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CHANGES IN THE THERMOELASTIC PROPERTIES CAUSED BY METAL FORMING PROCESSES IN Ni-Ti SHAPE MEMORY ALLOY

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Abstract. *Plastic forming processes have been applied in the shape memory alloys (SMA) to improve their mechanical properties. However, these processes lead to changes in its thermoelastic properties (temperatures and enthalpies of transformation, critical stress induced martensitic, reversible thermoelastic deformation and others). For technological applications of these alloys such as thermomechanical actuators, they should keep their constant characteristics throughout its use (thermoelastic properties). In this work are analysed these properties in the Ni-Ti shape memory alloys that have been processed mechanically by conventional rolling and Equal Channel Angular Extrusion (ECAE). The analyses were performed by differential scanning calorimetry, optical and electronic microscopy and under constant load bending tests (simulation of the memory effect in order to determine reversible thermoelastic strain). The results showed that the plastic forming processes drastically alter the properties, especially for those samples subjected to the ECAE that can block the martensitic transformation. Heat treatments were applied in order to improve the shape memory effect properties. Results of X-rays diffraction and micrographs indicate that each type of forming process and the presence of precipitates has great influence in the elastic property behaviours. These analyses are relevant for applications of these SMA which require large mechanical strength combined with functional properties of the shape memory phenomena.*

Keywords: *Shape Memory Alloys, Metal Forming Processes, Equal Channel Angular Extrusion – ECAE, Thermoelastic Properties.*

1. INTRODUCTION

The shape memory alloys (SMA) are active materials presenting the ability to recover apparently plastic deformation by appropriate thermal conditioning. The phenomena of Shape Memory Effect (SME) are closely associated with the phase transformations of the martensitic type that are crystallographically reversible (Otsuka and Wayman, 1998). The manufacture of the shape memory alloys of Ni-Ti family is especially important due to the fact that small variations in the chemical composition may change the critical temperatures of the martensitic transformation at about 100°C (Antunes *et al.*, 2013). Therefore, the Plasma for manufacturing process is used efficiently because it causes negligible loss of material by oxidation during melting, according to a study of De Araújo *et al.* (2009). The shape memory alloys Ni-Ti based are widely utilized because of its wide range of technological applications possibilities, which extend from aerospace, biomedical, petrochemical industries and others (Silva *et al.*, 2012 and Figueiredo *et al.*, 2009).

The SMA can be considered electric actuators when the SME is activated by applying electrical current pulses (Joule effect). In contrast, if the SME is activated directly through the controlled variation of temperature, are considered as thermal actuators. These alloys when subjected to plastic deformation processes have increased mechanical strength due to its hardening (large increase in the crystalline defects density) and decrease grain size. This change of mechanical properties causes changes in the thermoelastic properties of the SMA (critical transformation temperatures, enthalpies of transformation, thermoelastic deformation, thermal hysteresis and others) that are essential characteristics for use of these materials in technological applications.

ECAE (Equal Channel Angular Extrusion) or ECAP (Equal Channel Angular Pressing) is a metal forming process recently developed by Segal (1995), which is to promote the passage of the material between two sequential channels that intersect forming angles between 90° and 120°. These channels have identical geometrical dimensions, so the material does not change its dimensions after processing. The plastic deformation is produced during passage of the material at the intersection between the two channels. In this process, the material supports a severe plastic deformation that causes large amount of critical shear stress without modifying the cross section of the sample. Some studies show that the deformation phenomena that occur during ECAE process are independent of sample size (Figueiredo *et al.*, 2009). Several technological applications of these processed materials already are idealized, especially in parts that must have high mechanical strength obtained by plastic deformation processes, but should not have its dimensions changed during processing.

This study aims to obtain a Ni-Ti alloy with shape memory effect, submit these materials to mechanical forming processes by conventional lamination and angular extrusion (ECAE). In this paper are analysed the properties of the Ni-Ti shape memory alloy through analysis of differential scanning calorimetry, scanning electron microscopy and under constant bending load test. This latter test simulates the shape memory effect and from the curves obtained are determined the thermoelastic properties.

