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DSC-INVESTIGATIONS OF THE EFFECT OF ANNEALING TEMPERATURE ON THE PHASE TRANSFORMATION BEHAVIOUR IN Ni-Ti SHAPE MEMORY ALLOY

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Abstract. The variations in thermal transformation properties due to annealing within the temperature range from 400°C to 600°C were studied for the near equiatomic Ni-Ti shape memory alloy by the Differential Scanning Calorimetry (DSC) measurements. There was a critical temperature (about 600ºC), where the specimens demonstrated remarkably different transformation courses. There were also noticeable changes in transformation temperatures and heats depending on the annealing temperature. It is thought that the alterations of the microstructure in the Ni-Ti alloy during annealing are responsible for such behavior.

1. Introduction

The shape memory alloys (SMAs) belong to the group of new functional materials, not infrequently also determined as "smart functional materials". The functional properties that distinguish those materials from all others are the following [1-3]: free recovery, constrained recovery, actuator and work production, pseudoelasticity and high damping capacity. So far, among all the SMAs, Ni-Ti based alloys are the most commercially exploited ones (Example: Nitinol containing a nearly equal mixture of nickel and titanium [3-4]). As the most important functional property, the shape memory effect (SME) in such alloys is characterized by the thermoelastic reversible crystallographic phase transformation from a high-temperature phase (BCC structure) to a low temperature phase (monoclinic structure) [5]. In addition to these two phases, an intermediate phase may appear known as the intermediate R-phase which has the rhombohedral crystal structure [5-7]. Then, the direct transformation proceeded in a two-stage process, i.e. the material at high temperature in the parent phase (known as austenite) transforms to the intermediate R-phase and next to the low temperature phase – martensite. By the way, in some cases, the presence of a premartensitic transition is useful in engineering fields, mainly owing to the fact that SME with its participation exhibits excellent fatigue properties [6]. However, the occurrence of different transformation behaviours and changes in critical transformation temperatures depend on many factors, like for example thermo-mechanical processing [5, 8-9]. Thus, a systematic investigation all of them, including the material response to thermal heat-treatment with various process conditions, plays important role in controlling the transformation properties and as well as others of Ni-Ti type alloys [10-11].

There are a number of distinct techniques for studying the crystalline phase transformation behaviour [3, 12-14]. A review of the literature shows, that Differential Scanning Calorimetry (DSC) is the most popular and convenient test method to extract the thermal characteristics in different SMAs. Obviously, as each of methods it has some advantages and disadvantages [15]. The DSC technique yields a thermogram with characteristic peaks by measuring the amount of heat given off or absorbed by a tiny specimen of the alloy as it is cooled or heated through its phase transformations [16]. Thus, in the SMAs, the martensite to austenite transformation is endothermic reaction (heat absorbing), while the austenite to martensite transformation is exothermic reaction (heat emitting). On the calorimetric thermograms, the area under peaks indicates the energy of transformation. Using these peaks, the critical transition temperatures can be also determined [15].

The main objective of this paperwork is to present an experimental investigation of the effect of annealing heat-treatment temperature on the phase transformation behaviours in the Ni-Ti alloy close to near-equiatomic composition of Ni and Ti. The experimental research consists of DSC measurements, which were performed on the two types of SMA specimens, including the as-received and as-annealed conditions. In the present work, temperatures of a thermal treatment were selected to be within the range between 400 and 600°C. Calorimetric diagrams were used for the study of the phase transformation courses, the determination of the critical transformation temperatures and the measurement of the transformation energies.

2. Experimental aspects

Alloy, Specimens, Preparation. A nearly equiatomic polycrystalline Ni-Ti alloy (Nitinol) was used throughout the experiments. The as-received material in the form of sheet with a thickness of 0.5 mm was carefully spark-cut into small pieces with dimensions of about 2x2 mm. Specimens for the DSC measurements weighted between 10-16 mg. After spark-cutting, the specimens were heat-treated by annealing them in an electric muffle furnace (in air) at 400, 450, 500, 550 and 600°C for the same period of 30 minutes followed by free air-cooling to room temperature. The furnace temperature was controlled within ± 5°C. After each heat-treatment, the surface of the specimen was slightly polished by fine-grained emery paper to remove the oxide layer formed during mentioned above processing, washed in distilled water and alcohol, etched in a chemical solution of H_2O:HNO_3:HF (5:4:1) and again rinsed with distilled water and alcohol.

