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REVIEW

Advances in Biodegradable Orthopaedic Implants: Optimizing Magnesium Alloy Corrosion Resistance for Enhanced Bone Repair

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Abstract

Biomaterials revolutionize medicine, enabling cutting-edge applications like anchoring devices, substitutes, and advanced surgical equipment. Bio-implants are intended to sustain a damaged biological structure, substitute for an absent biological structure, or augment an extant biological structure. Utilized bioimplants can be classified as ceramics, metals, or polymers. Among the different types of implant materials, many are designed to remain permanently in the body, despite their temporary function. Biodegradable implants are particularly advantageous because they dissolve and are absorbed during the healing process. This invention spares patients from additional surgeries, reduces immobility, and cuts medical costs. In particular, biodegradable implants have improved orthopaedic surgical results, reduced complications, and promoted natural bone repair. With its outstanding biocompatibility and biodegradability, magnesium (Mg) stands out as a promising biodegradable orthopaedic implant. Its mechanical properties mimic natural bone, which helps to prevent stress shielding and enhances osteoblast attachment. Despite these advantages, the rapid degradation of magnesium poses challenges for sustained bone growth. Therefore, improving magnesium's corrosion resistance is crucial for its effective use in bone production. Mg-based metallic glasses, which are stronger, more elastic, and highly corrosion-resistant than crystalline materials, are being considered as biodegradable implant materials. The chemical homogeneousness, absence of secondary phases, and lack of grain boundaries in Mg metallic glasses reduce the formation of Mg^{2+} ions, H_2 bubbles, and OH^- ions. Successful implantation of tacks, screws, and other orthopaedic implants needs Mg metallic glasses to be a few centimetres thick. However, maximum-diameter glasses require a high glass-forming alloy. Thus, for Mg alloys to readily become glassy and larger in diameter, the composition of these glasses must be understood. This study explores current research, strategies, and technological advancements in biodegradable orthopaedic implants, with a particular focus on the performance of Mg. Furthermore, it provides an in-depth analysis of magnesium alloys' corrosion behaviour and discusses solutions to reduce their corrosion rate.

Keywords Biomaterial · Implant · Magnesium · Corrosion · Orthopaedics

Introduction

Biomaterials are substances that are surgically implanted or incorporated into living tissue [1]. They must have suitable physical, chemical, and mechanical characteristics to maintain structural integrity while avoiding any adverse effects on the patient [2]. Further critical attributes of biomaterials include fatigue resistance, mechanical strength, density, suitability for fabrication and storage, and appropriate patterning [3, 4]. Biomaterials have been utilized historically for more than four millennia; for instance, the Romans and Egyptians employed linen sutures, iron, gold, and wood for dental procedures and toe replacement, respectively. Nevertheless, during that era, their understanding of corrosion-related matters was relatively restricted. In biomaterial applications, materials such as teflon, nylon, silicone, stainless steel, and titanium rose to prominence after World War II [1]. Biomaterials are utilized in various medical contexts, including replacements, fixation devices, and surgical instruments. Hence, biomaterials have been instrumental in the development of substantial enhancements to surgical procedures, diagnostic instruments, and bioimplants.

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Bioimplants represent a significant application of biomaterials because they serve a vital function in substituting or reinforcing biological structures that are absent or impaired [5]. The applications of the various bioimplant materials are detailed in Table 1. Within the ever-evolving domain of bioimplants, current investigations are delving into state-of-the-art substances customized for particular medical fields. To achieve successful implantation, a multitude of factors must be considered. The most important of these is biocompatibility, which verifies that the implant lacks teratogenicity, immunogenicity, carcinogenicity, and toxicity and prevents adverse biological reactions. Prospective bioimplants such as advanced polymers, bioactive ceramics, biodegradable metals, and smart materials are demonstrating enhanced properties and performance across a range of medical applications.

Common bioimplants encompass orthopaedic, cardiovascular, neural, reconstructive, dental, ophthalmic, and general surgical applications [6]. Despite their temporary functionality, many of the bioimplants in use are engineered to remain in the body permanently because bioimplant removal necessitates an operation, which raises the patient's discomfort and expenditure. Though these bioimplants are biocompatible, they are not without their share of complications, including allergy and sensitization. Biodegradable implant materials can resolve these complications by undergoing suitable decomposition within the body. The body will dissolve and absorb a biodegradable implant once the healing process is fully concluded. Nevertheless, it is imperious that both the biodegradable implant and its degradation residues do not possess toxic properties [4]. Hence, by eliminating the need for an additional surgical procedure, a biodegradable implant reduces costs and facilitates the patient's mobility.

Although biodegradable implants are utilized in a multitude of medical domains, their significance in orthopaedics is emphasized due to several factors. Orthopaedic implants frequently support weight-bearing structures, including joints and bones. Biodegradable implants, by progressively degrading with the regeneration of bone, reduce the prospect of complications, including stress shielding, implant loosening, and fracture, in contrast to conventional implants. Additionally, orthopaedic research is constantly seeking novel fabrication techniques and biomaterials to enhance the efficacy and biocompatibility of biodegradable implants. Innovative advancements in materials science, tissue engineering, and additive manufacturing technologies are propelled by biodegradable implants, which are currently leading the way in orthopaedic treatment outcomes [9].

Recently, a novel category of biodegradable materials known as biodegradable metals (BMs) has surfaced as a viable substitute for conventional orthopaedic implants. After aiding in the healing of tissues, biodegradable metals typically undergo gradual corrosion in vivo, and prompted by the release of by-products, biodegradable metals typically trigger a host response before completely dissolving [10]. Magnesium, being one of the limited numbers of

Table 1 Bioimplant materials and their applications [7, 8]

Categories of implantable materials			Composition	Use
Ceramics			Hydroxyapatite, Phosphate tricalcium	Small cellular defects reconstruction, Small bone defect reconstruction
Polymers	Carbon based polymers		Gore-Tex (PTFE expanded), Poly-propylene (Marlex, Prolene), Poly-ethylene (Medpore), Poly-ethylene tereftalato (Dacron, Mersilene), Poliuretano, Polyesters aliphatic (ac. Poly-latic, poly-glycolic ecc.), Metil-metacrilato (MMA)	Thoracic and abdomen rebuilding Filling Defect of the soft tissue Cranio-facial reconstruction, Surgical Suture Vascular prosthesis, Coating of breast implants, Absorbable mini plates and screws
	Non carbon polymers		Silicon	Breast implants Prosthetics for increased facial characteristics
Composites			Fibre reinforced polymers	Hipjoint arthoplasty, bone cements
Metals		Permanent metal implants	316L stainless steel, Co–Cr–Mo, Cr–Ni–Cr–Mo, CP–Ti, Ti–Al–V, Ti–Al–Nb, Ti–13Nb–13Zr, Ti–Mo–Zr–Fe, Ti–Ni	Fracture fixation, stents, surgical instruments, dental implants, dental restorations, heart valves, pacemaker encapsulation, bone and joint replacement, fracture fixation, bone plates, orthodontic wires
		Biodegradable implants	Magnesium alloys	Mini plates, screws, surgical tools

biodegradable metals, presents a highly appealing amalgamation of mechanical attributes, biocompatibility, degradation susceptibility, and adaptability. Consequently, it emerges as a highly promising substance with the potential for the engineering of biodegradable orthopaedic implants and expanded medical uses. It is anticipated that future advancements and progress in the design and refining methods of Mg alloys will contribute to the continued improvement of the functionality and clinical applicability of implants composed of magnesium.

Although magnesium does have several benefits, its rapid degradation is a significant drawback. Magnesium has a significantly low corrosion resistance, resulting in its degradation before bone formation is completed [11]. It becomes imperative to lessen the biocorrosion kinetics of magnesium alloys to a level that corresponds to bone formation. Mg corrosion resistance has been effectively improved through purification, alloying, and surface modification. Consequently, Mg-based metallic glasses have emerged as promising biodegradable implant materials because of their superior strength, elasticity, and corrosion resistance compared to crystalline forms [10, 11]. Magnesium metallic glasses, due to their chemical uniformity and lack of secondary phases and grain boundaries [12], inhibit the formation of Mg^{2+} ions, H_2 bubbles, and OH^- ions [13]. Solid-state processes and liquid-state processes comprise contemporary manufacturing methods for Mg-based metallic glass. Amorphous powder synthesized through mechanical alloying or milling is necessary for solid-state processes. This powder is subsequently consolidated using methods such as isostatic pressing, hot and cold pressing, and spark plasma sintering [14]. Due to the necessity of maintaining their metallic glassy form, compacting these particles can be a difficult task [15]. In addition, the two-stage powder manufacturing and consolidation procedure may result in purity concerns as a result of potential contamination [16].

