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FABRICATION AND SHAPE MEMORY CHARACTERISTICS OF HIGHLY POROUS Ti-Nb-Mo BIOMATERIALS

Non-toxic Ti-Nb-Mo scaffolds were fabricated by sintering rapidly solidified alloy fibers for biomedical applications. Microstructure and martensitic transformation behaviors of the porous scaffolds were investigated by means of differential scanning calorimetric and X-ray diffraction. The $\alpha'' - \beta$ transformation occurs in the as-solidified fiber and the sintered scaffolds. According to the compressive test of the sintered scaffolds with 75% porosity, they exhibit good superelasticity and strain recovery ascribed to the stress-induced martensitic transformation and the shape memory effect. Because of the high porosity of the scaffolds, an elastic modulus of 1.4 GPa, which matches well with that of cancellous bone, could be obtained. The austenite transformation finishing temperature of 77Ti-18Nb-5Mo alloy scaffolds is 5.1°C which is well below the human body temperature, and then all mechanical properties and shape memory effect of the porous 77Ti-18Nb-5Mo scaffolds are applicable for bon replacement implants.

Keywords: Ti-Nb-Mo alloys, Porous scaffolds, Bio-medical materials, Shape memory alloys

1. Introduction

TiNi shape memory alloys have shown the most outstanding properties among the other shape memory alloys, and have already been extensively applied as metallic biomaterials in making biomedical apparatus and implant devices such as orthodontic arch wires, bone plates and stents due to their good biocompatibility and corrosion resistance. However, there are some people who are allergic to nickel. This has discouraged the use of TiNi as biomaterials to such people [1]. In fact, this has inspired the development of Ni-free biomedical shape memory alloys [2].

A major problem concerning metallic implants in orthopedic surgery is the difference of elastic modulus between the bone and metallic implants. For instance, the widely used Ti-based alloy, Ti-6Al-4V has an elastic modulus of about 110 GPa (the lowest value compared to other metallic biomaterials such as 316L Stainless steel and Co-Cr alloys) which is still higher than that of the bone (1-30 GPa). The elastic moduli of most metals are at least 10-20 times higher than those of hard tissues/bones. This mismatch results in bone being insufficiently loaded as called ‘stress-shielding’ resulting to osteoporosis, a disease characterized by decrease in bone mass and micro-architectural deterioration of bone tissue, leading to higher bone fragility and accordingly increase in fracture risk [3-5]. Therefore, stress-shielding is leading to retard bone remodeling, healing, and finally the bone loss [4,5]. The proposed solution to reduce the stiffness mismatches between bone and implant is to use porous materials. It has been found out that biomaterials which are low rigid are effective in improving bone healing and restoration [6]. An additional advantage of using porous materials is that the porous biomaterials provide room for body’s cells to grow into and intertwine with it. The ingrowth of body’s cells through the porous biomaterials improves biological fixation of the implant to the bone host [5,7-9]. In order to fabricate porous Ti and Ti alloys, a number of approaches have been carried out and these includes: loose powder sintering, slurry foaming, combustion synthesis, electron beam melting, solid-state foaming by expansion of argon-filled pores and polymeric sponge replication, hollow sphere sintering, reactive sintering and gas entrapped techniques. However, all of the above-mentioned methods provided a limited porosity.

A method to fabricate the porous Ni-free Ti-based shape memory alloys is proposed in this study. Very fine Ti-Nb-based alloy fibers were prepared by a melt overflow process. The porous bulk scaffolds, which have three-dimensional network structure, interconnected pores and high porosity, were produced using the solid-state sintering of the fibers and the effect of the high porosity on the mechanical performances was investigated using compressive tests

2. Experimental

Ti-Nb-Mo alloy ingots were melted under the high purity of argon atmosphere by an arc-melting method using high-purity titanium, niobium and molybdenum in a water-cooled Cu hearth.

