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Review

Applications of Magnesium and Its Alloys: A Review

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Abstract: Magnesium is a promising material. It has a remarkable mix of mechanical and biomedical properties that has made it suitable for a vast range of applications. Moreover, with alloying, many of these inherent properties can be further improved. Today, it is primarily used in the automotive, aerospace, and medical industries. However, magnesium has its own set of drawbacks that the industry and research communities are actively addressing. Magnesium's rapid corrosion is its most significant drawback, and it dramatically impeded magnesium's growth and expansion into other applications. This article reviews both the engineering and biomedical aspects and applications for magnesium and its alloys. It will also elaborate on the challenges that the material faces and how they can be overcome and discuss its outlook.

Keywords: materials; engineering materials; biomaterials; magnesium; magnesium alloys; properties; applications



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1. Introduction

As an alkaline earth metal, magnesium is shiny and silvery-white in appearance. It is also highly reactive and never found free in nature [1,2] with terrestrial and cosmic abundance [3]. It exists as a chemical compound until Joseph Black (in 1754), with prior contributions from Friedrich Hoffman (in 1729), recognized it as an element [4]. Even though Humphry Davy discovered the first magnesium metal in 1808 [1,4–8], the first production of pure magnesium was made by Antoine-Alexander Bussy in 1828 [4,6].

Since its discovery, magnesium has played an influential role in society. In its early days, military applications and wars fueled its growth [8]. For example, magnesium was weaponized to construct incendiary bombs, flares, and ammunitions that were subsequently deployed in World War II, and it caused massive conflagrations and widespread devastations [9]. Post-War, magnesium's availability and unique blend of properties were explored and were found to be highly attractive for an extensive range of applications. Today, magnesium is used for engineering applications in automotive, aerospace, and consumer electronics. In addition, it has a role in organic chemistry and pharmaceuticals [10] and is used to construct several general-purpose applications, such as sporting goods, household products, and office equipment [8].

Furthermore, with its superior biological properties, especially its ability to biodegrade in vivo, magnesium has received accelerated interest as a promising biomaterial by both the research and industry communities [11]. As a result, the global magnesium market is forecasted to grow at a compound annual growth rate of 4.9% and reach 1.6 million metric tons (Mt) by 2027, increasing from 1.1 Mt in 2020 [12]. China alone produced 0.9 Mt in the same year, accounting for more than 80% of global production [13].

Henceforth, given its continued interest and developments, both a comprehensive state of knowledge and a primer for readers interested in the properties and applications of magnesium and its alloys are imperative. Therefore, this article aims to synthesis and present the recent progress and developments of this domain. Mainly, this article focuses on its engineering and biomedical applications. First, the article succinctly introduces

the main methods in producing magnesium. It also delves into the recent progress and developments in its production methods. Then, it presents the key considerations enabling magnesium and its alloys to be considered for engineering and biomedical purposes. Finally, an extensive discussion on the recent progress and developments surrounding its applications follows.

2. Production Techniques

There are two basic methods of producing magnesium—(a) the electrolysis of fused anhydrous magnesium chloride and (b) metallothermic reduction of magnesium oxide by ferrosilicon [14]. A typical production process using the electrolytic and thermal methods is illustrated in Figure 1.

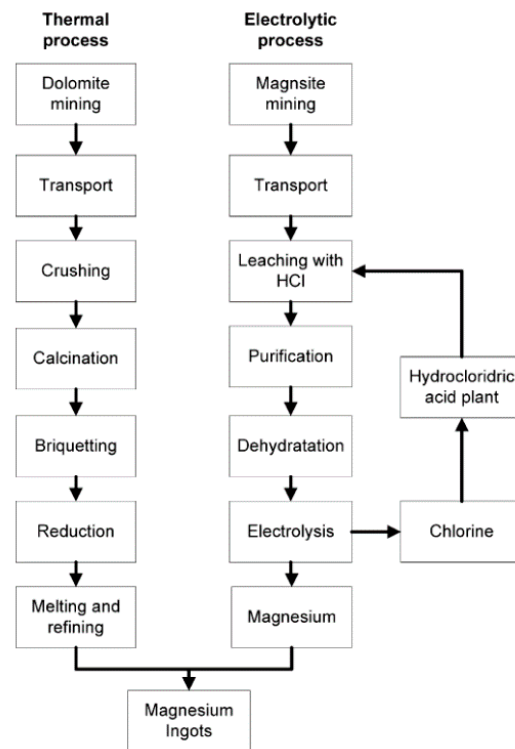


Figure 1. Process flowchart of primary magnesium production via a thermal and electrolytic process. Reproduced with permission from Cherubini, F., et al., LCA of magnesium production; published by Elsevier, 2008 [15].

Electrolysis is a two-step approach. First, it involves the hydrometallurgical preparation of the feedstock (dehydrated magnesium chloride), followed by feeding it directly through electrolytic cells [5]. Michael Faraday first discovered the core principles of producing magnesium metal with this method in 1833 [6].

In 1852, Robert Bunsen improved on Faraday’s process to achieve permanent separation of chlorine and magnesium, and that tweak in the process kickstarted the commercialization of magnesium [8]. Preventing the recombination of chlorine and magnesium was critical to Robert Bunsen’s success as anhydrous magnesium chloride is hygroscopic, which can lead to the formation of undesirable oxides and oxychlorides during direct dehydration [14]. Presently, it is still a technological challenge to produce anhydrous magnesium chloride with minimal or, ideally, no oxychlorides [16]. Bunsen’s electrolytic process is illustrated in Figure 1.

