Degradation behaviour of magnesium alloy and its composite used as a biomaterial

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Abstract. In the last six decades, it has been made a great advancement in the field of engineering material especially in biomaterials, including metal alloys, composites, polymers, ceramics, and metallic glasses. Different form of these biomaterial are used as a engrafts. Unlike conventional materials such as stainless steel, cobalt, or titanium-based alloy resulting in stress shielding effect, some of these materials are designed in such a way to degrade or to be resorbed inside the body rather than removing the implant after its function is served. Here, Magnesium based biomaterials are the most suitable and used as a newly developed biodegradable material. Inherent mechanical properties of magnesium like properties of elastic and modulus rigidity which are very much same as to those of human bone, make it biocompatible. There is limited use of pure Mg due to its corrosive nature, but when formed an alloy or the composite the degradation property can be improved and making them a material of choice for implantation. This paper aim is to review the degradation rate and the methods to control it. Due to high degradation rate of the Mg, as compare to other biomaterials, our final goal is to maintain the balance between the gradual loss of material and mechanical strength during degradation, by providing the strength to the newly forming bone tissue. Mg-based alloy or composite has the potential to be used as a biomaterial without the need for a second surgery, once this goal is achieved.

1. Introduction

At present, about 2.8 million demand for bone repair and implant cases are performed annually worldwide. Commonly biomaterials have faced the problem of fatigue, erosion, and corrosion. The biomaterial properties are important for accepted osseointegration. For any type of engraft, permanent or temporary the most important properties which are taken into consideration are biocompatibility and mechanical endurance [5]. When two or different implants are combined, corrosion resistance is important. Degradation rate is also an important factor for biodegradable material. Implant material should be lightweight to simplify motion. Implant materials should also have analogous characteristics as a bone. When the implant material is come into the contact with extracellular fluid, blood and soft tissues, it must be biological stable in vitro condition in addition to its mechanical properties. Therefore, the implant material should have similar properties as of human bone like mechanical properties, its biocompatibility, high corrosion, and wear resistance, and which enable osseointegration [3-7]. Polymer, ceramic, metal and their composites are mostly used as a biomaterial. At present conventional material like cobalt-chromium stainless steel, and titanium, are generally used [20].

Due to high mechanical strength and fracture toughness, metallic materials play an important role as a biomaterial to assist the healing or replace bone tissue that is diseased or damage as compare to polymer and ceramic materials. Therefore, metallic materials having the huge scope in the field of implant [10-12].

The materials that are used in temporary engraft can be moderately terminate and can be evacuated from the body of the human. As soon as the healing process is outright this biodegradable engrafts do not require a subsequent surgery. The central summons is to plan and adjust the rate of degradation to fit in a particular implementation. The by-products from the degradation should not evoke swelling and any other unpleasant effect. Those temporary engrafts are in huge demand, which is easily degradable and tarnished in biological environment. These characteristics can prevent the long-lasting problem of permanent engraft and do not required subsequent surgery. The best degradable engraft should provide good physiologic mend, renovation of local acquiescence, a interim brace of the damaged tissue, and the probability for flourishing and positive modification at later stage. Furthermore, it must be reconcilable with the resultant procedure and not limit to restore blood flow to any organ [21]. Medication and heritable transfer should be given specially for the stent material. Since an engraft requires to work

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completely for the time interval until the area which undertakes the surgery starts.

Presently, many of the researchers are mostly working on the development of the biocompatible material, which should also be a biodegradable and should not cause any type of inflammatory reaction.

Design, material constitute and surface properties like surface texture, surface chemistry and surface energy have great influence on implant interaction phenomena, including the biocompatibility of the implant material [22].