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The experimental studies were performed using a laboratory scale arc melt overflow. About 30 g of mother alloys was placed in a water-cooled hearth, and skull melted under argon atmosphere by plasma beam. Then the hearth was tilted about the rotating quenching wheel, which was made of molybdenum. The liquid metal overflowed over a relatively horizontal edge or pour spot, to contact the cooling wheel surface. The quenching wheel substrate served as a continuous permanent mold, against which the casting solidified. The thickness of fibers can be controlled by the rotating speed of the wheel. The dimensions of Mo cooling wheels are 122 mm in diameter and 10 mm in width. However, its tip was acutely machined in order to produce the shape of fibers or filaments. The linear speed of the wheel was kept at 5.1 m/s (1000 rpm), to produce relatively thin fibers.

The as-solidified fibers were cut into small fragments of less than 0.5 cm in length. Then the fibers with random directions were uniformly put into the predetermined packing chamber of the mold pressing equipment and the pressure was applied by screwing the bolts. Sintering was carried out at high vacuum conditions (about 1×10^{-3} Pa) and the sintering temperature and time were1100°C and 1.8 ks, respectively. The porous bulk samples were left to cool down to room temperature under the high vacuum conditions before being removed from the vacuum equipment after sintering was completed. All the samples were then heat treated at 850°C for 1.8 ks followed by quenching in ice water for the solution treatment. Microstructural and compositional investigations were performed by scanning electron microscopy (SEM) using a ZEISS (SUPER555VD) instrument and by energy dispersive X-ray spectrum (EDS) using a NORAN (THERMO Scientific Ultradry) instrument. Martensitic transformation temperatures of as-cast fibers and the sintered porous bulk were measured by differential scanning calorimetry (DSC), at a cooling and heating rate of 10°C/min, using a TA Instrument Q-20. Crystal phases of the specimens were identified by X-ray diffraction (XRD), using CuK_a radiation. The mechanical behaviors of porous Ti-Nb-Mo shape memory alloys were investigated by uniaxial compression experiments with a strain rate of 0.24 mm/min.

3. Results and discussion

The as-solidified fibers fabricated by the melt overflow processing were shown in Fig. 1a. As shown in Fig. 1b, their cross-sectional shape is semi-circle with about 100 μm in diameter because they had solidified rapidly on the sharp tip of a cooling wheel. The phase transformation temperatures of the Ti-Nb-Mo shape memory fibers is strongly dependent on the alloy composition. In order to use the excellent superelastic property of shape memory alloys in many medical applications, the austenite transformation finishing temperature (A_f) must be less than 36.5°C, which is human body temperature. Miyazaki et al. [10] have reported that the phase transformation temperature of α'' (martensitic phase) $\leftrightarrow$ β (austenite phase) in Ti-Nb-Mo alloys decreases by an average of 90°C with addition of 1% Mo, and by an average of 30°C with addition of 1% Nb. In this study, the transformation temperatures were controlled by substitution of Mo for Nb in 77Ti-23Nb (at. %) alloy. Finally, it was found that A_f of 77Ti-18Nb-5Mo alloy was less than the human body temperature. Fig. 2a shows the DSC curve of 77Ti-18Nb-5Mo alloy fibers, which exhibits two exothermic peaks on cooling and one endothermic peak on heating. Then, the martensitic transformation starting temperature (M_s) and austenite transformation finishing temperature (A_f) of $\alpha'' \leftrightarrow \beta$ phase transformation in77Ti-18Nb-5Mo fibers are –9.3 and 4.9°C, respectively.

