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# Biodegradable Mg alloys –A review

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## Abstract

The market for implant alloys, particularly those designed for orthopedic implants has expanded rapidly during the last decade. The medical sector has benefited greatly from the significant advances achieved in the study of Mg-based biodegradable alloy during this time.
Research is a step up in this area for a number of reasons, including the desire to improving people quality of life (a social as well as an economic driver). By decreasing the prevalence of permanent metallic implants (such as those made of stainless steel, cobalt-based alloys, and titanium alloys), which have their own set of drawbacks (including stress shielding and metal ion releases) that can have a negative impact on patients' mental and physical health.
Biodegradable Mg alloys are discussed in this paper, along with their history of development, important features that make them desirable for such applications (orthopedic implants), and features that must be modulated (corrosion rate and mechanical properties) to arrive at the optimal product for the intended application. It emphasizes the electrochemical characterization techniques/methods and strategies to enhance the corrosion behavior and mechanical characteristics of various kinds of biodegradable alloys, as well as the mechanism and features linked to the corrosion behavior of Mg alloys.
The criteria to be design, the requirements that implants of biodegradable alloys Mg-based must fulfill, and the features connected to their efficiency provided, as well as the methods of optimization, the category, and the influence of the alloying components.
**Key word:** Biodegradable, Mg alloys, Biodegradable implants**.**

## Introduction

Accidents and illnesses cause many bone fractures every year. Most of these breaks are too complicated to be treated conservatively and thus need surgical implantation of metal and plastic parts. Permanent metals implant, such as plates and screws composed of titanium alloys or steel used in conventional procedures of osteosynthesis and osteotomy to secure the bone before being surgically removed. This is particularly important for patients who are still young. After the first year or two, most people choose to have their metal implants removed.

Trauma treatment costs $56 billion per year in the United States [1], making it the second most costly medical issue behind heart problems. As an example, bone fractures account for over $ 32 billion in yearly costs. Over three million bone graft and transplant procedures performed annually throughout the globe [2]. As a result, improving the quality and efficacy of bone fracture therapies is crucial not just for patient (their emotional health and physical), but also for physicians, the health care system as a whole, and the bottom line. Bones are living tissues and have the potential to self heal after being fracture or even traumatized, second only to the skin in this regard. Mechanical force is crucial for the regeneration process of bones after a bone fracture. The biomaterials advancement used to mend replace joints and fractures has been crucial to modern orthopedic surgery. Except in the case of accidents, the likelihood of a fracture increases with sex, age, preexisting conditions and bone strength. Traumatic fractures, which are the most common kind, occur as a result of severe external pressures. In order to speed up the healing process or make up for lost bone tissue, orthopedic biomedical implants may be placed in or near a fracture. Once the fracture has healed, permanent metal implants often are surgically removed. Biodegradable implants, which break down naturally in the body, eliminate the need for removal after the healing process is complete for a shattered bone. The public health care system and individual patients alike will reap substantial financial benefits from this. In the range of small implants, temporary metal implant will take the role of permanent osteosynthesis materials for broken bone healing. These implants will provide as a temporary source of mechanical support until new bone can grow in and around them. Biodegradable metallic implants (Mg based) are difficult to produce because of the complex interplay between the technical and medicinal requirements for the material [3].
Recently developed Mg-based metal alloys have a high Osseo incorporation rate and are biodegradable. When compared to other metals used for orthopedic implants, including stainless steels, cobalt-chromium alloys, or titanium and titanium alloys, Mg alloys stand out due to their low elasticity, which is similar to that of human bone and eliminates the harmful impact of stress-shielding in bone structure. Mg biomaterials and their alloys are commonly used as short-term implants because they degrade fully in the biological environment (in vivo), being replaced by freshly created bone, eliminating the need for surgical reinter venation to eliminate the implant after 10-15 years, as is the case with permanent implants. Due to the transient nature of bone regeneration, they are a great solution for the supply of biodegradable metal implants. However, they have a downside in that they decay rapidly in the biological environment, requiring stringent monitoring of the rate of corrosion that is accordance with the healing of the damage bones tissues. The rapid corrosion process has detrimental consequences on the biological environment via interactions with other substances and the development of corrosion by products, in addition to the loss of mechanical properties that result from corrosion on an implant. Therefore, not only is the health of the patients at risk, but also is the total cost of the operation. That is why it is crucial to improve Mg alloys' corrosion resistance for applications like these.

## 1. History of Mg and its alloys in medical applications

Magnesium (Mg) entered the annals of science when Scottish physician and chemist Joseph Black identified it as such in 1755. Sir Humphrey Davy, a British scientist, separated magnesium (Mg) from magnesium oxide (MgO) and mercury oxide (HgO) in 1808. Around 1862, the first commercially produced magnesium metal was sold for use in pyrotechnic and

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photographic applications. Dr. Edward C. Huse employed Mg threads effectively to halt bleeding during radial artery and varicocele surgery in 1878. After using Mg threads on many patients, Huse found that their deterioration was gradual and proportional to the thread size [4].

In 1892, Austrian doctor Erwin Payr reported on the development of biodegradable Mg implants and developed flexible clinical uses. Approximately one hundred years ago, two of his publications claimed that Mg corrosion in vivo caused by the blood dissolve salts, tissues water content, and the cells chemical processes. Later, Belgian orthopaedist Albin Lam botte conducted clinical trials on humans, expanding on in vivo investigations first conducted on rabbits and dogs [5]. The Austrian firm I. Rohrbeck supplied the pure Mg used in Payr's research in the form of filaments, plates, and wires. Although they did sell Mg items, that business was not a "pioneer" in the industry. The electrolysis of molten carnallite (MgCl2.KCl.6H2O) was developed in 1886 in a German aluminum and magnesium company. Ten years later, in 1920, the Griesheim-Elektron firm had perfected the method and emerged as the industry leader, a position it held until 1916 [6]. Magnesium (Mg) was first produced commercially by the British firm Magnesium Elektron Ltd in 1937, which is still in business today. Although clinical experiments showed that Mg alloys were biocompatible [7], and their use in orthopedic and trauma surgery became common in the first half of the 20th century, their quick deterioration led to a substantial quantity of $H_2$ accumulating as subcutaneous bubbles of gas. This issue has halted research into Mg and its potential as a biomaterial for use in medicine [8]. Mg alloys were formerly the material of choice for orthopedic implants, but by the 1920, a new kind of stainless steel had emerged on the market. Mg and its alloys, on the other hand, have maintained widespread usage in a variety of non-medical uses, such as in the construction of vehicles, machinery, and aircraft. Due to their low density, high stiffness and, high strength at high temperatures and room temperature, Mg alloys now regarded as desirable for structural applications. In 1948, a uniform approach for designating alloy names and operating temperatures was introduced [9]. Mg regained attention as a metal implants applications in numerous medical field were due to the availability of high-tech equipment and alloying understanding at the time. Degradable metal implant consisting of Mg were alloys originally used in trauma surgery and orthopedic in the early part of the twentieth century. In recent years, researchers have revisited the potential of Mg alloys as biodegradable implant materials( see, for example, Witte [6], Staiger et al. and Xu et al. [8], [10], [11] Due to their widespread availability, magnesium alloys containing aluminum and zinc (AZ) have since become a popular research subject. The investigations revealed that the degradation rate of these Mg alloys varies with the alloying components used. Due to the incorporation of alloying elements, corrosion rates in Mg alloys kept to a minimum.

However, research conducted better understand the in vitro and in vivo corrosion mechanisms of Mg alloys and the role that the local environment and implant surface modification play in these processes. Znamenskii reported of two successful cases of bone fracture repair in 1945. The Mg alloy with 10% Al implants were undetectable in the fracture region 6 months after the bone transplant [12]. Implants made of Mg alloy with rare earth element additions were first utilized by Stroganov et al. in 1972. Rare earth metal made up 0.4–4.0% of the alloy, with cadmium, calcium, and aluminum making up 0.05–1.0% and manganese, silver, zirconium, and sil- icon making up the remaining 0.8–1.0%. According to in-vivo studies, this complex alloy degrades slowly over a period of 5–10 months; nevertheless, the author makes no mention of the dispersion of trace elements or other complications [13].



