JMEPEG (2011) 20:771–775
DOI: 10.1007/s11665-011-9920-5

1059-9495/$19.00

Stability in Phase Transformation After Multiple Steps of Marforming in Ti-Rich Ni-Ti Shape Memory Alloy

Andersandos Santos Paula, Karimbi Koosappa Mahesh, and Francisco Manuel Braz Fernandes

(Submitted May 15, 2010; in revised form February 14, 2011)

Nickel-titanium (Ni-Ti) alloys are the most attractive among shape memory alloys (SMA) due to their good functionality properties coupled with high strength and ductility. The transformation temperatures in Ti-rich Ni-Ti SMA can be altered by subjecting them to 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 stability of phase transformation characteristics, such as, type of sequence (one, two, and multiple steps) and transformation temperatures in Ti-Rich Ni-Ti SMA (Ni-51 at.%Ti), after being subjected to an initial heat treatment at 500 °C for 30 min in air followed by multiple steps of marforming (cold rolling, 30% thickness reduction) intercalated with heat treatments at 500 °C for 30 min in air and a final heat treatment at four different temperatures (400, 450, 500, and 600 °C) for 30 min in air atmosphere. Differential scanning calorimetry (DSC) and electrical resistivity (ER) were used to identify the phase transformation sequences and the stability of transformation temperatures during initial 10 thermal cycles for each sample with distinct thermo-mechanical treatment.

Keywords marforming, phase transformation stability, shape memory alloy, Ti-rich Ni-Ti alloy

1. Introduction

Thermomechanical treatments of Nickel-titanium (Ni-Ti) shape memory alloys (SMA) are important for the optimization of the mechanical properties and phase transformation characteristics. Although a large number of references may be found for the thermal and mechanical processing of Ni-rich Ni-Ti SMA, the Ti-rich alloys are rarely studied and most of them devoted to the processing of thin films.

An important characteristic in the Ni-Ti SMA is the stability on direct and reverse transformations, related with the sequence and transformation temperatures, and thermal hysteresis (Ref 1-5). Many researchers have studied the effect of cold working plus and aging on the thermomechanical response of SMAs. The transformation temperatures in NiTi SMAs have been shown in previous studies to be related to the presence of lattice defects introduced by cold working (Ref 6, 7). The follow-on heat treatments are found to rearrange/annihilate the lattice defects. Annealing at 500 °C or at temperatures above this point was noted to entail the development of recrystallization processes in the work-hardened matrix. It is observed that, apart from changes in the dislocation structure, the formation and dissolution of precipitates influences the chemical composition of the matrix related to the varying nickel content in the matrix bring shifts in the transformation temperatures (Ref 8, 9). Further, thermal cycling is again found to decrease the transformation temperatures. Transmission electron microscopy observation made by Perkins and Miyazaki et al. (Ref 1, 3) revealed that dislocations were introduced by thermal cycling and the density of the dislocations increased with the increasing number of cycling. The increase of dislocations density usually decreases the martensitic transformation start temperature (M_s), due to the resistance to the transformation caused by dislocations. The possible reason for this behavior is associated with the fact that the increase of dislocation density by thermal and/or mechanical cycles promotes sites for R-phase nucleation; another reason may be due to the fact that the internal stresses formed by these dislocations suppress the martensitic phase transformation (B19′).

The goal of the present work is to investigate the stability of the phase transformation characteristics, such as, type of sequence (one, two, and multiple steps) and transformation temperatures in Ti-Rich Ni-Ti SMA after being subjected to an initial heat treatment at 500 °C followed by multiple steps of marforming (cold rolling, 30% thickness reduction) intercalated with heat treatments at 500 °C and a final heat treatment at four different temperatures (400, 450, 500, and 600 °C) for 30 min in air atmosphere. Phase transformations are studied during the ab initio 10 thermal cycles. This work has been a continuation of the previously published report by the authors, in which, the initial annealing, preceding the thermomechanical steps, was performed at 800 °C (Ref 10), instead of 500 °C, as it is now the case.

