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 $^\circ$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 result 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$_{49.2}$Ni$_{50.8}$ 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$_{50.0}$Ni$_{49.7}$ alloy [3], Ni$_{49.8}$Ti$_{12.2}$Hf$_{8}$ [4] and Ti$_{50.3}$Ni$_{33.3}$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$_{12.2}$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.
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 eight passes using a die with a channel-intersection angle of Φ = 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 using a Tecnai G2 F30 transmission electron microscope, operated at 300 kV with a double-tilt sample stage. The foils 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 using an Instron 3365 tensile machine. The gauge length was fixed at 17 mm.

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 Gaussian 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_{2}Ni_{4} is precipitated or segregation may be caused by atomic shuffling during processing. This 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_{2}Ni_{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_{2}Ni_{4} precipitate can be observed. It has been reported that the aged Ti_{49.2}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_{2}Ni_{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 —→ R phase transformation. The second peak is related to the R —→ 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_{49.2}Ni_{50.8} alloy processed by ECAP at 400–500 °C [5] and other plastically deformed alloys [13], which might...
be due to the suppression of dislocations on martensitic transformation. Another important feature is that the transformation peaks do not shift after five thermal cycles. This sample was further thermally cycled for a total of 50 times. In order to accurately evaluate the cycling stability, the peak transformation temperatures were used, namely $R_p$, $M_p$, and $A_p$, representing the peak temperatures of the $B2 \rightarrow R$ transformation, $R \rightarrow B19'$ transformation and $B19' \rightarrow B2$ reverse transformation, respectively. Figure 2(b) shows the dependence of transformation temperatures on the thermal cycling number. After 50 cycles, the transformation temperatures decrease by less than 2°C, indicating the good thermal cycling stability of the as-ECAP-processed Ti$_{50.2}$Ni$_{49.8}$ alloy.

A different dependence of transformation behavior on the thermal cycling number was observed for the as-ECAP-processed Ti$_{50.2}$Ni$_{49.8}$ alloy. Figure 2(c) shows the DSC curves of the as-ECAP-processed Ti$_{50.2}$Ni$_{49.8}$ alloy for five thermal cycles. It can be seen that this sample shows a single-stage $B2 \rightarrow B19'$ transformation upon the first cooling and heating. After the third thermal cycle, this single exothermic peak splits into two peaks, corresponding to a $B2 \rightarrow R \rightarrow B19'$ two-stage transformation during cooling. This is different from the reported results [2], in which only single-stage transformation was observed even after 100 thermal cycles in the solution-treated Ti$_{50.2}$Ni$_{49.8}$ alloy.

The transformation temperatures of the as-ECAP-processed Ti$_{50.2}$Ni$_{49.8}$ alloy decrease significantly except for the $R_p$ temperature, as shown in Figure 2(d). It should be mentioned that the $M_p$ temperature refers to the peak temperature of $B2 \rightarrow B19'$ before the R-phase transformation was induced. After 50 thermal cycles, the $M_p$ and $A_p$ temperatures are reduced by 13 and 7°C, respectively. For the present solution-treated Ti$_{50.2}$Ni$_{49.8}$ alloy with an average grain size of 34 μm, the reductions of the corresponding transformation temperatures are 18 and 24°C, respectively. This indicates that the present ECAP treatment can improve the thermal cycling stability of Ti$_{50.2}$Ni$_{49.8}$ alloy to some extent.

The effect of thermal cycling on phase transformation behavior is generally related to the dislocations introduced during transformation [2]. The results shown in Figure 2 imply that the dislocations density resulting from thermal cycling is lower in Ti$_{49.2}$Ni$_{50.8}$ than that in the Ti$_{50.2}$Ni$_{49.8}$ sample. This is also confirmed by the results shown in Figure 3, which compares the tensile stress–strain curves of the as-ECAP-processed and thermal cycled samples. In order to obtain the same thermodynamical condition, the experiment was carried out at a temperature of $A_1 + 15$°C. After 50 thermal cycles, the stress–strain curve of Ti$_{49.2}$Ni$_{50.8}$ alloy does not show much difference with that of the as-ECAP-processed one. However, the stress–strain curve of the thermal cycled Ti$_{50.2}$Ni$_{49.8}$ sample is characterized by the disappearance of the stress plateau and the markedly increased critical stress to induce martensitic transformation, as compared to the as-ECAP-processed one. This is suggested to be related to the strengthening by dislocations introduced during thermal cycling.