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The fastest degrading, most biocompatible, and strongest Mg alloy has not been reported. It is important for researchers and clinicians to collaborate in order to gain the specific knowledge and careful/interdisciplinary procedures necessary for medical usage of Mg biodegradable alloys.

## 2. Based on Mg biodegradable products Characteristics

As the most lightweight structural metal, magnesium is often regarded as the greatest alloy of the 21st century. Recent years have seen a surge in research interest in magnesium alloys all across the globe. Magnesium is now the most widely used structural metallic materials, a 491% growth in research on Mg alloys between 2000 and 2019. Magnesium has a density of 1.738g/cm$^3$ and a melting of about 650 degrees Celsius. Magnesium is utilized often in the aerospace and automotive industries, as well as the electronics industry, because of the metal's light properties. Magnesium-based alloys are biodegradable, have mechanical qualities similar to human bone, and are the focus of recent research for medical applications due to their lightweight nature (cortical bone density is 1.75-2.1 g/cm$^3$)[15]. This final feature is crucial for operative uses. Rates of corrosion are relatively high hard, despite significant worldwide effort in research and development of Mg-based alloys. Because of this, the implant loses its mechanical qualities too soon, and the newly created bone is unable to support the required mechanical stress, such as the patient's weight, before the implant fails. Simultaneously, the process of fast biodegradation might be accompanied with the generation of hydrogen, which can be strong and have adverse consequences on the body [16]. Several approaches have been suggested to mitigate these processes, such as isolating the implants surfaces, using methods that allows the manipulation of the material's microstructure, and enhancing the surface quality by decreasing the roughness. Surface modification is a viable technique to enhance the performance of Mg-based biomaterials for orthopedic applications, corrosion resistance of Mg alloys may be enhanced by adding alloying elements like Al, Ca, Zn, Mn, and rare earth elements [17].

Complete corrosion biodegradable Magnesium alloys implants are preferable so that the duration of therapy with these implants is both helpful and brief [18]. The rate of corrosion of the Mg implant must be low enough to permit remodeling of the bone throughout the process of implant deterioration. Another drawback of Mg bio-resorbable alloys is the risk of gas embolism, which is caused by the passage of hydrogen gas into the circulation from a biodegradable Mg implant during the corrosion process. Callus development and cortical abnormalities may occur when the early cortical bone healing process is disrupted due to the generation of $H_2$ bubbles, which limit the good connection of osteocytes [19]. The biocompatibility, biodegradability, and excellent mechanical characteristics of transient magnesium alloys [20] are their greatest benefits. Mass gain from the interaction of magnesium with the elements of the human cell was first result that demonstrates magnesium and Mg alloys in vivo should have biocompatibility [21]. Researchers found that Mg was biocompatible and sped up the bone-building process, thus they concluded that it should be used clinically. Magnesium also has a high damping capability, meaning it can absorb energy better than any other metal in load applications [22]. The ultimate proportions easily achieved and remain stable when made from Mg. Making the Mg lightest working metal construction [23].

As a result, it is simple to generate complex forms, which is particularly useful for the often complex shapes required for medical applications [24]. Mg has a better strength-to-weight ratio (130 KNm/Kg) and more resistivity than biodegradable polymeric materials utilized in

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osteosynthesis. Magnesium orthopedic implants are preferred due to their high fracture toughness and elastic modulus that are both comparable to bone. However, the implant must not bend under the weight of the patient [25].

See the benefits and drawbacks of biodegradable Mg alloy implants in Figure (1). Using Mg-based metal implants rather than permanent ones reduces or eliminates stress shielding, which affects the bone formation, healing process, and implants stabile due to the discrepancy in stiffness/Young's modulus among the implant and the bone. When compared to other permanent implant materials like stainless steel (190-205 GPa), cobalt chrome alloys (230 GPa), and titanium (110-117 GPa) [26]. The release of dangerous substances owing to wear may also elicit inflammatory reactions, even though the materials employed in permanent implants are harmless and innocuous.

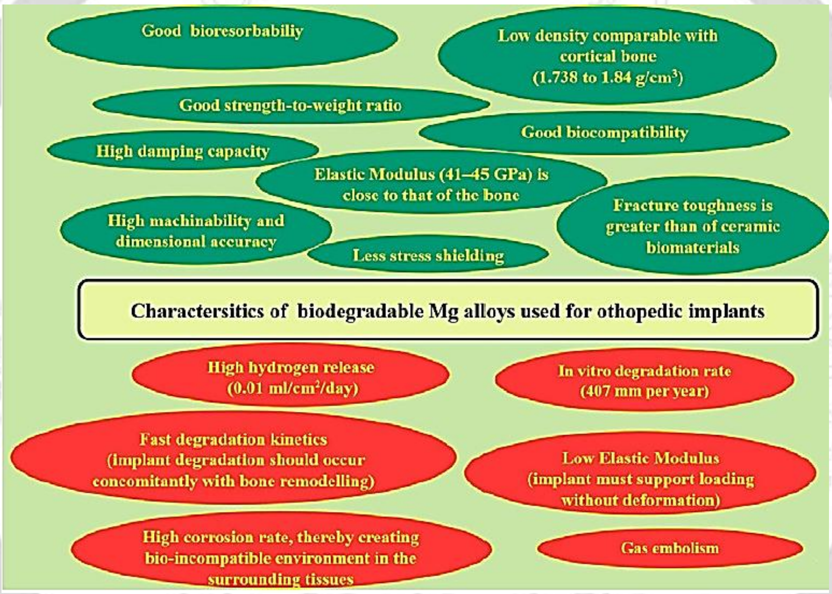


**Figure (1) Advantage and disadvantage of Mg alloys used for orthopedic implants [26].**

Table 1 compares the physical and mechanical qualities of several implants to those of natural bone, and Figure (2) illustrates the benefits and drawbacks of each [27].

Internal bone implant, such as the orthopedic implants, are often required for surgical repair of these fractures. Commercially available metal implants that meant to last a lifetime, such as bone plates or screws, often fabricated from stainless steel, cobalt-chromium or titanium alloys. Thus, the impact of correspondingly and, stress shielding, "the surgery" are now two main obstacles for permanent metals implant currently employed in practice of surgical. For starters, unlike the porous bones that surround them (10-30 GPa Young's modulus), permanent metal implant materials are overly hard (100-200 GPa) [28].

**Table 1 compared with natural bone and different metals mechanical properties [27].**

| Material | Density (g/cm$^3$) | E(GPa) | Compressive strength(MPa) | Fracture toughness(MPa•m$^{1/2}$) |
|---|---|---|---|---|
| Natural bone | 1.8–2.1 | 3–20 | 130–180 | 3–6 |
| Mg | 1.74–2.0 | 41–45 | 65–100 | 15–40 |
| Ti Alloy | 4.4–4.5 | 110–117 | 758–1117 | 55–115 |
| Co-Cr Alloy | 8.3–9.2 | 230 | 450–1000 | – |
| Stainless steel | 7.9–8.1 | 189–205 | 170–310 | 50–200 |
| HA Synthetic | 3.1 | 73–117 | 600 | 0.7 |
| PLA | 1.25–1.29 | 2.2–3.3 | – | – |

