Hydroxyapatite/poly(lactide-co-glycolide) micro-patterning on magnesium for biomedical applications

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Statement of Purpose: Magnesium has a great potential as a biodegradable implant material due to its favorable combination of mechanical properties, biodegradability and biocompatibility [1]. Recently it has been considered as a promising material for coronary stent applications because the biodegradability of Mg can eliminate potential long-term complications of other metal stents [2]. These beneficial characteristics notwithstanding, rapid corrosion of Mg in the physiological environment has limited its clinical use. Among the approaches to mitigate the degradation of Mg, the combination of bioactive ceramic and polymer coating could be very effective in terms of biocompatibility and flexibility for stents. In this study, hydroxyapatite and poly(lactide-co-glycolide) coating was form on the photo-lithographically patterned magnesium surface. The effects of the coating layer on corrosion properties were evaluated through degradation behavior in PBS. The coating stability was assessed in tensile strain condition using custom-built device.

Methods: Pure Mg plates polished up to 4000 grit with SiC papers. Prior to the coating process, microdot array-structure was designed on the Mg by photo-lithography. The samples were treated in 0.05M Ca-EDTA (ethylenediaminetetraacetic acid calcium disodium salt hydrate)/0.05M KH_2PO_4 (potassium dihydrogenphosphate) aqueous solution to form HA. During the treatment, pH was adjusted to 8.9 with sodium hydroxide (NaOH) and the temperature of the solution was raised from room temperature to 368K in an oven for 2 h. Then, 5wt% PLGA (75:25 in PLA:PGA) solution in chloroform (CF) was dropped on the surfaces and spin-coated at a spin speed of 2500 rpm for 1 min. Subsequently, the specimens were placed inside an oven at 70 °C and dried for 2 h. To evaluate the surface corrosion resistance, the Mg samples were soaked in phosphate buffered saline (PBS). After 4 days, the mass change of the samples was recorded. Also, to examine coating stability, tensile strain was applied to the samples at levels of 5%.

Results: Figure 1 shows the surface morphologies of bare Mg (A), micro-patterned HA (B) and micro-patterned HA/PLGA (C), (D) on Mg. In Fig.1 (B), microdot arrays of HA crystals were uniformly fabricated on the Mg surface. Arrays of HA appeared in needle-shape structure with the size of ~10μm in diameter. In Fig.1 (C) and (D), PLGA thoroughly filled the rest part of the Mg surface, resulting in advantageous combination with HA pattern in terms of flexibility. When the samples were immersed in PBS, the degradation mass of the surface-treated samples was significantly reduced compared with bare Mg (Figure 2). Especially, HA/PLGA micro-pattern showed considerably protection of the initial corrosion of Mg. After 4% of tensile extension, HA coating layer exhibited severe cracking on the surface, in contrast to the HA/PLGA micro-pattern. The pattern was resistant to tensile load since there was no evidence of cracking and delamination.

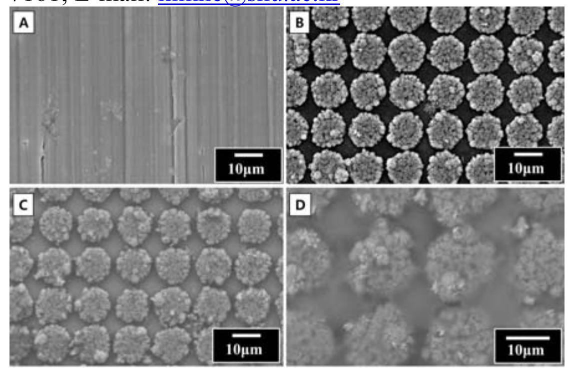

Figure 1. SEM micrographs of the bare (A), HA micro-patterned (B) and HA/PLGA micro-patterned (C), (D) Mg.

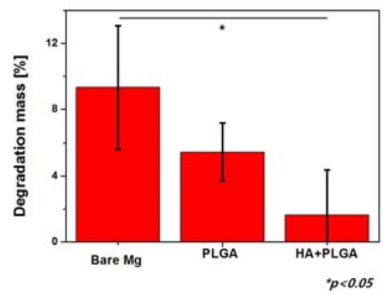

Figure 2. Degradation mass of the bare, PLGA coated Mg and HA/PLGA micro-patterned on Mg specimens after 4 days of immersion in PBS.

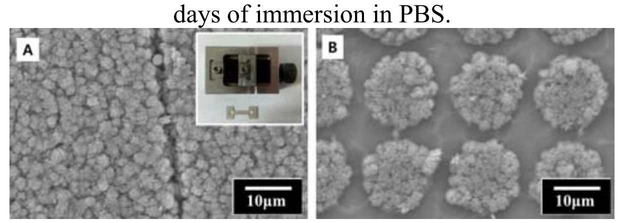

Figure 3. SEM micrographs of the HA coated and HA/PLGA micro-patterned Mg at 4% tensile strain level. The inset shows the lab-made device which gives tensile strain.

Conclusions: The micro-patterned HA/PLGA was successfully produced on photo-lithographically designed Mg surface by the treatment in Ca/P aqueous solution and PLGA spin coating process. The HA pattern covered the surface periodically and PLGA filled the rest densely. Corrosion resistance of the samples was highly improved compared to the bare Mg, resulting in the decrease of degradation mass in PBS. The SEM observations revealed that the patterned layer had better stability during deformation. In conclusion, HA/PLGA micro-patterning on Mg is a promising approach to reduce the corrosion rate of Mg and improve the coating flexibility.

References:

1. Staiger MP, Biomaterials. 2006;27:1728-34
2. Erne P, Cardiovasc Inter Rad. 2006;29:11-6.