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Investigation of thermal transformation properties under different annealing conditions of Ni-Ti shape memory alloy

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Abstract. In this paper, the influence of different annealing conditions on the phase transformation properties of a nearly equiatomic nickel and titanium (Ni-Ti) alloy was studied by using differential scanning calorimetry (DSC). Tiny samples, taken from the as-received material with the unknown history of thermo-mechanical processing, were subjected to the heat treatment at the temperatures varying from 400 to 600°C with a 50°C increment for 5, 20, 30, and 60 min. Based on the DSC testing, the phase transformation behaviour and temperatures were assessed. The results from this and previous studies indicate that thermal characteristics of the studied Ni-Ti alloy are sensitive to the annealing conducted under different parameters. When the heat treatment temperature increased, the phase transformation behaviour tended to convert from a two-stage sequence, i.e. through the intermediate R-phase to a one-stage reaction, as it was observed at 600°C. However, a certain exception appeared for the sample annealed for 5 min where the two-stage transformation on cooling was still preserved. Considering the effect of annealing time, there was no obvious change in the DSC profiles for annealing at 400 and 450°C. Higher annealing temperatures, in turn, resulted in variations of the peak shapes. Different annealing times were also shown to affect the transition temperatures where the most distinct alterations occurred for the M_s and M_f temperatures in comparison with the other ones. This type of studies, it is believed, may be useful especially from a practical point of view, i.e. in varying and controlling the properties of shape memory alloys (SMAs).
Keywords: Ni-Ti shape memory alloy, annealing conditions, DSC transformation properties

1. Introduction

In the previous article [1], the findings concerning the effect of different annealing temperatures on the phase transformation behaviour of the Ni-Ti shape memory alloy (SMA) were reported. Thermal treatment was done for a one period of time, and differential scanning calorimetry (DSC) measurements clearly showed that below a certain annealing temperature, the phase reactions exhibited the two-stage behaviour through the intermediate R-phase. However, progressive changes of the DSC peak shapes and related parameters appeared. The temperature of 600°C for 30 min was found to be the annealing treatment, after which a direct martensitic transition took place. There was also mentioned in the first section of Ref. [1] that the occurrence of different transformation behaviours and changes in critical temperatures depend on many factors including an applied heat treatment. On the other hand, the transformation behaviour in this class of materials can be affected not only by annealing temperature, but also by period of annealing time and cooling rate [2-5]. For nearly equiatomic Ni-Ti alloys (not too rich in nickel), a distinct sensitivity to transition properties can take place when the heat treatment is carried out within the confines of thermo-mechanical treatment [6, 7]. To the best available knowledge of the authors, there are a few reports in the literature showing the influence of annealing time on the transformation properties of Ni-Ti SMAs with a Ni content of less than 50.4 at.% [8-11]. The results presented there deal with the test samples after previous cold working, although in Ref. [11], for example, there is no clear information regarding the processing procedures of the initial material. In the present paper, the influence of annealing time on the phase transformation behaviour and critical temperatures of nearly equiatomic Ni-Ti alloy are presented based on the DSC measurements.

2. Procedure

A binary Ni-Ti SMA with 50.08 at. % Ni and balance Ti was used in this study. The initial material was received in the form of sheet of 0.5 mm in thickness without exact information about the thermo-mechanical processing history, i.e. prior working and final (possible) heat treatment. The transformation behaviour in the as-received condition revealed that the intermediate R-phase appeared during both heating and cooling, as reported previously [1, 12]. Prior to calorimetric characterization, small samples were subjected to an annealing at different temperatures (400, 450, 500, 550 and 600°C) for various times (5, 20, 30, and 60 min) in a muffle furnace followed by air cooling. After the annealing, a cleaning procedure was given to the samples, and its details along with the DSC experimental specification can be found elsewhere [1]. The critical temperatures of the transformations were estimated by the intersection of tangent lines to the DSC profiles, as illustrated in Fig. 1.

