Organic-Inorganic Hybrid Coating for Deformable and Bioactive Magnesium Implants

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Statement of Purpose: Magnesium (Mg) and its alloys have been regarded as promising materials for biodegradable implants because of their good mechanical performance relative to that of biopolymers. However, rapid corrosion in physiological conditions is a major obstacle for the clinical use of Mg [1]. Various protective coating techniques have been proposed to reduce corrosion rates and improve bioactivity of Mg [1]. Moreover, biomedical implants are often exposed to various dynamic loading situations that induce some degree of deformation, thus a protective coating layer on Mg needs to tolerate the deformation of its substrate [2]. Therefore, in this study, we have developed an organic-inorganic hybrid coating technique by introducing a groove pattern on Mg and selectively coating both hydroxyapatite (HA) and polyetherimide (PEI) on the groove surface to achieve a deformable, crack-free coating layer with improved corrosion stability and bioactivity.

Methods: Dog-bone shaped Mg specimens were prepared for the experiments. Microgroove patterns were created by either laser machining or CNC machining. The Mg specimens were treated in Ca/P solution to form HA as described in [3]. Mechanical behavior of Mg with or without groove patterns was simulated by finite element analysis (FEA) models at the applied tensile strain, ε=0.08 and predicted stress and strain contours were analyzed. The hybrid coating on the grooved Mg substrate was carried out. HA was formed on the grooved surface, followed by the spin-coating process with 10wt% PEI solution. Subsequently, the specimens were dried at 70℃ for 2 h. To eliminate PEI on HA, N-methyl-2-pyrrolidone (NMP) was applied on the coated surface. Coated groove surface of Mg was characterized by SEM/EDS.

Results: Brittle HA coating on flat Mg was fractured and delaminated at ε=0.08 as shown in **Fig.1a** while HA on grooved Mg was fractured at the valley part of grooves in **Fig. 1b, c**. The predicted strain contours of both flat and grooved Mg indicate that the grooved pattern creates the strain distribution, where the hills undergo minimal deformation, but the valleys experience large deformation, exceeding the applied strain, ε=0.08 (**Fig. 1d**). To optimize the groove geometry, the corresponding FEA models were created as indicated in **Fig. 2a**, varying three parameters, width, distance and depth. From the simulation results, increased width and decreased length and depth were found to reduce the maximum strain value, which suppress the risk of Mg failure during deformation (**Fig. 2b, c**). Based on the understanding geometry, the optimal groove geometry was chosen and was coated with brittle HA for hills and flexible PEI for valleys, covering the whole Mg surface with the hybrid coating (**Fig. 3a, b**). The EDS analysis in Fig. 3c confirmed that hills and valleys of Mg grooves were well-coated with HA and PEI, respectively.

Conclusions: The HA-PEI hybrid coating layer has been successfully fabricated on the grooved Mg surface where the less deformable hills and largely deformed valleys were coated with HA and PEI, respectively. To reduce the strain concentration at valleys, the optimal groove geometry was investigated. The grooved geometry of Mg in conjunction with hybrid coating has great potential as a crack-free, deformable protective and bioactive coating for various Mg-based implants.

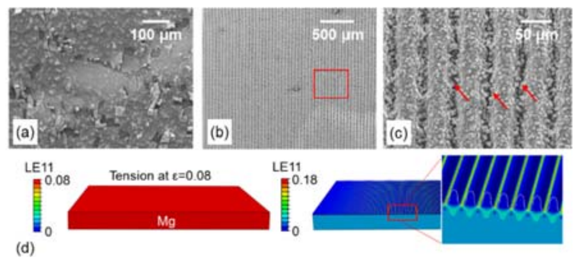

Figure 1. (a) Fractured HA coating on Mg, (b, c) fractured HA coating on grooved Mg at different magnifications, and (c) predicted strain contours of flat and grooved Mg substrates.

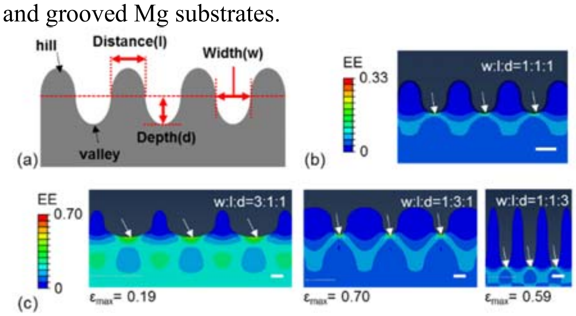

Figure 2. (a) Schematic diagram of FEA models with variables of width, distance and depth, (b) the strain contour of the groove at w:l:d=1:1:1, (c) strain contours of the different grooves (scale bar = 20 μm)

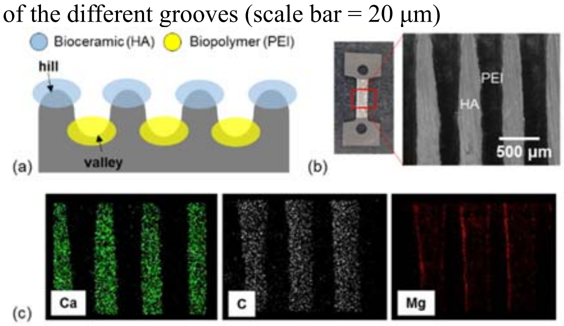

Figure 3. (a) Proposed design of a hydrid coating, (b) surface morphology of hybrid-coated grooved Mg specimen and (c) EDS data of hill and valley regions on the grooved Mg surface

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