JMEPEG (2012) 21:2546–2552
DOI: 10.1007/s11665-012-0391-0

1059-9495/$19.00

Effects of ECAP and Aging on Mechanical and Superelastic Behaviors of Ti-Mo-Based and Ti-25at.%Nb SMAs

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(Submitted March 13, 2012; in revised form September 7, 2012)

Ni-free Ti-based shape memory alloys (SMAs) are increasingly recognized as promising functional materials for medical applications. The mechanical properties of these metastable Ti-based SMAs are sensitive to aging and thermomechanical treatment. Effects of severe plastic deformation (SPD)-equal channel angular pressing (ECAP) and aging on superelastic behavior of Ni-free Ti-based SMAs, Ti-9.8Mo-3.9Nb-2V-3.1Al wt.% (TMNVA) and Ti-25at.%Nb, have been investigated. The results show that the yielding strength of TMNVA alloy increases sharply with the number of ECAP processes—to greater than 1,400 MPa after two passes ECAP—but elongation of TMNVA alloy decreases severely and the plasticity is lost completely after two passes ECAP. Both ECAP process and flash annealing treatment have weak contribution to the superelastic recoverable strains of Ti-Mo-based alloy. For Ti-25at.%Nb alloy, after one pass ECAP process at 400 °C, the yielding stress increases obviously, and the recovery strain increases a little. With the further increase in the number of ECAP processes, the yielding stress and the recovery strain change little. Aging treatment at low temperature after ECAP process is in favor of superelasticity of Ti-25at.%Nb alloy. An almost completely recoverable strain of 1.5% is obtained in Ti-25at.%Nb alloy after two passes ECAP and aging at 300 °C for 1 h. The mechanisms of the effects of SPD and aging are also discussed.

Keywords aging, ECAP, SMAs, superelastic behavior

1. Introduction

Ti-Ni shape memory alloys (SMAs) as biomedical materials have been used successfully owing to their superior shape memory effect (SME) and superelastic behavior. However, for Ti-Ni alloy, the possibility of Ni-hypersensitivity and toxicity have been pointed out (Ref 1, 2) because the Ni element content is usually more than 50 at.%. In order to avoid the potential hazard, some Ni-free Ti alloys have attracted attention as promising functional materials for medical applications, especially, the β-type Ti-Mo-based and Ti-Nb-based alloys (Ref 3, 4). There is no SME or superelasticity report for binary Ti-Mo alloys, though they usually exhibit low Young' modulus, such as Ti-7.5Mo alloy and Ti-15Mo alloy. However, some multi-component Ti-Mo-based alloy may possess the properties of SME or superelasticity. Ti-*x*Mo-Nb-V-Al alloys are newly developed metastable β-Ti Ti-Mo-based alloys with Mo-contents (*x*) in the range of 7.5-11.5 wt.%, which exhibit excellent superelasticity, and about 3% recovery strain can be obtained after solution treatment at 870 °C for Ti-*x*Mo-Nb-V-Al alloys. The recovery strain increases a little after flash annealing treatment at 350-550 °C for 10 s (Ref 5-7). For binary Ti-Nb alloys, Ti-(16-25)at.%Nb alloys exhibit the SME, and binary Ti-(25.5-27)at.%Nb alloys exhibit superelasticity at room temperature (Ref 8, 9). However, it has been reported that the low critical stress for slip deformation of binary Ti-Nb alloys results in a small recoverable strain (Ref 8, 9). In order to improve the SEM, superelastic recoverable strains, and the critical stress for Ti-Nb alloy, alloying elements were added to strengthen the parent phase and increase the mechanical properties, especially the yield stress. For example, Ti-Nb-Ga (Ref 10), Ti-Nb-Zr (Ref 11), Ti-Nb-Al (Ref 12), Ti-Nb-Ta (Ref 13). Ti-Nb-O (Ref 14), Ti-Nb-Ta-Zr (Ref 15) alloys with higher yield stress and ultimate tensile strength were developed, exhibiting better SME or superelasticity.

The thermomechanical treatment is another method to improve the mechanical properties and SME of alloys. Severe plastic deformation (SPD), including equal channel angular pressing (ECAP), high-pressure torsion (HPT), and multiple forging, is a powerful way to modify the microstructures and mechanical properties of metals and alloys. The microstructure and properties of shape memory Ti-Ni- and Ti-Ni-based alloys after ECAP and HPT have been studied by many investigators (Ref 16-22). The ultrafined grain, even the nano scale microstructure, can be obtained though the SPD process for NiTi alloys (Ref 16-20). The martensitic transformation (MT)

This article is an invited paper selected from presentations at the International Conference on Shape Memory and Superelastic Technologies 2011, held November 6-9, 2011, in Hong Kong, China, and has been expanded from the original presentation.