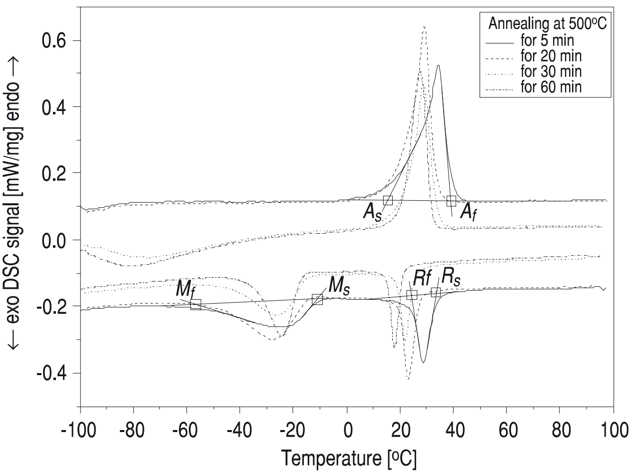

Fig. 1. DSC runs of the as-received Ni-Ti alloy after annealing at 500°C for different times

3. Results and discussion

Figures 1-3 show the DSC runs for samples annealed at temperatures in the range between 500 and 600°C for four different annealing times. As for this set of DSC curves, the phase transformation behaviour for 30 and 60 min of annealing along with the following other thermal characteristics were published previously [1, 12] and they are plotted here for comparison.

Despite variations of the DSC peak shapes after annealing at 500 and 550°C for different times, two-stage transformation behaviour with the existence of the R-phase was demonstrated every time on cooling. As shown in Figs. 1-2, with increasing annealing time, the heat flow peaks were becoming sharper with a tendency to displacement. On heating, a single peak corresponding to the direct reverse transformation was actually detected in all the samples; however, an annealing condition of 500°C/5 min resulted in a little asymmetrical character of the endothermic peak suggesting still the two-stage behaviour due to trace amount of the martensite→R-phase transformation (Fig. 1). It was found that after heat treatment for 5 and 20 min at 400 and 450°C, the DSC plots were very similar to those obtained for 30 and 60 min (see Refs. [1, 12]), and therefore are not displayed in the present paper. They also revealed the two-stage transitions both on heating and cooling, and with reference to the as-received material, small changes in characteristic temperatures were already noticeable. Heat treatment at the temperature of 600°C caused that the R-phase disappeared and hence the direct one-stage transformation was observed regardless of the periods of time (Fig. 3). The only exception appeared for the sample annealed during 5 min where the two-stage reaction on cooling was still preserved. It follows that this time period at

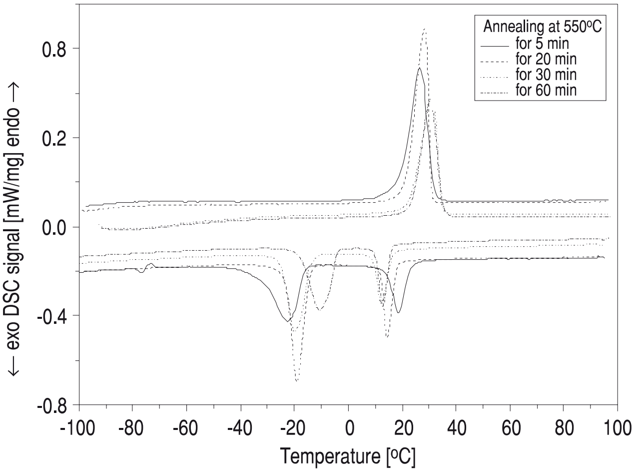

Fig. 2. DSC runs of the as-received Ni-Ti alloy after annealing at 550°C for different times

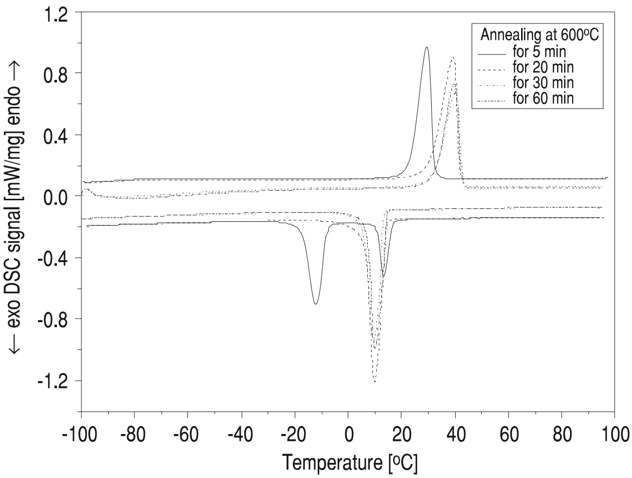

Fig. 3. DSC runs of the as-received Ni-Ti alloy after annealing at 600°C for different times

the highest annealing temperature was too short in order to introduce qualitative changes in the transformation sequences.

