

Review Article

Corrosion Protection and Surface Treatment of Magnesium Alloys Used for Orthopedic Applications

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An overview is reported about the history of prevailing magnesium alloys as orthopedic biodegradable materials. Important features of the effect of alloying additions, along with surface treatments for corrosion protection of magnesium alloys, are described. Hydroxyapatite (HA), the promising coat deposited by different direct and electrochemical methods to tailor corrosion resistance and biocompatibility, is discussed. Surface modifications, such as microarc oxidation or anodization which lead to nanostructures fabricated to provide better adhesion for HA coatings, are presented.

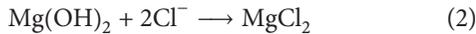
1. Introduction

Metallic materials continue to play an essential role as biomaterials to assist with the repair or replacement of bone tissue that has become diseased or damaged [1]. Metals are more suitable for load-bearing applications compared with ceramics or polymeric materials due to their combination of high mechanical strength and fracture toughness. Currently approved and commonly used metallic biomaterials include stainless steels, titanium, and cobalt-chromium-based alloys. A limitation of these current metallic biomaterials is the possible release of toxic metallic ions and/or particles through corrosion or wear processes [2–6] that lead to inflammatory cascades which reduce biocompatibility and cause tissue loss [2, 4–13]. Moreover, the elastic moduli of these alloys are not well matched with that of natural bone tissue, resulting in stress shielding effects that can lead to reduced stimulation of new bone growth and remodeling which decreases implant stability [14]. Current metallic biomaterials are essentially neutral in vivo, remaining as permanent fixtures, which in the case of plates, screws, and pins used to secure serious fractures must be removed by a second surgical procedure after the tissue has healed sufficiently [15]. Repeat surgery increases costs to the health care system and further morbidity to the patient.

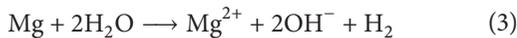
2. Magnesium Alloys as a Biodegradable Implant Material

Fortunately, magnesium, Mg, and its alloys which are chemically active can degrade naturally in the physiological environment by corrosion and are potential candidates in biodegradable hard-tissue implants. Mg²⁺ is the fourth most abundant cation in the human body and is largely stored mainly in bone tissues. It is vital to metabolism processes, a cofactor in many enzymes, and a key component of the ribosomal machinery that translates the genetic information encoded by mRNA into polypeptide structures [16–19]. Early clinical investigations and recent in vivo and in vitro studies suggest that Mg-based implants have good biocompatibility [20–22]. It has also been reported that Mg-based implants can stimulate the development of a hard callous at fracture sites [20, 23]. The unique mechanical properties of Mg alloys also render them desirable hard-tissue implants. Mg alloys possess a density of $\approx 1.7\text{--}2.0\text{ g cm}^{-3}$ that is close to that of natural bones ($1.8\text{--}2.1\text{ g cm}^{-3}$), and the compressive strength and tensile strength are much higher than those of biodegradable polymers. Compared with Ti alloys (110–117 GPa), stainless steels (189–205 GPa), and Co-Cr alloys (230 GPa), the elastic modulus of Mg alloys (41–45 GPa) is closer to that of natural bones. Hence, the stress shielding effect can be mitigated [16].

However, the major drawback of Mg alloys is their low corrosion resistance in the body. In this respect, Mg is undesirable because it is very active chemically, with a standard potential ≈ -1.7 V (standard hydrogen potential). The native MgO and/or Mg(OH)₂ surface layers are loose in nature and cannot provide sufficient protection to resist corrosion encountered in the physiological environment which contains a large amount of chloride ions (~ 104 mmol/L) [24]. Chloride ions can convert the surface Mg(OH)₂ into more soluble MgCl₂, and dissolution of Mg(OH)₂ makes the surface more active, decreasing the protected area and promoting further dissolution of Mg. The reactions are summarized as follows [16, 24]:



In addition, the high concentration of buffering agents in the body plasma is responsible for the high dissolution rate of Mg. When Mg is exposed to an aqueous solution, the following reaction takes place [24]:



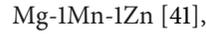
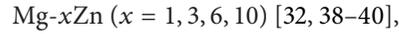
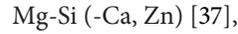
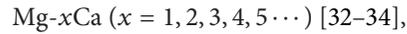
The buffering agents consume the generated OH⁻ quickly in turn, expediting the conversion from Mg to Mg²⁺. It has been demonstrated that inorganic components as well as proteins and amino acids influence the degradation rate. As a result, Mg-based biomedical implants can lose the necessary mechanical integrity before the tissue has sufficient time to heal completely. Hard-tissue repair typically requires implantation of the fixture for at least 12 weeks [16].