Figure 4(a) shows the effect of thermal cycling on $M_p$ temperature of the Ti$_{50.2}$Ni$_{50.8}$ samples annealed at different temperatures. The result of a solution-treated sample is also shown for a comparative purpose. When annealed at a temperature below 500°C, the $M_p$ temperature remains almost constant with increasing cycling number. If the annealing temperature was increased to a temperature above 600°C, the $M_p$ temperature would decrease with increasing cycling number, like the trend observed in the solution-treated sample. Other transformation temperatures also show similar dependence on thermal cycling and annealing temperature.

Figure 4(b) shows the effect of annealing temperature on the grain size and yield strength of the stress-induced martensite of Ti$_{49.2}$Ni$_{50.8}$ alloys. When annealed at a temperature below 500°C, the grain growth is not obvious, irrespective of the annealing temperature. Increasing the annealing temperature further leads to a rapid
increase in grain size, from the submicrometer to the micrometer range. Accordingly, the yield strength of the stress-induced martensite shows the opposite tendency to the annealing temperature. From the above results, it is proposed that there is a critical grain size between 0.4 and 3 μm. The alloy with a grain size below this critical value has a good cycling stability. This is also supported by previously reported results [3,4], in which both the Ti_{50.3}Ni_{49.7} alloy with a grain size of 0.2–0.3 μm and Ti_{45.2}Ni_{49.8}Hf alloy with a grain size of 0.3–0.5 μm showed good cycling stability.

Following the DSC results, the thermal cycling stability of ECAP-processed samples can be summarized as follows: (i) after the same ECAP processing, the phase transformation of the Ni-rich Ti_{49.2}Ni_{50.8} alloy is more stable against thermal cycling than that of the near-equatomic Ti_{50.2}Ni_{49.8} alloy; and (ii) annealing at a temperature below 500 °C does not change the thermal cycling stability of the Ti_{49.2}Ni_{50.8} alloy. Three factors that possibly influence the thermal cycling stability are dislocations strengthening, precipitation strengthening and grain refinement. From Figure 1, it is seen that both dislocations and precipitates are absent in most grains, indicating that the first two factors do not play dominant roles in determining the thermal cycling stability. Therefore, it is proposed that the main influencing factor can be ascribed to the grain refinement.

The difference in cycling stability between the two as-ECAP-processed samples can be explained by their different grain sizes. Figure 1 shows that the as-ECAP-processed Ti_{49.2}Ni_{50.8} alloy has a much finer grain than Ti_{50.2}Ni_{49.8} alloy. As a result, the former has a higher yield strength, which suppresses the dislocation generation and movement. This is confirmed by the results shown in Figure 3. Figure 4 shows that the dependence of the thermal cycling stability on the annealing temperature seems to be consistent with that of the yield strength of the stress-induced martensite on the annealing temperature, suggesting that this dependence can be correlated with the grain size evolution. This is reasonable, since the relationship between yield strength and grain size of SMAs also follows the Hall–Petch equation.

In summary, the thermal cycling stability of ECAP-processed Ti_{49.2}Ni_{50.8} alloy and Ti_{50.2}Ni_{49.8} alloy was investigated. The R-phase transformation is induced by SPD in the Ni-rich Ti_{49.2}Ni_{50.8} alloy and is absent in the Ti_{50.2}Ni_{49.8} alloy. After the third thermal cycle, a peak corresponding to R-phase transformation is visible in the DSC curve of Ti_{50.2}Ni_{49.8} alloy. During thermal cycling, the ECAP-processed Ti_{49.2}Ni_{50.8} alloy shows a more stable transformation behavior than the Ti_{50.2}Ni_{49.8} alloy. Annealing at a temperature below 500 °C does not change the thermal cycling stability of Ti_{49.2}Ni_{50.8} alloy. The relationship of thermal cycling stability with composition and annealing temperature can be explained by the grain size evolution.

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