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Shape memory effect of NiTi alloy processed by equal-channel angular pressing followed by post deformation annealing

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Abstract. Processing by Equal-Channel Angular Pressing (ECAP) is generally considered superior to most other SPD techniques because it uses relatively large bulk samples. However, due to their low deformability it has proven almost impossible to successfully process NiTi alloys by ECAP at room temperature and therefore the processing is conducted at elevated temperatures. Recently, a new billet design was introduced and it was used to achieve the successful processing of NiTi shape memory alloys by ECAP. In this procedure, a NiTi alloy was inserted as a core within an Fe sheath to give a core-sheath billet. In this research, a NiTi was processed by one pass ECAP with this new billet design at room temperature. The structural evolution during annealing was investigated by X-ray diffraction (XRD) and microhardness measurements. Post deformation annealing (PDA) was carried out at 400°C for 5 to 300 min and the results indicate that the shape memory effect improves by PDA after ECAP.

1. Introduction

NiTi alloys are known as the most important shape memory alloys because of their many applications based on the shape memory effect and superelasticity [1]. The NiTi alloy shows a thermoelastic martensitic transformation from the high temperature phase (Austenite) to the low temperature phase (Martensite) [2]. The thermoelastic transformation exhibits crystallographically reversible transformation. The plastic deformation such as slip or deformation twinning is irreversible, and such strains cannot be restored even upon heating. Thus, it is most important to increase the critical stress for slip in order for shape memory alloys to realize good shape memory and superelastic characteristics. In order to achieve a high critical stress for slip, work hardening and grain refinement can be useful . The increase of the critical stress is especially important for NiTi alloys, because slip is so easily introduced in these alloys [3]. In fact, it is well known that no superelasticity appears and the shape memory effect is also very poor in an ideal solution annealed condition, and good shape memory effect and superelasticity effects are realized only after the alloy is subjected to proper thermomechanical treatment because slip is easily introduced in the solution annealed condition [2].

Recent studies have shown that severe plastic deformation (SPD) processing enhanced shape memory and superelasticity in NiTi alloys [4, 5]. Processing by Equal-Channel Angular Pressing (ECAP) is generally considered superior to most other SPD techniques because it uses relatively large bulk samples and has other advantages [6, 7]. However, due to their low deformability it has proven almost impossible to successfully process NiTi alloys by ECAP at room temperature and therefore the processing is conducted at elevated temperatures [8-12]. It has been reported that the processing of a martensitic NiTi alloy for one pass at room temperature leads to form macro-shear bands due to austenite formation since this is the low formability phase. However, a sample deformed at room temperature followed by low-temperature annealing resulted in the most promising strength and shape memory characteristics under compression, such that a 5.3 pct recovered strain at a 2200 MPa strength level has been achieved, although the recovered strain decreases slightly in comparison with the as-received condition [8]. Therefore, shape memory characteristics after successful ECAP processing at room temperature followed by annealing is a unique subject for investigation. Recently a new design of billet has been introduced for achieving successful ECAP processing of NiTi alloys after two passes at room temperature by conventional die design [13, 14]. The successful ECAP processing of some of the NiTi specimens at room temperature using a core-sheath design is most likely due to the use of the Fe sheath which minimizes friction by acting in a manner similar to the movable die walls which are known to be advantageous in conventional ECAP processing. In addition, use of an Fe sheath provides an opportunity for easily processing NiTi billets having different cross-sectional areas. Furthermore, the Fe sheath appears to reduce the strain imposed on the NiTi core [13]. The present research was initiated to study the shape memory effect of NiTi after equal channel angular pressing at room temperature.

2. Experimental material and procedures

A NiTi alloy was used with nominal composition of Ni-50.2at%Ti and prepared using a non-consumable vacuum arc melting technique in a water-cooled copper crucible. After several remeltings for homogenization, the ingots were hot forged and then homogenized at 1000 °C for 720 minutes. Thereafter, hot rolling was used at 1000 °C to prepare rod-shaped samples with 7 × 7 mm^2 cross-sections. After solution annealing of the rods at 850 °C for 60 minutes and ice-water quenching, samples were cut with wire electro-discharge machining to 40 mm lengths and diameters of 3 mm. These samples were fitted in Fe sheaths with diameters of 30 mm and lengths of 50 mm. It should be noted that these Fe sheaths are in contact with the die walls during ECAP processing. The experimental procedure was described earlier for preparing the alloy [13, 14]. After solution annealing (SA) and ice-water quenching, the martensitic transformation start Ms and finish Mf temperatures were 43 and 26 °C, respectively upon cooling and conversely upon heating, the austenitic transformation start As and finish Af temperatures were 58 and 75 °C, respectively. This means the specimen after SA and subsequent ice-water quenching is full martensite [13].

