Surface modifications through dealloying of Fe-Mn and Fe-Mn-Zn alloys developed to create
tailorable, nanoporous, bioresorbable surfaces

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The effects and mechanisms of dealloying Zn-diffused Fe-Mn alloys over a wide range of processing parameters have been investigated using a four-step surface modification technique. The dealloying process was applied to construct tailorable, nanoporous Fe-Mn alloys for the development of functional, bioresorbable implants. The results showed that nanoscale features can be deliberately designed by selectively leaching out the less noble metals from the outer surface layer to create an extensive variety of porous topographies. It was found that initial microstructure, Zn diffusion time, etching rate, annealing temperature and time, and the type of etching media all play a role in customizing the resulting dealloyed morphology. The resulting nano-sized structures have the potential to enhance initial cell attachment for future bioactive, resorbable materials.

Keywords: Iron-manganese; Dealloying; Degradable; Nanoscale; Porous

1. Introduction

Biodegradable metals are emerging as an alternative to permanent, implantable fracture fixation devices, yet there remain challenges to be overcome as they become the next generation of biomaterials. Small fracture fixation implants such as pins, screws, and bone plates are needed

to mechanically support full tissue reconstruction after fracture of bone, cartilage, or ligaments and it would be beneficial if they were slowly replaced by healthy, natural tissue to complete healing. Currently, one of the biggest issues in metallic resorbability is controlling the ever-changing interface between the degrading implant and growing new tissue as outlined by Zheng et al.[1] Upon implantation, chloride ions start breaking down the oxide layer over the entire exterior of the degradable metal, while proteins begin adsorbing to its surface, thereby affecting the rate of metallic dissolution.[1,2] In the case of bone fracture fixation devices, apatite is also deposited on these surfaces, while the filopodia of migrating cells sense the implant's surface irregularities, adhere, and multiply to construct healthy hard tissues.[1–3] Amidst all these complex interacting mechanisms, the dynamic resorbable interface needs to encourage tissue attachment, cell proliferation, and ingrowth to reduce chance of loosening or failure as it slowly disappears. Dealloying, or chemically etching a material to selectively remove one or more less-noble components from the base metal, appears an attractive process to generate nanoporous or “sponge-like” metal frameworks for these unique biomaterials. The novel process of dealloying resorbable surfaces has the potential to enhance tissue/implant interactions through drastically increasing surface area, roughness, and possibly degradability.[4–7]

Traditionally, biomedical implants that require osseointegration for strong implant/tissue bonding are roughened by various physical or chemical means in order to increase surface area and contact of the interface, thereby enhancing osteoinductivity.[8] In addition, osteoblasts have been known to have a higher capacity to synthesize bone matrix on rougher surfaces.[9] Ryan et al. also mentioned that high surface area porous implants tend to show higher corrosion rates than non-porous implants.[10] Customarily, mechanical roughening treatments can include machining, polishing, and blasting with different types of particles, whereas chemical treatments

typically comprise of wet chemical etching and passivation treatments.[11–13] Alla et al. suggests that certain acid treatments used to roughen surfaces may actually accelerate bone apposition.[11] However, many of the existing treatments are applied to passivating surfaces such as 316L stainless steel, titanium, or cobalt-chromium alloys.[1,11] Little work has been conducted on dealloying of resorbable biomaterials. Being able to quickly tailor the nanoscale features of these resorbable surfaces so that the optimal initial cell attachment and growth occurs would be valuable for clinical applications. In this study, it was found that varying a wide set of dealloying processing parameters can yield a wide array of unique surface pattern formations, ranging from nanoscale pores to dendritic networks in the range of hundreds of microns.