This article is an invited paper selected from presentations at Shape Memory and Superelastic Technologies 2010, held May 16-20, 2010, in Pacific Grove, California, and has been expanded from the original presentation.

Andersandos Santos Paula, PPGEM - Post-graduated Program in Metallurgical Engineering, UFF - Universidade Federal Fluminense, Volta Redonda, RJ, Brazil; and **Karimbi Koosappa Mahesh** and **Francisco Manuel Braz Fernandes**, FCT/UNL, CENIMAT-I3N, Campus de Caparica, 2829-516 Caparica, Portugal. Contact e-mails: andersan@metal.eeimvr.uff.br and andersita@yahoo.com.br.

2. Experimental Procedure

Samples were extracted from straight annealed (as-received—AR) Ti-rich NiTi alloy (Ti51.0 at.%-Ni) plate of thickness 2 mm supplied by Memory-Metalle GmbH, Germany. In order to remove the oxide layer as well as the layer deformed by the cutting operation, the samples were subjected to chemical etching (10 vol.% HF + 45 vol.% HNO_3 + 45 vol.% H_2O).

The thermomechanical treatments comprised an initial heat treatment at 500 °C for 30 min, followed by a sequence of three successive 30% thickness reduction by cold rolling (marforming) plus heat treatment at 500 °C for 30 min [overall description of the type of thermomechanical processing is described elsewhere (Ref 10)]. Finally, all the samples were subjected to a final step of 30% thickness reduction by cold rolling (marforming) plus heat treatment at different temperatures (from 400 to 600 °C) for 30 min.

Specimens with a mass ranging from 40 to 50 mg were cut for differential scanning calorimetry analysis (DSC - SETARAM DSC92). The thermal cycle comprised heating up to 140 °C, holding for 360 s and subsequent cooling down to −30 °C, with heating and cooling rates being 7.5 K/min.

Electrical resistivity (ER) characterization have been performed by making use of a home made four-probe setup immersed, together with the sample, in a temperature controlled silicone oil bath. It consists of a block of four 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 input the current (500 mA) into the test specimen and a data acquisition board (National Instruments, USA) with a precision better than 1 μV is used to acquire and send the voltage signal to a PC. Samples have been scanned in the temperature range from 0 to 140 °C.

In DSC and ER profiles, identification of the phase transformation sequence and temperatures were done as explained in the previous publications by the authors (Ref 11, 12).

3. Results and Discussion

Phase transformation profiles are obtained after the initial heat treatment at 500 °C followed by series of marformings and final heat treatments at selected temperatures between 400 and 600 °C. In Fig. 1 and 2, the profiles acquired by DSC and ER techniques for a selected group of the 10 thermal cycles have been presented. In Fig. 1(a), from the DSC thermograms corresponding to the final heat treatment at 400 °C, it can be observed that while heating, there is a single endothermic peak attributed to one-stage phase transformation corresponding to M → A phase transformation. While cooling, two exothermic peaks are observed corresponding to two-stage A → R → M phase transformation. Further, in the ER profile shown in Fig. 1(b), the presence of sharp increase in ER while cooling attributes to the presence of R-phase transformation, which is completely stable during the 10 thermal cycles, so the first thermal cycle over the others in Fig. 1(b). The increase in ER becomes gradual with decrease in temperature, suggesting the finish of R-phase transformation and as the temperature is decreased, the ER decreases sharply due to R → M phase transformation, giving rise to the cap shape of the profile. Although, in Fig. 1(a), with increase in number of thermal cycles, the phase transformation processes both while heating