Metallic glasses are frequently synthesized in bulk using rapid solidification processing (RSP) [16]. Nevertheless, it is imperative to determine the most effective RSP technique for Mg-based glasses. Researchers have proposed a multitude of parameters to forecast the capability of glass-formation in metallic glasses. Empirical data guided the development of these parameters. Because these parameters are dependent on thermochemical properties, it is impossible to make theoretical predictions about glass-forming alloys without first synthesizing glassy alloys. On the contrary, researchers have used approaches such as solution thermodynamics, topological models related to cluster packing, and models that analyse the size difference among constituent species to make theoretical predictions of glass-forming compositions.

Bone Implant Materials

An orthopaedic implant is designed to replace a missing bone or joint or provide support for an injured bone [5]. Various types of orthopaedic implants are available to address issues in the hip, knee, shoulder, and elbow. Examples include intertwining wires, nails, pins, screws, tacks, rods, craniomaxillofacial implants, fragment implants, and external fixators, among others.

In recent years, millions of individuals have experienced significant benefits from orthopaedic implants. These implants primarily aim to alleviate pain and enhance the ease of joint movement. From an engineering perspective, the primary objective is to ensure the bone and the implant material's functionality and integrity. Therefore, materials with high bio tolerance and endurance to cyclic loading in a challenging bodily environment are considered suitable for implantation [4].

Materials used to fix bone defects can be put into four groups: metals, alloys, polymers, and ceramics. Metal-based biomaterials are better for load-bearing uses because they have a high critical fatigue strength that lets them handle the wear and tear of daily life. Surgeons commonly employ ceramic biomaterials for surface modifications of implants due to their hardness and wear resistance. Polymeric materials, known for their high flexibility and stability, find applications in low friction-related implants [8]. Composite materials have the advantage of combining the benefits of two or more phases or materials [4].

Ceramics

In the classification of inorganic compounds, ceramics are categorized into five primary categories of biomaterials: carbon, alumina, zirconia, bioactive glass, and calcium phosphate [4]. Notably, calcium phosphate ceramics consist of tricalcium phosphate (TCP) and hydroxyapatite (HA), each exhibiting distinct characteristics in vivo. Hydroxyapatite is renowned for its osteogenic properties, while tricalcium phosphate degrades at a faster rate [9].

The utilization of ceramics in orthopaedics dates back to the early 1800s. Initially applied for fracture fixation and filling bony defects, ceramics proved to be biocompatible and conducive to bony ingrowth [11]. However, limitations in strength and toughness constrain the widespread use of ceramics in bulk form, despite their advantages [4].

Polymers

Various polymeric implants encompass fibres, textiles, rods, and viscous liquids [4]. In comparison to ceramics, polymers

offer distinct advantages [17, 18]. They offer the ability to readily customize the mechanical properties and degradation behaviour of implants [19]. The biocompatibility of polymers is a significant concern. However, polymers, despite their striking resemblance to the components of native polymeric tissue, are more commonly utilized in replacing hip sockets. Nevertheless, the degradation of polymers within the body can lead to tissue irritation and a decline in mechanical properties [17]. Their application in load-bearing contexts is presently restricted by their adverse tissue reactions and limited mechanical properties [18].

Composites

The composite material must exhibit biocompatibility to prevent degradation at the constituent interfaces. Among the extensively studied composites for bioimplants are fibre-reinforced polymers (FRP). These composites find applications in various fields, including hip-joint arthroplasty, bone cement, fracture fixation devices, and articulation components. However, their limitations include low mechanical strength, an uncertain lifetime, and susceptibility to degradation under stress. Additionally, shape restriction poses a significant challenge. Therefore, ongoing technical advancements are necessary to address and improve these material limitations [17].

Metals

The utilization of metals as implants began in the early 1900s with the introduction of metal plates for bone fractures [20]. In the initial stages, metal implants encountered challenges such as corrosion and inadequate strength [21]. Nevertheless, the landscape underwent a major transformation in the 1920s with the introduction of 18–8 stainless steel, which was distinguished by its exceptional corrosion resistance. This development marked a significant step forward in the field of metal implants. Permanent metal implants and biodegradable metals broadly categorize metallic biomaterials. Table 2 outlines the properties of both bone and metal implant materials.

Permanent Metal Implants

Stainless Steel Implant-grade stainless steel has 18 wt% Cr and 8 wt% Ni, making it stronger and more corrosion-resistant than normal steel. The introduction of additional supplements, particularly molybdenum (Mo), led to the formation of 316 stainless steel, which exhibited enhanced corrosion resistance. Subsequent modifications in the carbon (C) content resulted in the creation of 316L, which displayed improved corrosion resistance, especially in chloride solutions [23]. Among orthopaedic implant materials, 316L stainless steel is widely preferred over Co–Cr alloys and Ti and its alloys due to its ease of fabrication and cost-effectiveness. Good load-bearing density, biocompatibility, tensile strength, and resistance to corrosion and fatigue are some of its other desirable properties [4].

Although beneficial, the body's diverse and sometimes toxic environment can cause corrosion and material release. Due to their strength and corrosion resistance, other alloys are favoured for permanent implants, although stainless steels are recommended for non-permanent implants. Stainless steel implants can be permanent in some cases [24].

Cobalt-Chromium Alloys Cobalt-chromium (Co–Cr) alloys are classified into two fundamental types: castable CoCrMo alloys and wrought CoNiCrMo alloys [4]. Renowned for their biomedical applications in orthopaedics and dentistry, these alloys have gained prominence in various medical procedures [25]. Co–Cr alloys are remarkable for several reasons, such as their biocompatibility, non-magnetic behaviour, wear resistance, heat resistance, corrosion resistance, and high strength [26].

Table 2 Properties of bone and metal implant materials [22]

Property	Cortical bone	Mg alloy	Ti alloy	Co–Cr alloy	Stainless steel
Density (g/cm^3)	1.8–2.1	1.74–2.0	4.4–4.5	8.3–9.2	7.9–8.1
Elastic Modulus (GPa)	3–20	41–45	110–117	230	189–205
Compressive Yield Strength (MPa)	130–180	65–100	758–1117	450–1000	170–310
Fracture Strength ($MPam^{1/2}$)	3–6	15–40	55–115	–	50–200
Tensile Strength (MN/m^2)	137.3	180–440	1000	690	650
Fatigue Limit (GN/m^2)	–	0.08–0.95 (AZ91)	–	0.30	0.28

In orthopaedics, these alloys play a crucial role in biomedical applications, particularly in prosthetics involving knee, shoulder, and hip replacements, as well as fixation devices for fractured bones [27].

One important use of Co–Cr alloys is in joint stems, where they offer a clear benefit by reducing the release of polyethylene wear particles that are common in polyethylene acetabular cup systems. This feature helps prevent tissue reactions and the subsequent relaxing of hip stems, contributing to the long-term success of orthopaedic implants [24].

Titanium-Based Alloys The remarkable physical, mechanical, and biological characteristics of alloys based on titanium (Ti) have led to a recent upsurge in their use as biomaterials. The biocompatibility and corrosion resistance of pure titanium (CP Ti) led to its early use as a substitute for 316 stainless steel and Co–Cr alloys. This was because 316 stainless steel and Co–Cr alloys contained detrimental elements namely nickel (Ni), cobalt (Co), and chromium (Cr) [28]. However, in cases requiring high strength, CP Ti's mechanical strength might not meet biomaterial requirements [29]. Researchers addressed this issue by introducing α and β-type Ti-based alloys namely Ti–6Al–4 V as substitutes for CP Ti [30]. Nevertheless, the poor biocompatibility of Ti–6Al–4 V, attributed to toxic elements namely aluminium (Al) and vanadium (V), prompted the development of β-type Ti-based alloys, such as Ti–6Al–7Nb and Ti–5Al–2.5Fe, replacing V with niobium (Nb) and iron (Fe) [31].

