Characterization of TiNi shape memory alloys obtained by spark plasma sintering process

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This paper presents the research results on the thermal behavior of the 48.5%at.Ti-Ni alloys, obtained by spark plasma sintering in vacuum under a pressure of 50 MPa, at temperatures of 850ºC and 900ºC and holding time of 5 minutes, and subsequently aged in argon for up to 30 minutes at 450ºC. Differential scanning calorimetry, dynamic mechanical and dilatometry analysis were used to characterize the transformation properties of the TiNi samples. All the results of differential scanning calorimetry and dynamic mechanical analysis confirmed the hypothesis that the stress-free thermally induced martensitic transformation exists in the investigated TiNi alloys. Annealing at lower temperatures (450ºC) in Ni-rich TiNi alloys led to precipitation process which facilitates the formation of the R-phase due to internal stress contributed by precipitates.

1. Introduction

The shape memory alloys (SMA) like TiNi show the best functional properties and occupy most of the world market. The use of TiNi shape memory alloys in old and new applications relies in obtaining enough stability of the functional properties, and the capacity to adapt to customer-required transformation characteristics. TiNi are the advanced materials that present mechanical responses due to thermal fields [1]. The property of recovering a plastic deformation by means of a suitable heating is one of the reasons why TiNi are widely applicable, besides the pseudoelasticity, impact absorption and vibration damping behavior [2]. As for the other requirements, production of TiNi by powder metallurgy technologies offers an opportunity to obtain near-net shape products while maintaining good mechanical properties. The TiNi shape memory alloys can also be obtained by other several methods.

At an industrial level, the Spark Plasma Sintering (SPS) is a new technique which takes only a few minutes to complete a sintering process compared to conventional sintering like melting in vacuum arc furnace (VAR), vacuum induction melting (VIM), self-propagating high temperature synthesis (SHS), hot isostatic pressing (HIP) which may take hours or even days. This high sintering rate of 100...600^{0}C/min is possible in SPS since it can be easily attained due to internal heating of the sample as opposed to external heating seen in case of conventional sintering. Also, sintering time is reduced in SPS due to small holding time at sintering temperature, while in conventional sintering it may extend to hours [3-5].

In the last years, SMA have attracted an increasing attention due to their superior damping properties compared to classical structural materials [6-10]. Because the utilization of TiNi is likely to depend largely on reliable property reproducitibility, it is essential that the factors affecting the properties be suitably controlled *[11]*. Thus the most of the properties of interest are directly related to the martensitic transformation. Near equiatomic binary phase, TiNi materials show on cooling a one-stage or two-stage thermoelastic martensitic transformation between the austenite phase (A) and the martensite phase (M) called martensitic transformation.

In this study the results concerning the evolution of the transformation behavior before and after annealing of 48.5%atTi–Ni obtained by SPS are reported and discussed in terms of the thermal aspects.

2. Experimental procedures

The TiNi alloys were obtained by spark plasma sintering from separate, very fine powders mixtures Ni (Merck, 10 μm particle size), Ti (Merck, 150 μm particle size) previously processed by mechanical homogenization. The mechanical homogenization was done in a glove box in argon protective atmosphere. After that, to obtain different structural states, exhibiting different microstructures characteristics, the TiNi powders mixtures were processed by SPS. The rectangular samples with dimensions of 40x40mm and height of 4-5 mm were obtained by SPS in vacuum by preheating at 450^{0}C with a heating rate of 100^{0}C/min and uniaxial pressing with 50

MPa for 5 minutes at two sintering temperatures of 900^{0}C (A4 sample) and 850ºC (A5 sample) and holding time of 5 minutes. The annealing of TiNi shape memory alloys for up to 30 minute at 450^{0}C was performed in a tubular furnace under argon flux followed by water quenching at