Selective dissolution (dealloying) typically penetrates only about nanometers to microns into the surface of a sample since it is diffusion limited.[14,15] In the past, this type of metal leaching was originally only regarded as undesirable due to the depletion of important stabilizing metals for corrosion resistant or structural applications.[14,16] When carefully controlled however, dealloying has been shown to improve material performance in electrical/chemical sensor, actuator, fuel cell, and catalysis applications.[4,15,17–21] In the past, dealloyed systems have preferentially etched a wide variety of elements in order to generate nanoporous surfaces of Au, Cu, Mn, Sn, Ag, Ni, Pt, Pd, and Ti.[4–7,14–20,22–28] The metal leaching process has been known to fabricate open pores, high surface areas, and tunable hierarchical networks of structures due to the more anodic components being dissolved away because of the driving force of surface diffusion.[16] Erlebacher et al. proposed that this development is then followed by a mass transport process occurring where the noble atoms diffuse from their original lattice positions at the bottom of the created pits and actually aggregate and assemble into a porous arrangement at the top, as the bottom of the pit branches or forks.[16] As the outer surface region

becomes depleted of the anodic species, a concentration gradient will form. Erlebacher et al. mentions that the diffusion of the more noble atoms from the base of the pores occurs against this concentration gradient, which brings to question why this unfavorable mechanism is happening since atomic diffusion customarily follows a concentration gradient.[22] Erlebacher et al. and others have suggested that this occurrence may be due to the noble atoms being left in a nonequilibrium state due to the increase in surface area after the anodic atoms are leached out.[22,23] The system then becomes balanced by the resulting surface energy reduction associated with noble atoms clustering at the surface.[22] An additional consideration that Erlebacher et al. advises is that dealloying is unlikely for abundantly high noble element concentrations due to the increased tendency of noble atoms diffusing into the newly-made vacancies, thereby obstructing further dissolution.[22]

The objective of the current study is to better understand the fundamental mechanisms behind dealloying Fe-Mn-Zn alloys in order to generate tailorable surface porosities. As Fe, Mn, and Zn are all nutrient metallic ions found in the body, the current study aims to specifically create and characterize a variety of viable morphologies that may further enhance interface compatibility with bone and orthopaedic soft tissues for bioresorbable implant applications.[29] An investigation into the influence of initial microstructure, Zn diffusion time, dealloying time, dealloying temperature, annealing time, and annealing temperature on the formation of nanoporosity was conducted. Future studies are underway and will focus on determining which of the outlined surfaces are most conducive for bone cell attachment, ingrowth, tissue/implant stability, and proliferation of cells.

2. Materials and Methods

2.1 Materials and sample preparation

Small, irregular pieces (≤ 12 mm [0.5in]) of pure Fe (Alfa Aesar, Ward Hill, MA, 99.9%) and pure Mn (Alfa Aesar, Ward Hill, MA, 99.9% Mn) were weighed out to create the alloy composition: Fe–30%Mn. This mixture was processed in a vacuum induction melter (VIM). The VIM was evacuated to a pressure of $\sim 10^{-3}$ atm and then purged with argon three times to reduce the oxygen content in the furnace. After the final purge, the chamber was backfilled with argon to minimize vaporization of the manganese. The alloy was melted and poured into a chilled, cylindrical copper mold resting on a water cooled copper plate to create a 1” diameter ingot 3.5” in length. The cast, Fe–30Mn ingot was then machined into 6 mm diameter discs, 3mm thick. Select samples were subjected to heavy cold-rolling (reduction of 50%) and further annealing treatment at a variety of temperatures and times. Prior to dealloying, all samples were ground to 600 grit sandpaper. Initial cast mechanical properties such as elastic modulus, hardness, and stiffness of this alloy were measured using nanoindentation (Hysitron TI-950 Triboindenter, Minneapolis, MN) with a Berkovich tip with a nominal radius of 150 nm. Peak load was varied from 8000 μN to 1000 μN while the segment times (loading, holding, unloading) were kept constant for each test. The maximum and minimum loading rates were 1600 $\mu\text{N/s}$ and 200 $\mu\text{N/s}$ respectively.

2.2 Solution preparation

The dealloying etchant used to immerse the alloys was conducted in 100mL of 5wt% HCl, or 0.1M KNO_3 , or 20 wt/vol% citric acid depending on the experiments, according to media outlined in several other studies with different material systems.[17–19] Dealloying was controlled at a variety of temperatures (from room temperature up to 60°C) and times (between 1 and 12 hours) to cover a wide spectrum of parameters. Dealloying with the above solutions was

always followed by a “soak” of the alloy in DI water to halt the kinetics of surface diffusion. Samples were then rinsed with 100% ethanol and dried in a desiccator prior to imaging.

