Materials Research Bulletin 82 (2016) 39–44

Contents lists available at ScienceDirect

Materials Research Bulletin

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

Microstructures and martensitic transformation behavior of superelastic Ti-Ni-Ag scaffolds

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ARTICLE INFO

Article history:
Received 3 November 2015
Received in revised form 15 February 2016
Accepted 21 February 2016
Available online 24 February 2016

Keywords:
A. Metals
B. Mechanical properties
B. Phase transformation
C. Differential scanning calorimetry (DSC)
C. X-ray diffraction

ABSTRACT

Ti-Ni-Ag scaffolds were prepared by sintering rapidly solidified alloy fibers. Microstructures and transformation behaviors of alloy fibers and scaffolds were investigated by means of electron probe micro-analyzer (EPMA), differential scanning calorimetry (DSC) and X-ray diffraction (XRD). The B2-R-B19′ transformation occurs in alloy fibers. The alloy fibers have good superelasticity with superelastic recovery ratio of 93% after annealing heat treatment. The as-sintered Ti-Ni-Ag scaffolds possess three-dimensional and interconnected pores and have the porosity level of 80%. The heat treated Ti-Ni-Ag scaffolds not only have an elastic modulus of 0.67 GPa, which match well with that of cancellous bone, but also show excellent superelasticity at human body temperature. In terms of the mechanical properties, the Ti-Ni-Ag scaffolds in this study can meet the main requirements of bone scaffold for the purpose of bone replacement applications.

1. Introduction

Quite recently, there has been a rise in the number of people suffering from osteoporosis, broken bones and skeletal defects around the world due to the increasingly active lifestyle, accidents, obesity and ageing population, which leads to a high demand for bone grafts and substitutes used to restore damaged bones [1,2]. Therefore, there has been increased interest in scaffold-based strategies for bone implant. TiNi alloys have been widely used in biomedical field due to their distinctive characteristics such as unique superelasticity, excellent shape memory effect, low elastic modulus, good corrosion resistance and biocompatibility [3]. Moreover, TiNi alloys have similar deformation behavior with that of bone compared with other metallic materials, which can guarantee the biomechanical compatibility [4]. However, the issue of the bulk TiNi alloys used for bone replacement is the elastic modulus mismatch between bulk TiNi alloys and human bones. The elastic moduli of bulk TiNi alloys range from 40 GPa to 90 GPa for austenite and 20 GPa to 50 GPa for martensite [3], which are still higher than that of cortical bone and cancellous bone ranging from 15 to 20 GPa and 0.1 to 2 GPa, respectively [5]. Another fact is that the bulk TiNi alloys lack the capability to allow the ingrowth of new bone tissue and vascularization [6]. Therefore, porous TiNi alloys have been developed due to their low density, capable of supporting early ingrowth of bone and adjustable modulus of elasticity [7].

Shape memory Ti-Ni-Ag alloys have attracted researcher's attention due to the effect of silver element on TiNi [8–10]. It has been reported that silver addition to TiNi alloys improved the corrosion resistance because of the presence of a stable passive film in artificial corrosion environment [11]. The high corrosion resistance can reduce the adverse effect of Ni release. Silver was incorporated into the Ti-Ni-Ag films as pure Ag nanoprecipitates [12]. In Ref. [3], it was showed that Ti-47.3Ni-1.4Ag (at.%) alloy can reduce the adhesion of bacteria due to the release of Ag ions from the tiny Ag particles that precipitate within the TiNi alloy matrix. Ag ions can penetrate into the bacterial cell and bring DNA molecule form change [8]. It is also reported that Ag ions can affect the bacterial viability by reacting with tissue proteins of cell membrane [9,10]. The martensitic transformation behaviors of Ti-Ni-Ag alloys were studied by Chun et al. [13]. Silver added TiNi alloys not only exhibit good biocompatibility and corrosion resistance but also show antibacterial function [3,11], comparable with binary TiNi alloys. Therefore, the primary motivation of this study is to fabricate Ti-Ni-Ag porous scaffolds with appropriate mechanical properties for the purpose of replacing damaged bones.

Although a lot of researchers have studied the mechanical properties of porous TiNi alloys in order to match properties of host bone, those porous TiNi alloys fabricated by conventional powder

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http://dx.doi.org/10.1016/j.materresbull.2016.02.031
0025-5408/© 2016 Published by Elsevier Ltd.

metallurgy techniques have their own limitations in terms of high level of porosity, regular pore shapes, appropriate pore size and homogeneous pore distribution [14]. Studies on the porous TiNi alloys are still lacking. In this study, the trail of manufacturing a different type of porous metallic scaffolds was carried out by sintering Ti-Ni-Ag alloy fibers and mechanical properties were investigated at human body temperature.

2. Experimental procedure

The 49Ti-50.3Ni-0.7Ag (at.%) pre-alloy ingots were fabricated from high purity elements of titanium, nickel and silver by arc melting six times under the high purity of argon atmosphere. The pure Ti ingots were also melted and used as the getter. The alloy fibers were prepared by using a laboratory melt overflow device [15]. About 20 g of pre-alloy ingot was placed in water-cooled Cu hearth and melt by plasma arc beam under pure argon atmosphere. Then the hearth was tilted to the rotating molybdenum wheel with sharp edge and the liquid alloy overflowed. The speed and diameter of Mo wheel are 1500 rpm and 120 mm, respectively. As-solidified fibers were cut into small segments with the length about 5 mm. In the present study, the designed porosity and volume of scaffold were 80% and $10 \times 10 \times 11\ \mathrm{mm}^3$, respectively. Then the mass of needed fiber segments calculated from the quality-volume formula [16] was 1.3759 g. The fiber segments were put into the packing chamber of graphite mold and sintered at 1173 K for 60 min in high vacuum conditions. The sample was cooled in the equipment to room temperature after sintering.

