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The Role of Silane Sol-Gel Coatings on the Corrosion Protection of Magnesium Alloys

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Abstract

Magnesium alloys, as the lightest structural metallic material with promising physical, mechanical, and biodegradable properties, have become very attractive for different technical applications, especially for industrial and biomedical fields. However, rapid corrosion is the most critical obstacle that limits its use to play a major role in large-scale applications. The simplest way to control the corrosion rate is to prevent a direct contact of the magnesium substrate with the environment by using surface modification technologies. Silica sol-gel coatings are considered a promising solution to enhance the corrosion resistance of magnesium alloys because sol-gel-based coating systems form very stable chemical bonds with the metallic surface. In this chapter, an insight about the advances in silica sol-gel coatings as an alternative method to control the corrosion of Mg and its alloys will be exposed. A wide overview of the most relevant aspects and their current applications, specifically for aerospace, automobile, and biomedical applications will be described. The modification of silica sol-gel matrix by the incorporation of different types of inhibitors to achieve an active barrier property on Mg alloys has been also considered. Finally, the future perspective based on the development of new silica sol-gel coatings on Mg alloy will be presented.

Keywords: Mg alloys, sol-gel, protective coating, corrosion, synthesis sol-gel, inhibitor

1. Introduction

The use of magnesium alloys in different industrial fields has increased mainly due to its very high strength-to-weight ratio in comparison to other structural alloys [1]. However, an important limiting factor is their high reactivity and thus, their susceptibility to corrosion [2]. The main objective of the research area has always been to increase the corrosion resistance of metallic substrates [3]. One method to reduce the effect of corrosion is to deposit a protective coating on a metallic substrate. Among the coating techniques, sol-gel process is considered a very efficient and economically viable solution for developing anticorrosion coatings on magnesium alloys. According to Segal [4], the sol-gel process can be defined as the production of inorganic oxides in the form of colloidal dispersion or metal alkoxides.

The sol-gel process was initially developed for producing pure inorganic materials, ceramic, and glass materials. However, pure inorganic sol-gel coatings do not provide

enough corrosion protection due to the presence of micro-cracks or defects [5]. The ability to process organic-inorganic hybrid composites at low temperature opened new opportunities in the design of free-crack sol-gel coatings that enhances the corrosion resistance of metals [6]. The research focused on the polymerization of organic-inorganic hybrid materials by sol-gel process increased significantly near the end of the twentieth century [7]. Thus, sol-gel process has got a strong technological impact on research related to protective and functional coatings because this method allows the surface modification of different materials without changing the substrate properties.

The citation report of the “Web of Science Core Collection” database reveals that the amount of literature containing “sol gel” and “Mg alloys” as keywords was 421 between 2000 and 2021; the research in this field is annually growing because of the new alkoxysilane precursors and functional species now available to obtain silica coatings with novel physicochemical properties.

1.1 A brief description of sol-gel synthesis process

The sol-gel technology is a wet-chemical process where the principal chemical aspect is the transformation of compounds, known as precursors, that contain Si-OR and Si-OH to form stable colloidal particle suspensions known as sol [8]. The sol can be applied on the substrates by different deposition techniques and then sintered to obtain a coating. During the aging step, a chemical transformation of the sol occurs leading to a rigid network, resulting in a gel [9]. Generally, inorganic or organic-inorganic sols are obtained via hydrolysis and polycondensation reactions between silicon alkoxides ($\text{Si}(\text{OR})_4$) such as: tetramethoxysilane (TMOS) or tetraethoxysilane (TEOS) and organoalkoxysilanes $\text{R}'\text{-Si}(\text{OR})_{n-1}$; where R' is the organic functional group linked to Si through a nonhydrolyzable covalent bond. During the hydrolysis stage, alkoxide groups are replaced with hydroxyl groups. Once the hydrolysis reaction has initiated, the condensation reaction occurs simultaneously. In this stage, the hydroxyl group and residual alkoxyl group react to form a three-dimensional Si-O-Si network [10]. From the reaction pathway point of view, two different Si-O-Si formation mechanisms can take place regarding if the reaction is performed under acidic or basic conditions. Therefore, the morphology and the structure of the resulting network strongly depend on the pH of the reaction.

Under acidic conditions [11], the oxygen atom of Si-O-R group is protonated in the first step to form a good leaving group. The central silicon atom turns to be more electrophilic and thus more susceptible to react by water to form Si-OH group (**Figure 1(1)**). An equilibrium condition is established between silanol groups and H^+ ions, resulting in positively charged species Si-OH_2^+ that interact with a silanol group to form Si-O-Si bonds (**Figure 1(2)**). In this case, the polymerization rate is directly proportional to the H^+ concentration. Therefore, a large number of monomers or small oligomers with reactive Si-OH groups are simultaneously obtained. The hydrolysis step reaction is favored, and the condensation step reaction is the rate-determining step. It was reported that the positively charged species, Si-OH_2^+ , react preferentially with the less acidic silanols (silanols attached to the least condensed (Si-O-Si) end groups), giving to chain-like networks [13].