Research suggests that α- and β-type Ti-based alloys may buffer stress better than human bone due to their greater elastic modulus [26]. Researchers have created β-type Ti-based alloys such as Ti–15Mo, Ti–13Nb–13Zr, Ti–12Mo–6Zr–2Fe, Ti–35Nb–5Ta–7Zr, and Ti–29Nb–13Ta–4.6Zr to solve this issue [32]. The Ti-based alloy Ti-35Nb-4Sn had the lowest elastic modulus at 40 GPa, although it was still greater than cortical bone (10–30 GPa) and cancellous bone (0.01–2 GPa) [33, 34].

Porous Ti-based alloys have been explored to address this, exhibiting a reduced elastic modulus. Porous materials not only make things less stiff, but they also help with biological repair and fixation by letting bone tissue grow inside the pores and making sure that the bone and implant share the same amount of load [35]. Porous Ti-based alloys are notable for combining high mechanical strength coupled with biocompatibility [36].

Biodegradable Metals

Biodegradable metals (BMs) have recently emerged as a suitable material for biodegradable implants, offering a unique advantage in their ability to slowly corrode in vivo. This controlled corrosion causes a slow host response, which is helped by the release of by-products. Eventually, the whole thing dissolves, having helped the tissue heal [10]. Biodegradable metals encompass metallic elements that are capable of being metabolized, demonstrating acceptable degradation rates and modes in the human body [10].

BMs are classified as biodegradable pure metals (BM–PM), alloys (BM–BA), and metal matrix composites (BM–MC) in materials research [37]. Pure metals have one metallic element and impurities below the commercial tolerance. In the BM-BA category, biodegradable alloys comprise metallic glasses and single-crystal metals with varied microstructures and several alloying elements. A biodegradable metal is the main component of BM–MC ceramic composites. Among the various metals studied, magnesium (Mg)-based alloys [38] have been extensively researched, incorporating varied additions of Zn, Ca, Li, Sr, Sn, and Mn to form diverse alloys.

Magnesium-Based Alloys Several studies have explored the medical applications of magnesium (Mg) in cardiovascular, musculoskeletal, and various other implants [39]. Mg wire has demonstrated successful use in treating haemorrhaging blood vessels [40]. Numerous cardiovascular applications of Mg implants encompass sutures, vessels, and nerve connectors. Mg connectors have facilitated the anastomosis of vessels, while Mg-based sutures have been used for the treatment of vascular parenchymatous organs [41]. Mg implants have been employed for various types of haemangioma treatments [42]. Magnesium implants, including pins, rods, screws, wires, sheets, and plates, have been developed for the treatment of bone fractures. Table 3 presents a historical overview of magnesium as a biodegradable implant [43].

Magnesium alloys have demonstrated exceptional potential as bio-implants in recent years [44], which is due to their favourable biological, mechanical, and physical characteristics. Notably, these alloys exhibit increased osteoblast adhesion [11], showcasing promising prospects for orthopaedic applications [45].

Nanomaterials in Orthopaedic Implants

Despite the numerous benefits of magnesium, such as stress shielding prevention and osteoblast attachment enhancement, its rapid degradation poses a challenge to the long-term development of bones. As a result, it is critical to improve magnesium's corrosion resistance to ensure its efficient use in bone production. Nanotechnology in bone tissue engineering presents new mechanical and biological performance prospects.

Recent nanoparticle manufacturing developments affect tissue engineering and regenerative medicine [46]. Nanoparticles' nanoscale size, high surface area, customizable

Table 3 Historical overview of magnesium as biodegradable implants [43]

S.nos	Author	Year	Material	Uses	Test species
1.	Huse	1878	Mg	Wires as ligature	Humans
2.	Payr	1892	Highly pure Mg	Pipes, plates, arrow, wires, sheets	Humans, guinea pigs,
3.	Hopfner	1903	Pure Mg	Vessel connectors	Rabbits, pigs, dogs
4.	Chumsky	1900	Highly pure Mg	Pipes, plates, arrow, wires, sheets	Humans, rabbits, dogs
5.	Lambotte	1906	Pure Mg	Rods, plates, screws	Humans, rabbits, dogs
6.	Lespinasse	1910	Metallic Mg	Ring plates	Dogs
7.	Andrews	1917	Pure Mg	Wires, clips	Dogs
8.	Seelig	1924	Pure Mg	Wires, strips, bands	Rabbits
9.	Verbrugge	1933	Mg–Al–Zn	Plate, screws, peg	Humans, dog, rat, rabbit
10.	McBride	1938	Mg–Mn	Sheet, plate	Humans, dogs
11.	Nogara	1939	Elektron	Rods	Rabbits
12.	Toponikunn	1940	Mg–Cd	Sutures	Humans
13.	Maier	1948	Mg	Wires	Humans, rabbits
14.	Stone	1957	Mg–Al	Wires	Dogs
15.	Fontenier	1975	Mg–Mn–Al	Anodes-Pacemaker	Dogs
16.	Wilflinseder	1981	Pure Mg	Wires	Humans
17.	Frank Witte	2005	AZ91D, LAE442	Rods	guinea pig femura
18.	Witte et al	2005	AZ91/AZ31	Rods	guinea pig
19.	Witte et al	2005	LAE442	Rods	guinea pig
20.	Huang Jingjing	2007	Pure Mg & AZ31B	Rods	rabbit
21.	Witte et al	2007	AZ91	Rods	rabbit
22.	Huang et al	2007	AZ31	Rods	Rabbit
23.	Xu et al	2007	Mg1.0Zn1.2Mn	Rods	Rat
24.	Liping Xu	2008	Mg–Mn–Zn	Rods	Rabbit
25.	Zhang et al	2008	Mg0.8Zn1.0Mn	Rods	Rat
26.	Zhang et al	2008	Mg6Zn	Rods	Rabbit
27.	Witte et al	2009	LAE442	Cylinders	Rabbit
28.	Loffler et al	2009	$Mg_{60}Zn_{35}Ca_5$	Discs	Pig
29.	Castellani et al	2010	Mg–Y–Nd–HRE	Rods	Rat
30.	S. Remennik et al	2011	B-BX, B-BS	Rods	Rabbit
31.	Tanja Kraus et al	2012	ZX50, WZ21	Pins	Rat

surface characteristics, scaffold tensile strength, and antibacterial/antiseptic capabilities might improve engineered tissues and solve tissue engineering problems [47, 48]. These nanoparticles are classified by shape, size, and chemical characteristics and come from several materials [49]. Several nanoparticles have improved scaffolds and tissue engineering together with polymers. These include gold, ceramic, silver, magnetic, and polymer nanoparticles [50]. Under optimal circumstances, electrospinning created fibrous nanostructures from eggshell waste cyclodextrin [51]. These cyclodextrin nanofibers are attractive dental nanocoating materials because of their homogeneous shape, limited particle size distribution, good heat stability, and superior abrasion resistance.

Nanomaterials integrated into orthopaedic implants have several benefits, including increased bone integration, enhanced mechanical qualities, antibacterial properties, superior drug delivery capabilities, and real-time monitoring. These advancements are revolutionizing the industry, resulting in increased success rates for implant procedures and improved long-term results for patients. As research progresses, the advancement of nanomaterial-based solutions is anticipated to enhance the safety, efficacy, and durability of orthopaedic implants.

Nanoparticles provide a flexible and potent set of methods for enhancing the functionality of orthopaedic implants and scaffolds, resulting in improved results in bone repair and regeneration. The addition of nanoparticles to scaffolds enhances their strength and durability, making them ideal for weight-bearing applications. Nanoparticles made from bioactive glass, calcium phosphate, or zinc, for example, can

help bone-forming cells (osteoblasts) work better and speed up the process of osteogenesis.

Graphene oxide nanosheets and hydroxyapatite nanoparticles, for instance, make hydrogels used for bone tissue engineering more conductive and stronger.

Nanoparticles including gold, silver, and hydroxyapatite nanoparticles have surfaces that help cells stick to them, grow, and change into different types of cells. For instance, studies have demonstrated that hydrogels containing hydroxyapatite nanoparticles facilitate the adhesion and growth of mesenchymal stem cells.

Nanoparticles namely chitosan, collagen, and silk fibroin make scaffolds more biocompatible, which means they work better with host cells and cause less inflammation. This makes them applicable in various medical scenarios.

Researchers have found that reduced graphene oxide (rGO) and hydroxyapatite (HA_p) nanocomposites can make osteogenic cells differentiate a lot better. To fix femur bones, Zheng et al. [52] used collagen, silver nanoparticles, and macrophages. Collagen made nanoparticles less harmful, and the support made it easier for new calluses and cartilage matrices to form, which speeded up the healing of fractures. Nanoparticles of silver boosted the growth of mesenchymal stem cells (MSCs) and the development of osteoblasts [53].