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would be suppressed because of the grain refinement, and the MT point (Ms) of TiNi alloys decrease after process of ECAP (Ref 20-22). After ECAP treatment, the B2 → R transformation occurred within a larger temperature range (Ref 18, 19, 21, 22). The mechanical properties, such as superelasticity, of TiNi alloy were improved by ECAP (Ref 17, 18, 22). With the increase in the number of passes of ECAP, the superelasticity becomes more stable, and a completely recoverable strain of 6% is obtained for TiNi sample after eight passes ECAP. The superelasticity becomes more stable after ECAP and was also observed in $Ti_{49.5}Ni_{25}Pd_{25}Sc_{0.5}$ SMA (Ref 23). There are very few reports about the study on the microstructure and properties of metastable β type Ti-Mo and Ti-Nb alloys processed by ECAP (Ref 24). In present article, the effect of ECAP and aging treatment on SME and superelastic behavior of Ti-9.8Mo-3.9Nb-2V-3.1Al wt.% (TMNVA) alloy and binary Ti-25at.%Nb alloy were investigated to explore a new strategy to improve the superelasticity of these alloys.

2. Experimental Procedures

TMNVA metastable β Ti alloy was received as hot rolled bars from Memry Corporation, USA. These as-received bars were solution treated (ST) at 870 °C for 1 h followed by quenching. The billets for ECAP treatment with a dimension of 10 mm × 10 mm × 120 mm were cut from the ST alloy bars.

Ti-25at.%Nb alloy was prepared from 99.7% sponge Ti and 99.6% Nb in a magnetic induction furnace with copper crucible. The ingots were hot forged into bars with a cross-sectional dimension of 12 mm × 12 mm, then, ST at 870 °C for 1 h, followed by quenching into water. Specimens for ECAP were cut from the ST bars by spark cutting, with a dimension of 10 mm × 10 mm × 140 mm. The ECAP process was applied at 400 °C for TMNVA and Ti-25at.%Nb alloys. ECAP processes were performed at Bc path, where the billets were rotated 90° along clockwise direction, between adjacent passages, with an ECAP set described in Ref 18 and 19.

Specimens of 3 mm × 0.8 mm × 50 mm for tensile test were cut from these square bars. Tensile tests were carried out under a strain rate of 1.0×10^{-4}/s. Strains were measured using a clip-on extensometer with a gage length of 25 mm. Specimen for microstructure observation was mounted, polished, and then etched in a solution of water, nitric acid, and hydrofluoric acid with a volume fraction of 80:15:5. Microstructure was examined by LeICA-MEF4M optical microscopy and JEOL-JEM-2010 Electron Microscope (TEM) with an accelerating voltage of 200 kV. For TEM observation, thin foil samples were obtained by mechanical grinding to 50-μm thickness and twin jet electropolishing (5% perchloric acid, 35% butyl alcohol and 60% methyl alcohol; 30 V; −30 °C). Phase constitution was identified by x-ray diffraction (XRD) with Cu Kα1 radiation, obtained from a tube operated at 200 mA, 40 kV, and the scan speed was 5°/s.

3. Results and Discussion

The tensile curves of TMNVA alloys after ST ECAP are shown in Fig. 1. The yielding strength of TMNVA alloy increases sharply after one pass ECAP as seen in Fig. 1, which is approximately 1,200 MPa. After two passes ECAP, the yielding strength increased to more than 1,400 MPa, but, the elongation property of TMNVA alloy decreases severely and the plasticity is lost completely.

The microstructures of TMNVA alloy are shown in Fig. 2. It is clear that there are equiaxed grains in ST TMNVA alloy. After SPD of ECAP process, grains were stretched and distorted obviously, as shown in Fig. 2(b) and (c). It is noticed that there appeared some small cracks on the forehead zone of TMNVA alloy specimens after two passes ECAP, as shown in Fig. 3. Hence, it is difficult to perform more than two passes ECAP at 400 °C for TMNVA alloy.