Under basic conditions [14], the hydrolysis reaction occurs directly by nucleophilic attack of OH^- to the silicon atom to form Si-OH bonds. In this case, deprotonated silanol (Si-O^-) anion is formed and then it gets condensed with a silanol group. The condensation reaction is favored, and the hydrolysis reaction is the rate-determining

Figure 1.
Mechanism of acid-catalyzed sol-gel process. (1) Hydrolysis mechanism and (2) Condensation mechanism reactions. Image adapted from reference [12].

step. The hydrolyzed species are immediately consumed because of the fast condensation. Due to the nucleophilic nature of the deprotonated silanol, the Si-O^- preferentially attacks the more acidic silanol (silanols attached to the highest condensed (Si-O-Si) end groups), leading to the formation of branched and highly condensed clusters.

1.2 Deposition methods and curing process of silane sol-gel coatings

A typical route of formation of silane sol-gel coating is described as the following process: synthesis of sol-gel > deposition > heat treatment. A sol-gel coating can be applied to Mg metallic substrates through various techniques, such as dip-coating, spin-coating, spraying, and electrodeposition, among others. However, dipping and spinning techniques are the two most used ones, especially for flat surfaces [10]. In the case of complex shapes, uniform coating can be obtained by electro-phoretic deposition method (EPD) [15].

By dip-coating, the surface treatment is attained by immersing the substrate into the sol-gel solution. The silanol groups Si-OH interact spontaneously with the Mg-OH groups that existed on the alloy surface via Van der Waals interactions. Upon the heat treatment, the Si-OH and Mg-OH bonds are attached firmly via a condensation reaction producing metallo-siloxane (Mg-O-Si) covalent bonds (**Figure 2**), and the remaining Si-OH groups of the deposited sol condense and form Si-O-Si bonds [16].

By controlling the curing temperature, the control of pore volume and size and mechanical strength can be achieved. High temperatures (more than 200°C) are normally used to cure inorganic sol-gel coatings and lower temperatures (less than 200°C) for drying/curing organic-inorganic sol-gel coatings [10]. Depending on

Figure 2.
Schematic representation of metallo-siloxane covalent bond formation.

the sol-gel precursors used, an optimal curing temperature should be defined since an inaccurate temperature could result in a decrement of the corrosion resistance properties of the coating and/or on the mechanical properties of the substrates. For instance, room temperature cured sol-gel coatings exhibit crack-free morphology, but a higher water sensitivity compared to coatings cured at a higher temperature. On the other hand, an increment of the curing temperature can lead to cracked coatings due to the stresses that appear during the sintering process [12]. A relatively new approach to densify sol-gel coatings is to use UV radiation [17]. Sol-gel films treated by UV radiation at room temperature can form denser sol-gel coatings able to improve the corrosion resistance of alloys.

1.3 Corrosion behavior of Mg alloys in aqueous environment

The poor corrosion resistance of Mg alloys can be mainly attributed to its high electronegative potential and the poorly protective properties of the quasi-passive oxide/hydroxide layer formed upon Mg. Generally, when the Mg alloys corrode in aqueous electrolyte, the metal changes its oxidation state, forms ionic species, and releases electrons. To maintain electroneutrality, the generated electrons must be consumed by other species. Therefore, the anodic reaction must be accompanied by a reduction reaction, where a molecule, ion, or atom gains electrons. In aqueous solution, water reduction is the dominant cathodic reaction. **Figure 3(1)** illustrates the anodic and cathodic reactions and the overall reaction that takes place during the corrosion of Mg in aqueous environment. The presence of chloride ions in the aqueous solution typically leads to accelerated corrosion processes (**Figure 3(1)**). $\text{Mg}(\text{OH})_2$ can convert to MgCl_2 , with higher solubility, promoting the dissolution of the Mg alloy [18].

On the other hand, the corrosive environment in the human body has a solution consisting of 0.14 M NaCl and other inorganic species, such as Ca^{2+} , PO_4^{3-} , and HCO_3^- . In this case, the presence of phosphates and carbonates promotes the formation of partially protective corrosion product layers [19]. It is clear that corrosion products depend on the type of the electrolyte. These corrosion products not only affect the corrosion rate but can also provide different protection properties to the substrate. **Figure 3(2)** shows a schematic representation of possible interactions between corrosion products of Mg alloy surface on a biological environment.

The deposition of a silane coating could control the corrosion of Mg alloys, although it could dissolve in contact with water due to the hydrolysis of the polysiloxane (Si–O–Si) network [20] that results in the release of silicic acid ($\text{Si}(\text{OH})_4$), which can be expressed as follows [21]:

It is important to determine the corrosion rate to explain the corrosion behavior and provide models that predict the kinetics of the corrosion in an engineering context. The most widely used technique for exploring the corrosion behavior of a coated Mg alloy involves immersing the samples in a corrosive solution, since the corrosion performance is faster than atmospheric corrosion tests [19]. To study the corrosion performance of coated Mg alloys in aqueous solution, a wide range of tests are used [2]. These tests are divided into two large groups: electrochemical and nonelectrochemical

Figure 3.
Schematic representation of reactions that take place between Mg alloy surface and (1) NaCl aqueous solution and (2) biological environment (reprinted from Ref. [19], Elsevier).

tests [22]. The most common electrochemical and nonelectrochemical methods used are mentioned below.

1.3.1 Electrochemical techniques

These methods are important and rapid tools for assessing the corrosion of coated Mg alloys. Between the electrochemical techniques, the most used are Potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS).

