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Thermal cycling stability of ultrafine-grained TiNi shape memory alloys processed by equal channel angular pressing

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The thermal cycling stability of martensitic transformation in two different TiNi alloys processed by equal channel angular pressing (ECAP) was investigated. The transformation behavior of the as-ECAP-processed $Ti_{49.2}Ni_{50.8}$ alloy was more stable than that of $Ti_{50.2}Ni_{49.8}$ alloy. Annealing at a temperature below 500 °C did not influence the thermal cycling stability of the $Ti_{49.2}Ni_{50.8}$ alloy. The relationship between thermal cycling stability and composition and annealing treatment was discussed based on the grain size evolution.

Keywords: Equal channel angular pressing, Shape memory alloys; Ultrafine-grained microstructure; Martensitic phase transformation; Thermal cycling stability

TiNi-based shape memory alloys (SMAs) have attracted much attention in many engineering applications due to their superior functional properties, including large work output force per unit volume and large displacement generated during shape recovery [1]. In practical applications, SMA devices experience a large number of thermal cycles, which often results in a change in the transformation temperatures and degradation of shape recovery properties. The mechanism behind the effect of thermal cycling has been ascribed to the introduction of dislocations, which usually compensate the incompatibility between the parent phase and the martensite during transformation [2,3]. Based on this mechanism, several approaches have been developed to suppress the dislocation movements and then improve the thermal cycling stability of SMAs, such as aging treatment of Ni-rich alloys [2], dislocation strengthening by thermo-mechanical treatment [2] and grain refinement [3,4].

Recently, equal channel angular pressing (ECAP), a severe plastic deformation (SPD) technique, has been regarded as a promising method to refine the microstructure of TiNi-based SMAs [5–7]. For example, an ultrafine-grained (UFG) state, with a grain size of about 300 nm, can be formed in bulk samples of $Ti_{49.4}Ni_{50.6}$ and $Ti_{49.8}Ni_{50.2}$ as a result of ECAP [5–7]. To date, the microstructure [5,8–10], martensitic transformation [10,11], conventional mechanical properties [5,8,9] and shape recovery properties [3,4,9,12] of ECAP-processed TiNi-based SMAs have been reported. One of the significant advantages resulting from ECAP processing is the increase in critical shear stress levels for dislocation slip, which is believed to give rise to good cycling stability. This has been demonstrated in $Ti_{50.3}Ni_{49.7}$ alloy [3], $Ni_{49.8}Ti_{42.2}Hf_8$ [4] and $Ti_{50.3}Ni_{33.7}Pd_{16}$ [12] high-temperature SMAs. Kockar et al. [4] first reported that the ECAP tends to produce a stable transformation temperature and strain in $Ni_{49.8}Ti_{42.2}Hf_8$ alloy due to the microstructural refinement and the increase in favorable dislocation density. Two years later, the same group [3] applied the same strategy to $Ti_{50.3}Ni_{49.7}$ alloy and reached similar conclusions. From the above studies, it seems that the previous studies have paved a way for the enhancement of the thermal cycling stability of TiNi-based SMAs. However, as yet, a comprehensive understanding of the thermal cycling stability of ECAP-processed SMAs is still missing; knowledge of how the composition and annealing treatment influence the thermal cycling stability is lacking.

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The purpose of this study is to investigate the thermal cycling stability of martensitic transformation in TiNi SMAs with different compositions subjected to the same ECAP processing. Based on the experimental results, the relationships of thermal cycling stability with composition and annealing treatment are discussed in terms of grain size evolution.

Two different TiNi alloys, with nominal compositions of $Ti_{49.2}Ni_{50.8}$ and $Ti_{50.2}Ni_{49.8}$ (at.%), were studied. Before processing, the alloys were annealed in a furnace at 800 °C for 1 h, then quenched into water. The as-quenched alloys have the microstructure with an average grain size of ~80 μm. The samples, in the form of 20 mm diameter × 200 mm length rods, were processed by ECAP at a temperature of 450 °C for eightpasses using a die with a channel-intersection angle of $\Phi = 120°$. The rod was kept at 450 °C for 15 min in a furnace prior to each pass, transferred to the pre-heated ECAP die as quickly as possible and then extruded at a rate of 8 mm s^{-1}. The pressing route Bc was used since it is the optimum one for producing an ultrafine structure [6]. After removing the surface oxide, the samples were sealed in vacuum quartz tubes, then annealed at various temperatures between 300 and 600 °C for 30 min followed by quenching in water. For comparison, the samples were also annealed at 900 °C for 2 h to obtain a coarse-grained microstructure.

Thermal cycling was performed on a Perkin-Elmer Diamond differential scanning calorimeter at a constant heating/cooling rate of 20 °C min^{-1}. The microstructure was carefully observed on a Tecnai G2 F30 transmission electron microscope, which was operated at 300 kV with a double-tilt sample stage. The foils for the transmission electron microscopy (TEM) were prepared by mechanical grinding, followed by twin-jet electropolishing using an electrolyte solution consisting of 95% acetic acid and 5% perchloric acid by volume. The mechanical properties of the as-ECAP-processed samples and thermally cycled samples were tested with an Instron 3365 tensile machine. The gauge length was fixed at 17 mm.

