Synopsis

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Title of thesis: **Effect of Processing Mg-6Zn-0.2Ce through High-Pressure Torsion on Its Use as a Biomaterial**

Conventionally, internal fixation devices used to repair fractured bones are fabricated from metallic materials, such as titanium alloys and stainless steel. Besides providing mechanical support, implants must be corrosion-resistant and are expected to facilitate tissue repair. As they are non-degradable, they persist even after the bone tissue is healed. If left inside, they can become sites of infection. Alternatively, they can be removed during a revision surgery, which increases cost and causes considerable discomfort to the patient. Furthermore, Young's modulus of these materials is significantly greater than that of bone tissue, which may cause stress shielding and lead to weakening and resorption of bone.

In contrast, bioresorbable implants hold great promise for internal fracture fixation since they can be resorbed by the body gradually over time, allowing damaged tissues to regenerate. After damaged tissue is restored and regenerated, these implants gradually degrade without the need for additional procedures. Magnesium (Mg) is an excellent bioresorbable implant candidate since it offers many advantages over traditional implant materials. For instance, Mg is a nutrient that the human body needs; an adult in good health should consume about 420 mg of Mg daily. Any surplus ions are stored in extracellular matrices and are excreted via urination. Mg has inherent bioactive properties that help heal tissues locally. Moreover, its Young's modulus is closer to the bone than traditional biomaterials, thereby reducing the stress shielding effect. However, the high corrosion rate and the relatively lower yield strength of Mg limit its clinical applications. Hence, it is essential for a synergistic improvement in both the mechanical and corrosion properties of Mg and its alloys for clinical applications. Mechanical strength and corrosion resistance can be improved via alloying and secondary deformation techniques. In this context, the addition of zinc (Zn) improves mechanical and corrosion properties, and cerium (Ce) helps in grain refinement, thereby improving mechanical properties. Overall, adding Zn and Ce to Mg synergistically improves mechanical and corrosion properties, and hence, a Mg-Zn-Ce alloy, such as Mg-6Zn-0.2Ce alloy, is a promising candidate biomaterial and was, accordingly, used for this study.

High-pressure torsion (HPT) is a severe plastic deformation technique in which samples are simultaneously subjected to torsional straining and hydrostatic pressure while being held between two anvils. As Mg has limited slip systems, its grain size cannot be refined further by standard secondary processes, such as rolling or extrusion, and deformation requires high temperatures. HPT is known to improve mechanical strength remarkably and can be performed at room temperature. However, the effect of HPT on corrosion is highly erratic; some have reported improvements, others have reported decrement, and some have shown no changes. Moreover, magnesium is also a very reactive substance, which makes it difficult to comprehend kinetics and mechanisms from electrochemical tests. Also, long-term corrosion testing, such as immersion tests, may differ greatly from short-term corrosion tests, like those using potentiodynamic polarization (PDP) methods and electrochemical impedance spectroscopy (EIS). Hence, the goal of the work in this thesis was to assess the effect of HPT on the mechanical behavior, corrosion properties, and cell response to Mg-6Zn-.02Ce alloy— prerequisites for evaluating materials as potential biodegradable implants.

Mg-6Zn-0.2Ce solution was heat treated at 400 °C for 12 h, followed by quenching in water: This condition is referred to as-received material. As-received alloy samples of dimension 10 mm diameter and 0.8 mm thickness were subjected to 1, 2, and 5 quasi-constrained HPT turns under a pressure of 6 GPa. After undergoing 1, 2, and 5 HPT turns, the grain sizes of the sample decreased from 300 ± 90 µm to 106 ± 31, 47 ± 19, and 74 ± 23 nm, respectively, resulting in ultra-fine grains (UFG). Notably, after HPT processing, mechanical strength improved significantly, with a reduction in ductility, compared to the as-received sample (see **Fig. 1**). The 2-turns sample showed the highest mechanical strength owing to the smallest grain size, consistent with the Hall-Petch-based grain boundary strengthening model.

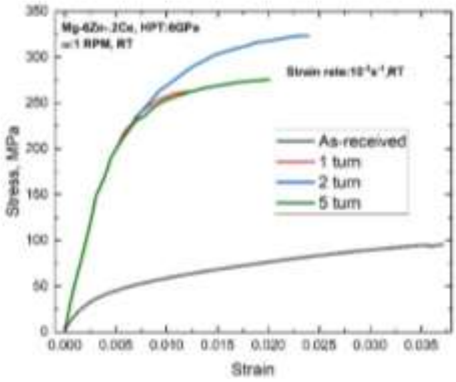

Fig 1: Representative plots showing the variation of nominal stress as a function of the nominal strain for as-received and 1, 2, and 5 HPT turns Mg-6Zn-0.2Ce samples.