In the 1930s the first-ever study on the practicability of Mg material engrafts for the bone fixtures, showing magnificent restorability and biocompatibility. Although the evolution of hydrogen gas is injurious if release in quantity. However, hydrogen evolution generally not play a significant role in small-scale engraft like stents, it can cause a problem when dealing with big parts required to brace osteosynthesis. The hydrogen bubbles can cause gas voids near mg engrafts in the flesh of humans because of the collection of hydrogen and insufficient transport mechanism. To avoid the risk of osteosynthesis hydrogen bubbles can be detached by penetrating. Therefore, it is better to prevent the hydrogen gas bubble formation [26].

The research is more concentrated on polymer and metal-based biodegradable material. Due to greater mechanical firmness and their corrosion by-products evoke less critical inflammation. For the usage in cardiovascular interference and osteosynthesis, magnesium and iron can be taken into consideration. Iron possesses low corrosion rates. Hence, for the orthopaedic engraft magnesium alloys have been significantly used and are very biocompatible.

The main problem possesses by using the conventional steel and titanium material is that it couldn't help in minimizing the stress shielding due to its high modulus, which can finally carry the majority of the load placed on the implant and bone, further this problem can easily overcome by the use of low modulus magnesium [28-30]. The outside load is necessary for the formation of a new bone structure. In bone fracture treatment stress shielding effect creates complications. If the transplant made of magnesium is used for fracture fixation, it reduces the stress shielding effect due to the property of low modulus possess by magnesium which is near to the modulus bone [20]. Therefore, magnesium and its alloy and composite has been highly recommended as a suitable base material for osteosynthesis process.

Now, we need to develop such a biomaterial which should be fulfil the requirement of biodegradability in the body fluid and having the similar mechanical properties, especially elastic modulus property is very similar to human bone as compare to other metal. Metals, like magnesium, zinc and iron are found to be a degradable in the human body fluids and having the good biocompatibility revealed by many researchers. Additionally, Magnesium is having a very similar elastic modulus that is 41–45 GPa as compare to human bone i.e. 10–20 GPa [29]. The main limitation with iron used as an implant is its very low degradation rate or non-

degradable nature and collection of by product iron hydroxide particles in many tissues. For the Zinc also slow degradation in the body fluid is limits its uses for temporary orthopaedic, application as it takes several years to complete full degradation. Calcium, Zinc Aluminium etc are used to make the magnesium alloy. These magnesium alloys can be further strengthened by solid solution, uniform dispersion, and precipitation hardening [25]. Magnesium metal matrix composites are now introduced as a new generation material in the area of orthopaedic engraft.

2. Biodegradability

Biodegradability is an ability of the material by which it can be degraded completely and safely without leaving any type harmful residues. Those material which are used as a biodegradable implant is that they do degrade after fulfilled their function, so that second surgery is not necessary to remove the implant. As the implant material degraded, it loses its mechanical properties and new grown bone stimulated with increasing load on healing tissue shown in fig 1. Recovery rate of bone tissue matches with the degradation rate of implant; therefore, it is necessary to investigate the mechanism, their behaviour and methods to regulate the degradation rate [30]

2.1. Degradable mechanisms

Principles of electrochemical are generally used to explain the mechanism of degradation for metallic implants. Following are the reactions which are involves during the degradation process of magnesium alloy and the main degradation products are H_2 and $Mg(OH)_2$ [30].

Now this Magnesium hydroxide on the surface of base metal i.e. Mg-based alloys is easily get eroded by body fluid which contain chlorine ions as per following reaction:

Thus, this magnesium oxide layer can't act as the protective layer fig 2 against the corrosion by which it accelerates the degradation rate. Composition and the structural states of the magnesium alloy decide the type of degradation. Here it starts the pitting corrosion which is usually undesirable because of which this $MgCl_2$ is come in contact with implant metal and become the reason to start the galvanic corrosion which further accelerate the degradation and there is significant reduction in the mechanical strength of implant.

