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POROUS MAGNESIUM AND ITS APPLICATION

The metallic biomaterials are being revolutionized with the development of biodegradable materials including several metals, alloys, and metallic glasses. As such, the nature of metallic biomaterials is transformed from the bioinert to bioactive and multibiofunctional ones. Magnesium-based biomaterials are candidates to be used as new-generation biodegradable metals. Magnesium can dissolve in body fluid; this means that the implanted magnesium can degrade during the healing process, and, if the degradation is controlled, it would leave no debris after the completion of healing. Researchers have been working on synthesis and characterization of Mg-based biomaterials with a variety of composition to control the degradation rate of magnesium since uncontrolled degradation could result in loss of mechanical integrity, metal contamination in the body, and intolerable hydrogen evolution by tissue. As observed, the applied methods of synthesis and the choice of components affect the characteristics and performance of the Mg-based biomaterials.

Keywords: biodegradable materials, Mg-based biomaterials, synthesis, characterization.

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1. Introduction

Biomaterials can be classified into four different groups as metals, ceramics, polymers, and composites. Among these groups, ceramics such as calcium phosphate are widely used as coating materials because they exhibit non-toxicity, good biocompatibility and osteoconductivity [1]. However, these ceramics have poor mechanical properties and high corrosion rates in acidic environments; this limits their use as bone implants in high load areas [1]. Polymer biomaterials are widely used for bone tissue engineering applications because they can be formed into complex shapes, and their surface properties are easy to modify. In addition, the chemical and mechanical properties of polymers can be changed to some degree during sterilization. However, polymer applications are limited due to their poor mechanical properties. In addition, some toxic additives such as plasticizers, anti-oxidizers, or stabilizers used in the synthesis of polymers can harm the host tissue causing it to combine with body fluids [2]. Metal implants are usually preferred for repairing fractures due to their excellent mechanical properties [3]. Stainless steels, cobalt and titanium alloys are most of the examples for commercially available bone implants. Metal is preferred for durable, load-bearing implants because it exhibits high strength and exceptional ductility leading to high fracture resistance [3]. In addition, metal objects with complex architectures can be produced through a variety of available production methods such as casting, machining, and powder metallurgy (PM) [3]. Biocompatibility and mechanical properties that match the bone are two important factors for implants [3]. The biocompatibility of metal plants is affected by corrosion and wear. In metal implants, harmful metal ions arising from corrosion and wear can cause inflammation, cell apoptosis and other damaging tissue reactions [3, 4]. It was reported that the release of Cr (Co–Cr alloys), Nb, V and Ni (Ti-based) ions can cause adverse tissue reactions by exceeding the concentration limits of these elements in tissue or body fluids [3, 4]. Ni, for example, is a highly cytotoxic, genotoxic, carcinogenic, and mutagenic element.

Mg and its alloys differ from other biomaterials by displaying compatible mechanical and physical properties in human bone. Their density and modulus of elasticity are close enough to each other to eliminate the elastic mismatch between plant and bone [5, 6]. In addition, Mg is naturally present in the composition of bones, and is one of the metals needed for metabolism [7]. However, the fundamental problem of Mg-based implants is their low corrosion resistance, which results in undesired and rapid degradation in living systems. Research investigations have been aimed at improving corrosion resistance and offering industrially applicable Mg-based biodegradable implants. Moreover, Mg-based

biodegradable implants are projected to change the direction of the medical sector soon as their commercial products begin to appear on the market. The implant material is desirable to have mechanical properties very similar to those of bone. However, in current practice, most of the metals used in biomedical applications exhibit much higher mechanical properties than bone. This causes the well-known stress-protective phenomenon; the result is decay of bone material and loss of strength. Stress shielding occurs when the implant carries a higher proportion of the applied load; adjacent bone is exposed to the reduced load and loses its density in response [4, 8]. Among metallic implants, Mg alloy stands out as having Young's modulus that is most similar to that of cortical bone (Mg: 40–45 GPa, cortical bone: 10–27 GPa) while Young's modulus for Ti and 316L-based stainless steels are respectively 110 and 193 GPa [4, 8]. Biodegradable metal implants are a new generation of metallic implants that exhibit increased corrosion resistance in body fluids during the healing process of host tissues [9]. Its main task is to support the host tissue with a slow corrosion rate in body fluids, and then dissolve completely after healing of the host tissue without implant debris [9, 10]. Among the biodegradable metal implants, Mg, Fe and Zn, also known as smart implants, have been extensively researched in recent years. The most significant challenge with biodegradable plants is to maintain their mechanical integrity during the healing period of host tissues [11]. Mg and Fe based implants showed good mechanical properties as hard tissue implants.

However, the high corrosion rate of Mg-based materials and very low corrosion rates of Fe-based materials limit their application as biodegradable implants. Thus, the degradation rate of pure Mg should be increased through alloying and surface engineering for use as biodegradable metal implants [11, 12]. This study aims to present a comprehensive and critical review of the latest research and technological advances in Mg-based biomedical implants.