Corrosion resistance was highest for 2 HPT turn sample, followed by 5 and 1 HPT turn samples, and the as-received sample (see **Fig. 2(a)**), as corrosion resistance is directly proportional to the diameter of the loop on the Nyquist plot. 2 HPT turn sample showed the lowest corrosion resistance because of its small grain size, which aids in the formation of an adherent oxide layer. When Mg is processed using HPT, a strong basal texture with the lowest surface energy and highest planar density is produced. Since the planes with the highest planar density have the highest coordination number (and, hence, fewer broken bonds), they often show the highest corrosion resistance. As can be seen in **Fig.2b,** the corrosion rate assessed following three days of immersion in simulated body fluid (SBF) is significantly higher than that estimated using the Stern-Geary approximation and Tafel extrapolation (i.e., short-term corrosion experiments). Even though the immersion test yielded a higher degradation rate for HPT-processed samples than the electrochemical test, it was still slightly lower for HPT samples than as-received samples. Variability in the long-term corrosion resistance of HPT-processed samples was statistically insignificant.

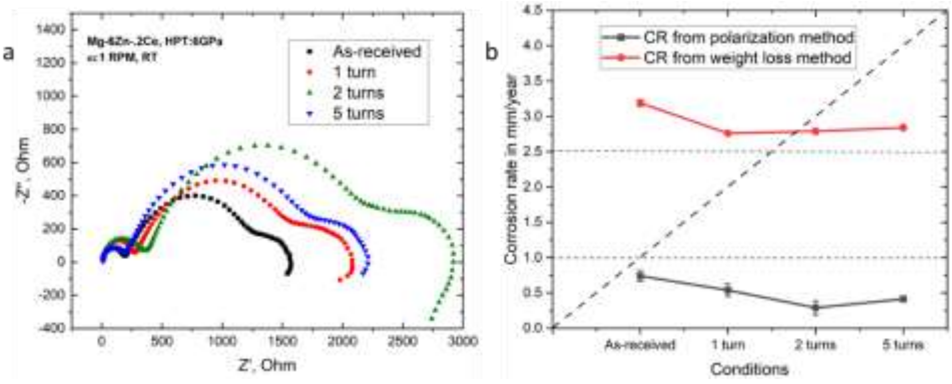

Fig 2: (a) Representative EIS-generated Nyquist plot for the Mg alloy examined in this study after stabilizing in SBF for 2 h. (b) Corrosion rate obtained from 2 h electrochemical polarization test and immersion test after submerging the samples in SBF for 72 h.

To discern the discrepancy in corrosion rate obtained from short-term PDP and long-term immersion-based weight loss test, the Tafel test was performed after submerging samples in SBF for 24 h. There is a remarkable difference between the Tafel curves of these two samples (**see Fig.3a**): The corrosion rate of samples after 24 h of immersion in SBF was significantly higher than the sample that was immersed for only 2 h. Mg-6Zn-0.2Ce forms pits when submerged in SBF for long periods (about 11.4 h), which accelerates corrosion. Corrosion pits formed in both as-received and 2 HPT turn samples, as shown in **Fig.3b and Fig.3c**.

