Full Length Article

Improved biodegradability of Fe–Mn alloy after modification of surface chemistry and topography by a laser ablation

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ABSTRACT

In this study we report the influence of laser ablation on the controlled biodegradability of a Fe–Mn alloy developed for medical implants. After texturing by a nanosecond Nd:YAG laser, the surface expressed extreme super-hydrophilic wetting properties, since laser ablation led to micro-channels and chemical modification resulting in nanostructured metal oxides. The influence of functionalized surface properties on corrosion behavior was examined on molecular level by using X-ray photoelectron spectroscopy. Results reveal that the oxide layer after the laser texturing of Fe–Mn alloy consists mainly of Fe_2O_3 and FeO, with the content of Mn in the oxide layer being significantly higher than in the bulk. The results of the electrochemical measurements clearly demonstrate the superior biodegradability of the Fe–Mn alloy samples functionalized by laser ablation. Here, the laser-triggered corrosion is self-driven by further production of corrosion products that leads to biodegradability of the whole sample.

1. Introduction

Versatile biodegradable metals for short-term medical implants have been intensively studied in recent years [1–4]. Some of the possible alloys for such applications, especially in orthopaedics (bone-fixation screws, pins, plates, disks), are those based on Fe [5–13]. At the beginning of the healing process, injuries need stable mechanical properties to provide sufficient support. However, as the healing process progresses, the mechanical properties of the implants can be reduced, until finally they are no longer required. Mg- and Zn-based alloys are not suitable for these applications because of their relatively poor mechanical properties, hydrogen evolution and high degradability. On the other hand, stainless steels and Ti-based alloys possess good mechanical properties, but are not intrinsically degradable, which means an additional surgical procedure must be performed for their removal [13–17]. This additional surgical procedure can be avoided by using implants made of tailored, degradable material. One of the possible routes is to add Mn to pure Fe or Fe-based alloys to moderately accelerate the corrosion and consequently make the material suitably degradable. Fe-based biodegradable metals offer a great potential for low, long-term exposure complications, chronic inflammation, side-effect risks or an inability to adapt to the implant [12,15,18–20]. Biodegradable metals are also expected to have a positive interaction during the healing process, and with metals, the degradation process and its products are not supposed to adversely affect the healing process. Fe–Mn-based alloys have suitable characteristics for interactions with human tissue [21,22].

To prepare a metal with a sufficiently high corrosion rate, some authors have added additional elements, such as Si, Pd, C, and S. In this context, many chemical modifications to Fe-based alloys were made during the past few years [5,7,11,15,23–29]. Despite this, just small improvements have been made so far in the enhancement of the biodegradability through chemistry modifications of the alloys. However, a bespoke corrosion rate can also be achieved by modifying the surface topography, which makes it possible to design material properties so as to ensure the correct life span for any particular application. Just recently, surface-roughness modifications, like sandblasting and laser texturing, have been shown to greatly modify the corrosion properties [30–35]. For example, the corrosion is significantly accelerated if the surface wettability after laser texturing is increased [35]. In this case, the interaction between a laser pulse and metal surface modify both, surface topography and its chemistry, since usually metal oxides are formed [36]. Therefore, the main aim of this study is to examine how laser ablation influences the biodegradability properties of an Fe–Mn alloy and to compare these results with different conventional surface treatments like polishing or sandblasting, which also increase the

instability of the alloy and the corrosion rate without changing its chemical composition.

The corrosion properties in the current study were investigated using Hank's solution, like the majority of the previous studies that used simulated physiological fluids [10,11,15,37] to simulate in-vivo conditions. Based on previous studies, we used electrochemical impedance spectroscopy (EIS) and potentiodynamic measurements to assess the degradation behavior of the laser-modified Fe–Mn alloy that we investigated. We then analysed the surface modification before and after immersion with a non-contact, optical, three-dimensional system and scanning electron microscopy (SEM). The surface degradation products were analysed and we measured the elemental distribution through the oxide film with an X-ray photoelectron spectroscopy (XPS).

2. Material and methods

2.1. Material preparation

Material Preparation – the investigated Fe-based alloy with 18 wt% Mn (Fe–Mn) was custom produced from pure Fe with the addition of Mn to the alloy. Both materials were melted in an induction furnace under an air atmosphere at approximately 1700 °C and cast into an iron mould. The cast Fe–Mn was hot rolled at approximately 1000 °C for a 33 % reduction. The literature [18,19,38] suggests that hot-rolled material without being annealed and/or homogenized has a higher corrosion rate. The chemical compositions of the alloy, revealed in Table 1, was determined using an X-ray fluorescence (XRF) spectrometer (Thermo Scientific Niton XL3t GOLDD +) and using a carbon and sulphur analyser (ELTRA CS-800).

