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Multiple-stage transformation behavior of $Ti_{49.2}Ni_{50.8}$ alloy with different initial microstructure processed by equal channel angular pressing

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Multiple-stage transformation of $Ti_{49.2}Ni_{50.8}$ 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 $A \rightarrow R$, $R_1 \rightarrow M_1$ and $R_2 \rightarrow M_2$, occurs in the as-ECAP processed alloy initially aged at 450 °C for 60 min. Only the $A \rightarrow R \rightarrow M$ forward transformation occurs provided that the aging duration was decreased/increased to 10/600min. The transformation sequence was discussed based on the microstructure evolution of as-ECAP processed alloy with different initial microstructure and pass number.

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 $Ti_{49.4}Ni_{50.6}$ and $Ti_{49.8}Ni_{50.2}$ 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, Ti_3Ni_4 precipitate is beneficial to refining the final microstructure of as-ECAP processed $Ti_{49.2}Ni_{50.8}$ alloy when processed by ECAP [8], but β-Nb particles retard the grain refinement of $Ti_{44}Ni_{47}Nb_9$ alloy [12]. During ECAP, shear plastic deformation is also applied on the Ti_3Ni_4 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 Ti_3Ni_4 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)$\rightarrow$R$\rightarrow$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 Ti_3Ni_4 precipitates having different sizes was obtained in $Ti_{49.2}Ni_{50.8}$ alloy by aging at 450 °C for different durations. The samples were processed by ECAP for different passes to obtain the various states of Ti_3Ni_4 precipitates. The multiple-stage transformation was paid particular attention and correlated with the microstructure evolution. This

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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 $Ti_{49.2}Ni_{50.8}$ (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 $\Phi = 120°$. 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 $\overline{21}3$ direction, indicating that the precipitates are Ti_3Ni_4 phase. The diffraction spots corresponding to R-phase are also revealed. For the A10 sample, the Ti_3Ni_4 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 Ti_3Ni_4 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 Ti_3Ni_4 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-

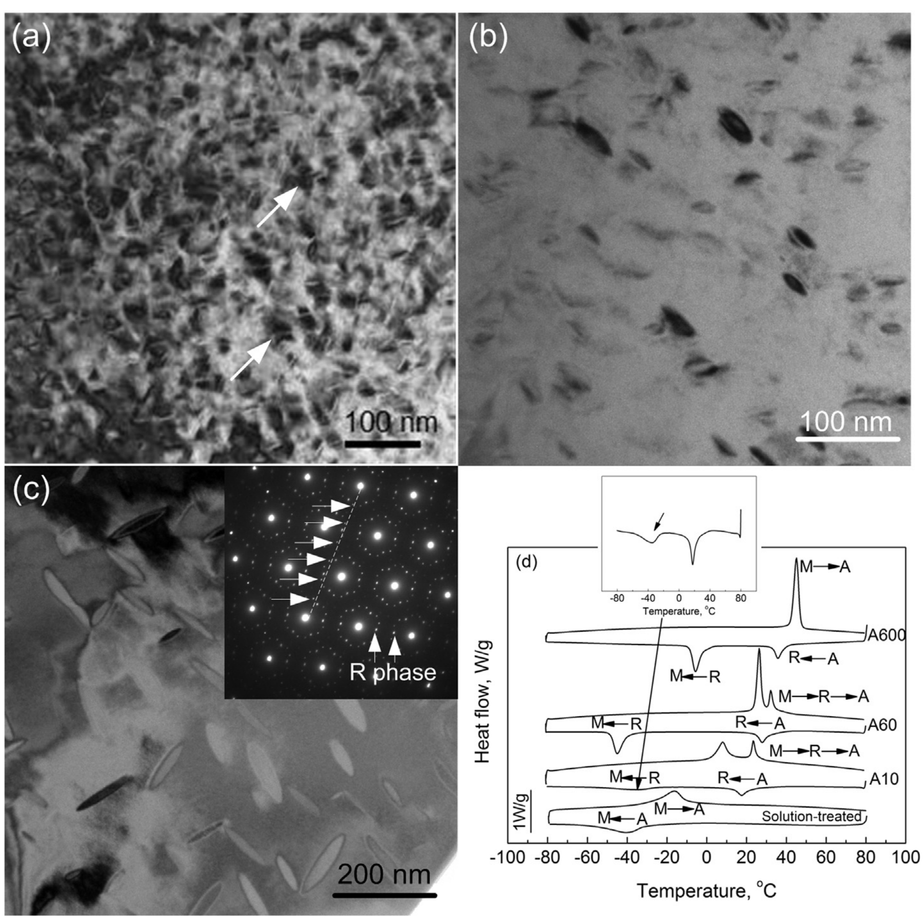

Fig. 1. TEM bright field images of the aged samples, (a) A10, (b) A60 and (c) A600. Diffraction patterns corresponding to the $[111]_{B2}$ were also inserted, respectively. DSC curves of the solution-treated and aged samples are shown in (d). The transformation sequences are also indicated.