Evaluation of adhesion and ion release of hydrothermally deposited strontium phosphate coating on Mg

R.J. Kavitha[1] & K. Ravichandran[1]* & T.S.N. Sankara Narayanan[2]
[1]Department of Analytical Chemistry, University of Madras, Guindy Campus, Chennai-600025, India.
[2]Hybrid Materials Manufacturing laboratory, School of Mechanical, Aerospace and Nuclear Engineering, (MANE), Ulsan National Institute of Science and Technology (UNIST), Ulsan, Republic of Korea.

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ABSTRACT *In this study, strontium phosphate coating was deposited on magnesium by hydrothermal treatment at 80, 120, 150 and 200 °C for 30 min. For implant applications, it is imperative to ascertain that the Sr-P coated Mg is capable of exhibiting a good adherence, limiting the extent of leaching of metal ions and not inducing toxic effect to the surrounding environment. These attributes are evaluated by standard test methods using uncoated Mg as control. The findings of the study reveal that the Sr-P coating obtained by hydrothermal treatment at 200 °C for 30 min is highly adherent to Mg, limits the loss in weight due to corrosion as well as the extent of leaching of Mg^{2+} and Sr^{2+} ions in simulated body fluid.*

Keywords*: strontium phosphate, adhesion, degradation, weight loss.*

1. Introduction

On account on their biocompatibility, biodegradability and mechanical properties, Mg and its alloys are acting as a smart biodegradable implant material for bone implants as well as for cardiovascular stents. However, Mg is being a highly reactive metal, it corrodes rapidly in the physiological pH (7.4-7.6) leads to generation of large volume of hydrogen gas and increase in the local alkaline pH, tend to loosen the mechanical integrity of the implant before the tissue has healed sufficiently and hence limits its clinical applications. Surface biomodification is the viable option to improve the corrosion resistance and biocompatibility. In addition, pitting corrosion of Mg is delayed in the presence of phosphate ions. Especially bioceramic coatings have an ability to promote osteointegration around Mg implants.[1-5] It is believed that Sr showed the ability to inhibit osteoclast activity and improves osteoblast activity which involves proliferation and differentiation in in vitro. Sr increases bone formation and reduces bone resorption invivo.[6-8] Among the various methods of coating, hydrothermal treatment (HT) has received considerable attention due to its simplicity, cost-effectiveness and energy efficiency. The ability to deposit uniform and compact coatings with excellent adhesive strength even on a 3-dimentional structure is the unique attribute of HT.[9]

In our previous study, the hydrothermally deposited Sr-P coating was successfully prepared and characterized for its morphology, chemical composition, phase content, surface roughness and corrosion behavior and bioactivity. According to this report, the coating is uniform and highly crystalline. The coating weight, density and R_a of the coating are increased following an increase in reactivity with temperature. XRD analysis showed that the Sr-P coating predominantly consist of mixture of Mg and Sr phosphate phases with the Sr/P ratio is ~1, suggesting the formation of coatings richer in $SrHPO_4$ phase when the deposition temperature increased from 80 to 200 ºC. Due to their higher coating weight, better surface coverage, increase in crystallinity and Sr-P phase content, the coatings prepared at 200 °C for 30 min offered excellent corrosion protection.[10] However, it is important to evaluate the adhesion and cytocompatibility of Sr-P coating. Therefore, in this present study adhesion, the ion release and weight loss after immersion in SBF of Sr-P coatings were investigated.