2.3 Microstructure analysis

Select Fe–30%Mn samples were mounted in Bakelite, mechanically ground and polished with 0.02 mm silica, chemically etched using Nital solution (2% HNO₃ in ethanol), cleaned with 100% ethanol and then placed in a desiccator for at least one hour. Optical microscopy was performed to examine cast and annealed microstructures, while scanning electron microscopy (SEM; FEI Philips XL-40) coupled with energy dispersive x-ray spectroscopy (EDS) was used to examine the surface structure and alloy compositions respectively. For all SEM analysis, the working distance was between 4.7-12.9 mm. For examining the surface morphology, the accelerating voltage was between 5-20 KV, whereas for performing EDS analysis, the accelerating voltage was 25 KV. X-ray diffraction (XRD) with CuK α radiation was also employed (Bruker D8 Discover X-Ray Diffractometer with GADDS [General Area Detector Diffraction System]) for the characterization of microstructural phases present in the cast Fe–Mn and Fe–Mn–Zn alloys.

3. Results and Discussion

3.1 Base material and the dealloying process

The average compositions of the as-cast alloys using energy dispersive x-ray spectroscopy (EDS) are listed in *Table 1* and include the regions of microsegregation typical of casting. *Table 2* lists the initial mechanical properties of the alloy before dealloying. *Figure 1* shows comparative XRD patterns for the dealloyed Fe–Mn–Zn alloy at the top surface with similar peaks to that of a cast Fe30Mn alloy.. Based on these results and according to the Fe–Mn–

Zn ternary phase diagram, dealloying fully removes the $Zn_{10}Fe$ intermetallic phase created due to zinc diffusion.[30] The bulk of the Fe-30Mn alloy was identified as a single γ (FCC) phase created during solidification, which is expected from the phase diagram and corresponds to similar results that other authors have found.[31,32] In the past, there have been a substantial amount of investigations conducted by several authors that demonstrate Fe-30Mn and Zn alloy biocompatibility and bioresorbability *in vitro*. [29,33–39] Since resorbability of these materials has already been established, although still too slow for clinical applications (about 0.7 mm/year in Modified Hank’s Solution for Fe30Mn and up to 0.2mm/year for pure Zn), [32,39] the current experiment focus more on the mechanisms involved with dealloying these alloys towards potentially improving attachment between the tissue/material interfaces.

Table 1. EDS Chemical composition of the Fe-Mn-Zn alloy at the surface throughout dealloying steps					
Element	Initial Concentration (Wt.%)	After Zn Diffusion (Wt.%)	Concentration Post-1st Dealloy (Wt.%)	Concentration Post-Anneal (Wt.%)	Concentration Post-2nd Dealloy (Wt.%)
Fe	69.82	74.16	66.69	60.32	70.33
Mn	30.18	22.65	28.03	31.79	29.34
Zn	N/A	3.19	4.34	2.64	0.33
O	N/A	N/A	0.94	5.25	N/A

Table 2. Mechanical Properties of Fe-30%Mn alloy	
Elastic Modulus (GPa)	208.86 (8.75)
Hardness (Vickers in GPa)	6.25 (0.41)
Stiffness ($\mu N/nm$)	195.82 (55.54)

After 24 hours of diffusing pure Zn at 600°C into the solid Fe-30%Mn sample (designated as STEP 1 in the dealloying process of *figure 2*), a $Zn_{10}Fe$ intermetallic layer about 200-230 μm thick developed between the pure Zn and Fe-Mn ingot interface. *Figure 3* illuminates that the concentration of Zn gradually decreases the closer one gets to the original

Fe-Mn alloy interface (from point 1 to 3), whereas the converse is true for both Fe and Mn concentrations, as expected due to diffusion of these atoms. Additionally, it can be viewed in *Figure 4* that the underlying cast microstructure of the alloy remains dendritic in nature even with Zn atoms diffused into it. As a side note, the size and mass of the base alloy were found to influence the amount of Zn diffused into the sample. It is key to use comparable masses of the base alloy and Zn, because it was observed that immersing Fe-Mn wires (0.020" diameter) in a significantly larger amount of molten Zn (1:2 mass ratio) caused the Fe and Mn to fully diffuse into the surrounding molten Zn just above the melting temperature of Zn.