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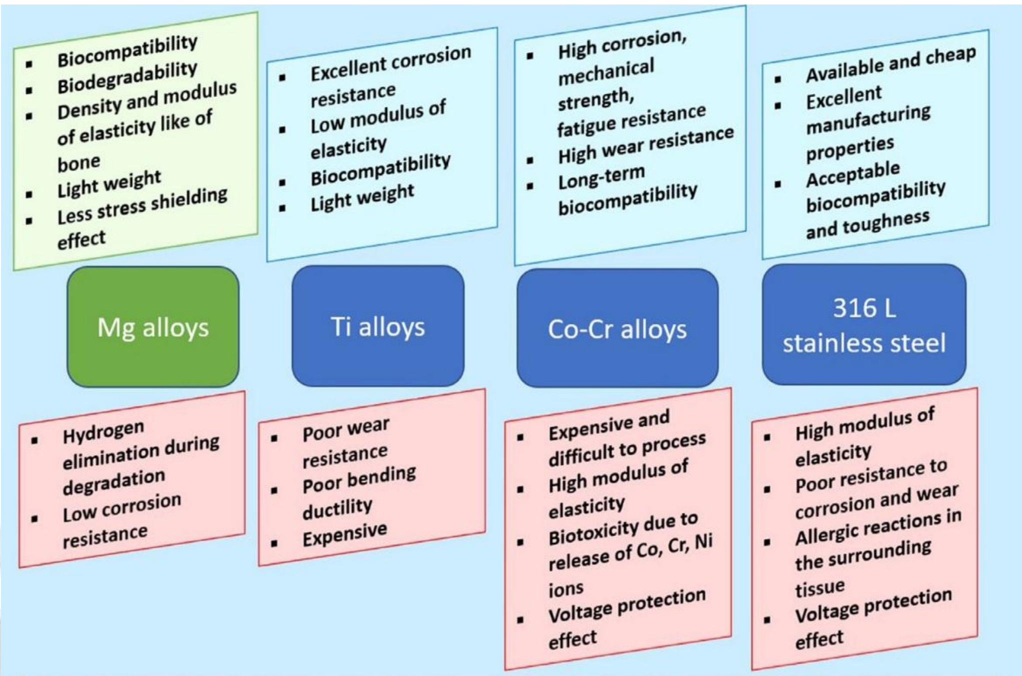


**Figure (2) Mg alloys compared with other metal implants (advantage and disadvantage)[27].**

The metal implant's primary function here is to shield the surrounding bone from the mechanical pressures that might otherwise cause damage. Because of this "protective" effect, patients often experience complications such as implant failure, poor fracture healing, damage to surrounding tissue, and persistent inflammation. Second, after a year or two, the metal implants should be taken out. This necessitates further surgical intervention, with all the attendant risks and expenses on several fronts. Biodegradable implant, which disintegrates in the body, a great answer for these situations because they eliminate two key obstacles: the impact of stress shielding and the procedure itself.

The three metals Magnesium, iron, and zinc often employed as basic components in medicinal applications as metals/biodegradable implants [29]. Table 2 lists the major features and how they compare to other steel products with the same purpose. Due to its mechanical qualities, iron is a promising material/implant option for biodegradation. The great elasticity contributes to its strong radial resistance. This has potential applications in the production of lightweight materials. Iron's high ductility is advantageous since it allows the material to be plastically bent, which is necessary for implantation.

**Table 2 parameters for pure metals used for medical applications compared to steel [29].**

| Material | Yield Strength, [MPa] | Tensile Strength, [MPa] | Elongation [%] | Degradation rate (*in vitro* tests)[mm/an] |
|---|---|---|---|---|
| Hardened steel, 316 L SS | 190 | 490 | 40 | - |
| Pure Fe, hardened | 150 | 200 | 40 | 0.16 |
| Pure Zn, cast | 17 | 20 | 0.2 | 0.2 |
| Pure Mg, cast | 20 | 86 | 13 | 407 |

In 2001 [30], researchers in New Zealand used (Fe > 99.8 %) to create the first biodegradable metal stent, which they inserted into the descending aorta of rabbits. No major inflammatory reaction or systemic damage was seen after surgical intervention. However, issues developed when these materials were employed as implanted devices owing to the nature of ferromagnetic pure Fe and the slow biodegradation rate (0.16mm/year) [31]. The deterioration rate was raised to 0.44 mm/year by adding a modest proportion of Mn, but this was still inadequate for large-scale applications. Biodegradable implants made from zinc-based alloys are potentially a possibility. The low melting point and reactivity of molten Zn-based metal alloys are the key benefits. Thus, they may be produced by hot forming, gravity casting, die-casting, or melting [32]. There was no evidence of toxicity or incompatibility with living organisms in zinc alloys [33]. However, pure zinc's poor strength and flexibility is a big drawback (as a possible biodegradable implant). However, magnesium is superior for this function since it is vital to metabolic processes and is quickly excreted from the body after being broken down [33]. Magnesium is slowly dissolved and absorbed by the body after implantation due to its low potentials of normal electrode (2.37V). The Mg 2 + ions formed are taken in by neighboring tissues or flushed out by bodily fluids. Biodegradation, natural bone-like elastic characteristics, and osteosynthesis potential make magnesium alloys ideal for use in restorative bone surgery. Cu, Ni, Fe, and Be are the most common impurities found in magnesium alloys. In general, the concentrations of Cu, Ni, Fe, and Be are capped at 100–300, 35–50, 20, and 5, respectively [18]. Toxicity limitations dictate that these contaminants be kept much below acceptable levels for use in biomedical applications.

## 3. Mg alloys corrosion mechanisms

Due to its great mechanical strength and breaking strength, metals implant continue to play an important role surgery in clinical for the repair or replacement of bone tissue. They are more suited to use in mechanically demanding situations than ceramic or polymeric alternatives [34]. Because of the high corrosion rate in the biological environment, metal implants deteriorate before the completion of the recovery process, necessitating a second operation to remove them after the body's tissues have recovered. Overall, degradable implants help the patient and the healthcare system since they eliminate the need for a second surgery to remove the implant. Further, in situations of pediatric surgery, degradable implants is also indicated when the body is still developing and a permanent implant has to be adjusted to fit the period of growth. Load is gradually transferred from the implant to the tissue, as seen in Figure (3), which promotes healing and remodeling of the damaged tissue. Magnesium has a poor corrosion resistance because of its normal electrochemical nature. Magnesium implants normally passivate when exposed to air, forming a thin coating of magnesium oxide that inhibits further chemical reactions [35].

Magnesium severely depleted in highly salty environment like human body. These properties make Mg alloys particularly well-suited for use as resorbable implants [35]. Magnesium, which is plentiful in bodily fluids, mostly combines with water to form hydroxide and hydrogen. Mg + 2 H2O = Mg(OH)2 + H2 (1) Magnesium hydroxide forms a persistent protective layer over magnesium implants in situations with pH > 11.5, while at (pH 11.5), it promotes corrosion of Mg alloys in the aqueous solutions [36].

This prevents the Mg hydroxide layers from covering the implants. Therefore, magnesium and Mg alloys implants surface corrosion is accelerated in vivo due to the highest chlorine electrolyte.



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Most engineering contexts, corrosion is to be avoided at all costs since it reduces the useful life of a material. However, biodegradable implants are of significant importance in the area of biomedical applications since they shield the patient from a second surgery to remove the permanent implant and get rid of the implant's long-term harmful effects. Because of its excellent strength and biocompatibility, magnesium is an appealing biodegradable substance. However, the loss of hydrogen that occurs with its decomposition is problematic for several biological uses. Damaged tissue may be further irritated by hydrogen generated during the decomposition of the implants in aqueous solution, as well as by the following rise in pH due to corrosion. Hydrogen gas builds up surrounding the implant, although it dissipates over time or may be punctured out, albeit this is more "uncomfortable" than dangerous [37]. Though it corrodes at a rather rapid rate, Degradation of magnesium results in the release of Mg ions, which are essential to human metabolism and known to stimulate the development of bone tissues [39]. These Mg-based materials advantages justify their usage in vascular stents and biodegradable orthopedic implants [40]. The biodegradation kinetics of different Mg alloys, in particular those with 3D structures, vary depending on the mechanical processing, alloying metals and coating processes used [41].

