Textural Evolution by Multiple Steps of Marforming in Ti-Rich Ni-Ti Shape Memory Alloy

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Abstract. The Nickel-Titanium (Ni-Ti) alloys are the most attractive amongst shape memory alloys (SMA) due to their good functionality properties coupled with high strength and good ductility. The transformation temperatures in Ti-rich NiTi SMA can be altered with suitable thermal and/or mechanical treatments to obtain martensitic transformation in one or more steps above 0°C. The goal of the present work is to investigate the textural evolution in Ti-Rich Ni-Ti SMA (Ni-51at%Ti) that will contribute to different phase transformation sequences (one, two and multiple steps) after being subjected to (i) two distinct thermal treatments (500 °C for 30 minutes in air and 800°C for 300 minutes in vacuum), (ii) followed by multiple steps of marforming (30% thickness reduction by cold rolling), intercalated with thermal treatment at 500°C for 30 minutes in air and (iii) four distinct final thermal treatments (400, 450, 500 or 600°C for 30 minutes in air). The textural results were obtained by X-Ray Diffraction (XRD) at room temperature (B19' phase) and at 150°C (B2 phase). Differential Scanning Calorimetry (DSC), Electrical Resistivity (ER) and X-Ray Diffraction (XRD) were used to identify the transformation temperatures and the phases that are present after all steps of thermomechanical treatments.

1. Introduction

In most of the polycrystalline materials, crystal orientations are present in a definite pattern and a propensity for this occurrence is initially caused during crystallisation from the melt or amorphous solid state and subsequently by thermomechanical processes. This tendency is known as preferred orientation or, more concisely, the texture. Many material properties (Young's modulus, Poisson's ratio, strength, ductility, toughness, electrical conductivity etc.) depend on the average texture of a material.

The transformation temperatures in Ti-rich NiTi SMA can be altered with thermal [3,4] and/or mechanical [5,6] treatments adequate to obtain martensitic transformation in one or more steps above 0°C [1,2]. Heat treatment can promote the nucleation and growth of Ti₂Ni precipitates. Ti₂Ni precipitates can disturb or impede the growth of martensite plates [7].

Several studies are dedicated to understand the influence of the texture on thermomechanical response of the SMAs [8-17]. Thermal cycling and mechanical working are found to develop specific texture in metals and alloys. They result in different anisotropy characteristics (mechanical, electrical and magnetic behaviour). NiTi SMAs are also sensitive to these effects. The texture is found to give rise to anisotropy in transformation recovery strain [10]. NiTi SMA in austenitic field has a bcc type texture [13,14]: α -fiber I $\langle 110 \rangle \parallel \text{RD}$ ($\{001\} \langle 110 \rangle$ - $\{112\} \langle 110 \rangle$ - $\{111\} \langle 110 \rangle$), α -fiber II $\langle 110 \rangle \parallel \text{RD}$ ($\{111\} \langle 110 \rangle$ - $\{110\} \langle 110 \rangle$), γ fiber $\langle 111 \rangle \parallel \text{ND}$ ($\{111\} \langle 110 \rangle$ - $\{111\} \langle 112 \rangle$), and η -fiber $\langle 100 \rangle \parallel \text{RD}$ ($\{001\} \langle 100 \rangle$ - $\{011\} \langle 100 \rangle$). The calculated lattice correspondence between parent phase and martensite using the notation of the correspondence variant from Miyazaki, where $\{110\} \langle 110 \rangle$ parent phase variant corresponds to $\{111\} \langle 211 \rangle$ and $\{002\} \langle 002 \rangle$ martensite variants; and $\{111\} \langle 110 \rangle$ parent phase corresponds to $\{210\} \langle 211 \rangle$ and $\{210\} \langle 002 \rangle$ [8].

In the present work, we have investigated how the multiple steps of marforming thermomechanical treatment in Ni-Ti SMA can affect the final crystallographic texture.

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2. Materials and Methods

The samples for the present study were extracted from straight annealed Ti-rich NiTi alloy (Ni-51.0at%Ti) plate of thickness 2mm supplied by Memory-Metalle GmbH, Germany. The as-received (AR) samples were subjected to the series of the following thermal/mechanical processes. Initially, the separate samples were subjected to two distinct thermal treatments (500°C for 30 minutes in air and 800°C for 30 minutes in vacuum, HTA and HTV, respectively), followed by multiple steps of marforming (30% thickness reduction by cold rolling), intercalated with thermal treatment at 500°C for 30 minutes in air. Finally, all the samples were thermally treated at four distinct temperatures (400, 450, 500 and 600°C for 30 minutes in air). The HTV was performed by heating the specimen at the rate of 3°C/s, holding at 800°C for 30 minutes and subsequently cooling at the rate of 3°C/s up to T_{room} . The samples were subjected to chemical etching (10% vol HF + 45% vol HNO₃ + 45% vol H₂O), in order to remove the oxide layer, as well as the layer deformed during the cutting operation.