2.2. Surface treatments

Surface treatments – pure Fe and some Fe–Mn samples were prepared by grinding down to 1200 grit and polishing down to 1 μm with a diamond suspension. The selected Fe–Mn samples were additionally processed by laser texturing. Here, a Nd:YAG (λ = 1064 nm) pulsed laser with a pulse duration of 95 ns (full width at half maximum) was used. The laser beam was focused on the surface by an F-theta lens with a focal distance of 160 mm. Since the surface was placed in the focal position, the beam spot size equalled 0.05 mm and it was led in lines with a velocity of 1.6 mm/s using a 2D scanner. For the processing, we used a 1-kHz pulse frequency and 0.6 W of average power, resulting in pulses with an energy of 0.6 mJ and spots separated by 1.6 μm, forming a channel. The distance between two adjacent lines, i.e., the scan line separation, was set to 50 μm.

2.3. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) depth profiles of the oxide layers were measured with a VG Microlab 310F SEM/AES/XPS. For all the XPS measurements Mg-K_α radiation at 1253.6 eV with an anode voltage × emission current 12.5 kV × 16 mA = 200 W power was used. For the investigation of the elemental composition with depth, Ar$^+$ ions with an energy of 3 keV at 1 μA ion were applied over the area of 4×4 mm^2. Similar ion-beam parameters were used for sputter-cleaning the sample, except that the raster area was closer to 10×10 mm^2 in this case. No exact calibration is available for this material, but a rough estimate for the sputtering rate at these profiling

parameters is of the order of 0.01 nm/s, which is consistent with some calibration measurements performed on metallic and oxide-type samples as well as with some reference data for the sputtering rates for Fe and its oxides. The ratio of our corrosion product (Fe_2O_3) and SiO_2 is 0.61 in the literature [39]. We used sample rotation during the depth profiling, since it is important to avoid shadowing for proper XPS depth profiling [40]. The spectra were acquired using Avantage® 3.41v data-acquisition & data-processing software supplied by the AES/XPS equipment manufacturer. Ar$^+$ sputtering for different time intervals estimated the thickness of the oxide layer. Casa XPS® software (http://www.casaxps.com) was used for the detailed data processing.

2.4. Scanning electron microscopy (SEM)

Scanning Electron Microscopy (SEM) analyses using a FE-SEM JEOL JSM-6500F were employed to investigate the morphology of the different Fe–Mn surfaces as well as the morphology and distribution of the corrosion products after a corrosion evaluation.

The surface topographies of the polished and laser-textured samples prior to and after the corrosion experiments were examined with a non-contact, optical, three-dimensional Alicona G4 InfiniteFocus (IF) system (Alicona Imaging GmbH, Graz, Austria). The 3D surface-roughness parameters, including the average height of the selected area (S_a), were obtained and calculated from the Alicona InfiniteFocus images using IF-MeasureSuite® 5.1 software.

2.5. Electrochemical measurements

Electrochemical measurements were performed on prepared specimens, ground with SiC emery paper down to 1200 grit and polished down to 1 μm with a diamond suspension. The laser-textured samples had no previous preparation other than the laser modification. The experiments were carried out at room temperature in a simulated physiological Hanḱs solution, containing 8 g/L NaCl, 0.40 g/L KCl, 0.35 g/L NaHCO₃, 0.25 g/L NaH₂PO₄·2H₂O, 0.06 g/L Na₂HPO₄·2H₂O, 0.19 g/L CaCl₂·2H₂O, 0.41 g/L MgCl₂·6H₂O, 0.06 g/L MgSO₄·7H₂O and 1 g/L glucose, stabilized at pH = 7.8. All the chemicals were from Merck, Darmstadt, Germany. The measurements were performed using a three-electrode, flat BioLogic® corrosion cell (volume 0.25 L). The test specimen was employed as the working electrode (WE). The reference electrode (RE) was a saturated calomel electrode (SCE, 0.242 V vs. SHE) and the counter electrode (CE) was a platinum mesh. Electrochemical measurements were recorded using a BioLogic® Modular Research Grade Potentiostat/Galvanostat/FRA Model SP-300 with an EC-Lab® software V11.10. The specimens were immersed in the solution 1 h prior to the measurement in order to stabilize the surface at the open-circuit potential (OCP). *The potentiodynamic curves* were recorded after 1 h of sample stabilization at the open-circuit potential (OCP), starting the measurement at 250 mV vs. SCE more negative than the OCP. The potential was then increased, using a scan rate of 1 mV/s. Long-term open-circuit *electrochemical impedance spectra* (EIS) were obtained for the investigated samples at the OCP, with a sinus amplitude of 10 mV peak-to-peak and a frequency range of 65 kHz to 1 mHz, directly after immersion for 1 h, 3 h, 6 h, 12 h, 24 h, 48 h and 72 h. All the measurements were made at room temperature and were repeated at least three times. The impedance data are presented in terms of Nyquist plots and Bode-Bode plots. For the fitting process Zview® v3.5b Scribner Associates software was used.

3. Results and discussion

3.1. XPS measurements

XPS analyses with depth profiles were acquired by fitting the spectra, as shown in Fig. 1. Narrow-range XPS scans show Fe $2p_{3/2}$ and Mn $2p_{3/2}$ transitions with the corresponding metallic and oxide

Table 1
Chemical composition of used materials in wt%.

Material	Mo	Mn	Cu	Ti	Si	C	Fe
pure Fe	< LOD	0.262	0.043	< LOD	0.051	0.19	Balance
Fe–Mn alloy	0.31	18.0	0.051	0.058	0.067	0.58	Balance