A Review on the Corrosion Performance of Magnesium Alloys in Biomedical Applications

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Abstract: Magnesium alloys have shown great potential for applications as both structural and biomedical materials due to their high strength-to-weight ratio, as well as their good biodegradability and biocompatibility, respectively. These properties make magnesium alloys suitable for structural and biomedical applications. This article offers an overview of the corrosion behaviour of various magnesium alloys being considered for applications involving biodegradable implants. There have been several studies that have provided multiple strategies for increasing the corrosion resistance of magnesium alloys. These studies aimed to enhance the possibility that magnesium alloys may be employed in biological environments. This article covers the strategies for tailoring corrosion resistance and the various approaches for enhancing corrosion resistance.

Keywords: Mg alloy; biodegradable behaviour; corrosion resistance

1. Introduction

Magnesium is attractive because it has a low density and high strength and toughness compared to other structural metals such as aluminium, copper, and stainless steel [1]. These properties make magnesium ideal for many applications, including aircraft construction, shipbuilding, marine construction, automotive components, sporting goods, and medical devices. Magnesium is abundant in the Earth’s crust, and magnesium alloys are readily available [2].

In recent years, magnesium alloys have grown more prominent as a possible biomedical material as they are biocompatible, biodegradable, and have mechanical properties similar to human bone tissue [3,4]. Magnesium alloys can be used in various medical applications, including bone implants and scaffolds, dental implants and fillings, orthopaedic prostheses such as screws and plates, vascular stents, etc. However, magnesium alloys are susceptible to corrosion in many environments, including human body fluids. The corrosion products formed can be toxic and cause adverse side effects [5]. Therefore, it is essential to investigate the corrosion performance of magnesium alloys in biomedical applications to ensure their long-term reliability and safety [6]. The corrosion resistance of magnesium alloys depends on several factors, including the composition and microstructure of the material. The corrosion behaviour is also strongly influenced by environmental conditions such as temperature, pH, and water activity [7]. In particular, magnesium alloys that contain a large amount of the Mg2Si phase tend to be more sensitive to corrosion than those with a low concentration because this phase has the highest solubility in biological media (about ten times higher than other solid phases) [8].
2. Magnesium Alloys for Biomedical Applications

Orthopaedic implants, such as bone screws, plates, and pins, are commonly used to fixate bone fractures. Magnesium alloys have shown promise in this field due to their mechanical properties, similar to bone, and their ability to biodegrade in vivo. Yang et al. reported that a magnesium alloy implant was shown to have good biocompatibility and integration with bone tissue in a rabbit model [9]. Similarly, it was found that a magnesium alloy screw had good biomechanical properties and biocompatibility in a rat model [10]. Table 1 shows the mechanical properties of some commonly used materials for biomedical applications. These properties are essential in determining the suitability of the alloy for a particular application.

Table 1. Comparison of properties of materials [11].

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Tensile Strength in MPa</th>
<th>Yield Strength in MPa</th>
<th>Elongation in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZ31B</td>
<td>280–305</td>
<td>175–210</td>
<td>8–21</td>
</tr>
<tr>
<td>AZ61A</td>
<td>320–350</td>
<td>205–240</td>
<td>5–15</td>
</tr>
<tr>
<td>WE43</td>
<td>300–330</td>
<td>210–240</td>
<td>10–20</td>
</tr>
<tr>
<td>Ti-6Al-4V</td>
<td>880–900</td>
<td>800–830</td>
<td>10–15</td>
</tr>
<tr>
<td>316L SS</td>
<td>485–620</td>
<td>170–310</td>
<td>40–60</td>
</tr>
</tbody>
</table>

Magnesium alloys were studied for their potential use in orthopaedic implants due to their effects on bone regeneration. The results revealed that they might promote the differentiation of bone marrow stem cells and accelerate bone mineralization [12]. Witte et al. evaluated the in vivo corrosion of four magnesium alloys and their associated bone response [13]. The results showed that the magnesium alloys positively affected bone regeneration and were well tolerated by the body. Magnesium alloys have also shown promising results for medical devices such as stents and joint replacements [14]. Magnesium alloys are used to manufacture these devices because they have proven to be strong and durable enough to hold up against the stresses of everyday use [15]. In addition, magnesium alloys had good biocompatibility and mechanical properties, making them a promising material for use in spinal implants [16].

Magnesium (Mg) alloys have several advantageous properties that make them suitable for medical implants [17]. They have a high strength-to-weight ratio, density, and modulus of elasticity, quite similar to cortical bone. Additionally, magnesium can be easily processed into complex shapes as it has excellent machinability [18]. Because Mg’s elastic modulus is close to that of bone, problems related to implant stress shielding can be reduced well [19]. Despite the promising results, magnesium alloys in medical implants still face challenges, such as the rapid degradation rate and the potential release of toxic byproducts. However, researchers continue to explore new ways to improve the properties of magnesium alloys and reduce their degradation rate.