3. Corrosion Protection of Mg Alloys

Improvement of corrosion resistance of Mg alloys could be achieved via alloying [22, 25], use of composites [26], or surface treatment.

3.1. Effect of Alloying Elements. An appropriate alloying composition can improve the corrosion resistance, mechanical properties, and the ease of manufacture of Mg-based materials. Two primary groups of Mg-based alloys are those contain 2–10 wt% aluminum (Al) with trace additions of zinc (Zn) and manganese (Mn), demonstrate moderate corrosion resistance and improved mechanical properties [27]. The second group uses a mixture of rare earth (RE) elements in combination with another metal such as zinc, yttrium, or silver and a small amount of zirconium which imparts a fine grain structure and enhanced mechanical properties [27]. As these materials are used in the body, care must be taken to choose alloying elements that are nontoxic. However, it is well known that Al is harmful to neurons [28] and osteoblasts [29] and is also associated with dementia and Alzheimer's disease [28]. The administration of RE (Pr, Ce, Y, etc.) could lead to hepatotoxicity [30]. Excessive Yttrium ions (Y⁺³) have been shown to change the expression of some rat genes and to have adverse effects on DNA transcription factors [31]. This has led to a demand for the development of a novel biodegradable Mg

alloys in which Ca, Zn, Mn, and Si could be an appropriate alloying elements, such as:



Ca or Zn is one of the most abundant nutritionally essential elements in the human body [34, 37, 42–45] and has basic safety for biomedical applications. Mn is an essential trace element (< 0.8 mg/L in blood serum), but high concentration may induce neurotoxicity [46]. Zn and/or Mn helps to overcome the harmful corrosion effect of iron (Fe) and nickel (Ni) impurities that might be present in Mg alloys. Ca reduces oxidation in the molten condition and during heat treatment. It also improves the rollability [47]. Mg-1Zn produced less hydrogen than many other binary Mg alloys in simulated body fluid (SBF) [48]. Ca and Zn act as grain refining agents which improve both corrosion resistance and mechanical properties [49, 50]. With increasing Ca content, more and coarser Mg₂Ca phase precipitates are along grain boundaries, weakening both the mechanical property and corrosion resistance of as-cast Mg-Ca alloy [51]. An as-extruded Mg-4Zn-0.2Ca ternary alloy [52] exhibited excellent mechanical integrity during in vitro degradation. After 30 days immersion in simulated body fluid (SBF) solutions, the values of the yield strength, the ultimate tensile strength, the elongation, and the elastic modulus of the alloy were degraded to values which still enough for bone fixing [52]. Ca ion concentration up to 50 mg/L, Zn ion concentration up to 60 mg/L, and Mg ion concentration up to 1000 mg/L did not cause cell toxicity [37].

Strontium (Sr), along with Ca and Mg, shares similar chemical, biological, and metallurgical properties. There is about 140 mg Sr in the human body, and 99% of the body content of Sr is located in the bones. Proper addition of Sr can refine the grain size of Mg alloys and enhance the corrosion resistance. Gu et al. [53] prepared hot rolled Mg-Sr binary alloys with a Sr content ranging from 1 to 4 wt% and found that Mg-2Sr alloy exhibited the highest strength and the lowest corrosion rate. The in vivo results showed that the degrading as-rolled Mg-2Sr alloy promoted bone mineralization and peri-implant new bone formation without inducing any significant adverse effects [54]. Ternary alloys, Mg-Zn-Sr [54], and Mg-Ca-Sr [55] were also developed, both of which suggest that the presence of higher amount of secondary intermetallic phases leads to poorer corrosion resistance.

Silicon (Si) has been regarded recently as an essential mineral in the human body [56]. It plays an important role in aiding the healing process and helping to build the immune system [57]. Moreover, it may be important for the growth and development of bone and connective tissue [58]. Therefore, it is also possible for Mg-Si alloy to be a biodegradable bone implant material. Refinement of microstructure by Ca

is an effective way to improve mechanical and corrosion properties [49, 50]. It is worthy to note that heat treatment of these Mg alloys can improve both mechanical and corrosion properties [59, 60].