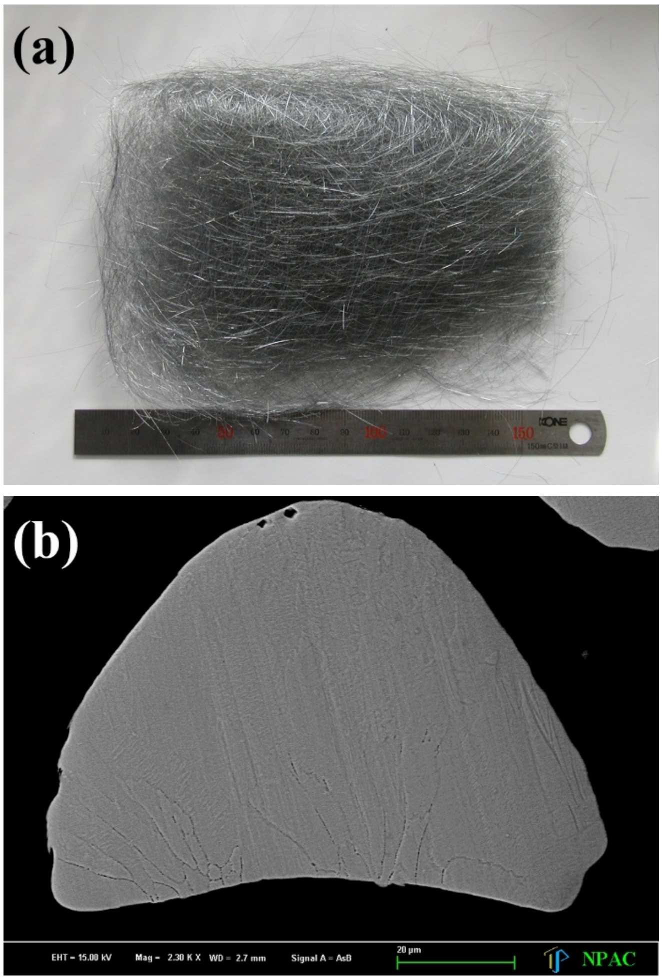

Fig. 1. (a) Photograph and (b) SEM micrograph of etched cross-section of as-solidified 77Ti-18Nb-5Mo fibers

Fig. 3a shows an optical image of the porous 77Ti-18Nb-5Mo scaffolds with 75% porosity. It is noted that the porous scaffolds have a wide range of porosity, a large pore size, and three-dimensional network structures as shown in Fig. 3b. The size of biological cells is known to be at most 3 μm. Therefore, the pore size of the 77Ti-18Nb-5Mo scaffolds, which were seen to be above 200 μm in Fig. 3b, is big enough to allow body's cells to grow through. The role of pores in the scaffolds is to make body's cell grow through and then increase the attachment of the implant to the bone making the implant to be part of the bone [7-9]. This may reduce losing the implants as the result of

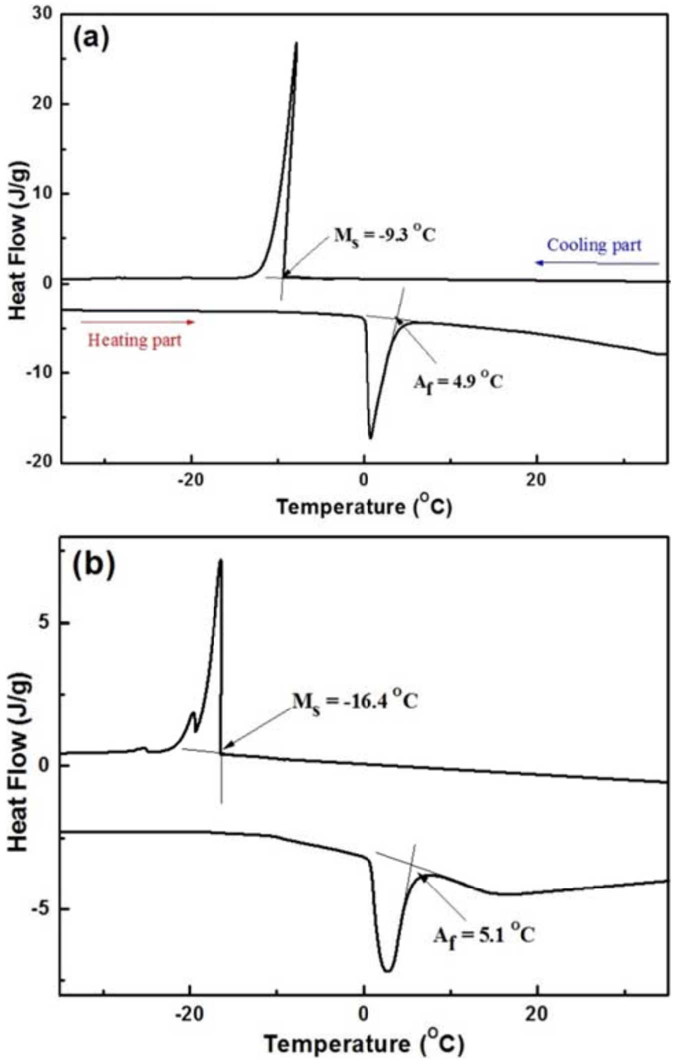

Fig. 2. DSC curves of (a) as-solidified fibers and (b) sintered scaffolds of 77Ti-18Nb-5Mo shape memory alloy