The second method of producing magnesium metal is with heat. Unlike electrolysis, intense heat in the thermal reduction process eliminates the need for an elaborate feedstock preparation [8]. The Pidgeon and Magnetherm processes are the main thermal routes. They are also batched processes [14] that use the same basic chemistry [5]. In the Pidgeon

process, dolomite and ferrosilicon are formed into briquettes with an externally heated retort to attain magnesium vapors. However, the Magnetherm process calcines a mixture of dolomite, ferrosilicon, and alumina to achieve the same by-product. The magnesium vapors obtained from both routes are then cooled and condensed separately before being extracted [5]. A typical thermal route is also illustrated in Figure 1. When the thermal reduction process was first introduced in the 1920s [16], it was touted to be the eventual replacement of electrolysis production. Today, the thermal routes, especially the Pidgeon process, are the most widely used due to their ability to produce high purity magnesium and the plethora of its raw material, dolomite [17].

2.1. Carbothermic Reduction as a New Production Technique

However, the current state-of-the-art Pidgeon process is known for its complex management and high operating cost [17]. In addition, it is notorious for consuming a massive amount of energy per production batch [18] to the extent that Ramakrishnan and Koltun estimated the global warming impact of producing magnesium metal in China to be ~60% higher than producing aluminum [19]. This led to a search for more efficient and sustainable production technologies. An identified alternative production route is a carbothermic reduction, where magnesia reacts with carbon to produce magnesium and carbon monoxide vapor.

Although this production method has had large-scale industrial trials in the mid-20th century, it has only garnered more attention in the recent decades as (a) carbon is a cheaper reductant than ferrosilicon, (b) carbon is readily available, and (c) if successful, the overall production cost is estimated to be significantly cheaper than the Pidgeon method [20]. Therefore, the condensation of magnesium vapors and its separation from carbon monoxide still presents a significant challenge.

Additionally, there is also a growing research interest in solar carbothermic reduction. Recent preliminary studies have concluded the process to consume less energy and emit less carbon dioxide at 32.3 mega-joules (MJ) of primary energy and 5.31 kg (kg) of CO₂ per kg of magnesium as compared to 181.4 MJ and 15.9 kg CO₂ in the Pidgeon process [21].

2.2. 3D Printing as a New Production Technique

Additive manufacturing, or 3D printing, is also an emerging production method for magnesium alloys. In general, there has been a growing interest in the 3D printing of metals due to its ability to customize and optimize each alloy to suit its respective applications and yield the best possible outcome. An example would be to print alloys in a more closely aligned configuration to the anatomical geometries of its patient's host tissues [22] to promote more significant cell growth, proliferation, and bone regeneration [23]. Another example would be to print alloys of complex geometries. This was previously not achievable with traditional manufacturing, and the literature has suggested these limitations to have hindered its growth [24]. Further, as opposed to conventional production methods, fabrication with additive manufacturing can also significantly reduce the technical difficulty and cost of customized production while improving its efficiency [25]. Overall, the pursuit and possibilities of additive manufacturing of magnesium alloys are very promising.

However, investigations on how magnesium alloys can be 3D printed are limited [26] as it is known to come with several challenges. Firstly, it is chemically reactive and flammable. It also has a low vaporization temperature, which increases the difficulty in mixing and printing magnesium alloys with the desired density, strength, biocompatibility, and corrosion behavior [23]. Lastly, the preparation of feedstock is also known to be dangerous as magnesium powders have a high tendency to explode [22]. Today, the two typical additive manufacturing methods to process magnesium alloys are wire arc additive manufacturing (WAAM) and selective laser melting, also known as the powder bed fusion method [26].

2.3. Secondary Magnesium Production

With the increased use of magnesium globally, more significant volumes of magnesium waste are to be expected. Fortunately, magnesium is highly recyclable, and recycling magnesium can be an additional supply source to primary production. Today, there are both flux and fluxless technologies to recycle magnesium. Recycled magnesium retains the same chemical, physical, and mechanical characteristics before it was recycled [27]. Additionally, recycling magnesium only consumes 5% of the energy needed to produce it [8]. Using secondary magnesium also reduces carbon footprint [28] and keeps the material in a circular economy.

However, magnesium alloys are only easily recyclable if their alloy composition is consistent and free of impurities [29]. This explains why most recycled magnesium comes from magnesium alloy scraps in the die-casting industry [27], which discards almost 30% of magnesium during the production process [30]. For magnesium recycling to truly take off, the industry needs to devise a recycling process that is both commercially viable and environmentally sound [29]. Presently, methods of recycling magnesium include distillation, salt-free or salt-based re-melting, solid-state recycling, and direct conversion [30].

3. Magnesium and Its Alloys as an Engineering Material

3.1. Engineering Properties

Magnesium is the lightest engineering metal. Pure magnesium has a low density of 1.74 g/cm^3 [31], and it exhibits a higher strength-to-weight ratio and better ductility and castability than aluminum and steel [32]. Compared to other metals and polymeric materials, magnesium presents no toxicity hazard [3] and performs better in thermal and electrical conductivity, vibration and shock absorption, and damping capacity [33]. Magnesium also possesses good machinability and can be shaped with any established method [3]. However, its notable weakness is in its proneness to corrosion. It corrodes quickly under two conditions: (a) when the alloy is constructed with specific metallic impurities or (b) exposure to aggressive electrolyte species. Coating technologies have since been developed and utilized to overcome this weakness, e.g., electrochemical plating, conversion coatings, and anodizing [34]. With a minimum purity of 99.8%, pure magnesium is available commercially [35], and it is suitable for most applications [14]. However, pure magnesium is ideal for metallurgical and chemical uses but not for engineering and structural purposes [31]. Therefore, it must be alloyed for engineering and structural applications to strengthen its weaker properties without sacrificing its key features [8].