The XRD results of TMNVA alloy after ST and ECAP processes are shown in Fig. 4. Phase analysis indicates that β + ω dual phase microstructure could be obtained in ST TMNVA alloy. After one pass ECAP process, the intensity of ω phase increases as shown in Fig. 4(b). After two passes ECAP process at 400 °C, α phase appears as shown in Fig. 4(c). The α-phase and ω-phase can strengthen the parent phase of β as secondary phases. However, the mechanism of the effects of α-phase and ω-phase on the mechanical property is still under investigation.

The effect of flash annealing treatment on the TMNVA alloy after one pass ECAP process is shown in Fig. 5. It is clear that there is little change on the stress-strain curve of TMNVA alloy after flash annealing at 600 °C for 10-20 s as shown in Fig. 5(a) and (b). After flash annealing treatment at 700 °C for 10 s, the plasticity of TMNVA alloy increases to 3%, as shown in Fig. 5(c), and the yielding strength decreases to about 1,100 MPa. As flash annealing time increases to 60 s (Fig. 5d), the plasticity was improved to about 9%, and the yielding strength is near to that of ST specimen because of recovery and recrystallization occurred during annealing at 700 °C.

It has been reported that thermomechanical treatment, cold-rolling. and flash-thermal treatment are effective to improve the superelastic performance of Ti-26Nb and Ti-20Nb-6Zr alloys, and the balanced properties on combining high martensitic critical stress over 400 MPa and the large fully recoverable strains up to 3.0% can be achieved by flash-annealing at 600 °C (Ref 25). These improvements are due to the flash treatment effects, resulting in ultrafine β grains with sizes 1-2 μm with