2. Magnesium Alloy Characteristics

Alloying is one of the methods in which different metals at different concentrations can be added to increase the ductility, strength, and corrosion properties of pure Mg. The increase in strength and corrosion is mainly related to the modification of the microstructural characteristics; particularly, the reduction in grain size compared to pure Mg. Most studies investigating Mg alloys have focused on improving all these characteristics for commercial purposes. Therefore, most of the research on biomedical Mg alloys is carried out with alloys originally developed for the aerospace, defence, and automotive industries [13]. Generally, Mg alloys contain aluminium (Al) or rare-earth elements

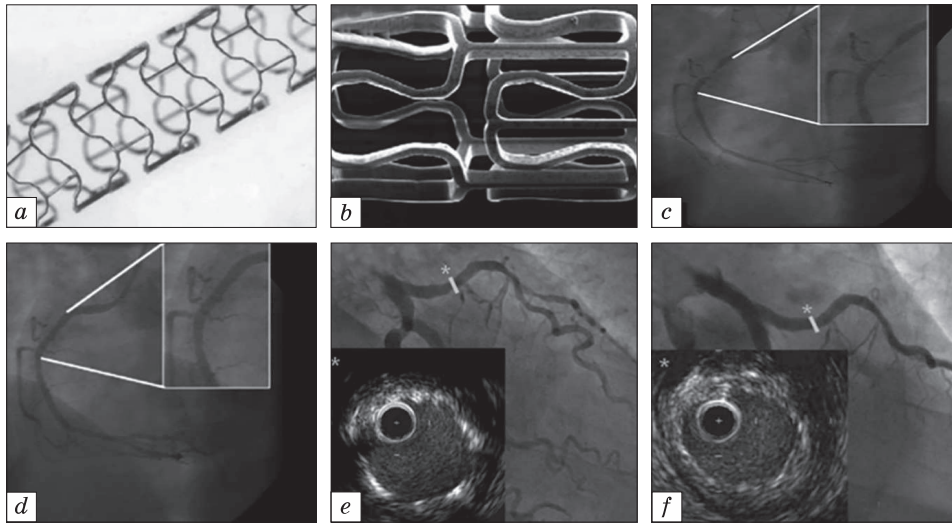


Fig. 1. Clinical trials of Mg-based alloys. Bioabsorbable Mg stent (BIOTRONIK, Berlin, Germany) after (a) expansion and before (b) expansion. High-grade stenosis of the proximal right coronary artery before (c) and after (d) Mg stent implantation. Coronary angiogram after Mg stent implantation (e) and after 4 months (f). The angiogram showed an open vessel lumen with no signs of luminal narrowing or edge effect. Adopted from Ref. [16]

(REE) [14]. Al is known to be neurotoxic, and its accumulation is associated with various neurological disorders such as Alzheimer's disease, dementia, and senility. On the other hand, severe hepatotoxicity was seen after application of REEs such as praseodymium, cerium, and yttrium. Thus, the researchers have recently concentrated on investigating the biologically safe Mg alloys, which consist of non-toxic elements such as Ca, Zr, Zn and Mn. Other alloying components under investigation include Sr, Li, Sn, Si, Bi, Cd, and Ag. Mg alloys can be binary, ternary or more. The components and composition of the alloy contribute to the various mechanical properties as well as the corrosion behaviour of Mg. Alloying with Al increases the corrosion resistance of Mg. AZ31, AZ61, and AZ91 are common Mg–Al–Zn alloys with moderate corrosion rates. Zn is one of the common alloying elements for Mg [15]. In Figure 1, it can be seen the properties of magnesium in bioabsorbable in implantation process which could control the corrosion rate [16].

Calcium is another well-known alloying element that accelerates bone growth. Mechanical properties and corrosion properties of Mg–Ca alloys can be adjusted by controlling the Ca content [14]. REE is another common combining element of Mg alloys. The addition of REE to the Mg–Al–Zn alloy is reported to increase further the corrosion resistance [1]. Incorporating of Ca in Mg alloys increases corrosion resistance

[17]. Li *et al.* [14] prepared a binary Mg–Ca alloy at a Ca content varying from 1 to 20 wt.% to investigate the biodegradability in bone. Alloys with high Ca content, including Mg–5, 10 and 20Ca, were found to be very brittle. Mechanical properties and biocorrosion behaviour of Mg–Ca alloys can be controlled by controlling the Ca content. The yield strength (YS), ultimate tensile strength (UTS), and elongation for as-cast Mg–Ca alloy samples decreased with increasing Ca content. The results of the cytocompatibility evaluation showed that the Mg–1Ca alloy did not cause toxicity to cells. Both in vitro and in vivo evaluations demonstrated the formation of a mixed layer of Mg(OH)₂ on the surface of the Mg–1Ca alloy during the immersion and implantation periods [14]. A similar study by Rad *et al.* [18] suggested Mg–0.5Ca alloys as promising candidates for biodegradable implants due to their high corrosion resistance. Knowing that incorporating Ca reduces the rate of degradation, Ca-containing Mg alloys have been investigated for their degradation behaviour and mechanical integrity. The addition of Ca is considered to increase the corrosion behaviour of Mg alloys. The immersion test of AZ91Ca into modified simulated body fluid (SBF) showed only a marginal reduction in UTS of 15% and extension to fracture of 20% [19]. The addition of Zn is also reported to increase the corrosion resistance of Mg alloys. In vivo degradation properties of Mg–Al–Zn alloy implanted intramedullary into rabbit femora was investigated in Ref. [20]. After a period of nine weeks, microscopic evaluation revealed the formation of a thin layer of calcium phosphate around the implant. The in vivo degradation rate of Al–Zn containing Mg alloy AZ31B is slower than that of pure Mg [20]. Other Mg alloys containing zinc Mg–6Zn have been investigated in Ref. [21]; obtained results are very similar to the previous study [20].