Researchers found that zirconium oxide nanocomposites with chitosan, organically modified montmorillonite (OMMT), and nano-hydroxyapatite (nHA_p) could grow bone tissue and kill microbes, potentially protecting orthopaedic implants from infections. The nanocomposites showed that they were pH-compatible, cell-compatible, and low-toxic [54]. Ceramic nanoparticles help cells stick together better in tissue engineering. Researchers incorporated copper and zinc nanoparticles into chitosan/gelatin/nanohydroxyapatite scaffolds. These scaffolds had a lot of holes and small pores. These nanoparticles made it easier for cells to stick together, move, and multiply, which led to quicker cell growth [55].

Copper-infused functional glass nanoparticles (Cu-BGN) transformed gelatin-coated structures into functional entities. Zheng et al. [52] found that these scaffolds were safe because they helped MC3T3-E1 cells make alkaline phosphatase, hydroxyapatite, and bone.

A different study made gelatin nanocomposites mixed with silver nanoparticles and bioactive glass. These materials stopped bacteria from growing and helped cells grow on electrospun scaffolds. Thinner fibres resulted from the incorporation of silver nanoparticles, which improved the outcomes of bone tissue engineering [56]. Nanoparticles of HA_p and iron oxide (Fe_3O_4) were mixed with chitosan and collagen to make a biocompatible structure. This scaffold worked well to fix a calvarial flaw by growing new bone tissue [57].

In 2017, Daniel et al. [58] made an antibiotic and bone-building hybrid scaffold This structure helped cells grow, divide, stick together, produce alkaline phosphatase, and differentiate into human bone marrow stromal cells (hBMSCs), showing that it was safe [59].

In 2015, researchers used colloidal chemistry to create three-dimensional hydrogels for bone tissue using graphene oxide nanosheets and hydroxyapatite (G/HA) nanoparticles. These nanocomposites were porous, safe, and have better mechanical and electrical properties. The hydroxyapatite nanoparticles in the G/HA hydrogel made it easier for mesenchymal stem cells to stick together, which led to longer cells than those on the rGO hydrogel [60].

Researchers investigated rGO/HAp nanocomposites in the same year to see if they could aid in bone growth and repair. These nanocomposites help cells differentiate through molecular signalling. [61]. Graphene oxide modification of tussah silk fibroin scaffolds and poly (L-lactic-co-glycolic acid) was also possible. Electrospun materials with a high Young's modulus and tensile strength made mouse mesenchymal stem cells better at turning into bone cells. These supports, which soak up proteins and water, helped cells stick together and grow [62].

The integration of nanoparticles with Mg-based orthopaedic implants provides substantial improvements in mechanical qualities, controlled degradation rates, biocompatibility, antibacterial effects, medication administration, and real-time monitoring. These developments mitigate the constraints of pure magnesium implants, rendering them more appropriate for therapeutic uses. By using the distinctive characteristics of nanoparticles, it is possible to design magnesium-based orthopaedic implants that demonstrate enhanced resistance to corrosion, compatibility with the human body, promotion of bone growth, and mechanical qualities. This ultimately results in superior clinical results and long-term success of the implants.

Performance of Magnesium Alloys in Orthopaedics

The stress shielding impact frequently observed in conventional implants is effectively mitigated by the elastic modulus of magnesium, which closely resembles that of natural bone. However, magnesium's principal drawback lies in its poor corrosion resistance. The rapid degradation of magnesium can lead to incomplete bone formation, hindering its effectiveness as an implant material [63]. Moreover, the accelerated degradation of magnesium alloys contributes to solution alkalization, potentially leading to necrosis [64]. This necessitates the imperative need to control the corrosion rate of magnesium alloys to align with the specific requirements of orthopaedic applications.

Magnesium alloys display high corrosion in aqueous solutions [65]. During corrosion of Mg in aqueous solutions,

the following electrochemical reactions are expected forming hydrogen gas and magnesium hydroxide [65].

Anodic Reaction

$$Mg \rightarrow Mg^{2+} + 2e \quad (1)$$

Cathodic Reaction

$$H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (2)$$

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2 \quad (3)$$

The magnesium hydroxide formed provides protection to the bulk due to its quasi passive nature [64]. The corrosion behaviour of Mg in an aqueous solution is pH-dependent. Mg dissolution occurs below a pH value of 11.5, above which there is $Mg(OH)_2$ formation [66]. Accordingly, Mg is actively dissolved at the blood pH (~ 7.3–7.4). The standard electrode potential of Mg is very low (– 2.37 V vs SHE) and is less noble than most of the matrix rendering the magnesium matrix anodic [67]. Hence Mg is more susceptible to galvanic corrosion. Various corrosion mechanisms are involved when Mg alloys are considered for bioimplant application in osteosynthesis. Some of which are discussed in this paper.

Galvanic Corrosion

The magnesium matrix, particularly when proximate to cathodic areas, is susceptible to galvanic corrosion. If magnesium is in contact with a nobler metal or there are cathodic secondary phases or impurities in the matrix, galvanic corrosion can occur within or outside a material [67].

Hanawalt et al. [68] emphasized that even minute traces of Fe, Ni, or Cu impurities in pure magnesium may have a detrimental impact on its corrosion behaviour. The limited solubility of these elements in magnesium, coupled with a low hydrogen overvoltage, may give rise to micro galvanic cells, thereby inducing internal galvanic corrosion. Aung & Zhou [69] delved into the grain size impact on the corrosion behaviour, while Hamu et al. [70] explored the role of microstructural changes in influencing the corrosion rate.

Stress Corrosion and Stress Corrosion Cracking

The evaluation of stress corrosion is essential for the use of magnesium implants in osteosynthesis, as the potential danger of stress corrosion cracking (SCC) can lead to abrupt implant failure. Miller suggested that the propagation of SCC in Mg alloys may occur either between grains or across grains, contingent upon the composition, microstructure, and environmental conditions [71].

Intergranular failure is an ongoing electrochemical process wherein the matrix near the grain boundaries experiences anodic dissolution, leading to the metal being pulled apart under applied stress [71]. On the other hand, transgranular SCC has two ways for cracks to grow: cracks can grow by dissolution, which includes preferential attack or film rupture; or cracks can grow by brittle fracture, which includes cleavage or hydrogen embrittlement [71].

Researchers have introduced several models to elucidate the mechanisms behind SCC. The discontinuous process proposed by Pardue et al. [72] is characterized by the alternation of mechanical and electrochemical process, while Pugh et al. [73] suggested a brittle-film model. Fairman & Bray [74] explored the role of dislocation movement in SCC and identified hydrogen embrittlement as a contributor to SCC [75]. However, the precise role of hydrogen in this context remains not fully understood.

Strategies Towards Enhancement of Corrosion Resistance in Magnesium Alloys

Numerous strategies, such as purification, alloying, surface modification, and metallic glass formation, have been employed to enhance the corrosion resistance of magnesium (Mg) implants.

Purification

Mg that is pure is pretty safe, but iron (Fe), nickel (Ni), and copper (Cu) that are mixed in can speed up corrosion reactions if their amounts are higher than acceptable levels [10]. High purity Mg, with significantly lower impurity levels, has demonstrated a thousand-fold reduction in corrosion rates compared to commercially pure Mg [63]. Impurity content ratios, such as the Fe/Mn ratio [76], influence the corrosion rate of pure Mg. Pure magnesium, on the other hand, isn't as strong, so it needs to be alloyed with less toxic elements to make its mechanical properties and corrosion resistance better.

Alloying

The use of pure Mg in orthopaedics is limited due to its low yield strength, making alloying essential for enhancing strength. The choice of alloying elements is critical to maintaining Mg's biocompatibility. Incorporating essential body elements as alloying elements reduces the risk of

toxicity, paving the way for biocompatible and biodegradable alloys [77].

Mg–Ca-Based Alloys

Mg–Ca alloys, containing calcium essential for bone signalling, have shown promise for bone healing. The co-release of Mg and Ca ions can be favourable for the assimilation of Ca into the bone. The ability of Mg–Ca alloys to resist corrosion and their ability to behave mechanically depend on the formation of Mg_2Ca phases. Smaller particles help the alloys resist corrosion and behave mechanically better. In vitro cytotoxicity tests have demonstrated the biocompatibility of the Mg–1Ca alloy, leading to in vivo degradation within 90 days and new bone formation [78].