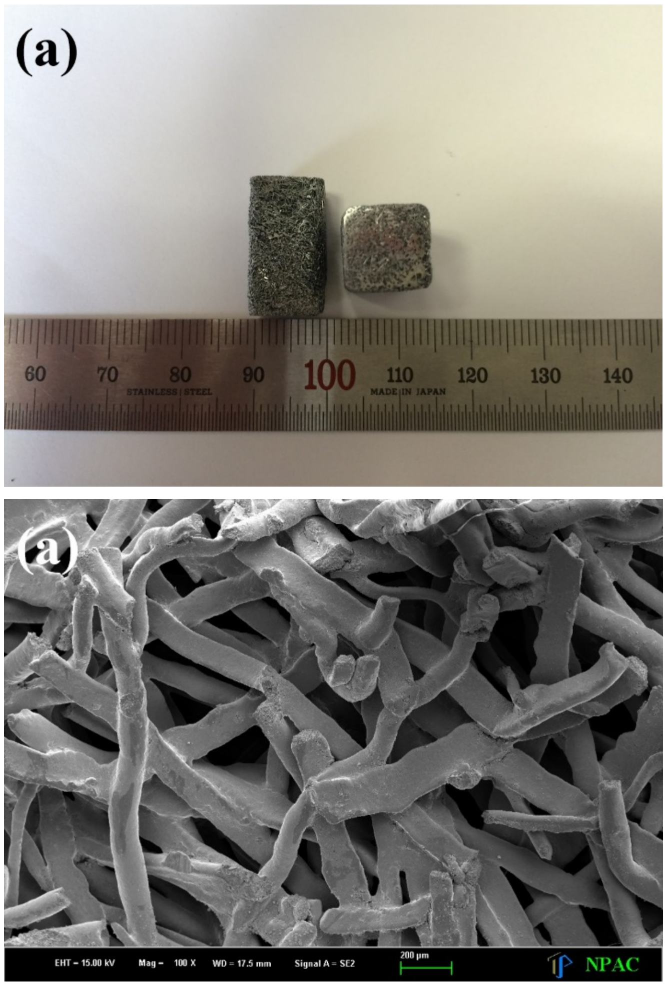

Fig. 3. (a) Optical and (b) SEM image of porous 77Ti-18Nb-5Mo scaffolds

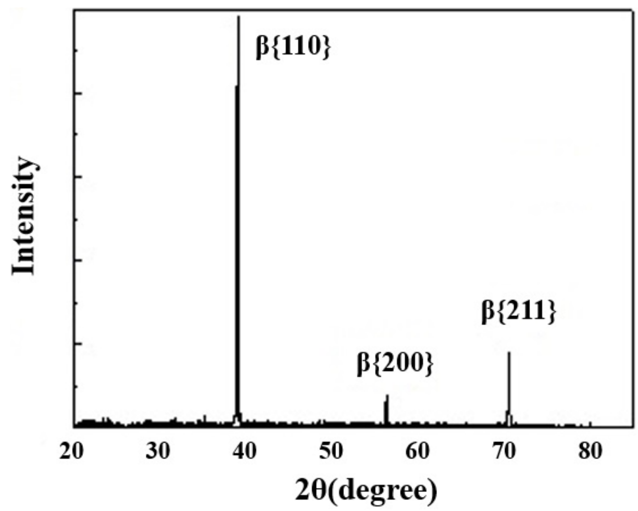

Fig. 4. XRD pattern of porous 77Ti-18Nb-5Mo scaffolds

failure of attachment between the implant and the surrounding tissues. Fig. 2b shows the DSC curve of porous 77Ti-18Nb-5Mo scaffolds. The M_s and A_f of $\alpha'' \leftrightarrow \beta$ phase transformation are –16.4 and 5.1°C, respectively. It was found that the M_s of the porous scaffolds was lower than that of the as-solidified fiber. It is well known that the internal strain such as dislocations have a strong effect on transformation temperatures [11]. In this study, crystallographic defects of dislocations and small grains introduced by rapid solidification are considered to be the reason for the high M_s of the as-solidified alloy fibers. Fig. 4 shows a XRD pattern of porous 77Ti-18Nb-5Mo scaffolds at room temperature. Only the diffraction peaks corresponding to β phase are found and the porous scaffolds are completely austenite state at room temperature. When these porous scaffolds are used as the implants, they must be cooled to a temperature below M_s. Then they are really soft and easy to be deformed before being inserted into the body. After implantation, the shape of porous scaffolds must be recovered by the shape memory effect during $\alpha'' \rightarrow \beta$ phase transformation at normal body temperature of a human being.

The mechanical behaviors of the porous 77Ti-18Nb-5Mo alloys were investigated by a uniaxial compression experiment. Fig. 5 shows the results of a loading-unloading compressive test, when it was compressed to the strain of 2.5% at room temperature (above A_f). On the loading, the plateau of a stress-strain curve was observed at about 4 MPa. The 1.5% elongation of the stress-plateau is associated with the