A new Mg-based alloy (LANd442) containing 90 wt.% Mg, 4 wt.% Li, 4 wt.% Al, and 2 wt.% Nd was developed by Hampp *et al.* [22]. The biocompatibility of this alloy was investigated in a rabbit model for 26 weeks. In this period, a relatively slow degradation was observed with the LANd442 alloy. Additional bone formation at the implant site, as well as the accumulation of a small amount of subcutaneous gas, is observed. The LANd442 Mg alloy causes a considerable non-inflammatory bone remodelling process in which new bone growth in the periosteal region predominates. For this reason, this study suggests that LANd442 appears to be a less suitable implant material for cortical bone applications [22]. Following this study, Hamp *et al.* investigated the early times of the healing process as this could represent a possible early occurrence of the bone-remodelling phase. They investigated the biocompatibility of two Mg-based alloys LAE442 and LANd442 and compared them with titanium in the first 4 and 8 weeks of implantation. This study identified interesting changes in bone structure at the earliest

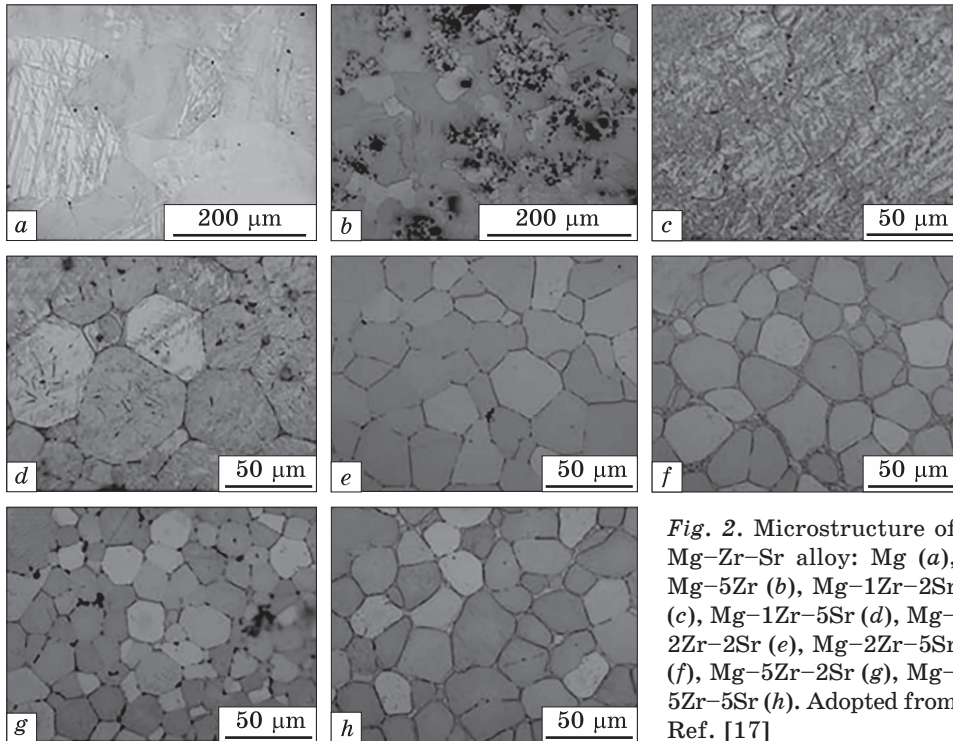


Fig. 2. Microstructure of Mg-Zr-Sr alloy: Mg (a), Mg-5Zr (b), Mg-1Zr-2Sr (c), Mg-1Zr-5Sr (d), Mg-2Zr-2Sr (e), Mg-2Zr-5Sr (f), Mg-5Zr-2Sr (g), Mg-5Zr-5Sr (h). Adopted from Ref. [17]

stages of implantation of Mg and Ti alloys. The studied Mg alloys also revealed good clinical tolerance, which allowed their assessment as suitable osteosynthesis materials. However, compared with studies with a longer implantation period, this short-term biocompatibility cannot infer a long-term effect. Thus, it is suggested that for a complete conclusion [23]. Most research studies report promising results for the application of Mg alloys as implant materials. Desired mechanical properties, biocompatibility, and biodegradability are attractive features for selecting implants. It is believed that Mg and Mg alloys are a new generation of biomaterials and will play an important role in revolutionizing orthopaedic, cardiovascular, and dental applications [24]. Microstructures such as grain size, grain boundaries, and phase distribution have a significant effect on the corrosion performance of Mg alloys. Grain refinement causes changes in grain boundary density and distribution, which changes the mechanical properties and corrosion properties of Mg alloys as shown in Figs. 2 and 3 [17]. The alloying elements applied by the metallurgical process and the process conditions have an influence on the microstructure of the Mg alloy [25–28].