Post-deformation annealing (PDA) after one-pass ECAP processing was performed at 400 °C for various times (5-300 min) in a vacuum furnace. It has been reported that the best superelasticity and shape memory characteristics are obtained, when the specimen is annealed at 400 °C immediately after cold-working [2]. Microhardness measurements were taken at the centers of the longitudinal sections of the billets parallel to the pressing direction (X direction). A load of 100 gf was applied for 10 s. At every point the local value of Hv was taken as the average of five separate hardness values.To study the phases, X-ray diffraction (XRD) was used in employing Cu Kα radiation at 40 kV and tube current of 30 mA. The XRD measurements were carried out over the 2θ range from 30° to 50°, using a step size of 0.02° with a counting time of 9.6 s at each step. The stress-strain curves were recorded for a study of the shape memory effect by miniature tensile specimen with 2 mm gage length using a Santam universal testing machine with a load capacity of 2 kN and the cross-head speed was set at 0.1 $mm.min^{-1}$, equivalent to a strain rate of ~7.4×10^{-4} s^{-1}. The strain recovery of the specimens was measured after loading to 6 and 8 pct strain followed by unloading and heating up to ~150 °C by dipping in hot oil followed by ice-water quenching.

3. Experimental results and Discussion

3.1 Microstructural evolution

Figure 1 depicts the microhardness measurements at the centers on longitudinal sections of the processed NiTi cores after one-pass ECAP processing followed by annealing at 400 °C for 0-300 min. Close inspection shows a significant increase of hardness value with reference to the SA condition (dashed line in Fig. 1). The hardness in the center of the core increases from the SA value of Hv ≈ 210 to a value of Hv ≈ 306 after one-pass of ECAP processing. The results indicate that the hardness values decrease by increasing the time of annealing as a result of activating recovery/recrystallization and grain growth mechanisms and finally achieve the hardness value of SA condition (Hv ≈ 211) after 300 min.

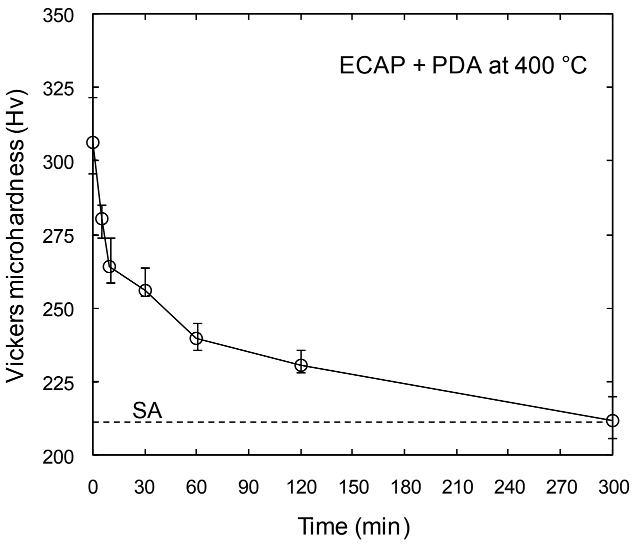

Figure 1 Microhardness measurement of NiTi after one pass ECAP processing followed by PDA at various times. The dashed line is the microhardness of SA specimen.

The X-ray diffraction patterns of samples after SA condition and ECAP processing followed by annealing at 400 °C for 0-60 min are represented in Fig. 2. The microstructure after solution annealing and annealing after the severe plastic deformation is full martensite. The broad austenitic phase peak is clearly revealed after processing by ECAP, thereby confirming the occurrence of the martensite-to-austenite transformation during ECAP processing which has been identified and expressed in the previous paper [13]. The R-phase characteristic peak appears after annealing in the X-ray diffraction patterns which is close to the peak of austenite. The results indicate that the intensity of the R phase peak decreases by increasing the annealing time and disappears after 60 min. Accordingly, the specimens after annealing are full martensite and these include B19' phase (martensite) and the minor amount of R phase (R-phase martensite shows shape memory behavior as in B19'-phase martensite [2]) .

It is well known that severe cold working, such as one-pass ECAP which imposes a strain ε_{eq}=1 [14], introduces defects, which are essentially dislocations. The PDA results in the martensitic transformation and is able to regenerate and decreases the thermal hysteresis [15, 16]. As already shown in the literature, this occurs with some changes, in particular the emergence of a two step transformation on cooling for low temperature annealings: B2 → R → B19' [17-19]. The X-ray patterns of PDA condition exhibit a minor R-phase peak after 5-30 min annealing at room temperature. The intensity of R phase peak decreases by increasing the annealing time and disappears after 60 min. It is important to remember that these specimens cooled down to 0 °C (quenching in ice-water mixture) after PDA. In fact, the existence of a minor R-phase after 5-30 min annealing in the microstructure and decreasing amount of R phase by increasing the annealing time indicate that Mf in these conditions is slightly lower than 0 °C and this temperature increases by increasing the annealing time. This argument is in the direction of previous research which expresses decreasing the thermal hysteresis and consequently increasing the Ms and Mf by increasing annealing temperature or time after cold working [15, 16].

