Acta Biomaterialia 17 (2015) 68–77

Contents lists available at ScienceDirect

Acta Biomaterialia

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

Influence of cross-rolling on the micro-texture and biodegradation of pure iron as biodegradable material for medical implants

Camillus Sunday Obayi [a,b,1], Ranna Tolouei [b,1], Carlo Paternoster [b], Stephane Turgeon [b], Boniface Adeleh Okorie [a], Daniel Oray Obikwelu [a], Glenn Cassar [c], Joseph Buhagiar [c], Diego Mantovani [b,*]

[a] Department of Metallurgical & Materials Engineering, University of Nigeria, Nsukka, Nigeria
[b] Laboratory for Biomaterials and Bioengineering, CRC-I, Department of Mining, Metallurgical and Materials Engineering & CHU de Quebec Research Centre, Laval University, Quebec City, Canada
[c] Department of Metallurgy and Materials Engineering, University of Malta, Malta

ARTICLE INFO

Article history:
Received 12 October 2014
Received in revised form 1 January 2015
Accepted 19 January 2015
Available online 30 January 2015

Keywords:
Biodegradable metals
Pure iron
In vitro degradation
Structure–properties relationships
EBSD

ABSTRACT

Iron-based biodegradable metals have been shown to present high potential in cardiac, vascular, orthopaedic and dental in adults, as well as paediatric, applications. These require suitable mechanical properties, adequate biocompatibility while guaranteeing a low toxicity of degradation products. For example, in cardiac applications, stents need to be made by homogeneous and isotropic materials in order to prevent sudden failures which would impair the deployment site. Besides, the presence of precipitates and pores, chemical inhomogeneity or other anisotropic microstructural defects may trigger stress concentration phenomena responsible for the early collapse of the device. Metal manufacturing processes play a fundamental role towards the final microstructure and mechanical properties of the materials. The present work assesses the effect of mode of rolling on the micro-texture evolution, mechanical properties and biodegradation behaviour of polycrystalline pure iron. Results indicated that cross-rolled samples recrystallized with lower rates than the straight-rolled ones due to a reduction in dislocation density content and an increase in intensity of {100} crystallographic plane which stores less energy of deformation responsible for primary recrystallization. The degradation resulted to be more uniform for cross-rolled samples, while the corrosion rates of cross-rolled and straight-rolled samples did not show relevant differences in simulated body solution. Finally, this work shows that an adequate compromise between biodegradation rate, strength and ductility could be achieved by modulating the deformation mode during cold rolling.

1. Introduction

High-purity polycrystalline iron (Fe) has generated extensive research, since its first experimental use as a biodegradable material for cardiovascular applications in 2001 [1]. This application demands a degradation rate matching the healing rate of the injured tissue, in addition to appropriate mechanical properties (such as ductility, yield and tensile strengths), adequate biocompatibility and low toxicity of the degraded compounds all along the implantation time [2].

The above desirable properties of a biodegradable cardiovascular stent have led to the re-assessment and improvement of some of the known properties of pure Fe. Recently, several metal processing steps have been used to adjust the mechanical, degradation and biocompatibility behaviour of pure Fe. These include selective alloying [3,4], electrodeposition/electroforming [5] and thermo-mechanical processing [6]. A thermo-mechanical treatment consists of a series of plastic deformation stages and heat treatments; it is aimed at obtaining semi-finished products with the desired shape and microstructure [7]. Plastic deformation, particularly cold working has a major impact on the final microstructure of the semi-finished product, affecting grain size, shape and microtexture. Cold working can significantly increase dislocation density, in turn affecting strain energy and residual stresses [8]. As-cold worked materials have higher tensile strength and hardness at

---

* Corresponding author at: Laboratory for Biomaterials and Bioengineering, Canada Research Chair I in Biomaterials and Bioengineering for the Innovation in Surgery, Department of Min-Met-Materials Eng & CHU de Quebec Research Centre, Laval University, Quebec City, Canada. Tel.: +1 418 656 2131x6270; fax: +1 418 656 5343.

E-mail address: Diego.Mantovani@gmn.ulaval.ca (D. Mantovani).

URL: http://www.lbb.ulaval.ca (D. Mantovani).

[1] These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.actbio.2015.01.024

the expense of ductility [9]. These properties can be restored by a subsequent heat treatment called annealing; however, the residual stresses may not be totally eliminated. In the case of severe plastic deformation, the amount of stored energy can induce recrystallization phenomena at lower temperatures [10].

Straight cold rolling, or uni-directional rolling (UD), introduces substantial microstructural heterogeneities or anisotropic properties [11]. All have implications for the physical, mechanical and degradation properties of metals. Cross-rolling, or bi-directional rolling (BD), is a process in which the rolling direction between two following passes is perpendicular. This process is used to reduce the directional effects of straight rolling [12] and to induce a more homogeneous final structure [13]. Bi-directional rolling significantly symmetrizes the rolling textures, modifies residual stresses and plastic strain anisotropy [12,14].

