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The Current Status of Research on the Effects of Different Alloying Elements on Medical Magnesium Alloys

Haoge Shou[1,2], Yang Yanga[1]*, Li Lia[1] and Liuyong Hec[3]*

[1]Zhumadian Central Hospital affiliated of Huanghuai University, China

[2]College of Intelligent Manufacturing, Huanghuai University, China

[3]College of Materials Science and Engineering, Chongqing University, China

***Corresponding author:** Liuyong He, College of Materials Science and Engineering, Chongqing University, 174 Shazhengjie Street, Shapingba District, Chongqing, China

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ABSTRACT

Magnesium (Mg) alloys with their natural biodegradability, excellent biocompatibility, and favorable mechanical properties, have become highly valuable materials for research in the biomedical field. However, the rapid degradation rate of Mg alloys limits their further development and application. This paper reviews the general principles of Mg and its alloy degradation in physiological environments, with a focus on the current research on the selection of alloying elements for magnesium alloys from a safety perspective.

Keywords: Medical Magnesium Alloys; Alloying; Biocompatibility; Corrosion Mechanism; Corrosion Rate

Introduction

As one of the most promising lightweight structural materials, magnesium (Mg) has been widely used in various fields, including automotive, aerospace, 3C products, and biomedical materials, over the years. Mg is also an essential nutrient for maintaining human health, participating in a series of metabolic processes and being necessary for the normal physiological functions of many tissues and organs, particularly the heart, brain, muscles, and skeletal system [1]. Mg alloys offer advantages such as low density, high specific strength, high damping capacity, good machinability, a density and elastic modulus similar to bone, minimal stress shielding effect, excellent biocompatibility, favorable safety degradation, and absorbability [2-5]. These properties make Mg alloys highly suitable for use as biodegradable temporary implants. Mg alloys were first used as ligation materials for bleeding blood vessels in 1878 [6], and since then, magnesium and its alloys have been extensively studied and applied in the medical field, including cardiovascular, musculoskeletal, and general surgery. In 2013, the orthopedic screw MAGNEZIX was approved for human use, with studies by Künneker et al. [7] reporting its use in fracture treatment. At the same time, the Mg-based K-MET screws received market approval from the Korean Food and Drug Administration and were used in fracture repair [8]. The Magmaris stent, a biodegradable magnesium alloy stent, was launched in Europe in 2016 and received CE certification. The Mg-based Magmaris stent has been used in the treatment of infant vascular stenosis [9], with Hauke et al. [10] reporting five-year data from human trials. Research on Mg-based biomaterials has shown that Mg and its alloys exhibit good biodegradability, with degradation products not causing disruption to human physiological functions, inflammation, or allergic reactions. However, the low corrosion resistance of Mg alloys and the premature loss of structural integrity remain significant challenges that limit their further development and application. Therefore, understanding the corrosion behavior of Mg and its alloys and improving their performance has been a hot research topic in the biomedical field.

Mg and its alloys are prone to corrosion in physiological environments. When Mg is placed in physiological solutions, degradation begins with an anodic reaction, resulting in the formation of Mg^{2+} on the Mg substrate surface ($Mg \rightarrow Mg^{2+} + 2e^-$). A cathodic reaction occurs at the cathode ($2H_2O + 2e^- \rightarrow 2OH^- + H_2$), and ultimately, Mg hydroxide ($Mg(OH)_2$) forms a thin film on the magnesium substrate surface ($Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$). This film limits further ion migration, reducing the corrosion rate of the alloy to some extent [2,11]. However, the hydrogen gas (H_2) produced at the corrosion site causes the magnesium hydroxide ($Mg(OH)_2$) precipitate deposited on the Mg substrate to split, preventing the formation of a uniform $Mg(OH)_2$ film on the surface. As a result, the $Mg(OH)_2$ film becomes loose and porous, allowing external corrosive media to further corrode the exposed alloy substrate through these pores. Therefore, the degradation of Mg and its alloys is not self-limiting and will continue until the substrate is completely degraded. Notably, chloride ions (Cl^-) can convert the corrosion product $Mg(OH)_2$ into the more soluble $MgCl_2$, which accelerates the degradation of Mg alloys in the body [11]. The concentration of chloride ions in the human body is approximately 100 mmol/L, and these ions disrupt the $Mg(OH)_2$ film, accelerating the degradation process. Additionally, other aggressive ions such as HCO_3^-, SO_4^{2-}, and HPO_4^{2-} also contribute to the corrosion of the alloy [12]. The corrosion behavior of Mg and its alloys in the human body is complex, and its corrosion mechanism depends on various factors, such as the corrosive medium, alloy composition, microstructure, and the properties of the alloy's surface film. Significant efforts have been made by researchers to understand the corrosion of different types and states of magnesium alloys in various regions of the human body, but a comprehensive understanding is still lacking. Therefore, the *in vivo* degradation of Mg alloys remains an area of long-term research. Alloying is one of the known methods to improve the corrosion resistance of magnesium alloys and can enhance the overall performance of Mg alloys by adding different alloying elements. This remains a key area of research in the biomedical field.

