Materials Science and Engineering C 79 (2017) 37–44

Contents lists available at ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

High degradation rate of Fe-20Mn-based bio-alloys by accumulative cryo-rolling and annealing

Hanning Li, Yanan Wang, Qiuming Peng *

State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, PR China

ARTICLE INFO

Article history:
Received 5 December 2016
Received in revised form 25 April 2017
Accepted 4 May 2017
Available online 4 May 2017

Keywords:
Alloy
EIS
Degradation

ABSTRACT

A new strategy of accumulative cryo-rolling (ACR) at liquid nitrogen temperature and annealing was performed to improve degradation rate of Fe-Mn-based implants. Differing from as-cast and ACRed Fe-Mn-based alloys with single-phase austenite, ACRed-annealed sample mainly consists of austenite and non-equilibrium Fe_5C_2 precipitate. ACR-annealed sample shows a degradation rate of 0.0388 $mA \cdot cm^{-2}$, which is 4.6 times higher than as-cast alloy. Pitting corrosion plays a dominant role in both as-cast and ACRed samples. Conversely, some micro-batteries are prone to form among different phase interfaces for ACR-annealed sample, resulting in general corrosion. It reveals that phase optimization is a possible strategy to achieve bio-Fe implants.

1. Introduction

Analogous to hybrid materials and inorganic materials which are effective materials for delivery [1–3], therapy [4–7] and sensors [8–11], the new developed Fe-based bio-metals have been regarded as a new generation implant to substitute the permanent stents with different bio-functions [12–14]. The pioneering research on pure iron confirms that local inflammations, systemic toxicity, and early restenosis due to thrombotic processes were hardly detected during *in vivo* investigation. For example, Peuster et al. proposed that degradable iron stents can be safely implanted without significant vessel obstruction caused by inflammation, neointimal proliferation, or thrombotic events [12]. The mean degradation rate of iron is about 20.4 μg/($cm^2 \cdot h$), and the lower iron concentration (<10 μg/ml) *in vitro* test is far below the threshold value of toxicity (>50 μg/ml) [15].

However, one of the most critical issues of pure iron lies in its too slow degradation rate, approaching to the behavior of permanent implant materials [12–13]. Thereafter, the efforts have been devoted to enhance its degradation rate. One method is adding less noble alloying elements below the solubility limit in iron to make the iron matrix more susceptible to degradation [16]. For instance, eight different alloying elements (Mn, Co, Al, W, Sn, B, C, and S) were chosen to investigate their effects on degradation rate of pure iron [17]. The other method is that the addition of noble alloying elements or nano-scale particles which forms small and dispersed intermetallic phases or composites to result in micro galvanic corrosion with iron matrix [16]. For example, the adding carbon nanotube into pure iron obtained a higher corrosion rate and a more uniform corrosion mode in physiological environment [18]. The third approach is relevant to mechanical processing and heat-treatment, such as cold-working deformation [19–22], and annealing treatment [23]. Compared with the other two methods, the mechanical processing technology is more appealing in view of industrial applications, due to its following uncomplicated toxicity evaluation procedures.

The recently developed Fe-Mn-based alloys-containing Mn between 20 and 35 wt% have exhibited high mechanical properties comparable to those of SS316L alloy and outstanding cell biocompatibility [24–27], and open a promising trajectory to develop degradable bio-Fe implants. In contrast to SS316L alloy, the adding of Mn element reduces magnetic susceptibility during magnetic resonance imaging. In addition, the presence of Mn will accelerate the degradation rate compared to pure iron. The degradation rate of Fe-30Mn alloy is about 10.70 $\mu A \cdot cm^{-2}$ in *Hank*'s solution, which is slightly higher than pure iron (8.96 $\mu A \cdot cm^{-2}$) [28]. A higher degradation rate of 0.21 $mm \cdot year^{-1}$ (18.0 $\mu A \cdot cm^{-2}$) [17] was observed in Fe-21Mn-0.7C-1Pd alloy, which indicates that only 1 wt% Pd additive is highly effective to improve the degradation rate [27]. However, taking into account the high cost of Pd and its potential biocompatibility, a new technique is desirable to improve the degradation rate of Fe-Mn based bio-implants [28].