room temperature to achieve martensitic transformation (A 4T and A 5T samples). The technological flux for TiNi materials obtained by SPS and thermal characterization steps are presented in figure 1.
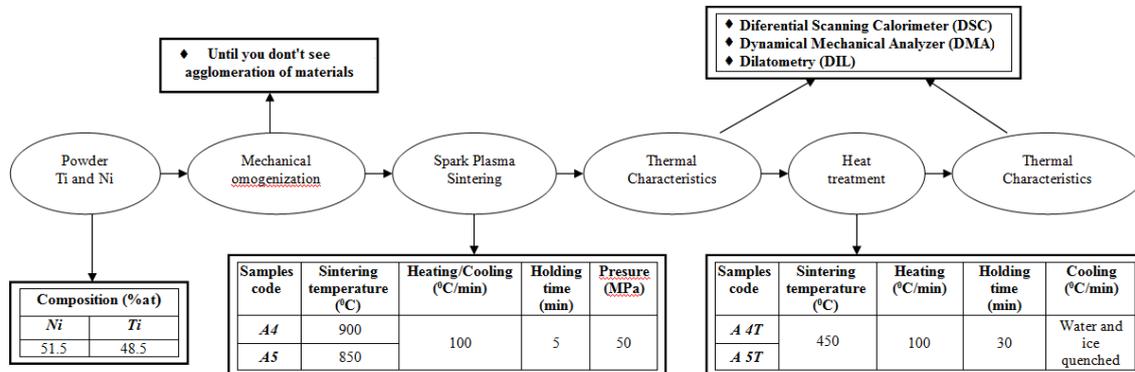
Fig. 1. Technological flux for TiNi materials obtaining by SPS and thermal characterization steps

Differential scanning calorimetry (204 F1, Netzsch), dynamic mechanical analysis (Q800 equipment TA Instruments, USA) and dilatometry (Linseis 75 Platinium Series) were used to characterize the phase transformation of the TiNi samples.

Differential scanning calorimetry (DSC) measurements were performed on samples with average weight of up to 5 mg, encapsulated in aluminum pans, to determine the phase transformation temperatures before and after annealing treatments. The cooling/heating rate was 5 K/min, at 250^{0}C.

Dynamic mechanical analysis (DMA) experiments were carried out in extension mode with 20μm amplitude and 1Hz frequency and 1^{0}C/min time for data acquisition. From the TiNi samples small beam specimens with dimensions of 40 mm x 5 mm x 0.4 mm were manufactured to perform the DMA tests. For DMA experimental characterization of TiNi samples, a heating rate of 5 K/min at 150^{0}C in air is required.

The dilatometry (DIL) measurements, were done from room temperature to 250^{0}C, using a 5 K/min heating and cooling rate for TiNi cylindrical form with 3 mm inside diameter and 12 mm length. For all the DMA and DIL measurement a constant force of 250 mN it was applied.

3. Results and Discussion

3.1. Temperature transformation characteristics

Fig. 2 shows the DSC curves of the tested alloys. DSC curves for the samples obtained by SPS at 850ºC and 900ºC show a small endothermic and exothermic peak A→M, M→A respectively for both samples (A4 and A5). The values of phase transformation of TiNi shape memory alloys depend on the manufacturing processes.
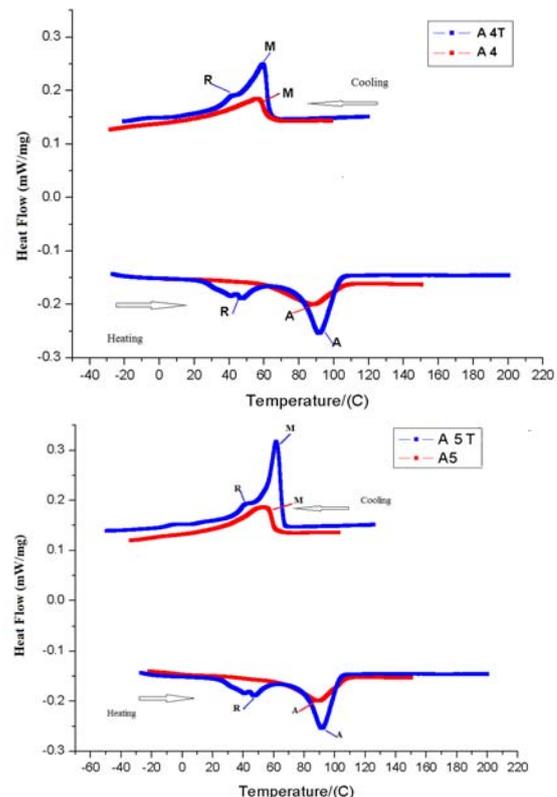
Fig. 2. DSC for A4 and A5 after heat treatment