Results

Selection of Elements for Magnesium Alloys

Alloying is a commonly used method in materials science to improve the properties of metallic materials. It is one of the most direct, simple, and effective ways to address issues such as the low elastic modulus, hydrogen gas release during degradation, and poor corrosion resistance of Mg alloys. The appropriate addition of alloying elements can improve various properties of Mg alloys by refining their grain structure [13], improving their microstructure [14], optimizing the type and distribution of second phases [15], and altering the potential difference between the precipitate phases and the matrix surface [5,16], thereby meeting the required performance standards. Therefore, specific alloying elements are often introduced into Mg and its alloys, and the properties of Mg alloys are adjusted through the preparation of binary and multi-component alloys to expand their range of applications. As Mg alloys have great potential as medical implant materials in the biomedical field, the biocompatibility of these alloys must be considered first. Biocompatibility refers to the ability of medical implant materials to withstand the effects of the host system and remain relatively stable during the body's dynamic changes without being rejected, and without causing toxic side effects. Thus, researchers must carefully select appropriate elements and feasible processing methods, optimizing the component design of new Mg alloys with biomechanical properties to ensure the product meets the required standards. Currently, commonly studied alloying elements in the biomedical field include calcium (Ca), bismuth (Bi), silicon (Si), aluminum (Al), zinc (Zn), manganese (Mn), lithium (Li), strontium (Sr), zirconium (Zr), molybdenum (Mo), and gallium (Ga). The effects of these elements on the properties of magnesium alloys are as follows:

- **Ca:** Ca is one of the essential elements for the human body and is non-toxic to cells. It is the most abundant mineral in the body. Ca^{2+} is one of the ions involved in forming bone matrix and is crucial for maintaining bone microstructure. Moreover, Ca^{2+} influences bone tissue regeneration and extends the lifespan of osteocytes through cellular signaling. It also facilitates the formation of the bone-implant interface, making Mg-Ca alloys highly advantageous as bone implant materials [4].

- **Bi:** The Mg-Bi alloy system is non-toxic and forms a stable Mg_3Bi_2 phase. When bismuth is in the solution state within the alloy matrix, it can inhibit the corrosion rate of Mg-Bi-based alloys, showing significant potential for development [17]. Further research by Wang et al. [18] shows that adding bismuth can refine the alloy's grain size, and with increasing bismuth content, the alloy's strength, ductility, and thermal stability improve.

- **Si:** Si is one of the trace elements required by the human body and helps maintain bone density and connective tissue function. It also promotes the proliferation, differentiation, collagen secretion, and bone matrix mineralization of osteoblasts, making it indispensable in bone formation [4]. Although silicon is commonly used for alloying Mg, its solubility in Mg is low (mass fraction of 0.006%), and the coarse Mg_2Si phase formed in Mg-Si binary alloys reduces the alloy's ductility, plasticity, and corrosion resistance. It is generally believed that silicon alone has limited effects on improving the properties of Mg alloys, and it needs to be combined with other elements to enhance the alloy's performance [4,19].

- **Al:** The addition of a moderate amount of aluminum to Mg alloys is highly beneficial. It can refine the alloy's grain size and enhance its strength, ductility, mechanical properties, and corrosion resistance [15,20,21]. Although Al is generally considered non-toxic, some studies suggest that it may have negative health effects on humans. The deposition of Al^{3+} in the nervous system can cause inflammation, leading to brain cell damage and pathological conditions, potentially accelerating brain aging and contributing to neurodegenerative diseases such as multiple sclerosis, Parkinson's disease, and Alzheimer's disease [22,23]. Nevertheless, research on Mg-Al alloys continues to be actively pursued [21,24,25].

- **Zn:** Zn is one of the trace elements essential for maintaining human health and is non-toxic to cells. It plays an important role in various cellular functions, including protein structural regulation, cell transcription, signal transduction, and enzyme activity [26,27]. Zn also has good osteogenic properties and potential for anti-bacterial and anti-inflammatory effects [28,29]. The addition of Zn refines the alloy's grain size and enhances its surface integrity, providing Mg-Zn alloys with good mechanical properties and high corrosion resistance [30]. Zn is one of the major research directions for new medical materials, significantly influencing the enhancement of Mg alloy performance. Notably, as the Zn content increases in Mg-Zn alloys, their corrosion resistance improves, primarily due to the formation of a protective Mg-Zn film on the alloy surface.

