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

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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.

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.

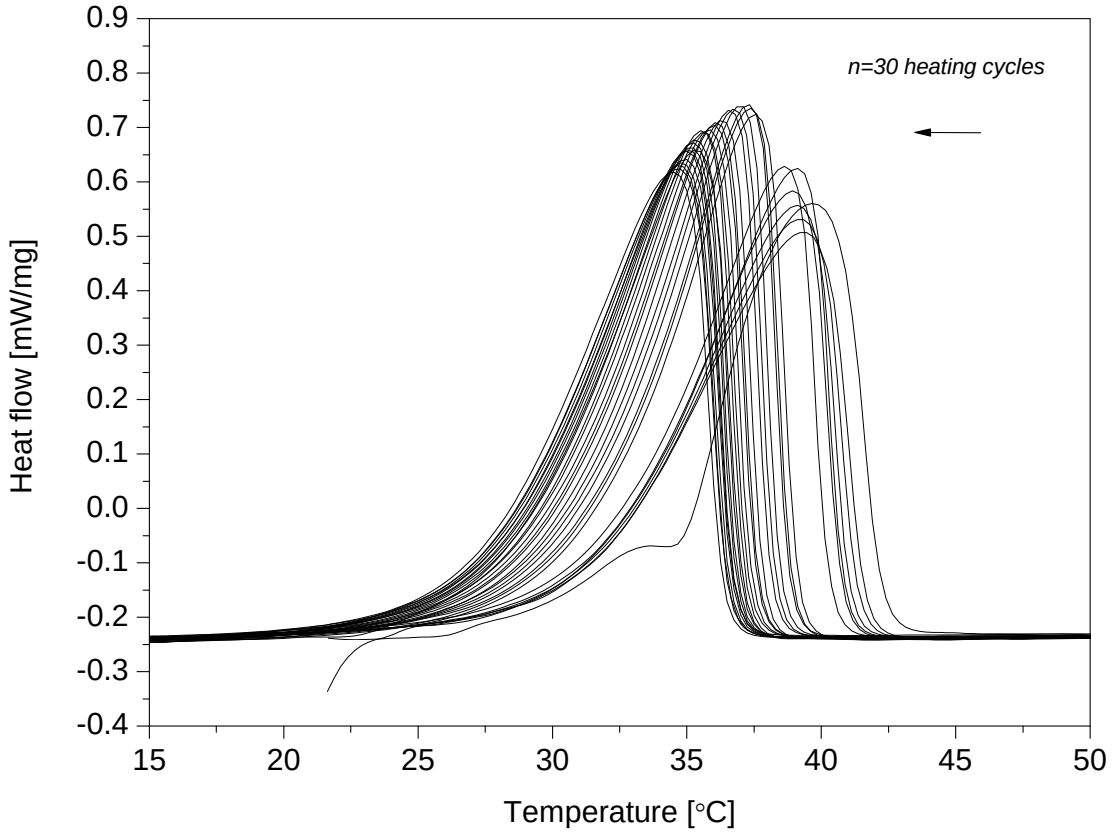

Fig. 2. Transformation behaviour during 30 consecutive heating cycles.

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

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.

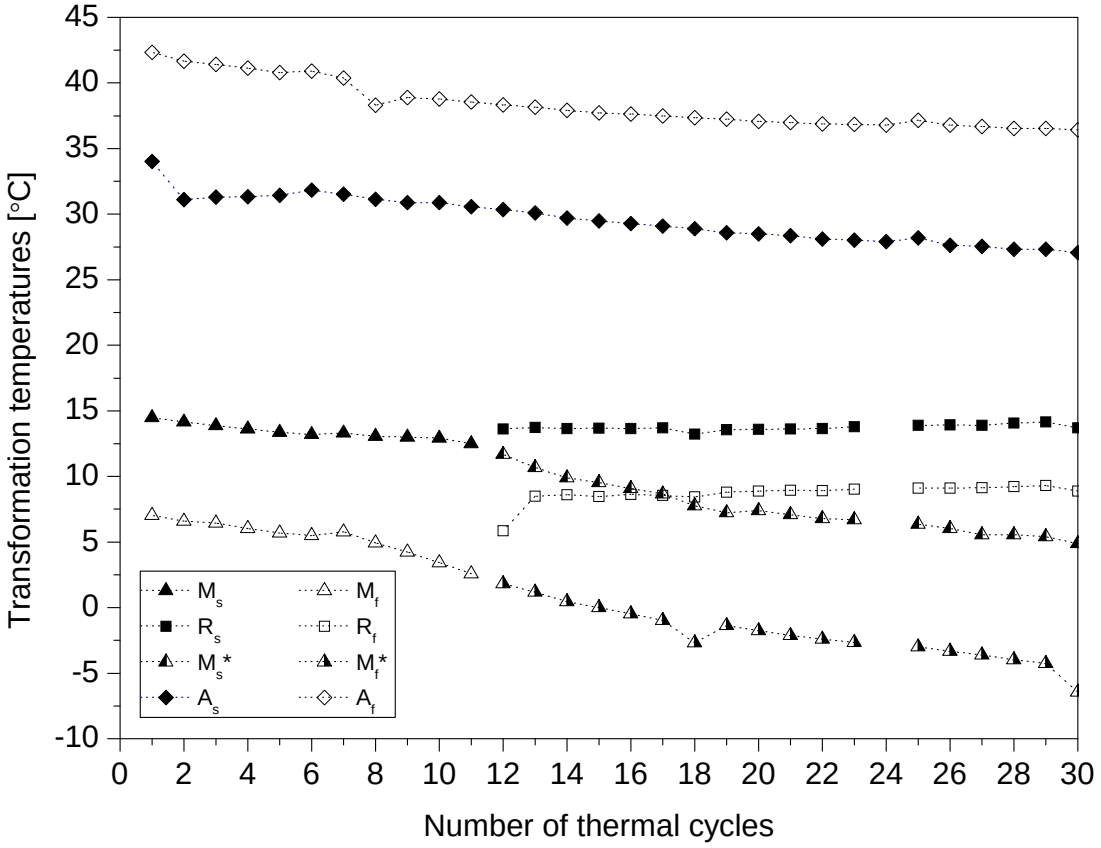

Fig. 4. Changes in phase transformation temperatures during thermal cycling.

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.

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