DSC measurements. The thermal studies were carried out on the as-received material and specimens after heat-treatment at various annealing temperatures in order to register the changes in phase transformation behaviours. The DSC measurements were made within 24 h after annealing treatments. Thermal parameters were collected by means of DSC 204 device by NETZSCH with a liquid nitrogen cooling accessory. The temperature and energy flow were calibrated using an indium reference standard. In the DSC procedure, the specimens were thermally treated in a range from -100°C to +100°C with a constant scanning rate of 10 K/min. This temperature rate is the most efficient one for measuring the intrinsic transition quantities and also a common value within published literature, therefore, was selected for research in this work [17]. Referring to earlier our laboratory tests, a maximum temperature of +100°C during calorimetric heating was determined to be well above the temperature required to obtain a fully austenite state for each of the studied specimens. Similarly, cooling to -100°C was established to be below enough the temperature at which the transformation to martensite was terminated. The applied temperature regime for each of specimens was the following: quick heating from room temperature to +100°C, then cooling to approximately -100°C at a constant cooling rate (10K/min) and finally heating again to +100°C at the same rate.

On the basis of the DSC profiles, the start and finish temperatures of each phase transformation were determined by the intersections of a base line and the tangents to a thermal peak. In accordance with the commonly accepted notation, these temperatures are expressed in the present paper as: R_s, R_f, M_s, M_f, A_s, A_f, (R-phase, martensite and austenite starting and finishing temperatures, respectively). Symbols such as R_p, M_p and A_p mean the peak temperatures for the concrete transformations, respectively. The transformation heats (absorbed and released), denoted further as ΔH with the proper subscripts, and were determined by calculating the area bounded by the peak and the base line. On the calorimetric diagrams, the exothermic phase transformations to martensite on cooling are ascribed to lower curves, and the endothermic phase transformations to austenite on heating to upper ones.

3. Experimental results and discussion

In this section, the DSC characteristics performed on the as-received specimen, without annealing heat-treatment, and on specimens that were heat-treated at selected temperatures for half an hour are reported and discussed. From the calorimetric observations follow thermal properties of the studied alloy such as the phase reactions (their sequences) involving different products during cooling and heating, the stress-free transformation temperatures, as well as the latent heats of transformations.

The DSC curves reported earlier [18] for the as-received Ni-Ti alloy are shown in Fig. 1. The added arrows on all the thermograms indicate the cooling and heating process. As can be seen from the figure, cooling of the as-received specimen from +100°C followed by heating from the sub-zero temperature caused two exothermic and endothermic peaks, respectively. During the forward transformation proceeding from austenite to martensite, a product of the first exothermic peak at higher temperature corresponded to the reaction from austenite (A) to R-phase (R), whereas that of the second exothermic peak at lower temperature corresponded to the reaction from R-phase (R) to martensite (M). Thus, the as-received material on cooling exhibited a well defined two-stage transformation sequence of A→R→M, whereat the A→R peak is narrow and the R→M one is shallow and strongly flattened. Two-stage transition with endothermic peaks also occurred upon heating, however; in this case the successive reactions were poorly separated. The two overlapping peaks corresponded to M→R transformation (visible smaller peak on the shoulder of the following) and R→A transformation (larger, higher temperature peak). Note this fact made difficult to estimate the finish of the M→R transformation and the start of the R→A transformation.