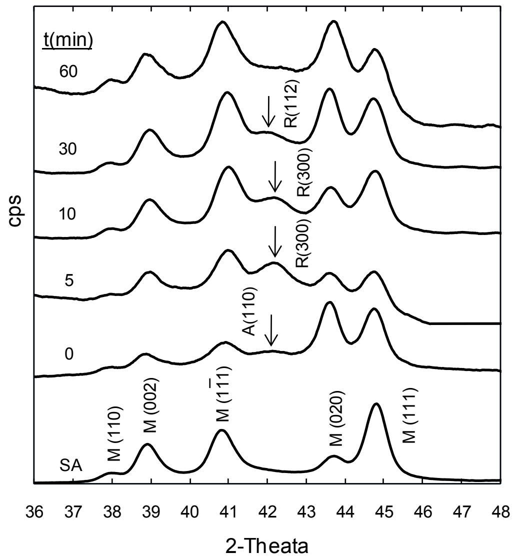

Figure 2 X-ray patterns of Ni50.2Ti after one-pass ECAP and PDA at 400 °C for 5-60 min.

3.2 Shape memory effect

The stress–strain curves of Ni50.2Ti alloy after one-pass ECAP processing followed by annealing at 400 °C for 0-30 min are represented in Fig. 3. The characteristic parameters of these stress–strain curves and also solution annealed and one-pass ECAP processed results are summarized in Table 1. The results indicate that the solution-annealed, one-pass ECAP processed and annealed specimen shows strain recovery after loading and unloading followed by heating up to 150°C (by dipping in hot oil) and ice-water quenching while the amount of recovered strain of one-pass ECAP is negligible. In addition, superelasticity in the one pass ECAP specimen is detectable which is expected according to the XRD result and the existence of an austenitic phase. The solution-annealed specimen shows poor shape memory effect in comparison with post-deformation annealing conditions (Table. 1). In the latter conditions, the results show fully recovered strain after annealing which characterizes good shape memory effect after loading up to 6 pct strain (Fig. 3). The characteristic detwinning plateau after the elastic region is revealed in the PDA condition which contrasts with the one pass ECAP condition (which is not shown but the data are in Table. 1). It seems martensite reorientation does not take place after the heavy deformation and the stress level decreases by increasing the annealing time from 0 to 30 min as a result of decreasing the density of dislocations which act as an obstacle for detwinning. These results indicate that the shape memory effect is improved significantly after PDA in comparison with SA and ECAP condition. In fact, the fully recovered strain at SA is 5.5 pct while in the case of PDA conditions this value is enhanced more than 6 pct. This may be attributed to the strengthening of the martensite matrix and grain refinement using ECAP followed by PDA. The results show annealing for 10 min is the optimum procedure with maximum recovered strain of 6.9 pct. It was reported earlier that annealing at 400 °C right after cold-working leads to the best superelasticity and shape memory characteristics up to 6 pct [2] and also the sample deformed by

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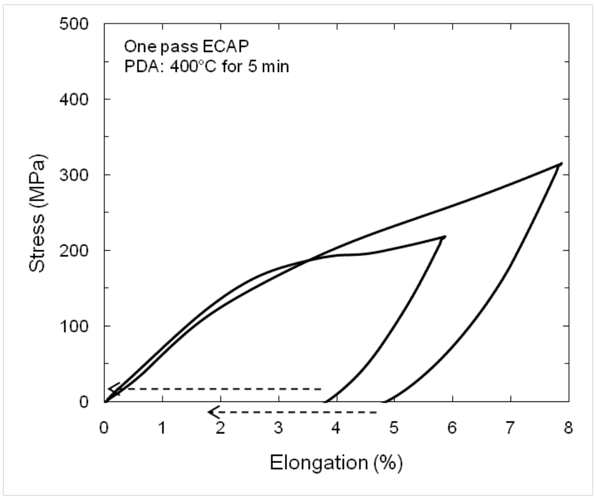
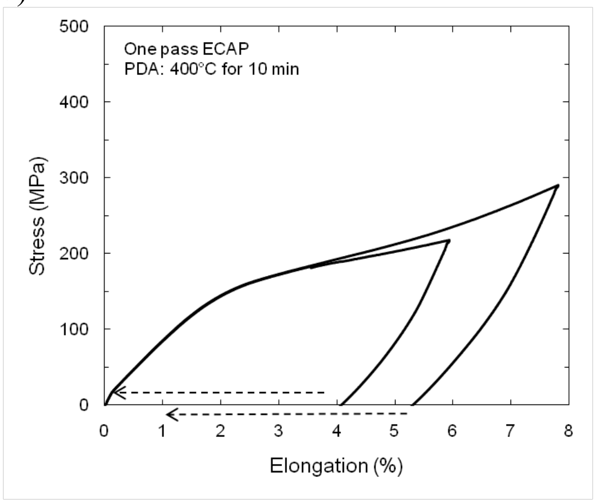
ECAP at room temperature followed by the low-temperature annealing resulted in a 5.3 pct recovered strain under compression [8].



