Magnesium and its Alloy for Biomedical Applications: a Review on Reinforcement philosophies, Mechanical and Corrosive properties

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Abstract

From recent decades extensive research is going on lightweight magnesium and its alloys for applications in medical science. Due to good biocompatibility and reasonable mechanical strength (similar to bone tissue), magnesium and its alloys are potential candidates for biomedical applications as biodegradable implant materials. However, poor corrosion rate and creep resistance of magnesium alloys are major limitations in its wider application for biomedical applications. Development of Magnesium (Mg) metal matrix composites (MMCs) reinforced with bioceramic particles can be sought as a solution to the above challenge. This review gives the comprehensive details of Magnesium (Mg) and its alloys along with the different reinforcement used to fabricate Mg MMCs, emphasizing on their method of fabrication and their mechanical and corrosive properties.

Keywords: *Biomaterials, MMCs, HAP, Stir Casting, Powder Metallurgy, Liquid Infiltration*

1. Introduction

Biomedical engineering stands for the application of the principles, design concepts and different problem-solving skills of engineering in the field combining medicine and biology for public health purposes. This field helps in advancements in health care from diagnosis to monitoring and treatment to recovery. Biomedical engineering has seen quite the advancements in recent times with the rapid increase in the implantable medical devices such as pacemakers and joints replacements in the orthopaedics field. Development in biomaterials has been a boon to the orthopaedics field.

Biomaterials are the materials engineered to interact with biological systems when implanted to heal the defected tissues. Biomaterials have been frequently used in orthopaedics as a substitute for bones and for cartilage regeneration.

Today in medical science, orthopaedic surgery depends on the advancements in biomaterials used for the fractures fixation and replacement of joint. The bone breaks, when the forces on the bone is greater than the strength of the osseous tissue in the bone. This is termed as 'fracture' [1]. Metallic pins with external frame are used to fix the fractured bone in place, after the fracture heals these pins along with the frame are removed. In some cases, surgery is carried out and the bone pieces are fastened together with rods, metal screws, etc. These implants cause infections due to their degradation at the implant site. The factors of major relevance in the advancement of biomaterials are non-toxicity in biological environment, good corrosion resistance and ample mechanical strength.

Biological materials being used are metallic, ceramic and polymeric materials. Compared to ceramics and polymers, metallic materials have find wide usage in orthopaedic applications because of their high mechanical strength [2]. Generally used metallic materials includes stainless steel, titanium alloy and cobalt-chromium alloy etc. However, these materials do not degrade in the body environment and after the bone heals requires secondary removal surgery. Moreover, these implants can lead to stress shielding effect because of the difference in Young's modulus between the bone and the implant [3]. Thus, developing biodegradable, light weight and biocompatible materials for implants without losing their strength are demanding.
Magnesium and its alloys are the promising candidates for the above-stated requirements. Magnesium provides good mechanical compatibility compared to the biodegradable polymer materials, such as polylactic acid (PLA) [4]. Magnesium due to its corrosive nature is biodegradable in the body environment. The densities of magnesium and magnesium alloys are 1.738 g/cm^3 and 1.75-1.85 g/cm^3 respectively. These densities are comparable to the human bone density (1.75 g/cm^3) [5]. Magnesium is the fourth most copious ion present in the human body and it plays a vital role in various metabolic reactions and biological mechanisms. Owing to its biodegradability, magnesium has attracted a great deal of attention because there is no need for another surgery for implant removal [6].

One of the major concerns associated with magnesium based implants is the rapid degradation in the body fluid, and hence their mechanical stability is lost before the bone tissues have wholly developed [5]. Complete degradation of magnesium implants is intended but at the pace of bone healing. One of the ways to enhance corrosion resistance of Mg and its alloys is to fabricate bioactive ceramics reinforced metal matrix composites (MMCs). The advantage of using MMCs lies in its adjustable mechanical and corrosion properties. These properties can be attained by the selection of suitable matrix and reinforcement in various concentrations.