Fig 1 (a) Bone healing & Mg Implant

Fig. 1. (b) Degradation behavior

According to the anodic reaction biodegradable metal release the electron and then oxidized to metal ions (Mn^{+}). Now this metal ion take part in cathodic reaction and result in local alkalization. Body fluid containing the Cl^{-1} ions are responsible for the erosion of the degradation layer of $M(OH)_n$ form on the metal surface. For cell adhesion, apatite is required which is formed by the local alkalization due to presence of Ca^{2+} and PO_4^{3-} ions present in the body fluid. As the cells are reproduce gradually, new tissues will be formed on the metal surface, as the time passes. This process is continuously be going on and as a result more degradation products are formed due to fall of the metal matrix and continue dissolve of metal matrix on the body fluid, further new fresh matrix expose to the body fluid and the process undergoes a new degradation [24]. The formation of the new apatite layer was occurred as per following equations.

The Apatite dissolution can be shown by Eqs. (8) and (9) as follow

3. Conventional biomaterial

3.1. Stainless steel (316L)

The main limitation of SS 316L is its less biocompatibility because of the presence of nickel which also cause allergic reactions, being a low resistance to corrosion its usage in temporary implant is limited [14]. SS 316L is having good mechanical strength property, elastic property, ductility and easily manufacturability, and easily available at low cost.

3.2. Co-Cr metallic alloy

Co-Cr metallic alloy replaced the SS 316L because of its very high corrosion resistance and good mechanical properties as a permanent implant. Many researchers revealed that, when it alloyed with molybdenum it shows a excellent resistance of corrosion and with high fatigue, it also have less biocompatibility and also shows some allergic reaction.

3.3. Titanium and titanium alloy

The main drawback of Ti and its alloy is stress shielding effect and non-degradation, but it has wide range of application because of its good mechanical strength, elasticity and cause no allergic reaction. But the further surgery is required to take out the engraft titanium alloy from the human body.

4. Regulation of degradation rate

To regulate the degradation rate of Mg-based alloys, there are various method when are generally used like alloying, heat treatment and surface coating etc. To reduce the corrosion rate of the magnesium metal different elements are used in varying proportional to control the grain size, micro structure and phase distribution.[23].

4.1. Mg based alloy

The Magnesium alloy can be classified in five group on the basis of material science and nutrition. Engineering magnesium alloying with Zn, Ca, AL, Cu, Sn, Cd, Fe, Th, Sr, Li, Mn, Zr, Ni, Pb, Cr, Si, Gd, Y, Sb, are very well documented [15]

4.1.1 Nutrient elements in human

Nutrient elements for the human body are Calcium, Zinc, Chromium, Manganese, Silica, and Tin. Cr and Mn are considered to be essential micro-nutrients but Cr may cause carcinogenic in humans. Ca is also a macro-nutrient present in human bone and very essential nutrient in chemical signalling with cells, with large minimal daily requirements. Sn and Si has not yet been

recognized as essential for human nutrition but it believe that having some health benefits.

4.1.2 Nutrient elements in animals and plants

Nutrient elements in animal and plants are Ag, Zr, Bi, Sr, Li, Al. Their importance in human body is still to be determined but present in animals and plants. Out of these element Aluminium is well known neurotoxicant and its accumulation can cause dementia or Alzheimer disease. For the treatment of manic-depressive psychoses, Li salts are used but shows toxicity when concentration is above 2 mM/L. By having the limited uses in medicinal application and show toxicity when consume in large quantity.

4.1.3 Toxic elements

Toxic elements are Pb, Th and Cd. Pb is highly toxic for nervous system, hematopoietic and also a nephrotoxic. Th is hazardous because of its radioactive nature. Cd is also recognized as a highly toxic, its effect is not only the limited up to Cardiovascular and hypertension but also on lungs, Kidneys, heart, liver, prostate, testes, heart, and liver [12].

4.1.4 Impurities

Impurities present in Magnesium are Fe, Ni, Cu. These all elements are commonly considered as undesirable to corrosion because of their very less solid solubility in Mg and their presence also cause of active cathodic site, resulting galvanic corrosion [28].

4.1.5 Others

Others alloying element in magnesium are Y, Gd, Sb, and RE. These elements are not found in human body and also not biologically essential for humans. Rare earth element having still some controversies on the biological effects. Many of the studies revealed that RE (rare earth metals) are not highly toxic, because they are directly used in chronic toxicity experiment, and therapy of cancer & synovitis.