2. Experimental details

2.1 Materials and methods used

Commercially pure magnesium (Mg) was used as a substrate material. The Mg samples were mechanically ground using SiC coated abrasive paper (grit size: 1000), ultrasonically cleaned using acetone for 15 min and dried. Deposition of strontium phosphate (Sr-P) coatings on Mg was performed using 0.1 M $Sr(NO_3)_2$ and 0.06 M $NH_4H_2PO_4$ by hydrothermal treatment (HT) at 80 °C, 120 °C, 150 °C and 200 °C for 30 min. The details of the deposition of Sr-P coatings on Mg by HT were reported elsewhere.[10]

2.2 Characterization of coatings

2.2.1 Adhesion test

The adhesive strength between the Sr-P coating and the Mg substrate was determined by ASTM (American Society for Testing and Materials) D 3359 standard test. The test was carried out following Test method B - cross-cut tape test.[11] An X-cut was made through the coated layer so that the bare substrate was exposed in the cut area. A pressure sensitive tape was applied over the cut region and pulled at one stroke without any jerk. Based on the extent of removal of the coated layer, the adhesive strength was assessed quantitatively on a 0B to 5B scale (5B: 0% removal of the coated layer; 4B: less than 5 % removal of the coated layer; 3B: 5 to 15% removal of the coated layer; 2B: 15-35% removal of the coated layer; 1B: 35-65% removal of the coated layer; and 0B: Greater than 65% removal of the coated layer).

2.2.2 Loss in weight due to corrosion of uncoated and Sr-P coated Mg and leaching of Mg^{2+} and Sr^{2+} ions after immersion in SBF

In order to evaluate the loss in weight due to corrosion and the extent of leaching of Mg^{2+} and Sr^{2+} ions, the uncoated and Sr-P coated Mg samples were immersed in SBF (composition in g/l: NaCl: 8.035; $NaHCO_3$: 0.355; KCl: 0.225; $K_2HPO_4.3H_2O$: 0.231; $MgCl_2.6H_2O$: 0.311; 1.0 M HCl: 39 ml; $CaCl_2$: 0.292; Na_2SO_4: 0.072; Tris buffer: 6.118; pH adjusted to 7.40 with an ionic concentration almost equal to those in human blood) under biomimetic conditions at 37 ± 1 °C for 240 h. The **c**orrosion products and remnant coatings were removed using chromic acid solution (200 g/L CrO_3 + 10 g/L $AgNO_3$) at room temperature in an ultrasonic bath.[12] The concentrations of Mg^{2+} and Sr^{2+} ions leached in to SBF after 1, 3, 5, 7 and 10 days were measured by inductively coupled plasma optical emission spectrometer (ICP-OES).

3. Results and discussion

3.1 Adhesion strength

The adhesion strength of the Sr-P coating to the Mg substrate is very important in determining the life time of the implant. Any detachment of the Sr-P coated layer would expose the bare Mg surface to the body fluid, which leads to the generation of galvanic cells between the areas in which the Sr-P coating is intact and where the coating is delaminated. The photographs of Sr-P coated Mg obtained by HT at 80, 120, 150 and 200 °C for 30 min after the adhesion test is shown in Fig. 1. The extent of adhesion of the Sr-P coatings is rated as per ASTM D 3359 standard. Accordingly, the adhesive strength of Sr-P coatings obtained by HT at 80, 120 °C for 30 min can be rated as 0B (i.e., greater than 65% removal of the coated layer) while the Sr-P coating prepared by HT at 150 °C for 30 min exhibits an adhesive strength rating of 2B (15-35% removal of the coated layer). In contrast, the adhesive strength of Sr-P coating prepared by HT at 200 °C for 30 min is very good and it can be rated as 4B (less than 5 % removal of the coated layer). The variation in the adhesive strength of the Sr-P coatings prepared by HT as a function of temperature is due to the difference in reactivity and the extent of formation an adherent layer during the initial stages of coating formation. Since detachment of the coated layer is likely to generate galvanic cells and accelerate the rate of corrosion of Mg, the Sr-P coated Mg prepared at 200 °C for 30 min can be considered suitable for implant applications.

