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Influence of recrystallization and subsequent aging treatment on superelastic behavior and martensitic transformation of $Ni_{50.9}Ti$ wires

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ABSTRACT

In the present study, influence of different stages of recrystallization process and subsequent aging treatment on the superelastic properties of Ni-rich NiTi shape memory wires is investigated. Characteristics of transformation temperatures were determined using differential scanning calorimetry. Results indicate that annihilation of cold work effects after annealing results in changes on the features of DSC curves. The amount of residual strain is higher in the samples with cold work value of $\varepsilon = 0.6$ compared to the samples with $\varepsilon = 0.4$. The combination of annealing and aging treatment leads to improve in the superelastic properties. Results showed that different stages of the recrystallization process would affect the precipitation process in subsequent aging treatment.

1. Introduction

Nickel–titanium alloys have great utilization in technology and medical applications due to unique functional properties such as shape memory effect (SME) and superelasticity accompanied with good biocompatibility and high corrosion resistance [1–4]. Superelasticity and SME are attributed to the thermo-elastic martensitic transformation [5]. Unlike one-way effect (1WE), which can only remember the high temperature (austenite) shape, two-way effect (2WE) can remember both high and low temperature shapes. Moreover, there is an interesting phenomenon that has been recognized in many different types of SMAs which was named temperature memory effect (TME) [6–9]. The TME is the ability of a material to remember the maximum temperature in the previous thermal history even under severe thermo-mechanical conditions [8].

It is well known that, Ni-rich NiTi alloys are capable of developing Ni_4Ti_3 precipitates during aging. Fine and coherent Ni_4Ti_3 precipitates affect both the martensitic transformation behavior and mechanical properties of NiTi alloys [10–12]. In the presence of Ni_4Ti_3 precipitates, an intermediate martensitic phase, known as R-phase with a trigonal lattice structure could be stabilized in NiTi alloys [13]. The effect of aging treatment on superelastic behavior, sequences and transition temperatures of martensitic transformations have been widely investigated in literatures [12,14–20]. It is well established that improvement of thermal shape memory and superelastic properties of Ni-rich NiTi alloys can be achieved by thermo-mechanical treatment [3,21,22]. It is also found that severe cold deformation could be affected the transition temperatures and also two way shape memory effect [23,24]. Moreover, depending on the annealing conditions, the resultant SMA may still have the 2WE. This, however; depends on annealing time to achieving the optimum two-way shape memory [24]. In order to improve the superelastic properties of NiTi alloys, thermo-mechanical treatment should be controlled so that a high density of dislocations accompanied with fine Ni_4Ti_3 precipitates be attained in the structure [19,20]. To control the microstructure and density of dislocations during thermo-mechanical treatment, recovery and recrystallization processes should be scrutinized. It is well known that primary recrystallization could be divided into two stages, (i) nucleation of new strain free grains and rapid growth of the new grains and (ii) slow growth of the newly recrystallized grains which reduces the overall transformation rate [21]. In the second stage of the recrystallization process the growing grains begin to impinge each other while the nucleation of new grains is underway [21]. Thus there are various densities of dislocations in each stage of the recrystallization. In the previous work [22] it was presented that recrystallization process occurs in a temperature range of 550–600 °C for $Ni_{50.9}Ti$ alloy. Therefore, present study concentrates

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on the effect of aging treatment at different recrystallization stages based on previous work on superelastic properties and martensitic transformation of $Ni_{50.9}Ti$ shape memory alloy.

It is declared that cold deformation up to 40% results in work hardening while more increase in the cold work amount does not significantly affect the mechanical properties of NiTi alloys [23]. Recent researches have illustrated that deformations about 60% and higher than that would lead to partial amorphisation that could result in nanocrystaline structures after post deformation annealing [24–27]. However, there is less systematic information about the influence of different recrystallization stages in deformed NiTi alloys on the microstructure, martensitic transformations and superelastic properties of Ni-rich NiTi alloys.

Finally, it seems that different density of lattice defects that varies during recrystallization and development of precipitates during subsequent aging treatment could strongly affect the superelastic properties.

2. Experimental works

NiTi wires with nominal composition of 50.9 atom.% Ni purchased from Memry Co. (USA) were used in this study. The as-received wire was in cold drawn state with a diameter of 0.34 mm. The wire was cut into 15 cm length samples. The NiTi wires were encapsulated in a quartz tube filled with high purity argon gas and they were annealed at 850 °C for one hour. In addition, some Ti foils were used inside the tube as a getter to purify the atmosphere. Diameter of the samples was reduced to 0.29 mm with etching out the surface layer of the samples. The samples were cold drawn after annealing using diamond dies lubricated by oil. The true strain after cold drawing was set to $\varepsilon = 0.4$ and 0.6 where the true strain "ε" is given by:

$$\varepsilon = 2\ln\frac{d_{t+1}}{d_t} \tag{1}$$

where d_{t+1} and d_t represent diameters associated with two consecutive drawing steps. The drawing speed was 0.5 m/min with no annealing step between drawing passes and the final diameter of the wire with $\varepsilon = 0.4$ and 0.6 was 0.215 and 0.235 mm, respectively. The cold drawn wires were annealed at 600 °C for 10, 30 and 90 min which were selected based on results of previous work [22]. Moreover, aging treatment at 450 °C for 45 min were performed after the cold drawing and annealing treatment. The samples were labeled according to the heat treatment cycle in Table 1.