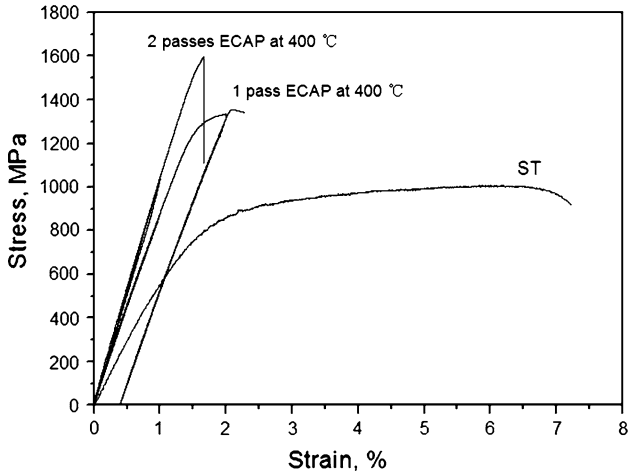

Fig. 1 Tensile curves of ST TMNVA alloy and processed by ECAP at 400 °C

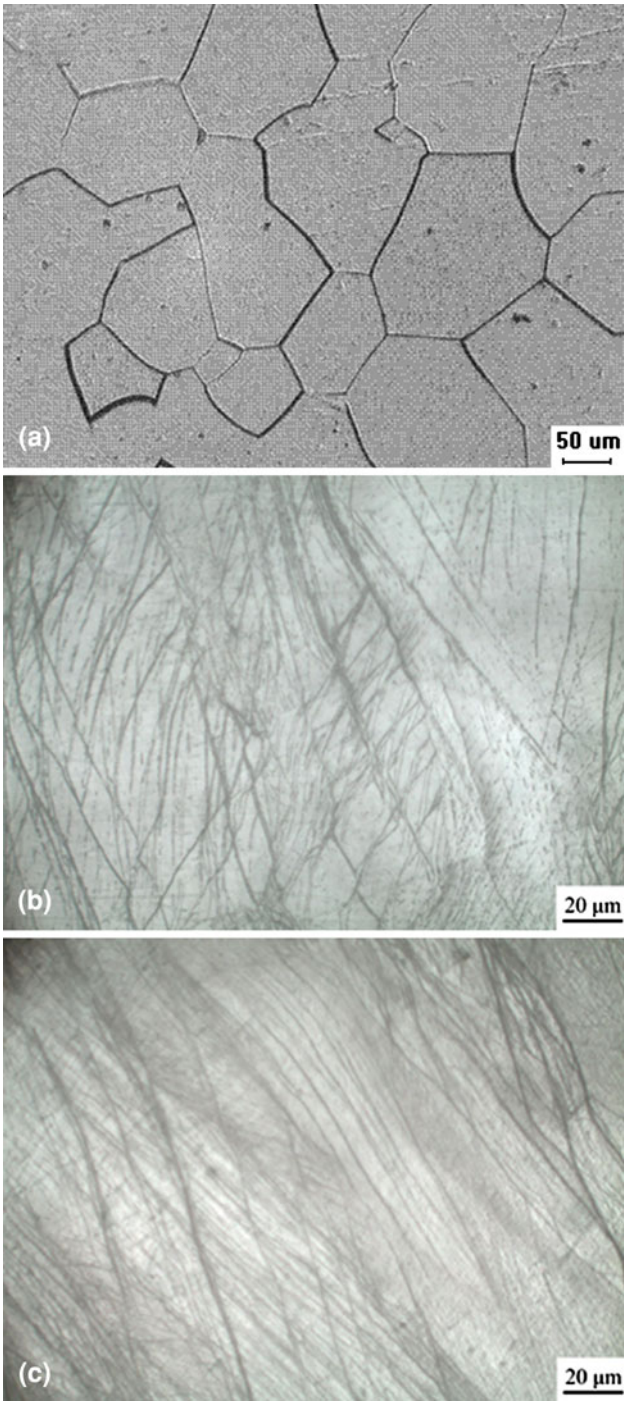

Fig. 2 Micrograph of TMNVA alloy after ECAP process at 400 °C, (a) ST, (b) one pass, and (c) two passes

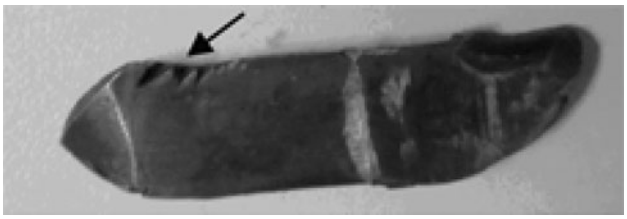

Fig. 3 Macrography of TMVAN alloy after two passes ECAP at 400 °C

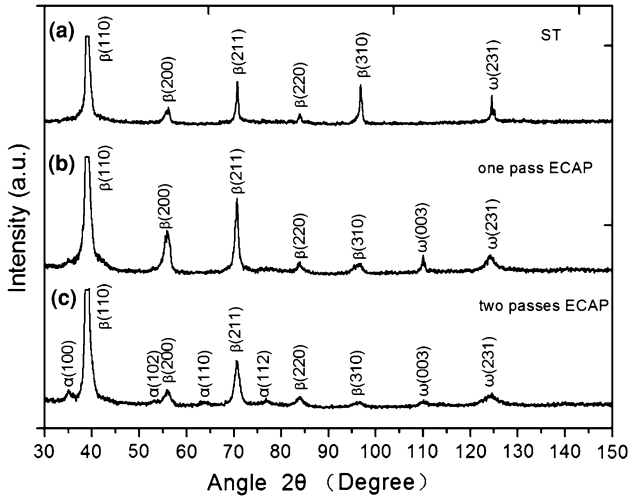

Fig. 4 XRD profile of TMNVA alloy, (a) before ECAP, (b) one pass ECAP, and (c) two passes ECAP at 400 °C

nano-sized α and ω phases' precipitation in the β matrix (Ref 25). However, in this study, it seemed that the effect of flash annealing on the Ti-Mo-based alloy is inconspicuous, as seen in Fig. 5(a) and (c). It is noted that the temperature (T_β) of β → α is 608 °C for Ti-26Nb alloy and 677 °C for Ti-Nb-Zr alloy, which are adjacent the flash-treated temperature (600 °C). Hence, there is a tendency for α → β phase transformation to occur, and nanosized α can be formed for cold-rolled Ti-Nb alloy and Ti-Nb-Zr alloy after the flash treatment. However, the T_β for Ti-Mo-based alloy is 850 °C (Ref 6), whereas, the flash-annealing temperature is 600-700 °C, which is much lower than that of T_β. It is easier for β → α phase transformation to occur, and α phase coarsening (Ref 26), during the flash annealing of Ti-Mo-based alloy, TMNVA. Hence, the effect of short-time annealing is different from that of the Ti-Nb alloy or Ti-Nb-Zr alloy. With the increase of the annealing temperature to 700 °C and the annealing time being increased to 60 s, the recovery and recrystallization of the β matrix and the α phase coarsening result in the decrease of yielding stress and the increase of the plasticity for TMNVA.