2. EXPERIMENTAL PROCEDURES

A Shape Memory Alloy (SMA) of equiatomic composition of Ni-50at.%Ti, corresponding to Ni-45wt.%Ti, was obtained by the Plasma Skull Push Pull (PSPP) process with controlled atmosphere melting chamber. This process is better described in the article of De Araujo *et al.* (2009). It was verified that, in order to assure the good homogeneity of the SMA, melting process should be repeated for five times. After, the ingot was homogenized for two hours in a muffle furnace at 900° C followed by quenching in water at room temperature.

The ingot was machined in a precision cutter with diamond disc, aiming at production of samples in form of prismatic bars for metal forming processes: conventional mechanical rolling process and Equal Channel Angular Extrusion (ECAE). The sample used in rolling process has 1.5 mm of thick and 5 mm of wide. The hot rolling was performed on conventional laminator machine. After each pass, the sample was heated in a muffle furnace at a temperature of 900ºC for one minute. The sample was deformed from 1.5 mm to 0.5 mm thick, with final deformation rate of 66.7% (20 steps of approximately 0.05 mm of deformation per step). For the angular extrusion, the sample was a bar of square cross-section of 5x5 mm^2. The matrix of the angular extrusion process has angle of 130 degree between internal channels. Angular extrusion was performed in a mechanical tests universal machine (EMIC), controlled to operate in the compression test mode at a rate of 0.5 $mm \cdot min^{-1}$ at room temperature.

In this work, samples were obtained after homogenization treatment (reference sample - no plastic deformation) and of mechanical rolling and angular extrusion processes. Samples obtained for each plastic deformation process were submitted to annealing treatment at 450 ° C for 15 minutes and cooled in water at room temperature for stress relief. Table 1 presents the nomenclature and procedures applied to each of the samples analysed in this study.

Table 1. Nomenclature and procedures of the Ni-Ti Samples

Sample	Procedures applied
H	Homogenized at 900°C for 2 hours
R	mechanical rolling process
RA	mechanical rolling process and annealed at 450°C for 15 min
E	extrusion process
EA	extrusion process and annealed at 450°C for 15 min

The calorimetric properties (temperatures and enthalpies of austenitic phase transformations, martensitic and rhombohedral and its thermal hysteresis) were performed by a differential scanning calorimeter (DSC Mettler TA3000), with a scan rate of 10°C·min^{-1}. Conventional metallographic procedures (sanding and polishing with diamond paste) were realised and the Kroll reagent (2 mL HF, 4 mL HNO_3 and 100 mL H_20) was used for etching. Microstructures of samples were taken by an electron microscope (Hitachi TM3000).

A special apparatus was developed to determine thermoelastic properties of SMA under constant bending load (cantilever test). The load is applied on the sample through a pulley system. A programmable silicon oil bath is used to realize heating and cooling cycles between -10 and 100°C. During cooling, the plate (sample) is deformed, and when heated the sample recovered its original form. A linear variable displacement transducer (LVDT) and a thermocouple measure the strain and the temperature, respectively. A control and data acquisition system is connected to a computer. More details about this special apparatus are in the article of Oliveira *et al.* (2010).

In this work, samples were individually tested under constant bending load of 80 MPa and thermally cycled 20 times between 20 and 100°C with a rate of 10°C.min^{-1} during heating and 3°C.min^{-1} for cooling. Samples have geometry of the prismatic bar with dimensions: 5 mm wide, 20 mm long and 0.5 mm thick.

Figure 1 shows deformation *versus* temperature curves obtained from data collected in the thermomechanical tests under constant load, in which are determined the thermoelastic properties [initial and final temperatures of the austenitic transformation (A_S and A_F), martensitic (M_S and M_F) and rhombohedral (R_S and R_F), thermoelastic deformations (ε_t) and thermal hysteresis ($Ht = A_{50} - M_{50}$) and strain (x)].

