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## The Development of Bioresorbable Fe-Mn alloys for Orthopaedic Implantation

Bioresorbable metals have immense potential to be used in the clinical treatment of a variety of soft and hard tissue injuries and disease. For many applications, the presence of a permanent device may cause severe negative effects and require re-intervention in the long-term. A transient support for a healing tissue is an attractive solution for orthopaedic and vascular interventions alike. For applications in bone fracture in particular, the human body requires fixation devices to support bone regrowth in the proper alignment, but only for a short period of time (typically 6-12 months). We aim to design bioresorbable materials to fill this gap in the current offerings of implants. One such material system with promising results is iron-manganese (Fe-Mn) alloys. Our goal is to tailor the material's corrosion rate, mechanical properties, and cellular interactions to support tissue healing and remodeling.

Here, we characterized the surface evolution and degradation kinetics of Fe-20% Mn while immersed in osteogenic media for 90 days. It was found that the thick, quickly-forming Fe-rich oxide layer that forms on the surface severely inhibits the degradation rate of the alloy. Comparisons were drawn between the degradation rates obtained from immersion mass loss testing and electrochemical experiments. Electrochemical experiments clearly overestimate the true degradation rate of the alloy in vitro, but quick evaluations can be made between materials processed differently. The composition of the alloy, final microstructure, and manufacturing method employed to create the implant were found to affect the structure of the rapidly formed, iron-rich oxide layer, which inherently affects the amount of ion release from the alloy while immersed in biological environments.

In an attempt to enhance the degradation rate, we then used large-strain machining (LSM), a novel severe plastic deformation (SPD) technique was utilized during these experiments to modify the degradation properties of a Fe-33%Mn alloy. It was discovered that Fe-33%Mn after LSM with a rake angle of  $\alpha$ =0° (effective strain=2.85) showed the most promising increase in degradation rate compared to as-cast, annealed, and additional deformation conditions (rolled and other LSM parameters) for the same alloy. It was discovered that to increase the degradation rate further for Fe–Mn alloys, (1) tailored shear-based deformation processing can increase the kinetic effects of corrosion up to a critical value, (2) the surface area of the implants should be increased to allow for more diffusion of the osteogenic media into the Fe–Mn bulk alloy, which would also provide more adhesion and ingrowth of the hard tissue environment, or (3) new elements or components should be added to the alloy to facilitate increased degradation.

Another step of the research involved the use of dealloying on Fe-30%Mn alloys to selectively leach out diffused Zn and create tailorable, nanoporous structures to facilitate increased initial cell attachment and ingrowth. The mechanisms of dealloying were explored and the major factors found that affect the final surface structures include: (1) Initial microstructure, (2) Zn diffusion rate, (3) Etching/dealloying rate, (4) Temperature and time of annealing treatment, (5) etching with different acid or basic media. Continuing this concept over to a cell attachment study, 11 various topographical configurations of the dealloying treatment were chosen to investigate initial bone marrow stromal cell attachment and improve tissue/implant interface adhesion. Cells were attached over a period of 24 hours and an MTS Assay was used to measure cell viability. Comparing this data with fluorescence microscopy, SEM, and roughness values experimentally found through AFM, certain surfaces were found to be more conducive to attachment of cells.