The important factors to be considered while using magnesium alloys in biomedical applications are alloying elements, surface condition, the type of medium, and stress conditions. Pure magnesium (Mg) has limited application as a biomedical material due to its low corrosion resistance and insufficient mechanical properties. However, alloying elements such as aluminium (Al), zinc (Zn), and lithium (Li) can be added [20] to improve the hardness, strength, and formability of Mg alloys. Adding Li can even change the crystal structure of Mg, resulting in enhanced formability [21]. Additionally, alloy composition affects the formation of protective films on the surface of Mg alloys, which can increase their corrosion resistance in simulated body fluids.

The surface conditions of Mg alloys, such as roughness and microstructure, are the primary determinants of their biomedical performance. The surface irregularity of these alloys influences their tendency to passivate and increases their susceptibility to pitting [22]. Fine grain improves magnesium alloys’ mechanical performance and corrosion resistance by promoting grain boundary growth [23].
The chemical composition of physiological fluids influences the biological activity of magnesium alloys. The major elements that influence the corrosion of magnesium alloys are inorganic ions, proteins, and cells. Various inorganic ions affect the deterioration of magnesium alloys in different ways [24]. The presence of $\text{HPO}_4^{2-}$ and $\text{Ca}^{2+}$ in NaCl solution can improve overall corrosion resistance and inhibit local corrosion, while the presence of $\text{HCO}_3^-$ ions accelerates the degradation rate.

Magnesium (Mg) implants, once placed inside the human body, are subjected to different stress conditions depending on the implant’s location. For instance, a Mg alloy vascular stent initially comes into contact with blood flow and encounters shear force [25]. As the tissue grows over the stent, fluid diffusion can influence the growth of intima on its surface.

3. Corrosion Mechanisms and Testing

The corrosion occurring in magnesium alloys is categorized as uniform, galvanic, pitting, intergranular, and stress corrosion cracking (SCC). In magnesium alloys, the prevalent form of corrosion is uniform corrosion. It occurs when the entire surface of the alloy is exposed to a corrosive environment and reacts uniformly, resulting in a loss of material thickness [26]. Galvanic corrosion takes place when two dissimilar metals come in contact with an electrolyte, causing an electron flow from the less noble (anodic) metal to the more noble (cathodic) metal [27].

Pitting corrosion can occur in magnesium alloys when the protective oxide layer on the surface is damaged or if there are impurities or defects in the metal [28]. Intergranular corrosion occurs along the grain boundaries of the alloy and can result in cracking and failure of the component. It is caused by the precipitation of second-phase particles along the grain boundaries, which can lead to a loss of corrosion resistance [29]. Stress corrosion cracking occurs if the metal is under tensile stress and exposed to a corrosive environment. In magnesium alloys, SCC can occur in the presence of chlorides, such as saltwater or road salt, and can lead to the catastrophic failure of the component [30].

One of the most common methods for testing corrosion resistance is salt spray testing, also known as the ASTM B117 test. This test involves exposing the magnesium alloy specimen to a salt spray mist in a chamber for a specified period while monitoring the formation of corrosion products. Although salt spray testing is widely used, it has some limitations, such as its inability to replicate real-world environments accurately [31]. Another method used for testing corrosion resistance is electrochemical testing, which involves measuring the electrochemical properties of the magnesium alloy in a corrosive environment. However, electrochemical testing requires specialized equipment and expertise, making it expensive and time-consuming [32]. Other methods for testing corrosion resistance include immersion testing, hydrogen evolution testing, and crevice corrosion testing. The suitable corrosion testing method is selected based on the specific requirements [33].

4. Corrosion Resistance Improvement

Various techniques have been developed to improve the corrosion resistance of magnesium alloys, encompassing surface modification, alloying, and protective coatings. Surface modification methods involve treating the surface of the magnesium alloy to form a protective layer, which can prevent the magnesium from coming into contact with the environment and thus reduce corrosion. This can be achieved through processes such as anodizing, plasma electrolytic oxidation, and chemical conversion coating [34]. Anodizing is an electrochemical process that forms an oxide layer on the surface of the magnesium alloy. Plasma electrolytic oxidation (PEO) involves exposing the magnesium alloy to an electrolyte and applying a high voltage to create a ceramic-like coating on the surface. Chemical conversion coating involves immersing the magnesium alloy in a solution that reacts with the surface to form a protective layer.

Alloying with other elements, such as aluminium, zinc, and rare earth metals, can also enhance their resistance to corrosion [35]. This is because these elements can form
intermetallic compounds with magnesium, which can improve the corrosion resistance of the alloy. For example, when aluminium is added to magnesium, it can form a protective layer of magnesium aluminate on the alloy’s surface, improving corrosion resistance.