For STEP 2 in the dealloying process, the sample underwent the 1st etching treatment, where it was immersed in 5wt% HCl and was allowed to freely corrode until the entire Zn coating surrounding the bulk Fe-Mn sample was chemically removed and bubbling was minimal (the length of immersion time varies for different coating thicknesses). *Figure 5(a-c)* demonstrates the surface evolution during the HCl etching treatment, where dissolution of mainly Zn metal ions into the electrolyte occurs until the underlying bulk Fe-Mn surface is completely exposed. It was found that the HCl reacts with Zn to release H₂ (gas) while creating products composed of ZnCl₂ (*Figure 5d*).

STEP 3 involved heat treating the etched sample for 1 hour at 400°C to allow for bulk diffusion of Zn atoms to the surface. A similar dealloying and coarsening treatment for a Ag-Au alloy was conducted by Qi et al.[6] The temperature for the current study was chosen to be 400 °C as it was below the melting temperature of Zn. *Figure 6(a-c)* shows that this heat treatment created a mild, coarsened structure on the surface.

Finally for STEP 4, the Fe-Mn-Zn sample was etched again in 5wt% HCl until bubbling was minimal (~1 hour) and nanoporosity was generated across the entire sample surface. The

average pore size was measured to be 80.49 ± 40.53 nm (*Figure 7a-d*). Taking a closer look at the cross section reveals that pores penetrated to depths of about 5-20 μ m depending on whether the area was a dendritic or interdendritic region (*Figure 7e-f*). As a goal, pore sizes that mimic cancellous (300-600 μ m) or cortical bone (10-50 μ m) would be ideal for porous, orthopaedic implants in order to facilitate cellular ingrowth. [40] However Vandrovcová et al. suggests that irregularities less than 100nm emulate the size of adhesion receptors on cells and moreover interact well with adsorbed cell adhesion-mediating molecules.[41] Murphy et al. also suggests that small pores may be beneficial for initial cell adhesion, whereas larger pores improve cellular infiltration.[42] As a side note, after dealloying, it was additionally observed that the grain boundaries were preferentially etched and a variety of other larger pores developed on the exterior at arbitrary intervals, possibly due to localized etching at defect sites.

SEM images of the cross sections of the samples after each step were taken in order to better understand the microstructural mechanisms involved in dealloying Fe-Mn-Zn (*Figure 8*). Based on the ternary phase diagram of Fe-Mn-Zn alloys and the intermetallic composition measured in *figure 3*, it can be seen that the thin $Zn_{10}Fe$ intermetallic layer that forms in STEP 1 (bright, white layer in figure) is completely etched away by STEP 2, along with some of the underlying material on the surface, leaving a rough surface behind. By STEP 3 a thick, Fe-rich oxide layer forms on the surface, with slightly higher concentrations of Mn and Zn at the surface (see *table 2*) due to heat treating. This surface is then etched in STEP 4, leaving behind a wide size-range of pores depending on how far the oxide layer is penetrated. The heat treatment step appears to simply allow for longer diffusion time of Zn and Mn species to the surface (an increase of about 3.76wt% of Mn with heat treatment). Dealloying was found to be largely controlled by the etching rate and length of etching time, where shorter times at STEP 4 (<1

hour) at room temperature achieved the wide-spread nanoporosity seen in *figure 7*, mid-length times (1-4 hours) created ligament structures similar to that reported by other authors with various other alloys (*figure 9*), [9-26] while much longer etching times always resulted in a dendritic, iron-rich skeleton, for cast alloys. In general, HCl preferentially targeted both of the less noble manganese and zinc elements, especially the interdendritic regions that are richer in manganese (*Figure 10*), which is expected since manganese is higher in the activity series and has a lower standard electrode potential compared to iron and zinc.[43,44] Based on these results, it appears that nanoporosity can be developed without the addition of zinc, since the etching media mainly targets the manganese. However, alloying Fe-Mn with zinc does seem to generally create smaller pore sizes than without, along with presenting more opportunities for surface modification through heat treatment.

