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Annealing behavior and shape memory effect in NiTi alloy processed by equal-channel angular pressing at room temperature

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ABSTRACT

A martensitic NiTi shape memory alloy was processed successfully by equal-channel angular pressing (ECAP) for one pass at room temperature using a core–sheath billet design. The annealing behavior and shape memory effect of the ECAP specimens were studied followed by post-deformation annealing (PDA) at 673 K for various times. The recrystallization and structural evolution during annealing were investigated by differential scanning calorimetry, dilatometry, X-ray diffraction, transmission electron microscopy and microhardness measurements. The results indicate that the shape memory effect improves by PDA after ECAP processing. Annealing for 10 min gives a good shape memory effect which leads to a maximum in recoverable strain of 6.9 pct upon heating where this is more than a 25 pct improvement compared with the initial state.

1. Introduction

NiTi shape memory alloys have unique characteristics by exhibiting shape memory and superelasticity based on a thermoelastic martensitic transformation which has attracted much attention in engineering applications [1]. The thermoelastic transformation exhibits a crystallographically reversible transformation. Nevertheless, plastic deformation such as slip or deformation twinning is irreversible and these strains cannot be restored even upon heating. Thus, it is important to increase the critical stress for slip by work hardening and/or grain refinement in order to realize good shape memory and superelastic characteristics for these shape memory alloys [1–3]. It has been shown that cold-working followed by annealing leads to good superelasticity as well as a shape memory effect of up to 6 pct and no plastic strains are observed [1].

It is well known that grain refinement by severe plastic deformation (SPD) can improve the physical and mechanical properties of metals and alloys. Recent studies have shown that SPD processing at relatively low temperatures may be used effectively to synthesize bulk nanostructured NiTi alloys with enhanced shape memory and superelasticity [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 such as simplicity in operation [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 generally conducted at elevated temperatures [8–12]. It was reported that the processing of a martensitic NiTi alloy for one pass at room temperature leads to the formation of macro-shear bands due to austenite formation since this is the low formability phase. Furthermore, a sample deformed at room temperature followed by low temperature annealing gave the most promising strength and shape memory characteristics under compression, such that a 5.3 pct recovered strain was achieved at a strength level of 2200 MPa although the recovered strain decreased slightly by comparison with the as-received condition [8]. However, there are no reports to date of the shape memory characteristics under tension of the NiTi alloy after successfully processing by ECAP at room temperature followed by annealing.

Very recently, a new billet design was introduced which permitted the successful processing by ECAP of NiTi alloys for up to two passes at room temperature using a conventional die design [13,14]. Accordingly, the present research was initiated in order to obtain a comprehensive description of the annealing

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behavior and the shape memory effect of NiTi after equal-channel angular pressing at room temperature.

2. Experimental materials and procedures

A NiTi alloy was used in these experiments having a nominal compositions of Ni-50.2 at% Ti. The experimental procedure for preparing the alloy was described earlier and involved a solution annealing at 1123 K for 60 min followed by ice-water quenching [13]. Samples were cut from the solution annealed material with wire electro-discharge machining to give rods having lengths of 40 mm and diameters of 3 mm. These samples were the core which fitted within Fe sheaths having diameters of 30 mm and lengths of 50 mm. The processing by ECAP was described in detail in earlier reports [13,14]. After one-pass of ECAP processing, post-deformation annealing (PDA) was performed at 673 K for various times from 5 to 300 min in a vacuum furnace. The heating rate of the specimens was $\sim$120 K min^{-1}. The transformation temperatures were measured using differential scanning calorimetry (DSC) with a liquid nitrogen cooling accessory having cooling and heating rates of 10 K min^{-1} during the thermal cycling. The DSC analyses were performed using non-isothermal (scanning) experiments upon heating at a scanning rate of 10 K min^{-1}.

Cylindrical samples of 10 mm length and 2 mm diameter were cut and inserted in an Adamel DT1000 dilatometer to provide an isothermal study of the ECAP and the solution annealed samples. The samples were heated to 673 K in vacuum using a heating rate of 120 K min^{-1} and then maintained at this temperature for 60 min. X-ray diffraction (XRD) was used to study the phases with Cu Kα radiation at 40 kV and a tube current of 30 mA at room temperature. The XRD measurements were carried out over a 2θ range from 30° to 50° using a step size of 0.02° with a counting time of 9.6 s at each step.