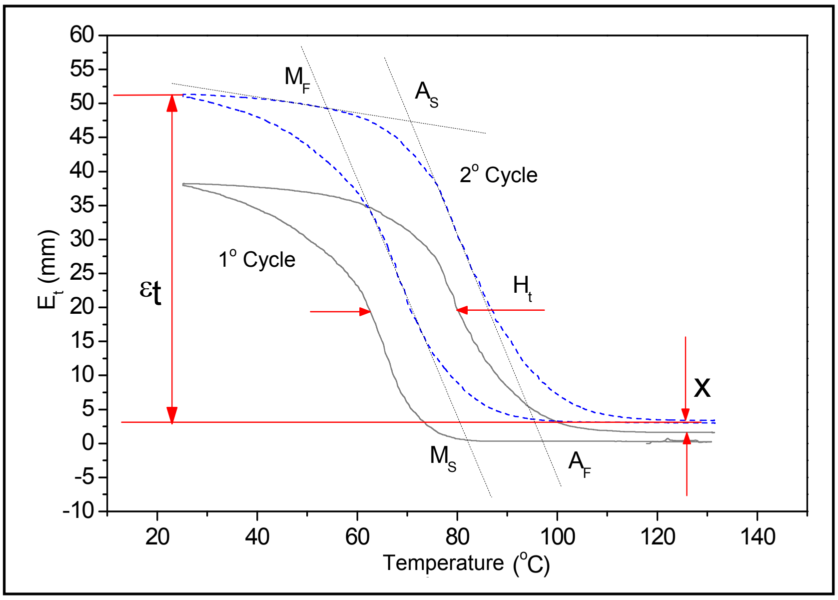


Figure 1. Representative strain *versus* temperature curves obtained during a typical test of thermomechanical cycles in simple bending mode. The investigated parameters are pointed out on this figure. (Gonzalez *et al.*, 2004).

3. RESULTS AND DISCUSSION

Figure 2 shows calorimetric curves for the samples submitted to the five conditions: a) homogenized (H), b) Rolled (R), c) Rolled and Annealed (RA), d) Extruded (E), e) Extruded and Annealed (EA). Table 2 summarizes the results determined by calorimetric tests for each condition applied the samples. The curve of the rolled sample indicates that the plastic deformation process causes a decrease in M_S temperature during cooling, from 31.2°C to about 20.4°C. The A_S temperature is also reduced compared to the reference sample (H) from about 7.2°C. In principle, it can be assumed that the initial inflection during cooling is due to the presence of rhombohedral phase (R phase) (Otsuka and Wayman, 1998). Plastic deformation process increases the linear defects density (dislocations) that may hinder or even inhibit direct (austenite => martensite) and reverse (martensite => austenite) martensitic transformations.

In the case of the rolled and annealed sample (RA), it's observed that the calorimetric curve and its data are practically similar to the reference sample (M), thus this treatment eliminates the effects of rolled mechanical process in this alloy.

The calorimetric curve of the extruded sample (E) (Figure 2d) clearly shows the peaks of the R phase and monoclinic martensitic phase (B19'). In the case of the laminated sample (R), the start temperature of R phase remains practically unchanged from to M_S temperature of homogenized sample (H). The R_S temperature of the extruded sample (E) decreases about 21°C (variation of -10°C from homogenized sample) and M_S temperature decreases to about -7°C (variation of -40^{o}C). This clearly shows that the angular extrusion process introduces a number of crystalline defects much larger than rolled process; however it produces no reduction in the geometric dimensions of sample.

