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Review Article

Review of degradation behaviour biodegradable magnesium MgZnCa alloys

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Abstract
Metals such as stainless steel and titanium have long been used in orthopedics due to their strength and wear resistance. However, magnesium-based alloys, with mechanical properties closer to those of bone, are gaining increasing attention for biomedical applications. Magnesium implants are biodegradable, lightweight and offer advantages such as reduced stress shielding and the elimination of secondary surgery. Despite the above-mentioned advantages, Mg-based biomaterials have poor corrosion resistance in physiological environments. This study focuses on biodegradable Mg-Zn-Ca alloys, which are characterized by high biocompatibility and satisfactory mechanical properties. The degradation process is influenced by various factors such as the qualitative and quantitative composition, heat treatment method, microstructure, grain size, phase presence, and other parameters. Alloying with elements such as Zn and Ca helps improve the mechanical and corrosion properties; however, it should be noted that at certain concentrations can reduce ductility and accelerate degradation. The corrosion process results in the formation of magnesium hydroxide, magnesium chloride, hydrogen gas, and other compound groups. Although the presence of hydroxyl, calcium, and phosphate ions can promote the formation of protective layers that slow down corrosion, the formation of magnesium chloride further accelerates the degradation process. The article discusses the degradation process of magnesium alloys, emphasizing the importance of optimizing their chemical composition and the choice of heat treatment method, as well as the influence of these factors on microstructural and phase characteristics.

Keywords: magnesium alloys, biodegradation, biomaterials, alloying, corrosion process.

1 Introduction

Advances in medical technology, coupled with the growing emphasis on enhancing both the quality and longevity of human life have led to an increased demand for biomaterials. The field of biomaterials focuses on the study and development of materials used in medicine. They are applied in the restoration of damaged tissues and in supporting the function of bones and joints [1, 2]. From a materials science perspective, biomaterials can be classified into four groups: ceramics, composites, polymers, and metals.Ceramic biomaterials, including mineral oxides and nitrides, possess non-toxic, biocompatible, and osteoinductive properties. They are often used as coatings for implants. Among ceramic biomaterials, calcium phosphates are particularly notable. Composite materials are combinations of two or more different components. This allows the integration of their individual properties, which positively influences both mechanical and biological characteristics. In modern orthopedics, carbon fiber-based composites are particularly popular due to their high strength, light weight, and good biocompatibility [3]. However, such materials exhibit poor mechanical properties and a high susceptibility to corrosion, which limits their application as bone implants [4, 5].

Today, several types of synthetic biodegradable polymers are widely known, including polylactide (PLA), polyglycolide (PGA), polycaprolactone (PCL), polyhydroxybutyrate (PHB), and polylactide-glycolide (PLGA), among others. As members of the aliphatic polyester family, PLA, PGA, and PLGA are the most commonly used materials for bone repair and tissue engineering. They exhibit biocompatibility, non-toxicity of degradation byproducts, and a controlled degradation rate. Polymers have a long history of use in biodegradable surgical sutures, and the U.S. Food and

Drug Administration (FDA) has approved them for clinical applications. Polymers such as PGA, PLA, and PLGA, which possess a relatively high elastic modulus, tensile strength, and low elongation at break, have also been investigated for bone repair. Notably, bone screw implants and splints made from PLA or PLGA are not susceptible to corrosion. Over time, their gradual biodegradation reduces implant strength, helping to prevent osteoporosis and eliminating the need for secondary surgery. Meanwhile, polymers with relatively lower strength can be effectively used for applications such as ankle, patella, and phalanx implants, as well as various types of fixation screws [5, 6].

However, the relatively low mechanical strength, radiolucency, and nonspecific foreign body reactions due to individual differences remain the main disadvantages of polymers. Additionally, certain toxic additives used in polymer synthesis, such as plasticizers, antioxidants, and stabilizers, may have harmful effects on the body [3, 6, 7].

Metal implants are commonly used to repair bone fractures due to their strength and durability. Stainless steel, cobalt-based (Co-based), and titanium-based (Ti-based) alloys are well-known examples of commercially available implant materials. Metals are preferred for long-term, load-bearing implants because of their high strength and ductility, which provide excellent resistance to fractures. Biocompatibility and appropriate mechanical properties are the two main factors in the selection and development of implants. However, the biocompatibility of metal implants can be compromised by corrosion and wear. During these processes, harmful metal ions may be released, leading to inflammation, cell death (apoptosis), and other adverse tissue reactions. Studies have shown that ions such as chromium (Cr) from Co-Cr alloys, as well as niobium (Nb), vanadium (V), and nickel (Ni), can cause harmful effects in tissues and biological fluids. Notably, nickel is highly cytotoxic, genotoxic, carcinogenic, and mutagenic [1, 2, 4, 3, 5].