Over the past years, the various fabrication methods and reinforcements has been used as presented in table1:

Table 1: Fabrication methods and Reinforcements used for development of Magnesium Composites for Biomedical Applications

Alloy	Reinforcement	Method	Remarks	Authors
AZ91D	HA (hydroxyapatite)	Powders of HA and AZ91D were mixed in an AZ31 can and extruded at 400^{o}C. Samples were obtained by machining the extruded rod.	Corrosive and mechanical properties are largely influenced by the size and distribution of reinforced particles. HA particles improved the corrosion resistance of Mg MMC.	Frank Witte et al [7].

Mg	HAP (hydroxyapatite)	**Stir Casting** HAP powder was added to molten Mg at 700°C and stirred homogeneously, then ingots were homogenized at 400°C, machined and extruded at 320°C to obtain samples.	Addition of HAP is responsible for grain refinement. Addition of HAP increases compressive strength and decreases tensile strength and hence brittleness.	Asit Kumar Khanra et al [8].
ZK60 A	CPP (Calcium polyphosphate)	**Powder Metallurgy** A 3-D blending machine was used to mix the powders. After that mixture was cold-pressed into a cylindrical compact. Under 150MPa pressure and at 380°C the compact was hot pressed. Finally, hot extruded to obtain sample material.	Higher compressive strength. Decrease in both ultimate strength and yield strength was observed with CPP addition. Elastic modulus (E) increased with CPP addition from 0% to 20% and then decreased. Composite more corrosion resistant as compared to ZK60A alloys.	Ailing Feng, Yong Han [9]
MgCa	HA/TCP (tricalcium phosphate)	**Liquid alloy infiltration technique** Composites were prepared by infiltrating molten MgCa alloy into porous scaffold using vacuum suction casting machine.	Composite compared to MgCa alloy exhibited inferior mechanical properties. Composite compared to original HA/TCP ceramic scaffold showed enhancement in the strength and the elongation [10]. Improved corrosion resistance.	X. N. Gu et al [11].
Mg	HA	**Powder Metallurgy** Powders were mixed by ball milling. And cold pressed into a cylindrical compact at 400MPa. The compact was after that hot pressed under 350MPa pressure and at 330°C. Finally, hot extruded to obtain sample material.	In reference to as-extruded bulk pure Mg, an increase in the yield tensile strength but a decrease in ultimate tensile strength and ductility was observed. Composite compared with as-extruded bulk pure Mg showed reduced corrosion resistance.	Xuenan Gu et al [12].

			Increase in HA content decreased corrosion resistance.	
ZM61	HAP	**Stir Casting** Calculated amounts of Mn and Zn and HAP powder were added to molten Mg at 700^{o}C and stirred homogeneously, then ingots were homogenized at 400^{o}C, machined and extruded at 320^{o}C to obtain samples.	Grain refinement occurs during extrusion because of HAP particles. Addition of HAP particles decreases ductility and tensile strength. With the addition of HAP an increase in compressive strength is observed. Brittleness increases with addition of HAP.	A.K. Khanra et al [13].
AZ91	FA (fluorapatite)	**Powder Metallurgy** A blend-press-sinter powder metallurgy (PM) method was used to prepare the composite. The particles of AZ91 and FA were mixed by ball milling and then under 880MPa pressure the mixture was cold compacted following by sintering at 400^{o}C. Sample material was thus obtained.	The compressive strength increased with addition of FA particles and reached maximum when 20wt.% of FA was added. As FA concentration increased, elastic modulus increased and ductility decreased. Micro-hardness increased with an increase in FA particles concentration. Corrosion resistance increased with addition of FA particles to AZ91 as compared to the AZ91 magnesium alloy [14].	M. Razavi et al [15].