As alluded to earlier, subsurface porous structures were also found to be generated by simply dealloying the Fe-30%Mn alloy without zinc added (*figure 11*). Average pore size for this surface was 147 ± 50 nm. This surface morphology was found to be less tailorable than with the addition of zinc, as illustrated in the next section. Nevertheless, the underlying mechanisms of dealloying both Fe-Mn-Zn and Fe-30%Mn appear to be similar at Step 4. *Figure 12* illustrates this believed progression for dealloyed Fe-Mn-Zn. In either case, the authors were able to explore and characterize a wide variety of factors that affect surface porosity and morphology in these dealloyed systems. When designing these structures, it is important to consider the complexity of cell attachment, since a variety of material surface properties affect it, including but not limited to: surface charge, stiffness, chemical composition, and roughness.[45] Future studies will focus on characterizing the visible increase in surface roughness and surface area and investigating how this specifically affects cell adhesion.

3.2 Major tailorable factors in dealloying that influence the final surface structure

It was discovered that the final morphology of these surfaces is fundamentally dependent on the original microstructure of the alloy, where chloride ions tends to attack the more anodic regions first and areas of high energy such as grain boundaries. However, varying the processing conditions, i.e. dealloying times and temperatures, annealing temperatures and times affect the rate of etching. Thus a variety of unique surfaces can be obtained discontinuing the dealloying process along this pathway. To specifically investigate microstructural effects, a few cast Fe-30%Mn samples were cold-rolled (CW50%) and then annealed at 1300°C for 1 hour to recrystallize the grains. Then the samples were immersed in Zn for 24 hours and dealloyed in the traditional four-step procedure as described above, producing rough, mountain-like structures covering the entire sample (*Figure 13a-b*) and not a dendritic skeleton. Interestingly, the grain boundaries were not visible on this structure, nor was there the formation of nano-sized pores.

Another factor that appears to influence the dealloyed surface structure is the degree of agitation of the etching. Keeping all other conditions the same, a stir bar set at the highest speed setting was added next to the sample during the last step of dealloying and the resulting surface was created (*Figure 13c-d*). Comparing this surface with *Figure 7*, it can be seen that nanopores develop, but are instead elongated in the direction of fluid flow as products are released. The edges of the pores also become more jagged and irregular in appearance rather than circular in shape, which may cause the actin cytoskeleton of a cell to elongate in the direction of the pores during cell migration and contribute to how well it attaches.[2] *Figure 13e-f* shows a dealloyed sample after 1 hour of etching where a stir bar had been placed on top of the sample, producing a “pinnacle” morphology covering its entirety. This peak-like surface is most likely due to the increased upward motion caused by the stirrer and the preferential extraction of Mn and Zn when

they combine with Cl, where the H₂ bubbles produced from this reaction rapidly float upwards to the surface of the air/liquid interface.

As mentioned earlier, changing the period of time that the media is able to corrode the surface also adjusts the surface morphology. Over-etching (4+ hours for the final step) annihilates nanoporosity due to the system being naturally driven towards reducing its surface energy by decreasing surface area.[22] For long periods of time, the etchant strongly targets grain boundaries, resulting in an instability of the surface and potentially leading to surface cracks.

Varying the span of time for Zn diffusion into the Fe-Mn alloy and thus altering the depth that the Zn penetrates into the surface was also found to influence morphology. The Zn/Fe-30%Mn diffusion couple was left in the furnace for 48 hours instead of the original 24 hours in the earlier experiments and nano-sized pores similarly developed. However, the shapes of the pores were “blockier” and the overall sizes of the pores were enlarged slightly (*Figure 14a-b*), which may be due to longer heat treatment times allowing for more surface diffusion of zinc that agglomerate near the surface.

For the 48 hour Zn-diffused samples, it was additionally observed that by increasing the heat treatment time in STEP 3 from 1 hour to 3 hours and keeping everything else unchanged, a rather inhomogeneous surface was created (*Figure 14c-d*). Nano-sized pores were visible, but they occurred arbitrarily and non-uniform. On the other hand, if only the annealing temperature for 1 hour of STEP 3 is increased to 600°C for the 48 hour Zn-diffused sample and all other parameters are kept the same, then a porous “lace-like” structure develops across the surface (*Figure 14e-f*). It is significant to note that this annealing temperature was chosen because it is above the melting point of Zn (~420°C).