After applying the heat treatment observed in A 4T and A 5T samples it was that the heat flow peaks show on the whole heating and cooling cycle a clear symmetrical transformation. While examining the scans on cooling/heating, we see an incipient R-phase transformation. This can be attributed to the fact that the composition fluctuated in the specimen because of insufficient mixing of powders or rapid heating/cooling rate of SPS. The TiNi materials show the transformation sequence A↔ R↔ M on cooling and heating after

annealing, with a small increase of the martensitic transformation temperature and a narrowing of the temperature range. This led to precipitation processes or crystallographic defects, as it is possible to be in A4T and A5T. Other papers report the same phenomenon [6,7,12-15], for materials with the same composition as ours, but produced by methods other than SPS, such as vacuum induction melting or thin films obtained by pulsed laser deposition technique (PLD), especially for melt spinning which involve rapid solidification [15, 16]. Crystallographic defects are thought to be introduced to depress the A→M transformation, and led to the A→R transformation. These processes appear when the melt spinning method is used for the fabrication of TiNi materials [15]. Also the precipitation of excess nickel from the TiNi matrix during the 450^0C annealing treatment produced a change in the transition temperatures of this alloy. The transformation start temperature on heating was as low as 35^0C and as high as 100^0C depending on the nickel content of the matrix due to the process condition of SPS (see tabel 1). The transition and inflection in the DSC curves (figure 2) for 30 minute during annealing at 450^0C represent a change in the rate of formation of a particular structure, the (R-phase), owing to the cumulative effect resulted from the composition and stresses generated by precipitation and crystallographic defects during heating or cooling annealing. The stresses associated with the precipitates appear to be sufficient to cause a decrease of the start and finish martensite temperature (M_s, M_f), respectively start and finish of the austenite temperature (A_s, A_f). Another consequence of forming precipitates phases instead of TiNi phase are the decrease of the heats of formation of the A↔M martensitic transformation that are ~ 3.5 J/g for A4T and ~ 3 J/g for A5T. Typical values found in literature [5, 15, 17, 18] are 3 to 12 J/g similar to our results. The decrease of the temperatures of transformation confirms that the precipitation phase caused an increase in the nickel content within the matrix [17,19].

Table 1. Transformation temperatures determined from DSC (^{0}C)

		M_s or R_s	M_s	M_f	R_f or A_s	A_s	A_f
SPS samples	A4		59	38		70	100
	A5	-	60	35	-	65	105
Heat treated samples	A4-T	51 to 62	-	39	29 to 60	-	100
	A5-T	42 to 68	-	40	30 to 75	-	103

3.2 DMA analysis

In order to examine the damping capacity of TiNi alloys, dynamic mechanical analysis was employed to record their Tan Delta versus temperature change. In figure 3a it was observed a change of damping peak for two regions at around 0.01 and 0.005 Tan Delta for the A4T and A4 samples. Thus between 30ºC and 60ºC, it was obtained a medium Tan Delta of 0.009 and corresponds to the damping capacity produced by R-phase or the M martensite phase while, between 60ºC and 110ºC there are increases in damping capacity due to the phase transformation of the martensite into austenite. In the case of A5 and A5T samples (figure 3b), only after annealing it was observed a change in the graphic and values of Tan Delta are around 0.004 and 0.012 respectively.

Also phase transition temperatures to the correspond start and finished R-phase temperature transformation (R_s and R_f) and start and finished austenite temperature transformation (A_s and A_f) were determined from the spectra of elastic modulus by using a DMA tests. The results are presented in Table 2. The critical values of the M→A or M→R→A transformation temperatures were in accordance with the DSC analysis and are almost similar to those for shape memory alloys thin films obtained by pulsed laser deposition technique [17, 20, 21].

Table 2. Transformation temperature determined from DMA (^{0}C)

		$R_s(^0C)$	$R_f(^0C)$	$A_s(^0C)$	$A_f(^0C)$
SPS samples	A4	-	-	84.8	95.6
	A5	-	-	72.7	93.3
Heat treated samples	A4T	65	50.7	87.4	97.8
	A5T	60.6	48.9	82.6	96.4