AZ91		**Casting Process** Using AZ91 porous scaffolds were casted in a negative salt-pattern molding process. Castings were then machined with salt spacers to protect the pores from collapsing during machining. In next step Molar sodium hydroxide solution was used to wash away the sodium chloride grains.	The mechanical properties of porous scaffold of AZ91 magnesium alloy were comparable to bone [16]. Compared to the bone, the degradation rate was too fast. The degradation rate can be controlled by providing protective coatings like calcium phosphates, magnesium fluorides etc. or using optimized alloys.	F. Witte et al [17].
Mg-Zn-Zr	HA	**Casting (as-cast)** Mg ingot having holes filled with Zn and HA particles was melted with master Mg-Zr alloy in a vacuum induction furnace with magnetic agitation at 720°C. Casted ingots were extruded to obtain sample materials.	Increased corrosion resistance was observed with addition of HAP to Mg-Zn-Zr alloy matrix. Favourable cytocompatibility observed with HAP particles addition.	Xinyu Ye et al [18].
Mg	Ca	**Powder Metallurgy** Powders were mixed by ball milling and cold pressed into a cylindrical compact at 400MPa. At 320°C and under a pressure of 350MPa, the compact was hot pressed. Finally, at 300°C materials were hot extruded to obtain sample material.	For the Mg/1Ca composite there is significant increase in the yielding tensile strength and concurrent decrease in ultimate tensile strength compared with that of the bulk Mg-1Ca alloy. Increase in corrosion resistance was observed. With an increase in Ca particulate, Mg/Ca composite showed reduction in corrosion resistance.	Y.F. Zheng et al [19].

2. Results and discussion

It was observed that addition of HA particles in magnesium based MMCs enhanced its corrosion resistance in artificial sea water and cell solutions [7]. Biodegradable Mg–HAP composite was produced by melting and extrusion route [8]. Grain refinement was observed with the addition of HAP to Mg matrix. For the Mg/1Ca composite there is significant increase in the yielding tensile strength and concurrent decrease in ultimate tensile strength compared with that of the bulk Mg-1Ca alloy. With an increase in Ca particulate, Mg/Ca composite showed reduction in corrosion resistance [19]. Increased corrosion resistance and favourable cytocompatibility was observed with addition of HAP to Mg-Zn-Zr alloy matrix [18]. F. Witte et al [17] achieved the mechanical properties of porous scaffold of AZ91 magnesium alloy were comparable to bone using casting process. Grain refinement occurs during extrusion because of HAP particles which further results in increases ductility and tensile strength [13]. Reinforcement of HAP in AZ91D magnesium alloys is responsible for grain refinement and hence increases compressive strength and decreases tensile strength and hence brittleness.

3. Conclusions

From the extensive literature study of magnesium alloys and composites for biomedical application following conclusions are withdrawn:

- Commonly used methods for fabrication of MMCs are powder metallurgy, Liquid alloy infiltration technique and stir casting.
- Reinforcement of HAP in AZ91D magnesium alloys is responsible for grain refinement and hence increases compressive strength and decreases tensile strength and hence brittleness.
- Porous scaffold of AZ91 magnesium alloy can be stir casted with comparable mechanical properties to bone.
- Addition of HAP to Mg-Zn-Zr alloy matrix increased the corrosion resistance and achieved favourable cytocompatibility.
- It was observed that addition of HA particles in magnesium based MMCs enhanced its corrosion resistance in artificial sea water and cell solutions
- Biodegradable Mg–HAP composite with good mechanical and corrosive properties was produced by melting and extrusion route.
- The degradation rate of magnesium alloys can be reduced by providing protective coatings like calcium phosphates, magnesium fluorides.
- The compressive strength increased with addition of FA particles and with increase in FA concentration, elastic modulus increased and ductility decreased.

4. *References*

[1] R. Radha and D. Sreekanth, "Insight of magnesium alloys and composites for orthopedic implant applications – a review," J. Magnes. Alloy., vol. 5, no. 3, pp. 286–312, 2017.

[2] Y. Su, Y. Su, W. Zai, and G. Li, "In Vitro Degradation Behaviors of Manganese-Calcium Phosphate Coatings on an Mg-Ca-Zn Alloy," vol. 2018, 2018.

