



Biodegradable magnesium alloys for orthopaedic applications: A review on corrosion, biocompatibility and surface modifications



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ARTICLE INFO

Article history:

Received 21 October 2015

Received in revised form 17 May 2016

Accepted 7 June 2016

Available online 10 June 2016

Keywords:

Biocompatible

Biodegradation

Coating

Corrosion

Mg alloys

Orthopaedic implants

ABSTRACT

Magnesium (Mg) and its alloys have been extensively explored as potential biodegradable implant materials for orthopaedic applications (e.g. Fracture fixation). However, the rapid corrosion of Mg based alloys in physiological conditions has delayed their introduction for therapeutic applications to date. The present review focuses on corrosion, biocompatibility and surface modifications of biodegradable Mg alloys for orthopaedic applications. Initially, the corrosion behaviour of Mg alloys and the effect of alloying elements on corrosion and biocompatibility is discussed. Furthermore, the influence of polymeric deposit coatings, namely sol-gel, synthetic aliphatic polyesters and natural polymers on corrosion and biological performance of Mg and its alloy for orthopaedic applications are presented. It was found that inclusion of alloying elements such as Al, Mn, Ca, Zn and rare earth elements provides improved corrosion resistance to Mg alloys. It has been also observed that sol-gel and synthetic aliphatic polyesters based coatings exhibit improved corrosion resistance as compared to natural polymers, which has higher biocompatibility due to their biomimetic nature. It is concluded that, surface modification is a promising approach to improve the performance of Mg-based biomaterials for orthopaedic applications.

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1. Introduction

Metallic orthopaedic implants have been used for the replacement and/or regeneration of damaged hard tissues [1]. Metallic implants are preferred for their high mechanical strength and toughness which make them superior to polymer and polymer-ceramic composites [2]. Orthopaedic metallic implants can be broadly classified into permanent (e.g. knee or hip prostheses) and temporary biodegradable implants (e.g. Screws, pins, etc.) [2]. Metals such as stainless steel, titanium and cobalt-chromium alloys have been employed as permanent implants [3,4]. However, there are some problems associated with the use of permanent metallic implants [5–7]. The first such problem includes incompatibility of mechanical properties of metallic alloys and natural bone; for example, metal alloys have greater elastic modulus to that of bone [8,9]. Under in vivo conditions, the mechanical mismatch between bone and implants leads to clinical phenomena called stress shielding [10,11]. In stress shielding, the implant carries much of the bulk load and the surrounding bone tissue experiences a reduced load stress. This triggers the resorption of surrounding bone tissue [11]. To address this problem, permanent metallic alloys such as Co-Cr-Mo and Ti-6Al-4V have been manufactured into porous forms to reduce the modulus mismatch with natural bone [12]. A number of techniques are available to produce a porous metallic structure (fully porous metals or surface treatments) such as sintered metal powders, gas injection to metal melt, plasma spraying, use of foaming agents etc. [12]. However, development of porous metallic implants suffers from limitations such as brittleness, impurity of phases and limited control over the size, shape and distribution of porosity [13]. This limiting their orthopaedic applications. The second problem associated with permanent implants is mechanical wear and corrosion associated with the long term implantation in the body. This results in the release of toxic metal ions (chromium, nickel, cobalt etc.) in the body which can trigger the undesirable immune responses, thereby reducing the biocompatibility of metallic implants. [14]. Such drawbacks have compelled researchers and clinicians to look at biodegradable implants, which once used, only remain for an appropriate time to fix the damage.

Biodegradable metals have several advantages when used in orthopaedic fracture fixation (e.g. Screws, pins, etc.) [8]. The mechanical properties of Mg and its alloys such as Young's modulus of elasticity ($E = 41\text{--}45\text{ GPa}$) and density ($1.74\text{--}1.84\text{ g/cm}^3$) are known to be similar that of bone ($E = 15\text{--}25\text{ GPa}$ and density $= 1.8\text{--}2.1\text{ g/cm}^3$). This is lower than other biodegradable materials such as Iron-Manganese (Fe-Mn) and Zinc (Zn) based alloys [2]. Furthermore, Mg ions are common metabolites in the body with a daily consumption range of 250–300 mg/day and are naturally stored in the bones [15]. Therefore, amongst biodegradable metals, the biocompatibility and the resemblance of mechanical properties of Mg and its alloys with bone makes it suitable for orthopaedic applications.