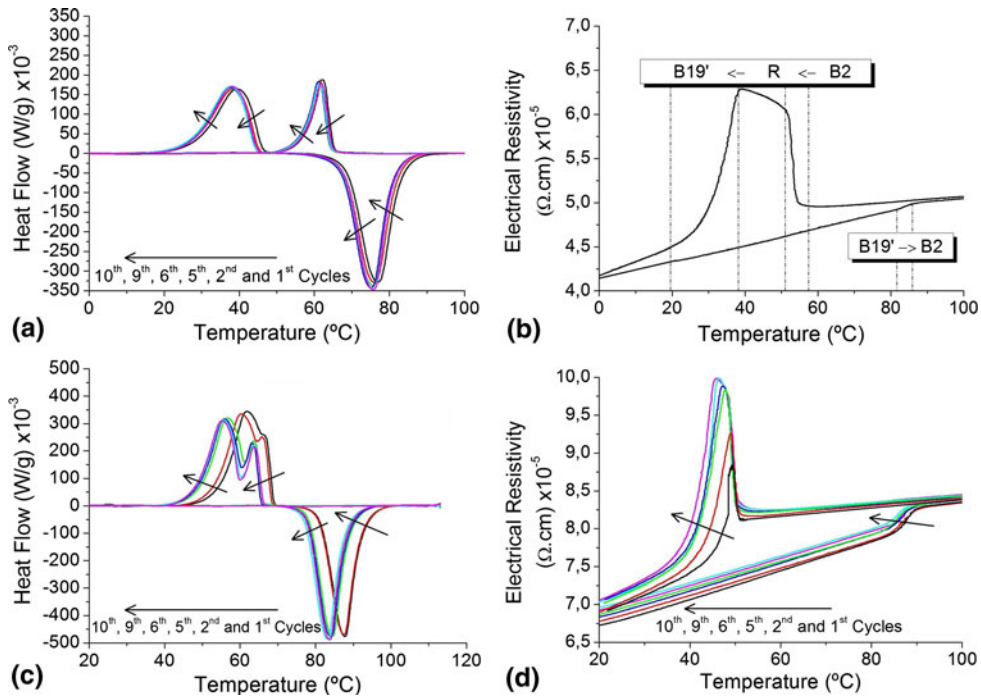

Fig. 1 Transformation characteristics stability for the multiple steps thermomechanical-treated samples, after final heat treatment at (a, b) 400 °C and (c, d) 450 °C. The arrows in endothermic/exothermic peaks in DSC (a, c) and ER (b, d) transition indicate the transformation evolution during thermal cycling (first to tenth cycle)

and cooling are found to shift toward lower temperatures, the extent of decrease in temperature is of the order of 2 K. Further, in Fig. 1(b), the ER profiles are found to virtually trace over the other leading to the conclusion that phase transformation process is quite stable over the 10 thermal cycles. In the DSC thermograms shown in Fig. 1(c) corresponding to the final heat treatment at 450 °C, while heating, one endothermic peak is observed related to one-stage M $\rightarrow$ A phase transformation. However, while cooling, the thermograms show exothermic peaks which are merged attributing to the overlap of the A $\rightarrow$ R $\rightarrow$ M phase transformation in a narrower temperature range. The overlap of the A $\rightarrow$ R $\rightarrow$ M phase transformation is further supported by the absence of the gradual increase in ER while cooling and, instead a sharp decrease, giving rise to the peak shape of the profile in Fig. 1(d). As the thermal cycling progresses, phase transformation processes are found to shift toward lower temperatures, both while heating and cooling. In Fig. 2(a), DSC thermograms corresponding to the specimen subjected to final heat treatment at 500 °C, for the first and second thermal cycles, the phase transformation peaks are observed to be symmetrical both while heating and cooling attributing to one-stage M $\leftrightarrow$ A transformation. Also, in the ER profile shown in Fig. 2(b) corresponding to the first and second thermal cycles, it is observed that the specimen undergo one-stage M $\leftrightarrow$ A transformation. As the number of thermal cycles is increased, DSC thermogram peaks is found to broaden asymmetrically and shift toward lower temperatures (from the fifth cycle onward), giving rise to increasing evidence of the intermediate R-phase transformation while cooling (Fig. 2b). For the specimen subjected to final heat treatment at 600 °C, the DSC and ER profiles obtained during different numbers of thermal cycles are presented in Fig. 2(c, d), respectively. From both the figures, it is clear that the specimen undergoes single-stage M $\leftrightarrow$ A phase transformation during the observed 10 thermal cycles, both while heating and cooling.