3.2. Surface Treatments of Mg Alloys. Surface treatment of Mg alloys is of particular interest for degradable implants because the corrosion rate is intended to be low in the initial phase due to the modified surface layer and then returns to the normal value when the layer corrodes away. Such a degradation pattern is desirable since the loss of strength of the implant would mirror the increase in strength of the healing union by providing sufficient support in the initial phase [61]. A large body of methods in the surface treatment of Mg alloys for improving corrosion resistance has been reported in the literature [62]. However, these methods are intended for industrial applications and might contain materials that are toxic. For implant applications, several approaches have also been reported to optimize and tailor the corrosion behavior as well as the biocompatibility.

3.2.1. Hydroxyapatite (HA) Coatings. For orthopedic applications, hydroxyapatite (HA) [25, 26, 43, 63–70] or other types of calcium phosphate (Ca-P) coatings are generally of high interest. Generally, the corrosion rate of Mg alloys is significantly decreased by different types of Ca-P coatings. As the detailed nature of the coatings studied varies over a wide range, of course also the measured degradation rates are different. From the preparation point of view, the most simple are Ca-P coatings that spontaneously form on Mg and Mg alloys upon exposure to simulated biofluids [71–74]. In addition to influencing the corrosion rate of Mg, Ca-P coating has been shown to be beneficial for biocompatibility [75, 76]. The layer that forms spontaneously on Mg alloys in SBF solution is not hydroxyapatite but instead an amorphous mixed (Mg, Ca)-phosphate (which can be carbonated and hydrated).

HA $[(Ca_{10}(PO_4)_6(OH)_2)]$ is currently used as a biomedical material due to its excellent biocompatibility and bioactivity, attributed to its chemical and structural similarities to bone and tooth minerals [77]. On account of its low strength and high brittleness, an important use of HA is as a bioactive coating on metallic substrates. Many methods have already been developed to prepare HA coatings on metallic substrates, such as sol-gel process [78], electrophoretic deposition [79], sputtering process [80], laser surface melting [81], pulse laser deposition [82], physical vapor deposition (PVD) [83], plasma spraying [84], and biomimetic methods [85]. However, these cannot be used to deposit HA coating on Mg alloys because of its low melting point and poor heat resistance. It is well established that HA deposited from aqueous solution has a composition and structure more close to that of human bones and teeth [66, 68, 86]. Thus, chemical or electrochemical method [63, 73–77, 87, 88] is the proper way to prepare HA coating on Mg substrates.

Certainly, a single-step coating process using nontoxic aqueous solution without applying electrical current is the most preferable from the view point of product cost and environmental load. However, this direct synthesis of HA [66–68] on Mg alloys was, and still now, a scientific challenge because

Mg ions prevent HA crystallization with the substitution of Mg atom for the Ca atom in the HA structure. Subsequently, the HA structure is destabilized by a decrease in the atomic ratio of Ca/P; that is, Mg ions inhibit apatite nucleation and growth. However, calcium-phosphate apatites were detected on alkali and heat treated Mg after they had been soaked in SBF for 14 days [68]. Direct HA coating was successfully carried out on Mg alloys in aqueous solution by Hiromoto and Yamamoto [74], but the coating time is up to 24 h. An electroless method to prepare a stable HA-containing conversion coating on Mg was also reported [89]. The utility of an equilibrium diagram generated by the use of advanced software allowed for the conversion coating solution concentration and pH to be selected to optimize coating preparation, which was specifically Ca-deficient HA-Mg(OH)₂. To overcome Mg ions inhibition just mentioned, one approach uses optimized solution chemistry to produce poorly crystalline HA on Mg alloy AZ31 [90]. Another approach uses Ca-chelate compound [74, 91] and optimized solution chemistry and temperature to obtain dense and uniform HA coatings, on pure Mg, that takes less than 2 hours [91].

Electrochemical deposition (ED) of HA on Mg alloys also has unique advantages due to its capability of forming a uniform coating on a porous substrate or one with a complex shape, its controllability with regard to the thickness and chemical composition of the coating, and its low deposition temperature [63, 69]. It is thus recognized as one of the most promising techniques for degradable Mg alloys.

Nevertheless, in a traditional cathodic electrodeposition process, when a static potential is applied, loose, porous, and low adhesive coatings can easily develop. The main reasons are: first, a polarization in concentrations is formed, since the speed of ion diffusion from the main body of the solution to the surface of the metallic substrate is too slow, and secondly, H₂ is produced on the cathode due to the reduction of H₂O. To solve this problem, it is suggested that pulsed power (pulse reverse current, PRC) be used for depositing the adherent coating [92–95]. The PRC parameters are demonstrated in [35].