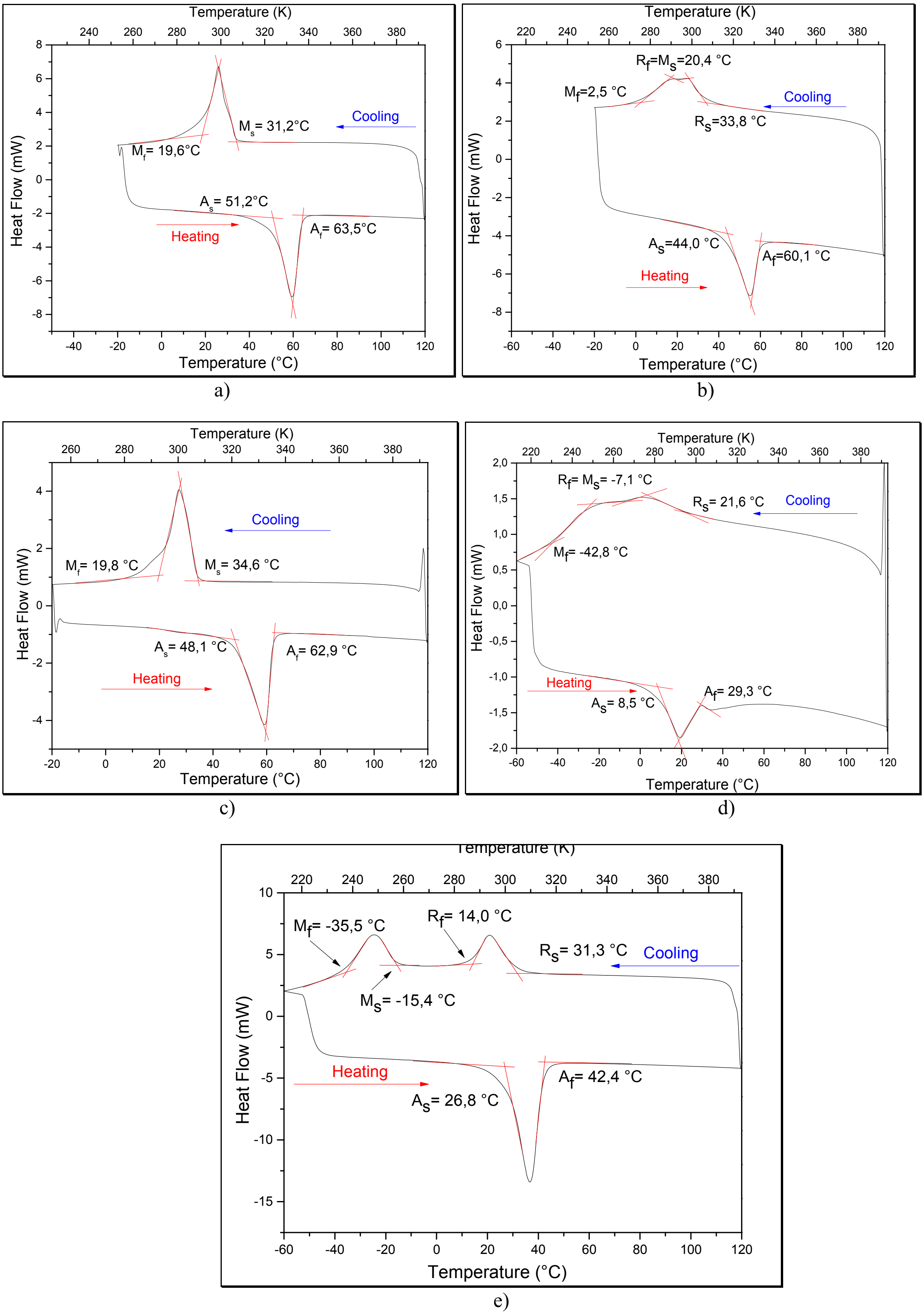


Figure 2. Calorimetric curves of the Ni-Ti alloy in the conditions: a) Homogenized (H), b) Rolled (R), c) Rolled and Annealed (RA), d) Extruded and Annealed (EA).