Melting and casting magnesium alloys in a vacuum-assisted inert atmosphere is the preferred manufacturing method as magnesium solidifies better than other cast metals. Further, a chemically inactive environment can prevent any contamination from reactive gases [36]. Solid solution strengthening and second phase strengthening are typically used to reinforce magnesium alloys further [35]. The alloying constituents and their chemical compositions can influence the enhanced physical properties of magnesium alloys. Typically, the alloying constituents make up roughly two-thirds of a magnesium alloy. The most common and preferred alloying elements are aluminum and zinc, where aluminum most commonly forms the base of a magnesium alloy [37]. Both aluminum and zinc are economical and highly soluble in magnesium [38]. Aluminum can be used to improve the alloy's strength, hardness, and melting range while tapering its corrosiveness [2]. A range of strength and ductility can be achieved by altering the aluminum content within the alloy [37]. When used together with zinc, it can further enhance the alloy's strength at room temperature. Adding zinc, by itself, can increase alloy fluidity in casting and improves its dimensional stability [2]. When zinc, together with magnesium alloys, is mixed with impurities like nickel and iron, it can strengthen the alloy's resistance to corrosion [31]. Favored magnesium alloys with aluminum include the AZ31 and AZ91 alloys. AZ31 is widely used in the aircraft industry due to its low mass density and good mechanical properties [39]. At the same time, AZ91 alloy remains one of the most popular cast type alloys due to its high strength, excellent corrosion resistance, and good castability [40].

In addition to traditional alloying, there have been, in recent years, significant research progress in magnesium alloy-based nanocomposites, where magnesium and its alloys are further reinforced with nano-sized particles [41]. The characteristics of these magnesium alloy-based nanocomposites are influenced by both the alloying constituents and the reinforced nanoparticles [42]. This domain's heightened research interest stems from the revelation that reinforcements with nanoparticles can improve magnesium's strength and ductility without any adverse effect [41]. While there may be limited commercial applications today, this discovery has posed magnesium alloy-based nanocomposites' to be a candidate for replacing traditionally alloyed magnesium in both engineering and biomedical applications [42].

To identify magnesium alloys and their principal alloy composition, one can refer to the alphanumeric designation system established by the American Society of Testing and Materials (ASTM), as well as relevant international and European standards. More diverse combinations of magnesium and its constituents and resultant effect have been discussed at great length and summarized in ASM's 2017 book [31]. Selected mechanical properties between magnesium, AZ31, AZ91D, its common alternatives, and biological tissues are also compared in Table 1 below. Compared with its common alternatives, magnesium's low density was the main reason this metallic material garnered interest in its early days. Presently, engineering applications for magnesium are still primarily found in the aerospace and automotive industries.

Table 1. Selected Mechanical Properties.

Materials	Density (g cm ³)	Compressive Strength (MPa)	Tensile Strength (MPa)	Elastic Modulus (GPa)	Reference
<i>Magnesium</i>					
Pure Magnesium	1.74	20–115	90–190	45	[43]
AZ31 Alloy (Extruded)	1.78	83–97	241–260	45	[43]
AZ91D Alloy (Die Cast)	1.81	160	230	45	[43]
<i>Alternative Metals</i>					
Aluminum Alloys	2.7	-	170–560	70	[44,45]
Stainless Steel	7.9–8.1	-	480–620	189–205	[43,46]
Cobalt-Chrome Alloys	7.8–9.2	-	450–960	195–230	[43,46]
Titanium Alloys	4.4–4.5	-	550–985	100–125	[43,46]
<i>Biological Tissues</i>					
Arterial Wall	-	-	0.5–1.72	0.001	[43,47]
Skin	-	-	2.5–16	0.006–0.04	[47]
Cancellous Bone	1–1.4	1.5–9.3	1.5–38	0.01–1.57	[43,47]
Cortical Bone	1.8–2	160 Transverse 240 Longitudinal	35 Transverse 283 Longitudinal	5–23	[43,47,48]

3.2. Engineering Applications

3.2.1. Aerospace Applications

As we briefly discussed, early applications for magnesium include fabricating incendiary bombs, pyrotechnics, and flash for photography [6]. These military applications led magnesium to play a considerable role in World War I and World War II. In World War II, magnesium was also used to construct military aircraft and its components [49]. That paved magnesium's entry into the civil aerospace industry as there are considerable environmental and economic benefits of using magnesium in constructing aircraft. Firstly, magnesium's excellent castability, machinability, and ductility make it advantageous over other conventional metallic materials. More importantly, using a lighter metal like magnesium in place of heavier metals can improve the aircraft's fuel efficiency and reduce emissions. This translates to savings on fuel and a lower operational cost. To illustrate the savings potential, we can use a standard Boeing 747 passenger model as an example.

By substituting all aluminum alloys with magnesium alloys, the aircraft could attain an overall weight reduction of ~60.4 tonnes (t) or 28% of its “operating empty weight” [50]. The potential benefits of using magnesium in the aerospace industry led to several experiments throughout history where aircraft were constructed entirely with magnesium or magnesium as the base material. Notable examples include the military aircrafts Northrop XP-56, Lockheed F-80, Convair B-36, and Convair XC 99 [51].

Through these experiments, the inherent limitations and critical aspects exhibited from the use of magnesium alloys emerged. It predominantly includes implications arising from its flammability, surface durability, and corrosion resistance. This led to restrictions imposed by various authorities, and consequently, these enactments significantly dented the prospects of magnesium in modern aviation.

