

Reduction of the corrosion rate of biodegradable metallic materials by Al₂O₃ PIII surface treatment

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Statement of Purpose: Metallic implants are often used for fracture fixation. However, long-term adverse effect or sometimes stress shielding maybe resulted if the implants are non-biodegradable. Therefore, biodegradable implant is an alternative to help reduce this complication and costs to health care system due to removal surgery. Magnesium is the potential candidate. However, the major challenges of using magnesium are the rapid degradation and hydrogen gas release after implantation. Therefore, improving its corrosion resistance is the primary objective prior to the clinical use. Various surface treatments such as Immersion Ion Implantation and Deposition (PIII&D)¹ and plasma anodisation² are applied to enhance the corrosion resistance. Our previous studies suggested that nitrogen and water plasma implantation were able to enhance the corrosion resistance of magnesium alloys^{3,4}, but little information was available on the biological integrity of these PIII treated magnesium alloys. In addition, our group has also applied an aluminium oxide layer onto the magnesium alloy with the use of PIII technique since both aluminium⁵ and aluminium oxide⁶ were found to be able to slow down the corrosion rate of magnesium. This present study aims to investigate the biocompatibility of the N₂, H₂O and Al₂O₃ plasma treated magnesium alloy.

Methods: PIII was conducted on the AZ91 magnesium alloy by using nitrogen, water and also aluminium and oxygen as the plasma sources.

To demonstrate the corrosion resistance test after the surface treatment, a preliminary immersion test by using DMEM medium was conducted at 37°C incubator for 1 and 3 days. In addition, the biocompatibility of the plasma treated samples was tested by culturing green fluorescent protein osteoblasts (GFPOB).

Results and Discussion: On observation, both the N₂ and H₂O plasma treated samples were corroded on day 1 and gas bubbles were observed from the samples' surface (as shown in Figure 1). However, there was fewer gas bubbles released on day 3 due to the formation of the magnesium hydroxide⁷. A colour change was observed for the N₂ plasma treated sample, where the sample colour changed from silver to black and the DMEM medium changed from orange red to pale purple. However, for the Al₂O₃ treated sample, although the surface of the sample changed from silver to black, no gas bubble was observed on day 1 and 3. The colour of the DMEM medium was still orange red throughout the immersion period. The result suggested that Al₂O₃ was able to slow down the corrosion rate as compared with N₂ and H₂O treatments. After conducting cell culturing test, no living GFP osteoblast was found on the N₂ and H₂O plasma treated magnesium alloys but cells tolerated very well on the Al₂O₃ treated sample as shown in Figure 2. This was

highly related to the oxidation rate of the samples. As correlated with the immersion test, N₂ and H₂O samples corroded vigorously so that their surfaces kept on oxidizing, therefore cells were not able to attach and proliferate.

As Tian et al.^{3,4} had reported that both N₂ and H₂O plasma enhanced the corrosion resistance of the magnesium alloys to a certain extent, however, by conducting the biological testing, the improvement was not enough to grow cells. Since the application of the magnesium alloys in this study was to use as an implant, it is apparent that both N₂ and H₂O treated magnesium alloys are not suitable. However, the Al₂O₃ plasma treated samples has certain potential to be used as an implant as its corrosion rate is slow, apart from the biocompatibility test, other tests include the mechanical testing during degradation and *in-vivo* studies are still needed.

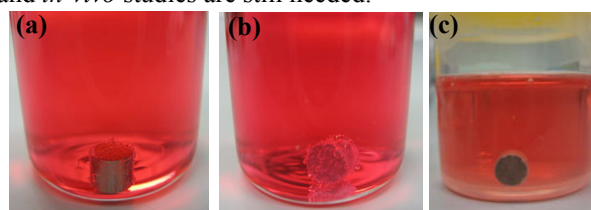


Figure 1. Immersion test of the plasma treated samples on day 1 by using DMEM medium. (a) N₂, (b) H₂O, (c) Al₂O₃. Gas bubbles were observed on N₂ and H₂O samples while not observed on Al₂O₃ sample.

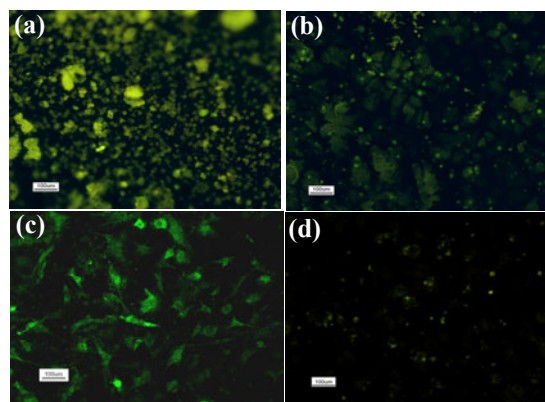


Figure 2. Microscopic view of GFP mouse osteoblasts cultured on (a) N₂, (b) H₂O, (c) Al₂O₃, (d) untreated samples after 3 days. Cells grow very well only on Al₂O₃ sample but not on N₂, H₂O and untreated samples. Instead there were significant amount of magnesium oxide and magnesium hydroxide formed on those samples other than Al₂O₃.

Conclusions: The corrosion resistance properties of N₂, H₂O and Al₂O₃ plasma treatments have been investigated. It is suggested that Al₂O₃ plasma modification has potential for further studies prior to clinical trial.

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