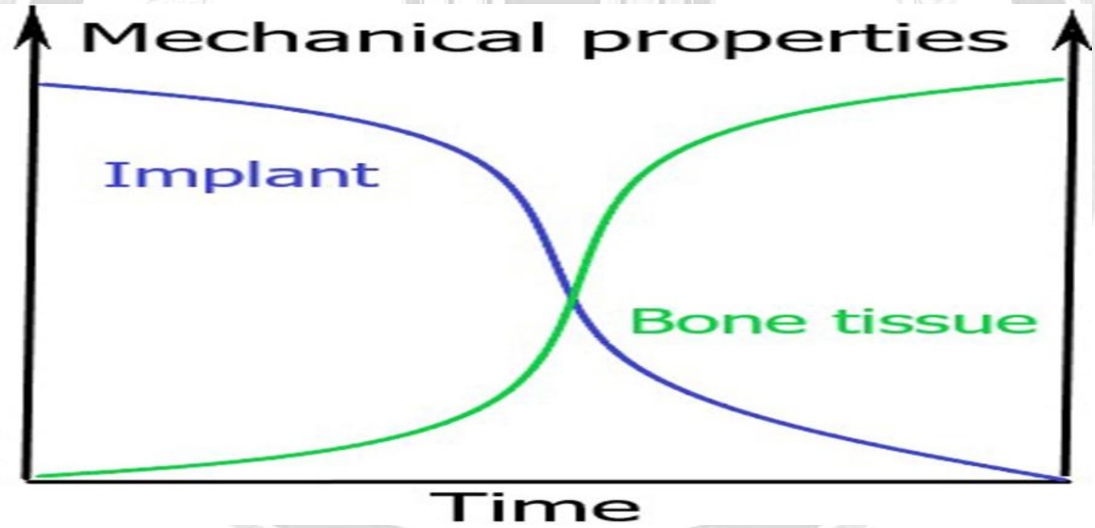


**Figure (3) diagram of representing implant (reduction of strength over time by degradation)[35]**

## 3.1 The corrosion process and effects potential negative biological

As magnesium alloys degradation, they will raise pH of surrounding environment and tissue. Toxic local consequences of alkaline poisoning might develop if the pH level in the area rises over (7.8). Magnesium biodegradation produces hydrogen gas bubbles, which raises concerns about tissue necrosis. Gas embolization in important organs was also proposed about this period. Rapid ion release from the alloy may cause pathological alterations to the ion organs, which may have far-reaching, deleterious impacts on organ function. Metal alloys used in medical implants corroded because they were thermodynamically unstable and had a propensity to revert back to their original condition as metal compounds. Galvanic corrosion and pitting corrosion are the most prevalent types of corrosion seen in alloys used in the medical metal alloys.

Using the X-ray synchrotron, Figure (4) depicts the dynamic corrosion process of a Mg (screw) biodegradable implant. The implant with the bruised ceramic composition and the one without it are both biologically compatible, with the coated implant degrading at rates of 0.161 0.075 mm/year after 1 month, 0.097 0.013 mm/year after 4 months, and 0.218 0.030 mm/year after 7 months [42]. Fragments of Mg implants, sometimes known as "debris," may wreak havoc on the surrounding biological matrix or trigger inflammatory reactions. Figure 4d (the screw head) illustrates such a fraction.
One month after implantation, the above diagram shows no significant changes; four months after implantation, a slight volume loss is seen and seven months after implantation, a clear deterioration (including disintegration) is shown [43].

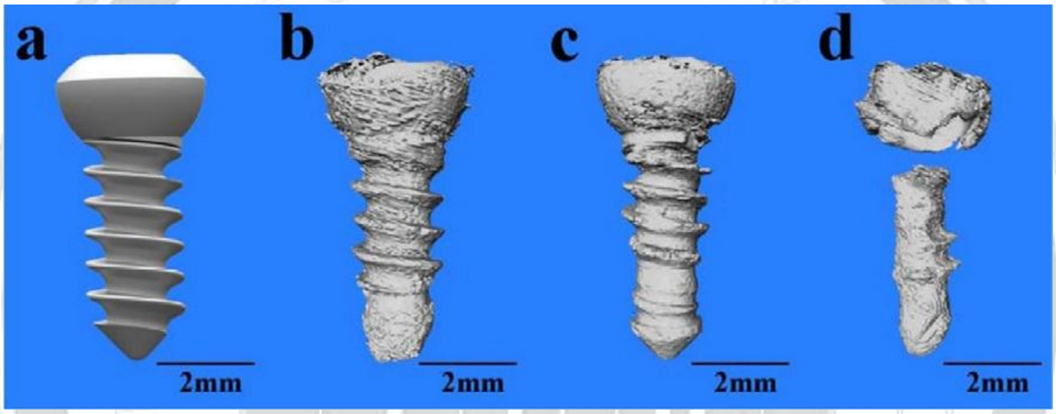


**Figure (4) Degradation process microphotography of the magnesium implant [42]**

**(a) The initial state , (b) after 1 month, (c) after 4 month, (d) after 7 month**

## 3.2 The mechanism of the corrosion process

Magnesium and its alloys corrode differently in water than they do in air because corrosion is an electrochemical process [44]. The reactions given explain corrosion's process in an aquatic setting (such as the body).

$Mg \rightarrow Mg^{+2} + 2e^{-}$ (anodic reaction) (2)
$2H_2O + 2e^{-} \rightarrow H_2 + 2OH^{-}$ (cathodic reaction) (3)
$2H_2O + O_2 + 4e^{-} \rightarrow 4OH^{-}$ (cathodic reaction) (4)
$Mg^{+2} + 2OH^{-} \rightarrow Mg(OH)_2$ (compound formation)

Magnesium and Mg alloys are highly susceptible to galvanic corrosion, which has significant implications for manufacturing technology, because the anodic reaction (2) generates a large amount of $H_2$ while the cathodic reaction (4) favors the formation of the hydroxide protection layer, which is insufficiently resistant. Under the effect of chlorine ions in the adjacent tissues, the protective coating of magnesium hydroxide generated on the surface of magnesium alloys in the human body would lose its protective ability. Magnesium hydroxide $Mg(OH)_2$ will react with chlorine to generate a water-soluble magnesium chloride, hence speeding up the corrosion process when the chloride content in the environment is over 30 m mol/L [45].
The chemical reactions shown below serve as symbols for these processes for example,

$Mg(OH)_2 + 2Cl^{-} \rightarrow MgCl_2$ (6)
$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$ (1)
$Mg + 2Cl^{-} \rightarrow MgCl_2$ (7)



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Despite being biocompatible and showing no evident cytotoxic consequences, the creation of the Mg $Cl_2$ layers on the implants surfaces will decide a reduction in the corrosion resistance [46]. However, the presence of hydroxyl ions boosts alkalinity, which, when combined with phosphate and calcium ions, causes a variety of calcium phosphates to precipitate and form a barrier on the surface [47]. Figure (5) and (6) depict the oxidation of the metal in response to contact with the biological fluid, which generates electrons that are then consumed by cathodic reactions, leading to the release of hydrogen gas and hydroxide and the formation of a protective layer on the surface [48], [49].