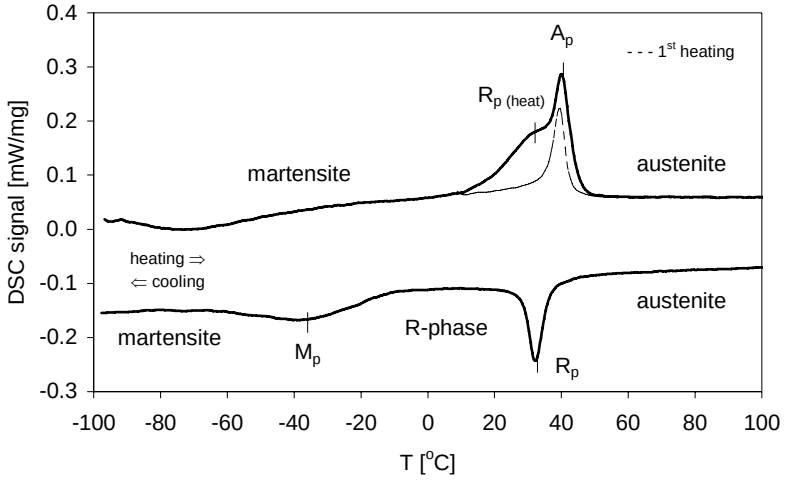

Figure 1. DSC cooling and heating curves of the as-received Ni-Ti alloy.

Figures 2-6 below show DSC curves for the as-annealed Ni-Ti specimens at various temperatures for 30 minutes. Transformation behaviour profiles for the specimens annealed at 400 and 450°C appeared like these obtained from the as-received material (Figs. 2-3). Here also, two-stage transformations through the R-phase happened during cooling and heating, but only along with the increase of annealing temperature the two overlapping endothermic peaks started to almost merge into one peak (Fig. 3). Thermal treatment of the as-received material in the range of 400-450°C caused a not large change in transformation temperatures and heats that will be discussed later on.

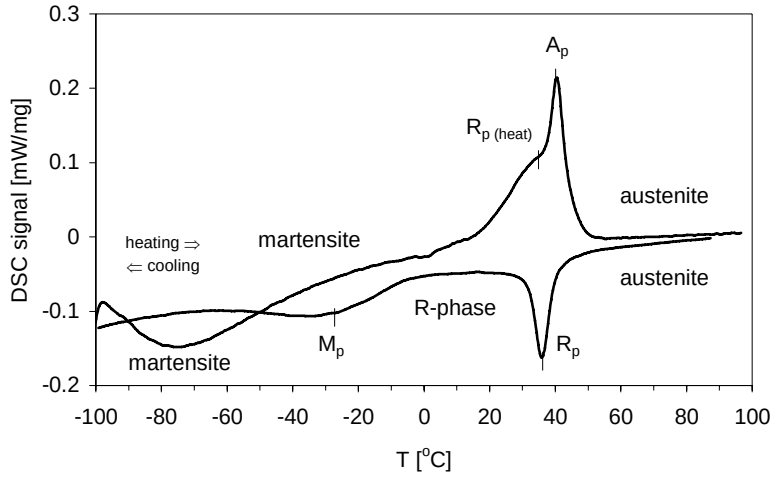

Figure 2. DSC cooling and heating curves of the Ni-Ti alloy annealed at 400° for 30 min.

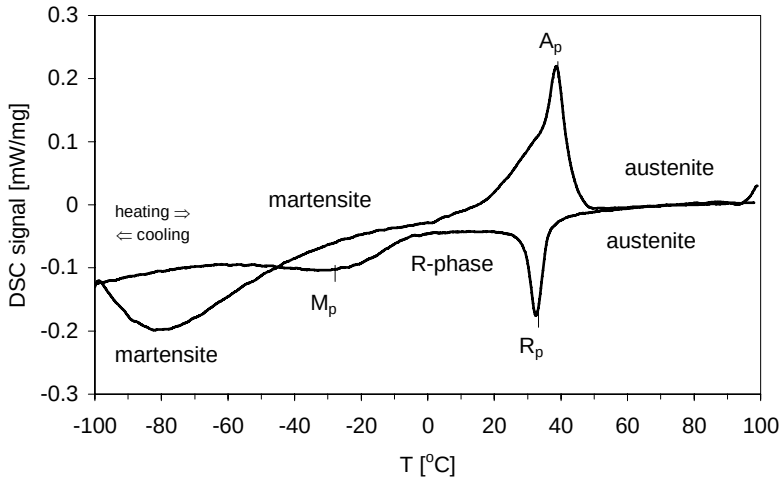

Figure 3. DSC cooling and heating curves of the Ni-Ti alloy annealed at 450° for 30 min.