Magnesium offers several advantages compared to conventional materials used for orthopedic implants. It constitutes approximately 60% of bone tissue and is an essential element for the human body, ranking fourth in abundance after potassium, sodium, and calcium. Due to its biocompatibility and non-toxicity, magnesium is well-suited for use in implants. The corrosion products of magnesium are safely excreted from the body through the urinary system [8, 3].

In this article, we examine Mg-Zn-Ca alloys that show potential for use as biodegradable implants in orthopedic applications, along with the key requirements for such materials. Special attention is given to both qualitative and quantitative methods of improving degradation behavior—specifically, how component concentrations and thermal treatment influence the formation of microstructure and phases, which in turn affect the degradation rate.

2 Main requirements for biomaterials

Human bone is primarily composed of organic and inorganic components. The organic portion mainly consists of collagen fibers and proteins, which provide elasticity and stability to the bones. The inorganic components, including phosphorus, calcium, magnesium, and others, contribute to the bones' hardness, serve as internal support, protect vital organs, support muscle function, and help maintain calcium balance. The human skeleton can be classified into two types of bone: cortical and cancellous bone. Although they share a similar composition, they differ in structure [5, 6].

Cortical bone, unlike trabecular bone, is primarily composed of mineralized tissue with a high mass per unit volume and low porosity, approximately 10%. In contrast, the porosity of trabecular bone can reach up to 90%, giving it a porous structure. Consequently, the Young's modulus and ultimate strength of trabecular bone are significantly lower [9, 10, 11].

According to clinical observations, the minimum recovery period for orthopedic injuries is 14 weeks. Of course, this period depends on various factors such as individual physiological characteristics, the chosen treatment method, and the type of injury. All these factors play a crucial role in selecting an appropriate fixation method to prevent complications and ensure proper healing [6, 10].

Thus, various implants such as screws, plates, and others can be used as fixation devices to ensure proper alignment and stability of damaged bone tissue. For example, screws and plates are used to provide correct fixation and structural support for bone segments in cases of fractures [9, 11].

Unfortunately, most metals possess mechanical properties that exceed those of bone tissue, which complicates their application. This challenge lies in the phenomenon known as stress shielding, which leads to reduced bone strength and further degradation. Bone tissue naturally adapts to external loads; however, the presence of an implant decreases stress on the surrounding bone, resulting in reduced bone density and weakening. Therefore, careful material selection is critical to avoid such complications. Magnesium alloys hold a special place in the field of bioimplants because the Young's modulus of magnesium (40–45 GPa) is much closer to that of natural bone compared to titanium (116 GPa) or stainless steel (110–193 GPa) [3, 12].

The primary function of biomedical implants is to provide reliable fixation and support throughout the bone tissue healing process. Therefore, implants must be effective, safe, and stable over time. Biomedical implants are designed to act as a temporary scaffold during tissue regeneration, and their material properties must meet specific requirements [11].

First and foremost, the mechanical properties of the

selected implant should closely match those of the damaged bone. The implant must remain effective and sufficiently stable throughout the healing process, facilitating bone regeneration without compromising the patient's health. These properties include strength, stiffness, Young's modulus, thermal conductivity, electrical conductivity, and others. Second, the material must exhibit good biocompatibility and safety. This includes the absence of toxic substances, significant tissue rejection reactions, and severe side effects such as allergic or inflammatory reactions. Third, the implant material should possess excellent anti-corrosion properties and be capable of degrading as the bone tissue heals. The ideal outcome occurs when the degradation rate of the material aligns with the bone tissue restoration rate. In this case, the implant is fully degraded by the end of the healing process, eliminating the need for repeat surgeries and preventing further harm to the body. Finally, the material should have osteoinductive properties, meaning it should contribute to accelerating bone tissue regeneration [6, 9, 13].

Materials intended for bone restoration are classified into two groups based on their degradation properties: bioinert and biodegradable materials. Bioinert materials, such as metallic alloys like steel and titanium, have a long clinical history and are among the most widely used medical materials. While inert implants have proven to be reliable for internal bone fixation, their use comes with several challenges that cannot be overlooked. For instance, inert implants remain in the human body until defects are identified during the "wearing" of the implants, which often leads to the need for repeat surgery. Secondary surgeries not only increase treatment costs but can also have negative consequences for the patient [5].

Thus, based on the literature data, we can highlight several advantages of using magnesium implants, including: excellent biocompatibility and biosafety properties, favorable mechanical characteristics, and an elastic modulus similar to that of bone tissue [14]. The above points provide a solid basis for further research on magnesium-based alloys.

3 Mg as bioimplant

The new generation of implants designed for temporary support of healing tissues primarily serves to maintain structural integrity during the bone regeneration process. Gradual resorption of the implant as the bone tissue heals prevents the accumulation of residual materials or fragments, thereby minimizing the risk of damage to surrounding tissues. Controlled degradation ensures a reduced likelihood of adverse outcomes and supports the natural healing process [5, 9].