1.3.2 Nonelectrochemical techniques

The most common nonelectrochemical methods used for Mg corrosion research are weight loss measurements, hydrogen collection, and pH measurements.

The electrochemical techniques for exploring the corrosion behavior of coated Mg alloys can be used independently or simultaneously with the nonelectrochemical techniques. The principles of each technique and an overview of the main advantages and limitations of different techniques were provided by Durán et al. [5]. A recent review by Kirkland et al. [23] considers the methodologies used to study the corrosion of biodegradable Mg implant materials.

2. Potential use of the Mg alloys in industrial applications

One of the key techniques to reduce fuel consumption and subsequently greenhouse gas emission is to shift to lightweight vehicles. Magnesium alloys with their low density, easy recyclability, and high strength-to-weight ratio are exceptional candidates in the automotive and aerospace sectors [24]. However, the high chemical reactivity and the low standard corrosion potential (~ -1.65 V.SCE), which is less electropositive than aluminum alloys ($\sim (-0.73$ V.SCE)), make them highly susceptible to corrosion, limiting their use in such areas [25]. In order to prevent corrosion of Mg alloys, surface modification techniques such as sol-gel technology have attracted increasing interest for many researchers.

2.1 Barrier effect of single protective silane sol-gel coatings against corrosion

The application of single sol-gel coatings on the surface of Mg alloys has been considered as a good initial approach to provide a protective behavior to the alloy, since the deposition of an inert silane coating avoids the direct contact between substrate and corrosive environment [26]. From the point of view of synthesis, the sol-gel route offers a versatile way to synthesize effective and denser coatings with specific properties.

2.1.1 Passive sol-gel coating barrier

Pure inorganic sol-gel coatings have been studied as an inert physical barrier to provide protection against corrosion. However, inorganic sol-gel coatings have some limitations such as: (i) brittleness, shrinkage, and internal stress after heat treatment process, and (ii) the high temperature required to sinter the coating that mismatches with the thermal expansion coefficient of Mg substrate [27]. A great effort has been made to incorporate organo-alkoxysilanes into the sol-gel synthesis to obtain crack-free hybrid coatings able to be sintered at lower temperatures (below 200°C, depending on Mg alloys) close to the thermal expansion coefficient of Mg substrate [28]. Due to the wide variety of organic-inorganic precursors, there is growing attention on producing hybrid-inorganic sol-gel coatings with different cross-linked structures and compositions. The final hybrid sol-gel coatings could reach fascinating mechanical and physical properties such as flexibility, hydrophobicity, exceptional dielectric properties, strength, ductility, hardness, and good thermal stability. Zucchi et al. [29] studied the protective performance of coatings obtained using organo-silanes with a long alkyl chain (octadecyl-trimethoxysilane) on AZ31 magnesium alloy. An improvement of the corrosion resistance properties of Mg alloy was observed, confirming that the modification of the siloxane network using a long aliphatic chain provides a positive effect regarding corrosion performance.

The corrosion protection of organic-inorganic hybrid thin films prepared with other organoalkoxysilane precursors such as methacryloxypropyltrimethoxysilane (MAPTMS) and tetramethoxysilane (TMOS) on AZ31 and AZ61 Mg alloys has been also studied by El-Hadaba [30]. The results showed an enhancement of the corrosion protection properties at the initial immersion time, but a quick degradation of the coated AZ31 Mg alloy after 1 day of immersion in 0.6 M NaCl aqueous solution. This behavior was attributed to microscopic pores defects in the sol-gel layer. The low pH of the sol-gel solution promoted the Mg dissolution during the deposition process together with the hydrogen evolution during the curing sol-gel coating.

As observed, although sol-gel technology allows the preparation of different hybrid organic-inorganic sol-gel coating compositions, the obtention of effective coatings for Mg-based alloys still is a huge challenge. One of the main aspects, related to the synthesis of the sol-gel coatings on Mg alloys, is the pH of the hydrolyzed sol-gel solution. Indeed, magnesium is not stable and spontaneously degrades during sol-gel deposition step when using acidic conditions. Hernández-Barrios et al. [31] evaluated the corrosion behavior of AZ31 Mg alloy pretreated with a hybrid silica sol-gel coating prepared using acetic acid as acid-catalyst, and 3-glycidyloxypropyltrimethoxysilane (GPTMS) and TEOS as silica precursors. The results revealed that the sol synthesized with the highest acid concentration reached more stable gelation kinetics, but with the worst corrosion resistance performance (i_{corr} : 1.3×10^{-6} A/cm²) compared with the sol synthesized with the slower acid concentration (i_{corr} : 2.4×10^{-7} A/cm²). The decay of the corrosion resistance of the sample coated with the more acidic sol is attributed to defects on the coating's morphology and to the corrosion process advancing in the substrate. Indeed, during the sol-gel deposition, corrosion products are generated together with hydrogen evolution.

In this sense, pH of the sol is a critical parameter and should be considered to get a nondefective SiO₂ coating not affecting the metallic substrate, and thus to provide a suitable corrosion resistance performance.