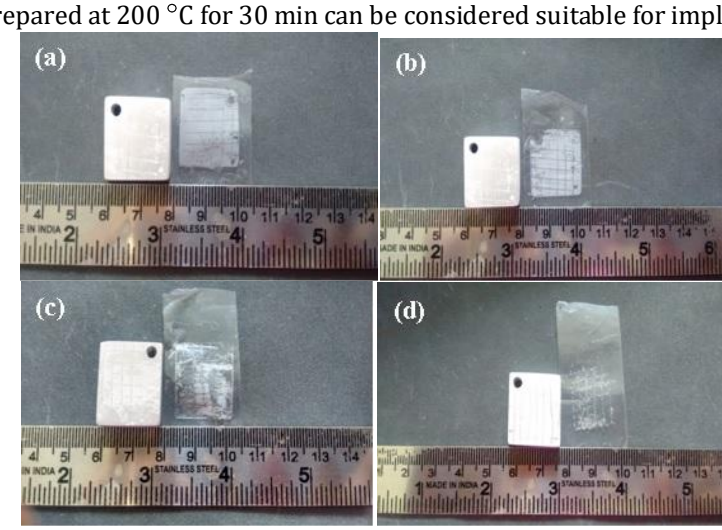

Fig. 1 Photographs showing the extent of adhesion of Sr-P coated Mg obtained by HT at various temperatures for 30 min after cross-cut tape test: (a) 80 ºC; (b) 120 ºC; (c) 150 ºC; and (d) 200 ºC

3.2 Loss in weight due to corrosion and leaching of Mg^{2+} and Sr^{2+} ions in SBF.

The loss in weight due to corrosion of uncoated and Sr-P coated Mg (obtained by HT at 80 and 200 °C for 30 min) after immersion in SBF at 37 ± 1 ºC for 24, 120 and 240 h is shown in Fig. 2.

Obviously, the loss in weight due to corrosion is increased with an increase in immersion time in SBF from 24 to 240 h and this trend is common for both uncoated and Sr-P coated Mg. However, when compared to the uncoated Mg, the loss in weight due to corrosion of Sr-P coated Mg is decreased significantly. Among the Sr-P coated ones, the sample coated at 200 °C for 30 min exhibits a very low weight loss irrespective of the immersion time. The presence of higher concentrations of aggressive Cl^- ions in SBF tends to promote dissolution of uncoated Mg and Sr-P coated Mg while the formation of $Mg(OH)_2$ and calcium phosphate based compounds limit the extent of corrosion attack. The lower loss in weight observed for Sr-P coated Mg indicates the ability of the Sr-P coating to prevent the ingress of the aggressive Cl^- ions and attack of the base metal. Among the Sr-P coated ones, the increased uniformity and higher coating thickness of the sample coated at 200 °C for 30 min helps to minimize the loss in weight due to corrosion. Based on the weight loss test, Sr-P coated Mg prepared at 200 °C for 30 min can be considered suitable for implant applications.

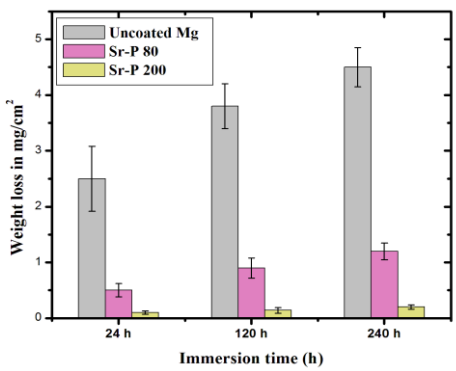

Fig. 2 Loss in weight due to corrosion of uncoated and Sr-P coated Mg obtained by HT at 80 and 200 °C for 30 min, after immersion in SBF at 37 ± 1 ºC for 24, 120 and 240 h

The concentrations of Mg^{2+} and Sr^{2+} ions leached from Sr-P coated Mg obtained by HT at 80 and 200 ºC for 30 min, after immersion in SBF at 37 ± 1 ºC for 1, 3, 5, 7 and 10 days are shown in Figs. 3(a) and 3(b), respectively. The concentration of Mg^{2+} ions leached from uncoated Mg is also included in Fig. 3(a) for an effective comparison. For both uncoated and Sr-P coated Mg, the concentration of Mg^{2+} ions is increased with an increase in immersion time up to 5 days. However, beyond 5 days of immersion, the trend is changed. For uncoated Mg, a large decrease in concentration of Mg^{2+} ions is observed, suggesting a reversal in trend beyond 5 days of immersion. This is due to the coverage of the surface of uncoated Mg by the corrosion products, mainly $Mg(OH)_2$. For Sr-P coated Mg, only a slight decrease in concentration of Mg^{2+} ions is observed beyond 5 days of immersion, which suggests that the extent of corrosion of Mg and formation of corrosion products are relatively less over the surface of Sr-P coated Mg. Among the Sr-P coated ones, the concentration of Mg^{2+} ions leached in to SBF is relatively less for the one coated at 200 °C for 30 min.

