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Microstructure and martensitic transformation of an ultrafine-grained TiNiNb shape memory alloy processed by equal channel angular pressing

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ABSTRACT

Microstructure, martensitic transformation and mechanical properties of an ultrafine-grained $Ti_{44}Ni_{47}Nb_9$ shape memory alloy processed by equal channel angular pressing were investigated. The as-ECAP processed sample is characterized by an inhomogeneous and refined microstructure. In β-Nb phase-rich region, the grains of matrix are elongated with high density dislocations. In β-Nb phase-free region, the microstructure is partial recovery and characterized by near-equiaxed grains. The heterogeneous microstructure is attributed to presence of β-Nb phase. Martensitic transformation behavior of the as-ECAP processed sample is characterized by a single-stage transformation. The thermal cycling stability of transformation and the mechanical properties are considerably improved due to a strengthening effect resulting from refined grain size and high dislocation density.

1. Introduction

In past decades, TiNiNb shape memory alloys (SMAs) have attracted much attention due to their wide transformation hysteresis, excellent mechanical properties and good shape memory effect [1–4]. Such advantages are beneficial to the engineering applications of the alloys as fastening and sealing parts which can be expanded and stored at an ambient temperature. In practical applications, two necessary conditions have to be met for a reliable fastening, i.e. stable transformation with a low martensitic transformation start temperature (M_s) and high yielding strength. The former is helpful to minimize the properties' instability caused by thermal or mechanical cycling. The latter can satisfy the practical requirements for high pressure tube joining. Until now, several methods have been proposed to develop the high-strength TiNiNb-based alloys, including cold working followed by proper annealing [5], addition of Co element [6] and optimization of Nb content [7].

Recently, equal channel angular pressing (ECAP) has been used to refine the microstructure of TiNi-based SMAs [8]. After ECAP, an ultrafine-grained (UFG) microstructure with a grain size of about 300 nm can be formed in bulk TiNi alloys [8–10]. This UFG microstructure may render the alloys good cycling stability and mechanical properties [11–13]. In addition, our previous report shows that Ti_3Ni_4 phase is beneficial to refining the final microstructure of the as-ECAP processed $Ti_{49.2}Ni_{50.8}$ alloy [13]. It is well known that the wide-hysteresis TiNiNb alloy usually has a hypoeutectic microstructure consisting of B2 matrix, dispersed β-Nb phase particles [1–4]. However, as yet, no reports on the UFG TiNiNb alloys are available.

The purpose of this study is to investigate the microstructure, martensitic transformation and mechanical properties of the UFG TiNiNb alloy processed by ECAP. Based on the experimental results, the effect of ECAP processing on microstructure and martensitic transformation behavior was also discussed.

2. Experimental

A commercial TiNiNb alloy with a nominal composition of $Ti_{44}Ni_{47}Nb_9$ (at.%) was studied. Before processing, the alloy was

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annealed in a furnace at 850 °C for 1 h, and then quenched into water (called as initial sample hereafter). The samples, in the form of 20 mm in diameter and 100 mm in length rods, were processed by ECAP at a temperature of 450 °C for 8 passes using a die with a channel-intersection angle of $\Phi = 120°$. The pressing route Bc was used since it is the optimum one for producing the ultra-fine structure [14].

Martensitic transformation was measured on a Perkin–Elmer Diamond differential scanning calorimeter (DSC) at a constant heating/cooling rate of 20 °C/min. Phase constitution was determined by X-ray diffraction (XRD) on a Panalytical X-pert'PRO diffractometer at room temperature using Cu Kα radiation. Microstructure of the initial samples was determined by a FEI Nano430 field emission gun scanning electron microscopy (SEM) equipped with an electron backscatter diffraction (EBSD) system. The EBSD data were analyzed by a commercialized EDAX software. The sample for EBSD was prepared by mechanical polishing down to 4000 grit papers followed by 1 h of vibro-polishing using a colloidal silica solution. Microstructure of the as-ECAP processed sample was carefully observed on a Tecnai G2 F20 transmission electron microscopy (TEM) which was operated at 300 kV with a double-tilt sample stage. The TEM foils were prepared by mechanical grinding, followed by twin-jet electropolishing using an electrolyte solution consisting of 80% methanol and 20% H_2SO_4 by volume. The mechanical properties were tested by an Instron 3365 tensile machine equipped with a thermal chamber. The gauge length was fixed at 17 mm.

3. Results and discussion

Fig. 1 shows the XRD patterns of the initial sample and as-ECAP processed sample. Both the patterns can be mainly indexed as a mixture of B2 parent phase, β-Nb phase and $(Ti,Nb)_2Ni$ phase using the following lattice parameters: B2, $a = 0.3018$ nm; β-Nb phase, $a = 0.3296$ nm and $(Ti,Nb)_2Ni$ phase, $a = 1.1326$ nm [2,4], respectively. However, the peak at 36.9° indicated by an arrow cannot be indexed at the moment, indicating an unknown phase appeared in this alloy. After ECAP processing, the relative intensity of several diffraction peaks changed. For example, the diffraction peak corresponding to (220) β-Nb phase disappeared and the diffraction peak of (211) B2 phase became stronger. This demonstrates that ECAP changes the orientation of grains in $Ti_{44}Ni_{47}Nb_9$ alloy, which requires further investigation to obtain the detailed information.