[3] R. J. M. Embryol, "Mg – Zn alloys , most suitable for biomedical applications," vol. 59, no. 1, pp. 49–54, 2018.
[4] K. Lietaert, L. Weber, J. Van Humbeeck, A. Mortensen, J. Luyten, and J. Schrooten, "ScienceDirect Open cellular magnesium alloys for biodegradable orthopaedic implants," JMAA, vol. 1, no. 4, pp. 303–311, 2013.
[5] N. Li and Y. Zheng, "Novel Magnesium Alloys Developed for Biomedical Application: A Review," J. Mater. Sci. Technol., vol. 29, no. 6, pp. 489–502, 2013.
[6] M. Haghshenas, "Mechanical characteristics of biodegradable magnesium matrix composites: A review," J. Magnes. Alloy., vol. 5, no. 2, pp. 189–201, 2017.
[7] F. Witte et al., "Biodegradable magnesium-hydroxyapatite metal matrix composites," Biomaterials, vol. 28, no. 13, pp. 2163–2174, 2007.
[8] A. K. Khanra, H. W. A. C. Jung, S. H. Yu, and K. U. G. S. U. N. Hong, "Microstructure and mechanical properties of Mg – HAP composites," vol. 33, no. 1, pp. 43–47, 2010.
[9] A. Feng and Y. Han, "The microstructure, mechanical and corrosion properties of calcium polyphosphate reinforced ZK60A magnesium alloy composites," J. Alloys Compd., vol. 504, no. 2, pp. 585–593, 2010.
[10] X. L. Ma, L. H. Dong, and X. Wang, "Microstructure , mechanical property and corrosion behavior of co-continuous b -TCP / MgCa composite manufactured by suction casting," vol. 56, pp. 305–312, 2014.
[11] X. N. Gu, X. Wang, N. Li, L. Li, Y. F. Zheng, and X. Miao, "Microstructure and characteristics of the metal-ceramic composite (MgCa-HA/TCP) fabricated by liquid metal infiltration," J. Biomed. Mater. Res. - Part B Appl. Biomater., vol. 99 B, no. 1, pp. 127–134, 2011.
[12] X. Gu, W. Zhou, Y. Zheng, L. Dong, Y. Xi, and D. Chai, "Microstructure, mechanical property, bio-corrosion and cytotoxicity evaluations of Mg/HA composites," Mater. Sci. Eng. C, vol. 30, no. 6, pp. 827–832, 2010.
[13] A. K. Khanra, H. C. Jung, K. S. Hong, and K. S. Shin, "Comparative property study on extruded Mg-HAP and ZM61-HAP composites," Mater. Sci. Eng. A, vol. 527, no. 23, pp. 6283–6288, 2010.
[14] M. Razavi, M. H. Fathi, and M. Meratian, "Effect of fluorapatite nano particles as reinforcement on the biodegradation behavior of magnesium-based nanocomposite," no. November, pp. 3–4, 2010.
[15] M. Razavi, M. H. Fathi, and M. Meratian, "Microstructure, mechanical properties and bio-corrosion evaluation of biodegradable AZ91-FA nanocomposites for biomedical applications," Mater. Sci. Eng. A, vol. 527, no. 26, pp. 6938–6944, 2010.
[16] F. Witte, H. Ulrich, C. Palm, and E. Willbold, "Biodegradable magnesium scaffolds : Part II : Peri-implant bone remodeling," 2007.
[17] F. Witte et al., "Cartilage repair on magnesium scaffolds used as a subchondral bone replacement," Materwiss. Werksttech., vol. 37, no. 6, pp. 504–508, 2006.
[18] X. Ye, M. Chen, M. Yang, J. Wei, and D. Liu, "In vitro corrosion resistance and cytocompatibility of nano-hydroxyapatite reinforced Mg-Zn-Zr composites," J. Mater. Sci. Mater. Med., vol. 21, no. 4, pp. 1321–1328, 2010.
[19] Y. F. Zheng, X. N. Gu, Y. L. Xi, and D. L. Chai, "In vitro degradation and cytotoxicity of Mg/Ca composites produced by powder metallurgy," Acta Biomater., vol. 6, no. 5, pp. 1783–1791, 2010.