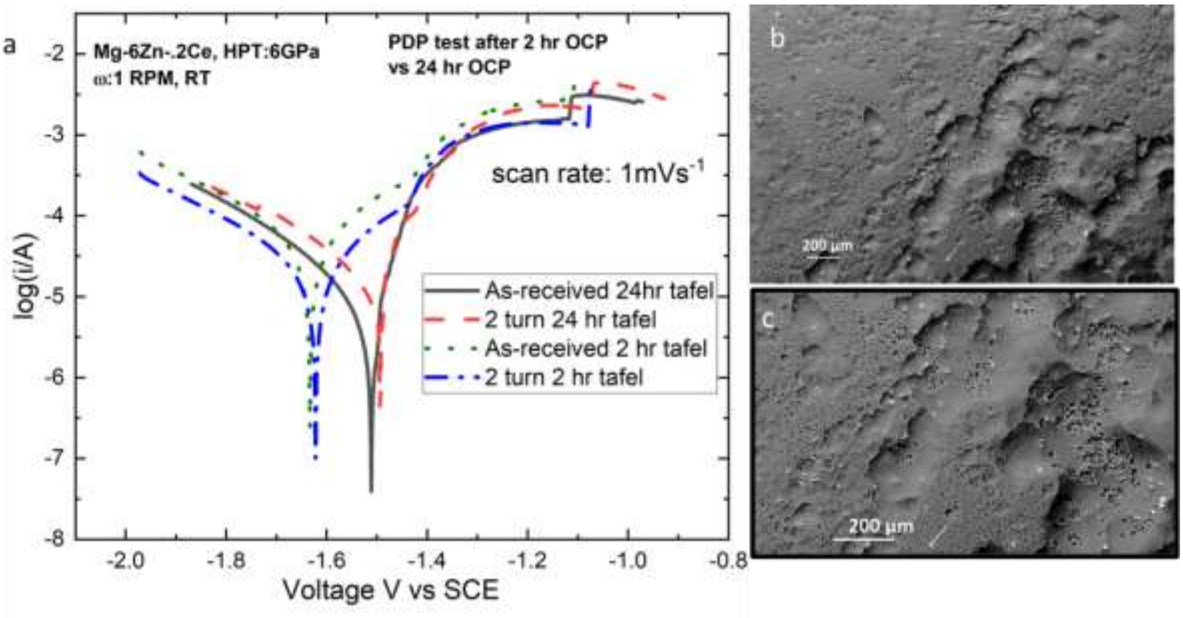

Fig 3: (a) Tafel curves of the Mg alloy obtained after immersing samples in SBF for 2 and 24 h, and the surface morphology after removing the corrosion layer formed on (b) as-received and (c) 2 HPT turn samples soon after 3 days of immersion in SBF.

Fig. 4 shows the morphology of MC3T3-E1 cells cultured in conditioned medium and fresh medium on Day 3 for as-received and 2 HPT turn samples. The green color represents actin filaments, whereas the blue color denotes the nucleus. Cells were uniformly distributed, and well-spread stress fibers were observed after exposure to 25 % conditioned media of as-received and 2 HPT turn alloy samples. However, the stress fibers bulged slightly and were not as well spread as the control for the cells exposed to 100% conditioned media. Significant increments in cell coverage can be observed by Day 3 with nearly full coverage of the well plates. Overall, the results of the cell morphology displayed in **Fig.4** indicate satisfactory compatibility.

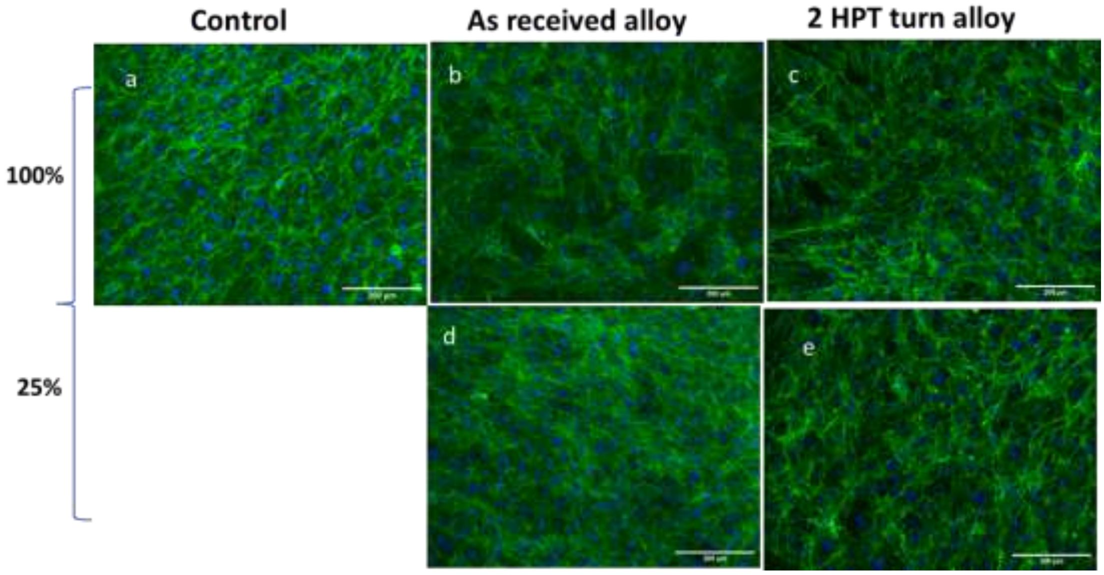

Fig. 4: Fluorescence micrographs showing the morphology of MC3T3-E1 cells cultured and 3 days (a-e) in conditioned media. The green color shows the F-actin (cell morphology), and the blue color shows the nucleus. The scale bar is 200 µm.

Overall, the 2 HPT turn sample showed significant improvement in mechanical properties, slightly improved corrosion resistance, and good biocompatibility, thereby improving its suitability for further evaluation to engineer bioresorbable implants for fracture fixation. This work highlights the potential of HPT as a viable technique to improve the biomedical performance of Mg alloys for engineering next-generation biomedical implants.