential applications of these coatings in automotive industries. Indeed, engineering selection of a proper coating

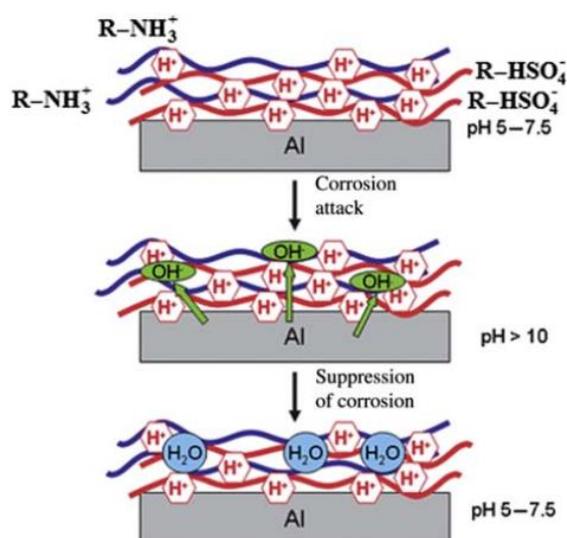


Figure 9.4 Schematic for the mechanism of buffering activity of a polyelectrolyte coating [72].

for magnesium alloys is the cornerstone in optimizing its functionality and improving its industry and probable applications [28]. On the other hand, many factors are included in magnesium alloy selection, among which are the working conditions of the alloy such as room temperature (e.g., Mg–Al–Zn alloy) versus elevated temperature (e.g., Mg–Zn–Zr alloy) [11]. Chen et al. [34] prepared a novel self-healing system composed of poly(lactic-co-glycolic) acid (PLGA) porous particles loaded with BTA as a corrosion inhibitor. This coat was applied on magnesium alloy (AMlite) via direct electrospray deposition with subsequent epoxy spraying. PLGA has been extensively used in controlled drug delivery because via hydrolysis it easily degrades its ester linkages on exposure to water. Therefore, PLGA particles demonstrate rapid response to both water and pH increase induced by magnesium corrosion (Fig. 9.5). This would lead to the instantaneous release of BTA at alkaline pH to self-heal the protective coat and retard further corrosion (Fig. 9.5A). A PLGABTA micro-composite was prepared in dichloromethane and speedily evaporated during the electrospray process. BTA was released through the nanopores in the PLGABTA microparticles. A scratching test was performed for specimens coated with epoxy only and with epoxy and PLGABTA composite immersed in 0.1 M NaCl electrolyte for 30 min, thereby revealing that

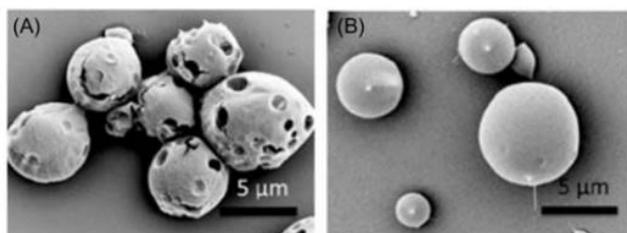


Figure 9.5 SEM images of PLGA – BTA microparticles in a (A) pH 10 and (B) pH 7 environment after 8 h of immersion [34].

the scratches in the former coat exposed the underlying magnesium material to severe corrosion attack, while in the latter coat BTA was released and healed the formed scratch and protected the metal underneath.

Eco-friendly vanadate smart conversion coating has been reported by Hamdy et al. [4] as an effective protective approach against corrosion, which may be applied as a pretreatment top-priming onto magnesium alloys to provide a suitable surface for subsequent application of a protective paint. The authors have assessed the self-healing performance of this coating for improving the corrosion resistance of a newly developed AZ31 HPO magnesium alloy in 3.5% NaCl solution. Results of various electrochemical techniques, SEM-EDS, and optical microscopy showed a marked enhancement in the localized corrosion resistance of magnesium substrate after applying a vanadia conversion coating specifically with a concentration of 50 g/L¹ at pH 7 due to self-healing effect (Fig. 9.6).

The coating durability depends on the vanadia solution concentration and pH where changing the solution pH from neutral (pH 7) to alkaline (pH 9) adversely affects the corrosion protection.