The hierarchical structure of the bone must be considered in the design of bone implants [29, 30]. For example, human compact bone is

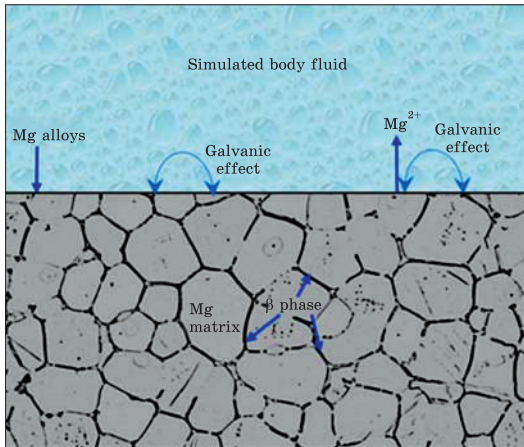


Fig. 3. Galvanic effect on the Mg matrix and the second phase produced during accelerated corrosion of Mg alloys. Adopted from Ref. [17]

a composite material with a hierarchical architecture from the macro to the nanoscale. Human compact bone can be described as follows. Osteons are fibres with a diameter of 200 m consisting of parallel lamellae and pores.

Lamellae are made of them, which are constructed from fibrils. Thus, multiple scales must be considered to achieve a high degree of compatibility with the host tissue [29]. There are important factors that must be considered to improve implant biocompatibility such as corrosion rate, strength, wear resistance, flexibility, and water solubility [29]. In addition, porosity, cavities, or channels at the microscale play an important role in cell proliferation and growth into implants [29]. Individual surface parameters such as roughness, chemical composition, electric charge, wettability, and crystallinity play an important role in terms of compatibility [29]. The most important factor for achieving a high degree of compatibility between the implant and the host tissue is the surface properties of the implant. In addition, the surface properties have a significant influence on stress protection, wear resistance and fatigue failure. In addition, the implant surface is a major factor in the success or rejection of implant material because it is in direct contact with the surface of the host tissue. Surface roughness is a key factor for the degree of osseointegration and mechanical fixation of implants to bone [31]. It has been demonstrated that surface roughness in the microscale range increases the rate of new bone formation due to increased protein adsorption and cellular activity [31]. As shown [32], the shear strength of bone implants increased by increasing the surface roughness from 0.058 to 4.25 μm . In another study, bond strength was increased (0.38–9.70 MPa) by increasing the surface roughness (S_a) value (0.2–4 μm) [33]. The S_a value of the Mg plate was measured between 5.66 and 6.44 m. Previous studies have shown that optimal surface roughness increases the bond strength of bone implants. Rønold *et al.* [33] investigated the effect of surface roughness on the integrity of bone implants. They showed that the best bone implant integrity was achieved at $S_a = 3.90$ m and there was a significant decrease in bone implant integrity by increasing the S_a value from 5.07 to 11.03 μm [34]. In another

study, there was a significant increase in bone cell activity by increasing the surface roughness from 0.37 to 3.29 μm [35]. Pore size and pore morphology have a significant effect on cell attachment and proliferation. It is proven that pores with hexagonal morphology increase cell attachment more than round pores. In addition, in vivo studies show that the risk of infection decreases with increasing pore size after implantation (0.1 mm). On the other hand, the increase in pore size has a negative impact on the mechanical properties of the implant. The implants exhibited brittle behaviour when the pore size was increased from 100–200 to 350–450 μm . Thus, increasing the pore size decreases the modulus of elasticity, shear strength and compaction strength [36].

The combination of random macro-, micro-, and nanoscale roughness on the implant surface enhances the integrity between the implant and the host tissue. Roughness of the implant surface increases protein accumulation and as a result increases cell adhesion [37]. Thus, mimicking the bone surface with micro and nanotextures can enhance osteointegration due to increased mineral deposition [38]. Prodanov *et al.* [36] producing three different surface patterns (150, 300, and 1000 nm). In vitro results prove that the best mechanical integrity is achieved on surfaces with a roughness of 300 nm [37]. Brändemark *et al.* [38] modify the implant surface using laser technology. It was reported that the rate of new bone formation in the contact area was increased due to bone bonding at the nanolevel. In addition, pore size has a significant influence on implant behaviour in vivo. The shear stress is increased by increasing the pore size from 100 to 200 μm whereas by increasing the pore size from 200 to 300 μm , the pore size is decreasing [39]. Optimal surface roughness should be found to enhance cell attachment, but it is not a major factor in cell integration. The optimum size for roughness may depend on the actual size of the cells used in the in vitro study. Mirhosseini *et al.* [39] investigated the effect of laser pattern on cell attachment for Ti6Al4V implants. The patterned surface promotes 2T3 osteoblast cell growth and uniform cell adhesion. While surface smooth cells accumulate on implants in areas close to the nursery centre [40].