Presently, with advancements in magnesium research, it is possible to manage these prevailing concerns with maintenance and repairs. However, performing these servicing activities will inevitably drive up its total cost of ownership [51]. Thus, despite significant improvements since the restrictions were first imposed, magnesium is still found mainly in engine- and transmission-related castings and landing gears only and not in external or structural applications [52]. The same is true for helicopters. Today, aluminum and its alloys are still highly favored over magnesium and its alloys for aerospace structures.

However, that is set to change with more significant advancements in applied magnesium research, such as its material development and novel manufacturing technologies. After all, if its drawbacks can be mitigated, magnesium’s intrinsic material properties will make it ideal for the aerospace industry. For example, recent progress in applied magnesium research focused on addressing its ignition and flammability issues. These efforts cumulated to the discovery of less-flammable magnesium alloys, which opened the possibilities for them to be incorporated in passenger cabins. Accordingly, the Society of Automotive Engineers revised its standards, specifically AS8049C, in 2015 to allow magnesium alloys for aircraft seat construction if it complies with the Federal Aviation Administration requirements [24,51]. Another area with significant progress addresses magnesium’s meager mechanical strength for engineering applications. Progress in this area is driven by the potential benefits of using magnesium in weight-sensitive applications, such as aircraft [51]. As a result, it led to the introduction of high-performance magnesium alloys like the Elektron 21, which has already received an Aerospace Material Specification (AMS 4429), and Elektron 675, which is reported to exhibit twice the strength of aluminum while only bearing half the weight of titanium [53].

3.2.2. Automotive Applications

The earliest automotive applications of magnesium and its alloys can be traced back to 1918, where magnesium-based racing engine pistons for the Indy 500 were introduced [52]. However, it was not until the 1930s when Volkswagen outfitted a magnesium-based engine block for its Beetle series that set off a widespread adoption of magnesium in the automotive industry [8]. Since then, magnesium has been used for various powertrain, chassis, and body structure applications. Today, magnesium remains the third most used metallic material in the automotive industry [10]. Figure 2 provides a pictorial summary of the contemporary automobile components constructed with magnesium and its alloys.

In many ways, the growth story of magnesium applications for the automotive industry is similar to the aerospace industry. Firstly, due to its inherent limitations, it is mainly adopted for its “in-use” benefits. Hence, despite having many automotive applications, its overall share of metallic materials in the automotive industry remains minuscule compared to steel and aluminum [10]. However, given the industry’s increased pressure by authorities and the wider community to reduce its emissions and pursue a more sustainable pattern of growth, magnesium has increasingly garnered attention for its potential to reduce the vehicle’s weight, provide energy savings, and limit environmental impact without compromising its overall strength and functions [32]. This fueled industry and research interest in magnesium. It also contributed to a surge in its adoption in the automotive

industry even though it comes with a higher price point than other conventional metallic materials.

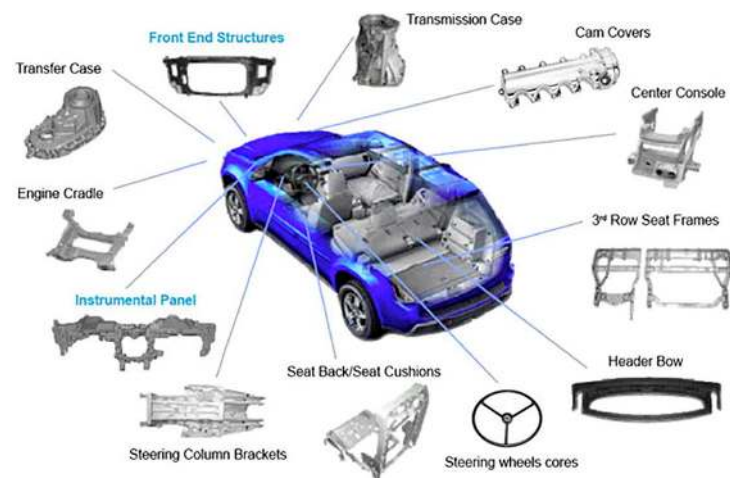


Figure 2. Use of magnesium-based materials in the automotive industry. Reproduced with permission from Sankaranarayanan, S. and M. Gupta (2021). “Emergence of god’s favorite metallic element: Magnesium based materials for engineering and biomedical applications.”; published by Elsevier, 2021 [54].

Presently, cast magnesium alloys remain the most used type for automotive applications due to their excellent characteristics. In addition, there have also been progress and several developments in casting fill and solidification, which enabled the production of a broader and higher quality range of cast products. Cast magnesium alloy applications include instrument panel structures, cross-car beams, roof frames, seat frames, and more. Noticeably, they tend to be located in automobiles’ front and top portions, where weight reduction is essential [10]. The dominant types of cast magnesium alloys in the automotive industry include the Mg-Al-based alloy series, such as the AZ and AM alloys; Mg-rare earth-based alloys, e.g., WE43 and E21; and ZK alloys.

Furthermore, for applications requiring elevated temperatures, high-strength magnesium alloys and alloy nanocomposites can be considered as they possess superior thermal and dimensional stabilities [55]. However, apart from cast magnesium alloys, other types of magnesium and its alloys—e.g., sheet magnesium and extruded magnesium—seemed to have limited to no reported applications in the modern automotive industry. Several materials, processes, and performance challenges plaguing magnesium need to be resolved to drive greater magnesium uptake in the automotive industry [10].

4. Magnesium and Its Alloys as a Biomaterial

As we reiterate, magnesium’s heightened interest and possibilities have encouraged more research to discover more efficient ways of producing magnesium metal and its alloys for new and extended applications [8]. Beyond engineering applications, magnesium, by itself or as an alloy, is also primarily used in the health and biomedical industry [31].