Table 2. The results of calorimetric curves of the Ni-Ti alloy samples

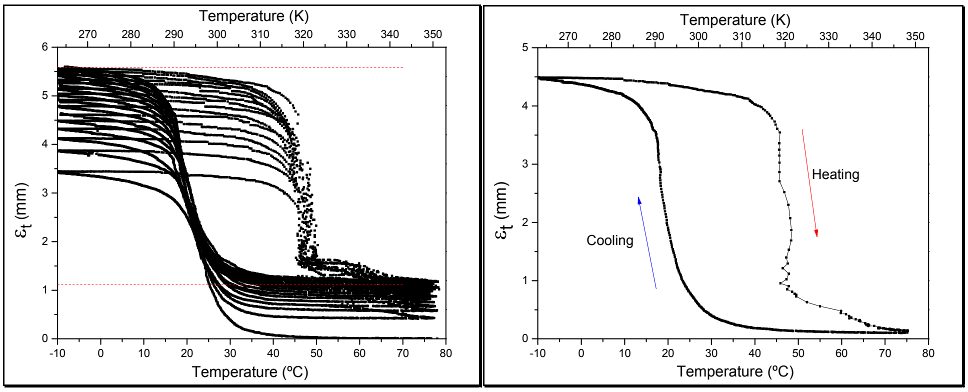
Sample	Parameters								
	A_s (°C)	**A_f (°C)**	**ΔH(J/g)$_{Heating}$**	**R_s (°C)**	**R_f (°C)**	**M_s (°C)**	**M_f (°C)**	**ΔH(J/g)$_{Cooling}$**	**H_t (°C)**
H	51.2	63.5	10.3	-	-	31.2	19.6	10.9	32.3
R	44.0	60.1	13.4	33.8	20.4	20.4	2.5	14.7	39.7
RA	48.1	62.9	15.0	-	-	34.6	19.8	13.4	28.3
E	8.5	29.3	17.2	21.6	-7.1	-7.1	-42.8	18.2	36.4
EA	26.8	42.4	17.0	31.3	14.0	-15.4	-35.5	16.0	57.8

In the figure 2e, the calorimetric curve of the extruded and annealed sample (ER) shows a complete separation between the peaks of the R phase and of the martensitic phase, with a temperature interval between peaks of about 45°C (temperature interval = $R_{50\%}$ - $M_{50\%}$). After annealed heat treatment, the temperature of the R phase (R_S) rises to about 30°C, i.e. it returns to the value of the standard sample (H). The R_F temperature in this sample is easily determined to 14°C and the thermal hysteresis of the R phase is 16.1°C. The M_S temperature decreased to -15.4°C and M_F to -35.5°C, generating a thermal hysteresis in the martensitic phase of 20.1°C. Thus, the M_S temperature decreased about 8°C relative to the extruded sample. This heat treatment was able to restore the R_S temperature of the phase R, in this way, it was effective to eliminate (or minimize) the effects of angular extrusion process in this crystal structure. For martensitic phase, this treatment has become ineffective or even complicates the process to initiate the transformation.

Figure 3 shows the thermomechanical cycling curves of the Ni-Ti samples in the bending tests under constant load. Table 3 summarizes the results obtained in these tests. The maximum reversible thermoelastic deformation was 4.5 mm for the homogenized sample. In the calorimetric tests, the critical temperatures of phase transformation of the rolled sample (R) returned to be pretty much the same ones obtained for the reference sample (H) after annealed thermal treatment. However, this treatment was not sufficient to restore the reversible thermoelastic deformation obtained in the reference sample, since the maximum value obtained for the annealed sample was of 2.21mm. From the table 2, which shows the results of the calorimetry, it can be seen that the enthalpies of transformation does not return to the values of reference sample (H). From the results of thermoelastic tests, it can be claim that this treatment has not been able to eliminate all the effects of the rolling process.

The extruded sample practically did not show any thermoelastic deformation. This was probably due to limitation of the thermal bath, which has a minimum temperature of -10, and also by blocking of transformation due to large increase in dislocation density. When an external stress is applied to a shape memory alloy promotes the increase of the critical transformation temperatures. Apparently, the load applied was not sufficient for these temperatures to increase sufficiently to be detected by the device. The extruded and annealed sample showed only a recovery deformation of 0.7 mm, i.e. not reached 25% of the value obtained by the deflection reference sample, indicating a high degree of hardening.

Figure 4a shows a micrograph of the rolled sample. The grains have become elongated in the direction of the lamination process. The arrows in the micrograph indicate the direction of lamination. Figure 4b shows the micrograph of the extruded sample. Unlike the laminated sample, the grains are rounded and without preferred orientation. The micrographs of rolled and extruded samples show that the latter process produces grains without preferential orientation. Probably, the configuration of the stress fields generated by the increased dislocation density must be highly disoriented. These facts seem to be responsible for the greatest loss of thermoelastic properties in the extruded samples.