Mg–Zn-Based Alloys

Zinc (Zn) solubility in Mg alloys improves mechanical behaviour, and the addition of Yttrium (Y) reduces corrosion rates [79]. In vitro and in vivo studies have shown osseointegration, biocompatibility, and corrosion resistance with zirconium (Zr) addition. Manganese addition reduces corrosion rates by removing heavy metal elements [80]. The influence of Zn content on microstructure, corrosion resistance, and mechanical properties varies, with the Mg–Zn–Ca alloy exhibiting outstanding mechanical integrity during in vitro degradation [81].

Mg–Si-Based Alloys

Silicon (Si) is essential for bone tissue progress. The Mg_2Si phase in Mg–1Si alloys can make them hard to shape, but adding Ca and Zn elements to improve the morphology of Mg_2Si makes it less expected to rust and improves its mechanical properties [82].

Mg–Sr-Based Alloys

Strontium (Sr) addition refines grain size and enhances corrosion resistance. The Mg–2Sr alloy has the lowest rate of corrosion and the most strength. On the other hand, the Mg–Zn–Sr and Mg–Ca–Sr alloys have high rates of corrosion because they contain a lot of secondary intermetallic phases [83].

Mg–RE-Based Alloys

Rare earth elements in Mg improve strength and corrosion resistance. Gadolinium (Gd) and Dysprosium (Dy) show higher solubility than Yttrium (Y), while Europium (Eu), Neodymium (Nd), and Praseodymium (Pr) show lower solubility. Various Mg-RE-based alloys, such as WE43, Mg–Y, and Mg–Gd, have been reported for biomedical applications, with the WE43 alloy being renowned for its excellent corrosion resistance and mechanical behaviour [84].

Surface Modification

Surface modification is a distinctive strategy to enhance the corrosion resistance of magnesium (Mg) alloys while preserving mechanical integrity and improving biocompatibility.

Anodic Oxidation and Micro-Arc Oxidation (MAO) Coatings

Anodizing pure Mg yields porous and non-porous films, with the magnesium oxide layer formed during anodization slowing down the corrosion process. Micro-Arc Oxidation (MAO) treatment on the AZ91D alloy improves wear and corrosion resistance. The addition of calcium (Ca) and phosphorus (P) to the ceramic coating of MAO-treated AZ91D alloy reduces corrosion rates. The MAO treatment makes the Mg–Ca alloy more resistant to corrosion and helps cells stick together better [85].

Calcium Phosphate Coatings

Chemical conversion, alkali-heat treatment, and electrodeposition can all be used to make calcium phosphate coatings. These coatings are biocompatible and non-toxic, which makes them perfect for orthopaedics**.** Chemical conversion, especially for brushite (DCPD) and hydroxyapatite, is a simple and cost-effective method. Alkali-heat treatment enhances the corrosion resistance and biocompatibility of pure Mg, while DCPD and fluoridated hydroxyapatite (FHA) layers show promising results on the Mg-6Zn alloy. It is better for biocompatibility and less corrosion when there are fluorinated coatings and biodegradable polymer coatings namely Poly (Lactic-Co-Glycolic Acid) (PLGA) [86].

Fluorinated Coatings

Fluoride treatments reduce the corrosion rate of Mg alloys and promote osseointegration. Studies on fluoride-coated Mg–Ca alloys show improved mechanical behaviour, increased corrosion resistance, and high biocompatibility. However, several studies have reported contradictory results [87]. Biodegradable polymer coatings, such as polycaprolactone, chitosan, and PLGA, decrease corrosion rates, improve

mechanical properties, and enhance biocompatibility when applied to Mg alloys [87].

Other Treatments

Laser shock peening (LSP), ion-beam aided deposition (IBAD), and plasma immersion ion implantation and deposition (PIII&D) have been investigated for surface modification. IBAD coating reduces the corrosion rate of AZ31, while ion implantation of Al into Mg reduces degradation rates. The PIII & D technique introduces Ti, Al, and Zr individually into AZ91, with Al implantation and coating providing the best corrosion resistance. LSP slows down the corrosion rate in Mg-Ca alloys due to high compressive residual stress [88].

Metallic Glasses

Glasses are amorphous materials [89–91] that are obtained by rapid quenching from the liquid state [92]. Figure 1 depicts the change in specific volume by temperature. The competing process exists between liquid and crystalline phases during cooling. As per thermodynamics, materials must exist at the lowest energy state. During slow cooling crystalline materials are formed due to sufficient time available for the mobility of the atoms to form ordered structures. During cooling, there is a decrease in the mobility of atoms due to a rise in the melt viscosity. Rapid quenching reduces the mobility of atoms by reducing the driving force (i.e. Gibbs energy) and forms glass. The ease of glassy phase formation by suppressing crystalline phases is the Glass Forming Ability (GFA). Critical Cooling Rate (R_c) is the lowest cooling rate available to form a glass and it is a measure of GFA. As demonstrated in Fig. 2, a higher GFA is associated with a lower R_c, whereas a higher R_c is associated with a lower GFA. Critical Diameter (D_{max}) is another criterion to measure GFA which is the maximum thickness at which a glassy material can be developed [93]. Glass transition Temperature (T_g) is observed when glassy metals are heated. From T_g the mobility of atoms increases as a function of temperature. This increase in mobility allows the glassy material to form various shapes. Heating the glass allows the transformation of the amorphous state of glass to crystallinity at the crystallization temperature (T_x). The temperature interval between glass transition temperature and crystallization temperature is called the supercooled liquid region ($\Delta T_x = T_x - T_g$) [94].

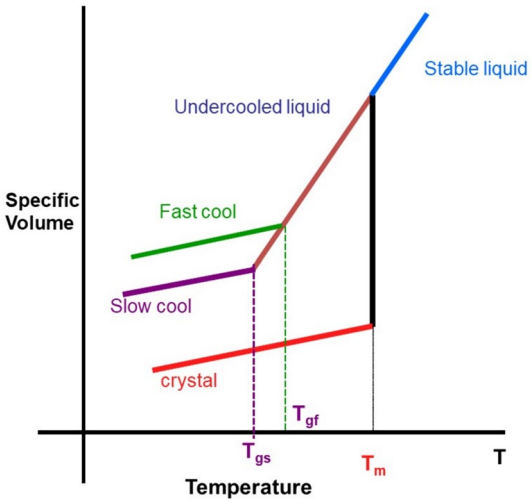

Fig. 1 Specific volume vs temperature for a normal and glass-forming material [16]

Reduced Glass Transition Temperature (T_{rg})

In order to forecast the GFA of the alloys, Turnbull introduced a critical parameter known as $T_{rg} = T_g/T_l$. T_g and T_l are the glass transition temperature and liquidus temperature, respectively [16]. The viscosity increases as the T_{rg} value increases, and the alloy melt can readily solidify into a glass at a minimum cooling rate (i.e. Higher T_g value and lower T_l value may aid easy glass formation). It was suggested by Turnbull based on nucleation theory that when $T_{rg} \geq 2/3$, there is suppression of homogeneous nucleation of crystalline phase [94]. T_{rg} should possess a minimum value of ~ 0.4 to form a glass. When T_{rg} is higher, glass formation becomes easier [16].

Supercooled Liquid Region ($\Delta T_x = T_x - T_g$)

ΔT_x is the supercooled liquid region, which is defined as the temperature range between the crystallization temperature (T_x) and the glass transition temperature (T_g). The stability of the glassy phase, which resists crystallization, is reflected in the larger width of the supercooled liquid region,

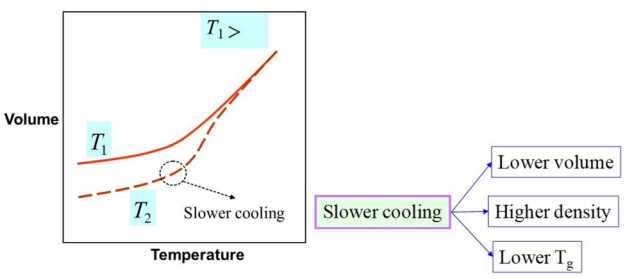

Fig. 2 Relation between critical cooling rate and glass-forming ability [16]

as suggested by Inoue [16]. As a result, the glass-forming capacity is reliant upon the supercooled liquid region.