The results of the calorimetric tests after annealing at temperatures exceeding 450°C are submitted in Figs. 4-5. It follows from the curves that the cooling transformations were still in two-stages among austenite, R-phase and martensite. What's interesting, in these cases, the R→M peaks tended to be narrower and definitely deeper with increase in the heat-treatment temperature. On the DSC heating curves, only one distinct endothermic peak was detected. This means that the reverse transformations from martensite to R-phase and further to austenite were overlapped together practically resulting in the one-stage process of M→A. Nevertheless, some subtleties on the low temperature side of the endothermic peaks can be still noticeable pointing at a trace amount of the R→A transformation.

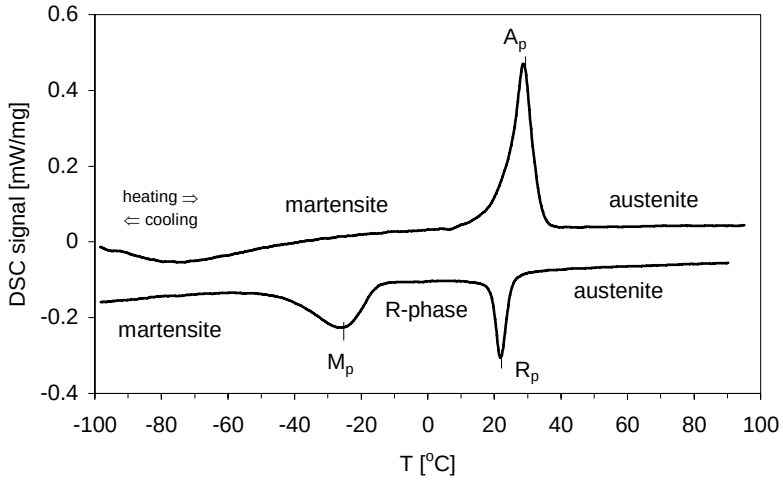

Figure 4. DSC cooling and heating curves of the Ni-Ti alloy annealed at 500° for 30 min.

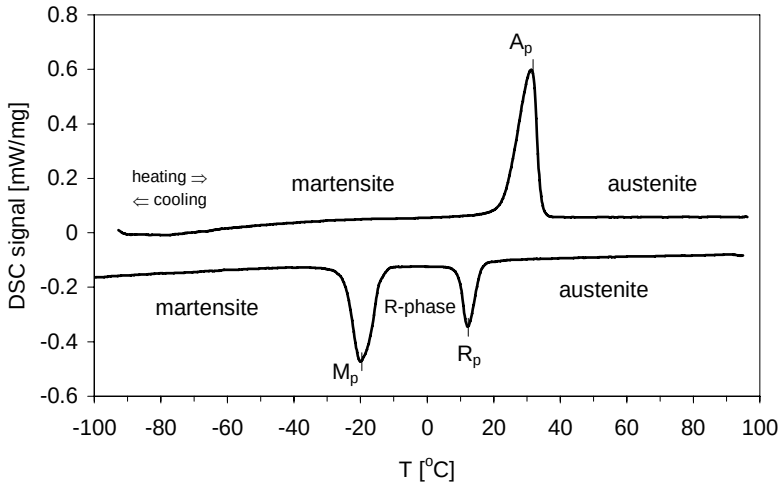

Figure 5. DSC cooling and heating curves of the Ni-Ti alloy annealed at 550° for 30 min.

