Materials Physics and Mechanics 13 (2012) 64-69 Received: March 13, 2012

CHANGE IN THE TRANSFORMATION SEQUENCE DUE TO STRESS-FREE THERMAL CYCLING OF NI-TI SHAPE MEMORY ALLOY

Krzysztof Kuś[1*], Teodor Breczko[2]

[1] Chair of Functional Materials and Nanotechnology, Faculty of Technical Sciences,
University of Warmia and Mazury in Olsztyn, 10-266 Olsztyn, 1A Okrzei Str., Poland

[2] Chair of Material Computer Science, Faculty of Mathematics and Computer Science,
University of Bialystok, 15-887 Bialystok, 64 Sosnowa Str., Poland

*e-mail: krzysztof.kus@uwm.edu.pl

Abstract. The stress-free thermal cycling with help of a differential scanning calorimeter (DSC) is executed through the transformation range of a fully annealed Ni-Ti alloy sample, continuously observing the variations in the calorimetric profiles and related thermal parameters. The influence of two different cooling rates right after annealing on the transformation properties is extra and separately examined. It is found that as the thermal cycle number increases, the transformation sequence changes into a two-stage behaviour on cooling, and the first visible symptoms related to the appearance of intermediate R-phase occur after 10^{th} full cycle. Apart from a progressive decrease of the critical temperatures, there is no DSC evidence for the two-stage reaction on heating within the whole thermal cycling test. As a result of the higher cooling rate after annealing, somewhat higher transformation temperatures are measured for the Ni-Ti alloy.

1. Introduction

In the case of Ni-Ti shape memory alloys (SMAs), belonging to the group of "intelligent functional materials", it is known that the response to the various thermal/mechanical treatments is highly important from the perspective of engineering applications. These procedures can lead to changing the functional properties, including transformation behaviour and transformation temperatures. Among the thermal/mechanical treatments, a stress-free thermal cycling has been extensively studied, both for complete and incomplete cycles [1-6]. Consequently, more and more better knowledge is obtained enabling the control and improvement of the functional properties with reference to utilization of SMAs. It is necessary to finish saying that there are other factors having an influence on the transformation characteristics, for example Ni concentration [7], and with regard to the group of thermal treatments, heat treatment conditions, especially after cold working of Ni-Ti alloys, seem to be ones of the most serious variables that determine the forward and reverse transition [8-10]. Within the present article, the differential scanning calorimetry (DSC) results of investigations concerning the effect of thermal cycling with no applied stress on the continuous change in the transformation characteristics of Ni-Ti alloy are mainly presented. In this alloy, an influence of different cooling rates right after annealing heat treatment on the thermal parameters is extra examined.

2. Experimental

The experiments were carried out using a binary near-equiatomic NiTi alloy. In this work, additionally to the DSC thermal cycling, the effect of different cooling conditions after heat treatment on the transformation behaviour was examined. To this end, after being subjected to annealing at 600 °C for 30 min in an argon gas atmosphere, one of sample (denoted as A600/30) was freely air cooled to room temperature (~23 °C), while the second one (denoted as W600/30), was rapidly cooled by immersing in a water bath maintained at ~18.5 °C. Owing to the fact that thermal history of the as-received material was not exactly known, the chosen heat-treatment guaranteed the lack of presence of the intermediate R-phase (Rhombohedral phase). The sample cooled in air was designed for thermal cycling tests. Details concerning the sample preparation and setting conditions for the DSC tests were described in a previous paper [11]. Critical temperatures, as the principal thermal parameters of the transformations, were determined by drawing tangent lines to the heat flow curves.

3. Results and discussion

The DSC measurements result in plots of heat flow as a function of temperature, and for both annealed samples show one sharp exothermic peak on cooling corresponding to the direct transformation from austenite to martensite, and one sharp endothermic peak corresponding to the reverse transformation from martensite to austenite (Fig. 1). Such one-stage transformation behaviour is observed regardless of different cooling conditions after annealing treatment. However, it can be seen from the presented thermograms that there is a noticeable shift in the transformation temperatures (M_s, M_f, A_s, and A_f) towards higher values as cooling rate increases. The thermal hysteresis of the transitions, as the difference between the maximum of the heat flow peaks, is about 29 °C.