Biodegradable metal implants include magnesium (Mg), zinc (Zn), and iron (Fe), often referred to as smart implants, which have been extensively studied in recent years. As previously noted, the key challenge in working with biodegradable implants is ensuring that the supporting structure maintains sufficient mechanical strength throughout the body's recovery process. Mg- and Fe-based implants, in particular, exhibit favorable mechanical properties, making them suitable for load-bearing applications [3, 12].

Magnesium is a lightweight metal with a density of 1.74 g/cm^3, which is significantly lower than that of titanium (4.32 g/cm^3) and steel (7.9 g/cm^3) [15]. Compared to other commonly used metal implants, magnesium exhibits an elastic modulus and compressive yield strength that are closer to those of natural bone tissue. As previously mentioned, magnesium is the fourth most abundant cation in the human body and is naturally present in bone tissue. In a person weighing 70 kg, the total magnesium content is approximately 1 mole, and it plays a crucial role in metabolic processes. Research has also shown that magnesium has a stimulating effect on bone growth [14].

The use of magnesium alloy-based biomaterials dates back to the 20th century and continues to be an active area of research. Interest in magnesium alloys stems from their excellent mechanical properties, biocompatibility, biodegradability, and relatively low cost. Magnesium alloys possess mechanical and physical properties that closely resemble those of human bone tissue. This makes them a promising material for biomedical applications. Among magnesium-based bioimplants, their low density (1.8–2 g/cm^3) and low elastic modulus (41–45 GPa) are particularly noteworthy, as they are significantly lower than those of conventional materials such as stainless steel, cobalt-based alloys, and titanium (see Table 1) [9, 16]. Moreover, magnesium is the eighth most abundant element in the Earth's crust, which guarantees an ample supply for its extensive use in a wide range of industries [17, 18].

However, a major challenge with magnesium is its low corrosion resistance and unpredictable degradation in biological environments, which limits its application as a biodegradable implant. To overcome this limitation, the degradation rate of pure magnesium must be improved through alloying and surface engineering, enabling its further development for biomedical use [10].

A comparison of key mechanical properties, including tensile strength, yield strength, and elastic modulus, between implanted materials and natural bone is presented in Table 1 [9]. It can be observed that the difference in Young's modulus between implant materials and bone tissue is quite significant. This discrepancy can lead to slower tissue healing and may even contribute to complications such as osteoporosis. Additionally, biological drawbacks must also be considered. Inert materials, which remain in the body for extended periods, either do not degrade or degrade extremely slowly. Over time, they may undergo corrosion, releasing ions with varying degrees of toxicity, potentially causing inflammation and allergic reactions (see Table 2). Table 2 presents data on the applications, advan-

Table 1. Comparison of some physical properties of implants with biological bone [16]

Materials	Density ((g/cm^3))	Young's modulus (GPa)	Compressive Yield Strength(MPa)
Cortical/Compact bone	1.8–2.0	5–23	130–180
Magnesium	1.74–1.84	41–45	65–345
Titanium alloys	4.4–4.5	110–117	758–1117
Stainless steel (316 L)	7.9	190	170–310
CoCr alloys	8.3–9.2	210–253	450–1000
Synthetic Hydroxyapatite (HA)	3.1	73–117	600

tages, and disadvantages of various biomaterials. A review of this table confirms that no single material currently meets all the necessary requirements, highlighting the need for further research to enhance specific properties [6].

4 Degradation process

In 1906, magnesium was first used as a fixation device for the internal fixation of bone fractures. However, several attempts were unsuccessful due to the rapid degradation of magnesium, which led to a significant decrease in its mechanical properties (Fig. 1). Magnesium is highly reactive and tends to degrade through corrosion. The corrosion process of magnesium and its alloys is an electromechanical process. It is known that the oxidation process in air and the corrosion process in aqueous environments are distinctly different. During corrosion in an aqueous environment, magnesium hydroxide and hydrogen are formed, as depicted in Fig. 1. The corrosion mechanism of magnesium and its alloys can be described as follows: [5, 19].