Fig. 2(a) shows the back-scattered electron (BSE) image observed in the initial alloy. The initial alloy has a typical hypoeutectic microstructure consisting of B2 matrix, dispersed β-Nb phase particles indicated by the black arrow. The $(Ti,Nb)_2Ni$ particles with an irregular shape indicated by the white arrow are also observed. The formation of $(Ti,Nb)_2Ni$ particles are possibly due to the introduction of oxygen during melting [15] and will not be discussed hereafter. In order to investigate the grain size of initial alloy, EBSD tests were carried out. The result is shown in Fig. 2(b). This image is based on the Kikuchi band contrast and Euler angle. The electron backscatter pattern (EBSP) along grain boundaries tend to show poor band contrast which usually corresponds to dark region. The different colors are related to different Euler angles. As shown in Fig. 1 and the references [2,4], both the B2 matrix and the β-Nb phase have a body centered cubic (b.c.c.) crystal structure with quite closed lattice parameter at room temperature. It is impossible to identify these two phases from Fig. 2(b). Therefore, they are determined by the combined results from BSE observation and EDX measurements. It is seen from Fig. 2(b) that the B2 matrix is characterized by the irregular grains having an average grain size of about 3 μm. The β-Nb phase particles with a grain size of about 0.8 μm mainly distributed along the grain boundaries of matrix. It is also seen that some nanosized β-Nb particles were located in the grain interior of matrix, as indicated by the arrows, being consistent with the previously reported results [16].

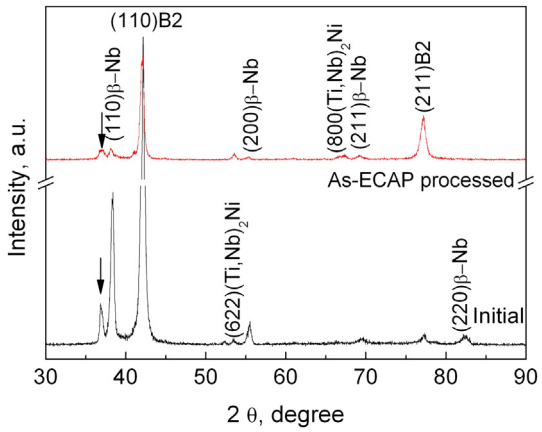

Fig. 1. Comparison of XRD patterns from the samples deformed with ECAP and the initial material.

The microstructure elongated after ECAP processing, as shown in Fig. 2(c). This is quite similar to the rolled microstructure [4]. Fig. 2(d) and (e) show the typical TEM bright field images of the as-ECAP processed sample from different regions, namely, one is β-Nb particle rich and another is β-Nb particle free, respectively. The EDX result showed the black spots in Fig. 2(d) contain 81 at.% Nb, 10% Ti and 9% Ni. Therefore, they are determined to be β-Nb phase, which is too thick to be penetrated by electron beam. This is because that the β-Nb phase is more chemical stable against the electrolyte than the matrix. The morphology of β-Nb particles did not show distinct difference with that of the initial alloy. The following two important features can be observed in the matrix. First, a heterogeneous microstructure was observed. To be more exact, Fig. 2(d) shows that the matrix had a heavily deformed grain structure with a high dislocation density. Most of the grains were elongated and grain boundaries were not well defined but rather poorly delineated and curved in general. However, Fig. 2(e) shows that the matrix had near-equiaxed grains with well-defined grain boundaries and is partial recovery. Second, the grains were greatly refined from about 3 μm (Fig. 2(b)) to about 0.3 μm (size of near-equiaxed grains) or 0.6 μm (width of elongated grains). The first feature is different from the TiNi alloys subjected to the same processing, in which microstructure is characterized by a homogeneous microstructure, i.e. the equiaxed grains with a size of 0.25–0.5 μm [13,17,18]. The heterogeneous microstructure in the present alloy is possibly due to the original eutectic structure which shows a strong plastic mismatch of the constituents and the inhomogeneity of the β-Nb particle distribution in the B2 matrix. This may produce a strong stress redistribution within the material during processing. It is generally recognized that the β-Nb particles are softer than the matrix [2]. We can assume that during ECAP processing, in the region with β-Nb particles (Fig. 2(d)), a relatively low effective strain is obtained, resulting in less efficiency in refining the original structure of matrix. In the region without β-Nb particles, as shown in Fig. 2(e), the stress imposed on the matrix can be effectively transferred among the grains, therefore, a large effective strain can be obtained. The hypothesis is also supported by the microstructure evolution with pressing pass in which the microstructure of TiNi alloys changes from the elongated grains with a high density of dislocations to the equiaxed ones with increasing effective strain [19]. The role of soft β-Nb particles is in contrast to that of hard particles in other alloys which is beneficial to the grain refinement,