Fig. 6 gives the DSC diagram of the specimen annealed at 600°C. Compared with all the DSC curves already presented, a qualitative difference in phase transformation behavior was observed on the material at the highest annealing temperature. It results from the fact that the R-phase transformation was not recorded. In this case, the transformation on both cooling and heating occurred in one-stage from austenite to martensite (A→M) and from martensite to austenite (M→A), respectively. About such behavior (direct A↔M phase transformation) testifies to an occurrence only of the single exothermic and endothermic peak on the DSC graph (Fig. 6).

According to the obtained results, the annealing temperatures within the range of 400-600°C have a significant influence on the transition characteristics in the as-received material. In particular, an annealing temperature in the nearness of 600°C suggests being the critical temperature where the distinct change in phase behavior was found. Below this critical value, the transformations proceeded with a participation of the intermediate R-phase. As the heat-treatment temperature moved toward higher values the R-phase aimed to be unstable and when reached 600°C, it disappeared and the direct martensitic transformation occurred in both directions.

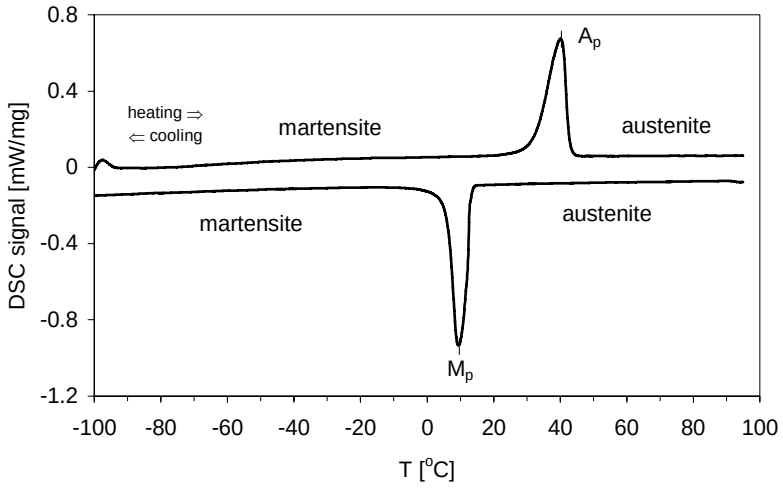

Figure 6. DSC cooling and heating curves of the Ni-Ti alloy annealed at 600° for 30 min.

By using the exothermic and endothermic peaks the transformation temperatures and heats were assessed, as summarized in Table 1. The calculated area under each peak represents the latent heat of the proper transformation. The terms $\Delta H_{A\rightarrow R}$, $\Delta H_{R\rightarrow M}$ and $\Delta H_{A\rightarrow M}$, collected as negative data, are the transformation heats for the A→R, R→M and A→M processes upon cooling, respectively. The terms $\Delta H_{M\rightarrow R\rightarrow A}$ and $\Delta H_{M\rightarrow A}$, expressed as positive data, describe the transformation heats for the M→R→A (here combined area due to superimposed peaks) and M→A processes upon heating, respectively.

Table 1. Transformation temperatures and heats for the as-received material and annealed specimens as measured with DSC.

Annealing temperature [°C]	R_s cool [°C]	R_f cool [°C]	M_s [°C]	M_f [°C]	A_s [°C]	A_f [°C]	$\Delta H_{A\rightarrow R}$ [J/g]	$\Delta H_{R\rightarrow M}$ [J/g]	$\Delta H_{A\rightarrow M}$ [J/g]	$\Delta H_{M\rightarrow R\rightarrow A}$ [J/g]	$\Delta H_{M\rightarrow A}$ [J/g]
as-received	37	28	-10	-64	15[a]	45[b]	-6.207	-6.728	-	18.45	-
400	40.5	31.5	-4	-61	17[a]	45.4[b]	-4.8	-4.946	-	15.9	-
450	37	28.8	-5.5	-62	16.5[a]	44.5[b]	-4.976	-6.723	-	16.32	-
500	25.5	19	-15	-44	22.5	34	-5.834	-12.24	-	-	21.78
550	16.5	9.4	-14	-25	23	34.2	-6.167	-15.18	-	-	23.05
600	-	-	12.8	5.2	32	43	-	-	-26.52	-	25.87

Legend: a – starting temperature of M→R transformation,
b – final temperature of R→A transformation.