When the Mg alloy comes into contact with body fluids or simulated body fluids (SBF), it undergoes oxidation, leading to the release of Mg^{2+} (equation 2) cations and electrons (Fig. 1(a)).

$$\text{Cathode Reaction:} 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (1)$$

The released electrons participate in the reduction of water, generating hydroxyl ions OH^- (equation 1) (Fig. 1(a)).

$$\text{Anode Reaction:} \quad Mg^{2+} + 2e^- \rightarrow Mg \quad (2)$$

$$\text{Overall Reaction:} \quad Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2 \uparrow \quad (3)$$

The formation of an $Mg(OH)_2$ (3) film on the surface provides protection against further corrosion.(Fiq. 1(b)) At the same time, biomolecules in body fluids, such as amino acids, proteins and lipids, may adsorb onto the alloy surface and influence its corrosion behavior

$Mg(OH)_2$ layer is not able to effectively protect the magnesium matrix from further degradation, which leads to pitting corrosion (Fig.1(c)). As OH^- ions are produced, the pH of the medium near the Mg surface rises, creating an alkaline environment. The $Mg(OH)_2$ film remains stable at a high pH (>11.5), but at a lower pH (<11.5), this layer tends to dissolve. As a result, the $Mg(OH)_2$ layer begins to degrade.(4) It reacts with chloride ions present in the body fluids (or SBF), forming soluble, biocompatible and non-cytotoxic $MgCl_2$, which leads to pitting corrosion on the surface [9, 16].

$$Mg(OH)_2 + 2Cl^- \rightarrow MgCl_2 + 2OH^- \quad (4)$$

Furthermore, the high concentration of hydroxyl ions in the medium promotes the presence of calcium and phosphate ions, facilitating the formation of a protective calcium phosphate layer on the surface [9, 21]. Calcium and phosphate ions in body fluids trigger the formation of a biological apatite layer due to the alkaline environment (Fig. 1(c)). The formed pits act as initiation sites for cracks due to local stress concentration, and over time, these corrosion processes intensify. Eventually, the damaged areas detach from the implant [16].

Chloride ions cause pitting corrosion in magnesium alloys, especially at concentrations above 30 mmol/L, by turning magnesium hydroxide into soluble magnesium chloride, which accelerates degradation. On the other hand, phosphate ions PO_4^{3-} help reduce corrosion by forming a protective magnesium phosphate layer. Bicarbonate ions HCO_3^- first promote corrosion but later help passivation through the formation of magnesium carbonate. Sulfate ionsSO_4^- increase the dissolution of magnesium. Proteins like albumin can form a protective coating enriched with calcium phosphate, while amino acids tend to increase magnesium degradation [5].

Zinc, (5) often used as an alloying element because it can replace hydrogen ions in solution, also participates in additional reactions within magnesium-zinc alloys, complementing the previously mentioned mechanisms (7) [22]:

$$Zn + 2H_2O \rightarrow Zn(OH)_2 + H_2 \uparrow \quad (5)$$

$$Zn \rightarrow Zn^{2+} + 2e^- \quad (6)$$

Table 2. Properties of orthopedic implants [6]

Material	Application	Advantages	Disadvantages
Stainless steel	Surgical instruments, stands, temporary fixation materials	Good biocompatibility, low cost, folded processing technology	Young's modulus is increased and can cause inflammation
Cobalt-based alloys	Replacement prostheses for the knee and hip	The best indicators of wear resistance and tensile strength	Biotoxic, allergenic, high cost
Titanium alloys	Total endoprosthetics, fracture fixation	Biocompatibility, lightness, low modulus	Low corrosion resistance, lower hardness
Magnesium based alloys	Biodegradable fixing plates and other medical devices	Good biocompatibility, low modulus, positive effect of magnesium ions on bone restoration	High corrosion rate and hydrogen release during corrosion