Samples with a mass ranging from 40 to 50mg were cut from all specimens for DSC analysis (SETARAM DSC92). The following thermal cycle was used for the DSC tests: start temperature at T_{room} , heating to 180°C, holding for 360s and subsequent cooling down to -30°C, with heating and cooling rates of 7.5°C/min.

ER characterisation has been performed by using the home made four-probe set up, which was immersed together with the sample in a silicone oil bath with a temperature control system. It consists of a block of 4 copper rods with wedge-shaped tips. The position of the rods, as well as the pressure that they exert on the test specimen, is individually controlled. A controllable power supply is used to apply the current (1660 mA) into the test specimen. Data acquisition board (National Instruments, USA) with a precision better than 1 μ V was used to obtain the signal and to interface with a PC. Samples were scanned in the temperature range from -20 to 150°C.

XRD analysis was performed using a Bruker diffractometer (rotating anode – XM18H, CuK α radiation, 30 kV/100 mA, D5000 goniometer) with texture analysis at T_{room} (B19' phase) and 180°C (B2 phase). The rolling direction (RD) was kept aligned in $\phi = 0^\circ$ and the transversal direction (TD) in $\phi = 90^\circ$.

3. Results and Discussion

Figs. 1, 2, and Table 1 show the evolution of the transformation temperatures and the transformation sequence, respectively, for the separate samples undergone HTA and HTV followed by four steps of marforming + thermal treatments. Figs. 1a & 2a and Figs. 1b & 2b represent the data of the specimens initially subjected to HTA and HTV, respectively.

Fig. 1. Evolution of transformation temperatures, extracted from DSC curves of the specimens after thermal/mechanical (multiple steps of marforming) treatments: (a) HTA, and (b) HTV.

Based on the DSC (Fig. 1) and ER (Fig. 2) results, independent from the initial thermal treatments (HTA and HTV), it is observed that in both the cases, there is a clear tendency for the increase of the transformation temperatures of B19' (M'_s & M'_f (B2→B19'), or M''_s & M''_f (R→B19')) and B2 (A_s & A_f (B19'→B2)) phases with increasing annealing temperatures during the final thermal treatments. R-phase transformation occurs for the samples annealed up to 450°C, during the final thermal treatments. For the sample thermal treated at 400°C, there exist a clear separation between the transformation temperatures of B2→R (R_s and R_f) and R→B19' (M''_s and M''_f). In the present set of study of the samples subjected to series of thermal/mechanical treatments, with respect to the observed phase transformation steps, there can be three distinct behaviour subgroups [18-21]. For the final thermal treatment temperature at 400°C the highly deformed

structure partially recrystallise, giving rise to a two-steps transformation on cooling: $B2 \rightarrow R$ and $R \rightarrow B19'$. On heating, the transformation apparently occurs by one step ($B19' \rightarrow B2$).

Table 1. Transformation Temperatures and Sequences extracted from DSC and ER results.

Samples Conditions	Transformation Temperature (°C)							
	On cooling						On heating	
	$B2 \rightarrow R$		$R \rightarrow B19'$		$B2 \rightarrow B19'$		$B19' \rightarrow B2$	
	R_s	R_f	M_s''	M_f''	M_s'	M_f'	A_s'	A_f'
HTA+TMT400	65,8	53,9	47,9	25,1	-	-	66,7	87,7
HTV+TMT400	65,2	52,4	45,9	22,4	-	-	63,1	86,0
HTA+TMT450	67,1	*	*	*	*	47,5	78,9	96,1
HTV+TMT450	68,9	*	*	*	*	47,3	75,9	99,7
HTA+TMT500	-	-	-	-	74,8	55,6	82,2	106,0
HTV+TMT500	-	-	-	-	72,8	54,9	87,6	112,0
HTA+TMT600	-	-	-	-	81,2	59,4	88,2	116,4
HTV+TMT600	-	-	-	-	80,5	54,4	88,6	117,5

“s” – 1% transformed; “f” – 99% transformed; “-” – non-detected; “*” – undefined.

Fig. 2. Evolution of sequence transformation and transformation temperatures represented by ER curves of the specimens after thermal/mechanical (multiple steps of marforming) treatments: (a) HTA, and (b) HTV.