The storage moduli for the A4 sample are 11 GPa and increasing after annealing up to 41 GPa (A4T). The same increase it was obtained for the A5 sample where the storage moduli are 39.5 GPa and up to a value of 43 GPa respectively for A 5T sample. This variation of storage modulus with temperature can be correlated with the phase transition dilatometry results presented below.
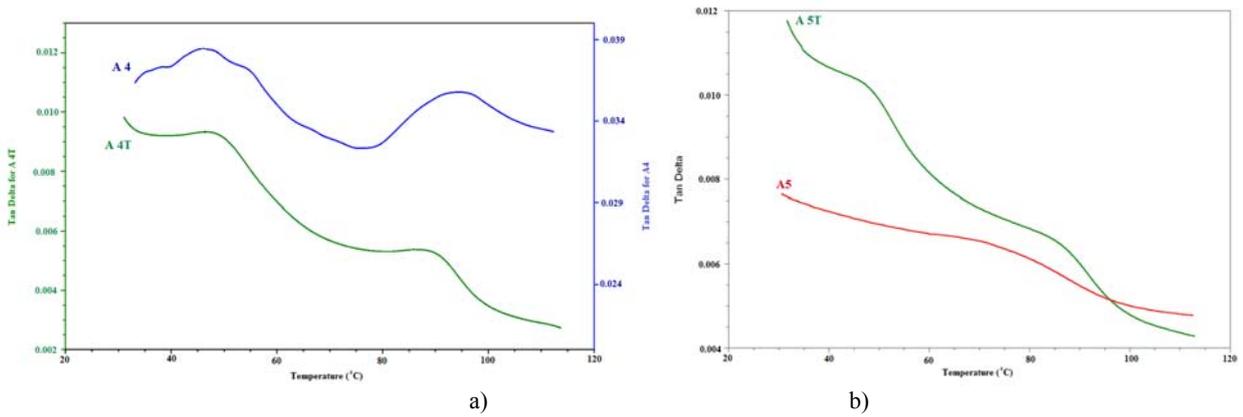
Fig. 3. Damping capacity (Tan Delta) versus temperature for A4 and A 4T (a); A5 and A5T (b) samples.

a)

b)
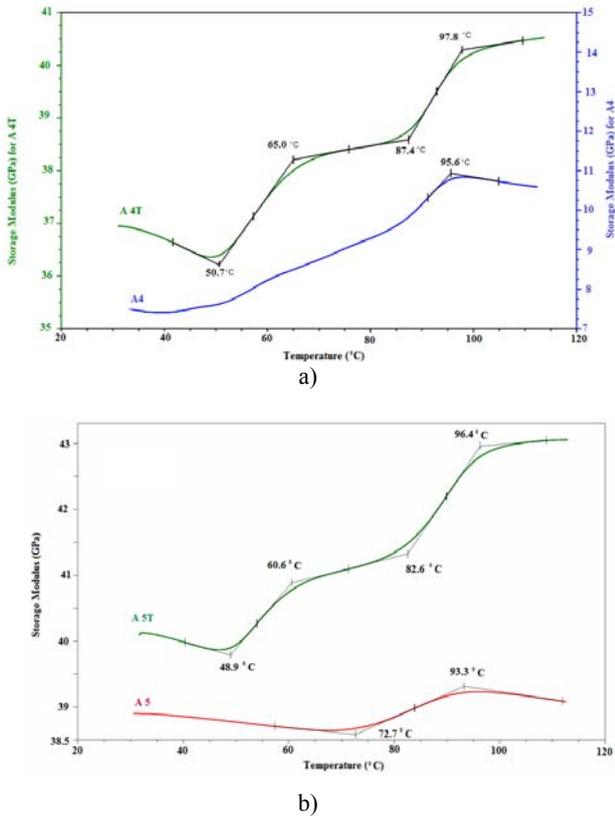
Fig. 4. Storage modulus versus temperature for A4 and A4T (a); A5 and A5T (b) samples

3.3. Dilatometry analysis

Fig. 5 shows the temperature dependence of relative linear thermal expansion of the TiNi samples. For A4 and A5 samples we found a change in dilatation during M→A transformation more than 0.7% within a temperature difference of 40^0C. When the materials are heated from room temperature to 200°C, it was observed a large increase of the linear thermal expansion up to 130°C and

decrease after 130^0C temperature due to an increase of the grain size and as a result the observed contraction decreases (figure 6). Also the linear thermal expansion of the materials showed an expansion in the 50-100^{0}C region due to the combined thermal and internal stress for A 4T and A 5T. From literature it is found that the precipitation in TiNi based alloys plays an important role in phase transition behavior A→ R→ M [22].

a)