Our objective focuses on the improved degradation rates of Fe-20Mn-1.2C (wt%) alloy in terms of accumulative cryo-rolling (ACR) in the liquid nitrogen temperature followed by annealing. The main strategy is that ACR in the liquid nitrogen temperature can effectively entrap dislocations and create a large number of defects, such as slip banding and vacancy [21,29]. Then both of them provide some preferential sites to form some non-equilibrium intermetallic phases by appropriate annealing owing to their high activation energy. These non-equilibrium phases possibly possess more a positive electrode potential by varying the concentration of C element. As a result, since the volume fraction

* Corresponding author.
E-mail address: pengqiuming@ysu.edu.cn (Q. Peng).

http://dx.doi.org/10.1016/j.msec.2017.05.004
0928-4931/

of secondary non-equilibrium intermetallic phases and defects increase simultaneously, the electrochemical corrosion rate is expected to be improved correspondingly.

2. Material and methods

2.1. Sample preparation

A high pure Fe-20Mn-1.2C (wt%, all compositions given thereafter in wt%) alloy ingot with a diameter of 100 mm was prepared by electromagnetic stirring casting process. It was heat-treated at 1050 °C for 60 min and immediately quenched into cool water to obtain a uniform austenitic microstructure (denoted as Fe-20Mn-1.2C-1 alloy). The round sheet with the thickness of 4 mm, were immersed in liquid nitrogen for 10 min. Then it was rolled immediately from 4 to 3.2 mm (*i.e.*, 20% accumulative strain, denoted as Fe-20Mn-1.2C-2 alloy). The accumulative cryo-rolling (ACR) process was divided into ten steps. After each rolling, the sheet was quickly immersed in liquid nitrogen for 10 min before next step. After ACR in the liquid nitrogen temperature, the sample was annealed at 380 °C for 30 min, and cooled naturally (denoted as Fe-20Mn-1.2C-3 alloy).

The chemical composition of Fe-20Mn-1.2C alloy was measured by X-ray fluorescence spectroscopy (XRF, X-123SDD Amptek). The X-ray source was an Amptek Mini-X-Ag emitting. 10 kV and 100 μA were used to excite the characteristic X-rays of the sample between 0 and 10 keV. The detailed composition was18.3 Mn, 1.20 C, 0.060 Si, 0.016 S and 0.022 P (wt%), with the balance of Fe.

2.2. Microstructural characterization

The microstructural investigations were performed using optical microscope (OM, AMPLIVAL, Zeiss) and field emission scanning electron microscopy-gun (FESEM, JEOL JSM-7001F). The standard metallographic procedures were applied, including grinding, polishing and etching. The samples were etched in 4% nitric acid alcohol solutions. The elemental concentrations in the matrix and phases were investigated by FESEM equipped with energy dispersive X-ray analysis (EDX) with a system-Oxford INCA device. A low loaded voltage of 8 keV with the spot of ~1 μm in diameter was used to study the phase composition. The average values were obtained based on at least five random spots.

The phase composition of the Fe-20Mn-1.2C-x alloys (x = 1, 2 and 3) and corrosion products on the sample immersed up to 160 h in the test solutions were studied by X-ray diffraction (XRD) techniques. XRD technique was done with a CuK_α radiation at a scan scope from 30° to 100° with a step size of 0.02°. The filament current and acceleration voltage were 30 mA and 40 kV, respectively [30].

2.3. Electrochemical testing

Degradation performance was evaluated during a potentiostat/frequency response analysis system (Bio-logic, VSP). Experiments were performed in a three-electrode electrochemical cell in 0.9 wt% NaCl solutions at 37 ± 1 °C, with a saturated calomel electrode (SCE) as the reference electrode, a platinum mesh as the counter electrode and the specimen under investigation as the working electrode [31]. The working electrodes were ground with silicon carbide paper to 3000 grit and then rinsed with distilled water and degreased with ethanol and acetone. The distance between the three electrodes is about 1.5 cm, and the ratio of solution to surface is 600 ml to 0.5 cm^2. The stir at the speed of 150 rpm was performed to effectively reduce the pH fluctuation.