Inoue Criteria

To predict GFA, Inoue proposed three empirical rules based on thermodynamics, kinetics, and topological aspects [16]. As per Inoue's prediction, firstly, a multi-component alloy containing at least three components is easy for glass formation. Secondly, constituent elements in the multi-component alloy should possess a significant atomic size difference of approximately 12%. Thirdly, major constituent elements should exhibit negative heat of mixing.

Bulk Metallic Glasses (BMGs)

Noncrystalline solids with section thicknesses higher than one millimetre obtained through the liquid state process are termed to be bulk metallic glasses [16]. BMGs.

possess a minimum of three components and can be produced at slow solidification rates ($\lesssim 10^3$ K s^{-1}). Figure 3 represents the Time–Temperature–Transformation (*T–T–T*) curve for liquid to solid transformation. The transformation curve having a C-shape, depicts the time required for the initiation of stable crystalline phase [16]. Curve a and b represent crystallization start and end, respectively. Curve 1, 2, and 3 in Fig. 3 depict the cooling rate for coarse-grained crystals, fine grained crystals, and glassy phase, respectively. If the liquid alloy is cooled at a rate faster than curve 3, the glassy phase is formed because the liquid is maintained on supercooled state. The cooling rate represented by curve 3 is called critical cooling rate [16]. Figure 4 represents the *T–T–T* curve for multicomponent alloy. With increase in the number of alloying elements, the C curve shifts to the right.

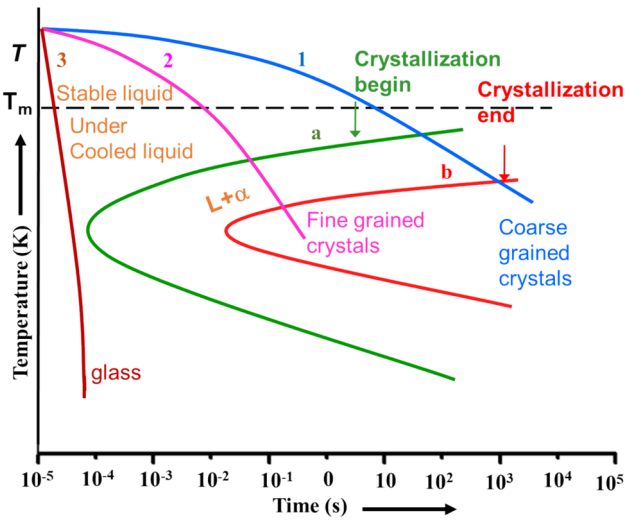

Fig. 3 TTT Diagram for liquid-to-solid transformation [16]

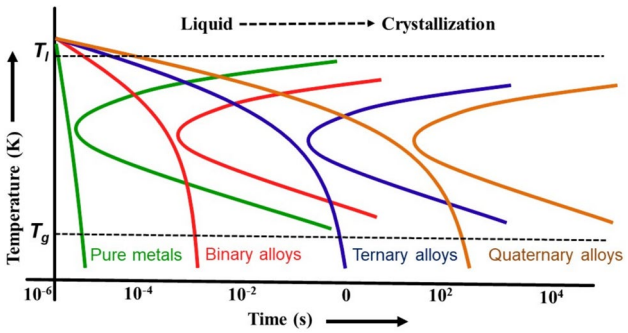

Fig. 4 TTT Diagram for multicomponent alloy [16]

Hence, glassy alloy can be easily formed even at slow solidification rates. The bottom cooling rate reported by Nishiyama & Inoue [95] for BMGs is 0.067 K s^{-1} (i.e. 4 K min^{-1}) while the highest diameter reported is 72 mm by Inoue et al., [96] in a $Pd_{40}Cu_{30}Ni_{10}P_{20}$ alloy.

Processing of BMGs

In the realm of metallic glasses, the generation of an amorphous phase by eliminating crystalline phases requires extremely rapid cooling. However, creating bulk metallic glasses (BMGs) is a complex and challenging process due to the need for rapid cooling. Conventional production techniques are time-consuming and resource-intensive. Researchers have introduced recent advancements in fabrication procedures with high throughput to overcome these barriers. Studies indicate that the incorporation of metallic glass composites significantly enhances the corrosion resistance of Mg-based materials compared to pure Mg [97].

Over the past decades, extensive research has focused on improving the capacity for BMG formation by modifying synthesis, production, and processing techniques. Strategies include producing alloys with multiple constituents [98]. Ramya et al. successfully synthesized a 4 mm-diameter Mg-based BMG using the copper mould casting approach [98].

Various synthesis strategies for Mg-based BMGs have been explored, employing techniques such as induction heating, copper mould casting, high-pressure diecasting, suction casting, and melt spinning [98, 99]. For example, researchers have used the induction heating method to enhance the hardness, ductility, and strength of $Mg_{67}Zn_{28}Ca_5$ BMGs by incorporating nano-alumina particles [100]. High throughput techniques, in particular the blow forming process, have been introduced to develop simultaneous Mg–Cu–Y metallic glasses [101].

While traditional methods involving copper mould casting and metal spinning are effective, they produce BMGs with limited size, making them impractical for certain applications, such as orthopaedic implants [102]. Researchers

have employed advanced techniques namely laser remelting to produce corrosion-resistant Mg-based BMGs [102]. Additive manufacturing, though still in the research phase, provides an alternative approach for producing metallic glasses [103].

Surface treatment is crucial for Mg-based alloys due to their natural corrosiveness. Traditional surface treatments include micro-arc surface treatment and anodic surface treatment, but they involve the use of alkaline solutions, which can be environmentally harmful. Dry methods, particularly sputtering, have been explored for surface treatment to enhance the properties of metallic glasses [104].

The study emphasizes that the synthesis and fabrication processes significantly influence the properties and structure of BMGs. Composite materials, as demonstrated in various studies, often outperform monolithic Mg-based BMGs [105]. Tailoring the size of BMGs is crucial, particularly for biomedical applications, where mechanical strength and degradation properties are essential factors for implant success [106]. The choice of synthesis methods, materials, assembly techniques, and mould utilization plays a pivotal role in determining the final size and properties of Mg-based BMGs.

Magnesium-Based Metallic Glasses as Orthopaedic Implants

Metallic glass formation is one of the latest strategies [10] which is used to circumvent the difficulty of poor corrosion resistance of Mg implants. Glassy Mg implants are acquiring substantial significance as biodegradable implants due to their higher strength, elasticity, and inflated corrosion resistance in contrast to crystalline counterparts [91]. By virtue of the above features, Mg metallic glasses diminished the generation of Mg^{2+} ions, H_2 bubbles, and OH^- ions [45]. However, the poor ductility of these glassy samples limits their practical usage as viable implants. Hence, there is a need to improve the section thickness, corrosion resistance, ductility, and biocompatibility in order to transmit these implants into biomedical use.

Current methods for processing magnesium-based metallic glasses encompass solid-state techniques (e.g. mechanical alloying/milling) and liquid-state techniques (e.g. copper mould induction melting/melt spinning) [107]. The solid-state process involves mechanical alloying or milling for synthesis along with suitable consolidation techniques such as spark plasma sintering and isostatic pressing [108]. However, the perpetuation of the glassy state is difficult during compaction [109]. Moreover, the two-stage process of powder production and consolidation is more susceptible to contamination [16]. On the contrary, the liquid-state process is considered to be a more perfect technique to synthesize glasses in bulk [16] but identifying the absolute rapid solidification processing (RSP) technique is strenuous. Nevertheless, melt spinning has proven to construct glassy $Mg_{60+x}Zn_{35-x}Ca_5$ alloys ($x = 0, 3, 6, 9, 12, 15$) with improved corrosion resistance [13] but the critical thickness reported was only about 50 µm. This thickness limitation is a major drawback for transforming these biodegradable glasses into viable implants and it has been circumvented through the amalgamation of induction melting and copper mould [11]. The maximum critical diameter reported in $Mg_{66}Zn_{30}Ca_4$ which is one of the better glass-forming compositions is 5 mm [15]. Figure 5 illustrates the various techniques utilized in the processing of metallic glasses.