Pure HA coating suffers relatively high dissolution rate in the biological environment [95], which is unfavorable for long-term stability of the implant and makes the interface between bone and implant unstable [96, 97]. Recently, many researchers have focused on the application of fluorine-doped hydroxyapatite Ca₁₀(PO₄)₆(OH)_{2-x}F_x (FHA) as a bioactive coating to provide early stability and long-term performance [98, 99]. In comparison with pure HA coating, FHA coating could provide significant dissolution-resistant property, better apatite-like layer deposition, better protein adsorption, better cell attachment, and improved alkaline phosphatase activity in cell culture [98, 100]. Since FHA and Mg alloy are all degradable, Mg alloy with FHA coating has received more and more interest as biodegradable materials [66, 100]. Pulse reverse current (PRC) technique was also used to deposit FHA coating on Mg alloys [35]. Besides, H₂O₂, a strong oxidative reagent, was introduced into the electrolyte, which was first induced on cathode to only produce OH⁻ ions during the electrodeposition process [101]. Therefore, H₂O₂ could reduce the effect of H₂ evolution on

the nucleation and growth of nano-FHA coating by PRC technique.

Microarc oxidation (MAO) [67, 102–106] followed by electrochemical deposition (ED) of HA is another attempt to overcome the single HA coating obtained through ED which has a low bonding [107, 108] strength (about 4–6 MPa) and may lead to peel off after implantation [107]. MAO, which is an electrolytic process, can fabricate porous ceramic coating with high adhesion to the substrate. It is outlined that this porous coating can be used as the intermediate layer for depositing HA because it can generate pinning force when HA is deposited in the pores [109] and enhance the corrosion resistance of the porous layer. At the same time, recent developments in biomineralization have already demonstrated that nanosized crystals and particles play an important role in the formation of hard tissues of animals [110]. As reported in [111, 112], mechanical properties, such as compressive strength, hardness, and indentation fracture toughness, of HA increased with a decrease in grain size, and the nanosized HA can promote bone cell adhesion and proliferation in comparison with microsized HA [111, 113]. Therefore fabricating a nanosized HA coating on the MAO coating may be a promising way to improve the biocompatibility and corrosion resistance of Mg alloys. The MAO coating is prepared under a pulse voltage mode, and the cell potential is increased gradually till 165–175 V; then the working electrode is oxidized for about 30 min. [67]. The electrolyte is prepared by dissolving 0.1 mol/L $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, 0.028 mol/L $\text{CH}_{14}\text{N}_2\text{Na}_2\text{O}_8 \cdot \text{H}_2\text{O}$, 0.01 mol/L $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, and 0.28 mol/L $\text{KF} \cdot 2\text{H}_2\text{O}$ in distilled water. According to another publication [104], MAO was conducted at a fixed applied voltage in the range 360–400 V for 10 min to obtain promising results for the surface treatment of Mg-Ca alloys which exhibit good corrosion resistance and surface biocompatibility. The electrolyte was prepared from the solution of 10 g/L sodium silicate with 3.5 g/L sodium hydroxide. Shi et al. [106] performed MAO in 500 mL aqueous solution containing 50 g/L NaOH, 40 g/L Na_2SiO_3 , 20 g/L $\text{Na}_2\text{B}_4\text{O}_7$, and 40 g/L $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ at a constant potential of 90 V for 40 min.

Anodization is the third type of techniques to fabricate nanostructure coatings. It is also an electrolytic oxidation process in which the metal as anode is converted to oxide film having desirable corrosion protective, decorative, and functional properties [114–120]. Anodization can increase the film thickness, hardness, corrosion resistance, and wear resistance and provide better adhesion for primers than the bare metal. The anodizing behavior of Mg alloys is strongly influenced by the voltage or current applied. Different passive and active states can be found depending on the applied voltage/current, time, substrate, and electrolyte [121]. Studies have investigated many aspects of anodizing Mg, such as electrolyte composition [122–125], anodizing parameters such as constant voltage or constant current density control modes [120, 124, 126], substrate effects including substrate type, Mg purity, and alloying element concentration [38, 72, 120, 124, 127], and time of anodization [114]. Different electrolytes have been proposed: either an aqueous [114–116, 123–125, 128–132] or nonaqueous [119, 133] solutions. However, when anodization is used in the bioenvironment, there are certain requirements for the

coating. The coating should be thick, strong, and nontoxic. That is to say electrolyte should be carefully designed.