The earliest medical use for magnesium can be traced back to 1695 when Nehemiah Grew extracted naturally occurring magnesium sulfate from a spring in Epsom town of southern England [6]. In 1878, Edward C. Huse used magnesium wires as blood vessel ligatures [4], and this was the first reported use of magnesium metal for medical purposes. Since then, several notable experiments have been conducted to assess magnesium’s suitability as a biomaterial.

Erwin Payr was one such influential pioneer who extended magnesium’s prospects as a biomaterial into various surgical areas and further hypothesized the factors leading to magnesium’s corrosion in vivo [7]. Another early pioneer is Albin Lambotte and his assistant, Jean Verbrugge, who further extended it to orthopedic applications and concluded

that magnesium implants are not toxic or irritant [56]. Other early experimental application also includes fabricating tubes, plates, wires, sheets, and screws out of pure magnesium, and they were tested on both humans and animals [7].

The first use of magnesium alloys in the medical field was reported much later, in 1948, by Troitskii and Tsitrin using magnesium cadmium to treat cases of pseudarthrosis [56]. Following Troitskii and Tsitrin's experimental application, there have been no reported clinical studies of magnesium-based orthopedic implants [57], while other clinical studies were conducted on a small scale [56]. An extensive review of magnesium's rich history as a biomaterial has been documented by Frank Witte [7].

4.1. Biological Competencies

There is growing literature on magnesium and its alloys as a biomaterial, especially as a temporary implant. The strong interest stems from magnesium's remarkable engineering properties and its natural occurrence in the human body. Magnesium is the second most abundant and essential intracellular cation [6]. It is an essential mineral that supports physiological functions in the human body, including the structural stabilization of proteins, nucleic acids, cell membranes, and the promotion of specific structural or catalytic activities of proteins, enzymes, or ribozymes [1]. Moreover, magnesium is also non-toxic and non-irritant. It promotes tissue healing in the human body and can be excreted through urine or feces [57]. Magnesium is also primarily found inside cells or bones, where it is known to support osteoinductivity [4]. Hence, with these factors combined, magnesium is naturally biocompatible to the human body.

Magnesium's greatest strength lies beyond biocompatibility. It excels in biodegradability and bioabsorbability [46]. It is also bioresorbable and a bioactive material [4]. Often, the body only requires the temporary presence of an implant or device [33] to support its tissue regeneration and restoration of impaired physical functions [58]. However, if the implant is not removed promptly, it may lead to undesirable responses like chronic physical irritation and inflammatory response, or worse, introduce biotoxicity [59].

When evaluating for use as a temporary implant, biodegradability is of the utmost importance. Ideally, the implant should biodegrade and completely dematerialize after the tissue has been fully recovered. As the host tissue gradually heals and recovers its load-bearing capacity and mechanical integrity, the strength and stiffness of the implant should degrade at an inversely proportionate rate [59]. Therefore, the closer the host tissue is to a complete recovery, the lesser degree of support and reliance it should receive from an implant, which corresponds to the gradually reduced presence of the implant. This inverse relationship is illustrated in Figure 3.

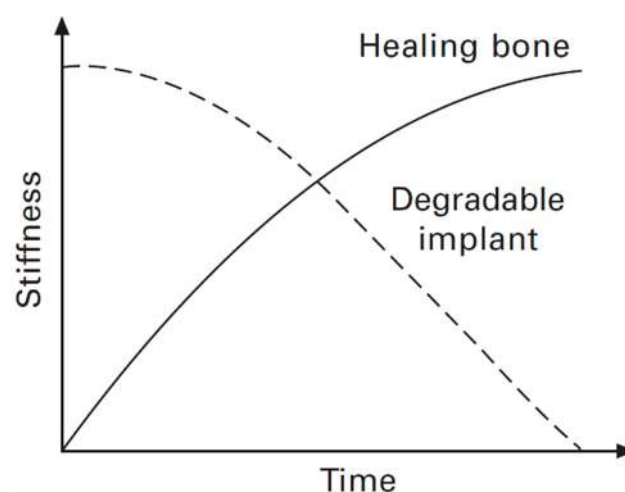


Figure 3. A Stiffness–Time inverse relationship between degradable implants and healing bone. Reproduced with permission from Witte, F., et al., Magnesium (Mg) corrosion: a challenging concept for degradable implants; published by Woodhead Publishing, 2011 [60].

Additionally, the biodegradation process should also occur without any adverse effects on the human body. Unlike traditional metallic implant materials, such as stainless steel, cobalt-chromium alloys, and titanium alloys, which are bio-inert, magnesium is biodegradable and bioabsorbable. This eliminates the need for follow-up surgery to remove the implant after the impaired physical functions have been restored [46].

4.2. Mechanical Functionality

As previously discussed, magnesium has outstanding engineering and mechanical properties, especially its lightweight and density. However, as a biomaterial, and in comparison with its bio-inert counterparts, magnesium possesses several mechanical limitations, which impeded its widespread adoption. Metallic implants are preferred over other biomaterials (such as ceramics or polymers) for their superior load-bearing capabilities, corrosion behavior, and fracture toughness [59]. However, magnesium exhibits weaker abilities in the above areas despite being a metallic implant material, limiting its biomaterial applications [58].

Nonetheless, magnesium alloys have a lower elastic modulus than their bio-inert counterparts (refer to Table 1), which is advantageous as a biomaterial. A higher elastic modulus is directly proportionate to the increasing stiffness of the materials, and an overly stiff implant can cause stress shielding, which hinders the healing process. It may even lead to bone loss and possibly a secondary bone fracture [57,59]. Therefore, as magnesium's elastic modulus is closer to the stiffness of natural bone, it is preferred [59].