It is very important to have adequate and proper mechanical properties for a biomedical implant during its life cycle. The durability of the implant structure is a top priority issue for patient safety because the implant's role is to support physically damaged tissue during the healing process. In addition, a biodegradable implant that has the highest mechanical properties does not necessarily mean that it will perform the best. For example, a very large difference between the modulus of elasticity of the implant and the damaged bone can cause elastic mismatches and lead to stress shielding especially in metallic biomaterials used for orthopaedic applications. There are many ways to improve the mechanical performance of biodegradable implants, at least but not less

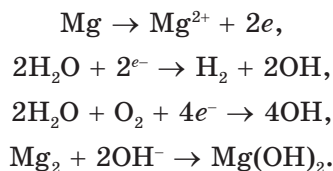
[41]. Mg is one of the most important elements built in the human body where it is involved in many enzymatic reactions. It is reported that Mg occurs in the processes of protein and nucleic acid synthesis, plasma membrane stabilization and many other cellular activities [13]. The amount of Mg in the average adult human body is about 21–28 g and more than 50% of it is in bone tissue. Soft tissue contains 35–40% of this content and less than 1% is sequestered in serum [13]. Elemental Mg sequestered in bone, acts as a reservoir for acute changes in serum Mg levels. The bivalent ion Mg 2⁺ plays an important role in determining bone fragility. It is also known that Mg 2⁺ ions occur in the process of transforming immature bone into mature bone. The content of Mg ions in bone mineral is about 6 mol.% but this content decreases during

Table. Mechanical properties of the Mg alloy powder formation process

Mg alloy	Tensile strength, MPa	Yield strength, MPa	Elongation, %	Young modulus, GPa	Compression strength, MPa	Bending strength, MPa	Refs.
Mg-4.0Zn-0.2Ca (extruded)	297	240	21.3	45	–	–	[43]
Mg-Zn-Y-Nd (hot-extruded)	316	183	15.6	–	–	–	[44]
Mg-Zn-Y-Nd (CECed)	303	185	30.2	–	–	–	[44]
Mg-1.5Y-1.2Zn-0.44Zr (hot-extruded)	236	178	28	–	471	501	[45]
Mg-3Sn-0.5Mn	240	150	23	–	–	–	[46]
Mg-3Al-4Zn-0.2Ca	198	–	10.3	44.1	–	347	[47]
Mg-2Zn-0.5Ca-Mn (heat-treated)	205	–	15.7	–	–	–	[48]
Mg-5.3Zn-0.6Ca + 1.0Ce/La (extruded)	202	–	–	–	–	–	[49]
Mg-1Mn-2Zn-1.5Nd (extruded)	>285	–	>14	–	>395	–	[50]
Mg-Gd-Zn-Zr-Mn (extruded)	341	315	21.3	–	–	–	[51]
Mg-Gd-Nd-Zn-Zr (extruded)	267	217	–	–	–	–	[52]
Mg-Zn-Y-Nd (ECAP)	239	96	30.1	–	–	–	[53]
Mg-Zn-Y-Nd (CEC)	280	194	29.4	–	–	–	[53]
Mg-Zn-Y-Nd (extruded)	242	170	20.9	–	–	–	[53]

the bone maturation process. Immature cartilage and bone tissue contain high concentrations of Mg 2^+ ions but these concentrations change depending on aging. In addition, the presence of Mg in the bone composition increases the elasticity of the bones [13]. The effect of Mg on bone formation has been investigated in previous studies. The presence of Mg has a significant effect on the differentiation of osteoblast cells. Bone formation around and above the degraded Mg implant has been shown to influence accelerated bone healing. In addition, it is proven that the human body can tolerate the H gas released during the degradation process of Mg and its alloys. However, the high amount of hydrogen gas released can cause complications during the healing period. Thus, the corrosion rate of Mg must be controlled to reduce the risk of gas accumulation. The amount of gas expelled from the implantation site also depends on the implant site and available blood flow [42]. The mechanical properties of the Mg alloy powder formation process can be seen in Table.

Corrosion of Mg and its alloys is an electrochemical process [54]. It is known that the process in an aqueous environment is different from the oxidation process in air [55]. The mechanism of Mg corrosion in aqueous environment can be explained by the following reactions [54–56]:



The large amount of hydrogen gas evolution during the anodic reaction results in a decrease in the speed of the cathodic reaction, which is known as the phenomenon of negative difference effect [1, 57]. The formation of a moderate protective layer during the cathodic reaction reduces the rate of the cathodic reaction. However, this protective layer was not strong enough. Therefore, they break down before initiating anodic polarization [57]. The degradation behaviour of Mg and its alloys is affected by different parameters such as aqueous environment, composition, structure, surface structure, alloying elements, impurities, secondary phase, and manufacturing method [56]. Mg and its alloys exhibit unexpected behaviour in physiological environments due to the presence of dissolved oxygen, proteins, amino acids, chloride, and hydroxide ions in Fig. 4 [56, 59]. Adsorption of amino acids, proteins and lipids on the surface changes the rate of degradation of Mg and its alloys [56, 59]. In addition, $\text{Mg}(\text{OH})_2$ acts as a protective layer resulting in increased corrosion resistance. However, the high chloride ion concentration in the physiological environment damages the protective layer of $\text{Mg}(\text{OH})_2$ causing pitting corrosion [9, 60]. The mechanism of cor-