Over the past decades, a variety of self-ordering electrochemical processes have been found to produce oxide nanostructures from aqueous or nonaqueous fluoride-containing solutions [134]. Under optimized conditions resulting surface features are regular tubular (nanotubular) or porous structures. There are many works reported in the literature on the formation of ordered porous oxides of metals including valve metals, such as Al [135, 136], Ta [137], Zr [138, 139], Nb [140, 141], Ti [142–144], and Hf [145], but only a few attempts can be found based on Mg and Mg alloys. Since Mg hardly forms defined oxide films in aqueous solution, it may be a promising approach to use nonaqueous solutions for anodization, particularly with the aim of reducing chemical dissolution during anodization. Brunner et al. [133] showed the formation of a black, porous oxide layer on Mg from water free methanol or ethanol electrolytes containing nitrate ions. Ono and Asoh [146] studied anodization of pure Mg in nonaqueous solutions where they showed the formation of a barrier layer in a solution consisting of a mixture of amine, ethylene glycol, and water. They also investigated the formation of anodic oxide films on Mg surfaces in alkaline-fluoride solutions [125] and for the first time, using alkaline aluminate solution, they reported formation of cylindrical cellular structures [124].

In order to optimize the biological performance, the corrosion behavior of the material as well as its interactions with cells needs to be tailored. For instance, in the case of Ti, drastic influence of nanotubular TiO_2 layers on the cell behavior has been reported as compared with compact TiO_2 layers [147]. Moreover, such nanotubular surface layers were found to enhance the formation of HA on the Ti surface [148]. In the case of Mg, electrochemical anodization approaches to achieve similar surface morphologies as reported for Ti have been explored, and even though nanoporous [133] as well as nanotubular [119] surface layer has been reported. These nanostructures until now show a poor order. Moreover, possible enhancement of biological functionalities by such nanostructured surface layer has not yet been explored.

3.2.2. Miscellaneous Coating Approaches. Apart from the above mentioned Ca-P coatings, many coating techniques have been developed to reduce the corrosion of Mg alloys, such as hydrogenated amorphous silicon [149], alkaline heat treatment [68, 150], carbonate treatment [151], fluoride conversion coatings [152–157], biodegradable polymers [158–160], or composite coatings of polymers and calcium phosphates [161–163]. Moreover, the degradation behavior of Mg alloys can be significantly influenced by self-assembled monolayers [164, 165] or by protein adsorption layers which can be covalently bound to Mg surface using silane coupling chemistry [166]. The latter approach may have the advantage that in addition to the demonstrated strong effects on Mg dissolution rate, binding of specific proteins on the surface prevents nonspecific adsorption from the body fluids and hence may offer a wide range of possibilities to tailor the biological performance to match the requirements of the specific application targeted.

Fluoride chemical conversion coatings own merits such as low cost and simplicity in operation [167]. Fluoride is one of the few known agents that can stimulate osteoblast proliferation and increase new mineral deposition in cancellous bones. It is essential in the diet of human beings and is thought to be required for normal dental and skeletal growths [168]. Fluoride incorporated into the bone increases the size and, thus, decreases the solubility of the bone apatite crystals [169].

4. Concluding Remarks

The key to develop Mg-based alloys that are suitable as biodegradable orthopedic implants is how to control their degradation rates and mechanical integrity in the physiological environment [35, 153]. That is to say, Mg alloys would remain in the body and maintain mechanical integrity over a time period of 6–12 weeks for upper limbs or 12–24 weeks for lower limbs [170, 171], 12–18 weeks [35], 12 weeks [45], or three phases: 3–7 days, 3–4 months, and months to years [170, 172], while the bone tissue heals, eventually are replaced by natural tissue. It is also important that the degradation products, such as, Mg^{2+} , H_2 , and OH^- should be within the body's acceptable absorption levels [35]. If pH change and H_2 evolution increase are too drastic, cell death [118] and spalling off the coat as well as susceptibility to stress corrosion cracking and H_2 -embrittlement [173, 174] of the implant material can take place. However, if the corrosion rate of Mg-implant can be controlled by developing novel alloys or surface modifications, the biological environment may be better able to deal with H_2 -gas and OH^- ions generation.

Conflict of Interests

The authors hereby certify that there are no financial or competing interests that exist in this work.

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