When the nature of phase transformation during the first thermal cycle of the specimens subjected to final heat treatment at different temperatures are compared, it is clearly observed that the specimen after final heat treatment at 400 °C, undergoes intermediate R-phase transformation and R-phase is stable in a well-defined temperature range while cooling. For the specimen subjected to final heat treatment at 450 °C, the R-phase transformation is taking place in a narrower temperature. Further, for the specimens, after heat treatments at 500 and 600 °C, there appears no R-phase transformation. Phase transformation temperatures during the first thermal cycle after final heat treatments at different temperatures are listed in Table 1. It may be noted that as the heat-treatment temperature is increased, phase transformation temperatures also increase with disappearance of the R-phase transformation. This is in agreement with the earlier findings that R-phase has higher dislocation density than the martensitic and austenitic phases and becomes unstable with decrease in the density of defects during heat treatments at temperatures higher than 450 °C (Ref 8). Therefore, the temperature at which, the heat treatment is performed, found to play a major role in fixing the phase transformation nature and the transformation temperatures.

The stability of the phase transformation after multiple steps of marforming in the present Ti-rich Ni-Ti SMA specimen, when subjected to thermal cycling is found to sensitive and depend on the final heat-treatment temperatures. Further, the thermal cycling process also found to affect the nature of phase transformation. The stability of the phase transformation temperatures and Hysteresis during thermal cycling is schematically represented in Table 2. From the table, it is evident that a well-defined R-phase transformation present during the

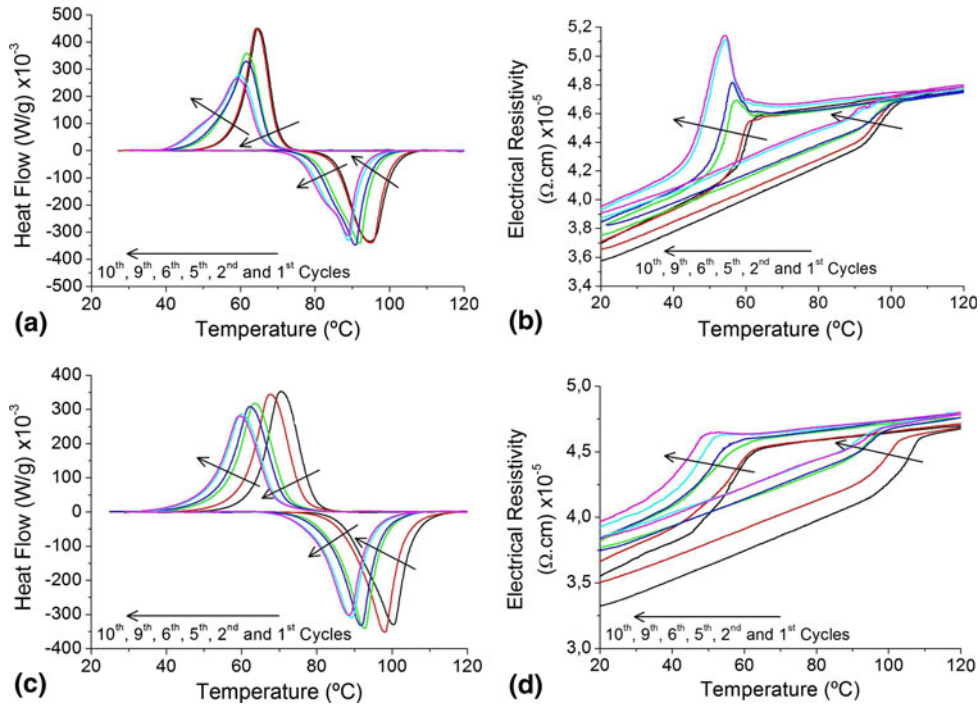

Fig. 2 Transformation characteristics stability for the multiple steps thermomechanical-treated samples after final heat treatment at (a, b) 500 °C and (c, d) 600 °C. The arrows in endothermic/exothermic peaks in DSC (a, c) and ER (b, d) transition indicate the transformation evolution during thermal cycling (first to tenth cycle)

