Mitigating Degradation of Additively Manufactured Porous Magnesium Scaffolds Using Hydroxyapatite Coating

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INTRODUCTION: Bone implants typically consist of metals such as titanium, stainless steel, and cobalt chromium due to their mechanical strength.[1] However, the strength of these materials exceeds that of bone which can lead to stress shielding, atrophy of bone, and/or pain, requiring revision surgeries.[2] As an alternative biodegradable material, magnesium promotes osteogenesis but can degrade too fast causing gas pockets and/or insufficient mechanical strength. Coatings such as hydroxyapatite (HA) are an effective means to modulate degradation, as we have demonstrated on solid pure magnesium.[3] The objective of this work was to evaluate the effects of hydroxyapatite (HA) coating on the degradation kinetics of additively manufactured porous magnesium (Mg) scaffolds. Our hypothesis was that the HA coating would mitigate the initial bulk degradation of the magnesium scaffolds.

METHODS: Additively manufactured WE43 Mg alloy scaffolds (n=6, 6x1.4mm (dxh)) with diamond unit cells (400 μm strut width; 600 μm pore size)[4] were coated using a solution deposition method at 90°C, pH 8.9, for 16 hours on each side. Non-coated samples (n=6) served as the control. A degradation study was performed in DMEM (ISO 10993-12) on a rocker plate at 90 RPM, 37°C[3] through 20 days. Sample mass and solution pH were recorded at days 0, 1, 4, 7, 10, 15, and 20. SEM imaging was performed on days 0, 4, 10, and 20. Surface profilometry scans were performed on day 20 samples to measure line roughness, surface roughness, average step height, maximum height, and minimum height. For mass and pH data, a repeated measures ANOVA was performed, and for surface profilometry data, an unpaired t-test was performed (GraphPad Prism, v8.4.3).
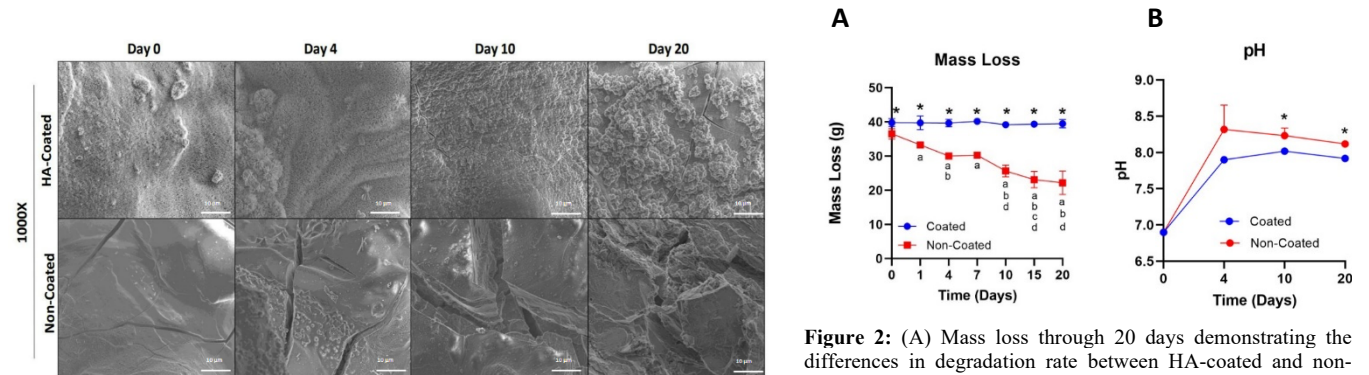
RESULTS: The SEM images confirmed the presence of the HA coating on the samples, which was partially dissolved by day 20, exposing the WE43 substrate. Large cracks in the non-coated sample appeared to deepen over 20 days (**Fig. 1**). Only non-coated scaffolds had a reduction in mass (~35% by day 20); no change in mass of HA-coated scaffolds were observed (**Fig. 2A**). Likewise, pH was higher for non-coated scaffolds at days 10 and 20 compared to that for coated scaffolds (**Fig. 2B**). Line and surface roughness were not different between the coated and non-coated scaffolds on day 20 (**Fig. 3A-B**). In contrast, the average step height, maximum height, and minimum height were higher for the coated scaffolds (**Fig. 3C-E**), indicating they had undergone less degradation.

DISCUSSION: Mass for coated samples remained constant throughout the 20-day study, demonstrating the HA coating was an effective means to slow the degradation of WE43 scaffolds. Less change in pH in the coated scaffolds over time also supports this finding. The equivalent line and surface roughness at day 20 were likely attributable to the relatively large baseline roughness induced by the AM process. Higher height values for the HA-coated scaffolds indicates they had degraded less than the non-coated scaffolds, further supporting our hypothesis. Collectively, these results demonstrate the utility of the HA coating for mitigating degradation of magnesium alloys. Ongoing work includes finite element modeling to estimate degradation patterns and mechanical integrity of degraded HA-coated and noncoated scaffolds beyond 20 days over their expected lifespan, and degradation of the scaffolds in a bioreactor environment.

SIGNIFICANCE/CLINICAL RELEVANCE: Additive manufacturing of degradable, osteogenic biomaterials such as magnesium with customizable geometries and mechanical properties will accelerate the translation of next-generation orthopedic implants. Here, we demonstrate the functionality of HA coating to slow the degradation of additively manufactured porous Mg scaffolds, which may ultimately enhance osseointegration and bone repair.

REFERENCES: 1. Li, Y., *Acta Biomat,* 2018; 2. Munir, K., *Acta Biomat,* 2020; 3. Rourke, A. *J Mat Res,* 2022; 4. Jahr, H., *Acta Biomat,* 2017

Figure 1: HA-coated and non-coated scaffolds imaged using SEM at 1000X. HA is visible on the surface of coated scaffolds and begins to wear away by day 20. Cracks are more prominent on non-coated scaffolds and appear to grow over time. Scale bar=10μm.

Figure 2: (A) Mass loss through 20 days demonstrating the differences in degradation rate between HA-coated and non-coated WE43 scaffolds (n=6, *p<0.05). (a) indicates significant difference to day 0. (b) indicates significant difference to day 1. (c) indicates significant difference to day 4. (d) indicates significant difference to day 7. (B) Solution pH over 20 days of degradation (n=6, *p<0.05).
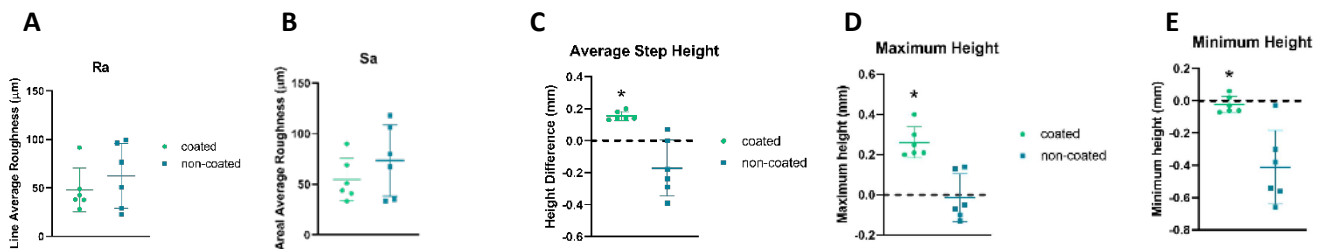
Figure 3: Surface profilometry data at day 20. No differences were observed for Ra (A) or Sa (B) for coated and non-coated samples. Average step height (C), maximum height (D), and minimum height (E) were greater for HA-coated scaffolds compared to non-coated scaffolds (*p<0.05).