PAPER

Fabrication and characterization of A Zn-0.5Fe alloy membrane by powder metallurgy route for guided bone regeneration

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Abstract

A Zn-0.5Fe membrane with a thickness of 0.1 mm was produced by powder sintering and then hot extrusion and hot rolling. The microstructure, mechanical properties, corrosion properties and cytotoxicity of the Zn-0.5Fe membrane were investigated. The Zn-0.5Fe membrane had a finer and uniform microstructure in comparison to as-sintered Zn-0.5Fe and as-extruded Zn-0.5Fe alloys. Among the three alloys, the Zn-0.5Fe membrane exhibited the best mechanical properties, due to the fine grain strengthening, which is caused by the grain refinement and porosity reduction of the Zn-0.5Fe alloy after processing. The corrosion results of the Zn-0.5Fe alloys in Ringer’s solution show that the corrosion resistance was improved after hot working because of the decrease of microgalvanic corrosion caused by intermetallic compound. Furthermore, the cytotoxicity test assessed by MC3T3-E1 subclone 14 cells showed the Zn-0.5Fe membrane had an acceptable biocompatibility. Therefore, the Zn-0.5Fe membrane has great potential for biodegradable guided bone regeneration.

1. Introduction

Biodegradable metal materials have been introduced as GBR membrane materials to overcome the negative effects of non-degradable materials and degradable polymer materials. Non-degradable materials such as titanium membranes require surgical removal of implants [1] and degradable polymer materials cannot provide enough space for bone reconstruction, which have low strength and rapid degradation [2]. At present, the most studied biodegradable metal materials are Fe-based alloys, Mg-based alloys and Zn-based alloys. Among the three alloys, Zn-based alloys are a promising candidate material with many advantages [3] Zn-based alloys have moderate corrosion rates and produce little hydrogen during degradation as implants. Because pure Zn membrane had low ultimate tensile properties [4], alloying it with the other elements is a good way to improve mechanical properties [5]. Alloying elements must be selected with consideration for biocompatibility. Since Fe is one of the essential elements in the human body, it was recognized a suitable element that be added to biodegrade Zn metal.

Alon Kafri showed that the as-casted Zn-1.3Fe (wt%) alloy prepared by melting casting had good biocompatibility in male mice [6]. Z. Shi prepared Zn-0.3Fe (wt%) alloy by bottom circulating water cooling casting and traditional melting casting, which the ultimate tensile strength (UTS) of as-cast Zn-0.3Fe alloys were less than 80 MPa [7]. Powder metallurgy is an effective way in preparing homogeneous alloys with widely different melting points, which the melting points of Zn and Fe are 419.3 °C and 1538 °C respectively. A series of as-sintered Zn-Fe alloys have been prepared by powder metallurgy for scaffold, which Zn-1Fe and Zn-2Fe (wt%) alloys were potential biodegradable implants [8]. However, in the author’s knowledge, there is no relevant literature report on Zn-Fe alloy membrane with thickness of 0.1 mm which produced by powder sintering.

The purpose of this study is to develop a new GBR membrane to test the properties of basic materials, so as to select samples for subsequent implantation experiments. Base on previous studies [6–9] and Zn-Fe phase diagrams [10], adding trace Fe to the Zn alloy could improve the properties. In this paper, we detailed
investigation on the Zn-0.5Fe (wt%) alloy membrane in its microstructure, mechanical properties, corrosion properties and cytotoxicity.

2. Materials and methods

A Zn-0.5Fe membrane with a thickness of 0.1 mm was produced by powder sintering and then hot extruded and hot rolling. The high-purity Zn powders (>99.9%, 23.0 μm) and Fe powders (>99.9%, 23.0 μm) were mixed together for 4 h in mixer (Turbula, WAB, Czech Republic) and then pressed into shape (Ø56 x 120 mm) in a stainless-steel mold using a pressure of 500 MPa under argon gas. Subsequently, the raw billets were sintered at 400 °C for 2 h under argon atmosphere. The alloys were annealed at 360 °C for 48 h and then water quenched. Then as-sintered alloys were preheated at 320 °C for 2 h and extruded into bars with 16 mm diameter. The as-extruded bars were then hot multi-pass rolled that preheated at 220 °C for 2 h with reduction per pass by 15%, to obtain membranes with a thickness of 0.1 mm.