Cross-rolling is of prime interest in many metal working operations because it affects the formability of metals [15], which enables the formation and control of preferred crystallographic texture. Formability of metal sheets is influenced by specific crystal orientations; low carbon steel sheets with high (111) and low (100) textures show high plastic strain ratios and exhibit adequate deep drawing properties [16]. Adequate formability is mandatory for successful cold forming of metals into products of extreme small thicknesses. The complex geometry of coronary artery stent dictates fabrication from materials that display consistent, predictable and uniform non-directional properties and characteristics. They also need to be produced from materials with a proper formability by tube drawing process during stent manufacturing.

Past investigations on cold working of pure Fe with subsequent annealing have been found to impact the grain size evolution [17], corrosion rate in acidic media [18,19] and mechanical properties [20]. Nevertheless, the effect of BD on microstructural changes, mechanical properties and degradation behaviours of pure Fe was not thoroughly addressed in previous studies particularly in relation to crystallographic texture [12] and recrystallization behaviour [21].

Taking into account the relevance of pure Fe as a base metal for biodegradable stents, the aim of the present work was to assess the effect of cross-rolling on the microtexture evolution, mechanical and degradation behaviour. Its mechanical properties and corrosion rates after processing by uni-directional rolling or bi-directional rolling were studied and compared in this work.

2. Materials and methods

The material used in this work was an Armco® soft ingot iron (>99.8% purity) in the form of 2 mm thick as-rolled sheets (Good fellow Limited, Cambridge, United Kingdom). The chemical composition of the as-received material is given in Table 1.

The rolling reduction of 75% was carried out to achieve 0.5 mm thickness, with thickness reduction limited to 0.2 mm per pass at a rolling speed of 220 mm s^{-1} (Stanat, Rolling Mill; model TA-315) in two different ways: uni-directionally rolling (UD) and bi-directionally rolling (BD). In this latter case, the specimen was turned by 90° between each successive pass. The as-received material properties were investigated without further processing, to have a reference material. Samples with square cross-sections of 10×10 mm^2 were cut from both UD and BD rolled strips and subsequently annealed at two temperatures of 550 °C and 900 °C; the annealing process was carried out in a tube furnace under a high purity argon atmosphere. The heating rate was 6.5 °C per minute; the sample was soaked for two hours at the annealing temperature and then air quenched. Sample codes of the treated and untreated samples are listed in Table 2.

2.1. Microstructure and texture evolution

The as-received, as-rolled and annealed samples were mechanically ground and polished; an etching with 2% Nital solution for optical metallography was performed after the polishing. An optical microscope (Nikon Epiphot 200, Japan) equipped with CLEMEX Vision image analyser (Clemex, Longueuil, Canada) was used for microstructural observation on the transverse direction (TD) of the samples after etching.

2.1.1. XRD

The average texture and preferred crystallographic orientation of the samples (on normal direction (ND)) were analysed using a Siemens D5000 X-ray diffractometer, operated using Cu-Kα radiation ($\lambda = 0.15406$ nm) at an accelerating voltage of 40 kV and a current of 30 mA. The scan rate was 0.05° s^{-1} in the range of 20–120° at a step size of 0.02°.

A study of the texture index was performed following the procedure established in the literature [5] based on the following formulas:

$$I_{exp}(hkl) = \frac{I_{exp}(hkl)}{I_{exp}(110) + I_{exp}(200) + I_{exp}(211) + I_{exp}(220)} \tag{1}$$

$$I_{ref}(hkl) = \frac{I_{ref}(hkl)}{I_{ref}(110) + I_{ref}(200) + I_{ref}(211) + I_{ref}(220)} \tag{2}$$

$$M(hkl) = \frac{I_{exp}(hkl)}{I_{ref}(hkl)} \tag{3}$$

where $M(hkl)$ is the texture index, $I_{exp}(hkl)$ is relative intensity of the (hkl) plane reflection for the experimental pattern and $I_{ref}(hkl)$ is relative intensity of the (hkl) plane reflection for the reference pattern of body-centred cubic (bcc) iron (JCPDS card No. 06-696).

2.1.2. EBSD

The specimens were hot mounted (on normal direction, ND) in conductive Bakelite, suitable for electron microscopy, using a specimen mounting press. They were then prepared for further metallographic investigation using standard laboratory metal grinding and polishing techniques, with 240–4000 SiC paper. A final mirror finish was obtained using a Metprep Chemicloth with a water-based colloidal silica suspension of mean particle diameter of 0.06 μm.

Degreasing of the surface was carried out by thorough acetone and isopropyl alcohol cleaning. Electron backscatter diffraction (EBSD) was performed using a Merlin Gemini scanning electron microscope (SEM) equipped with an EBSD/EDX Ametek detector. The total tilt between the EBSD detector and the sample surface was set to 70° in order to project the electron diffraction pattern onto the EBSD detector. The working distance was set to 15 mm while the working voltage was set to 20 kV and the probe current

Table 1
Chemical composition of the as-received Armco iron (wt.%).

C	Ni	Cr	Mn	Cu	Mo	S	Sn	P	Si	Al	Fe
0.006	0.037	0.032	0.041	0.017	0.002	0.014	0.014	0.019	0.008	0.010	Bal.