Enhanced degradation properties of biodegradable Fe-Mn solid solutions containing divalent elements

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Statement of Purpose: Metallosis from the undesirable wear and debris formation related to long-term use of Ti, Co-Cr, and Fe-based inert biometals created a clinical need for developing biodegradable metals. Mg-based alloys have been vigorously researched as candidate biodegradable metals with advantages of biodegradability and density similar to human bone [1]. Rapid corrosion of Mg however, has not been resolved yet causing physiologically unfavorable amounts of hydrogen gas evolution and premature mechanical failure in in vivo experiments. On the other hand, iron-manganese alloys were introduced as a potential candidate for biodegradable metal albeit displaying slow degradation, but higher mechanical strength and anti-ferromagnetic properties [2]. However, design of the alloy to exhibit higher degradation rate could be envisaged to exhibit desirable degradation profiles of different medical devices such as craniofacial screw, plate or mesh. Therefore, in this study, Fe-Mn compositions were modified by introducing Ca and Mg identified by theory and developed using high energy mechanical alloying to enhance the degradation rates of biodegradable Fe-Mn while still maintain the anti-ferromagnetic property for magnetic resonance imaging.

Methods: Pure Fe, Mn, Ca and Mg powder in high purity were weighed, sealed with stainless steel balls in air-tight vials under argon atmosphere, and mechanically alloyed using P5 planetary milling machine Fe-Mn, Fe-Mn-Ca, and Fe-Mn-Mg powder alloys were consolidated using cold isostatic press at 60kpsi and sintered at 1200 °C for 3 hours under gettered ultra-high purity argon. Sintered alloy specimens were machined for biocorrosion and cell cytotoxicity assessment in dimension of 7.5 mm in diameter and 1.5 mm in thickness. Potentiodynamic polarization (Tafel test) was carried out employing a three electrode cell with platinum counter electrode, Ag/AgCl reference electrode, and the epoxy mounted specimen as the working electrode. The test was performed in DMEM +10% FBS at 37.4 °C. Indirect MTT (3-(4,5-Dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) assay was used to assess the cytotoxicity of the degradation product after 72 h immersion of sectioned specimens in culture medium. 10%, 25%, 50%, and 100% extract media were added to the 24 h cultured MC3T3-E1 cell, and MTT assay was performed after 72 h [2].

Results: Corrosion potential (E_{corr}), current density (i_{corr}) and associated corrosion rate (mm/year) calculated from the potentiodynamic polarization test shown in Figure 1 are tabulated in Table 1. It was found that the corrosion current density (i_{corr}) of the ERC alloys due to addition of suitable alloying elements, Ca and Mg, was elevated compared to Fe-Mn. Calculated corrosion rate of Fe-Mn were enhanced from 0.05 to 0.11 and 0.18 mmpy after replacement of Mn with Mg and Ca respectively. X-ray diffraction (XRD) of Fe-Mn-Ca, Fe-Mn-Mg, and Fe-Mn is shown in Figure 2. Adding Mg and Ca instead of Mn did neither affect the phase of iron and manganese nor exhibit distinctive pure Mg or Ca peaks. It is intended to maintain Y-phase Fe and Ɛ-phase Mn to achieve anti-ferromagnetic behavior and minimize the interference with magnetic resonance imaging. In Figure 3, indirect MTT assay assessing extract medium containing the degradation product after 72h immersion of the sintered Fe-Mn-Ca, and Fe-Mn-Mg pellets exhibited cell viability comparable to the cell culture plastic (negative control) even at 100% and 50% extract media.

Materials	Corrosion potential, E_{corr} (V)	Corrosion current (μA)	Corrosion rate (mmpy)
Fe-Mn	-0.65	-2.69	0.05
Fe-Mn-Ca	-0.56	-17.32	0.18
Fe-Mn-Mg	-0.60	-11.46	0.11

Table 1. Corrosion properties of processed Fe-Mn, Fe-Mn-Ca, and Fe-Mn-Mg alloys derived by powder metallurgy.

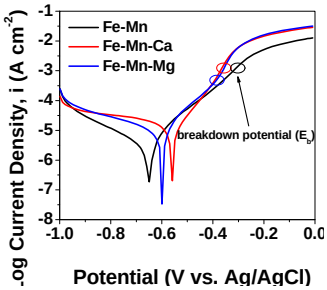

Figure 1. Tafel plot of Fe-Mn, Fe-Mn-Ca, and Fe-Mn-Mg powder alloys.

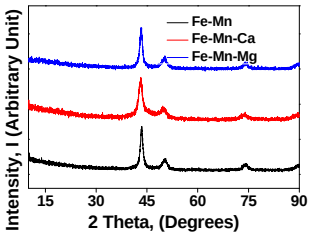

Figure 2. X-ray diffraction patterns of Fe-Mn, Fe-Mn-Ca, and Fe-Mn-Mg powder alloys.

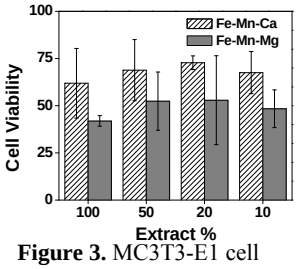

Figure 3. MC3T3-E1 cell viability after MTT assay of Fe-Mn-Ca, and Fe-Mn-Mg powder alloys.

Conclusions: Fe-Mn-Ca and Fe-Mn-Mg developed by high energy mechanical alloy exhibited higher degradation rates without compromising the anti-ferromagnetic property and cell cytotoxicity. Mechanical testing, immersion corrosion testing, mineralization assay, and alkaline phosphatase assay will be further studied to assess the potential of these modified Fe-Mn alloys for degradable medical device applications.

References:

[1] Staiger MP. Biomaterials. 2006. 27:1728-1734.
[2] Hermawan H. Powder Metallurgy. 2008. 51:38-45(8)