The cyclic stress-strain curves of the Ti-25at.%Nb alloy after ST and ECAP are shown in Fig. 6. As seen in Fig. 6(a). The superelastic recovery strain of ST specimen is small. When the specimen is unloaded from tensile strain of 1.5%, the recovery strain is 1.3%, and the remained stain is 0.2%. As the strain increases, the recovery strain maintains at 1.3%, and the remained strain increases. The superelasticity of Ti-25at.%Nb alloy can be improved by aging treatment at 300 °C for 1 h, as seen in Fig. 6(b). It is noticed that after one pass ECAP process at 400 °C, the yielding stress increases obviously, and the recovery strain increases also, as seen in Fig. 6(c). The work hardening phenomena is clear. When the specimen is unloaded from tensile strain of 1.5%, the recovery strain reaches to 1.4% and the remained strain is only 0.1%. A maximum recovery strain of 1.6% is obtained when the specimen is unloaded from strain 2%. However, with the further increase in the number of ECAP processes, the yielding stress and the recovery strain change little, as shown in Fig. 6(e) and (g).

Usually, the grain refinement suppresses the MT, and the MT temperature (Ms) decreases. Hence, the critical stresses for

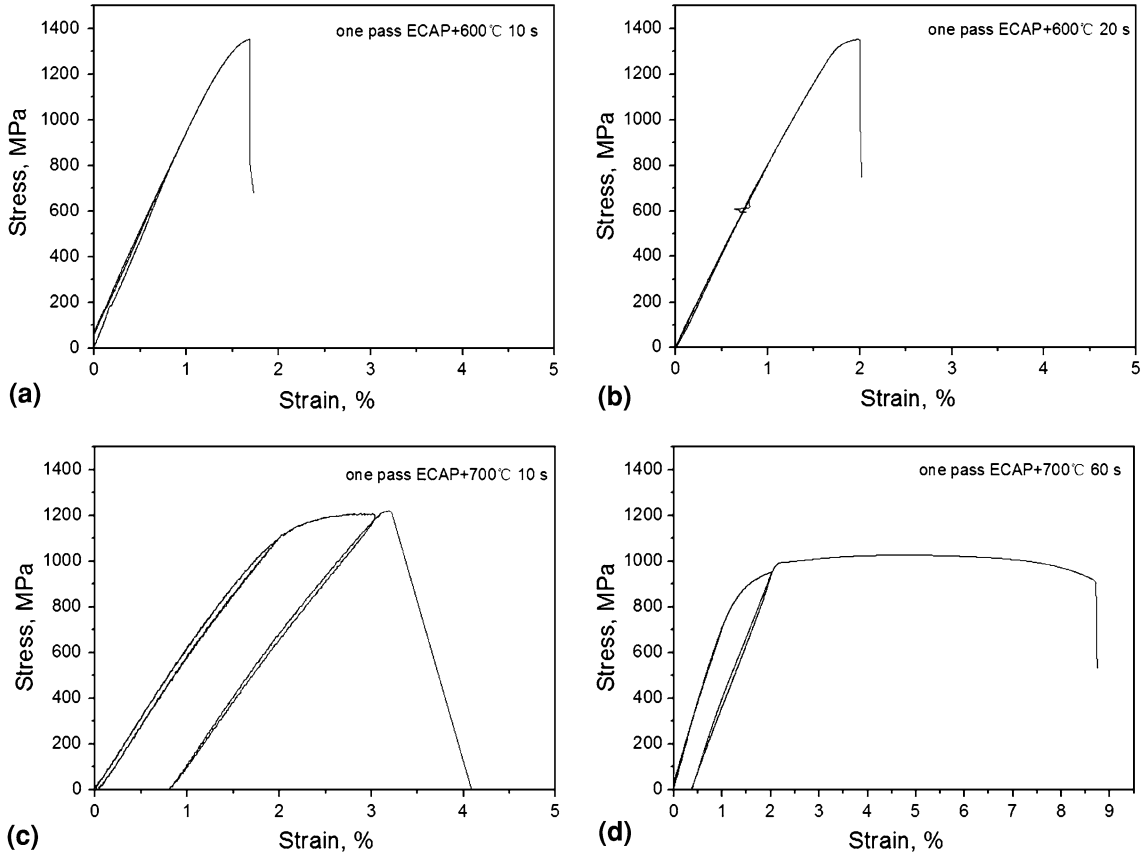

Fig. 5 Tensile curves of TMNVA alloy after one pass ECAP followed by flash annealing at 600-700 °C for 10-60 s, (a) 600 °C 10 s, (b) 600 °C 20 s, (c) 700 °C 10 s, and (d) 700 °C 60 s