stress-induced martensitic transformation. After a loading-unloading cycle, the porous scaffold was heated at 100°C (the temperature higher than A_f) and held for 30 min, and then cooled to room temperature. The changes in the length of the specimen, which occurred during the austenite transformation, were measured. The recovered stain, which are ascribed to the shape memory effect, is 0.75%. Apparent elastic modulus was evaluated in the linear unloading portion of the stress-strain curve and the elastic modulus of the porous 77Ti-18Nb-5Mo alloys was as small as about 1.4 GPa. This small value of elastic modulus in the porous 77Ti-18Nb-5Mo scaffold is reflecting that the porous structure of the material undergoes higher deformation than dense materials and thereby avoiding yielding [12].

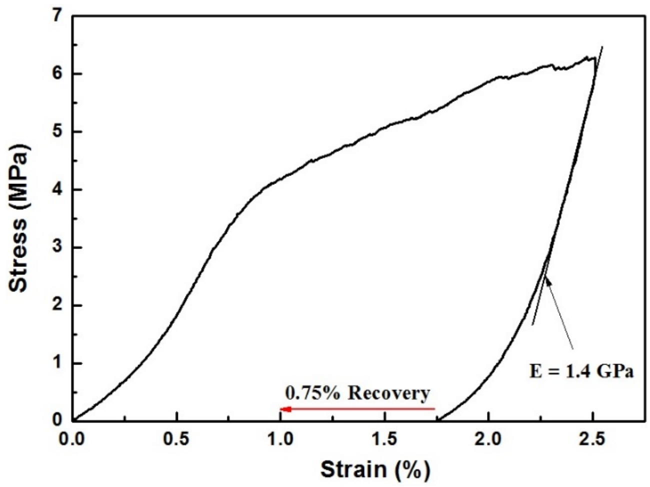

Fig. 5. Compressive strain-stress curve of porous 77Ti-18Nb-5Mo scaffolds

4. Conclusions

77Ti-18Nb-5Mo shape memory alloy fibers were prepared using the melt overflow process. The Ti-Ni-Mo scaffolds with 75% porosity were synthesized with a large pore size and three-dimensional network morphology, using the rapidly solidified fibers. When the compression test of the porous alloy was carried out at room temperature, the plateau of the stress-strain curve was observed at about 4 MPa and the strain of the stress-plateau associated with the stress-induced α'' (martensitic phase) $\rightarrow \beta$ (austenite phase) transformation was 1.5%. The elastic modulus of the porous alloy was as small as 1.4 GPa because of the high porosity of Ti-Nb-Mo shape memory alloys. The A_f of 77Ti-18Nb-5Mo scaffolds is 5.1°C which is well below the human body temperature, and then the shape of porous scaffolds must be recovered by the shape memory effect after their implantation in the body.

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