$Mg_{60+x}Zn_{35-x}Ca_5$ ($0 \le x \le 7$) alloys with high Zn content were reported to show nil hydrogen evolution in the in vivo studies conducted by Zberg et al. [109]. Gu et al. [108] reported the improved corrosion resistance and cytocompatibility of $Mg_{66}Zn_{30}Ca_4$ sample. Mg–Zn–Ca BMGs showed higher strength but then less plasticity than their crystalline counterparts. For example, the compressive strength of $Mg_{66}Zn_{30}Ca_4$ BMG (716–854 MPa) was higher than the crystalline alloy AZ91D (400 MPa) and the tensile strength of $Mg_{67}Zn_{28}Ca_5$ glassy wire (675–894 MPa) was higher than the crystalline alloy WE43 (270 MPa) [13]. However, intrinsic brittleness is baneful for Mg–Zn–Ca-based BMGs as bioimplants. Moreover, the biodegradable material should be suitably tuned to exhibit an ideal corrosion rate of 0.02 mm/year [63] such that it exhibits suitable performance and stability for the minimum required period around 12 weeks [44] satisfying the acceptable corrosion rate of 0.02 mm/

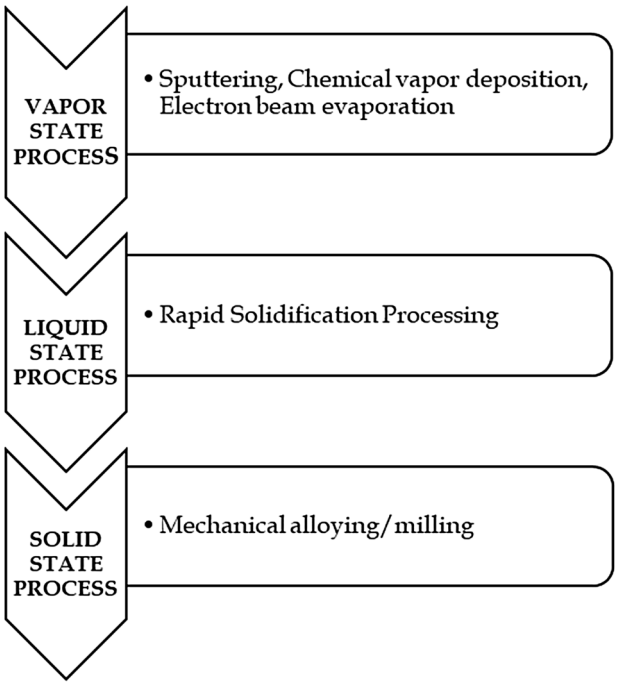

Fig. 5 Different Processing Methods for Metallic Glasses [16]

year [63]. The majority of in vitro investigations on metallic glasses have been conducted on samples with a thickness of only a few μm [110] to a maximum of 1–4 mm [111].

Hence, transforming Mg–Zn–Ca metallic glasses into viable implants involves the improvement of their ductility as well as their corrosion resistance. Palladium (Pd) alloying of 2 at % in $Mg_{72}Zn_{23}Ca_5$ showed delayed corrosion and a harder surface due to the formation of crystalline phases [112]. Yttribium (Yb) addition of 2 and 4 at % to Mg–Zn–Ca BMGs exhibited an improvement in ductility under bending and tensile loading [113]. The improvement in ductility was credited to the increased shear band density at the fracture ends and increased plastic zones at the fracture surface. The Yb alloyed samples also showed improved biocompatibility. Li et al. [114] reported that Strontium (Sr) alloying to Mg–Zn–Ca bulk metallic glasses showed improvement in glass-forming ability and corrosion behaviour. Significant effort has been made to improve the mechanical properties of Mg–Zn–Ca BMGs through Yttrium (Y) addition [111], since Y inclusion forms Long Period Stacked Ordered (LPSO) phases which improve the mechanical properties [12]. Li et al. [115] examined the influence of Silver (Ag) addition on the glass formation, mechanical behaviour, corrosion properties, and biocompatibility of Mg–Zn–Ca metallic glasses. Though Ag addition decreased the glass-formation, it showed a slight improvement in corrosion resistance and cytocompatibility.

BMG Composites

While bulk metallic glasses (BMGs) exhibit high strength, their limited plasticity restricts their application in structural contexts. Overcoming this limitation calls for the improvement of BMG mechanical properties, a challenge that can be addressed through the generation of BMG composites using either in-situ or ex-situ methods [116]. These methods aim to enhance ductility and toughness.

In in-situ composites, second-phase precipitation occurs during the casting or subsequent processing of the glassy alloy. On the other hand, ex-situ composites involve the external addition of reinforcement particles during the casting of the glassy alloy. The interface between the matrix and reinforcement tends to be stronger in in-situ composites compared to ex-situ composites [16].

In the past, metallic glass composites were made by adding ceramic particles to melt-spun glassy ribbons [117], using an amorphous metal ribbon as reinforcement in a polymer or glassy ceramic matrix [118], and strengthening BMG matrices with ceramic or ductile metal particles [119]. Adding an extra phase to metallic glass composites improves their mechanical properties by making it easier for multiple shear bands to form during deformation. This makes the composites more flexible. However, this approach exhibited challenges, including poor fatigue resistance attributed to debonding between phases [119]. In specific instances, such as Mg–Zn–Ca–HAp composites, the glass-forming ability of the $Mg_{66}Zn_{30}Ca_4$ alloy decreased with hydroxyapatite (HAp) addition, resulting in a partially amorphous structure. Furthermore, the addition of HAp resulted in a significant enhancement in corrosion resistance [116].

It is crucial to note that BMGs and BMG composites with thicknesses of a few millimetres are insufficient for manufacturing orthopaedic implants namely pins, tacks, and screws. To be viable for such applications, BMGs must have thicknesses in the range of a few centimetres. Achieving BMGs with larger diameters requires an alloy composition with high glass-forming ability (GFA). Consequently, it is imperative to possess a thorough comprehension of the composition of a variety of Mg–Zn–Ca alloys, which are capable of undergoing a conversion to an amorphous state with increased dimensions.

Thermodynamic Predictions of Glass-Forming Alloys

The glass-forming ability of metallic glasses has been predicted by a variety of factors. Experimental data, including the glass transition temperature(T_g), crystallization temperature (T_x) [120], liquidus temperature (T_l), reduced glass transition temperature $T_{rg} = \frac{T_g}{T_l}$ [13], $\Delta T_x = (T_x - T_g)$ [121] $\gamma = \frac{T_x}{T_g + T_l}$ [122] $\alpha = \frac{T_x}{T_l}$ [123] and $\beta = \left(\frac{T_x}{T_g}\right) + \left(\frac{T_g}{T_l}\right)$ [124] is used to derive these parameters. The above parameters are contingent on thermodynamic variables making it difficult to augur glass formation without the synthesis of glassy alloys. Gallego et al. [125] predicted the glass-forming compositions based on solution thermodynamics. Egami & Waseda [126] predicted glass-forming compositions using models based on size differences of integral elements. Miracle [127] used topological models grounded on cluster packing to analyse glass formation.

The Miedema model [128] has been extensively employed due to its adaptability in incorporating multicomponent alloys [107], which is a characteristic of the numerous theoretical models used to predict glass-forming compositions. An approach such as Miedema's is a significant starting point in situations involving multicomponent alloys that lack an existing thermodynamic database. Researchers including Gallego et al. [125], Murty et al. [129], Busch and Johnson [130], Takeuchi and Inoue [131], Basu et al. [132], Bhatt and Murty [133], and Ramakrishnarao et al. [134] have extensively employed this model.

Despite the significant progress that has been made in predicting the glass-forming ability (GFA) of various alloys since the inception of the Miedema model, the contribution of elastic enthalpy to GFA has frequently been

intentionally disregarded or presumed to be substantially reduced [132–135]. An effort has been made to incorporate the contribution of elastic enthalpy in the estimation of glass-forming tendencies in Mg–Zn–Ca alloys by introducing a new thermodynamic parameter, P_{HHS}, which considers the enthalpy of chemical mixing (ΔH_{chem}), elastic enthalpy ($\Delta H_{elastic}$), and configurational entropy ($\Delta S_{config}/R$). This was initiated recently. The model's predictions have been corroborated by experimental results and literature [136].

