



REVIEW ARTICLE

Similarities and differences in coatings for magnesium-based stents and orthopaedic implants



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Summary Magnesium (Mg)-based biodegradable materials are promising candidates for the new generation of implantable medical devices, particularly cardiovascular stents and orthopaedic implants. Mg-based cardiovascular stents represent the most innovative stent technology to date. However, these products still do not fully meet clinical requirements with regards to fast degradation rates, late restenosis, and thrombosis. Thus various surface coatings have been introduced to protect Mg-based stents from rapid corrosion and to improve biocompatibility. Similarly, different coatings have been used for orthopaedic implants, e.g., plates and pins for bone fracture fixation or as an interference screw for tendon-bone or ligament-bone insertion, to improve biocompatibility and corrosion resistance. Metal coatings, nanoporous inorganic coatings and permanent polymers have been proved to enhance corrosion resistance; however, inflammation and foreign body reactions have also been reported. By contrast, biodegradable polymers are more biocompatible in general and are favoured over permanent materials. Drugs are also loaded with biodegradable polymers to improve their performance. The key similarities and differences in coatings for Mg-based stents and orthopaedic implants are summarized.

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Introduction

Magnesium (Mg) is one of the lightest metals, exhibiting good mechanical properties, biodegradability, and biocompatibility [1,2], and has thus received great attention in the field of percutaneous coronary intervention (PCI) [3] and orthopaedic applications [4,5]. The main applications of Mg-based implantable medical devices currently include cardiovascular stents, bone fixation plates and pins, and screws for tendon-bone or ligament-bone insertions. The nature of their biodegradability makes Mg alloys look promising in implant applications because there is no need for secondary surgery to remove the implants [6]. Unfortunately, due to low corrosion resistance, many problems including hydrogen elution and decreasing mechanical strength prior to the healing of the surgical regions have also arisen during *in vivo* studies [7,8].

To prevent rapid corrosion, various surface modification techniques have been used [9,10]. Among them, the application of coatings has been documented as one of the most effective [11]. In addition to corrosion prevention, coatings can also provide a drug reservoir for Mg-based biomedical implants. Many coating technologies have been developed for Mg alloys, including inorganic coatings, metal coatings, metallic oxide coatings, metallic hydroxide coatings, chemical conversion coatings, nanoporous inorganic coatings, and polymer coatings [11–17]. This paper reviews the various coating techniques applied to Mg alloy device scaffolds and also determines the role that coatings play in stent functionality and orthopaedic implants. The differences and similarities of coatings used in stents and orthopaedic implants are also addressed.

Metal, metallic oxide, and metallic hydroxide coatings

Metal coatings

Titanium (Ti) implantation has been shown to improve the corrosion resistance of AZ91 alloy [18]. The vapour deposition of aluminium (Al) has been applied to Mg-based alloys and has been shown to decrease the degradation rate [19]. The downside of this Al deposition, however, is its low biocompatibility. Al has also shown signs of corroding in sodium chloride (NaCl) solution, an outcome that does not suggest efficiency for an implant coating material [13]. Therefore further analysis of other more effective materials is needed for a better understanding of deposited metal coatings that produce low toxicity values when implanted. Gold was also investigated as a coating for Mg alloy in another patent [20]. However, others workers have demonstrated that stents coated with gold increase the risk of restenosis [21].

Metallic oxide and metallic hydroxide coatings

A thin film of metallic oxide can provide an interface with vascular milieu for a stent as well as enhancing its biocompatibility [22]. Therefore some metallic oxides, such as titanium dioxide and zirconium oxide, were coated on

stents to improve their performance. A titanium-nitride-oxide coating was investigated to reduce neointimal hyperplasia. Compared with stainless steel, two stents coated with different titanium-nitride-oxide coatings showed better biocompatibility and reduced neointimal area [23]. Another study investigated converting metallic polycrystalline oxides into an amorphous oxide to increase the corrosion resistance of stents. The results indicated that an amorphous oxide-coated stent was safer and more biocompatible [24]. Earlier research suggests that nickel (Ni)–Ti stents may have a native oxide layer. By an electropolishing, heat treatment and passivation process, the deformed native oxide layer on a Ni–Ti stent can be removed and a new uniform oxide layer will form. These processes improved the corrosion resistance of Ni–Ti stents due to the uniformity of the oxide layer grown on the stent surface [25]. Zirconium oxide [26], iridium oxide [27], and noble metal oxides [28] have also been reported in patents as coatings for stents. Another patent reported a multilayer metal and metallic oxide coating for a stent: the inner metallic layer was a noble metal or alloy and the outer layer was iridium oxide [29].

The simplest method of generating a coating on an Mg sample is to simply expose it to the environment (air and water). This process, called passivation, exposes the sample to atmospheric humidity at a level sufficient to create a Mg hydroxide layer on the outer surface; continuing to store the sample in air creates an additional, beneficial, carbonate layer. Oxide layers usually provide better corrosion protection than hydroxide layers. The $\text{Mg}(\text{OH})_2$ layer actually increases in thickness on the implant surface over time, whereas the MgO layer stays at a relatively constant thickness, but can be increased through thermal treatment [30]. Also, alkaline solution treatment was also believed to create a layer of $\text{Mg}(\text{OH})_2$, MgCO_3 , and MgO on the surface of Mg alloys [14].

Chemical conversion coating

Chemical conversion coating involves taking the surface of the metal implant material and converting it into the desired coating via a chemical or electrochemical process. In the past, the process was performed to create chromate layers because of its ability to provide effective corrosion resistance. However harmful environmental outcomes arise from the use of chromium (Cr) in chemical conversion baths, therefore a Cr substitute must be found [31].

Metal phosphate compounds as a possible replacement were investigated. The results of Chen et al [12] suggested that the performance of these metal phosphate layers were significantly dependent on the pre-treatments used to make the layers more or less functional. For biomedical applications, research shows that two potential coating materials, fluoride-based layers and calcium phosphates, can be applied.

Zhang et al [169] explored the preparation of calcium phosphate coatings on an Mg–1.0Ca alloy using electrochemical deposition. Enhanced corrosion resistance was observed in Hank's solutions. The thickness and morphology of the coating had a significant effect on the corrosion behaviour of this Mg alloy. Another investigation showed

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