Table 1 Phase transformation temperature and transformation hysteresis at first thermal cycle

Final heat treat temperature, °C	Phase transformation temperature, °C						Transformation hysteresis, °C			
	Direct (on cooling)				Reverse (on heating)					
	R_s	R_f	M_s	M_f	A_s	A_f	A_s-R_s	A_f-R_f	A_s-M_s	A_f-M_f
400	65.8	53.9	47.9	25.1	66.7	87.7	+0.8	+33.8	+18.7	62.7
450	67.1	*	*	47.5	78.9	96.1	+11.8	*	*	+48.7
500	···	···	74.8	55.6	82.2	106.0	···	···	+7.5	+50.4
600	···	···	81.2	59.4	88.2	116.4	···	···	+7.1	+57.0

"s": 1% transformed, "f": 99% transformed, "···": not detected, "*": undefined

Table 2 Stability of the phase transformation temperatures and hysteresis during thermal cycles

Final heat treat temperature, °C	Phase transformation temperature, °C						Transformation hysteresis, °C	
	Direct (on cooling)				Reverse (on heating)			
	R_s	R_f	M_s	M_f	A_s	A_f	A_s-R_s	A_f-M_f
400	=	=	=	=	=	=	=	=
450	↑3.6	*	*	↓13.7	↓8.4	=	↓11.9	↑13.4
500	(69.3)	(*)	↓*	↓4.5	↓9.1	↓9.8	(+3.9)	↑4.7
600	(78.9)	(*)	↓*	↓24.0	↓17.1	↓10.2	(-10.1)	↑7.8

"(×°C)": new phase, "↑": increase, "↓": decrease, "=": insignificant modification (<2 K), "*": undefined

Table 3 Nature of phase transformation observed during different thermal cycles

Final heat treat temperature, °C	Phase transformation sequences (Cycles)					
	Reverse (on heating)			Direct (on cooling)		
	First	Fifth	Tenth	First	Fifth	Tenth
400	X	X	X	XX	XX	XX
450	X	X	X	*	*	*
500	X	X	X	X	*	*
600	X	X	X	X	X	*

X: one stage (B2 → B19′ or B19′ → B2), XX: two stages (B2 → R → B19′), *: multiple stages (B2 → R; B2 → B19′; R → B19′)

thermal cycles after final heat treatment at 400 °C is quite stable, whereas, variation in the phase transformation temperatures are noted for specimens after final heat treatment above 450 °C. In Table 3, the nature of phase transformation in terms of number of stages is schematically shown. In the table, it is clear that two-stage A → R → M phase transformation is present during the 10 thermal cycles for specimen after final heat treatment at 400 °C. For the specimen heat treated at 450 °C, overlapped two-stage phase transformation (A → R → M) is found to be present during the first thermal cycle while cooling and continues to be present in the overlapped nature during the 10 thermal cycles. For heat treatments above 450 °C, one-stage phase transformation (A → M) is present during the first thermal cycle while cooling; it is eventually, overlapping with a minor R-phase transformation.

In the present set of results, different treatments applied on a specimen are found to have opposing effects on the nature of phase transformations. In contrast to the heat treatments, which tend to increase the phase transformation temperatures, thermal cycling tends to decrease them. Defects (such as dislocations) that are transformation induced during the thermal cycling, tend to hinder the martensitic phase transformation, thereby, promoting the intermediate R-phase transformation (Ref 1, 5). Further, it is noteworthy that, once the well-defined R-phase transformation is present, during the thermal cycling, then it is found to be stable throughout the 10 thermal cycles.