Discussion & Future Prospects

Improving both the mechanical strength and corrosion resistance of Mg–Zn–Ca metallic glasses is essential for their suitability as orthopaedic implants [137]. For orthopaedic applications, a biodegradable implant material should possess robust mechanical strength, ductility, and corrosion behaviour that meets the allowed corrosion rate of 0.02 mm/year for at least 12 weeks [138]. Even though research is still going on, Mg–Zn–Ca metallic glasses are not thought to have enough mechanical and corrosion resistance for use in bioimplants [139]. To solve this problem, new research has looked into adding yttrium (Y) to magnesium-zinc alloys. This makes the alloys stronger and more flexible by creating different intermetallic phases [140].

The icosahedral I phase Mg_3YZn_6, the hexagonal H phase $MgYZn_3$, and the hexagonal Z phase $Mg_{12}YZn$ are some of the intermetallic phases that help improve the mechanical properties [141]. Biocompatibility is crucial for any potential biomaterial, and for orthopaedic applications, it must facilitate osteoblast contact [142, 143]. Research into multifunctional materials that simultaneously exhibit strong cytocompatibility and corrosion resistance holds significant potential. Recent studies suggest that the corrosion resistance of Mg–Zn–Ca metallic glasses can be tuned by adjusting the alloy composition [109].

To avoid harm to the organism caused by the alloy's disintegration of toxic components, biodegradable implants must be biocompatible. The corrosion of metal implants can trigger various immunological reactions, including Form IV delayed hypersensitivity, which involves immune suppression and a foreign body reaction [143]. Incorporating silver (Ag) into Mg alloys can enhance biocompatibility and resolve infection issues during implant surgery due to Ag's antibacterial properties [115]. There isn't a lot of research on alloying Ag with Mg alloys], which shows how important it is to find biodegradable materials that are better at resisting corrosion, getting along with living things, and having better mechanical properties [144].

A promising approach involves reinforcing Mg–Zn–Ca glass-forming alloys with suitable particles, such as hydroxyapatite (HAp) [116], a mineral component of natural bone known for its outstanding biocompatibility and bioactivity [145]. Mg–Zn–Ca–HAp composites could be used as bioimplants because they help osteoblasts grow and bone cells stick together. However, HAp doesn't dissolve well in the body [146]. Despite the extensive literature on Mg–Zn–Ca–HAp composites, researchers have conducted limited studies on composite production in Mg–Zn–Ca glass-forming alloys [116].

These new findings make it easier to choose Mg–Zn–Ca metallic glasses for use in biomedical settings. They also make it possible to create multifunctional materials that are better at mechanical properties, resist corrosion, and work well with cells. Combining Mg–Zn–Ca-based glass-forming alloys with HAp reinforcement holds promise for developing an ideal bioimplant material with suitable mechanical properties, corrosion behaviour, and cytocompatibility. Figure 6 illustrates a comparison of corrosion current density for various Mg–Zn–Ca-based metallic glasses, showcasing the potential of partially amorphous samples in enhancing corrosion resistance, even in larger diameters. This mix of partially amorphous Mg–Zn–Ca–Ag/Y/Sr glass-forming alloys and HAp reinforcement could be a higher step forward in the progress of making bioimplant materials.

Thus, section thickness, corrosion resistance, ductility, and biocompatibility must be improved to make these implants useful in biomedical applications. Creating magnesium-based biodegradable orthopaedic implants with an ideal mix of mechanical characteristics, corrosion resistance, and cytocompatibility, combined with a considerable sample diameter growth, is crucial. As advancements are made in the area of modern materials [147], it is very probable that magnesium-based nanocomposite implants will have a significant impact on the future of orthopaedic surgery. These implants will offer safer, more efficient, and more durable options for bone repair and regeneration.

Conclusion

Magnesium stands out among various metals as a capable contender for biodegradable orthopaedic implants owing to its inherent biocompatibility and biodegradability, coupled with mechanical properties that align with those of natural bone. However, a crucial challenge lies in mitigating the corrosion rate of Mg alloys to extend their degradation period until complete bone formation occurs. Among the various strategies employed to enhance corrosion behaviour, Mg-based metallic glasses have recently emerged as a breakthrough for biodegradable implants. These materials surpass their crystalline counterparts, offering high strength, elasticity, and superior corrosion resistance. Mg–Zn–Ca metallic glass, in particular, has demonstrated significant promise due to its physiological compatibility. Previous attempts to

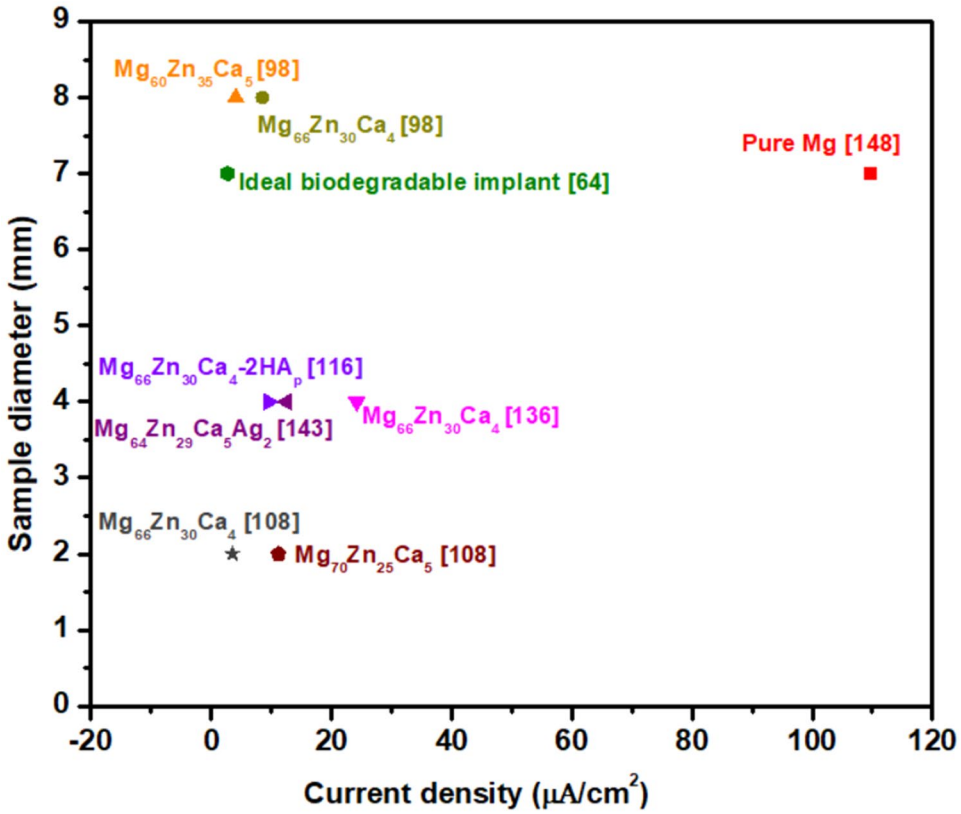

Fig. 6 Comparison of corrosion current density for various Mg–Zn–Ca-based metallic glasses

produce Mg–Zn–Ca bulk metallic glasses using solid-state, liquid-state, and vapour-state methods resulted in a maximum diameter of only 4–5 mm and a higher corrosion rate than ideal for biodegradable implants. Additionally, their limited ductility hinders conventional usage. Consequently, there is a pressing need to enhance section thickness, corrosion resistance, ductility, and biocompatibility to propel these implants into practical biomedical applications. Hence, in the field of orthopaedic implants, creating magnesium-based biodegradable implants with an optimal balance of mechanical properties, corrosion resistance, and cytocompatibility, along with a significant increase in sample diameter, is of paramount importance.

This article aimed to explore larger diameter Mg-based glassy bio-implants with improved corrosion behaviour, ductility, and biocompatibility for biodegradable orthopaedic implants. This review demonstrates that by optimizing alloy elements, superior corrosion resistance, mechanical behaviour, and biocompatibility can be achieved in Mg-based biodegradable alloys. The creation of biodegradable implants made of Mg that have better sample diameter, excellent corrosion resistance, and biocompatibility is a higher step forward in the field of multifunctional materials that combine mechanical properties, corrosion resistance, and cytocompatibility. These investigations pave the way for the development of the ideal biodegradable orthopaedic implant. The review covers topics including biomaterials, thermodynamics, materials engineering, corrosion studies, mechanical behaviour, biodegradation, and biocompatibility. Hence, this review article advances the potential for a biodegradable implant in orthopaedic applications.

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Data Availability Upon reasonable request, the corresponding author will provide the datasets that were generated and analysed during the current study.

Declarations

Conflict of interest The author has no relevant financial or non-financial interests to disclose.

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