Table 1. Corrosion rate of Mg alloy.

Alloy	Condition	Corrosion medium	Corrosion rate mm/Year
Mg	As-cast	SBF	1.94~
Mg		Hank's	0.36
Mg	As rolled	SBF	0.84
Mg		Hank's	0.32
Mg-1Ca	As cast	SBF	12.56
Mg-1Zn	As cast	SBF	1.52
Mg-1Sn	As cast	SBF	2.45
Mg-1Sn	Sub rapid solidification	Hank's	0.121

Mg-3Sn		Hank's	0.168
Mg-5Sn		Hank's	0.337
Mg-7Sn		Hank's	0.507
Mg-2Sr	As rolled	Hank's	0.87
Mg-1Mn	As cast	SBF	2.46
Mg-1Ag	As cast	SBF	8.12
Mg-0.5Ca		SBF	4.08
Mg-0.5Ca		SBF	2.79
Mg-1Ca		SBF	0.66
Mg-0.5Ca-0.5Zn		SBF	2.3
Mg-0.5Ca-1Zn		SBF	4.3
Mg-1Ca-1Zn		SBF	1.6
Mg-0.5Ca-0.5Mn		SBF	4.2
Mg-0.5Ca-0.5Mn		SBF	0.83
Mg-1Ca-1Mn		SBF	4.02
Mg-1Ca-1Mn		SBF	2.82
Mg-0.5Ca-0.25Zn-0.25Mn		SBF	6.9
Mg-0.5Ca-0.25Zn-0.25Mn		SBF	0.62
Mg-1Ca-0.5Zn-0.5Mn		SBF	4.05
Mg-1Ca-0.5Zn-0.5Mn		SBF	2.09
Pure Mg		Kokubo	8.47
Mg-2Ca		Kokubo	6.89
Mg-4Ca		Kokubo	9.04
Mg-2Ca-0.5Mn-2Zn		Kokubo	1.78
Mg-2Ca-0.5Mn-4Zn		Kokubo	2.27
Mg-2Ca-0.5Mn-7Zn		Kokubo	3.98
Mg-1.2Zn-0.5Ca	As cast	SBF	8.2
Mg-1.2Zn-0.5Ca	Heat treated	SBF	4.8

4.2. Mg-based composites

Presently investigation is going on magnesium-based composite for its feasible use in the human body as a temporary implant. Many researches show that magnesium-based composites exhibit improved refined grain structure, mechanical strength and reduced corrosion resistance. Magnesium metal matrix composites (MMCs) having good mechanical strength, hardness, toughness and wear resistance properties, which make it as promising orthopaedic biomaterials.

Particularly for biomaterial application several reinforcing materials including metallic powder and ceramic material like calcium polyphosphate, hydroxyapatite, tricalcium phosphate, fluorapatite, ZrO_2 , Al_2O_3 , TiO_2 , ZnO , MgO , TiB_2 , SiO_2 , TiC , TiN , Si_3N_4 , CNTs, Zn, Sr, Zr, Ti etc., are used to produce Mg metal matrix composites [16].

Hydroxyapatite (HA) is one of the inorganic compounds that having a biological importance to human bones (make up 50% by vol) and teeth. Hence HA is a biocompatible material. Hydroxyapatite ceramic powder exhibits excellent biocompatibility, bioactivity, and osseointegration. Since HA stimulates bone ingrowth it enhanced osseointegration. Due to increase in the biomineralization by adding the HAp to magnesium the resultant Mg substrate, which act as a nucleating site for mineral deposition, will increase the corrosion resistance in physiological environment and hence decrease the degradation rate. It has been proved by the researcher that the mechanical strength, corrosion and bio-properties of Mg based bio-composite will be enhanced by adding the HAp in magnesium-based composite [28].