In order to better understanding the recrystallization process, electrical resistance was measured at 600 °C for 2 h using a direct current four-probe method as explained in the previous work [22].

Optical microstructural evaluation was performed after grinding, electro-polishing and chemical etching of the samples. Electro-polishing treatment was carried out using a 21% perchloric acid and 79% acetic acid at 10.5 V and 35 °C. The etchant was composed of 100 ml hydrochloric acid, 20 ml distilled water, 2.4 g ammonium hydrogen difluoride and 34.5 g sodium metabisulfite.

Table 1
Label of the samples according to the heat treatment cycle.

Sample	True strain value	Heat treatment cycle
A_{10}	0.4	Annealed at 600 °C for 10 min
A_{30}	0.4	Annealed at 600 °C for 30 min
A_{90}	0.4	Annealed at 600 °C for 90 min
B_{10}	0.6	Annealed at 600 °C for 10 min
B_{30}	0.6	Annealed at 600 °C for 30 min
B_{90}	0.6	Annealed at 600 °C for 90 min
A'_{10}	0.4	Annealed at 600 °C for 10 min and aged at 450 °C for 45 min
A'_{30}	0.4	Annealed at 600 °C for 30 min and aged at 450 °C for 45 min
A'_{90}	0.4	Annealed at 600 °C for 90 min and aged at 450 °C for 45 min
B'_{10}	0.6	Annealed at 600 °C for 10 min and aged at 450 °C for 45 min
B'_{30}	0.6	Annealed at 600 °C for 30 min and aged at 450 °C for 45 min
B'_{90}	0.6	Annealed at 600 °C for 90 min and aged at 450 °C for 45 min

Tensile tests were carried out at 37 °C and the cross-head speed of 0.1 mm/min using Adamel Lohmargy DY26 which was equipped with a 100 kg load cell and a furnace with accuracy of ±0.5 °C. Overall length of the sample between the grips was set to be 40 ± 0.02 mm. The strain rate of $4.1 \times 10^{-5}\ s^{-1}$ calculated based one moving speed and gauge length. Diameters of the samples were measured using a digital micrometer with accuracy of 1 μm. Tensile tests were performed in loading and unloading cycle up to 4% and 6% strain. The experiments were repeated three times in order to enhance the accuracy of results.

Differential scanning calorimetry was performed in helium atmosphere with a cooling and heating rate of 10 °C/min using a Netzsch DSC 404 C calorimeter. The samples were heated up to 100 °C, where they were held for 3 min to stabilize thermal equilibrium. Then the DSC measurements started by cooling the samples down to −100 °C. The samples were held for 3 min at −100 °C and then were heated up to 100 °C.

3. Results and discussions

Fig. 1(a) shows the DSC curve of solution annealed sample. Moreover, microstructure of the solution annealed sample and the samples with $\varepsilon = 0.4$ and 0.6 are shown in Fig. 1(b–d), respectively. As shown in Fig. 1(a), two peaks during cooling and heating cycles can be seen which are attributed to the B2 to B19' and reverse transformation. The average grain size of this sample was 29.5 μm (Fig. 1(b)). Fig. 1(c) and (d) showing elongated grains in the cold drawn samples, reveal that the grains length increases by increasing the cold work value.

Fig. 2 shows stress–strain curves of the solution annealed sample and the samples with $\varepsilon = 0.4$ and 0.6. As shown in Fig. 2(b) and (c), cold drawing of the NiTi wires results in reducing the residual strain after unloading, in comparison with the solution annealed sample (Fig. 1(a)). However, the stress plateau is annihilated in the cold drawn samples. It is well known that the cold deformation of NiTi alloys results in the formation and stabilization of stress-induced martensitic phase. The stress plateau is related to stress-induced martensitic transformation accompanied by coalesced martensite variants and detwinning of the lattice invariant shear (LIS) twins.

In order to clarify the different annealing stages, in situ electrical resistance measurements were performed on the cold drawn NiTi wires. Fig. 3 shows the changes in R/R_0 value as a function of annealing time, up to 2 h at 600 °C after applying the true strains of 0.4 and 0.6, in which R is electrical resistance during the annealing treatment and R_0 is initial electrical resistance of the samples.

According to the previous work [22] and Fig. 3, it is recognized that the recrystallization occurs at 600 °C and grain growth starts later (after point "C" in Fig. 3). To study the effects of different annealing stages on superelastic properties, the samples were selected in different annealing times (which are labeled in Table 1). In the samples A_{10} and B_{10}, recrystallization process is started, but not completely performed. In the samples A_{30} and B_{30}, the recrystallized grains begin to grow and collide to each other while the nucleation of new grains is still continuing. Finally, in the samples A_{90} and B_{90}, it could be declared that the recrystallization process is completed and grain growth is underway. According to the Huang [28] work, transformation front propagate in the martensitic/austenitic materials. However, in the present study, the recrystallization process was investigated by electrical resistance test and it seems that the transformation front removed during the initial stages of the test. As it can be seen from Fig. 3 that the electrical resistance plunged in the first stage after primary sharp increase and this is showed that the materials is fully austenite and it seems that the effect of transformation front is removed during electrical resistance tests.

Optical micrographs of the samples A_{10} to A_{90} and B_{10} to B_{90} (different stages of annealing treatment) are shown in Fig. 4. From Fig. 4(c) and (f) it is clear that the recrystallization process is occurred and newly crystallized grains are observed.