In another work, Hamdy and Butt [28] developed a smart stannate-based coating to improve the corrosion resistance of AZ91D Mg alloy. These are also industrially applicable and economically attractive as only two steps are needed for the coating preparation and the chemical used is simply a diluted tin oxide solution. Results showed that a stannate-based coating inhibits localized corrosion at microcracks due to the formation of a tin oxide-rich magnesium hydroxide layer. Moreover, this coating has a self-healing functionality for magnesium surfaces that heal the pitting sites and repair microcracks without external intervention.

Gnedenkov et al. [73] developed a self-healing intelligent coating formulation based on the plasma electrolytic oxidation (PEO) method through the incorporation of the corrosion inhibitor 8-hydroxyquinoline

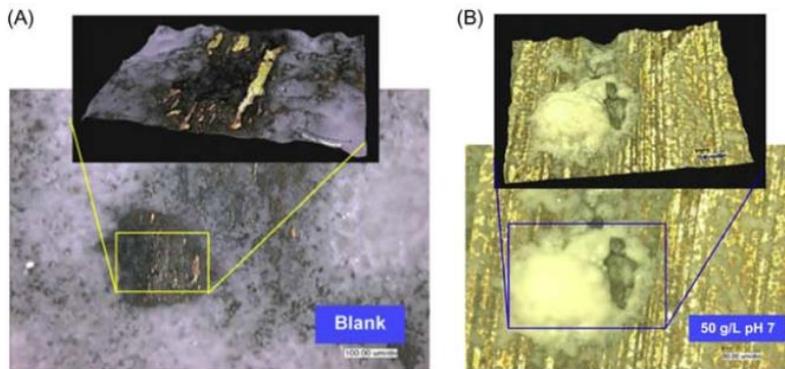


Figure 9.6 Microscopic images for Mg AZ31 HPO samples in the (A) absence and (B) presence of vanadia coating after 7 days of free immersion in a 3.5% NaCl solution [4].

(8-HQ) into the PEO-layer and tested its efficacy against the corrosion of MA8 magnesium alloy. The produced coating exhibited enhanced protective properties against corrosion with self-healing properties. Zhang et al. [74] fabricated a smart Cr(III)-based chemical conversion coating (Cr(III) CCC) with self-healing properties for the AZ31B magnesium alloy. The coat composed of amorphous/nanocrystalline Cr and Cr₂O₃, modified by stearic acid had a hierarchically porous structure. Therefore this coat has superhydrophobic properties and its water contact angle (CA) was measured and found to be 157 degree. Fig. 9.7 reveals the change in CA value of a water droplet (4 μL) for the ultrasonic prepared Cr(III) CCC for 60 min as a function of modification time in the stearic acid or ethanol solution. The CA value increased rapidly from 56 to 140 degrees during the first 30 min of modification, and then gradually increased. Superhydrophobic Cr(III) CCC surface (CA > 150 degrees) can be obtained by modification for more than 90 min. Although the CA value can reach 157 degrees by modification for 120 min, the water droplet can hardly roll off freely from the Cr(III) CCC even if when the substrate is upside down. Such a superhydrophobic surface with high water-adhesive force can be found widely in the nature, typically in petals (i.e., the petal effect). The superhydrophobic property of the coating can prevent the initial contact of the corrosive liquid from the substrate. In the case of a nonwetting state, the subsequent breakdown of the coat facilitates the formation of a chromium oxidant layer that is responsible for the self-healing activity.

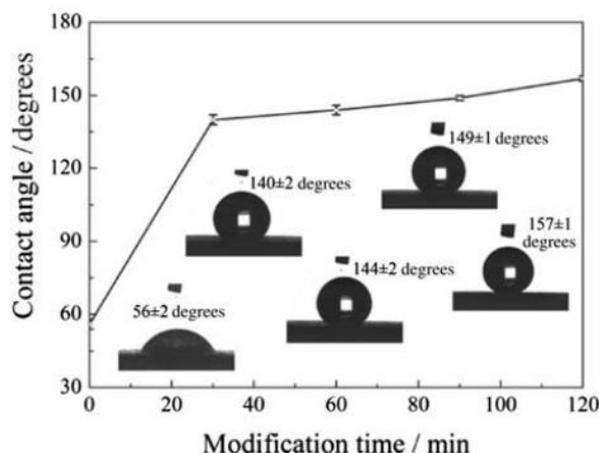
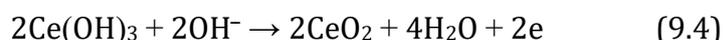
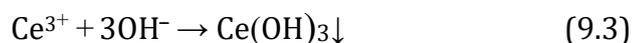


Figure 9.7 Change in the contact angle value of the prepared Cr(III) CCC for 60 min as a function of modification time by immersion in an ethanol solution of 10^{-3} M stearic acid at room temperature. The volume of the water droplet is about $4 \mu\text{L}$ [74].