To better understand the step-by-step process of how these structures are generated through the dealloying process, it is key to examine how the oxide layer develops on the surface of these alloys during the annealing period during STEP 3. *Figure 6(d-f)* illuminates how as the annealing temperature is increased to 600°C, there is a coarsening of oxidation products at the surface due to surface diffusion, forming a distinct network of large, micron-sized ligaments. It appears that for longer Zn-diffusion times (48 hours), the higher amount of Zn in the alloy actually diffuses out and forms ZnO whiskers or “wire-like” structures when above its melting temperature (*figure 6g-i*). This “extrusion” of ZnO out of the Fe-30Mn matrix is potentially due to thermal expansion and a volume change of the Zn during melting. Thus, the porous metal membrane in *figure 14e-f* is created due to preferentially etching out these extended Zn nanowires and the Mn dispersed within the rest of the surface.

Interestingly, increasing the etching temperature during STEP 2 of the dealloying process significantly increases the etching rate more than if temperature is increased during STEP 4. As seen in *Figure 15*, the Zn and Mn are completely etched away from the interdendritic regions near the surface after dealloyed at 50°C, leaving a dendritic frame behind. The remaining surfaces of both the 24 and 48 hour Zn-diffused alloys appear similarly faceted or “step-like” and any nano-sized pores have been destroyed. The biggest difference between the 24 and 48 hour Zn-diffused surfaces with all other parameters kept similar is the penetration depth of the etching media. For the 24 hour Zn-diffused sample, pores reach about 150µm into the bulk of the alloy, whereas they go about 590µm for the 48 hour Zn-diffused sample (*Figure 16*). From a biological standpoint, larger and deeper interconnected pores have been shown to result in enhanced oxygen and nutrient supply to cells, increasing the amount of bone formation.[46] However, it is important to note that as the pores get deeper, the dendrite arms become thinner.

Additionally, it is key to point out that during this particular process the acid appears to preferentially etch metal following the growth path of the dendrites (*Figure 15f*), starting at the grain boundaries and continuing through the bulk of the sample. This brings about the point that dealloying tends to occur following the slip planes in the microstructure and crystallographic orientation of the grain that it passes through. Gilbert et al. mentioned similar developments for leached Co-Cr alloys, but the resulting decrease in corrosion resistance was detrimental for the intended applications of Co-Cr.[47] The current authors hypothesize that the high energy grain boundaries act as rapid transport pathways for Zn, where grain boundary diffusion dominates, and the hydrochloric acid follows these less noble routes.

Finally, a dealloyed surface can also be tailored by altering the type of etching media utilized. 0.1M KNO₃ was employed to etch the Zn-free, Fe-Mn surfaces. The resulting structures can be viewed in *Figure 16a-b*. It can be seen that the Mn-rich interdendritic regions were again preferentially etched, causing nano-sized pillars or “plateaus” to form rather than circular or ligament type pores (*Figure 16b*). KNO₃ appears to also attack the Mn-rich interdendritic regions (darker areas in *Figure 16a*), yet the dendritic regions are fairly “untouched” and nonporous, even though there still exists Zn and Mn within it. When the temperature of the etchant was raised to about 40°C for 1 hour of immersion, an unstable oxide layer formed instead on the surface that appeared “fuzzy” or plate-like (*Figure 16c-d*). Any temperatures above 40°C caused complete annihilation of these structures. Unfortunately, large, patches of pits occurred in regions where bubbles formed and remained adsorbed to the surface. When a stir bar was used to keep the media flow moving to remove these bubbles, the passive layer broke apart and fell away (*Figure 16c*). This ‘segmentation’ of the unstable oxide layer during immersion in KNO₃ appears similar to that of a previous study with a Fe-30Mn alloy immersed in osteogenic media during a

ninety day time period.[48] This ‘flaking’ behavior is not ideal for a stable interface and should be avoided. Fe-30Mn samples were also immersed in citric acid for an hour and homogenous “jagged” structures were created (*Figure 16e-f*).