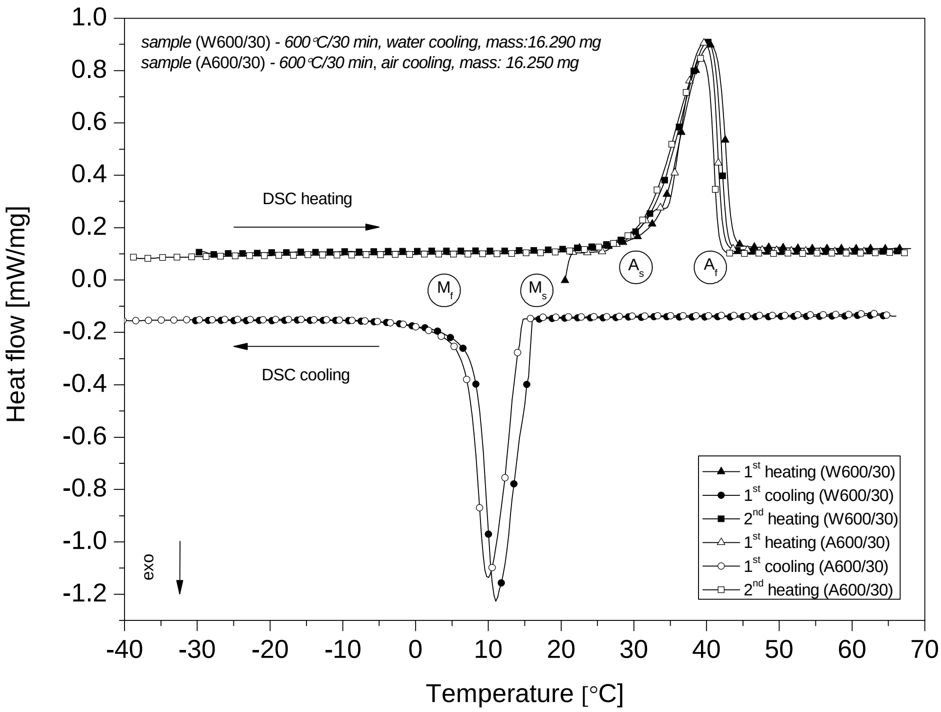

Fig. 1. DSC curves obtained from the annealed Ni-Ti samples at two different cooling rates. Detailed transformation parameters for both samples are collected in Table 1. In Fig. 1 the endothermic curves denoted as "1st heating" represent an initial calorimetric heating of the samples from room temperature to +70 ºC. The 1st cooling cycle and the 2nd heating cycle were used to obtain the thermal properties presented in Table 1.

Table. 1. Thermal parameters of the transformations as determined from DSC curves.

Sample	M_s (°C)	M_f (°C)	A_s (°C)	A_f (°C)	Transformation heat (on cooling) (J/g)	Transformation heat (on heating) (J/g)
W600/30	15.98	8.14	31.95	42.93	-34.42	34.24
A600/30	14.50	7.04	31.10	41.66	-31.22	31.44

In spite of visible shifts of the peak positions in the calorimetric scans, on the basis of which the transformation temperatures were followed, one should be aware that there are a lot of different factors that affect the results obtained from DSC analysis. Among the material elements, sample mass, geometry, or also sample preparation can be distinguished [8, 12-14]. In the present paper, however, weights of the two differently cooled samples and their shapes were practically identical, thus these features rather did not impinge on the received DSC data. The sample A600/30 is chosen for experiments of thermal cycling. The effect of repeated heating and cooling cycles on the transformation behaviour of this alloy (DSC curves every fifth cycle), has been reported elsewhere [11]. Figs. 2 and 3 demonstrate the transformation behaviour, in turn, from the first to the 30th full cycle, including details of a few DSC profiles obtained during cooling.