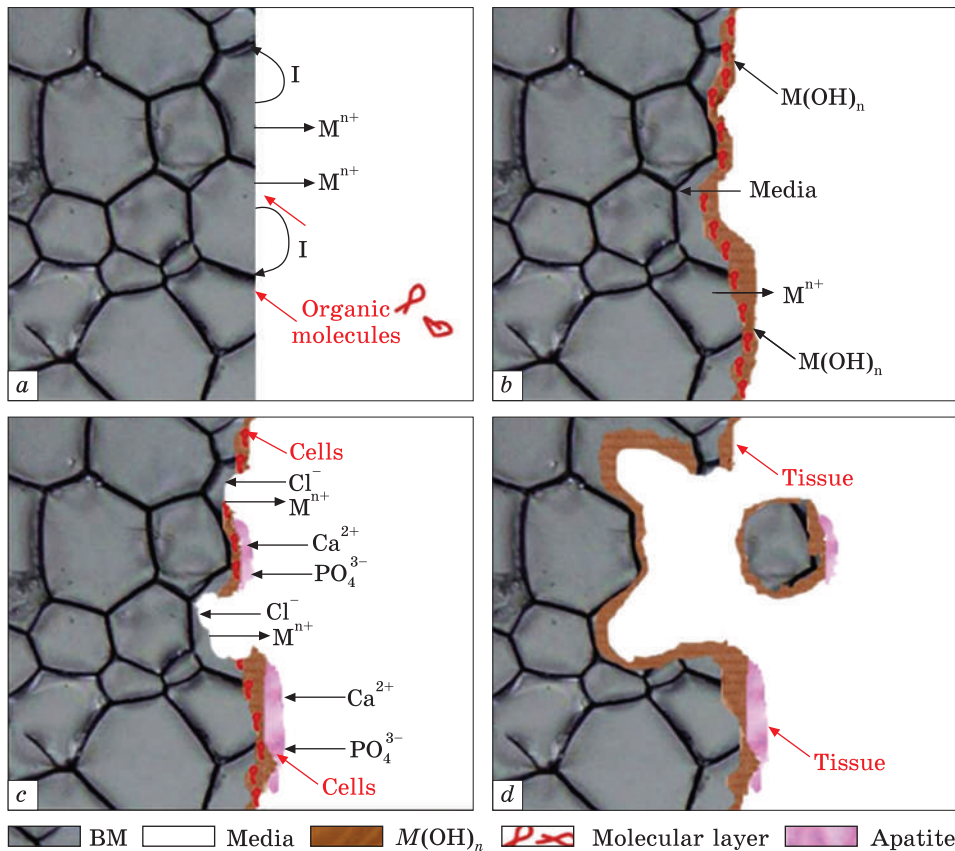
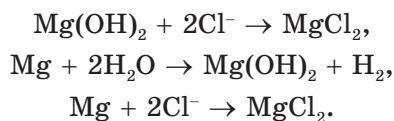


Fig. 4. Illustration of the degradation mechanism at the BM/medium interface, where BM is so-called ‘biodegradable metal’ — Mg in our case. Adopted from Refs. [9, 55]

rosion of Mg in the presence of chloride ions is described as follows:



The formation of a layer of MgCl_2 on the surface reduces the corrosion resistance because it is known that MgCl_2 is quite soluble [9, 60, 61]. However, it is biocompatible and shows no cytotoxic effect [9]. Furthermore, the high concentration of hydroxyl ions in the environment increases the alkalinity and the presence of calcium and phosphate ions causes the deposition of a protective layer of calcium phosphate on the surface [56]. The presence of buffering agents such as HCl-Tris and Hepes, which are used to neutralize the pH value of SBF, accelerates the corrosion rate of Mg-based implants by consuming OH ions [9]. Thus, the consumption of OH ions causes a decrease in the formation of cor-

rosion products and an increase in the corrosion rate. On the other hand, adsorption of protein (fetal bovine serum) on the surface of Mg implants increases the corrosion resistance [9]. It is known that insoluble salts precipitate on the surface of Mg in the presence of proteins which form an insoluble solid layer on the surface. This protective layer increases corrosion resistance [55, 57]. It is reported that impurities and secondary phases play an important role in the corrosion resistance of Mg and its alloys. There is a difference between the potential of the Mg reference electrode and the impurity/secondary phase resulting in a micro-galvanic cell [1, 54, 57, 59]. The corrosion rate of pure Mg increases in the presence of impurities such as Fe, Ni, Cu, and Co due to the higher potential of the standard electrode [57]. It is recognized that the secondary phase has a significant effect on the galvanic corrosion resistance of Mg and its alloys. The secondary phase can act as a corrosion barrier or act as a galvanic cathode [63–65]. The number of secondary phases, grain size, depositional sites and reference electrode potential must be considered to determine their effect on the corrosion rate [63–65]. It was reported that the second phase with finer grain size deposited along the grain boundaries increased the corrosion resistance while the high corrosion potential of the secondary phase increased the corrosion rate [65, 66].

3. Mg-Based Composites for Biomedical Implant Applications

The biodegradability of Mg alloys makes them suitable for orthopaedic implants. Many studies have shown that the design of Mg alloys with a controlled degradation rate is needed. The development of new composites based on Mg alloys with other systems could be a promising solution to meet this demand [67]. Researchers have combined different types of ceramic and polymeric materials with Mg and Mg alloys to form Mg-based composites through various manufacturing routes and investigated their effects on corrosion resistance, mechanical properties, and biocompatibility. In ceramic composites, Mg and Mg alloys are used as a matrix and the matrix is reinforced with ceramics. While in polymer composites, Mg and Mg alloys are usually added to strengthen the polymer matrix.