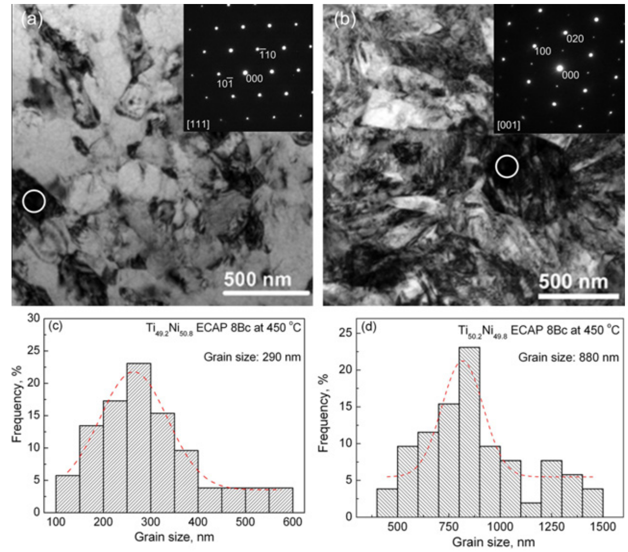

Figure 1. TEM images of the as-ECAP-processed $Ti_{49.2}Ni_{50.8}$ alloy (a) and $Ti_{50.2}Ni_{49.8}$ alloy (b), and the corresponding histograms of the grain size distribution ($Ti_{49.2}Ni_{50.8}$ alloy (c) and $Ti_{50.2}Ni_{49.8}$ alloy (d)). Diffraction patterns corresponding to the $[1\,1\,1]_{B2}$ and $[0\,0\,1]_{B19'}$ zones of the regions indicated by the circle are inset.

The microstructures of the as-ECAP-processed samples were observed by TEM at room temperature. Figure 1(a) and (b) show bright-field images of the microstructures of as-ECAP-processed $Ti_{49.2}Ni_{50.8}$ and $Ti_{50.2}Ni_{49.8}$ samples, respectively. It is seen that the ECAP processing results in near equiaxed grains, with well delineated grain boundaries. Most grains are free of dislocations, consistent with the results reported by Pushin et al. [5]. The two-dimensional average grain size was determined from the TEM images. At least 300 different grain sizes were measured for each sample. Figure 1(c) and (d) show the size distributions of the grains for the two alloys. The average grain sizes are also indicated in these figures. The Gauss fitting curves are plotted as dashed line in Figure 1(c) and (d). The actual size distributions agree well with the fitting curves. Both alloys are greatly refined compared to their initial grain sizes. After the same ECAP processing, the as-ECAP-processed $Ti_{49.2}Ni_{50.8}$ alloy possesses a much finer grain (290 nm) than the $Ti_{50.2}Ni_{49.8}$ alloy (880 nm).

It is generally accepted that the grain refinement by ECAP consists of the following steps as the number of passes in ECAP is increased: (1) an increase in dislocation density; (2) the formation of a homogeneous dislocation structure; and (3) a transition from arrays of low-angle grain boundaries to high-angle grain boundaries [6]. According to the Ti–Ni binary phase diagram [1,14], in the Ni-rich $Ti_{49.2}Ni_{50.8}$ alloy, Ti_3Ni_4 is precipitated or segregation may be caused by atomic shuffling during processing. These hinder the movement of dislocations and act as Frank–Read dislocation generation sources, resulting in increased dislocation density. This leads to the finer grains in the $Ti_{49.2}Ni_{50.8}$ alloy than in the $Ti_{50.2}Ni_{49.8}$ alloy that cannot form any precipitates. On the other hand, the Ti_3Ni_4 precipitate or the segregation redissolves into the matrix during processing because of the large number of dislocation defects [15,16]. This is also confirmed by the diffraction pattern inset in Figure 1(a), in which no diffraction spots corresponding to Ti_3Ni_4 precipitate can be observed. It has been reported that the aged $Ti_{49.3}Ni_{50.7}$ alloy shows a smaller grain size than the Ti-rich $Ti_{51.5}Ni_{48.5}$ alloy after the same high-pressure torsion process at 350 °C; this was attributed to the blocking effect of Ti_3Ni_4 precipitates [8]. A similar effect of precipitates on grain evolution was reported in a 7050 Al alloy processed by equal channel angular rolling [17]. The above reported results support the present assumption.

Figure 2(a) shows the differential scanning calorimetry (DSC) curves of the as-ECAP-processed $Ti_{49.2}Ni_{50.8}$ alloy for five thermal cycles. There are two exothermal peaks in the cooling curves. The first peak indicated by the blank arrow corresponds to the $B2 \rightarrow R$ phase transformation. The second peak is related to the $R \rightarrow B19'$ transformation. The R-phase transformation also was observed in the $Ti_{50.3}Ni_{49.7}$ alloy processed by ECAP at 425 °C (route Bc) for four passes [3], the $Ti_{49.4}Ni_{50.6}$ alloy processed by ECAP at 400–500 °C [5] and other plastically deformed alloys [13], which might