4. Conclusions

When Ti-rich Ni-Ti alloy subjected to thermal cycling, after multiple steps of marforming and final heat treatments, the stability of the phase transformation is found to sensitive and depend on the final heat-treatment temperatures. Further, the thermal cycling process also found to affect the nature of phase transformation. It is evident that a well-defined A → R → M phase transformation present during the thermal cycles after final heat treatment at 400 °C is quite stable. For heat treatments above 450 °C, one-stage phase transformation (A → M) is present during the first thermal cycle while cooling; it is eventually, overlapping with a minor R-phase transformation.

Further, different thermomechanical treatments applied on a specimen are found to have opposing effects on the nature of phase transformations. In contrast to the heat treatments, which tend to increase the phase transformation temperatures, thermal cycling tends to decrease them.

Acknowledgments

The authors acknowledge FCT/MCTES for the pluriannual financial support of CENIMAT/I3N and the project Smart Composites (PTDC/CTM/66380/2006). KKM gratefully acknowledges the fellowship with Ref. No. C2007-443-CENIMAT-6/Ciência2007. ASP gratefully acknowledges FAPERJ (Brazil) for the financial support in the APQ-1 project E-26/110.414/2010.

References

1. S. Miyazaki, Y. Igo, and K. Otsuka, Effect of Thermal Cycling on the Transformation Temperatures of TiNi Alloys, *Acta Metall.*, 1986, **34**, p 2045–2051
2. K. Otsuka and X. Ren, Factors Affecting the Ms Temperature and its Control in Shape-Memory Alloys, *Mater. Sci. Forum*, 2002, **394–395**, p 177–184
3. J. Perkins, Lattice Transformations Related to Unique Mechanical Effects, *Metall. Trans.*, 1973, **4**, p 2709–2721
4. V. Pelosin and A. Riviere, Effect of Thermal Cycling on the R-phase and Martensitic Transformations in a Ti-Rich NiTi Alloy, *Metall. Mater. Trans. A*, 1998, **29**, p 1175–1180
5. J. Uchil, K.G. Kumura, and K.K. Mahesh, Effect of Thermal Cycling on R-phase Stability in a NiTi Shape Memory Alloy, *Mater. Sci. Eng. A*, 2002, **332**, p 25–28
6. H. Morawiec, D. Stróz, and D. Chrobak, Effect of Deformation and Thermal Treatment of NiTi Alloy on Transition Sequence, *J. Phys. IV*, 1995, **5**, p 205–209
7. L. Yinong and P.G. McCormick, Factors Influencing the Development of Two-Way Shape Memory in NiTi, *Acta Metall. Mater.*, 1990, **38**(7), p 1321–1326
8. T. Todoroki and H. Tamura, Effect of Heat Treatment After Cold Working on the Phase Transformation in TiNi Alloy, *Trans. J. Inst. Met.*, 1987, **28**(2), p 83–94
9. P. Filip, J. Rusek, and K. Mazanec, Effects of Work Hardening and Heat Treatment on the Phase Transformation Behaviour of Ti-50.6 at% Ni Alloys, *Mater. Sci. Eng. A*, 1991, **141**(2), p 5–8
10. A.S. Paula, K.K. Mahesh, and F.M. Braz Fernandes, Evolution of Phase Transformations After Multiple Steps of Marforming in Ti-rich Ni-Ti SMA, *Eur. Phys. J. Spec. Top.*, 2008, **158**, p 45–51
11. A.S. Paula, K.K. Mahesh, C.M.L. Santos, J.H.P.G. Canejo, and F.M. Braz Fernandes, One- and Two-Step Phase Transformation in Ti-Rich NiTi Shape Memory Alloy, *Int. J. Appl. Electromag. Mech.*, 2006, **23**, p 25–32
12. A.S. Paula, Thermomechanical Treatments of Ni-Ti Alloys System: Structural Characterization and Optimization of the Properties Associated to Shape Memory Effect, PhD Thesis, FCT/UNL - Portugal, 2006