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

Michael Heiden, David Johnson, Lia Stanciu*

School of Materials Science and Engineering, Purdue University, West Lafayette, IN 47907, USA

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ABSTRACT

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.

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

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* Corresponding author.
E-mail addresses: mheiden@purdue.edu (M. Heiden), davidjoh@purdue.edu (D. Johnson), lstanciu@purdue.edu (L. Stanciu).

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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

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 ~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, 3 mm 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 μN/s and 200 μN/s respectively.

2.2. Solution preparation

The dealloying etchant used to immerse the alloys was conducted in 100 mL of 5wt% HCl, or 0.1 M 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 h) 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

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 (μN/nm)	195.82 (55.54)