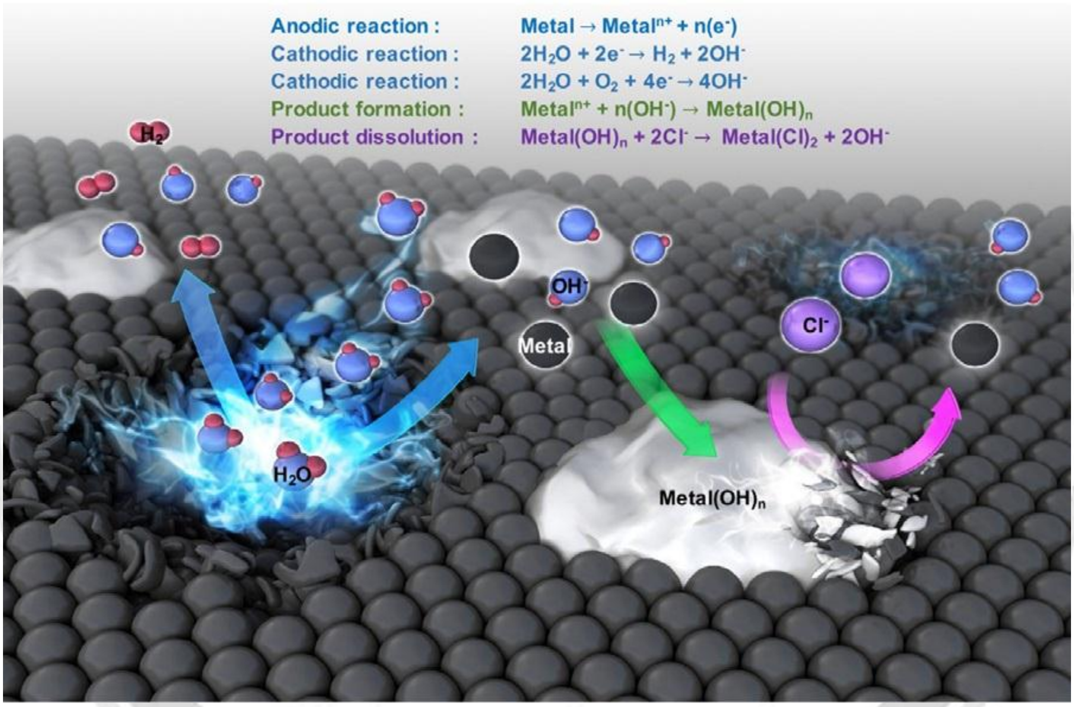


**Figure (5) metal degradation Mechanism [48]**

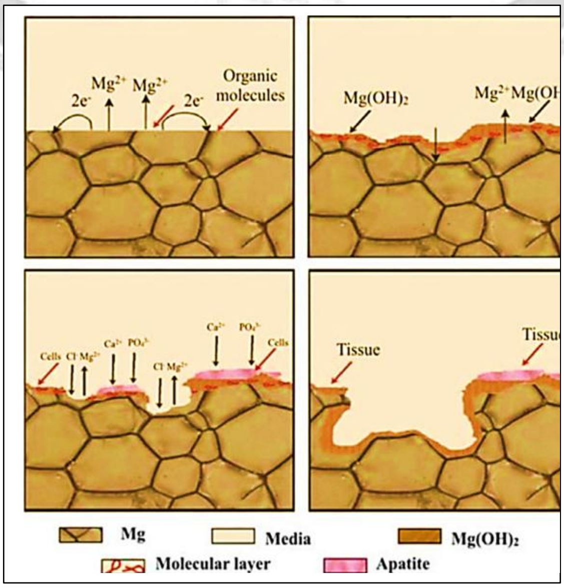


**Figure (6) mechanism degradation of Mg in vivo [49]**

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Biodegradable implant materials based on Mg should be strong enough to withstand breaking or fracture in the body. Walking, running, and other natural bodily motions all put stress on orthopedic implants. Implant failure results from stress loading in addition to corrosion in the surrounding tissue. Below the yield stress, this process manifests as stress corrosion cracking (SCC) [89]. Stress corrosion behavior of Mg-based implants has been the subject of several investigations, although crucial aspects are still lacking. When stress corrosion conditions exist, two primary mechanisms contribute to the development and propagation of cracks:
Anodic degradation at film-free crack tip causes intergranular stress corrosion cracking, which in turn causes crack extension and fracture propagation. Hydrogen atoms formed during the cathodic reaction of Mg alloys penetrate the Mg matrix and produce breaking, shown as trans granular stress corrosion cracking. That when mechanical stress applied to Mg, the SCC process causes fracture propagation to delay and sub-critical [51]. When a fracture becomes large enough, it interacts with the load and causes the material to shatter violently. A material's characteristics, particularly the passive film behavior that emerges on its surface during corrosion, may have an impact on the stability and coherence of SCC. Pitting corrosion may result from localized disintegration of the magnesium hydroxide ($Mg(OH)_2$) layer caused by chloride ions from human body fluid. When it comes to behavior at SSC, deformation velocity is crucial because it breaks the film, allowing localized dissolution or hydrogen penetration. The susceptibility of implants to SCC also depends on other parameters, such as the presence of flaws and the chemical makeup of the Mg alloy. Rapid solidification was used to create a biodegradable Mg-based alloy (Mg-6% Nd-2% Y-0.5% Zr (EW62)) with enhanced corrosion resistance, mechanical characteristics, and SCC behavior, as shown in research [49]. Surface film stability and the lack of a major detrimental micro-galvanic impact from secondary phases explain why increasing the Nd content of a Mg-5%Zn alloy by up to 3% [50] had no appreciable effect on the alloy's susceptibility to stress corrosion. Kannan et al. [52] found that the addition of rare-earth elements to Mg alloys, such as EV31A (0.48 wt pct Zn, 2.85 wt pct Nd, 0.50 wt pct Zr, and the rest Mg), considerably increased SCC. Both the presence of additional key elements like Ag and Zn and the degree of fineness of the microstructure contribute to the SCC resistance.

## 4. Biodegradable magnesium-based orthopedic implants: pathophysiology and toxicity of magnesium and alloying components

Corrosion of biodegradable Mg alloys may liberate metal ions, which have been shown to produce both local and systemic toxicity in vitro. A serum Mg level in the blood between 0.73 to 1.06 mmol/L is considered normal. Mg is an activator of several enzymes and plays an important role in adenosine triphosphate (ATP) generation, just two of its many roles in intracellular physiological processes. Moreover, it acts as a coregulatory of protein synthesis and as a stabilizer of both RNA and DNA [17]. Increased amounts of Mg ions, caused by the implantation of magnesium and Mg alloys, may promote new bone development and have anti-osteoporotic action. long-term potentiation and Short-term synaptic facilitation, as well as improvements in learning and memory, have all been shown in mice treated with Mg in laboratory experiments [53]. Magnesium (Mg) is the least harmful of the body's plentiful elements; yet, further research into its biological effects is required. Due to the physiological environment and corrosion rates in the implantation sites, the quantity of alloying element employed in the production of Mg based biomedical implants has to be adjusted. In general,

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below a certain critical threshold level, the body may be able to withstand the release of ions of poisonous elements, but any release over that level will have negative consequences [54]. When designing biomedical implants, it is essential to maintain localized release of ions of metal below critical threshold values. Table 3 Summarizes the toxicology of the most frequently used elements in Magnesium alloys. [17], [53], [55].

**Table 3 the toxicology of the most frequently used elements in Magnesium alloys [17, 53, 55].**

| Alloying Element | The effect of the alloying process | Pathophysiology/toxicology |
|---|---|---|
| Al | Increases hardness, strength, and casting capacity (fluidity), while density increases little. | Normal blood serum level 2.1-4.8 $\mu g/L$; Established alloying element in titanium implants; Risk factor in generation of Alzheimer's disease; Can cause muscle fibre damage; Decrease osteoclast viability |
| Ca | Improves thermal and mechanical properties, helps refine granulation and increases elongation resistance; reduces surface stresses. | Normal serum level 0.919-0.993 mg/L; Most abundant mineral in the human body (1-1.1 kg); Mainly stored in bone, teeth; Is tightly regulated by homeostasis of skeletal, renal, and intestinal mechanism. |
| Cu | Helps increase resistance to both room temperature and high temperature. | Normal blood serum level 74-131 $\mu mol/L$. |
| Mn | Increases corrosion resistance in salt water in some aluminium-containing alloys. | Normal blood serum level <0.8 $\mu g/L$; Essential trace element; Important role in metabolic cycle of e.g., lipids, amino acids, and carbohydrates; Influences the function of the immune system, bone growth, blood clotting, cellular energy regulation and neurotransmitters; Neurotoxic in higher concentration (manganism). |
| Ni | Increases both efficiency and maximum force at room temperature. It has a negative impact on elongation and corrosion resistance. | Normal blood serum level 0.05-0.23 $\mu g/L$; Strong allergenic agent which can induce metal sensitivity; Carcinogenic and genotoxic. |
| Sr | Increases elongation resistance (used with other elements); increase bone mass and reduce the incidence of fractures. | 140 mg in the human body; Neurological disorder |
| Sn | Improves ductility and reduces the tendency to fracture during processing, when used with Al; Improves compressive strength and corrosion resistance | 9-140$\mu g/L$, located in higher levels in liver and less toxic; Carcinogenic |
| Y and Lantanides | Y- increases high temperature resistance and elongation resistance when mixed with rare earth metals; increases the fluidity of alloys when casting. Ce - Improves corrosion resistance; increases plastic deformation capacity and Mg elongation and hardening ratio; reduces deformation strength. Nd- improves the strength of the material. | <47$\mu g$ in blood serum level; Substituted for $Ca^{2+}$ and matters when the metal ion at the active site; compound of drugs for treatment of cancer; Basic lanthanides deposited in liver; more acidic and smaller cations deposited in bone |
| Zn | Improves corrosion resistance when added to Mg alloys (with Ni and Fe impurities); at 2wt% or more, there is a tendency for hot cracking. | Normal blood serum level 12.4-17.4 $\mu mol/L$; Trace element; Essential for the immune system; Co-factor for specific enzymes in bone and cartilage; Neurotoxic at higher concentrations |

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## 5. Possible uses of magnesium alloys in medicine. Market tendencies.

