Multiple-stage transformation behavior of Ti49.2Ni50.8 alloy with different initial microstructure processed by equal channel angular pressing

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Multiple-stage transformation of Ti49.2Ni50.8 alloy processed by equal channel angular pressing (ECAP) was investigated as a function of pass number and aging treatment before ECAP. When the pass number is no more than four passes, three stage transformation, namely A → R, R1 → M1 and R2 → M2, occurs in the as-ECAP processed alloy initially aged at 450 °C for 60 min. Only the A → R → M forward transformation occurs provided that the aging duration was decreased/increased to 10/600 min. The transformation sequence was discussed based on the microstructure evolution of as-ECAP processed alloy with different initial microstructure and pass number.

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1. Introduction

TiNi-based shape memory alloys (SMAs) have attracted much attention in many engineering and biomedical applications due to their superior functional properties, including large work output force per unit volume, large displacement generated during shape recovery and the excellent biocompatibility [1]. In order to further enhance the properties of TiNi-based SMAs, equal channel angular pressing (ECAP), a several plastic deformation technique, has been employed to refine the microstructure of TiNi-based SMAs [2–4]. For example, the ultrafine grained microstructure, with a grain size of 0.2–0.3 μm, can be obtained in bulk samples of Ti49.4Ni50.6 and Ti49.8Ni50.2 as a result of ECAP [2]. As compared to the coarse-grained counterpart, the ultrafine grained TiNi-based alloys show several advantages, including improved shape recovery stress and strain [5], enhanced cycling stability [6–9], and biocompatibility [10].

Microstructure of the as-ECAP processed TiNi-based alloy can be naturally affected by processing conditions, including processing temperature [7] and pass number [11] etc. Very recently, our works [8,12] indicate that the second phase also greatly influences the microstructure of as-ECAP processed TiNi-based SMAs. To be more specific, Ti3Ni4 precipitate is beneficial to refining the final microstructure of as-ECAP processed Ti49.2Ni50.8 alloy when processed by ECAP [8], but β-Nb particles retard the grain refinement of Ti49Ni42Nb9 alloy [12]. During ECAP, shear plastic deformation is also applied on the Ti3Ni4 phase besides the matrix which may cause the re-dissolution of second phase [8,13,14]. In the coarse-grained Ni-rich TiNi alloys, the Ti3Ni4 phase as a result of aging can cause the multiple-stage transformation [15–17]. It is generally accepted that the as-ECAP processed TiNi alloys usually show a two-stage A(B2 parent phase) → R → M(B19 martensite) transformation upon cooling resulting from the refined microstructure and dislocations [8,11,18]. However, as yet, a comprehensive understanding of the effect of initial microstructure on martensitic transformation of as-ECAP processed TiNi SMAs is still missing; knowledge of how the re-dissolution of precipitates influence the transformation behavior is lacking.

In the present work, the initial microstructure with Ti3Ni4 precipitates having different sizes was obtained in Ti49.2Ni50.8 alloy by aging at 450 °C for different durations. The samples were processed by ECAP for different passes to obtain the various states of Ti3Ni4 precipitates. The multiple-stage transformation was paid particular attention and correlated with the microstructure evolution. This
understanding may allow optimization of transformation behavior through control of the initial microstructure and the processing condition.

2. Experimental procedure

A commercial TiNi alloy with a nominal composition of Ti49.2Ni50.8 (at.%) was studied. Before processing, the alloy was solution-treated in a vacuum furnace at 900 °C for 1 h, and then quenched into water. The as-quenched alloy has the microstructure with an average grain size of 70 µm. In order to obtain the precipitate with different sizes, the solution-treated alloys were aged at 450 °C for 10 min, 60 min and 600 min, respectively. The samples were sealed in the evacuated quartz tubes for heat-treatments. Hereafter, the aged samples were represented by A10, A60 and A600 for simplicity, respectively. After aging, the grain size keeps almost constant, as confirmed by optical microscopy observation.

The samples, in the form of 10 mm in diameter and 60 mm in length rods, were processed by ECAP at a temperature of 450 °C for up to 8 passes using a die with a channel-intersection angle of Φ = 120°. The rod was kept at 450 °C for 10 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 15 mm/s. The pressing route Bc was used in which the sample was rotated by 90° in the same sense, since it is the optimum one for producing the ultra-fine structure [19].

Thermal cycling was performed on a Perkin-Elmer Diamond differential scanning calorimeter (DSC) at a constant heating/cooling rate of 20 °C/min. DSC samples have a mass between 10 and 35 mg. Microstructure was carefully observed on a JEOL 2010 transmission electron microscopy (TEM) which was operated at 200 kV with a double-tilt sample stage. The samples were cut by a low-speed diamond saw to avoid any change of microstructure. The TEM 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.