As a side note, there are too many types of etchants that could be used to dealloy this system for this paper to fully cover and characterize. Furthermore, it is postulated that initial bulk Fe-Mn composition also plays a role in the dealloying process, however that particular variable was not investigated in this study. In addition, it was found that the general outlined morphologies are reproducible if the parameters are carried out accurately in the same conditions. However, the authors would like to stress that the nanotopographies will fluctuate considerably since every material differs microstructurally and corrosion itself is a variable process. Thus it is challenging to have comparable measured values of roughness and so consequently, no roughness values were measured during this study. However, future studies will focus on comparing how these specific topographies (based on the systematic procedures used to create them) influence cellular behavior (attachment, proliferation, differentiation) *in vitro*. Lastly, it is also important in future implant design to avoid major stress gradients between the outer porous layer and bulk properties because stress corrosion cracking and other undesirable materials failures may occur.[22]

4. Conclusion

Dealloying Fe-Mn-Zn and Fe-Mn alloys was shown to generate a wide range of tailorable nanotopographies on the surface by varying any of the parameters in the outlined ‘four-step’ dealloying process. The overall mechanisms behind this selective dissolution were established as being a preferential attack on the less noble components (Mn and Zn) while immersed in a chosen acid or base, followed by the bulk diffusion of these components to the surface and the

formation of an oxide layer during annealing, ending with another preferential attack on the more anodic components that were newly exposed. It was found that diffusing zinc into Fe-Mn alloys may only generate a stronger dealloying response, since similar structures can be obtained without zinc, yet a wider range of porous structures can be created through a post-coarsening treatment. The major factors during this ‘four-step’ process that were discovered to affect the final surface structure and the extent of porosity in these alloys include:

- 1) *Initial microstructure* (depends on the percentage of anodic elements added to base metal: Mn and Zn in this study, type of processing/deformation treatments previously applied that alter the shape of the crystallographic orientation, and the direction of solidification for cast materials)
- 2) *Zn diffusion rate* (depends on the temperature that diffusion is occurring and the amount of time that diffusion takes place in this study, along with availability of anodic regions for attack)
- 3) *Etching/dealloying rate* (depends on the concentration of anodic elements, material volume, and concentration of the acid or base employed, the temperature at which etching takes place, total etching time, and degree of media agitation)
- 4) *Temperature and time of heat treatment after 1st etch* (depends on the concentration of alloying elements and their respective diffusion coefficients, which affects the rate of elemental diffusion and affects the thickness of the oxide layer that develops)
- 5) *Selectively dealloying with different acid or basic media* (depends on the initial microstructure, concentration and volume of etching medium, which affects whether anodic or cathodic etching occurs)

The current study illuminates a diverse set of possible processing paths to modify the surface of Fe-Mn-Zn and Fe-Mn alloys. It is expected that some of these topographical configurations will enhance initial cell attachment and improve tissue/implant interface adhesion in future experiments, thereby leading to potentially new bioactive biomaterial interfaces. Additional tests will examine how bone marrow stromal cells adhere and proliferate on these varied surfaces in osteogenic environments in order to evaluate the viability of these surface modifications. In any case, our results help broaden the knowledge of the mechanisms behind dealloying and its potential applications, along with extending the range of techniques for creating nanoporous surfaces.

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Figure Captions:

Figure 1. XRD patterns of cast Fe₃₀Mn and top surface of a dealloyed Fe-Mn-Zn sample. Peaks of γ (FCC) phase are indexed at the bottom.

Figure 2. General overview of the process used to dealloy Fe-30%Mn.

Figure 3. SEM of a cross section of the Zn-diffused sample and the corresponding EDS plots.

Point 1: (Zn coating)	Fe: 8.36 wt%,	Mn: 0.75 wt%,	Zn: 90.89 wt%
Point 2: (Intermetallic Layer)	Fe: 9.64 wt%,	Mn: 1.53 wt%,	Zn: 88.83 wt%
Point 3: (Bulk Fe-Mn)	Fe: 74.16 wt%,	Mn: 22.65 wt%,	Zn: 3.19 wt%

Figure 4. Etched diffusion couple of Fe-Mn (middle) and Zn (top and bottom layers) showing the dendritic microstructure of the cast sample and the surrounding Zn₁₀Fe intermetallic layers.

Figure 5. Surface evolution during STEP 2 of the dealloying process. a) Initial partially-etched Zn coated layer. b) Partially-etched surface with underlying Fe-Mn surface exposed. c) Fully etched Fe-Mn-Zn surface. d) Corrosion products after 1st dealloy composing of: Zn: 58.85 wt%, Cl: 27.50 wt%, and O: 13.65 wt%.