Patients who participated in clinical trials using magnesium-based screws to heal/repair bone abnormalities saw no serious adverse effects [56], [57]. In 2013, doctors discovered the removal of the first commercially available magnesium screws (Magnezix, Syntellix, Hannover, Germany) [58]. In addition, a new MgYREZr alloy interference bolt (Mi- lagro, DePuy Mitek, Leeds, UK) has been released to the public [59]. It has been observed that radio-translucent regions occur temporarily surrounding magnesium implants [60]. Mg alloys vascular stent, which have been evaluated in clinical studies [61], [62], have been shown to up to six months mechanically stable in animal studies. Resorption effectiveness of up to 95% after a year has been shown in clinical trials and commercialization of polymer-coated biodegradable, drug-controlled stent manufactured by Swiss businesses [63]. Magnesium implants for both orthopedic and vascular use show promise, but their widespread clinical application has yet to be established [60], [64]. This is especially true when compared to smaller orthopedic implants like bolts and screws. Figure (7) depicts illustrative clinical applications [3].

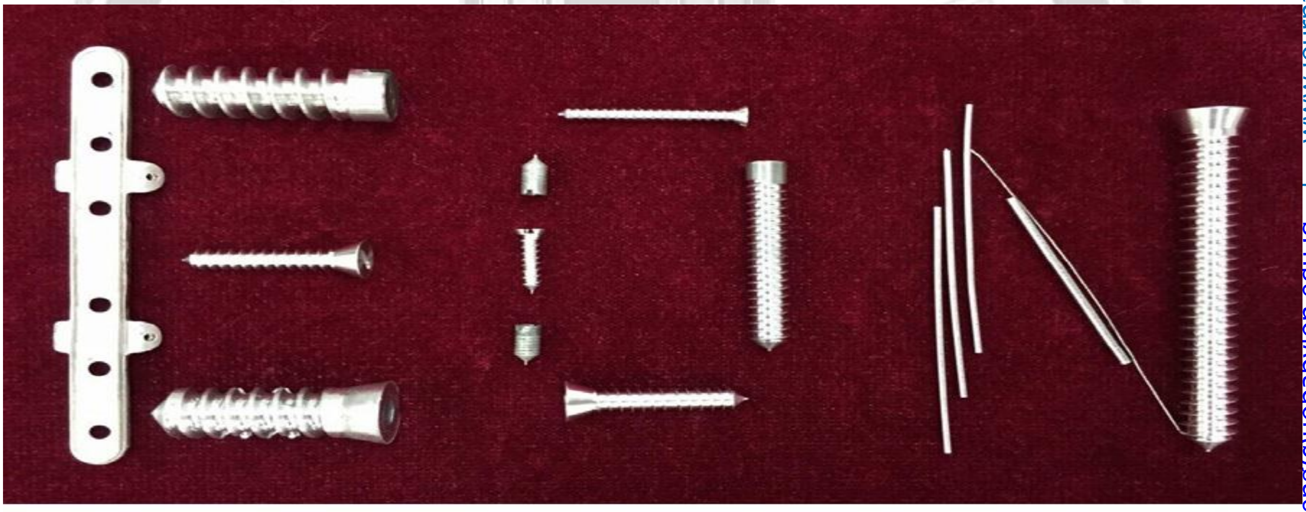

**Figure (7) biodegradable metal implants types [3]**

Shanghai Jiao Tong University [65] has recently produced a novel Mg-Nd-Zn-based alloy (Jiaoda BioMg, abbreviated as JDBM) by combining molecular dynamics modeling with experimental data. Neodymium, zinc, and zirconium were chosen as the key alloying constituents for this family of alloys. Although Nd and other rare earth elements exhibited modest cytotoxicity, alloys containing them (such as magnesium-neodymium binary alloys) have shown substantial improvements in mechanical characteristics [66] and reduced galvanic corrosion. The addition of Zn, which is an important nutrient, improves the Mg alloy's ductility and deformability. In Figure (8) JDBM-1 alloy is used to create bone plates, screws, and even 3D porous structures for bone tissue, while in Figure (9) cardiovascular stents are fabricated using JDBM-2 alloy (which has excellent ductility and moderate resistance). Magnesium alloys were found to be excessively brittle, have inadequate mechanical qualities, and decay too rapidly in the first clinical studies into their potential medicinal uses. Therefore, magnesium alloys' formerly widespread usage in healthcare has all but dried up. However, technological advancements and new types of high pure Mg alloys

with superior corrosion and mechanical performance have sparked interest in biodegradable Mg-based alloys for use in medical field, as evidenced by the research conducted by Heublein et al. between 2000 and 2003 [67]. Orthopedic implants, even those not made of magnesium, are now in widespread clinical usage. Figures 10 and 11 highlight the wide range of medical uses for adsorbent metal stents (AMS) produced from materials like WE43 and modified Mg-based alloys, as well as MAGNEZIX type screws [64], [68], [69]. Although significant progress has been achieved in the development of magnesium-based biodegradable alloys in recent years, a number of basic issues need to be solved before these materials may be used in medical applications. Due to their quick deterioration and subsequent development (due to degradation) of hydrogen gas bubbles, the spectrum of medical uses of Magnesium based alloys is currently restricted [70], [71].
Ideally these metals will maintain their mechanical integrity over the necessary healing time. Analysis of metal toxicity in vitro and in vivo for biocompatibility study; enhancement of mechanical properties of metals through alloy design (compositional) and metallurgical processes; and regulation of corrosion behavior through substrate or surface modification (coating and other surface treatments) are the three main thrusts of fundamental research into bioresorbable metals. It is anticipated that the novel resorbable metals would progressively corrode in vivo, eliciting a suitable host response before dissolving entirely as the tissues recover [72]. Iron, magnesium, zinc, and their alloys make up the family of absorbable metals. Iron-based stents, according to a recent paper [73], have shown excellent long-term bio- compatible when tested on animals. There has been no thrombosis or cardiac mortality reported in human clinical trials using magnesium alloy stents, which have been ongoing for 24 months [63]. Pure zinc stents have been shown to be biocompatible and resistant to corrosion in the vasculature of rabbits [74]. Several scientific studies have been published on this topic recently, and several reviews have zeroed in on certain metals (e.g., magnesium, iron, or zinc) and their uses in cardiology and orthopedics [75]. While there are many ongoing efforts to create uniform standards for bioresorbable materials, three standards have been established that specifically address bioresorbable implants and the materials they are made of. Standard guide for evaluating absorbable stents (ASTM 2013) [76]-[79], ISO/TR 37,137: 2014: Cardiovascular biological assessment of medical devices - Guide for absorbable implants (ISO 2014a), and ISO / TS 17,137: 2014: Cardiovascular implants and extracorporeal systems (ISO 2014b). These criteria are more broad in scope, but they might be beneficial for evaluating absorbable metal installations that call for a more all-encompassing approach to bioresorbable metals. Understanding the need of developing uniform standards for evaluating the metallurgy, corrosion, and biocompatibility of bioresorbable metals, ASTM and ISO have joined forces to provide coordinated standardized recommendations [80], [81]. When these guidelines are fully implemented, they will undoubtedly speed up the development of cutting-edge technologies for producing bioresorbable metals/alloys for both clinical and commercial applications. There will be a noticeable improvement in patients' quality of life, and the immediate gains will mostly be economic. Companies like AAP Implantate AG, Abbott, Bausch & Lomb In-corporated, BIOTRONIK, Inc., Edwards Lifesciences Corp., LifeNet Health, MiMedx, Smith & Nephew Plc, and Zim- mer Biomet are among the most prominent names in the global market. Cardiovascular, dental, ortho- pedic, ophthalmological, neurological, and trauma problems are just some of the areas where bioimplants have shown promise as a treatment option. The worldwide market for metal bioimplants was valued at $78 billion in 2016, and is projected to reach $124 billion in 2023 [82]. The primary reasons of market growth include the increased incidence of orthopedic, cardiovascular, and spinal illnesses that may be addressed with bio



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implants. The increasing trend (globally) of an aging population and the rising incidence of chronic illnesses are driving forces in the expansion of the implant market [82]. Depending on the site of injury or illness. Market expansion is also influenced by raising public awareness about these problems and by the rapid scientific progress being made in the area of bio implants [2].