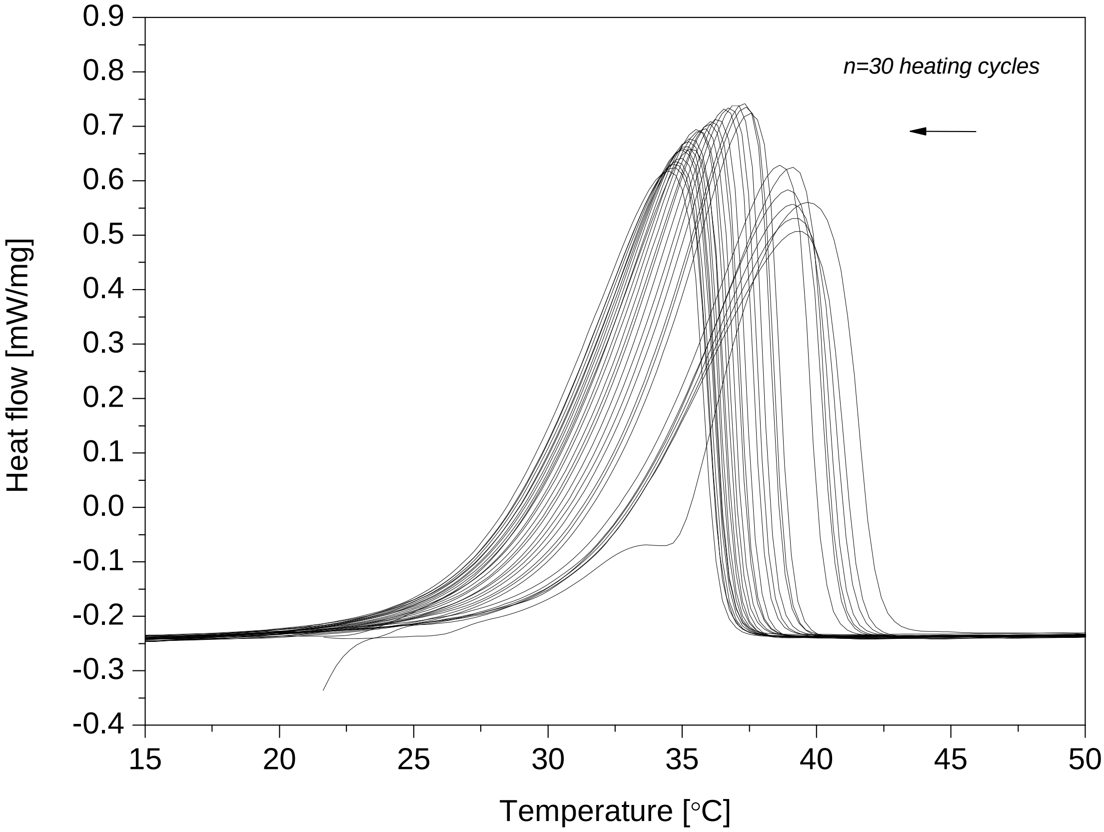

Fig. 2. Transformation behaviour during 30 consecutive heating cycles.

It is seen that during the first few thermal cycles, the sample displays identical phase transformation behaviour, i.e. the forward (austenite-to-martensite) and the reverse reaction occur as the single sequence. However, as the 10th cycle is achieved, some noteworthy changes are found to appear on the DSC graphs. A closer observation of the successive cooling curves (Fig. 3) allows perceiving an asymmetrical character of the peaks with simultaneous variation in the height.