b)
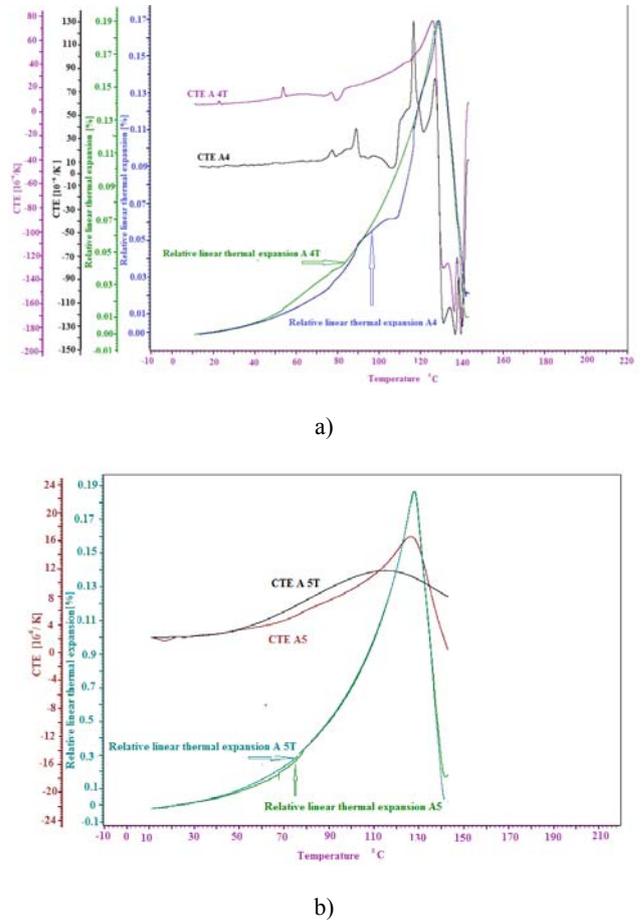
Fig. 5. Variations with temperature of relative thermal expansion in time and thermal expansion coefficient (CTE) for TiNi materials

The coefficient of thermal expansion (CTE) increases with the increase in temperature, from 50 to 130°C (Table 3). Also, negative values are observed for coefficient of thermal expansion for A4 and A 4T samples which point to the fact that tensile recovery stresses can occur when the materials are heated and constrained at constant force [8,10,23]. This tensile stress caused the M→R→A transformation and apparition of the precipitate particles, which displays low and nonlinear thermal expansion values in temperature range from room temperature to 250^0C [27]. This fact is possible due to R-phase transformation that is observed before the M→A transformation. Also, due to the R-phase transformation, these alloys can be used for devices such as thermal actuators, where a small temperature hysteresis and reliability are required [23, 25-28]. These values are consistent with those obtained by F. Cardarelli [13].

Table 3. Result of coefficient thermal expansion

Temperature (C)	140.1	138.5	136.6	134.1	131.1	127	116.7	114.5	109.9	106.4	99.3	91.4	88.9	83.9	79.1	77.4	74.5	A 4
CTE (10^{-6})/K	-134.1	-93.6	-141.4	-118.2	-131.5	76.6	124.8	51.9	40.1	0.6	9.8	10.1	34	16.6	10.5	15.4	9	
Temperature (C)	139.6	137.7	136.2	133.2	125.8	114.6	83.9	79.6	76.9	55.4	53.6	52.3						A 4T
CTE (10-6)/K	-188.3	-127.9	-171.4	-131.2	71.6	37.4	15.2	5	11.4	8.7	16	7.4						
Temperature (C)	142.1	134	126.6	106.1	89.6	83.3	76.9	20.5	16.1	12.2								A5
CTE (10-6)/K	0.6	9.7	16.2	9.9	7	6.2	5.2	1.7	1.3	1.7								
Temperature (C)	142.8	134.1	116.1	53.9	32.9													A 5T
CTE (10-6)/K	7.6	9.3	11.3	3.4	2													
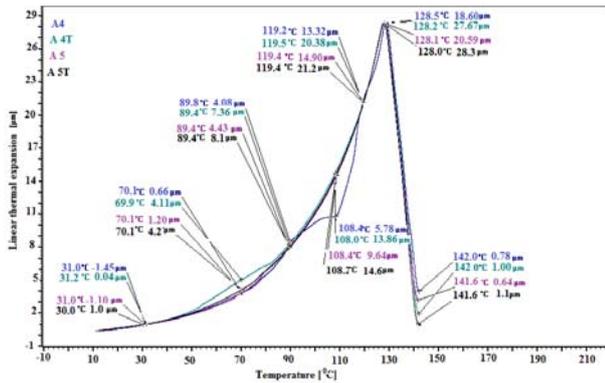
Fig. 6. Linear thermal expansion for TiNi shape memory alloys

4. Conclusions

TiNi samples are prepared by powder metallurgy technology combined with SPS and annealing treatment. All the results of TiNi samples confirmed the hypothesis that the stress-free thermally induced martensitic transformation appears in these alloys. Annealing at lower temperatures (450^0C) in Ni-rich TiNi alloys allowed the formation of the R-phase due to internal stress induced by precipitates. The DSC analysis confirms the presence of the martensite transformation in these materials. An increase of storage modulus with the increasing the temperature of sintering from 850^0C at 900^0C was observed, especially after applying the annealing treatment at 450^0C. Also it was observed that the TiNi shape memory alloys presents a peak of damping more pronounced for A4 and A 4T that is associated to martensitic transformation and is more than 0.7% .

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