- **Mn:** Mn is a trace element essential for maintaining human health and normal system functions, playing a key role in defending against oxidative stress, promoting growth, digestion, and immune responses [31]. Mn is widely studied in medical Mg alloys. Xie et al. [16] added a certain amount of Mn to ZK30 alloy to study the effect of manganese content on the alloy's properties. The results showed that Mn addition refined the grain size and formed a relatively protective Mn oxide film on the alloy's surface, reducing the corrosion rate. The degradation rate of the alloy first decreased and then increased as the Mn content increased, reaching its lowest point at 0.8% (mass fraction). However, excessive Mn exposure can cause oxidative stress and mitochondrial energy imbalance by triggering free radical formation and affecting antioxidant enzyme activity, which may influence cholinergic systems and lead to neurodegenerative diseases such as Alzheimer's and Parkinson's diseases.

- **Li:** Li has a long history of use in treating mental health conditions, and at low concentrations, lithium is generally considered non-toxic. Li exhibits significant antibacterial properties and can inhibit the growth of osteosarcoma cells, while also stimulating mesenchymal stem cell proliferation and osteogenic differentiation, thus promoting bone regeneration and healing. As a result, Li is considered a promising bioactive element [32-34]. Mg-Li alloys are particularly notable for their superior ductility and formability, making them promising lightweight materials. Studies have shown that the Li content (mass fraction) in Mg-Li-Zn alloys significantly influences their mechanical properties, with Mg-xLi-Zn alloys exhibiting higher yield strength, tensile strength, and elongation compared to cast Mg-Zn alloys. Additionally, Mg-Li-Zn alloys show a concentration-dependent cytotoxicity against osteosarcoma cells and promote bone growth.

- **Sr:** Sr is a trace element in the human body and an important component of bone. It is non-toxic to cells. Sr promotes osteoblast growth, bone formation, and inhibits the activation and differentiation of osteoclasts [2,5]. Alloys containing strontium are considered promising materials for bone implants. Studies on the effect of strontium addition to Mg alloys show that an appropriate amount of strontium can improve the alloy's corrosion resistance by refining grain size and strengthening the second phase. However, excessive Sr can lead to the formation of more $Mg_{17}Sr_2$ phases, which significantly reduce the alloy's plasticity.

- **Zr:** Zr has good biocompatibility, low cell toxicity, and bone compatibility. The addition of Zr to alloys not only effectively refines the grain size but also enhances the strength of the alloy's grain boundaries [13]. Furthermore, Zr improves the alloy's mechanical properties and promotes the formation of a stable passive film on the alloy surface, enhancing its corrosion resistance. Additionally, MA et al. [35] prepared Mg-2% Zn-0.5%Y-1%Nd-0.5%Zr (ZE21C) alloys and studied the degradation behavior of ZE21C suture anchors *in vitro* and *in vivo*. They found that these alloys promoted bone healing and the regeneration of the fibrous cartilage interface at the tendon-bone junction, achieving better results than Ti6Al4V (TC4) alloys.

- **Mo and Ga:** Mo is a trace metal involved in various enzymatic processes in the human body [36-38]. It is a material with high strength and excellent mechanical properties. While pure Mo implants show low toxicity in animal studies, excessive molybdenum can be excreted through metabolic processes in the body. Although there is limited information on its toxicity, molybdenum's potential as an alloying element is significant. Recent studies have shown that molybdenum alloys exhibit long-term mechanical stability, making them ideal for stent materials. Ga has antibacterial activity, enhances bone tissue regeneration, and can treat conditions such as osteoporosis. As an alloying element, it improves the mechanical properties of alloys.

Summary and Outlook

With the deepening research on alloying, the mechanisms by which alloying elements affect the corrosion resistance and other properties of Mg alloys are becoming increasingly clear. In biomedical Mg alloys, adding a small number of alloying elements can achieve improved properties. However, the more elements added, the greater the uncertainty in the performance testing of the alloy, and the challenges in assessing its biological safety increase. Therefore, a comprehensive consideration of the alloy's biological safety, degradation rate, and mechanical properties is necessary to optimize the composition ratio. Tailored development of alloy compositions can enable Mg-based biomaterials to exhibit customized degradation behaviors, meeting specific needs. Although alloying has been a key focus in enhancing the performance of biomedical Mg alloys due to its convenience and ability to impart various properties, simple alloying alone can no longer fully satisfy the demand for diverse performance characteristics.

Thus, it is necessary to combine alloying with other modification techniques, such as surface treatment. While current Mg alloy products show great clinical potential and their performance as implant materials has been improving, the high degradation rate of Mg alloys in physiological environments remains a major limitation for clinical applications. A good balance between ideal biological compatibility, mechanical properties, and corrosion resistance has yet to be achieved. The future focus will be on controlling the corrosion rate and improving corrosion behavior through various optimization methods. Similarly, the design of Mg alloys should evolve into an integrated approach that considers both structure and function, and even the development of composite materials. Specific alloy types should be developed according to the requirements of different implant sites, thereby expanding the applications of Mg alloys in the biomedical field.

Author Contributions

Haoge Shou: Writing - original draft, Writing - review & editing, Conceptualization, Resources, Supervision, Project administration, Funding acquisition. Liuyong He: Methodology, Investigation, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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