Wang et al. [75] reported an epoxy coating containing Ce–MCM-22 zeolites that has exhibited effective corrosion resistance with self-healing performance for the binary Mg–Li alloy. Self-healing properties of this epoxy coating was attributed to the active Ce^{3+} species that can be released from MCM-22 zeolites precipitated to the scratched areas of the Mg–Li alloy (Fig. 9.8).

The presence of Ce^{3+} ions in the coating was ascribed to higher cation concentrations based on cation exchange properties of the MCM-22 zeolite [26]. The hydroxyl groups originated from the increased pH due to corrosion process. This leads to formation of $\text{Ce}(\text{OH})_3$ which can spawn in the precipitation of CeO_2 [Eqs. (9.3) and (9.4)]. Therefore the Ce inhibition process is mainly triggered by the increase of concentration of hydroxyl groups in the corrosion sites.



Zeng et al. [76] synthesized a ZnAl layered double hydroxide consisting of uniform hexagonal nanoplates via coprecipitation and hydrothermal treatments. They applied this coat on the AZ31 magnesium alloy, and then a PLA coating was sealed on the top layer of the

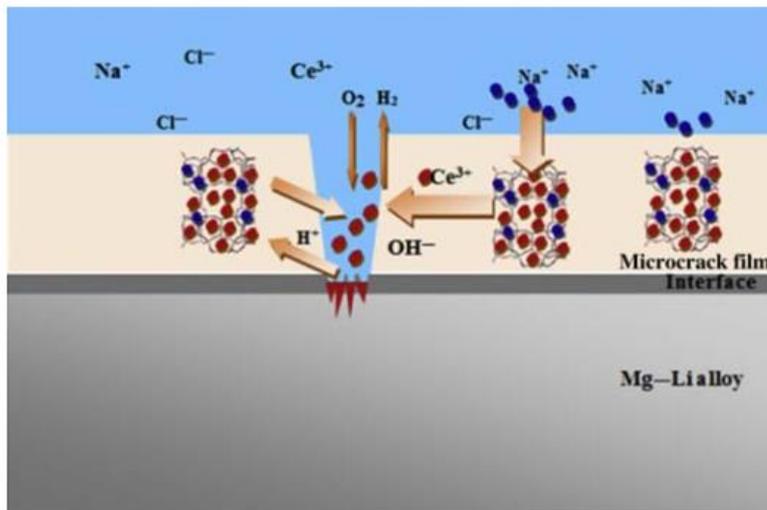


Figure 9.8 Schematic representation of the stimuli-triggered release process in the epoxy coating containing CeMCM-22 zeolites [75].

ZnALDH coating using vacuum freeze-drying. It was found that this coating consisted of a compact inner layer and a porous outer layer. The CO_3^{2-} ions leached from the layered double hydroxide react with dissolved Mg^{2+} to form a protective MgCO_3 film. Then, MgCO_3 is dissolved to form $\text{Mg}(\text{OH})_2$ under alkaline conditions at the corrosion sites which spread to cure the pitting sites resulting from corrosion on the alloy surface.

Ding et al. [77] incorporated mechanized silica nanoparticles (MSNPs) as nanocontainers into a host self-assembled nanophase particle (SNAP) barrier coating. MSNPs, in turn, consisted of mesoporous silica nanoparticles and supramolecular nanovalves in the form of pseudorotaxanes. These nanocontainers enclosed the corrosion inhibitor, 2-hydroxy-4-methoxyacetophenone (HMAP), and it was found that they were capable of trapping HMAP under neutral solution conditions and release it upon presence of environmental stimuli (alkali or Mg^{2+}) at corroding microregions on the magnesium alloy surface. Due to the stimuli-responsive release property of this coat, it has a self-healing potential: once the surface was mechanically scratched, HMAP is released from MSNPs and form a compact molecular film on the damaged alloy surface, finally inhibiting the corrosion propagation and executing the self-healing function.