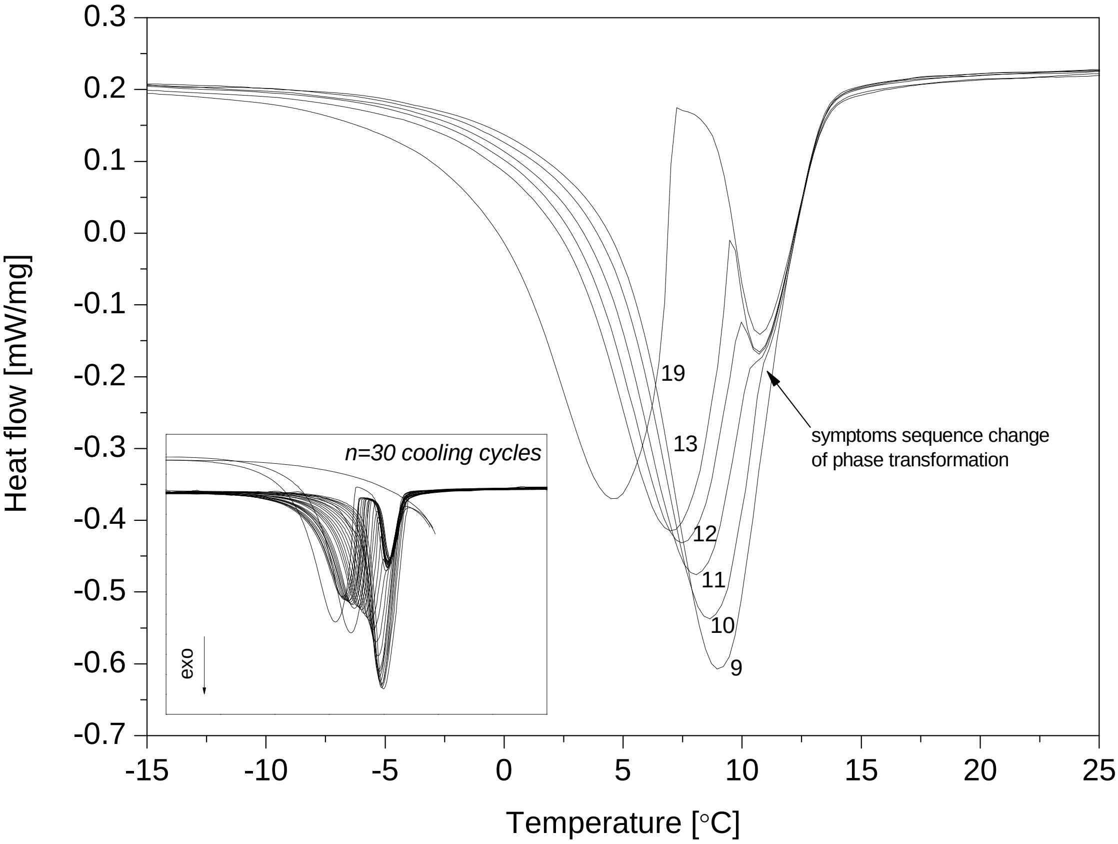

Fig. 3. Transformations during 30 consecutive cooling cycles.

These features, preceded by decreasing of the martensite transition temperatures with each cycle, result in an appearance of double peak clearly indicating that an intermediate R-phase is introduced into the sequence of forward transformation. This peak undergoes the process of splitting into two distinct peaks as the thermal cycle number increases, where the first one, appearing at a higher temperature, corresponds to austenite→R-phase transformation and the second one, at a lower temperature, is for R-phase→martensite. Although not shown here, there is a progressive expansion of the R-phase temperature range with further thermal cycling [11]. Regarding the transformation sequence change, it is interesting to note that there exist a critical number of thermal cycles for the complete development of R-phase and this critical number is a function of heat treatment temperature [3]. Whereas the type of transformation changes from one-stage to two-stage during successive cooling, no qualitative difference is observed on the DSC runs with the repetition of heating process (Fig. 2). Here, apart from the displacement of profiles, the transformation behaviour is still characterized by a single peak leading to the conclusion that normal one-stage reaction occurs only. The DSC results in this work are consistent with [2, 4, 15], although the first visible traces related to the appearance of R-phase and then its full development can be detected for different number of thermal cycles. This may be depending on the material history, as mentioned above. Figure 4 shows the continuous changes of the critical transformation temperatures for 30 full thermal cycles. Both the austenite and the martensite start and finish temperatures decrease during thermal cycling, however data related to the forward transformation show a more dynamic fall (on average, 11.5 °C between 1st and 30th cycle in comparison to 6.4 °C for A_s and A_f).