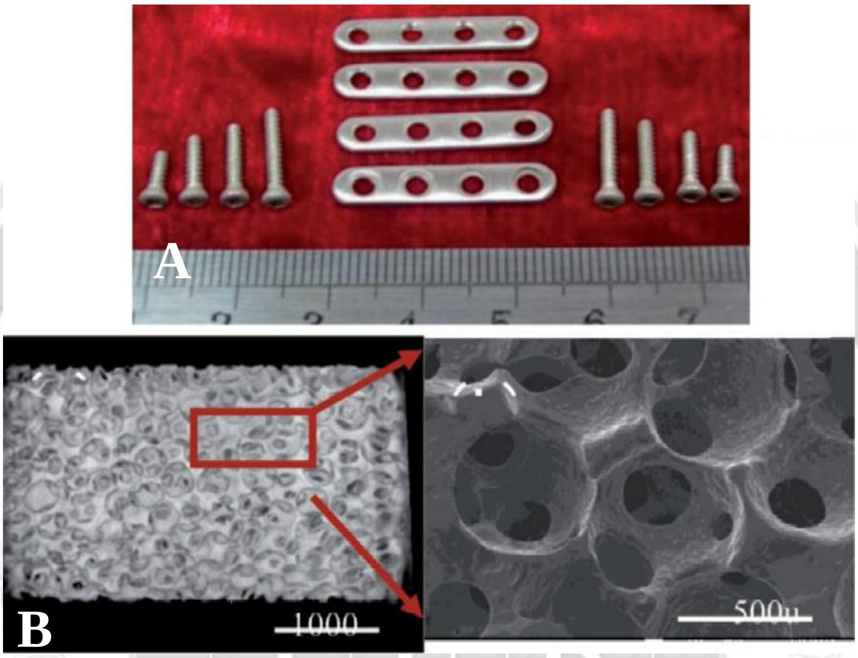


**Figure (8) JDBM-1 alloy [69].**

**A) Screws and rods. B) Porous structure)**

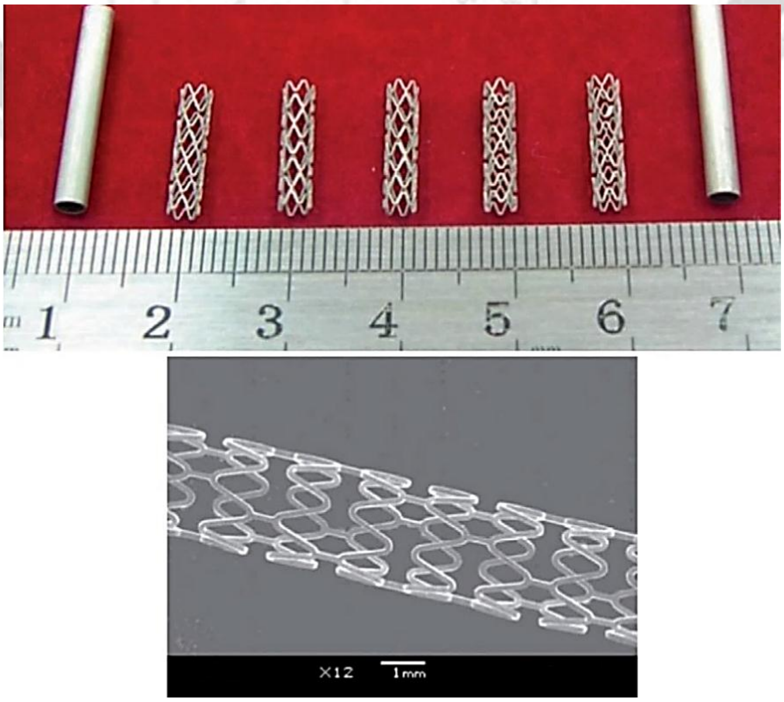


**Figure (9) Various (JDBM-2 alloy) cardiovascular stent [69]**

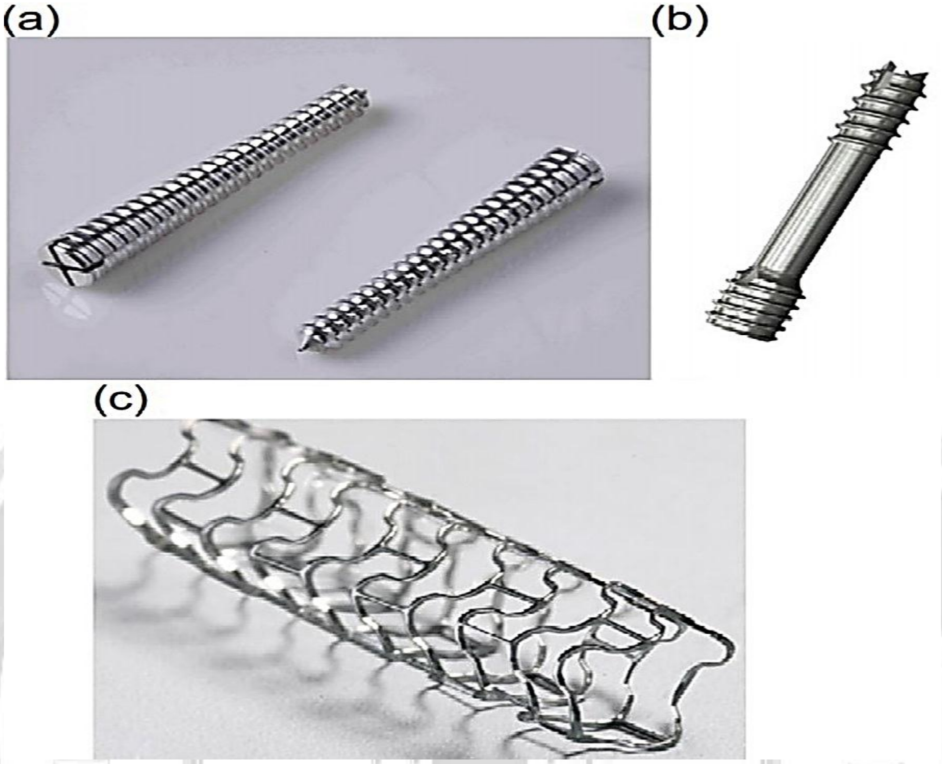


**Figure (10) Mg alloys Commercial implants:**
**(a) Orthopedic devices. (b) Screws. (c) Stent. [64].**


**Figure (11) important applications of implants made of Mg alloys**
**(a) Stents (b) Orthopedic**

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## 6. Mg biodegradable alloy requirements for implants

The materials most often used in modern biodegradable implants are resorbable polymers and bio-ceramics. However, their use as support devices is typically limited by the materials' inherent weaknesses. Magnesium, iron, and their alloys have considerable promise as biodegradable, short-term implant materials. However, the research, testing, and optimization stage are still in progress for biodegradable metals with improved mechanical characteristics, non-cytotoxicity, biocompatibility, and acceptable degrading qualities. Magnesium and its alloys are a relatively new kind of biodegradable metallic materials that are receiving increasing interest as a potential orthopedic implant material. For many different types of temporary implants, including plates and screws in orthopedics and stents in cardiovascular implant ology, biodegradable metal alloys have become more popular.

**(i)** magnesium and its alloys are easily corroded in aqueous solutions, particularly those containing chloride ions, which give them a natural biodegradation capability. Implants made from Mg alloys deteriorate more quickly in physiological settings compared to those made from Fe and its alloys.

**(ii)** Magnesium's biocompatibility is second to none in normal metabolism, the magnesium (Mg) ions ($Mg^{2+}$) produced during implantation and degradation are used.