Composites consisting of various Mg alloys as matrix and various ceramics as reinforcement, with different fabrication routes, have been extensively investigated to assess their viability in biomedical applications. A group of biomaterials having similar characteristics to the bone mineral moiety appears very promising for hard tissue engineering applications. This group includes calcium phosphate, especially hydroxyapatite (HA), beta-tricalcium phosphate (β -TCP) and biphasic calcium phosphate (BCP) which is a combination of HA and β -TCP [67]. Calcium

phosphate induces ion adsorption and deposition of calcium phosphate minerals on the composite surface, which stimulates bone growth. However, its mechanical properties cannot compete with bone. A possible solution to this can be obtained through the development of a calcium phosphate composite with an alloy matrix of Mg and Mg. The research group evaluated the incorporation of HA into pure Mg and Mg alloys such as AZ91D and MgCa. Metal matrix composite (MMC) consisting of Mg AZ91D alloy matrix and HA reinforcement. The mechanical properties of the composite were found to be very similar to those of natural bone. HA particles stabilize the corrosion rate in artificial seawater and cell solutions. During the immersion test, bone cells were able to adhere and persist on the surface of the MMC-HA composite [68]. Significantly higher compressive strength was observed with the AZ91/HA composite as compared to the HA. Alloy AZ91 shows lower corrosion resistance compared to HA. Therefore, it can cause the recurrence of porous HA and promote bone cell adhesion and proliferation [69]. Compared with the casting method, PM is reported to be a more suitable method to obtain a homogeneous distribution of ceramic particles in the Mg matrix [67]. Therefore, the PM method used by Gu *et al.* [69] to make Mg/HA composites with various HA content (10, 20, and 30 wt.%). The Mg/10HA composite showed a uniform distribution of HA particles. Compared with extruded bulk pure Mg, enhanced YS but reduced UTS and elongation were observed with the Mg/10HA composite. The increase in HA content also increased the corrosion rate of the composite. Cytotoxicity evaluation showed that Mg/10HA was compatible with L-929 cells [70]. To synthesize the nanohydroxyapatite (nHA) reinforced magnesium composite (Mg-nHA), the friction stir processing method was used. The applied method fine-tunes the grain size from 1500 nm to as low as 3.5 nm. The addition of nHA and fine grain size increased the biomineralization in SBF.

The ideal biodegradable material should dissolve gradually along with the process of new bone formation. BCP can be a promising option that is a biomaterial consisting of different proportions of HA and TCP. Appropriate proportions can make it possible to obtain the desired level of degradation. Despite excellent biocompatibility and degradation rates, BCP does not have the required mechanical strength [67]. The strength of the biphasic calcium phosphate scaffold was increased by 200-fold, corresponding to half of the strength of the bulk MgCa alloy, by forming the MgCa-HA/TCP composite by incorporating the MgCa alloy. A slower corrosion rate was obtained with the MgCa-HA/TCP composite compared to the bulk MgCa alloy. In addition, the cytotoxicity evaluation showed that the Mg/10HA composite extraction medium did not cause toxicity to L-929 cells [70]. Mg composites with silica and silicate

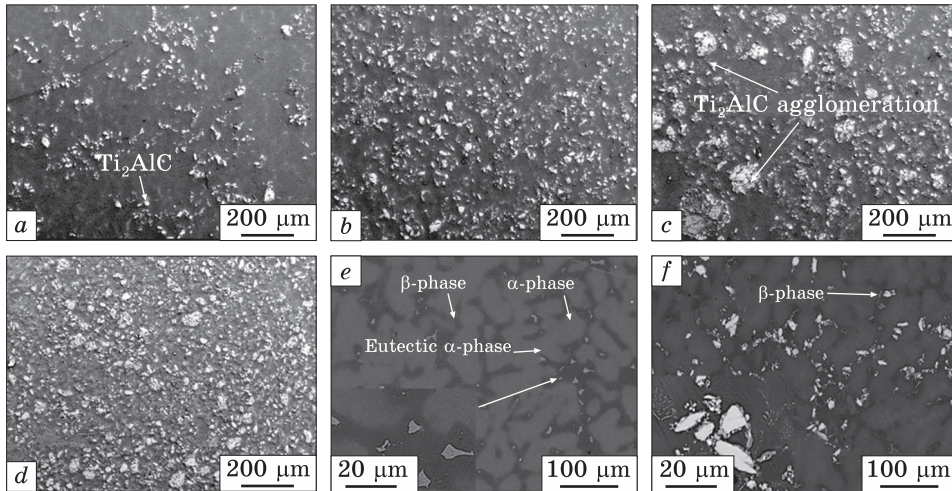
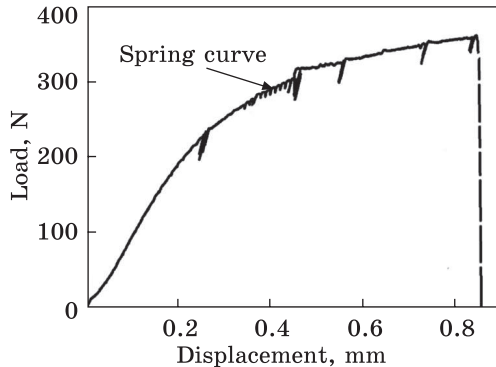