When we use the nano reinforcement instead of micro level reinforcement in magnesium composite, we get relatively good mechanical properties like mechanical strength, yield strength and ductility due to increase in wetting property. The recent development of reinforcement is by using the naturally derived nano HAp to develop magnesium metal matrix composite, Fish bone is recently used in some research.

Table 2. Corrosion resistance of Mg composite.

Composites	Effect on corrosion resistance by adding HAp on Mg / Mg alloy	Medium
AZ91D-20 wt.% HA	1.25- 0.16 mm/year for AZ91D-20 wt.% HA composite, although no data were reported for bare AZ91D	Artificial sea water
Mg-HA (10, 20, 30 wt.%)	Decrease the corrosion resistance of Mg by ~ 31% by adding 10wt% HA	SBF
(Mg-Zn-Zr)-1 wt.% nHA	Polarization resistance improved by ~57% and E_{corr} was also shifted towards the positive side	SBF
Mg-HA (10, 20 wt.%)	Addition of 10% HA has shown ~ 10% higher corrosion resistance as compared to pure Mg and after PEO treatment of composite has improved the corrosion resistance of Mg-10HA by ~ 250%	SBF
(Mg-3Zn-0.5Zr)-HA (0, 0.5, 1 and 1.5 wt.%)	E_{corr} value shifted by ~ 11% towards +ve side by adding 1%wt HA in alloy	SBF
Mg-HA (5, 8, 10 and 15 wt.%)	E_{corr} value shifted by 95% towards the +ve side, with ~ 10 times decrease in the corrosion current density by adding 10 wt % HA	3.5% NaCl solution

(Mg-Zn-Y)-0.5 wt.% HA	Improvement in the corrosion rate to ~ 62% by adding 0.5 wt % HA	SBF
(Mg-3Zn)-HA (0, 2, 5, 10 wt.% HA)	Improvement in the corrosion resistance to ~ 42% by adding 5 wt% HA	SBF
(Mg-2Zn-0.5Sr)-HA (0, 0.1, 0.3 wt.%)	Increase in the corrosion resistance about ~ 44% by adding 0.3 wt% HA in alloy	SBF
(Mg-5Zn-0.3Ca)-HA (0, 1, 2.5, 5 wt.% HA)	Decrease in corrosion current density by ~ 66% after addition of 1 wt.% HA	SBF
(Mg-1Zn-1Ca)-HA (0, 1 3 wt.% HA)	Increase in corrosion resistance by ~ 76% after adding 1 wt% HA in alloy	(PBS)
Mg-15 wt.% HA	Decrease in corrosion current density about ~ 57% by adding 15 wt% HA in Mg	SBF
AZ31-nHA	Increase in corrosion resistance about ~ 72% by adding nHA in alloy	SBF
Mg-HA (5, 10, 15 wt.%)	Decrease in the corrosion current density about ~ 60% by adding 10 wt % HA	SBF
Mg-2.5 wt.% HA	Negligible changes in the corrosion resistance by adding 2.5 % wt HA in Mg by FSP process	(DPBS)
ZE41-fish bone derived HA	Increased corrosion resistance about ~ 52% by adding fish bone derived HA	Ringer's Solution

5. Conclusion

Magnesium as a “biodegradable” metal is the most emerging as promising metal for bone implants. Presently, the research in the field of biomedical especially for the Mg-based alloys and its composite are in demand. It is believed that magnesium-based alloy possesses the similar modulus of elasticity and very good biocompatibility. Although, they are degraded faster than development of new bone. a considerable efforted has been made continuously for developing the new metallic implants with matched biodegradability and mechanical properties as bone repair. For example, a series of Magnesium MMC alloy such as LAE442, WE43, and ZEK100 etc., has been developed and it shows improvement in corrosion resistance. Addition of HAp used to make the Mg based composite reduce the ductility and yield strength of implant, but at the same time improve the corrosion resistance. These Mg based composites used as bone replacement and body implants as it provides great strength-to-weight ratio as well as bio-compatibility and bio-degradability.

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