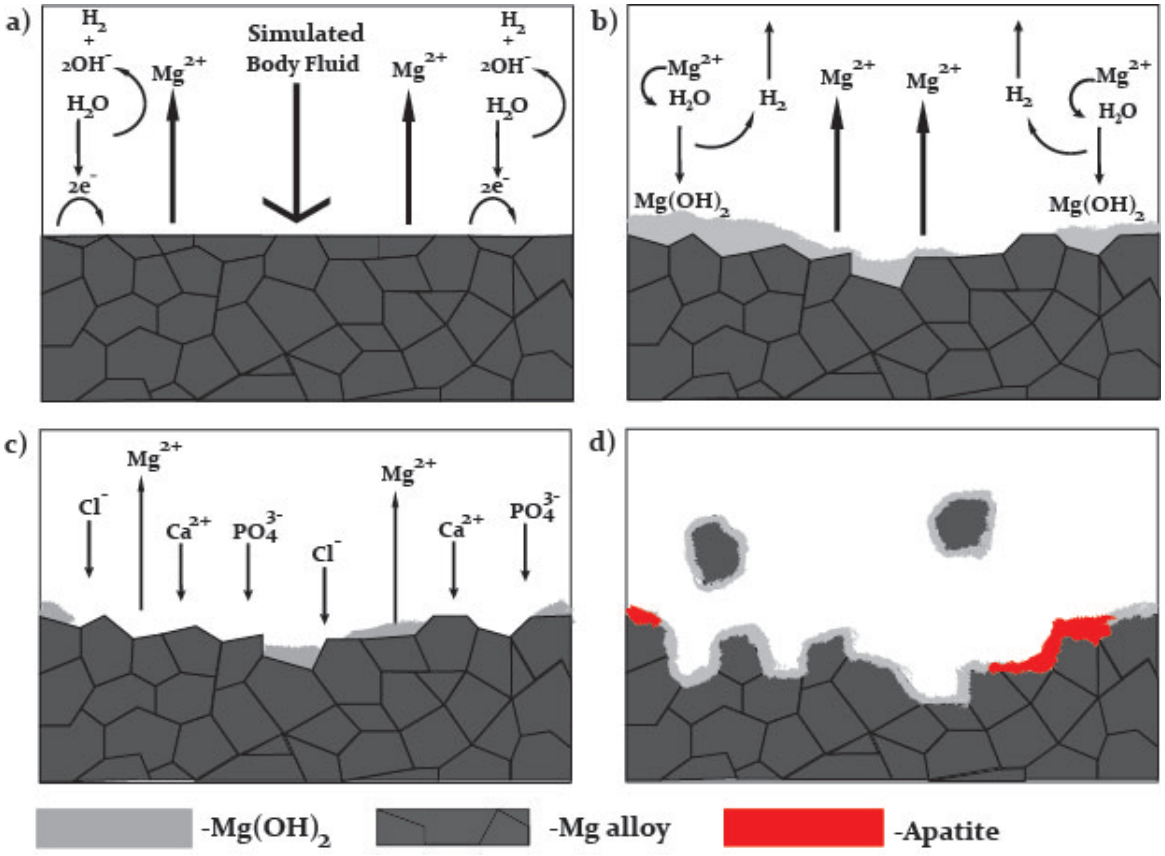

Figure 1. Mechanism of magnesium alloy degradation [16, 20]

Mg could also remove Zn ions from solution:

$$Mg + Zn^{2+} \rightarrow Zn + Mg^{2+} \tag{7}$$

Due to corrosion, the mechanical integrity of the implant is compromised, leading to its degradation before complete bone healing occurs. Additionally, as shown by the reactions, the hydrogen gas (5) released during corrosion causes the formation of hydrogen cavities. Given these critical issues, it is essential to control the degradation rate of magnesium-based implants, as it leads to hydrogen bubble accumulation and a rise in local pH, which may result in cell death and tissue inflammation [5, 21].

Table 3. Mg and Mg alloys degradation factors [23]

Alloy Factors	In-vivo factors	In-vitro factors
Type of material (plate, rod, etc.)	Tissue pH	Dynamic/static
Grain size	Chlorine ion level	Solution pH
Alloying elements	Place of implantation	Solution Temperature
Metal purity	Type of animal	Degradation media

5 Corrosion factors and methods of improving the corrosion properties of the MgZnCa alloys

The corrosion behavior of magnesium and its alloys is influenced by microstructural defects (e.g. dislocations, twin deformation) and environmental factors. Residual stress from defects and mechanical stress both contribute to increased corrosion rates. Chloride ions in body fluids accelerate degradation, while other factors, such as inorganic ions, oxygen, and organic buffers, also play significant roles. The buffer system HCO_3^-/CO_2 protects magnesium alloys by forming $MgCO_3$, but amino acids reduce this protective effect [9].

In addition, it is important to note that the implantation site significantly affects the rate of implant degradation. It has been found that the degradation of plate implants is much higher than that of screws when used for elbow fractures. These differences in degradation rates are attributed to the implant location: the screw is placed directly in the bone, while the plate is surrounded by muscle tissue, which accelerates the degradation process [9, 24].

The MgCa alloy exhibits mechanical properties similar to those of bones, which significantly contribute to the process of bone restoration. However, its high degradation rate limits its application. The secondary phases of Mg_2Ca formed at the grain boundaries of the alloy, act as an anode, accelerating corrosion through galvanic reactions [24]. An ideal bone implant should have an appropriate degradation rate, allowing for gradual bone restoration after implantation, during which the bone progressively replaces the implant until complete recovery [25, 7].

Pure magnesium alloys show a broad spectrum of degradation times, ranging from 4 to 52 weeks, depending on their composition and processing methods [26]. However, most of these alloys tend to degrade rapidly, which can compromise their mechanical integrity within the body. To mitigate this, researchers have developed a variety of physical and chemical strategies to manage the degradation process during implantation. By alloying magnesium with different metals and non-metals, it is possible to control phase distribution, grain size, and microstructure, leading to improved degradation behavior [14, 17].