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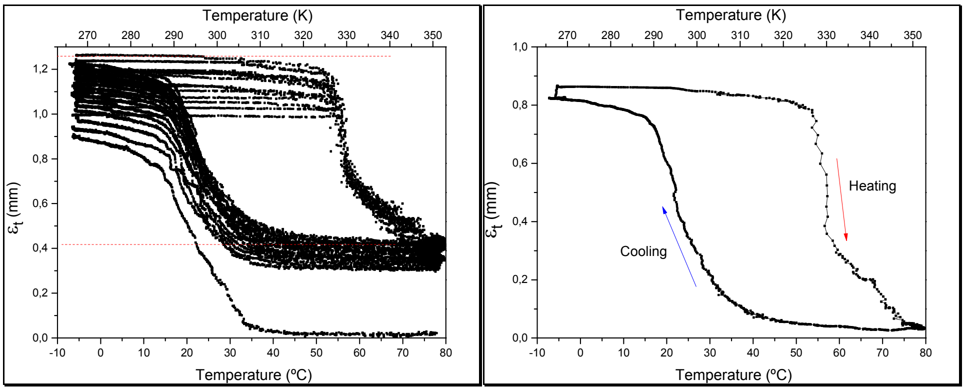

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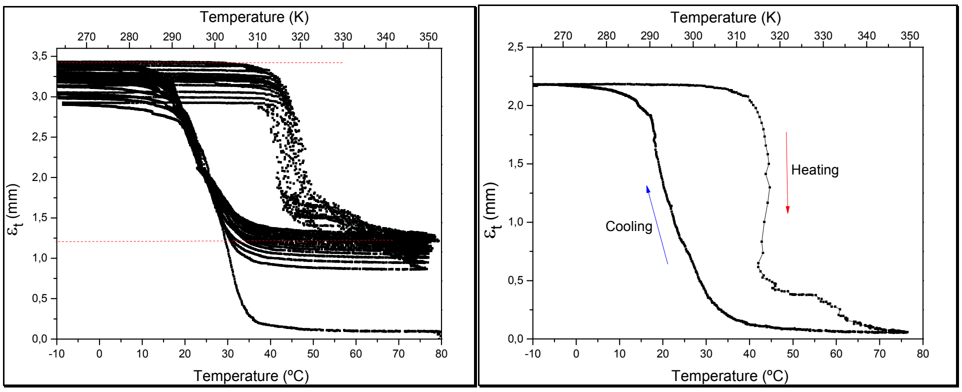

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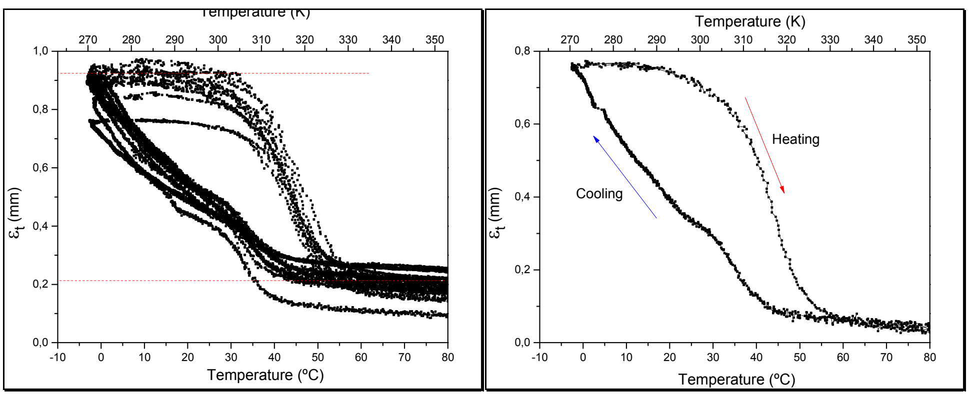
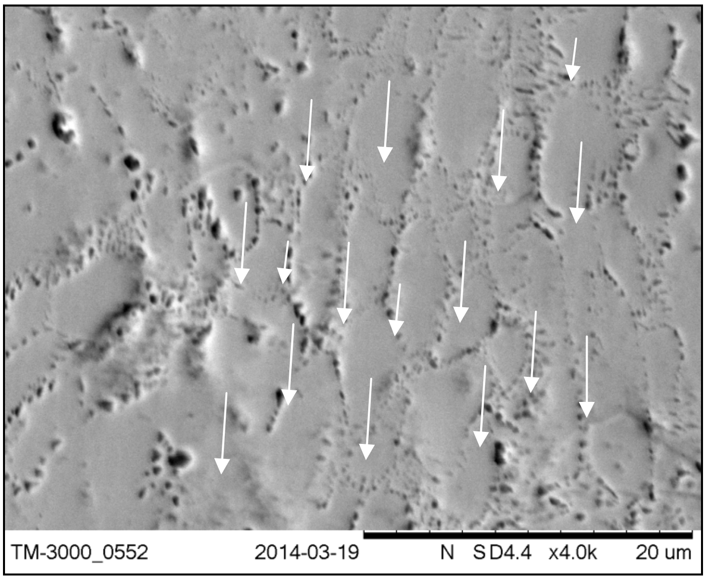