Within the initial 10 cycles, a decrease of M_s temperature by about 2 °C is observed. Note that Fig. 4 distinguishes the martensitic transformation temperatures on these measured before (M_s and M_f) and after (M_s^* and M_f^*) the formation of an intermediate structure. In the same figure some discontinuities of the data take place as a result of technical breaks during DSC tests for the replenishment of liquid nitrogen.

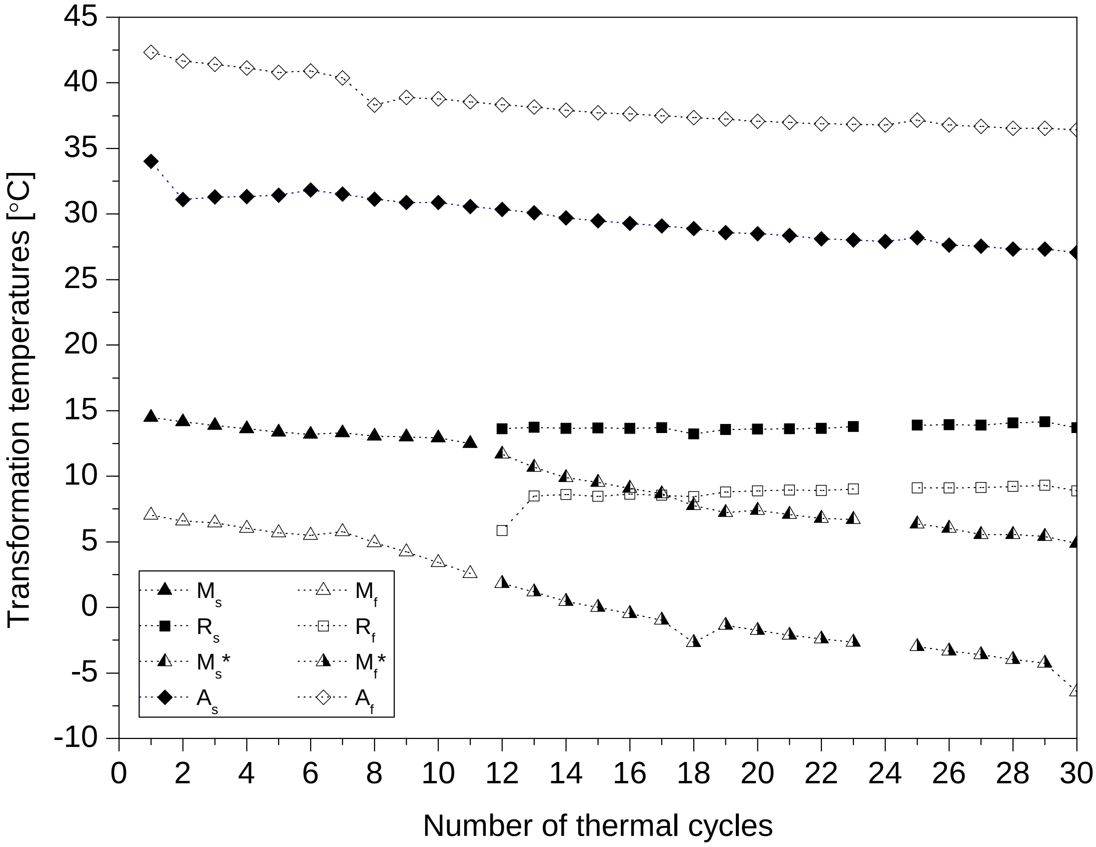

Fig. 4. Changes in phase transformation temperatures during thermal cycling.

Regarding the R-phase temperatures (R_s, R_f), these remain practically unaltered throughout thermal cycling, although a slightly increasing trend is recognized. According to obtained results one may say that used in the present studies thermal treatments influence the transformation characteristics of Ni-Ti SMA. Their changes seem to be correlated with a modification of the material microstructure, during both repeated thermal cycling [11] and annealing. Although tested samples show a noticeable change in the critical temperatures depending on the rate of cooling, it is necessary to point out that the influence of heat treatment parameters mostly play role after previous cold-working, when the near-equiatomic Ni-Ti alloys are considered [8, 10, 16-17].