SMA with fine grain would increase to induce MT. However, in this study, for Ti-25at.%Nb alloy, the critical stresses for MT decrease after process of ECAP. As to the binary Ti-Nb alloys, it is reported that the Ms temperature decreases with the increase of Nb contents following a linear dependence (Ref 27). The Ms temperature is close to the room temperature with the addition of 26 at.% Nb. Hence, Ti-26Nb alloy can exhibit superelastic behavior and possess the lowest critical stress in all of Ti-(16-28)at.%Nb alloys (Ref 27). It is well known that α phase and ω phase precipitate during aging treatment at medium temperature which can increase the content of the β-stable element (Nb) in the β phase matrix located near α phase and ω phase, because α and ω phases are Ti-rich phases and element of Nb diffuses out of α phase and ω phase. It is reasonable to suggest that the composite content of Nb in Ti-25at.%Nb alloy matrix around and near α phase and ω phase will increase to near 26 at.%. As the Nb content increases, the critical stress to induce MT of Ti-25Nb alloy will decease. In fact, the mechanism is still unclear and under investigation now.

After aging at 300 °C for 1 h, the yielding stresses of ECAPed Ti-25at.%Nb alloy specimens decrease a little, but the ultimate strengths increase obviously, as shown in Fig. 6(f) and (h), which should be attributable to the precipitation of ω phase (Ref 26, 28). The recoverable superelastic strain increases a little. An almost completely recoverable strain of 1.5% is obtained in Ti-25at.%Nb alloy after two passes ECAP and aging at 300 °C for 1 h, as shown in Fig. 6(f).

The microstructure of Ti-25at.%Nb alloy after ECAP and aging is shown in Fig. 7. After two passes ECAP process, grains were elongated and the width of the fiber band becomes narrow, about 500 nm. After aging treatment at 300 °C for 1 h, lots of ω-phase, of several nanometer sizes, precipitated on the matrix for Ti-25at.%Nb alloy, as shown in Fig. 7(c). After four passes ECAP, the fiber band structure disappears, and the grains become equiaxed grains entirely. It is evident that a homogenous, ultra fine-grained structure with a mean grain size of about 200 nm is formed as shown in Fig. 7(e) and (f). Considering the results in Fig. 6, for Ti-25at.%Nb alloy, it is unclear as to why the mechanical behavior changes little after the fourth pass ECAP, while the grains are further refined to 200 nm, compared to that after the second pass ECAP process, which is still under investigation.

There are some effective thermomechanical methods to refine the metastable Ti alloy (Ref 13, 29). It is reported (Ref 29) that a combination processing technique of warm swaging and warm rolling applied for a β-type Ti-24Nb-4Zr-8Sn (wt.%) alloy resulted in significant grain refinement and formed a microstructure comprising β phase with a size less than ~200 nm and the precipitation of nanosized α phase. The ultrafine-grained alloy exhibited a recoverable strain of up to ~3.4% (Ref 29). Comparing the difference between the ECAPed Ti-25at.%Nb alloy and Ti-24Nb-4Zr-8Sn (wt.%) alloy processed by warm swaging plus rolling processing (Ref 29), or that of Ti-22Nb-6Ta alloy processed by cold rolling and aging (Ref 13), a strong