The microstructure was studied via optical microscopy, scanning electron microscopy (SEM) (FEI Quanta 200, NL) with an energy dispersive spectrometer (EDS) and x-ray diffraction (XRD, D/Max 2550). Tensile tests were performed on a universal testing machine (Instron 3369, USA) according to the ASTM-E8-04 standard. The corrosion properties were evaluated by electrochemical tests, which were performed on an electrochemical workstation (CHI 660E, CHN), in Ringer’s solution (NaCl 8.6 g L⁻¹, KCl 10.3 g L⁻¹, CaCl₂ 0.33 g L⁻¹, pH 7.4).

The murine MC3T3-E1 cell line (MC3T3-E1 subclone 14, Cell Bank of Chinese Academy of Sciences, CHN) were used to assess cytotoxicity of Zn-0.5Fe membrane. According to ISO 10993-12 standards, extract of Zn-0.5Fe membrane was incubated in serum-free alpha-Minimum Essential Medium (α-MEM medium) for 72 h with surface area to volume ratio as 6 cm² ml⁻¹. According to ISO 10993-5 standard, MC3T3-E1 subclone 14 cells were cultured on 96-well plates with densities of 1 × 10⁴ cells ml⁻¹ in α-MEM medium with 10% fetal bovine serum and 1% penicillin/streptomycin for 24 h. The medium was replaced with alloy-diluted 12.5%, 25% and 50% extracts. The negative control group was set as the original medium, and the cell activity was detected by Cell Counting Kit-8 (CCK-8 kit, beyotime, CHN) assay cultured in different medium for 1, 3 and 5 days.

3. Results and discussion

Microstructure changes of Zn-0.5Fe alloy membrane during preparation are present in figures 1, and 1(a)–(c) shows the optical microstructure of the Zn-0.5Fe alloys. The as-sintered Zn-0.5Fe alloy could be observed with an average size of 21.3 μm Zn matrix and pure 6.8 μm Fe particles. After extrusion, the grain was refined and the pure Fe particles were crushed and formed intermetallic compounds with the Zn matrix. In the as-extruded Zn-0.5Fe alloy, the average grain size of Zn matrix was 2.44 μm, and intermetallic compound was 6.89 μm. After rolling, the Zn-0.5Fe alloy grain was further refined, and the average grain size of matrix and intermetallic compound was 0.93 μm and 2.21 μm respectively. The bands in figures 1(b)–(c) displayed along the processing direction. The change of the weight ratio was observed by line scanning the local microstructure of the Zn-0.5Fe alloy (figures 1(d)–(f)), indicating that Zn-Fe intermetallic compounds were formed during the machining process.

This could be attributed to the Zn-0.5Fe alloy sintering temperature was 400 °C, the local temperature exceeded the melting point of Zn (419.3 °C), but far from reaching the melting point of Fe (1538 °C), so pure Fe was wrapped in the part of a molten Zn alloy. In the process of hot extrusion and hot rolling, deformation and heat treatment caused the phase transformation between broken Fe particles and Zn matrix, forming intermetallic compounds. EDS results showed that the weight ratio of Zn: Fe in intermetallic compounds of the membrane was almost 89:11, which was close to that of Zn: Fe in FeZn₁₃ phase. XRD patterns showed that the Zn-0.5Fe membrane consists of Zn and FeZn₁₃ phase, which was matching with the Zn–Fe equilibrium phase diagram [10] and EDS results. The morphology of FeZn₁₃ phase in the membrane was different from that reported in previous literatures [11], which was caused by membrane produced by powder sintering.

Table 1 shows the electrochemical parameters and corrosion rates of Zn-0.5Fe alloys obtained by the polarization curve of the action potential in Ringer’s solution. The results showed that the corrosion potential and current density of Zn-0.5Fe membrane were −1.28 V and 7.67 μA m⁻², compared with those of as-sintered Zn-0.5Fe alloy (−1.16 V, 9.76 μA m⁻²). The corrosion rates of as-sintered, as-extruded and as-rolled Zn-0.5Fe alloys were 0.146 mm year⁻¹, 0.125 mm year⁻¹ and 0.115 mm year⁻¹ respectively. The microstructure of Zn-0.5Fe membrane was finer, and FeZn₁₃ phase reduced the galvanic corrosion of the Zn and Fe particles, which improved corrosion resistance. The corrosion rates show that corrosion resistance of the Zn-0.5Fe membrane was much higher than that of as-sintered and as-extruded Zn-0.5Fe alloys in Ringer’s solution.
Table 2 illustrates the porosity and mechanical properties and figure 2 shows Tensile fracture morphologies of the Zn-0.5Fe alloys. The porosity of as-sintered, as-extruded and as-rolled Zn-0.5Fe alloys were 1.82%, 0.93% and 0.58% respectively. After hot extrusion and hot rolling, the porosity of Zn-0.5Fe alloy decreased. The Zn-0.5Fe membrane had the highest hardness and tensile strength, which were more than 380% and 179% of as-sintered Zn-0.5Fe alloy respectively. It is noteworthy that the Zn-0.5Fe alloy membrane produced by powder sintering shows UTS was 168.8 MPa, which was higher than 108 MPa of the pure Zn membrane in Guo’s study [4]. After hot extrusion, the hardness and strength of the Zn-0.5Fe alloy were improved, and the plasticity was increased from 0.5% to 19.9%. The main reason for the improved mechanical properties was fine grain