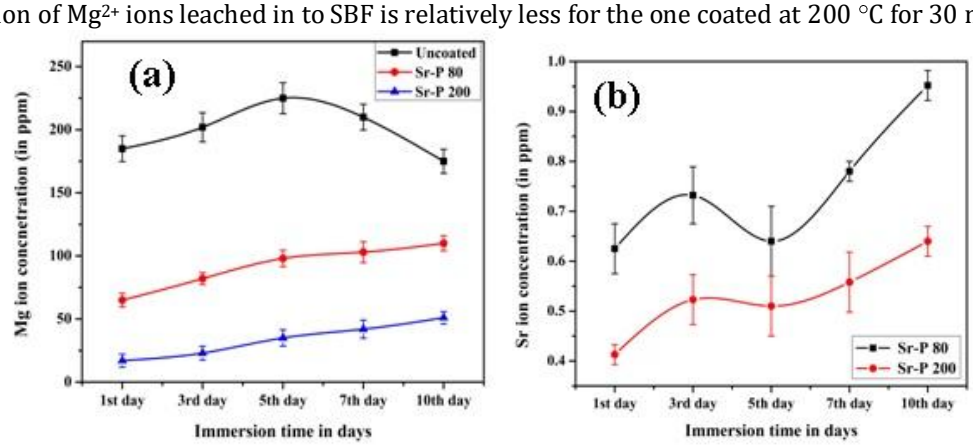

Fig. 3 Concentrations of (a) Mg^{2+} ions and (b) Sr^{2+} ions leached from Sr-P coated Mg obtained by HT at 80 and 200 ºC for 30 min, after immersion in SBF at 37 ± 1 ºC for 1, 3, 5, 7 and 10 days (concentration of Mg^{2+} ions leached from uncoated Mg is also included in (a) for an effective comparison)

When compared to the concentration of Mg^{2+} ions, the concentration of Sr^{2+} ions leached in to SBF is significantly lower (Fig. 3(b)). Hence, it is clear that the Sr^{2+} ions leached in to body fluid is not likely to induce any toxicity to the surrounding environment. The concentration of Sr^{2+} ions leached in to SBF, in general, is increased with an increase in immersion time from 1 to 10 days. The fluctuations in the concentration of Sr^{2+} ions is observed from 3rd day to 7th day could be due to the accumulation of corrosion products. Among the Sr-P coated ones, the concentration of Sr^{2+} ions leached in to SBF is relatively less for the one coated at 200 °C for 30 min. This is due to its better stability in SBF. Based on the loss in weight due to corrosion and concentration of Mg^{2+} and Sr^{2+} ions leached in to SBF, Sr-P coated Mg prepared at 200 °C for 30 min can be considered suitable for implant applications.

Conclusion

A simple hydrothermal coating process was exploited successfully to produce an Sr-P conversion coating on Mg with an ability to inhibit an initial degradation rate. Further, the adhesive strength also confirms the coated layer remains intact and the dissolution behavior of the coating was very less, mass loss was significantly reduced and also found that the protected layer will maintain higher mechanical strength for longer time. Toxicity around the implant in physiological environment is also very less which is evidenced from the release of Mg^{2+} and Sr^{2+} ions profile. Further toxic fewer environments would be supportive for cell proliferation and growth. Hence, based on the all observations, Sr-P coated Mg prepared at 200 °C for 30 min can be considered suitable for implant applications.

Referances

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