Open circuit potential (OCP) measurements were made between the working electrode and the reference electrode without current. It revealed the potential between the anodic and cathodic reaction currents at the working electrode/solution interface were balanced [32]. The OCP were tested immediately after the specimens were immersed in the solutions, and were measured for 7200 s duration.

The polarization curves were performed from −1000 mV(SCE) to −450 mV(SCE) after immersion for 120 min. The scan rate was 0.166 mV/s and the step height was 1 mV. The polarization curve was used to estimate the corrosion potential (E_{corr}), and corrosion current density (I_{corr}) at corrosion potential (E_{corr}) by the Tafel extrapolation. These experiments were repeated five times to ensure reproducibility. The samples have been grinded and polished again after every test. The Tafel behavior was obtained under cathodic polarization (β_c) up to 250 mV below the rest potential. The Tafel behavior of anodic polarization (β_a) was obtained under anodic polarization up to 200 mV above the rest potential.

The electrochemical impedance spectroscopy (EIS) was carried out at open circuit potential with an applied signal of 10 mV/rms. The scanning frequency ranged from 1000 kHz to 0.01 Hz. The fitting circuits were achieved by EC-Lab software [31]. The EIS testing was performed on the samples after immersing for 2 h, 6 h and 10 h, respectively.

2.4. Immersion testing and product analysis

The immersion tests were to investigate corrosion mechanism by revealing the growth of corrosion film of Fe-20Mn-1.2C alloys. The samples were immersed in 0.9 wt% NaCl aqueous solutions at 37 ± 1 °C for different time intervals to elucidate corrosion process. Eight cylinder specimens with a diameter of 8 mm and a length of 3 mm were immersed in 0.9 wt% NaCl solutions for different intervals (10 min, 30 min, 60 min and 16 h). They were rinsed with pure water, and then rinsed by ethanol and dried in air prior to SEM observation and both X-ray photoelectron spectroscopy (XPS) analysis. XPS tests were performed with a spectrometer (ESCALAB-2) equipped with an MgK_α ray source (1253.6 eV protons).

3. Results

3.1. Microstructural variation

Fig. 1 shows the microstructures of Fe-20Mn-1.2C-x alloys. It can be seen that the grains are about 80 ± 5 μm for three samples. The Fe-

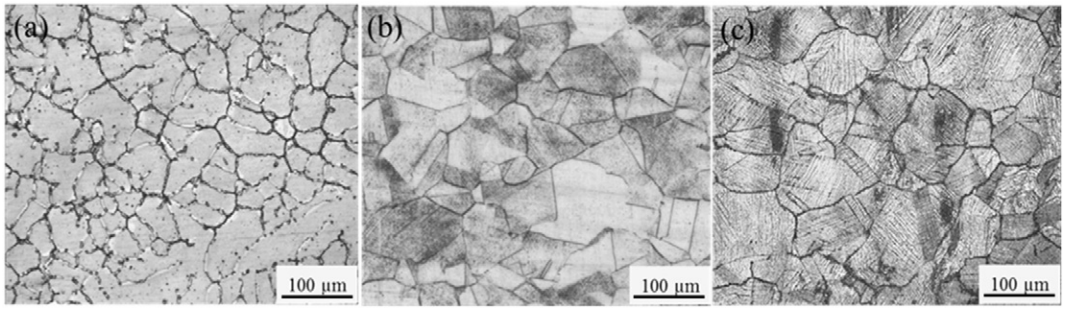

Fig. 1. Optical graphs of Fe-20Mn-1.2C samples under different states, (a) Fe-20Mn-1.2C-1; (b) Fe-20Mn-1.2C-2; (c) Fe-20Mn-1.2C-3.