Table 1. Electrochemical data of Zn-0.5Fe alloys in Ringer’s solution.

| Alloy          | $E_{corr}$(V) | $I_{corr}(μ\text{A cm}^{-2})$ | $V_{corr}$(mm year$^{-1}$) |
|---------------|--------------|-------------------------------|-----------------------------|
| As-sintered   | −1.16        | 9.76                          | 0.146                       |
| As-extruded   | −1.19        | 8.36                          | 0.125                       |
| Membrane      | −1.28        | 7.67                          | 0.115                       |

Table 2. Porosity and mechanical properties of the Zn-0.5Fe alloys.

| Alloy          | Porosity (%) | Density (g cm$^{-3}$) | YS (MPa) | UTS (MPa) | Elongation (%) | HV$_{0.1}$ |
|---------------|--------------|-----------------------|----------|-----------|----------------|------------|
| As-sintered   | 1.82         | 6.65                  | —        | 100.53    | 0.51           | 30.41      |
| As-extruded   | 0.93         | 6.74                  | 101.31   | 150.92    | 19.93          | 52.76      |
| Membrane      | 0.58         | 6.81                  | 110.20   | 168.81    | 16.25          | 142.68     |
Figure 2. Tensile fracture morphologies of Zn-0.5Fe alloys: (a) As-sintered alloy; (b) As-extruded alloy; (c) Membrane.

Figure 3. Cytotoxicity results of the Zn-0.5Fe membrane: (a) Optical images of MC3T3-E1 subclone 14 cells, (b) Relative growth rate (RGR) of cells cultured in different extracts, *p < 0.05.
strengthening, which could be seen from figures 1(a) (b) that the prior particle boundary of the as-sintered Zn-0.5Fe alloy basically disappeared after extrusion, and the grain was obviously refined. Compared with the as-extruded Zn-0.5Fe alloy, the UTS of the as-rolled Zn-0.5Fe membrane also increased slightly, but the elongation decreased to 16.2%, which may be the reason for the increase of hard FeZn$_{13}$ phase in the Zn-0.5Fe alloy. The large increase in hardness was due to work hardening, which was due to the large deformation in the rolling process from the 16 mm extruded bar to 0.1 mm rolled sheet. From the tensile fracture morphology of the as-rolled Zn-0.5Fe alloy, obvious cleavage plane and a few dimples can be seen, which indicates that the fracture mode was brittle-toughness mixed fracture.

Figure 3 shows the results of the cytotoxicity test of the Zn-0.5Fe alloy membrane. Results showed that no obvious cell death was observed in the cells and cell viability were more than 95% incubated with the 12.5% and 25% extract. However, MC3T3-E1 subclone 14 cells in the 50% extract did not perform as well on 1 day, possibly due to the metal ion content in the culture medium. Fortunately, an increase in cell numbers and cell viability was seen in subsequent cultures, and the cell activity had exceeded 70% on 5 day, indicating that the cells gradually developed tolerance in the 50% extract, meeting the requirements for cytotoxicity in the GBR applications.

4. Conclusion

This work studied microstructure, mechanical properties, corrosion properties and cytotoxicity of Zn-0.5Fe (wt%) membrane prepared by powder sintering. The conclusions are as follows:

(1) A novel Zn-0.5Fe membrane, which was produced by powder sintering, had uniform fine microstructure and FeZn$_{13}$ phase was formed in hot deformation.

(2) Zn-0.5Fe alloy membrane had higher tensile strength and corrosion resistance compared to as-sintered and as-extruded Zn-0.5Fe alloys, which were due to the grain refinement and formation of intermetallic compounds during machining.

(3) Zn-0.5Fe alloy membrane had adequate biocompatibility, and the cell viability of MC3T3-E1 subclone 14 cells cultured was higher than 95% in 12.5% and 25% Zn-0.5Fe alloy membrane extract mediums for 1, 3 and 5 days.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Declaration of interests

All authors disclosed no relevant relationships.

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