3. Results and discussion

The microstructure of aged samples were observed by TEM at room temperature. Fig. 1 (a), (b) and (c) show the bright field images of the microstructure of A10, A60 and A600, respectively. As expected, numerous thin precipitates with a lens shape present in the samples, as indicated by the arrows. The selected area electron diffraction (SAED) patterns is characterized by the 1/7 superlattice spot in the 2T3 direction, indicating that the precipitates are Ti3Ni4 phase. The diffraction spots corresponding to R-phase are also revealed. For the A10 sample, the Ti3Ni4 precipitates are surrounded by strong stress-field, which means that the precipitates are coherent with the matrix. With increasing aging duration from 10 to 60 and 600 min, the average size of Ti3Ni4 precipitate increases from about 20 to 38 and 108 nm, respectively. The observation area is in the grain interior. It should be mentioned that the distribution of Ti3Ni4 precipitate is uniform across the sample. Fig. 1 (d) shows the DSC curves of the solution-treated and aged samples. It is seen that upon cooling, all of the three samples show a two-
stage A → R → M forward martensitic transformation. Upon heating, the A10 and A60 samples show the two-stage M → R → A reverse transformation, and the A600 sample shows the single-stage M → A reverse transformation. The transformation sequence was determined by the partial DSC cycling method [15]. The above results are consistent with the reported results on the effect of aging on martensitic transformation of Ti49.2Ni50.8 alloy [16,20,21]. It has been reported by Karbakhsh et al. that Ti49.2Ni50.8 alloy was aged at 450 °C after sealing into an evaluated quartz tube, then the aged sample shows normal two-stage transformation upon cooling [16]. According to their work [16], the two-stage transformation is possibly related to the higher degree of Ni supersaturation in the sample aged at 450 °C which may result in the uniform distribution of Ti3Ni4 phase. Therefore, the normal two-stage transformation are expected.

Fig. 2(a) shows the TEM bright field image of the microstructure of A10 sample processed for one pass. After the shear deformation imposed by the one pass ECAP, the initially equiaxed and coarse grains were greatly elongated and refined. A large number of dislocations can be observed in the grains having widths of about 1 μm. The SAED pattern does not show any superlattice spots related to Ti3Ni4 precipitates, implying that the precipitates have re-dissolved into the matrix due to the plastic deformation. This is consistent with the reported results [8,13,14]. The brightly spherical

![Fig. 2](image-url)
phase is Ti4Ni2O which formed during melting [22]. This phase does not dissolve into the matrix [14] and will not be discussed hereafter. After processed for eight passes, the elongated grains turned into the equiaxed shape with an ultrafine grain size of about 0.4 μm, as shown in Fig. 2(b). The evolution of grain morphology with pass number is a general tendency observed in the as-ECAP processed TiNi alloys [11,14] and other alloys [19,23]. The Ti3Ni4 precipitates were not found in the matrix.

Fig. 2(c) and (d) show the bright field images of the microstructure of the A60 samples processed for one pass and eight passes, respectively. After eight passes, the grain size was reduced to about 0.3 μm. From the inserted SAED pattern, it is seen that the Ti3Ni4 precipitates exist after one pass, but re-dissolve into the matrix after eight passes. Fig. 2(e) and (f) show the bright field images of the microstructure of the A600 sample processed for one and eight passes, respectively. It is seen that the Ti3Ni4 precipitates exist even after eight passes, as confirmed by the SAED pattern. According to the results shown in Fig. 2, it is proposed that the degree of redissolution of Ti3Ni4 phase is controlled by the plastic deformation strain and initial size of precipitate.

Fig. 3(a) and (b) show the DSC curves of the A10 samples processed for different passes. Upon cooling, as compared to the results shown in Fig. 1(d), the transformation sequence does not change, the transformation temperatures are reduced and the transformation peaks become diffused. The reduced transformation temperatures can be attributed to the suppression of refined grain and dislocations introduced during ECAP [11,12,18]. The diffused transformation peak is possibly related to the large number of dislocations [24]. Upon heating, after one pass, the as-ECAP processed A10 sample shows the single-stage M→A reverse transformation, which is different from that of the A10 sample.