Another aspect to consider is related to the promotion of insulating coatings with high-density structures for blocking the penetration of electrolytes. In this case, complexing agents are added during the synthesis of the sol to react with the organic group of some organo-alkoxysilanes and therefore stimulate the organic polymerization. For instance, Qian et al. [32] prepared a hybrid sol-gel through hydrolysis and condensation reactions of TEOS and GPTMS. The opening of the epoxy group of GPTMS results in coatings with novel physical and chemical properties. The authors further incorporated triethylenetetramine (TETA) as an organic crosslinking agent to bond with the open epoxy groups. The corrosion behaviors of the coatings deposited on AZ31B magnesium alloy were evaluated by polarization curves measurements in the 3.5% NaCl solution. The results revealed that a compact and smooth silane film was formed on the substrate's surface, which provided good barrier protection, improving the corrosion resistance ability (i_{corr} : 3.7×10^{-9} A/cm²) in comparison to untreated magnesium alloy substrate (i_{corr} : 4.1×10^{-6} A/cm²) (**Figure 4**).

Furthermore, the corrosion resistance properties of silane films can be significantly improved by the incorporation of some nanoparticles into the sol-gel film. The beneficial effects of the addition of different nanoparticles on the corrosion resistance for Mg alloys have been reported by different researchers. For instance, the effect of incorporating SiO₂ nanoparticles [33], graphene oxide [34, 35], carbon nanotubes [36], alumina, titania, zirconia [37], and Montmorillonite (MMT) [38] on the sol-gel synthesis has been evaluated.

For example, the addition of a colloidal silica nanoparticles suspension into the sol-gel coating is considered a good approach to increase the hardness, density, and wear resistance, and thus the corrosion resistance properties of hybrid silane coatings. Peres et al. [33] investigated the effect of adding different amounts of SiO₂ nanoparticles into a hybrid silica sol based on TEOS and GPTMS on the corrosion resistance of AZ31 magnesium alloy. The results showed that the incorporation of nanoparticles improved the corrosion resistance of Mg alloy. However, the maximum amount of SiO₂ recommended to obtain a coating with the best anticorrosive performance was between 100 and 300 mg l⁻¹; coatings doped with a higher amount of SiO₂ showed nanoparticles agglomeration and consequent defects and cracks. Thus, two critical issues should be

Figure 4. Potentiodynamic polarization curves of bare alloy and the hybrid coating in 3.5 wt.% NaCl (reprinted from Ref. [32], ESG).

considered to avoid a detrimental effect on the anticorrosion behavior of the film: (i) the dispersion of nanoparticles into the film, and (ii) the amount of loaded nanoparticles.

On the other hand, graphene oxide (GO), which is a two-dimensional sp^2 carbon material, with many inherent characteristics such as good mechanical strength, chemical inertness, and good thermal stability, has also been considered to reinforce organofunctional silane coatings for corrosion protection of Mg alloys [34]. However, the high specific surface area of graphene and the strong Van der Waals force (–stacking) between graphene layers made it to agglomerate easily, resulting in hybrid coatings with a decrease in corrosion performance and microhardness properties. As graphene-based compound [39], oxidized fullerene [40], and carbon nanotube [36] have also been considered as a novel promising reinforcement for hybrid composite silane coatings for Mg alloys due to their properties including high strength, lightweight, thermal and mechanical stability, hydrophobicity, corrosion resistance, and high specific surface area. The anticorrosion and protective action of a zeolite-filled silane sol-gel coating on AZ31 magnesium substrate was studied by Calabrese et al. [41]. The zeolite composite coating evidenced very high hydrophobicity behavior (contact angle up to 140° showed good adhesion and good barrier properties during immersion in 3.5 wt.% NaCl solution.

Although significant advances have been made regarding modified sol-gel coatings composition, there is still a large gap in this research since most of the studies only provide information about the instantaneous corrosion rate, but not about the kinetic of the sol-gel film degradation in standard aqueous solution of 3.5 wt.% NaCl, which is helpful for a comprehensive choice of anticorrosion strategies and a systematic control of the degradation of sol-gel films.

2.1.2 Active sol-gel coatings barrier

Up to now, conventional physical barrier coatings with suitable composition designs have been considered to improve the corrosion resistance of Mg alloys; however, in very harsh environments when the aggressive agent and water reach the metal surface, the silane coatings are not capable to stop the corrosion process, reducing the lifetime of the coating protection. For this reason, smart self-healing protective coatings should be considered to provide long-term protection to the material. The smart

self-healing effectiveness relies on a dissolving-reprecipitation interaction in the local defect, able to repair the defects entirely or partially, restoring the functionality of the coatings. The incorporation of corrosion inhibitors into the silane sol-gel coatings is the most studied strategy to obtain a self-healing ability of the silane coating thus enhancing the corrosion resistance of the metal.

Inorganic corrosion inhibitors such as rare earth inhibitors (cerium and lanthanum) have been demonstrated to be effective in the protection of magnesium alloy. For example, the rapid formation of oxygen vacancies in ceria lattice plays a crucial role in self-healing coating formulation since cerium cations interact with the OH^- ion released during the corrosion process, forming stable and insoluble cerium oxide/hydroxide species that precipitate in the surface and prevent further corrosion process. Prolonging the corrosion time, the deposited film gradually grows reducing the oxygen and electron transfer [42].