Figure 6. SEM after STEP 3, no 2nd dealloying. (a-c) 24hr Zn diffusion, anneal at 400°C. (d-f) 24hr Zn diffusion, anneal at 600°C. (g-i) 48hr Zn diffusion, anneal at 600°C. Left to right, images are simply increasing in magnification.

Figure 7. The Fe-Mn-Zn surface after STEP 4 (2nd etch), displaying a wide array of nanopores covering the entire surface. a) 2500X, b) 6500X, c) 12000X, d) 20000X. (e-f) Cross sections of the surface displaying nano-sized pores at 5000X and 12000X.

Figure 8. Fe-Mn-Zn alloy cross sections after each step in the four-step dealloying process. Note for Step 1: Top region is Zn, middle is intermetallic region, and bottom is Fe-30% Mn bulk. The white/black glow at the top in Step 2 and Step 4 is due to electron charging in the SEM from epoxy resin.

Figure 9. (a-b) Fe-Mn-Zn dealloyed ligament structure (etched for 4 hrs.) at 10000X and 20000X respectively.

Figure 10. EDS results of compositions at different points on the cross section of the cast Fe-Mn-Zn alloy at 1000X. a) Dendritic region. b) Interdendritic region.

Figure 11. The Fe-Mn surface after dealloying in HCl for 1 hour, exposing variable sizes of nanopores covering the entire surface. a) 5000X, b) 25000X.

Figure 12. Progression of Fe-Mn-Zn surfaces during dealloying with increasing time: (a) Nanoscale pores immediately develop upon immersion, (b) media penetrates through the oxide layer, (c) media attacks underlying surface according to crystallographic orientation of planes, (d) surface is infiltrated deeper, (e) localized corrosion attacks creating deeper pits, (f) and the end result is an iron-rich dendritic skeleton for cast Fe-30Mn alloys.

Figure 13. (a) Recrystallized etched structure at 10X that underwent cold-rolling (CW50%) and then annealing at 1300°C for 1 hour. (b) Corresponding dealloyed structure. (c-d) The cast Fe-Mn-Zn surface after STEP 4 with stir bar added next to it to agitate the HCl media; displays elongated nanopores compared to those seen in *figure 7*. a) 2500X, b) 25000X. (e-f) The Fe-Mn-Zn surface after adding a stir bar placed atop the specimen. a) 5000X, b) 25000X.

Figure 14. (a-b) Fully dealloyed surfaces after 48 hours of Zn diffusion during STEP 1 instead of the original 24 hours. a) 5000X, b) 25000X. (c-d) Fully dealloyed surfaces after 48 hours of Zn diffusion and annealed for 3 hours instead of the original 1 hour. a) 6000X, b) 25000X. (e-f) Fully dealloyed surfaces after 48 hours of Zn diffusion and annealed at 600°C instead of the original 400°C. a) 2500X, b) 20000X.

Figure 15. Fully dealloyed surfaces and respective cross sections at 50°C for ~12 hours during STEP 2 after 24 hours of Zn diffusion (a,c,e), or after 48 hours of Zn diffusion (b,d,f).

Figure 16. (a-b) Fe-Mn surface after static, dealloying with 0.1M KNO₃ for 1 hour. (c-d) Fe-Mn surface after dealloying with 0.1M KNO₃ using a stir bar at 40°C for 1 hour. (e-f) Fe-Mn surface after dealloying in citric acid for 1 hour.

Figure 1

Figure 2

Step 1 – Zn diffusion into initial alloy

Step 2 – 1st etching of Mn and Zn in acid

Step 3 – Coarsening treatment

Step 4 – 2nd etching of Mn and Zn in acid

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Step 1- Zn diffusion into Fe-Mn

Step 2- 1st HCl Etch

Step 3- Annealing

Step 4- 2nd HCl Etch

Figure 9

Figure 10

Element	Wt%	At%
MnK	27.40	27.76
FeK	71.75	71.51
ZnK	0.85	0.73

Element	Wt%	At%
MnK	31.56	31.95
FeK	67.76	67.47
ZnK	0.68	0.58

Figure 11

Figure 12

Figure 13

Figure 14

Figure 15

Figure 16

Graphical Abstract