Fig. 3(c) and (d) show the DSC curves of the A60 samples processed for one and eight passes, respectively. Upon cooling, the samples processed for less than 4 passes show three-stage forward transformation. The sample processed for eight passes shows the A→R→M transformation, same as that of A10 sample. Upon heating, after one pass, the as-ECAP processed sample shows three-stage reverse transformation. After two or four passes, the DSC curves of as-ECAP processed samples are characterized by the two-stage reverse transformation. The sample processed for eight passes show the two-stage M→R→A reverse transformation. Fig. 3(e) and (f) show the DSC curves of the A600 samples processed for different passes. The transformation sequence is the same as that of the aged one, irrespective of pass number.
In order to identify the transformation peaks of the A60 samples processed by ECAP, the partial DSC cycling method was used [15]. The results of the sample processed by one pass are shown in Fig. 4, as an example. The full cycle DSC curves were also shown in Fig. 4(a) for the comparison purpose. First, the sample was cooled to a temperature between peaks 1 and 2. It is seen from Fig. 4(b) that the peak 1 corresponds to the peak 5, the transformation hysteresis between peaks 1 and 5 is about 3.6 °C. Therefore, this pair results from the R-phase transformation, which is characterized by a small hysteresis due to its small lattice deformation [25]. When cooled to a temperature between peaks 2 and 3, the heating DSC curve shows the peak 6 besides the peak 5 which are overlapped. This suggests that the peak 2 corresponds to the peak 6. It is found that upon heating during the second partial cycle (Fig. 4(c)), the size of peak 5 is reduced as compared to that in the first partial cycle (Fig. 4(b)). This implies that R phase partially transformed to another phase (M1) during the second cooling, which is quite similar to the previous reported results [26]. In addition, the peak 6 locates at the higher temperature side of peak 5. Therefore, peaks 2 and 6 are identified to be R1/M1 and M1/A, respectively. When further cooling from the cool end temperature of second partial cycle, the residual R phase transformed to martensite (R2/M2), corresponding to peak 3. During heating, M2 transformed to R phase,

![Fig. 4. Partial DSC curves of the A60 sample processed for one pass. The original full DSC curves of this sample has been shown in (a).](image)

![Fig. 5. Schematic illustration of microstructure evolution and corresponding transformation sequence for the as-ECAP processed samples with different initial microstructure, h and c represent heating and cooling, respectively. A and B present precipitate-dissolved and precipitate-rich regions, respectively.](image)
resulting in the presence of peak 4. The detailed transformation sequence was also marked in Fig. 3(c). It should be mentioned that the subscripts 1 and 2 do not mean that there are two kinds of R phase or B19’ martensite. Using the same method, the reverse transformation sequence of the A60 samples processed for two or four passes was determined to be M1 → A and M2 → A.

Fig. 5 schematically illustrates the microstructure evolution and the induced transformation sequence in the as-ECAP processed samples with different initial microstructure. It is generally accepted that the multiple–transformation of the aged Ni-rich TiNi alloys results from the inhomogeneous distribution of Ti3Ni4 phase [15]. However, in the case of A10 sample, this mechanism is not applicable since the Ti3Ni4 phase re-dissolves into the matrix even after one pass due to the severe plastic deformation, as shown in Fig. 5(a). With increasing the pass number, the microstructure was greatly refined and the dislocation density increase. This is responsible for the two-stage transformation in the as-ECAP processed A10 sample.

Once the initial aging duration was increased to 60 min, the average size of Ti3Ni4 precipitates increases, as shown in Fig. 5(b). Based on the results shown in Fig. 2(a) and (c), it is reasonably suggested that there is a critical size of Ti3Ni4 precipitates between 20 nm and 30 nm for the present ECAP conditions. The precipitates having a size below this critical value are re-dissolved into the matrix after one pass ECAP. The precipitates having a size above this value may fracture or partially re-dissolve into the matrix, which requires further investigation. The microstructure of part region is similar to that of the as-ECAP processed A10 sample and characterized by the full re-dissolution of Ti3Ni4 phase and high density dislocations. Correspondingly, martensitic transformation occurs in the two-stage A → R(R1) → M1 manner. The microstructure of other region is characterized by the residual Ti3Ni4 phase and high density dislocations. This should be responsible for the A → R(R2) → M2 transformation. After eight passes, the residual Ti3Ni4 phase disappeared. The microstructure of as-ECAP processed A60 sample is quite similar to that of A10 sample other than the slightly different grain size, as shown in Fig. 2(b) and (d). Therefore, martensitic transformation occurs in the same manner with that of as-ECAP processed A10 sample.

In the case of A600 sample, after eight passes, the Ti3Ni4 phase is still visible, as confirmed by the TEM results shown in Fig. 2 (f), because the precipitate size is much larger than the proposed critical value of re-dissolution. The overlarge precipitates also retard the grain refinement, as demonstrated by the elongated grains of A600 sample. The precipitate size even increases possibly due to the interpass annealing. This is supported by the increased transformation temperatures with the increase of pass number. The microstructure of as-ECAP processed A600 sample is still characterized by Ti3Ni4 precipitates and high density dislocations introduced by ECAP. This gives rise to the two-stage A → R → M transformation shown in Fig. 3(e) and (f).

4. Conclusions

The transformation behavior of Ti49.2Ni50.8 alloy with different initial microstructure processed by ECAP depends on the pass number and initial aging treatment. When the alloy was initially aged at 450 °C for 10 min/600 min, the as-ECAP processed alloy shows the A → R → M forward transformation. When the alloy was initially aged at 450 °C for 60 min, if the pass number is no more than four, the forward transformation occurs in the three-stage manner, namely, A → R, R1 → M1, and R2 → M2. This can be ascribed to the partial re-dissolution of Ti3Ni4 phase. If the pass number is eight, the forward transformation occurs in the two-stage A → R → M sequence.

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