Measurements of the Vickers microhardness, Hv, were taken at the centers of the longitudinal sections of the billets parallel to the pressing direction, equivalent to the X direction. A load of 100 gf was applied for a dwell time of 10 s. Every point in the reported values of Hv was taken as the average of five separate hardness values. The ECAP core was also used to prepare foils for transmission electron microscopy (TEM) using focused ion beam (FIB). The different phases were analyzed by selected area diffraction applying different beam directions in a JEOL-2100 TEM operating at 200 kV. Stress–strain curves were recorded for studying the shape memory effect using tensile testing and gauge lengths of 8 mm measured parallel to the pressing direction as shown in Fig. 1. A Santam universal testing machine was used for the tensile testing with a load capacity of 2 kN and operating with a cross-head speed of 0.1 mm min^{-1} which is equivalent to an initial strain rate of $\sim 7.4 \times 10^{-4}$ 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 $\sim$423 K by dipping in hot oil followed by ice-water quenching.

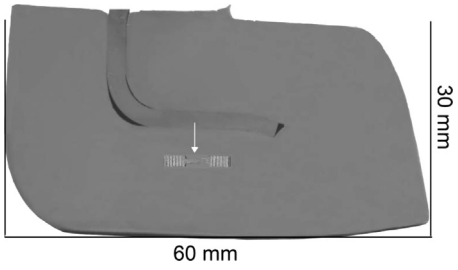

Fig. 1. Longitudinal section of a billet after ECAP: Fe sheath 30 mm in diameter × 50 mm in length and NiTi core 3 mm in diameter × 40 mm in length. The white arrow shows the area for the tensile test specimen and also the area of DSC, dilatometric measurements, microhardness measurements and X-ray analysis.

3. Experimental results

Fig. 1 shows a longitudinal section of the billet including the NiTi core (3 mm in diameter and 40 mm in length) contained within the Fe sheath (30 mm in diameter and 50 mm in length) after one-pass by ECAP. It is readily apparent that the NiTi alloy was successfully processed by ECAP at room temperature by containing the NiTi sample within the Fe sheath. Processing was performed successfully for up to two passes of ECAP by controlling the processing variables as described in detail in an earlier report [13].

Non-isothermal DSC measurements of the Ni50.2Ti alloy after solution annealing and one-pass of ECAP are illustrated in Fig. 2. The exothermic peak is visible for the ECAP processed sample and this contrasts with the solution annealed sample and demonstrates energy storage during the severe plastic deformation. The appearance of the exothermic peak in the non-isothermal DSC measurements is related to the occurrence of recovery and recrystallization phenomena after cold working. This result shows that the recovery and recrystallization start at $\sim$598 K and the integral of the exothermic peak as a stored energy (E_{stored}) is $\sim$540 J mol^{-1}.

The isothermal dilatometric measurements of Ni50.2Ti at 673 K after solution annealing and ECAP processing are given in Fig. 3. These measurements reveal that, after expansion of the cylindrical samples up to 673 K after $\sim$3 min, there is significant contraction as a result of recovery and recrystallization. Based on this evidence, it appears that the recrystallization is completed after $\sim$11 min. The occurrence of a small contraction for the solution annealed sample is probably a consequence of thermal shock during the high heating rate.

The kinetics of isothermal recrystallization are usually expressed by the well-known Johnson–Mehl–Avrami–Kolmogorov (JMAK) equation [15,16] and through the isothermal study. Thus, it is possible to qualitatively assess the nature of the recrystallization and grain-growth phenomena [17,18]. Assuming the volume fraction of the transformed material is proportional to the dilatation measured under the dilatometric peak, as shown in Fig. 3a, the volume fractions (x) of the transformed material may be plotted against time, t, as shown in Fig. 3b. The Avrami plot of ln[ln $(1-x)-1$] versus ln(t) (with the time in s) then yields a straight

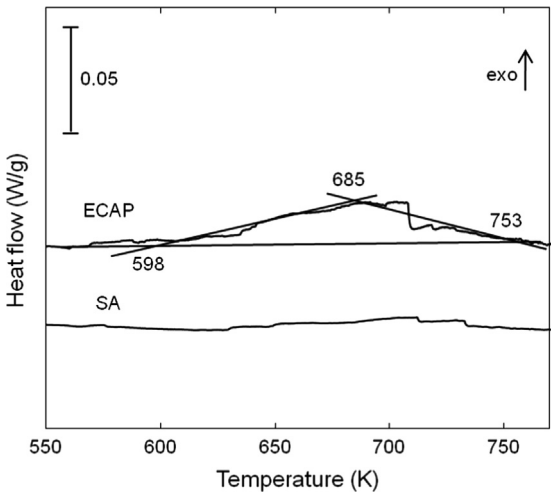

Fig. 2. Non-Isothermal (scanning) DSC measurement of Ni50.2Ti after solution annealing and ECAP processing: the heating rate is 10 K min^{-1}.