Coatings are another method that can be applied to magnesium alloys to enhance their corrosion resistance [36]. Coatings can be organic, inorganic, or hybrid. Organic coatings are typically polymer-based and can provide good corrosion protection, but they may be prone to degradation over time. Inorganic coatings, such as ceramic coatings, can provide excellent corrosion protection and are more durable, but they can be more expensive to apply. Hybrid coatings combine the benefits of both organic and inorganic coatings, providing good corrosion protection and durability.

Each method has its own pros and cons, and the selection of method relies on the particular application and performance requirements. For instance, surface modification methods can enhance the corrosion resistance of magnesium alloys without substantially modifying their mechanical properties [37]. Nonetheless, these procedures can be expensive and time-consuming. Coatings, such as anodizing and plasma electrolytic oxidation, can provide excellent corrosion protection but can be prone to delamination and cracking [38,39]. Hence, the choice of method depends on the specific application and performance requirements.

The corrosion behaviour of the AZ31B magnesium alloy after the surface coating has been investigated in several studies. Ahmed et al. [40] evaluated the corrosion resistance of AZ31B alloy after it was coated with an electroless Ni-P coating followed by a layer of sol–gel coating. The results showed that the coated AZ31B alloy exhibited significantly improved corrosion resistance compared to the uncoated alloy. The coatings acted as a barrier, reducing direct exposure to corrosive environments and preventing the initiation and propagation of corrosion. Similarly, Park et al. [41] investigated the corrosion resistance of AZ31B alloy after it was coated with graphene oxide (GO) nanosheets. The GO coating effectively inhibited corrosion by acting as a physical barrier and reducing the contact between the alloy surface and corrosive media. The researchers observed a significant reduction in the corrosion rate and improved corrosion resistance compared to the uncoated alloy. Furthermore, another study by Farnoosh et al. [42] investigated the corrosion behaviour of AZ31B alloy after it was coated with a composite ceramic coating consisting of Al₂O₃ and SiO₂ nanoparticles. The coated alloy exhibited enhanced corrosion resistance as the ceramic composite coating provided a protective layer that effectively reduced the corrosive attack.

The corrosion behaviour of AZ61A magnesium alloy after surface coating has been widely studied as AZ61A is used for numerous applications where corrosion resistance is crucial. El-Aziz et al. [43] investigated the effect of a ceramic coating of Al₂O₃ on the corrosion behaviour of AZ61A magnesium alloy. The results showed that the ceramic coating significantly improved the corrosion resistance of the alloy, as the ceramic layer physically and chemically inhibited the direct exposure of the alloy surface to the corrosive environment. The results showed a lower corrosion rate and higher corrosion potential compared to the uncoated samples. Kharrat et al. [44] evaluated the effect of graphene oxide coatings on the corrosion behaviour of AZ61A magnesium alloy. The results showed that the coatings reduced the corrosion rate of the alloy by acting as a corrosion barrier that prevented direct exposure to corrosive media. The researchers observed that the graphene oxide coatings also increased the corrosion resistance of AZ61A magnesium alloy by improving its passivation behaviour. Furthermore, Markovic et al. [45] investigated the influence of a silane coating on the corrosion behaviour of AZ61A magnesium alloy. The results showed that the silane coating protected the alloy from corrosion by passivating the surface and improving its resistance to corrosion. The researchers observed that AZ61A samples coated with a silane film exhibited lower corrosion rates and higher corrosion potentials compared to uncoated samples.

The corrosion behaviour of WE43 magnesium alloy after surface coating has been extensively studied in recent years. The use of a cerium conversion coating as a protective layer on WE43 magnesium alloy was studied. The researchers found that the cerium
conversion coating effectively reduced the corrosion rate of the alloy and provided improved protection against corrosion. In another study, investigation was made on the corrosion behaviour of WE43 magnesium alloy with silane-modified micro-arc oxidation coatings. The results showed that the silane-modified micro-arc oxidation coatings significantly improved the corrosion resistance of the alloy by enhancing adhesion and reducing coating porosity. The examination on the corrosion behaviour of WE43 magnesium alloy with a polyaniline/nano-SiO$_2$ protective coating was carried out and the results demonstrated that the protective coating effectively reduced the corrosion rate of the alloy in simulated physiological solutions by acting as a barrier and lowering the permeability of corrosive ions.

5. Conclusions

The corrosion performance of magnesium alloys investigated by many researchers is reviewed for biomedical applications. Even though Mg and Mg-based alloys have similar mechanical properties to natural bone and are biocompatible, the rapid corrosion rate of these alloys in the body’s physiological environment is a significant challenge. The results of various research studies show that optimising microstructure and surface properties, alloying with other elements, and applying coatings or surface modification techniques are effective strategies to control the corrosion rate. In addition, the corrosion testing methods must be selected based on the biomedical application and performance requirements. In future, investigations are required to combine the corrosion improvement techniques to enhance magnesium alloys’ mechanical properties and resistance to corrosion.

Author Contributions: Paper writing, N.S.; Supervision, K.L.H. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are contained within the article.

Conflicts of Interest: The authors declare no conflicts of interest.

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