The effect of adding Ce and La salts as inhibitors as well as nanoparticles in silane solution has been explored as an opportunity and a challenge for researchers. Zanotto et al. [43] studied the corrosion resistance efficiency of 3-mercaptopropyltrimethoxysilane (PropS-SH) coatings modified with cerium nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) deposited on AZ31 magnesium alloy. Moreover, Qiao et al. [44] studied the corrosion resistance behavior of 3-methacryloxypropyltrimethoxysilane coatings modified by lanthanum nitrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) deposited on AZ31 Mg alloy. Both studies demonstrated that either cerium or lanthanum ions can be added as inhibitors to the silane solutions to enhance the corrosion of the pretreatments for magnesium alloy. However, they reported that silane coatings doped with cerium nitrate salt showed poorer corrosion behavior than those doped with cerium nanoparticles, CeO_2NPs . Coatings doped with CeO_2NPs were more “compact,” avoiding the electrolyte penetration, and therefore providing improved corrosion protection [45]. Under this perspective, Calado et al. [46] modified a hybrid epoxy-silane coating with ceria nanoparticles to improve the barrier protection of AZ31 Mg alloys. EIS results showed an improvement in corrosion resistance because the modified ceria-coating was capable to provide active corrosion protection. The ceria nanoparticles react with water and/or hydroxyl ions, producing a cerium (IV) oxide or hydroxide layer onto the AZ31 surface. Electrolyte diffusion pathways are blocked; thus, the localized corrosion activity is reduced.

The use of organic compounds with heteroatoms such as N, S, and O can provide inhibitory effects to silane coatings. The major role of heteroatoms in corrosion protection is the formation of a complex chelate with Mg^{2+} ions which create insoluble deposits on the metallic surface, blocking the active sites and preventing the local pH increases, which is responsible for the intensification of intermetallic dealloying [47]. Toorani et al. [48] proposed a silane coating with active corrosion properties using γ -amino propyltriethoxysilane (APS) and TEOS as silica precursors, and adding different organic inhibitors: 8-hydroxyquinoline (8-HQ), indole-3-carbadehyde (I3C), 2-mercaptobenzoxazole (MBO), and sodium diethyldithiocarbamate (DDTC) to silane precursors. The results showed that organic inhibitors provide better active corrosion protection properties to the silane coating compared to the bare AZ91D magnesium alloy, especially when the 8-HQ inhibitor was added. In search of new organic inhibitors for corrosion protection of Mg alloys, Ashassi-Sorkhabi et al. [49] reported the effect of adding amino acids (L-alanine, L-glutamine, L-methionine, and L-aspartic amino acids) as eco-friendly inhibitors into sol-gel coating matrix. The corrosion ability of amino acids was associated with their tendency to form hydrogen bonds with the oxide or hydroxide groups on the metal surface and to the lone

pair electrons present in their heteroatoms that can complex Mg cation. The paper described that all amino acids improved the anticorrosion performance of the silane coating, but L-aspartic exhibited the best enhancement effect.

2.2 Barrier effect of multilayer protective coatings

Even though silica sol-gel coatings have shown to be successful as a physical and active barrier, it is sometimes not enough for a long-term protection system in harsh environment. Some micro-defects or micro-cracks appear, allowing the penetration of corrosive agents and producing oxide-hydroxide-carbonate deposits beneath the coating, causing its rapid delamination. Thereby, the application of single-layer coating does not provide a full protection of Mg alloys. For this reason, great effort is underway to identify efficient alternative systems with desirable surface properties. In this context, the combination of different systems has been suggested, based on the deposition of a first oxide layer using conventional anodization or plasma electrolyte oxidation (PEO) processes followed by the deposition of silica sol-gel coating seems to be a good alternative.

PEO is an electrochemical process that has increasingly been employed to improve the surface properties of Mg alloys. This process produces an adhesive micro-porous oxide layer on the surface that provides a moderate protection on the metal and alloys. The ceramic-like film can be sealed with a silane coating to reduce the infiltration of the aggressive medium through the micro-pores, providing a long-term corrosion protection. Tan et al. [50] reported the preparation of a multilayer system obtained by anodizing the AZ91D Mg alloy and post-sol-gel treatment using MEMO (3-methacryloxypropyl trimethoxysilane), TPTMS (3-mercaptopropyl trimethoxysilane), and silica nanoparticles as reinforcement. The preliminary results showed that after the deposition of various silane layers by spray method, the silane coatings seal the pores of the anodized coating providing a physical corrosion protection in 3.0 wt.% NaCl.

Recently, Merino et al. [51] studied the corrosion resistant of an integrated system for AZ31B Mg alloys combining PEO and sol-gel process. In this case, the sol was prepared by using TEOS, GPTMS, colloidal SiO₂ nanoparticles, and 1-methylimidazole (MI), and then deposited onto optimized oxide coating. The results revealed that the multilayer system exhibits a good corrosion performance in 3.5 wt.% NaCl, since the polarization resistance (R_p) for the integrated system samples showed a quite high value ($31546.8 \Omega \text{ cm}^2$) compared to Mg alloy ($207.3 \Omega \text{ cm}^2$) (**Figure 5**).

Figure 5. Bode plot and phase angle plot for bare AZ31B Mg alloy, anodized sample and multilayer system tested in 3.5 wt.% NaCl (reprinted with permission from Ref. [51], Wiley Online Library).

This is an interesting alternative to significantly improve the corrosion resistance of Mg alloys. However, only a few papers present complete and decisive results. Additionally, different factors need to be considered to reach a good compromise between stacking and anticorrosion properties, such as sealing pore effectiveness and micro-cracks formation during the deposition of multiple silane layers [52].