d)

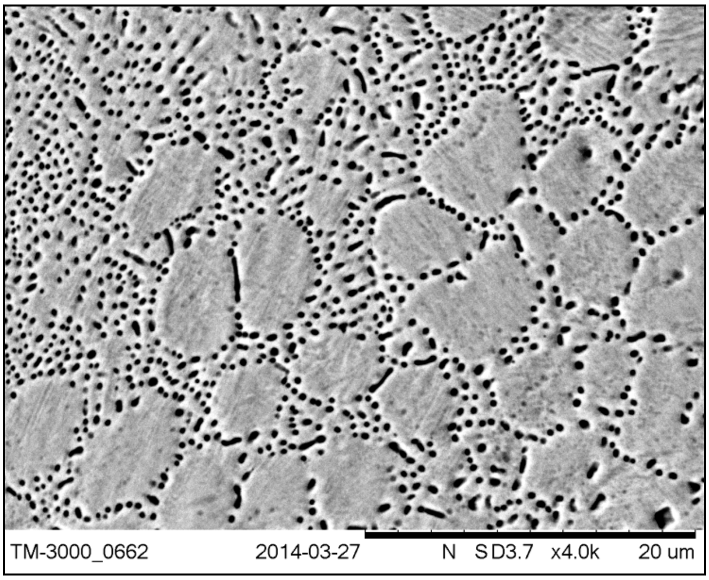
Figure 3. Thermomechanical cycling curves of the Ni-Ti alloy in the conditions: a) Homogenized (H), b) Rolled (R), c) Rolled and Annealed (RA), d) Extruded and Annealed (EA).

Table 3. Results of the thermomechanical cycling curves of the Ni-Ti samples.

Sample	Rs (ºC)	$R_f = M_s$ (ºC)	M_f (ºC)	A_s (ºC)	A_f (ºC)	ε_t (mm)
H	-	26.5	15.1	44.9	49.8	4.50
L	-	33.2	12.6	53.2	74.6	0.86
LR	-	30.9	15.1	42.9	50.2	2.21
E	-	-	-	-	-	0.09
ER	41.7	29.1	-2.6	33.2	50.8	0.74



a)



b)

Figure 4. SEM micrographs of samples: a) Rolled and b) Extruded.

4. CONCLUSION

The plastic forming processes by lamination and angular extrusion promoted increased mechanical resistance of samples due to the reduction of the grain size caused by shear stress during plastic deformation and introducing defects in the crystalline structure. These processes have significantly affected the thermoelastic behaviour of the shape memory alloy. Although one cannot compare directly (quantitatively) the influence of the two processes on the properties of shape memory, but it became evident that the process of angular extrusion seems to be much more effective in hardening of sample.

The results of the calorimetry curves when compared with data curves under constant load tests are complementary. The critical phase transformation temperatures of the samples were reduced by plastic deformation processes, since there is a higher need of energy to perform the transformations.

The micrographs of rolled and extruded samples show that the latter process produces grains without preferential orientation. Probably, the configuration of the stress fields generated by the increased dislocation density must be highly disoriented. These facts seem to be responsible for the greatest loss of thermoelastic properties in the extruded samples.

In the technological applications of the SMA is important to take into consideration the fact that the increased mechanical strength is achieved at the expense of reduced transformation temperatures and of the thermoelastic properties of the shape memory effect, and may be recovered partly by heat treatment.

5. ACKNOWLEDGEMENTS

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