Ceramics which are inorganic non-metallic materials that have been employed in hard tissue engineering applications, are collectively known as Bioceramics [16]. Bioceramics possess desirable properties for biomedical applications such as (i) thermo-chemically stable, (ii) good wear resistant and (iii) are easily mouldable. Additionally, they are biocompatible, non-toxic and non-immunogenic [17,18]. However, bioceramics like hydroxyapatite (HAP) are brittle and possess low tensile strength when compared to Mg based alloys [18]. Ceramics have been used commercially in various applications like coatings for implants, maxillofacial reconstruction and drug delivery devices [19–21].

Polymeric materials have been employed for tissue engineering applications due to their ductility, biocompatibility and biodegradable

nature. Polymers are composed of small repeating monomers which give the polymer its characteristic properties. The degree of cross linking of monomers determines the physiochemical nature of polymers [24]. In general, polymeric materials are broadly classified into synthetic and natural polymers.

Synthetic polymers such as aliphatic poly-ester (poly lactic acid, poly glycolic acid, poly co-(lactic-co-glycolic acid)) can be synthesized in controlled conditions to regulate properties such as molecular weight and derivatization. These advantages of synthetic aliphatic polyesters enable their use in biomedical applications. Natural polymers such as collagen and protein based gels, hyaluronic based derivatives, polysaccharide chitosan and heparin based scaffolds have been successfully used in various tissue engineering applications [22]. Natural polymers share properties similar to materials in the body and thus may encourage expeditious tissue healing by directing cell adhesion and function. Both classes of polymer can be chemically modified to produce tuneable scaffold and biomedical implants with controlled degradation rates. [23]. Moreover, several reports showed that the by-products of biodegradable polymers are highly biocompatible [24]. These polymers can be engineered into various shapes and sizes, such as disk, rod, pellets, plates, films and fibres as required. Some applications include biodegradable sutures, bone grafting materials, pins, screw and load bearing orthopaedic devices [25]. Despite possessing many desirable properties, polymers have low mechanical strength when compared to bioceramics and metal implants, thereby hindering their applications in hard tissue engineering. Therefore polymers have been largely employed in soft tissue engineering and low-load bearing medical devices [25]. Comparatively, Mg and its alloys have advantages over polymers due mechanical strength similar to bone.

From the above discussion, it can be observed that Mg based alloys have mechanical properties (density, yield strength, tensile strength, elongation to break and elastic modulus) similar to that of natural bone as compared to other biodegradable alloys, permanent implants, ceramics and polymers as showed in Table 1. Despite many advantages, the major limitation of Mg based alloys as biomedical materials is their high corrosion rate [26]. Corrosion results in the formation of H_2 gas; which, if rapidly absorbed can lead to balloon effect in vivo [27]. Additionally, shift in alkaline pH in the region surrounding the corroding surface is also a concern for biomedical applications [28].

There are some strategies to improve the corrosion behaviour and biocompatibility:

- Optimising the composition and microstructure, including grain size, crystalline structure phase and texture of the base metal through the development of manufacture process/methods.
- To improve the corrosion behaviour and biocompatibility of Mg based implants through protective polymer deposit coatings on Mg and its alloys.

2. Corrosion behaviour of Mg and its alloys

The usual degradation of biomedical metals is through the corrosion process. Generally, the corrosion process involves electrochemical reactions to produce oxides, hydroxides and H_2 gas species. In physiological conditions, the corrosion reactions of biodegradable metals including Mg and its alloys, involve the following anodic dissolution of metals and cathodic reduction reactions [8].



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