a)



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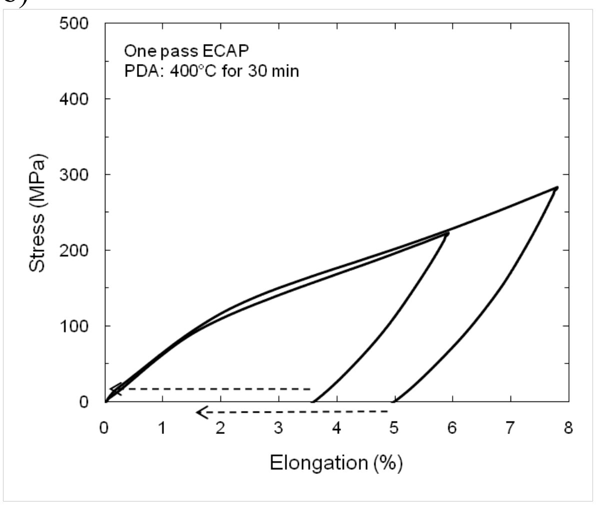

c)

Figure 3 Stress–strain curves of Ni50.2Ti after ECAP processing followed by various PDA at 400 °C for 5-30 min. The arows show the strain recovery upon heating after unloading.

In fact, severe plastic deformation followed by optimum PDA leads to an appropriate microstructure for achieving a good shape memory effect. Accordingly, annealing behavior and finding the best PDA condition is important to achieve good shape memory effect. Annealing at 400 °C for 10 min exhibits much superior shape memory effect compared to annealing at 400°C for 5 and 30 min and probably more time. However, the shape memory characteristic of PDA for 10 and 30 min are almost similar which means the microstructure does not change drastically after 30 mins and this is supported by the X-ray patterns and hardness measurements. It is expected that the growth of grains by recrystallization after 10 min annealing leads to a decrease in the recovered strain as a result of mechanical strength deterioration. This explains why the shape memory effect in solution-treated specimens is poor in Table. 1.

Table 1. The characteristic parameters of stress–strain curves after loading and unloading followed by heating up to ~150 °C.

Condition	Recovered Strain (pct)	Stress at 6 pct (MPa)
SA	5.5	230
ECAP	5.1	440
PDA for 5 min	6.1	260
PDA for 10 min	6.9	235
PDA for 30 min	6.4	229

Finally, the severe plastic deformation of a NiTi alloy in the martensitic state at room temperature and the post-deformation annealing resulted in the most favorable microstructure for high recoverable strains, thereby a shape memory effect as compared to the SA condition. The main reason for this difference is that at room temperature the initial deformation mechanism is martensite reorientation and then mostly martensite slip. The plastic deformation followed by the PDA leads to strengthening of the matrix by grain refinement, which eventually suppresses the irreversible slip deformation during the martensite reorientation by raising the critical shear stress for slip.

4. Summary and conclusions

The martensitic Ni50.2Ti alloy was successfully processed by ECAP at room temperature and post deformation annealing at 400 °C carried out for improving the shape memory effect. The hardness increased drastically from the SA value of Hv ≈ 210 to a value of Hv ≈ 306 after one-pass ECAP processing. The hardness after annealing at 400°C indicated significant decrease after 10 min and decreased gradually to the hardness of the solution annealed condition with further increasing annealing time up to 300 min. The X-ray diffraction patterns showed the specimens after annealing are full martensite and these include martensitic B19' phase and a minor amount of martensitic R phase. The shape memory effect was improved significantly after PDA in comparison with SA and ECAP condition. This may be attributed to the strengthening of the martensite matrix and grain refinement using ECAP followed by PDA. The results show that all specimens recover 6 pct strain and the maximum recovered strain, 6.9 pct, is related to the 10 min annealed specimen, a unique shape memory effect in comparison with the results of other researchers.

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