3. Bio-applications

Mg alloys are considered as suitable candidate materials for biomedical applications due to their mechanical properties and their confirmed biocompatibility. In biological environments, magnesium alloys biodegrade with kinetics that depend on the surrounding tissue, eliminating secondary surgical procedure of implant removal [53]. The desirable Young's modulus of Mg alloys (41–45 GPa), which is close to the cortical bone (3–20 GPa), and the excellent ability of the Mg ions to promote bone regeneration make them attractive as orthopedic implants [54]. Currently, researchers are underway to improve bioresorbable cardiovascular stents based on Mg alloys, which are designed to provide short-term supporting structures and to combat coronary heart and peripheral artery diseases [55].

Soluble magnesium ions (Mg^{2+}), hydroxide ions (OH^-), and hydrogen gas (H_2) are well known for being the primary magnesium corrosion products. Many studies have confirmed that Mg^{2+} ions are essential for living cells and the excess can be excreted in the urine without causing damage to excretory organs such as the liver or the kidney. However, the rapid corrosion rate of Mg-based alloys in physiological conditions promotes an intense hydrogen evolution [56]. Hydrogen gas is nontoxic and is easily diffusible, but excessive corrosion leads to the formation of undesirable gas bubbles (emphysema) in surrounding soft tissue. The rapid evolution of H_2 bubbles can get accumulated and form gas pockets, leading to intensifying necrosis and inflammation within the living tissues [57]. On the other hand, depending on the type of the implant, the excessive corrosion leads to secondary problems. In the case of orthopedic implants, an excessive corrosion can produce early losing mechanical strength properties avoiding the implant assist the fracture of the bone firmly at least in the early healing stages (typically 12 weeks) [58]. Moreover, the uncontrollable and uneven degradation behavior for a vascular implant will produce huge amounts of hydrogen within a short time disfavoring the healing of neovascularization tissues which easily result in restenosis. Studies have shown that the critical period of vascular healing normally ends 3 months after implantation [58].

Both orthopedic and vascular magnesium implants look promising, but these drawbacks limit their applications. Thus, the use of Mg alloys as biodegradable implants is still in its infancy due to its high susceptibility to corrosion.

3.1 The effect of a silane coatings to control Mg alloy degradation

Since, silane coatings have demonstrated excellent biocompatibility, favorable cellular adhesion, and proper protein absorption, they have been employed as bio-functional coatings to control the high in-vivo degradation rate of Mg and its alloys. It has also been reported that organofunctional silane coatings do not cause adverse tissue reactions, and the degradation product ($\text{Si}(\text{OH})_4$) produced into the body can be easily eliminated through the renal system. For this reason, some researchers have developed different compositions of organo-inorganic silane coatings for this

application. For instance, Gaur et al. [59] studied the effect of a phosphonosilane coating, trying to improve the corrosion resistance of Mg-6Zn-Ca magnesium alloy in a physiological environment. In this study, the authors used a phosphonate (silane diethylphosphatoethyltriethoxysilane (DEPETES)) and bis sulfur silane (bis-[3-(triethoxysilyl) propyl] tetrasulfide (BTESPT)) precursors to synthesize the silane coating, considering that both precursors were found to be nontoxic. The in-vitro investigation showed that the silane coating provided significant and durable corrosion resistance. Moreover, the presence of hydrated magnesium phosphate was also identified after 216 h of immersion test in m-SBF; component reported to support osteoblast formation and tissue healing. Two years later, the same authors [60] reported the preparation of other silane coating composition obtained by using GPTMS and MTEOS to improve the in-vitro corrosion resistance and biocompatibility of the Mg6ZnCa alloy. The results demonstrated that the deposition of a silica coating obtained by combining both precursors slow down the dissolution of a biodegradable magnesium alloy in the early stages (280 h), enhancing cells growth on the coated specimen. Furthermore, the formation of magnesium/calcium phosphate on the surface of the Mg alloys after immersion time showed good bioactivity and osteo conductivity of the coating. The results suggested that the sol-gel coating developed for the Mg6ZnCa alloy is a promising solution for biomedical application such as bio-absorbable surgical skin staples (needs to be removed after 10–12 days of postsurgery), micro-clips (needs to degrade within 2 weeks), and pins used in fingers dislocation or fracture that are predicted to heal quickly.

To enhance the corrosion resistance of magnesium alloys, a modified epoxy-silane coating obtained by using GPTMS and diethylenetriamine (DETA) as organic cross-linker was also proposed by Zomorodian et al. [61]. Although hydrogen evolution, pH, and in-vitro cell culture tests were not carried out, the EIS data showed an improvement of the corrosion resistance properties in Hank's solution associated with a dense and homogenous coating deposited on the Mg alloy. On the other hand, Castro et al. [62] also investigated the corrosion degradation rate of Mg alloys (AZ31B and AZ91D) by the deposition of two different silica sols prepared with and without colloidal silica particles for biodegradable implant materials. The results showed that the corrosion resistance behavior of Mg alloys, characterized in SBF using three different in-vitro tests: hydrogen evolution, pH variation, and potentiodynamic curves, enhanced after the deposition of the silane coating that contains nanoparticles as cross-linked network reinforcement (**Figure 6**).