The transformation behaviors of all specimens were investigated by differential scanning calorimetery (DSC) measurements at heating and cooling rate of 0.17 K/s using TA instrument DSC Q20. Crystal structures were studied at various temperatures by X-ray diffraction (XRD, D8 advance) using Cu Kα radiation with a scanning rate of 2°/min. Microstructural investigations were performed by electron probe micro-analyzer (EPMA, JXA-8100). TA instrument dynamic mechanical analyzer (DMA) was used to measure the tensile properties of alloy fibers at temperature $A_f + 5$ K. The dimensions of specimens were 30 mm in length and 0.09 mm in approximate diameter. The compressive tests of scaffolds were performed by using shape memory simulator at human body temperature. The size of sample was 8 mm × 8 mm × 10 mm.

3. Results and discussion

Fig. 1(a) shows the backscattered electron micrograph of 49Ti-50.3Ni-0.7Ag alloy bulk. By EDS analysis, the gray-colored TiNi matrix has Ag content of 0.40 at.% and the black-colored particles are known to be Ti_2Ni phase including Ag of 0.24 at.%. The chemical composition analyzed by EDS for each phase was taken from 5 measurements and expressed as average value. White-colored particles include 34.10 at.% Ag, 35.97 at.% Ti and 29.93at.% Ni, which are considered to be TiAg phase. The large amount of Ni is included in TiAg particles can be ascribed to the size of TiAg particles that are too small to be measured accurately by EDS analysis [13] and thus the influence from surrounding TiNi matrix should not be neglected. The diffraction peaks of TiAg phase were identified by XRD as shown in Fig. 3(a). Ti_2Ni and TiAg phases were not observed in as-processed alloy fibers as shown in Fig. 1(b). However, 0.57 at.% silver was included in the alloy fiber matrix, which was much higher than that in alloy bulk matrix. The fact can be ascribed to the rapid solidification of liquid alloy made much more Ag atoms supersaturate in the matrix of alloy fibers. The high content of silver in matrix is of interest due to its antibacterial function. Fig. 1(c)–(f) shows backscattered electron micrographs obtained from alloy fibers annealed at 673 K, 773 K, 873 K and 1073 K for 3.6 ks, respectively. The second phase particles appeared in the matrix with raising annealing temperature from 673 K to 1073 K, which are considered to be TiAg phase.

Fig. 2(a) shows the DSC curve of alloy bulk. One DSC peak on cooling curve and one DSC peak on heating curve were observed. For alloy fibers, two DSC peaks on cooling curve and one DSC peak on heating curve were observed as shown in Fig. 2(b). Phase identification was further investigated by XRD to illustrate the DSC curves. B2 phase, Ti_2Ni and TiAg diffraction peaks were observed simultaneously at room temperature in alloy bulk as shown in Fig. 3(a). Cooling the specimen down to 243 K, diffraction peaks of R phase and B19′ martensite appeared. On further cooling to 173 K, the intensity of diffraction peaks of B19′ martensite increased with decreasing the intensity of diffraction peaks of R phase. Therefore, B2-R-B19′ martensitic transformation occurred in alloy bulk. Only

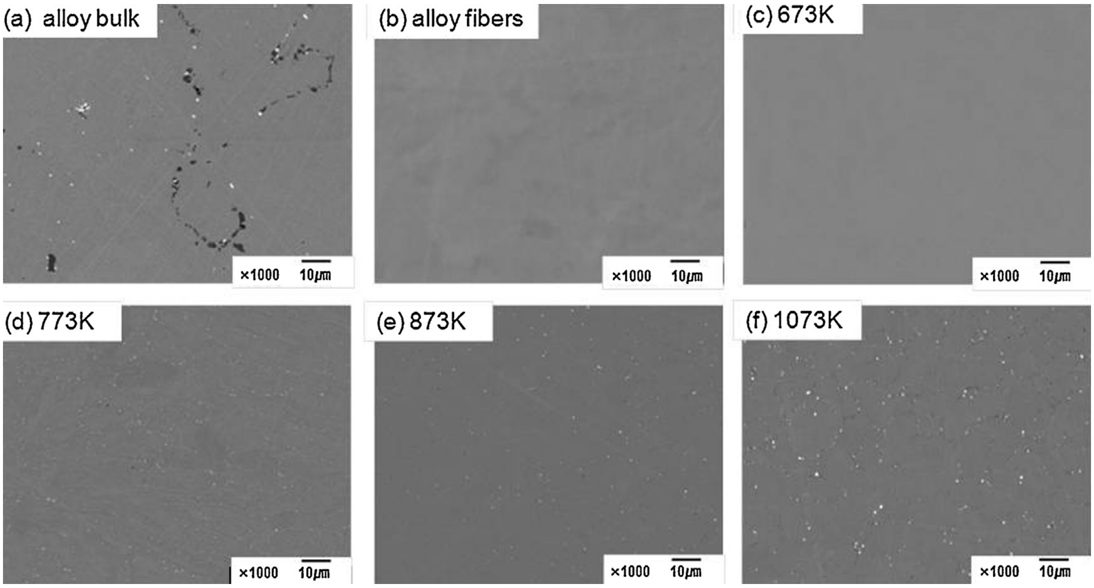

Fig. 1. Backscattered electron micrographs of specimens: (a) alloy bulk, (b) alloy fibers, which were annealed at various temperatures for 3.6 ks; (c) at 673 K, (d) at 773 K, (e) at 873 K and (f) at 1073 K.