During heat treatment, the secondary phase disperses uniformly within the matrix. This uniform distribution minimizes galvanic corrosion between the secondary phase and the magnesium matrix, promoting even degradation and reducing the risk of localized pitting corrosion [10, 12]

One way to improve the corrosion resistance of magnesium-based alloys is by adding a special coating or layer to their surface. This protective barrier helps reduce corrosion, especially at the beginning of implant use. Another method is plasma electrolytic oxidation (PEO), an affordable, simple and environmentally safe process that forms strong oxide-ceramic coatings on metal surfaces [27, 24]. For example, researchers studied how different amounts of zinc and surface treatment using plasma electrolytic oxidation (PEO) affect the corrosion behavior of the Mg xZn 0.3Ca alloy, where $x = 1, 3, \text{and} 5\%$ by weight. They discovered that higher zinc levels led to the formation of molten magnesium areas and intermetallic compounds $Ca_2Mg_6Zn_3$ along grain boundaries. The corrosion rate increased with more zinc in the alloy. However, PEO surface treatment, as shown in in vivo tests, significantly reduced the corrosion rate [27].

In [10], it was revealed that the degradation rate of the Mg-3%Zn-0.3%Ca alloy changes after various heat treatments. The study demonstrated how the volume fraction of the secondary phase and grain size are key factors controlling the biocorrosion rate of the alloy. Samples with the smallest grain size, but with the largest volume fraction of the secondary phase, exhibited the highest corrosion rate, as the secondary phase causes galvanic corrosion, which outweighs the positive effect of a smaller grain size. Conversely, the sample with the smallest volume fraction of the secondary phase but the largest grain size also showed a high corrosion rate, as the larger grain size predominates (the corrosion rate increases with increasing grain size). The minimum corrosion rate was observed for a sample subjected to heat treatment at 420°C for 24 hours,

which had a balanced volume fraction of the secondary phase and grain size.

Y. Zhang et al. [26] investigated Mg–3Zn–0.2Ca (wt.%) alloys with varying columnar microstructures and solidification rates. Corrosion tests showed that alloys possessing an equiaxed (cellular) crystalline structure exhibited more uniform (homogeneous) corrosion behavior and demonstrated the lowest corrostion rate.

C. Gong et al. [28] investigated the degradation behavior of $Mg_xCa_{1-x}Zn$ alloys (x = 0, 2, 5, and 8 wt.%). It was found that the grain size decreased with increasing Zn content, an effect attributed to the growth-limiting role of Zn. During solidification, the sharp decrease in the solubility of Zn and Ca in the Mg matrix at lower temperatures leads to their enrichment at the solid–liquid interface, which induces supercooling and suppresses grain growth. The microstructure of the alloys consisted mainly of an α-Mg matrix and secondary intermetallic phases, predominantly distributed along the grain boundaries. As the Zn concentration increased, the volume fraction of secondary phases also grew, with their distribution along grain boundaries changing from discontinuous to continuous. Electrochemical and immersion tests ranked the corrosion resistance of the alloys in the following order: XZ15 < XZ10 < XZ18 < XZ12 (where the first digit indicates the Ca content and the second the Zn content, in wt.%). Among these, the XZ12 alloy exhibited the most uniform corrosion behavior. This improvement was attributed to the presence of Zn-enriched Mg_2Ca phases. In contrast, the discontinuous ternary intermetallic phase in XZ15 served as a cathodic site, accelerating localized corrosion, whereas the continuous ternary phase observed in XZ18 acted as a physical barrier, reducing corrosion propagation.

Studies have shown that adding rare earth elements to magnesium alloys helps improve their strength by forming a stable phase at the grain boundaries. For example, when the alloy has more 10% cadmium (Cd), it forms Mg_5Cd particles at the grain edges, increasing the mechanical properties. In addition, with 15% Cd, the resistance of the alloy to corrosion improves. Adding lanthanum (La) also helps, as it forms a protective layer that protects the surface. However, there are not many animal tests on how these alloys behave [7].

Zinc is a vital element for the human body. When added to magnesium alloys, it improves both mechanical strength and corrosion resistance. Zinc also helps create secondary phases in the alloy, which makes it more stable, and it reduces the negative effects of unwanted impurities. Additionally, zinc forms a protective surface layer that shields the alloy from corrosion [20].

Calcium, an essential element in bones, teeth, and other tissues, also supports hormone regulation and muscle function. When added to magnesium alloys, calcium helps clean up impurities and refines the grain structure. At concentrations between 0.5–1%, calcium slows grain growth, which can improve the alloy's properties. However, if the calcium content is too high, it can form a brittle Mg_2Ca phase along the grain boundaries, which weakens corrosion resistance and makes the material less ductile [24].

Seo-Young Kim et al.[29] studied Mg-35Zn-xCa alloys, based on the Mg-35Zn alloy, where x = 1–5 wt% Ca. To determine the optimal composition for an ideal biocompatible alloy, the structural characteristics, corrosion resistance, and cytotoxicity of the resulting samples were assessed. The purity of the starting components used was Mg – 99.3%, Zn – 99.9%, and Ca – 99.5%. The developed alloys showed superior hardness compared to existing magnesium alloys. Structural analysis revealed that Mg-35Zn-xCa alloys exhibited a dendritic composition. The volume fractions of the second phases (Mg_2Ca and $Ca_2Mg_6Zn_3$) increased with the Ca concentration. Notably, the Mg-35Zn-2Ca alloy demonstrated the best mechanical properties, corrosion resistance, and response to cytotoxicity. Based on these results, the authors suggest that the alloy with 2% calcium content is the most promising material for use in orthopedic implants, though further in-vivo studies are needed.

