

## ABSTRACT

The present study aims to develop a Mg alloy for temporary orthopedic implantation by incorporating essential body-nutrient elements. The concept behind designing this alloy system stems from the fact that the ions and molecules generated during degradation of such alloy can be effectively utilized by bodily organisms for different activities, without inducing toxicity. However, the effectiveness of the method relies on controlled degradation of the alloy since each and every metallic ion has a definite regular intake limit, beyond which they might exhibit adverse effects in human body. Considering this, a Mg-4Zn-0.5Ca-0.8Mn alloy system was selected for the current study where each of the alloying elements are essential trace elements for body and the presence of 0.8 wt.% Mn ensures the formation of a Mn-oxide enriched product film that effectively inhibit the penetration of chloride ions, leading to substantially higher corrosion resistance compared to low Mn containing Mg-4Zn-0.5Ca alloys. The fabricated Mg-4Zn-0.5Ca-0.8Mn alloy in as-cast (AC) condition exhibited interconnected network of coarse precipitates along the grain boundaries, leading to poor tensile and bio-corrosion properties. To ensure adequate precipitate dissolution and simultaneous solute redistribution, the alloy was subjected to a homogenization heat treatment. Instead of adopting a tedious and time taking 'hit and trial' approach through experimentation, the homogenization parameters were optimized in the study employing thermodynamic calculations and diffusion-based kinetic modelling. An optimum balance in tensile (yield strength, YS~125 MPa and elongation,  $E_f$  ~6%) and biocorrosion properties (corrosion rate, CR~3 mm/year) was achieved in the alloy homogenized at 633 K for 24 h (H24) due to a substantial dissolution in coarse precipitate network as well as the presence of lower fraction of fine Mn-Zn phases. Since the properties of the homogenized alloy were far lower than the minimum requirements for temporary implantation, the H24 specimen was subjected to further thermomechanical treatment employing an economical hard-plate hot forging (HPHF) method. The aim has been to induce microstructural modifications in terms of grain orientation and grain size in order to alter the slip system activity. The HPHF at varied temperatures (i.e., 523 K, 623 K, and 723 K) produced microstructures predominantly comprising of {0001} // ND oriented grains, in contrast to the H24 (homogenized) specimen which consisted of randomly oriented grains. To examine the variation of slip/twin activity in the studied specimens throughout the span of tensile deformation, the visco-plastic self-consistent (VPSC) simulation method was adopted in this study. The VPSC simulation revealed that the randomly orientated grains resulted in enhanced basal slip activity at the onset of deformation, whilst, the non-basal slip activity was primarily facilitated by basal-oriented grains after adequate nominal stress required for the corresponding non-basal slip mode was achieved. Among the hot-forged specimens, the specimen forged at 623 K (FH24-623) exhibited the best strength-ductility synergy (YS~225 MPa,  $E_f$  ~16%) due to bimodal grain structure with lower average grain size and a higher pyramidal  $\langle c+a \rangle$  activity. A

quantitative analysis, carried out using empirical equations, revealed that bimodal microstructures containing lower average grain size show lesser degradation than a unimodal microstructure having higher average grain size, provided that the specimens develop a protective product layer which retains their corrosion current density below  $10 \mu\text{A}/\text{cm}^2$ . The FH24-623 specimen exhibited the lowest CR ( $\sim 0.35 \text{ mm/year}$ ), attributed to the optimum size distribution of fine and coarse grains as well as the prevalence of basal oriented grains in the specimen. The least corrosion resistance was noted in the specimen forged at 523 K (FH24-523) owing to the high retained strain, induced due to the forging treatment at a temperature (523 K) below the recrystallization temperature of the alloy. Considering this, the specimens homogenized for different durations were subjected to HPHF at 523 K temperature to investigate the implications of retained strain on bio-corrosion behaviour. The deformed specimen exhibited accelerated degradation compared to its homogenized counterpart, attributed to high dislocation density that led to defect (oxygen vacancies) generation and nonuniform product films formation. An even distribution of retained strain mitigated the nonuniformity of the product film to certain extent by providing greater film coverage and resulted in higher film resistance. Finally, the *in-vitro* cytocompatibility tests revealed that all specimens maintained a cell-viability over 70%, confirming acceptable cytocompatibility of the alloy. The FH24-623 specimen demonstrated the highest cell-viability and cell-proliferation due to its minimal degradation rate, allowing controlled ionic release, which assisted cell-growth without inducing toxicity. Moreover, the lower degradation rate of FH24-623 specimen resulted in minimal rise of pH, which promoted rapid dissociation of  $\text{Zn}(\text{OH})_2$  into Zn ions, leading to enhanced antimicrobial activity. Besides the favourable biocompatibility, the tensile and biocorrosion properties exhibited by the FH24-623 specimen exceed the minimum thresholds reported for orthopedic fixtures, making it a prospective material for temporary orthopedic implants.

**Keywords:** Antimicrobial activity; Body-nutrient elements; Bimodal grain structure; Cytocompatibility; Grain orientation; Grain size distribution; Homogenization treatment; Hard-plate hot forging; *In-vitro* bio-corrosion; Kinetic modelling; Mg-alloy; Thermomechanical processing; Temporary orthopedic implants; Tensile Deformation; VPSC simulation.