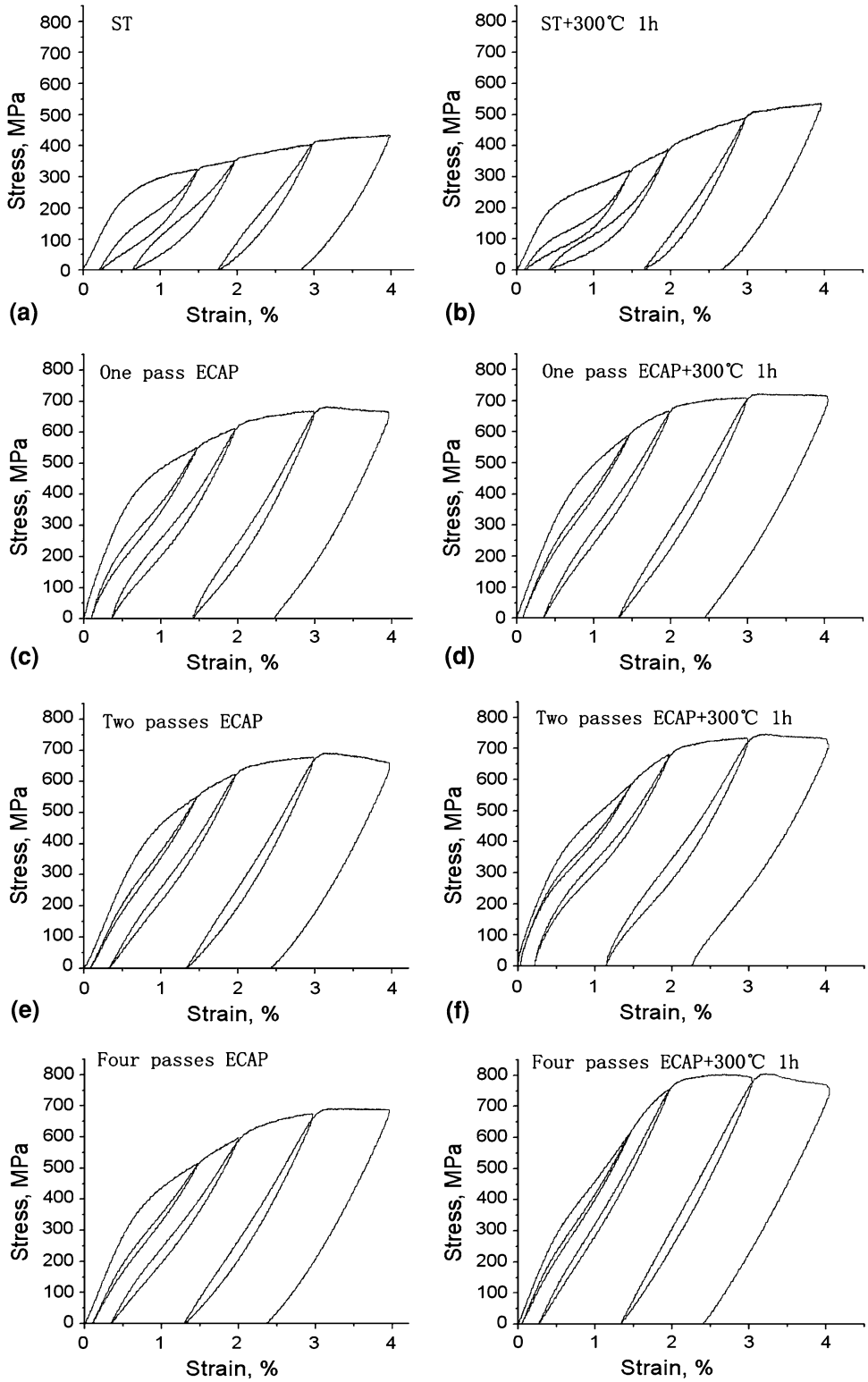

Fig. 6 Cycle loading-unloading tensile curves of Ti-25at.%Nb alloy after ECAP at 400 °C and aged at 300 °C for 1 h: (a) ST, (b) ST + aging, (c) one pass ECAP, (d) one pass ECAP + aging, (e) two passes ECAP, (f) two passes ECAP + aging, (g) four passes ECAP, and (h) four passes ECAP + aging

texture formed after warm rolling or cold rolling deformation may give rise to the larger recoverable strain of ~3%, besides the third alloying element's strengthening effect. It is reasonably considered that there may be little benefit from the texture formed in the alloy after multipass warm ECAP process along Bc route, which needs further experimental support.