Recent studies consider the development of double nano-composite coatings [63], based on the first deposition of $\text{Mg}(\text{OH})_2$ or MgO enriched oxide layer and a subsequent deposition of a silane sol-gel coating, to achieve longer corrosion protection systems. Dou et al. [64] prepared double composite coatings using a conventional micro-arc oxidation process, and then the sol-gel technique. The in-vitro degradation performance of the composite coatings showed an improvement of the corrosion resistance properties by reducing the corrosion current density.

Different approaches have been considered to improve the biocorrosion resistance of the Mg alloys for cardiovascular stent application since it is a disease with high mortality and an increasing incidence [65]. For example, Liu et al. [66] reported the use of layer-by-layer self-assembly technique, based on the deposition of a first APTES-based silane coating followed by the deposition of a graphene oxide (GO) suspension. The results showed that the silane/GO composite coating improves the corrosion and wear resistance of Mg alloy, suggesting its use in biomedical fields as a vascular stent.

Figure 6. Variation of hydrogen evolution as a function of immersion time in SBF solution for coated and uncoated AZ31B and AZ91D substrates; MTL coating corresponds to the silane coating that contains nanoparticles and TG to the silane coating without nanoparticles. (reprinted with permission from Ref. [62], Springer Nature).

3.2 Factors affecting the bio-functionality of silane coatings

3.2.1 Cyto-compatibility

The biocompatibility of Mg alloys is determined by the toxicity of the released corrosion products and the interaction effect between metal surface and living tissues. Not all the studies mentioned in the previous section included in-vitro cell viability tests as complementary information, necessary to determine the response of the silane coatings deposited on Mg alloys.

Although AZ91D showed a better corrosion resistance performance with respect to AZ31B Mg alloys, the AZ91D shows lower biocompatibility and bioactivity due to its higher Al content. To improve the cyto-compatibility of AZ91 Mg alloys, Witecka et al. [67] studied the effect of the deposition of different silane coatings on its surface; ethyltriethoxysilane (S_1), 3-aminopropyltriethoxysilane (S_2), 3-isocyanatopropyltriethoxysilane (S_3), phenyltriethoxysilane (S_4), and octadecyltriethoxysilane (S_5). S_1 was used to introduce a simple polysiloxane precursor to the substrate; S_2 and S_3 were selected to introduce positive and negative charges on the alloy surface, and finally, S_4 and S_5 were chosen to examine the π electrons and the long alkyl chain effect on the surface. Cell culture experiments showed that the cyto-compatibility was not affected by the surface modification. However, Silane S_1 was the only system able to improve cell growth during 7 days of incubation. Because cyto-compatibility is a basic and important parameter in the design of silane coating to bio application, other strategies have been considered to improve the bioactivity of Mg alloys, the deposition of sol-gel derived bioactive glasses coatings being one of them. These coatings based on pure silica, SiO_2 -CaO- P_2O_5 or SiO_2 -CaO, have been shown the largest level of bioactivity based on their reaction rate and bone binding ability. The bone-bonding ability occurs through the development of a biological apatite layer when the materials are exposed

Figure 7.

Schematic representation of the deposition sol-gel glass-like bioactive sol for enhancing the implant performance of AZ91D magnesium alloy (reprinted with permission from [70]; Elsevier).

to body fluids or simulated body fluids. In-vivo studies have shown that biological species are incorporated into the silica-rich and apatite layers. Consequently, coatings react with the physiological fluid for obtaining an adequate interfacial bonding with bone by forming hydroxyapatite layer (HA). Their main applications are focused on bone repair and regeneration in the field of tissue engineering. Regarding the synthesis, some attempts have been made to obtain bio-glass silane coatings [68, 69]. Recently, Omar et al. [70] synthesized two compositions of bioactive silica-glasses, 58S and 68S, by using tetramethyl orthosilicate (TMOS), methyltriethoxysilane (MTES) and calcium L-lactate hydrate (**Figure 7**).

The lactate was used to avoid the use of calcium nitrate as a precursor due to the presence of nitrate residuals in the coatings is not beneficial to the body. The results showed that both coatings showed a quick apatite formation, good corrosion resistance properties, good cell adhesion, and proliferation, representing a promising coating system for degradable AZ91D implants.

Other strategies considered in the synthesis of silane-coatings to potentially improve the biocompatibility of Mg alloys consisted of the incorporation of hydroxyapatite nanoparticles. Nikbakht et al. [71] synthesized a modified silane coating with hydroxyapatite nanoparticles to promote biocompatibility and bone healing through producing calcium phosphorus-rich corrosion products. The results showed that a correct amount of hydroxyapatite nanoparticles not only helped to optimize the barrier properties of the silane coating, but also improved cell growth, especially the MG-63 osteoblastic.