From the collected results in Table 1 is evident that the annealing within the range of 400 to 600°C produced the shift in start and finish transformation temperatures of the R-phase on cooling to lower values, whereat a small growth at 400°C was perceived with reference to the as-received alloy. In the case of martensite phase, the M_s temperature decreased after a slight growth for annealing at 400°C and then clearly increased from specimen annealed at 500°C. The M_f temperature showed a strong displacement to higher temperatures from 450°C and this trend was seen up to 600°C. Owing to the extremely broadened and flattened DSC peaks, the M_s and M_f temperatures given in the table are not very accurate for the as-received and annealed specimens at 400-450°C. They become better defined with increasing annealing temperatures. Calorimetric measurements indicate that in the specimens heat-

treated between 400-550°C, the M_s and M_f temperatures were below room temperature due to the R-phase which the possibility of forming reduced as the M_s temperature moved toward higher values. Such transformation behaviour, i.e. without revealing a rhombohedral R-phase took place at higher annealing temperatures. As a result of heat-treatment, the A_s temperature for reverse transformation insignificantly increased in the range of 500-600°C, whereas the A_f showed a similar trend to the M_s temperature.

Changes in thermal properties can be also illustrated by means of other transformation critical points, which correspond to temperatures of maximum DSC runs during cooling and heating, as marked in Fig. 1 through 6. The symbols R_p, M_p and A_p are the peak temperatures of the DSC curves for the A→R, R→M and M→A transformations, respectively. Changes in the peak temperatures are plotted in Fig. 7 as a function of annealing temperature, whereat A_p presented value for the as-received and annealed specimens in the range of 400-450°C correspond to the peak temperature of R→A transformation.

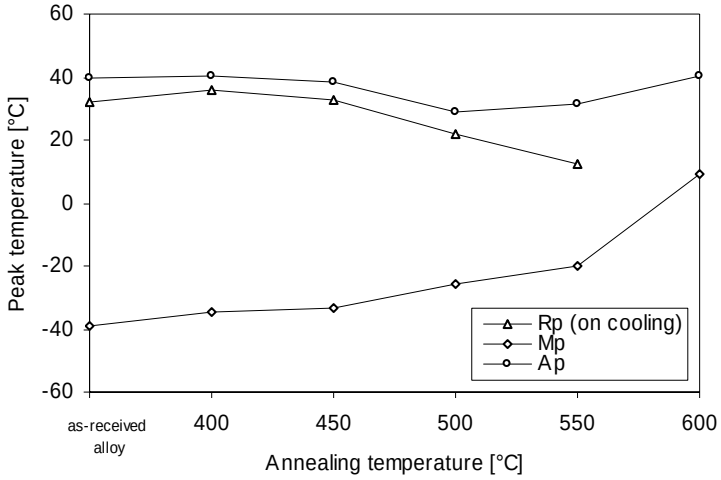

Figure 7. Phase transformation peak temperatures as a function of annealing temperature.

It is apparent from the curves that the R_p peak temperature on cooling shifted to the low temperature region by an annealing at the desired temperatures, although at 400°C a little increase with relation to the as-received specimen occurred. The M_p shifted considerably to higher temperatures with increasing heat-treatment temperature. This means, thereby, that the temperature difference between the R_p and M_p peaks diminished continuously with the annealing temperature until the two exothermic peaks became superimposed, what took place after a heat-treatment temperature of 600°C. A unique A→M transformation peak on cooling was then observed. For the A_p peak temperature, a gentle decrease in the value was visible reaching its minimum for material annealed at 500°C. Above this temperature the A_p raised with further increasing annealing temperature. For the material annealed at 600°C, the transformation hysteresis defined as the difference between A_p and M_p peak temperatures was about 31°C.