4.3. Corrosion

Corrosion is a form of biodegradation. Magnesium's ability to biodegrade is its greatest strength, while the speed at which it degrades is its greatest weakness. Magnesium degrades rapidly in a physiological environment. Such accelerated degradation can compromise the mechanical integrity and strength of its respective applications. Besides, it can result in possible deleterious and consequences [4], such as premature failure of the implant [46], interference with the healing process, and in extreme cases, death [61].

With limited research and technologies in its early days, surgeons faced great difficulties managing magnesium corrosion in vivo. As such, they preferred the use of corrosion-resistant V2A steel in place of magnesium, and that waned interest in magnesium as a prospective biomaterial [7]. Despite significant advances today, managing magnesium corrosion is still a major technological challenge [61].

The types of magnesium corrosion can be classified into general/uniform or localized. Predominately, magnesium can be exposed to galvanic corrosion, pitting corrosion, filiform corrosion, intergranular corrosion (IGC), exfoliation corrosion (EFC), crevice corrosion, stress corrosion cracking (SCC), corrosion fatigue (CF), and erosion-corrosion [62].

Magnesium corrosion in vivo accelerates in the presence of chloride ions, which can be found in human body fluid or blood plasma [63]. Magnesium corrodes in an aqueous environment via an electrochemical reaction to produce hydroxide and hydrogen gas [60]. The produced hydroxide layer quickly gets converted away into highly soluble magnesium chloride, and this reinforcing process loop hastens the rate of magnesium's corrosion [61].

Extensive literature has identified magnesium's rapid degradation to contribute to hydrogen evolution and alkalization [33]. Hydrogen evolution refers to the production of subcutaneous hydrogen bubbles adjacent to the implants [63]. The rate at which these hydrogen bubbles are produced is directly correlated to the corrosion rate of magnesium [64]. When hydrogen is produced faster than absorbed, it will create a balloon effect [33], which can tear and destroy the tissues and their layers as it gets separated. The destruction of tissues can delay the healing process, and in extreme cases, it can be fatal if the balloon hydrogen bubbles get too large and disrupt the bloodstream [63].

Local alkalization around a rapidly corroding magnesium implant is also a primary medical concern. While the human body can manage slight fluctuations in pH level, a greater alkaline concentration can create an adverse physiological reaction. For exam-

ple, if the *in vivo* pH value of the localized region exceeds 7.8, it can lead to alkaline poisoning [63].

A review of the literature suggests three key strategies to overcome magnesium's corrosive behaviors. They are purification, alloying, and surface modification. These strategies employ the same principle of slowing the biodegradation process. By incorporating them, it can reduce the speed of hydrogen accumulation and localized alkalization. It will also provide room for the human body to adjust and deal with the magnesium implants [63]. However, while purifying magnesium is an option to reduce its corrosion rate materially, it will produce a pure magnesium metal with several mechanical limitations, as discussed above, and render it unsuitable for most medical applications [59].

Instead, similar to how pure magnesium is alloyed for engineering and structural applications, alloying is widely used to improve magnesium's mechanical and corrosive performance as a biomaterial. Many variables can affect the alloy's mechanical and corrosive performance and its implications to the human body [63]. These variables include the alloying elements, their level of purity, their microstructure, and how the materials are processed and alloyed [4,64]. Therefore, a careful and holistic assessment of the alloying element is critical. It must be biocompatible, not known to produce any biotoxins or avoidable inflammatory response, and optimized for its respective biomedical applications [33,42,59]. Aluminum (Al), calcium (Ca), zinc (Zn), zirconium (Zr), and strontium (Sr) are commonly used as alloying elements [56]. Rare earth elements, such as yttrium (Y), gadolinium (Gd), lanthanum (La), and dysprosium (Dy), are also considered even though their biocompatibility remains a question [4].

Presently, alloying, by itself, seems to be limited in clinical practice as its ability to improve corrosion resistance is insignificant [65]. However, modifying the surface with a coating layer effectively controls the initial degradation of magnesium and its alloys [66]. Compared to alloying, surface modification can retain the material's critical properties while achieving enhanced corrosion resistance and biocompatibility [67].

Taking a step further, current trends suggest combining both methods (coating on alloys) to be widely accepted and adopted. Similar to alloying, the applied coating should be optimized to its substrate and its intended biomedical purpose. Surface modification methods include micro-arc oxidation (MAO), chemical transformation, electrodeposition, and biomimetic deposition [65]. The main types of coating include polymeric coatings, calcium-phosphate coatings, and graphene coatings [46]. For an in-depth discussion on surface modifications for magnesium and its alloys, one can refer to publications by Mousa et al. [66] and Zeng et al. [62].

4.4. Anti-Microbial Strategies

As all medical devices are subjected to microbial colonization and infection [68], effective prevention of bacterial infection is a top priority. Failure to do so can compromise the efficacy of the implant and, in some cases, result in infection persistence, implant failure, and even death of the patients [69]. When an infection occurs, additional surgery and repair of the implant are needed, which adds to the patient's medical burden. Bacterial biofilms are estimated to cause two-thirds of human bacterial infections. Essentially, it is a densely packed community of microbial cells that are challenging to eradicate when formed. Furthermore, their resistance to the immune system and antibiotics has been observed [68]. As such, antibiotic-loaded biomaterials and, more recently, stimulus-responsive biomaterials have also been developed to intensify the bacteria-killing process before it attaches to the implant surface [69].