**(iii)** Magnesium's modulus of elasticity (40-45 GPa) is closer to that of natural bone (3-20 GPa) than that of common metals like stainless steel ( 200 GPa), cobalt-based alloys (230 GPa), and titanium alloys (115 GPa), which helps to mitigate the stress-shielding effect.

**(iv)** Lighter implants are possible because the density of Mg alloys is between (1.74 and 2g/$cm^3$), making them lighter than titanium alloys (4.4-4.5g/$cm^3$) and more in line with natural bone (1.8-2.1g/$cm^3$).

Materials designed to be absorbed into the body must have physicochemical qualities that are compatible with those of the surrounding tissues. Their primary functionality has to be biocompatibility and biodegradability. Biocompatibility refers to an implant's capacity to be made of materials that will not cause a negative biological reaction in the surrounding tissue. To be biodegradable means that a substance may undergo chemical breakdown or break down into simpler substances when subjected to biological conditions. It is preferable for bone resorption and remodeling to happen concurrently when an orthopedic implant is involved. Therefore, a resorbable implant should be biodegradable, biocompatible, and bioactive.

## 6.1 Biodegradable metal the criteria of design

Biodegradable metals have distinct design requirements than permanent (inert) metal implants. The following fundamental scientific considerations must taken into account when designing metal implant materials [71]:

(i)Biosafety and biocompatibility. In the medical field, Al is not ideal, thus it is best to leave it out of the alloying process altogether.

(ii) Sufficient toughness and pliability for mechanical use. To provide an effective "life" of the implant of 90-180 days, orthopedic implant materials must have a mechanical strength value of > 200 MPa, an elongation of min. 10%, and a degradation rate of 0.5 mm/year in SBF at 37 °C. However, cardiovascular stents benefit from a combination of moderate resistance and increased ductility (> 20%).

(iii) Managed decomposition. Most reported Mg alloys are particularly vulnerable to local corrosion effects; thus, it is essential to have a uniform and predictable deterioration in order to properly anticipate the "life expectancy" of the implants.

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## 6.2 Methods for Enhancing Mechanical Performance and Decay

Casting magnesium results in a high deterioration rate and poor strength. Alloying and processing under the right circumstances may enhance properties. Self-absorbable Mg alloys should have their alloying elements chosen with degradation and biocompatibility in mind, in addition to the enhancement of mechanical qualities. Microstructure, phase distribution and particle size distribution all known to have a major impact on the corrosion behavior of Mg alloys. The mechanical characteristics, eventually, the corrosion behavior of magnesium alloys will be affected by the process of "refining" the granules, which alters the density and, correspondingly, the distribution and connectivity of the granules. Mechanical characteristics and corrosion resistance may enhanced in Mg-based alloys by refining them.

Impurities and/or second phase precipitates are often present in Mg alloys. The presence of these phases, which are cathodic with respect to the Mg matrix, may cause the anodic reaction to proceed more quickly, leading to the destruction of the $Mg(OH)_2$ protective coating. When the protective layer compromised, the surrounding solutions will permeate the porous film and accelerate the corrosion of the Mg matrix. The corrosion of an alloy will be more concentrated in areas where the larger corrosion potential is a second phase than elsewhere in the material. Uniform corrosion of the Mg alloy is very rare [83]. According to the study, uneven corrosion affects 29 out of 31 different Mg alloys [84]. Most recently a new Mg-based material (Mg3Zn1Ca15Nb) with enhanced mechanical properties and corrosion resistance obtained via the PM method, proving once again in biomedical field applications that importance absence of secondary phases [85]. Metal matrix refinement and hardening are very sensitive to processing conditions including powder metallurgy, casting, and plastic deformation procedures. Surface modification is another option for lowering and controlling the degrading behavior of Mg alloys and, by extension, increasing their biocompatibility. Many studies have demonstrated that the Mg implants in the body may greatly improved corrosion resistance by changing the surface and applying certain treatments [86]-[88].

## 6. Conclusions

Magnesium-based alloys are unquestionably the most advanced biodegradable metals due to their superb integration. There is no need to remove biodegradable implants once the mending process for a fractured bone is complete since they are absorbed by the human body. Significant monetary gains will accrue to both the public healthcare system and individual individuals. The properties of Mg alloys make them ideal for use as temporary biodegradable biomaterials in orthopedics, including their excellent biocompatibility, natural biodegradation capabilities, minuscule modulus of elasticity (like biological bone), and low weight. A lot of research is still being done to improve Mg alloys corrosion resistance for medical applications. In order to ensure compatibility and an improvement in mechanical qualities and corrosion behavior, the manufacturing process should only use pure raw materials, choose certain elements to alloying in prescribed proportions, and adhere to strict quality control standards. In addition to using effective processes like severe plastic deformation, ultra-fast solidification, and adequate heat treatment, corrosion behavior can also be influenced by treating/coating the surface of materials with biocompatible coatings with special corrosion resistant. The composition and longevity of the surface coating that develops during usage determines the susceptibility of Mg alloys to stress corrosion cracking. Specific implant manufacturing processes, such as plastic deformation, can reduce the micro-galvanic effect induced by second phases that are homogeneously and uniformly distributed in the matrix, and heat treatments can be used to determine the microstructural modifications with impact on the failure modes in Mg alloys for implants. All of these characteristics

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continue to be studied in depth for optimal medicinal applicability. In conclusion, the design criteria for the future generation of biodegradable Mg alloys must accommodate for both desired mechanical properties and tolerable corrosion behavior, while also ensuring remarkable bioactivity. When designing these biodegradable materials, it is crucial to think about how dependable they will be to use, how inexpensive they will be to produce, how easy they will be to process and sterilize, and how aesthetically pleasing they will be. A combination of academic and clinical knowledge is essential for developing useful medical applications.

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مـجلـة جـــامعة بـــابل للعلـــوم الهندسية مـجلـة جـــامعة بـــابل للعلـــوم الهندسية مـجلـة جـــامعة بـــابل للعلـــوم الهندسية

# سبائك المغنيسيوم القابلة للتحلل بيولوجيا – مراجعة عامة

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**الخلاصة**

لقد توسع سوق السبائك المستخدمة للزرع الجراحي، وخاصة تلك المصممة لزراعة العظام، بسرعة خلال العقد الماضي. حيث استفاد القطاع الطبي بشكل كبير من التقدم الكبير الذي تم تحقيقه من خلال دراسة السبائك القابلة للتحلل الحيوي القائمة على المغنيسيوم. حيث يعد البحث في هذا المجال خطوة للأمام لعدد من الأسباب، منها الرغبة في تحسين نوعية حياة الناس (محرك اجتماعي واقتصادي). من خلال تقليل الاعتماد على الغرسات المعدنية الدائمة المصنوعة من (الفولاذ المقاوم للصدأ، والسبائك القائمة على الكوبالت، وسبائك التيتانيوم)، والتي لها مجموعة عيوب خاصة بها والتي يمكن أن يكون لها تأثير سلبي على الصحة النفسية والجسدية للمرضى.

تتم مناقشة سبائك المغنيسيوم القابلة للتحلل في هذه الورقة، إلى جانب تاريخ تطورها، والميزات المهمة التي تجعلها مرغوبة لمثل هذه التطبيقات (زراعة العظام)، والميزات التي يجب تعديلها (معدل التآكل والخواص الميكانيكية) للوصول إلى المنتج الأمثل للتطبيق المقصود. ويركز على تقنيات/طرق واستراتيجيات التوصيف الكهروكيميائية لتعزيز سلوك التآكل والخصائص الميكانيكية لأنواع مختلفة من السبائك القابلة للتحلل، بالإضافة إلى الآلية والميزات المرتبطة بسلوك التآكل لسبائك المغنيسيوم .المعايير التي سيتم تصميمها، والمتطلبات التي يجب أن تلبيها لغرسات السبائك القابلة للتحلل الحيوي التي تعتمد على المغنيسيوم، والميزات المرتبطة بكفاءتها، بالإضافة إلى طرق التحسين وتأثير العناصر المضافة لصناعة تلك السبائك.

**الكلمات الدالة:** المواد القابلة للتحلل , سبائك المغنسيوم , الزرع الجراحية