Figs. 3, 4, 5 and 6 show the texture results for the thermal/mechanically treated samples (multiple steps of marforming + thermal treatments) with final thermal treatments at 400, 450, 500 and 600°C, respectively.

Figs. 3a,b, 4a,b, 5a,b and 6a,b show the pole figures $(11\bar{1})_{B19'}$ for the thermal/mechanically treated samples with final thermal treatment at 400, 450, 500 and 600°C, respectively. It is possible to identify the samples which have undergone similar thermal treatments (HTA or HTV) during the first stage. It is observed that the specimens subjected to similar thermal treatments have the same texture components. The reinforcements increase with increasing thermal treatment temperatures. Further, for both sample groups (HTA+TMT and HTV+TMT), a crescent increase in the central texture component contribution in parallel with a decrease of the texture components close to $\chi=45^\circ$ shows a trend to increase with increasing annealing temperature. In the martensitic state, the central reinforcements are associated to the $1:(11\bar{1})[2\bar{1}1]_{B19'}$ and $4:(11\bar{1})[\bar{2}1\bar{1}]_{B19'}$ texture variants related to $\{110\}<110>_{B2}$ and the reinforcement close to $\chi=45^\circ$ are associated to the $2:(10\bar{2})[211]_{B19'}$, $4:(10\bar{2})[\bar{2}1\bar{1}]_{B19'}$ and $6:(10\bar{2})[0\bar{2}0]_{B19'}$ texture variants related to $\{111\}<110>_{B2}$, that are more intense in the sample group HTA+TMT [19-21].

Figs. 3c,d, 4c,d, 5c,d and 6c,d show the pole figures $(110)_{B2}$ for the thermal/mechanically treated samples with final thermal treatment at 400, 450, 500 and 600°C, respectively. In the austenitic state, central reinforcements are associated to the $(110)[110]_{B2}$ texture component. However, the reinforcement close to $\chi=45^\circ$ is associated to the $\{001\}<110>_{B2}$ texture components only present in the sample group HTA+TMT and in the condition HTV+TMT600. In the sample group HTV+TMT, with the final thermal treatment above 600°C, the reinforcement close to $\chi=45^\circ$ is associated to the $\{111\}<110>_{B2}$ texture components [19-21].

Fig. 3. Pole Figures (a,b) $(11\bar{1})_{B19'}$ and (c,d) $(110)_{B2}$ for the thermal/mechanically treated samples (multiple steps of marforming) with final thermal treatment at 400°C samples and previous thermal treatment: (a,c) HTA; (b,d) HTV.

Fig. 4. Pole Figures (a,b) $(11\bar{1})_{B19'}$ and (c,d) $(110)_{B2}$ for the thermal/mechanically treated samples (multiple steps of marforming) with final thermal treatment at 450°C samples and previous thermal treatment: (a,c) HTA; (b,d) HTV.

Fig. 5. Pole Figures (a,b) $(11\bar{1})_{B19'}$ and (c,d) $(110)_{B2}$ for the thermal/mechanically treated samples (multiple steps of marforming) with final thermal treatment at 500°C samples and previous thermal treatment: (a,c) HTA; (b,d) HTV.

Fig. 6. Pole Figures (a,b) $(11\bar{1})_{B19'}$ and (c,d) $(110)_{B2}$ for the thermal/mechanically treated samples (multiple steps of marforming) with final thermal treatment at 600°C samples and previous thermal treatment: (a,c) HTA; (b,d) HTV.

4. Conclusions

After the initial thermal treatments followed by multiple steps of marforming + thermal treatments for the Ti-rich Ni-Ti SMA, it was possible to obtain:

- three groups of phase transformation sequences with respective finish transformation temperatures (for martensitic and austenitic transformations): (i) $B2 \rightarrow R \rightarrow B19'$ and $B19' \rightarrow B2$ for the samples with the final thermal treatment at 400°C (HTA+TMT400 and HTV+TMT400); (ii) $B2 \rightarrow R$, $B2 \rightarrow B19'$, $R \rightarrow B19'$ and $B19' \rightarrow B2$ for the samples with the final thermal treatment at 450°C (HTA+TMT450 and HTV+TMT450); and (iii) $B2 \leftrightarrow B19'$ for the samples with the final thermal treatment above 500°C (HTA+TMT500, HTA+TMT600, HTV+TMT500 and HTV+TMT600);
- a maximization of the central reinforcement intensity close to the $(110)[110]_{B2}$ and a decrease of the secondary reinforcement intensity close to the components associated to $\{001\} \langle 110 \rangle_{B2}$, in other words, a mixture of α -II and α -I fibers.

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