In [29], L. Yu et al. investigated the effect of varying amounts of silver on the microstructure, mechanical properties, and electrochemical behavior of the Mg-Zn-Ca alloy. The study found that the addition of silver improved not only the mechanical properties but also the corrosion resistance of the alloy. This improvement is attributed to the formation of smaller grains and more uniformly distributed secondary phases. The alloy Mg-3Zn-0.2Ca-xAg was used as a base, where x = 0%, 0.1%, 0.3%, 0.5%, and 0.7% by weight. Microstructural analysis showed that with 0.3% Ag, the alloy exhibited a smaller grain size of 2.08 µm. Additionally, the Mg-3Zn-0.2Ca-0.3Ag alloy demonstrated improvements in mechanical properties, including elongation (by 4.57%), yield strength (by 5.7%), and tensile strength (by 2.4%) compared to Mg-3Zn-0.2Ca. After immersion in artificial body fluids at 37°C for 15 days, the hydrogen evolution and degradation rates of Mg-3Zn-0.2Ca-0.3Ag were significantly lower than those of Mg-3Zn-0.2Ca. Furthermore, cytotoxicity testing indicated that the Mg-3Zn-0.2Ca-0.3Ag alloy exhibited good biocompatibility. In the article [30], F. Qin et al. investigated the corrosion behavior and mechanical properties of amorphous Mg-Zn-Ca alloys, as well as the influence of the Ag component on these properties. The study revealed that the 65Mg30Zn5Ca (%) alloy exhibited a high fracture strength of over 720 MPa, which increased further with the addition of 1% Ag. Among the amorphous alloys tested, the highest polarization resistance in Hanks' solution was observed in the 65Mg30Zn4Ca1Ag alloy (8542 Ohm/cm^2), while the lowest was found in the 63Mg30Zn4Ca3Ag alloy (4125 Ohm/cm^2). The 65Mg30Zn5Ca alloy showed an

intermediate result (5640 Ohm/cm^2). The study concluded that with higher Ag content, both the strength and corrosion resistance of the alloys decreased due to reduced glass-forming ability and galvanic corrosion.

Xuenan Gu et al. [31] investigated the metallic glass of Mg-Zn-Ca alloys with different compositions (Mg66Zn30Ca4 and Mg70Zn25Ca5 (%wt) and explored their potential use as biomaterials by studying microstructural, mechanical properties, corrosion, and cytotoxicity. The research found that the Mg66Zn30Ca4 alloy exhibited a more uniform corrosion morphology compared to pure magnesium and Mg70Zn25Ca5 . It also demonstrated improved corrosion potential and lower current density than pure magnesium. The alloy surfaces showed a much more uniform corrosion morphology with evenly distributed micropores, unlike the larger, more irregular pores seen on the surface of rolled pure Mg. The corrosion products identified were Mg(OH)2 and Zn(OH)2. Cytocompatibility tests revealed that the Mg66Zn30Ca4 and Mg70Zn25Ca5 samples had higher cell viability compared to pure Mg.

Magnesium-based biodegradable glasses are promising due to their single-phase, chemically homogeneous alloy system and the absence of secondary phases that could degrade mechanical properties and corrosion resistance. The article [32] describes a method for enhancing the corrosion resistance of magnesium-based glass biomaterials. Biodegradable $MgZnCa$ glasses with high Zn content and reduced hydrogen evolution during the degradation process were studied. It was found that when the Zn content exceeds a certain threshold (28% by mass), a passivation layer forms on the surface of the alloy, preventing rapid corrosion. A model was developed based on the calculated Pourbaix diagram using corrosion analyzer software. As a result, glassy alloys $Mg(60+x)Zn(35-x)Ca5$ (where $0 \leq$ x $\leq$ 7%) show significant potential for use in the next generation of biodegradable implants [32].

Based on the reviewed studies, it can be concluded that researchers aim to determine the properties of various composition variations (%) of MgZnCa alloys and the factors influencing them. Given the complexity of biological environments and the numerous factors influencing the degradation rates and properties of magnesium alloys, current research is focused on finding the optimal composition ranges. Additionally, significant attention is being paid to processing techniques that can be adapted for different biomedical applications. Various alloying elements are used to refine microstructure, enhance corrosion resistance, and improve mechanical performance. It has been shown that rare earth elements like La and Cd can enhance the biodegradability of magnesium alloys. However, it is important to consider the potential toxicity of these elements, as the biocompatibility of degradation products is critical for their safe use as biomaterials.