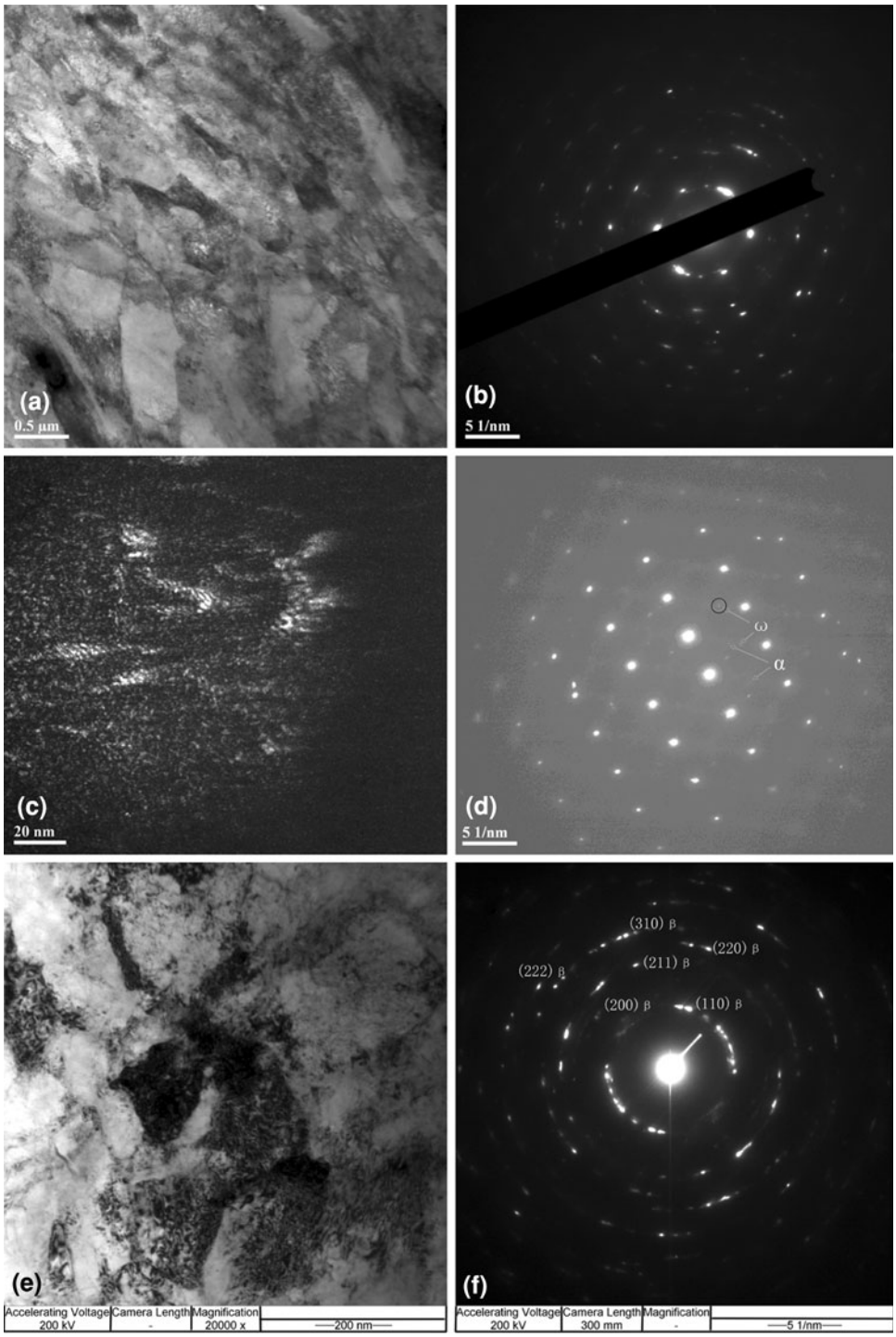

Fig. 7 Microstructure Ti-25at.%Nb alloy after ECAP process at 400 °C and aging at 300 °C for 1 h: (a) bright field image after two passes ECAP, (b) SAED of (a), (c) dark-field micrograph of precipitated ω phase after two passes ECAP and aged at 300 °C for 1 h, (d) SAED corresponding to (b), (e) bright field image of Ti-25at.%Nb alloy after four passes ECAP, and (f) SAED of (e), showing polycrystalline diffraction rings

4. Conclusion

The effects of ECAP process at 400 °C and aging on the mechanical and superelastic behaviors of Ni-Free Ti-Mo-based SMA (TMNVA), and Ti-25at.%Nb alloy have been studied. The conclusions are as follows:

1. For TMNVA alloy, the strength increased obviously, and the plasticity decreased sharply after one pass ECAP at 400 °C. After two passes ECAP process, the plasticity is lost completely. It is difficult to perform more than two passes ECAP process at 400 °C, since there are some cracks after two passes ECAP process. Both ECAP

process and flash-annealing treatment have weak contribution to the superelastic recoverable strains of Ti-Mo-based alloy.

2. For Ti-25at.%Nb alloy, after one pass ECAP process at 400 °C, the yielding stress increases obviously, and the recovery strain increases a little. With the increase in the number of ECAP processes, the yielding stress and the recovery strain change little. Aging treatment at low temperature after ECAP process is in favor of superelasticity of Ti-25at.%Nb alloy. An almost complete superelasticity of 1.5% recovery strain was obtained after two passes ECAP process at 400 °C and aging at 300 °C for 1 h. Equiaxed grains with 200 nm can be obtained after four passes ECAP process at 400 °C.

Acknowledgments

The authors gratefully acknowledge the financial support from the National Science Fund of China (No. A50671067), and the support from The Science and Technology Committee of Shanghai Municipal (09JC1407200).

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