3.2.2 Protein absorption-platelet adhesion

The initial interaction of biomaterials with the biological environment is based on the absorption of protein on the surface and the interaction with ions and water molecules to form various reactive interfaces. Understanding protein adsorption mechanisms, kinetics, and thermodynamics are essential to improve the design of silane biocompatible coatings [72]. Appropriate protein adsorption on the modified Mg surface alloys is essential for application in bone tissue regeneration and the effective

integration of Mg implants. In relation to biomedical implants, such as cardiovascular stents, protein adsorption kinetics play a crucial role in the platelet adhesion process. Implanted biomaterials in contact with blood *in vivo* need to retain a low degree of platelet adhesion to prevent thrombosis, implant failure, and other complications [73]. A rapid adsorption of proteins might cause a higher number of platelet adhesion on the surface, which can trigger thrombus formation by platelet activation and ultimately result in blood coagulation. Considering that the protein adsorption can be roughly controlled through roughness and wettability, Majumder et al. [74] proposed the deposition of a hydrophobic silane-PMMA coating to improve the corrosion resistance and the hemo-compatibility nature of AE42 Mg alloys for cardiovascular stent applications. The results showed that an improvement in hydrophobicity resulted in a significant reduction of protein adsorption and hemolysis ratio, making it a favorable candidate for biodegradable stent application. Surface modification by the addition of Heparin (anticoagulant reagent) has also been considered to increase the thrombo-resistance of biomedical implants. Liu et al. [73] developed a biofunctionalized anti-corrosive coating on Mg AZ31 alloy containing heparin reagent. The modified silane coating system reduced platelet adhesion on the surface, thus increasing its interest in biodegradable implant applications as cardiovascular stents.

3.2.3 Drug release silane coatings

On the other hand, bacterial infections or inflammations are one of the reasons for biomedical implants failure. Bacteria can form recalcitrant biofilms on implant surfaces, resisting conventional antibiotic treatments. As a consequence, the entire implant must be removed to allow an efficacious antibiotic treatment. Thus, it is necessary to find an effective local drug-releasing coating to simultaneously provide high anticorrosion and antibacterial ability for Mg alloys. Sol-gel coatings have attracted great attention since they offer the possibility to introduce antibiotics in the coating, and also to control the mechanism and kinetics of the drug release. Under this context, Xue et al. [75] designed a composite coating on AZ31 Mg alloy by depositing a drug-loaded coating obtained by crosslinking ciprofloxacin (CIP) (antibacterial drug) and polymethyltrimethoxysilane (PMTMS) as precursors. Cyto-compatibility and antibacterial performance of the coating were probed using *in-vitro* cytotoxicity tests (MTT), live/dead cell staining, and plate counting method. The results showed that the coating displayed a controllable long-term drug release ability against *Staphylococcus aureus* and *Escherichia coli*, implying that this coating provides a new approach for the anti-infection Mg bone implants. Although this coating system showed a good antibacterial performance, the drug-releasing time of the coating was too long to be used in the human body, since the period in the wound healing cycle is normally 1–2 weeks.

This approach can be a promising alternative, but it is necessary to continue studying ways to shorten drug-release time by modifying the synthesis of the sol. The control of the sol-gel synthesis and processing parameters together with the selection of the precursors are key issues.

4. Conclusions and perspectives

This chapter summarizes the advances of the silica sol-gel coating as a surface modification technique to control the corrosion of Mg and its alloys. The most

important advantages of the sol-gel technique are the opportunity to introduce a wide range of alkoxysilane precursors and organic molecules in the synthesis for obtaining hybrid organic-inorganic sol-gel coatings with desirable cross-linking structure and good protective corrosion behavior. The organically modified sol-gel coatings provide the possibility to obtain thick, crack-free coatings with good corrosion performance. The hybrid films can be reinforced by doping with nanoparticles to obtain denser coatings, and with inhibitors to obtain active barrier protection. Although relevant advances have been made in recent years, some aspects related to the sol-gel technique on Mg alloys should be considered before obtaining a successful industrial application, especially for aerospace, automobile, and biomedical applications.

Since the corrosion behavior of sol-gel coatings depends on the synthesis parameters, organic-inorganic precursors, and the mechanical and chemical features of the comprising organic and inorganic networks, a variety of sol-gel coating with different compositions and cross-linked structures have been developed. However, the different protective properties and the service life between those coating on Mg alloys are still not known clearly. Therefore, systematic and long-term comparisons need to be conducted in future research to better understand the corrosion mechanism, as well as the advantages and disadvantages of each coating. Furthermore, the kinetics of hydrolysis and condensation reactions, gelation kinetics, and curing process parameter should also be studied and considered to avoid cracks coating formation during the heat post-treatment. Sol-gel films treated by UV radiation at room temperature can form a denser sol-gel coating that can improve the corrosion resistance of alloys.

Although a sol-gel coating is a promising alternative, recent works show that the deposition of a single layer of sol-gel coating faces many difficulties and does not stop the corrosion of Mg alloys. On that basis, the combination of different deposition processes, such as anodization or PEO processes, and sol-gel technique could be more effective methods to mitigate the corrosion damage. However, different factors such as sealing pore effectiveness should be considered to reach a good compromise between stacking and anticorrosion properties. The preparation of efficient composite coatings for Mg-based alloys is still a huge challenge.

To achieve a practical application in the biomedical field, the design of sol-gel coatings should be more purposeful. For example, for bone implant applications, the hybrid coatings should be pro-osteogenesis and biocompatible. Moreover, the corrosion resistance studies of the silane coatings deposited on Mg alloys should be complemented with in-vitro cell viability tests to determine the bifunctionality response of the silane coatings.

However, many challenges need to be faced and solved, intelligent multilayer systems are promising alternatives to significantly increase the use of Mg alloys in many relevant applications, from corrosion protection to bioactive devices. Continuous research is the best way to get them.

Acknowledgements

This chapter is a part of the dissemination activities of the project FunGlass, which has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement number: 739566.

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