Degradation properties are influenced by many factors (Tab.3), the most significant of which are described below. Impurities and secondary phases also play a crucial role in the corrosion resistance of magnesium and its alloys. The corrosion rate of pure magnesium increases in the presence of impurities such as Fe, Ni, Cu, and Co due to their high electrode potential. It is well-established that the secondary phase significantly affects the galvanic corrosion resistance of magnesium and its alloys. Galvanic corrosion appears between two metallic implants with different electrochemical potentials and leads to accelerated degradation [12, 20]. The secondary phase can either act as a corrosion barrier or as a galvanic cathode. The number of secondary phases, their grain size, precipitation, and electrode potential must all be carefully considered in order to control the corrosion rate. Studies have shown that a secondary phase with a finer grain size, particularly one that is segregated along grain boundaries, improves corrosion resistance [12]. Thus, we can confidently assert that even seemingly insignificant factors can significantly influence the degradation process. The careful selection of composition and ratio, along with appropriate heat treatment techniques, can bring the properties closer to the ideal. Undoubtedly, ongoing research and development of MgZnCa alloys will drive significant progress in the coming years.

6 Future research directions

As we have previously mentioned, the main issue associated with magnesium and its alloys is the rapid degradation rate, which leads to the loss of mechanical strength in implants and excessive hydrogen gas release. Both of these problems are highly undesirable in the context of biomedical implants. Current research mainly focuses on improving the biocorrosion resistance of Mg and its alloys, and this involves areas such as alloying, heat treatment, and surface coatings. However, the application of coatings has a short-term effect, as after their degradation, the biomaterial is again exposed to physiological conditions, and controlling hydrogen release becomes extremely challenging.

Future research should focus on alloying Mg and studying the thermal effects on alloys to find long-term solutions. When alloying MgZnCa, the biocompatibility of the added elements must be taken into account to effectively improve corrosion resistance without adversely affecting the body. An important consideration is also the regulation of the biodegradation rate, which depends on several factors such as the implantation site, tissue damage, the time the implant remains in the body, the surface area of interaction between the alloy and body fluids, the material's structure and composition, and others.

It is necessary to investigate the creation of biomaterials from MgZnCa and alloying them with elements that are safe for the body, such as Ag or Cu. A significant issue is the change in mechanical strength dur-

ing implant degradation, which complicates the precise prediction of its performance in the body. This highlights the need for developing a complex model that can accurately predict changes in mechanical properties during material degradation. Looking at the rapid progress in the field of computational simulations, there is a need for improvements in the computational tools for the performance prediction of Mg and its implants.

Another important aspect is the environment in which the implant will be used. To create an accurate model that mimics the implant's surroundings, thorough research and determination of boundary conditions are required. This necessitates additional in vivo studies to better understand the long-term effects of MgZnCa alloys on surrounding tissues, as well as their potential to cause inflammation or hydrogen gas pocket formation during degradation.

Studying the interaction between these alloys and the immune system will also be critical to understanding their safety and effectiveness. In the future, with the development of personalized medicine, the development of customizable MgZnCa alloys that can meet the individual needs of patients, such as varying bone density or healing rates, may become an important area of research. Creating models that account for the loss of strength and degradation of Mg implants in a corrosive environment represents a significant area for future research, as it has not been sufficiently explored in the past.

7 Conclusions

Magnesium alloys with Mg-Zn-Ca composition are promising for biomedical use because they naturally degrade in the body. However, their corrosion behavior depends a lot on their composition and microstructure. Certain phases like Mg_2Ca, can speed up corrosion by creating galvanic cells, acting as anodes. Factors such as grain size, defects, and the amount of secondary phases also affect how quickly these alloys degrade. By carefully selecting heat treatment parameters, it's possible to distribute the secondary phases more evenly, reducing pitting corrosion and improving the alloy's resistance.

Surface treatments like plasma electrolytic oxidation (PEO) are effective in creating protective coatings that slow down corrosion. Still, improving the long-term stability of magnesium alloys in the body requires a balanced approach—optimizing the composition, microstructure, and processing techniques.

Adding zinc and calcium improves the alloy's mechanical and corrosion properties, but excessive amounts can reduce ductility and increase the risk of corrosion. For example, if too much calcium is added, it can form brittle Mg_2Ca along grain boundaries, weakening the material.

Despite progress, challenges remain. Researchers need to refine alloy compositions, understand how microstructure affects properties, and develop new methods to ensure magnesium alloys stay stable and safe when used in the body.

Author Contributions

K. Amirmatova: Conceptualization, investigation, writing—original draft. E. Aliyev: methodology, editing, data analysis.

Conflict of Interest

There are no conflicts of interest.

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