4. Final remarks

- In studying the effect of two different cooling rates after annealing, it is shown by DSC that the phase transformation temperatures of Ni-Ti alloy shift slightly towards the higher values in case of faster cooling. Regardless of the cooling conditions, both samples demonstrate the one-stage transformation behaviour.
- In studying the effect of thermal cycling in Ni-Ti alloy, it is found that before an introduction of the R-phase into the forward transformation, the continuous changes in DSC profiles occur on cooling. These changes, preceded by decreasing of the martensite

transition temperatures within the initial cycles, result in an appearance of the two clear exothermic peaks which represent the two-stage transformation. There is no DSC evidence for the two-stage reaction on heating, regardless of achieved thermal cycles. It is also shown that the characteristic temperatures of transformations shift during the whole test run, however in the case of R-phase, variations are not much noticeable.

- The published literature indicates that changes in the transformation properties due to stress-free thermal cycling are generally attributed to the alteration of the alloy microstructure. In this respect, structural defects like dislocations are crucial to promote the R-phase.
- Although considered in this work problems have been extensively studied in the literature, this type of investigations seem to be still justifiable with respect to the effective utilization of SMAs in various engineering areas, and even to create new applications. Besides regulating and tailoring the shape memory characteristics due to processing, the repeated actuation cannot be avoided in most cases, and in this respect the stability of thermal properties is of great importance.

References

[1] S. Miyazaki, Y. Igo, K. Otsuka // *Acta Metall.* **34** (1986) 2045.
[2] P.G. McCormick, Y. Liu // *Acta Metall. Mater.* **42** (1994) 2407.
[3] J. Uchil, K. Ganesh Kumara, K.K. Mahesh // *Mater. Sci. Eng. A* **332** (2002) 25.
[4] H. Matsumoto // *J. Alloys Comp.* **350** (2003) 213.
[5] Y. Liu, J. Laeng, T.V. Chin, T-H. Nam // *Mater. Sci. Eng. A* **435-436** (2006) 251.
[6] Y. Liu, J. Laeng, T.V. Chin, T-H. Nam // *J. Alloys Comp.* **449** (2008) 144.
[7] M. Schwartz (Ed.) // *Encyclopedia of Smart Materials* (John Wiley, 2002) Vol. **1-2,** p. 954.
[8] T. Todoroki, H. Tamura // *Trans. Japan Inst. Metals* **28** (2) (1987) 83.
[9] E. Abel, H. Luo, M. Pridham, A. Slade // *Smart Mater. Struct.* **13** (2004) 1110.
[10] S.H. Yoon, D.J. Yeo // *Proc. of SPIE* **5648** (2005) 208.
[11] K. Kus // *Technical Sciences* **13** (2010) 203.
[12] A. Serneels // *Shape memory alloy characterisation and optimisation. AMT - @ Medical Technologies*, Belgium, pp. 1-18.
[13] Z. Sierpiński // *Thermal analysis in metal science – possibilities and applications, Part 1. Differential Scanning Calorimetry. Lectures on Instrumental Methods of Testing, designed for master extra-mural courses with a specialty of mechanical working*, pp. 1-37, http://home.agh.edu.pl/~blaz/wyklady/pliki/analiza.pdf
[14] J.A. Shaw, C.B. Churchill, M.A. Iadicola // *Experimental Techniques* **32** (2008) 55.
[15] H. Matsumoto // *J. Mater. Sci. Lett.* **10** (1991) 408.
[16] T. Saburi, In: *Shape Memory Materials*, edited by K. Otsuka and C.M. Wayman (Cambridge University Press, Cambridge, 1998), p. 49.
[17] L.K. Kabayama, O.D. Rigo, J. Otubo // *Mater. Sci. Forum* **643** (2010) 43.