Zomorodian et al. [57] investigated the effect of a composite coating composed of polyether imide with minor contents of diethylene triamine

(0.3%) and hydroxyapatite (2%) and applied on AZ31 magnesium alloy. The coated samples were immersed in Hank's solution and it proved to be able to slow down the corrosion rate of AZ31 magnesium alloy to more than 12 weeks.

Sun et al. [78] loaded halloysite nanotubes (HNT) with the corrosion inhibitor BTA and added this composite to a silicate-based electrolyte to produce a PEO-based coating. The formed coating was applied on AM50 alloy which effectively enhanced its corrosion resistance. The self-healing functionality of this coat was achieved by the formation of a dense nanocrystalline $\text{Mg}(\text{OH})_2$ film at the corrosion sites. The film nucleation was induced by the pH increase in pores of the corroding PEO coating, thus triggering the mechanism of active corrosion protection of the Mg alloy (Fig. 9.9).

Lastly, Luo and Cui [79] developed a conducting polymer-based smart coating for magnesium via direct electrodeposition on the active metal in ionic liquid under mild conditions where the magnesium substrate was

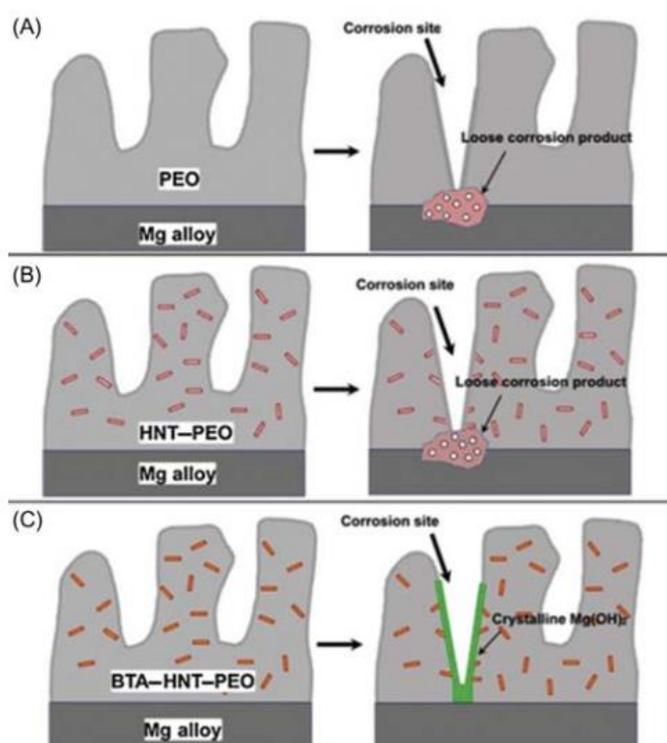


Figure 9.9 Corrosion degradation and protection mechanisms of AM50 Mg alloy with (A) PEO, (B) HNTPEO, and (C) BTAHNTPEO coatings in NaCl solution [78].

highly stable during the electrodeposition process. The authors electrodeposited poly(3,4-ethylenedioxythiophene) coatings on magnesium which were uniform and could significantly improve the corrosion resistance for magnesium or its alloys.

9.9 Future of smart coatings for magnesium protection

As a result of the global concern regarding fossil fuels having the major responsibility for atmospheric pollution, all countries must adopt more clean and ecofriendly technologies in industry and transportation sectors. Turning to light-weight vehicles based on Mg alloys provides an excellent strategy for reducing CO₂ emissions. In spite of the high reactivity and corrosion tendency of Mg alloys, this issue can be treated by means of an effective coating. As an alternative to toxic chromium-based coatings, this chapter provides the most recent advances of state-of-the-art coatings for Mg and Mg alloys with outstanding abilities to protect Mg materials against corrosion with self-healing properties if corrosion occurs. However, these coatings are still confined to the laboratory scale, and we have collected as many related works as we could so that they can be utilized by manufacturers of Mg-based vehicles in the future.

9.10 Conclusion

This chapter provides an introductory review on the use of magnesium in industries, its importance and applications, and various protection methods against its corrosion. The definition of smart or intelligent coatings having self-healing properties, their advantages, and designs are discussed. A number of smart coatings that have been developed and reported in the literature for magnesium and its alloys were reviewed to shed light on the potential applications of these advanced coatings in transportation industries. As a future perspective, this chapter reports on these coatings to transfer them from lab scale to industry as effective protectors for Mg-based vehicles against deterioration.

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