Biodegradable Mg implants: how to improve the surface properties?

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INTRODUCTION: Due to their ability to resorb in the human body and to provide specific biological responses, Mg-based implants can be classified as bioactive and biodegradable materials. In the past decades, they were successfully used as cardiovascular and orthopedic implants. To provide mechanical integrity in the body over several months, the corrosion process must be precisely controlled. Plasma Electrolytic Oxidation (PEO) surface treatment has been proven an efficient method for corrosion protection of Mg alloys. We showed how PEO improves the corrosion resistance of AZ31. Different post-treatments improving biological properties of the Mg alloys can be considered in the fabrication chain of future resorbable implants.

METHODS: Polished AZ31 discs (30 mm diam.) were anodized by PEO using a CIRTEM® bipolar pulsed current source (f=100 Hz; J+= 30÷60 A/dm^2, J-= 0÷30 A/dm^2). The electrolyte contained 4 g/l NaOH and 6.3 g/l calcium glycerophosphate (pH=12.5). Treatment time was 5 min resulting in the anodized layer thickness of 15-20 µm. Two post-treatments were performed after PEO: 1) 50 nm-thick TiO_2 layer was deposited by Atomic Layer Deposition (ALD) and 2) a PLLA (poly-L-lactic acid) layer (10 µm-thick) was deposited by dip-coating. The surface and cross-section morphology were examined by Scanning Electron Microscopy (SEM) and optical microscopy. Corrosion tests were performed by potentiometry. Hydrogen gas evolution was measured by immersing the samples in HCl (0.25 M) solution. Biological assays with mouse fibroblast L929 cells were performed on the treated samples in order to assess their cytocompatibility. L929 cells were grown in contact with sample extracts, degraded during 24 and 72 hours in DMEM/F12 medium supplemented with 10 % FCS and 1 % PenStrep. WST-8 proliferation assays were used to assess cell viability in presence and absence of the coated sample extracts. Cell viability in absence of the sample was taken as 100 % viability.

RESULTS: The surface of anodized samples presents a morphology typical for PEO layers, showing a high percentage of open pores originating from arc discharges and gas emission through the growing PEO layer (Fig. 1, left). The potentiometry results show that PEO treatment enhanced the corrosion resistance by a factor of 300 (compared to non-treated AZ31). The emission of hydrogen gas, resulting from a reaction between Mg and HCl, was significantly retarded by PEO treatment. No hydrogen bubbles were observed during first 30 days of tests for PEO-treated samples, while 250 mL of gas was collected after 15 min of test with untreated AZ31 sample (same test conditions).

The results of biological tests indicated a poor cell viability for PEO-treated AZ31. The cell viability increased significantly (> 80%) after ALD post-treatment (Fig.1, right). PLLA coating resulted in a cell viability of 60% (compared to the reference).

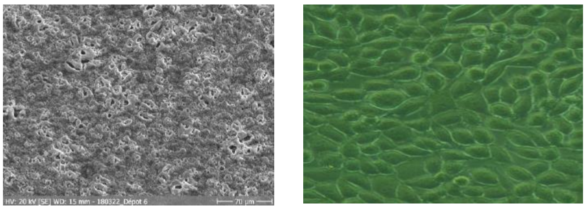

Fig. 1 (left): SEM image of the surface of PEO-treated AZ31; (right): optical microscopy image (200x) of L929 cells exposed during 24 h to the PEO-ALD sample.

DISCUSSION & CONCLUSIONS: PEO is a suitable surface treatment enhancing the corrosion resistance of Mg-based alloys. However, open pores in the PEO layer are problematic as they could initiate Mg ion release from the substrate in contact with a physiological medium, resulting in a pH increase in the surrounded area and poor biological response. Post-treatments (TiO_2 by ALD, dip-coating with PLLA) can further improve the corrosion resistance of the PEO-treated Mg alloys. They are necessary to obtain a favourable biological response in contact with viable cells.