Magnesium's rapid corrosive behavior is a blessing in disguise. Its rapid corrosion increases the concentration of magnesium ions locally, which alters the pH value and prohibits bacterial activities *in vivo* [70]. Though recent studies have further confirmed the significant antibacterial effect of magnesium ions on *Staphylococcus epidermidis* and *Escherichia coli* (*E. coli*) [71], it is essential to note that with biofilms, bacteria can withstand external pH alterations and continue infecting the tissues [68].

Magnesium, by itself, cannot attain excellent antibacterial performance. Therefore, novel magnesium alloys (with alloying elements that possess antibacterial, such as silver, copper, zinc, and gallium) and antibacterial coatings are developed [68].

4.5. Biomedical Applications

Magnesium may not be the perfect biomaterial, but the compromise between its merits and weaknesses has paved the way for specific medical applications. Presently, magnesium and its alloys are widely used for musculoskeletal and orthopedic applications. It is also extensively investigated for cardiovascular applications, and it can also be found in general and oral applications. Musculoskeletal and orthopedic applications will be the focus of this section. We will also briefly discuss the state of magnesium and its alloys in cardiovascular applications.

4.5.1. Musculoskeletal and Orthopedic Applications

Autografting is the yardstick of contemporary bone repair materials. It contains the necessary elements to stimulate new bone growth. However, it is resource-scarce, and it requires secondary surgeries to remove the implant after the impaired physical functions have been restored [72]. As previously discussed in Section 4.1, the need for secondary surgeries is also a challenge faced by bio-inert metallic implants, in addition to stress shielding [46].

Hence, the medical community has been actively seeking prospective implant solutions that are biocompatible, biodegradable, and exhibit similar characteristics to the human bone. Novel biomaterials like biodegradable polymers have been investigated for their suitability as they also share properties similar to materials found in the human body [61]. However, biodegradable polymers possess inferior mechanical strength and brittleness to magnesium and its alloys, resulting in surgery failure when employed in load-bearing applications [57]. Further, employing biodegradable polymers is also observed to induce long-term inflammatory responses in peri-implant tissue and discourage osseous ingrowth [57,73]. Hence, except for its rapid corrosive behavior, magnesium remains a more promising biomaterial than biodegradable polymers for bone substitution and scaffolding of bone tissue [56]. Notably, magnesium-based orthopedic implants positively affect the regeneration of new blood vessels and bone tissue. Others could not achieve this feat and, thus, may provide magnesium-based orthopedic implants with an edge over the rest, especially when dealing with challenging bone conditions [73].

Present clinical applications of magnesium-based orthopedic implants remain relatively nascent and sparse. Notable implants in recent years include the MAGNEZIX[®] (Syntellix AG, Hanover, Germany) MgYREZr alloy bioabsorbable compression screw and the K-MET[™] (U&i Corporation, Seoul, Korea) MgCaZn alloy bioresorbable bone screw, and both demonstrated positive clinical results in several case applications. For example, the use of MAGNEZIX[®] MgYREZr alloy screw for osteochondral fracture fixation at the humeral capitulum is reported to be clinically and radiologically uneventful as the degradation of the magnesium alloy did not hinder the healing process [74]. Another case trial (Figure 4A) uses MAGNEZIX[®], and a similar specification titanium alloy—the incumbent choice—for hallux valgus surgery in 13 patients reported comparable pain assessment and range of motion scores of the first metatarsophalangeal joint [73]. Following these positive results, MAGNEZIX[®] was accepted for clinical use by the medical community, and its availability proliferated in more than 50 nations. Today, it is explicitly recommended for intra- and extra-articular fractures, nonunions, bone fusion, bunionectomies, and osteotomies treatments. Its average price is reported to be ~20% higher than comparable titanium implants [74,75]. Similarly, for K-MET[™], long term studies were conducted, and favorable results were reported. In a clinical study of 53 cases, K-MET[™] alloy screws were observed to support early bone healing, leading to the growth of a new bone capable of replacing the K-MET[™] implant entirely within a year of its implantation (Figure 4B) [76].