Regarding the changes in the transformation heats data, the exothermic heat for the A→R transformation on cooling remained almost unchanged with increasing annealing temperature, achieving the absolute average value of about 6 J/g. Otherwise, the absolute exothermic heat for the R→M transition was seen to decrease slightly at first and then increased gradually till the specimen annealed at 550°C. The $\Delta H_{R\rightarrow M}$ had the minimum value of 5 J/g and the maximum value of 15.18 J/g. It is well obvious that the sum of the exothermic heats, i.e. from A→R and R→M transformations in the function of annealing temperature demonstrates the same trend as the $\Delta H_{R\rightarrow M}$.

For the endothermic heat of reverse transformation during heating it insensibly decreased until reaching a minimum value of about 16 J/g in the alloy annealed at 400°C, and then started to increase as the annealing temperature shifted to higher values. Note that in the above discussion areas under unresolved peaks associated with the two successive reverse transitions for the as-received and annealed specimens at 400 and 450°C (see Figs. 1-3) were combined together in order to estimate the endothermic heat. According to Ref. [19], the increase of the latent heat with increasing annealing temperature is attributed to the increase of the A↔M phase transformation reversibility.

As for the total exothermic and endothermic heats, there was a difference between values which generally decreased with increasing annealing temperature. A minimum value of about 0.6 J/g was measured after annealing at 600°C, what consequently means an almost reversible character of the A↔M transformations.

From the experimental results presented in the current section it is deduced that the heat-treatment temperature applied to the as-received Ni-Ti alloy is important factor which determines phase transformation behaviour. In the as-received material and after annealing at temperatures not exceeding 450°C, the two-stage transformation sequence on cooling (A→R→M) and on heating (M→R→A) was seen, although the reverse transformations in these specimens appeared as unclear (superimposed thermal peaks). When the annealing temperatures were higher than 450°C, the same order on cooling, but a one-stage transformation on heating (M→A) was observable. A value of 600°C was ascertained to be the critical heat-treatment temperature at which the test specimen was free from R-phase. In this case, only one-stage transition of A↔M was demonstrated.

The changes in peak shapes of the DSC curves due to the annealings, entailed the changes in transformation temperatures and heats. Regarding the difference between M_s and M_f during cooling, it was observed to decrease with increasing annealing temperature, being the highest for annealing at 400°C (57°C) and the lowest for annealing at 600°C (~8°C). The difference between R_s and R_f upon cooling was found to be almost independent of annealing temperature in the range of 400-550°C. Similarly, difference between A_s and A_f during heating remained almost constant for the specimens annealed above 450°C.

Summarizing the findings shown in this paper one may state that the general trends in the thermal properties measured as a function of annealing temperature correspond for example to those presented in the literature for the Ni-Ti SMA [20-23]. However, it is should be said here, that the precise history of processing for the as-received Nitinol alloy was not revealed from the supplier friend. From the other side, the sequences of transformations as well as the characteristic temperatures are influenced by prior thermo-mechanical history of the alloy, according to Ref. [24]. Based on the DSC results received, also Refs [3, 10] and publications mentioned just above, therefore, it is reasonably to suspect that the as-received alloy could somehow be thermo-mechanically treated before the tests. A characteristic issue here is that the material in this condition exhibited the SME, although its magnitude was not measured in this study. In any case, the observed behaviour in phase transition characteristics of the Ni-Ti alloy subjected to heat-treatment may be explained by the modification its microstructure.

4. Conclusions

It is generally stated that the annealing temperature applied to the as-received Ni-Ti SMA turned out to be a valid parameter which affects the transformation behaviour and associated thermal quantities. Calorimetric tests showed that below a certain annealing temperature the transformations proceeded in the presence of R-phase. 600°C was found to be the value where only one-stage phase transformation of A↔M took place.

The marked changes in transition temperatures due to annealing occurred for martensite, while much smaller ones appeared for austenite and the R-phase. In spite of some inaccuracies as for the thermo-mechanical history of the as-received Ni-Ti alloy, it is believed that the changes in measured thermal properties can be attributed to the evolution of the alloy microstructure as a result of annealing heat-treatment. It requires further and deeper research.

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