Fig. 5. Scanning electron microscopy images of composites with different fractions of Ti_2AlC : (a) 5 %, (b) 10 %, (c) 15 %, and (d) 20% in the secondary electron (SE) mode; (e) AZ91D cast alloy and (f) 5% in the back-scattering electron (BSE) mode. Adopted from Ref. [74]

Fig. 6. Applied load as a function of displacement for AZ91D/5% Ti_2AlC composite. Adopted from Ref. [74], where detailed description of the interruption points is presented



materials also showed an increase in mechanical properties and bioactivity as well as a decrease in the rate of degradation. Bio-ceramic-based composites are made by mixing HA powder and bioactive glass through the sintering method. Retaining the sample for 14 days in SBF reduced its compressive strength by 65%. In addition to its cytocompatibility confirmed by in vitro biologic evaluation, significant release of silicon ions in SBF was interpreted as a sign of osteoinductivity [71]. In another study, MMC consisting of pure Mg as matrix and bioceramic calcium silicate (CS) as reinforcement was synthesized. The addition of calcium silicate particles increased the compressive strength of the Mg matrix by 30%. The immersion test in SBF showed that the corrosion resistance of Mg increased due to accelerated HA precipitation on the composite surface. Release of Si ions from the calcium silicate phase increased the ability of the composite to stimulate ALP expression of osteoblast-like cells compared to pure Mg [72]. The Mg matrix composite reinforced with bredigite was developed by Dez-

fuli *et al.* [73]. 67% higher ultimate compressive strength and 111% better ductility were achieved through incorporation of 20 vol.% bredigite particles in the Mg matrix. In vitro degradation rate of bredigite Mg-20%, the composite was observed to be 24 times lower than that of monolithic Mg. Therefore, after 12 days of immersion in cell culture media, the mechanical properties of the composites were still comparable to those of cortical bone [73].

Many studies have been conducted to determine the Mg composite reinforced with the MAX phase ($M_{n+1}AX_n$, where $n = 1$ to 3, M is an early transition metal, A is an A-group element, and X is either C and/or N). The MAX phase is applied to a group of more than 60 ternary nitrides and carbides that share a layered structure. The $M_{n+1}AX_n$ layer is characterized by strong covalent $M-X$ bonds that are inserted with the A layer *via* weaker $M-A$ bonds. This inherent nanocoated structure provides a unique combination of metal-like and ceramic-like properties as Fig. 5 [74]. The AZ91D composite reinforced with Ti2AlC by casting method resulted in higher values of yield strength, ultimate and Young's modulus were obtained, and these values increased with increasing volume fraction of Ti2AlC as shown in Fig 6.

4. Summary

Mg is degraded in a physiological environment without eliminating any toxicity. Therefore, this procedure eliminates the need for a second surgical operation for implant removal if the degree of degradation is commensurate with the rate of tissue healing. Several synthesis methods have been applied to synthesize Mg-based biomaterials with different types of material components. The main objective is to achieve controlled degradation. In this regard, after synthesis, in vitro and in vivo studies have been carried out. In addition, the performance of the material and the synthesis process has been evaluated through computational studies. This can result in interconnected porous microstructures with desired pore sizes and distributions, which are important for enhanced biological interactions of the material and the planted environment. Apart from the microstructure, the role of the surface characteristics of the material is very important for biocompatibility. The textured surface enhances cell attachment and proliferation.

Mg alloys, and the formation of Mg composites with ceramics and polymers using several synthetic methods have been studied to improve the mechanical properties and corrosion resistance of Mg. Certain concentration limits for alloying elements, above which are toxic to the biological environment and cannot affect the mechanical properties of the material. The synthesis process and degradation behaviour of Mg-based biomaterials have been studied in silico. There is a need to select

a method to achieve the desired surface roughness, porosity, corrosion resistance and mechanical properties at the same time.

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ПОРУВАТИЙ МАГНІЙ ТА ЙОГО ЗАСТОСУВАННЯ

Металеві біоматеріали зазнають революції з розробленням матеріалів, які розкладаються мікроорганізмами, включаючи кілька металів, стопів і металевих стеккол. Таким чином природа металевих біоматеріалів трансформується з біоінерт-

них у біоактивні та мультибіофункціональні. Біоматеріали на основі магнію є кандидатами на використання в якості металів нового покоління, які розкладаються мікроорганізмами. Магній може розчинятися в рідині організму; це означає, що імплантований магній може руйнуватися під час процесу загоєння, а якщо розпад контролювати, то він не залишатиме відходи після завершення загоєння. Дослідники працюють над синтезом і характеристикою біоматеріалів на основі Mg з різноманітним складом, щоби контролювати швидкість розщеплення магнію, оскільки неконтрольоване розщеплення може призвести до втрати механічної цілісності, металевого забруднення в організмі та неприпустимого виділення водню тканинами. Помічено, що застосовані методи синтезу та вибір компонентів впливають на характеристики та продуктивність біоматеріалів на основі Mg.

Ключові слова: матеріали, які розкладаються мікроорганізмами, біоматеріали на основі Mg, синтез, характеристика.