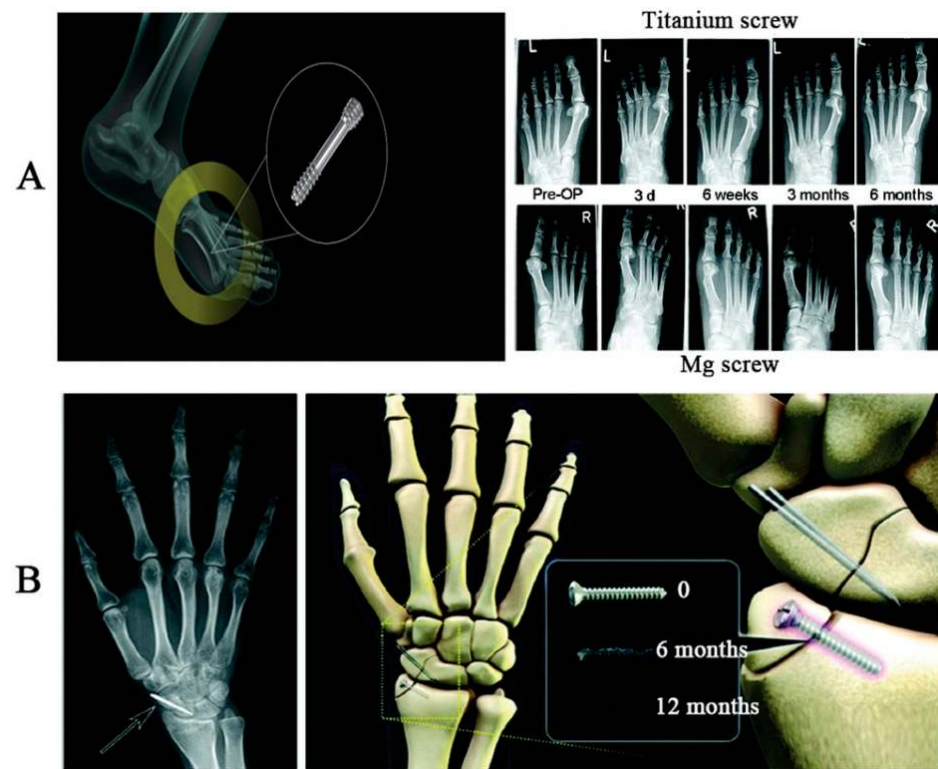


Figure 4. Examples of magnesium applications in orthopedics. (A) Use of MAGNEZIX[®] MgYREZr alloy bioabsorbable compression screw to treat hallux valgus fracture in 13 patients. Reproduced with permission from Wang, J.L., et al. (2020). “Biodegradable Magnesium-Based Implants in Orthopedics—A General Review and Perspectives.”; published by Wiley, 2020 [73]; (B) Use of K-MET[™] MgCaZn alloy bioresorbable bone screw to treat distal radius fracture in 53 patients. Reproduced with permission from Lee, J.-W., et al. (2016). “Long-term clinical study and multiscale analysis of in vivo biodegradation mechanism of Mg alloy.”; Copyright 2016, National Academy of Sciences [76].

Recent developments further include the exploration of using ultra high-purity magnesium orthopedic internal fixation implant to treat avascular necrosis of the femoral head in China [73], using magnesium-based implants to treat facial fractures in Singapore [77], and the first clinical trial to investigate the effects of a coated magnesium implant [78].

In summary, while there has been an initial loss of interest in using magnesium as a biomaterial from the medical community, in part due to its corrosive behavior, interest for clinical applications has since renewed in the recent decade. There have been momentous research and technological advancements in metallurgy that made fabricating magnesium and its alloys with better mechanical and corrosive performance possible. With sustained interest and efforts to continuously improve its properties for clinical use, magnesium and its alloys will be highly desirable as an orthopedic biomaterial. Eventually, it may be an ideal replacement to bio-inert metallic implants in typical musculoskeletal and orthopedic applications like bone substitutes, fixatives, and stabilization devices for fractured bones, ligament and tendon repair, and total hip arthroplasty [57].

4.5.2. Cardiovascular Applications

Presently, there are limited applications for magnesium and its alloys in cardiovascular medicine, as they are primarily experimental or preclinical [79]. Magnesium and its alloys are being investigated for their suitability to replace bio-inert metallic implants in typical cardiovascular therapeutic applications. These include prosthesis implantation and stent insertions, such as artificial valves, stents, pacemaker cases, and stent-grafts [80].

As with any medical application, metallic implants are preferred over ceramics and synthetic polymers for their biocompatibility and superior mechanical properties [81]. Similar to musculoskeletal and orthopedic applications, its ability to biodegrade is critical. It can reduce the need for risky and expensive surgical operations to remove or replace the metal at each stage of the patient's recovery. Specific to cardiovascular medicine, it will reduce the likelihood of thrombogenesis, restenosis, endothelial dysfunction, and other clinical complications [80,81].

However, bare magnesium alloy stents are notorious for rapid corrosion or biodegradation, leading to devastating effects described in Section 4.3. Hence, as magnesium-based biodegradable coronary stent implantation is highly regarded as a potential therapeutic application to coronary heart disease, one of the leading causes of death globally [79–81], extensive ongoing investigations centered around strategies to control its degradation rate [82,83]. The strategies proposed are consistent with our earlier discussion in Section 4.3. It includes improving the design of the alloy and modifying the surface with coating technologies. Thus far, the literature has suggested that incorporation of both strategies would work [82], although early in vivo trials have demonstrated mixed clinical outcomes [81]. Nonetheless, more research and advancements in this direction will likely persist in the coming years. Technological breakthroughs are critical for magnesium-based cardiovascular applications to be widely adopted for clinical uses.

5. Conclusions

Magnesium's availability and unique blend of properties has made it very attractive for engineering and biomedical applications. Furthermore, alloying magnesium can modify or enhance its existing properties to make it suitable for even more applications. As an engineering material, magnesium's notable characteristics include its lightweight, specific high strength to weight ratio, and superior machinability and castability. These factors enabled magnesium to find its footing in aerospace and automotive applications, where the industry is actively seeking lighter-weight alternatives to harness additional environmental and economic benefits. As a biomaterial, magnesium's notable characteristics include its biocompatibility, biodegradability, and bioabsorbability on top of the engineering properties. In addition, it also includes its elastic modulus and innate anti-microbial mechanisms. Hence, magnesium is mainly used in musculoskeletal and orthopedic applications while extensively being investigated for cardiovascular medicine.

While its ability to biodegrade is celebrated, the rate at which it biodegrades is problematic. It biodegrades rapidly, and as a result, this impeded magnesium's widespread adoption in both engineering and biomedical applications. Nonetheless, with the ongoing research progress and technological advancements, the mitigation strategies to overcome magnesium's overly rapid degradation are widely investigated.

Magnesium is a promising material, and market research has demonstrated its projected increased demand. However, today's primary magnesium is energy-intensive and inefficient to produce, which inspired research in additive manufacturing of magnesium alloys and using solar energy to perform the carbothermic reduction. Recycling magnesium is also an option to keep the supply circular, and there are ongoing investigations to determine the most commercially viable and environmentally sound recycling process.

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