Figures 4-8 show the phase transformation temperatures of Ni-Ti samples annealed at various temperatures, plotted as a function of annealing time. Note that due to the overlapping of two thermal peaks on the DSC heating curve, some temperatures related to the reverse transformations were impossible to deduce in samples after annealing at 400 and 450°C. At these annealing temperatures, the R_s, R_f, A_s, and A_f temperatures were almost unchanged when the annealing time increased from 5 to 60 min. There was also no distinctive trend in the M_s and

M_f temperatures, although their small variations were noticed with increasing annealing duration (Figs. 4-5). This behaviour may result from the inaccuracy in the determination of transformation temperatures because the R-phase→martensite peaks had strongly broadened and flattened shapes (see Refs. [1, 12]).

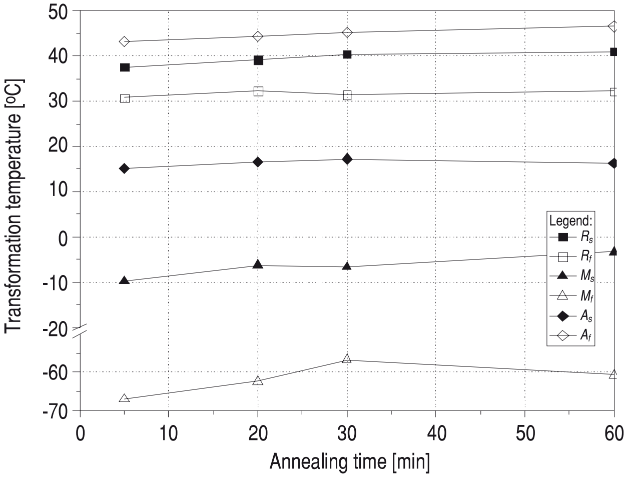

Fig. 4. Transformation temperatures vs. annealing time for the samples annealed at 400°C

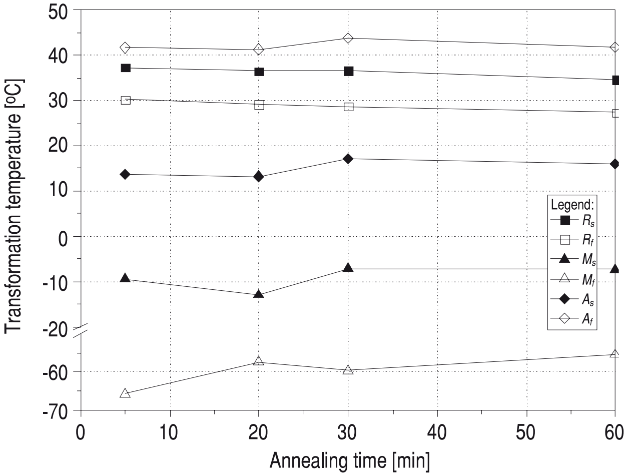

Fig. 5. Transformation temperatures vs. annealing time for the samples annealed at 450°C

For a heat treatment temperature higher than 450°C, different annealing times were shown to affect clearly the measured temperatures, as illustrated in Figs. 6-7. At 500°C, apart from A_s and M_f temperatures, the increase in annealing time caused an apparent decrease in the others, when the biggest one occurred between

5 and 20 min. The A_s and M_f temperatures increased steadily by annealing time, as shown in Fig. 6.

At the annealing temperature of 550°C, the R_s and R_f temperatures decreased while the A_s and A_f increased with the variation of the annealing time from 5 to 30 min (Fig. 7). Then, they appeared to be almost unaffected with extending the annealing duration to 60 min. Regarding the M_s and M_f temperatures, they were generally found to increase; however, the M_f increased initially up to 20 min, subsequently decreased somewhat with increasing annealing time, and then again increased for 60 min. It is worth noticing that although a temperature of 550°C was already fairly

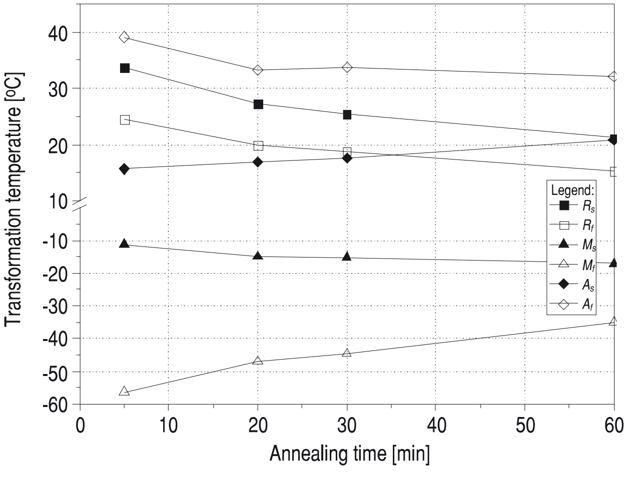

Fig. 6. Transformation temperatures vs. annealing time for the samples annealed at 500°C

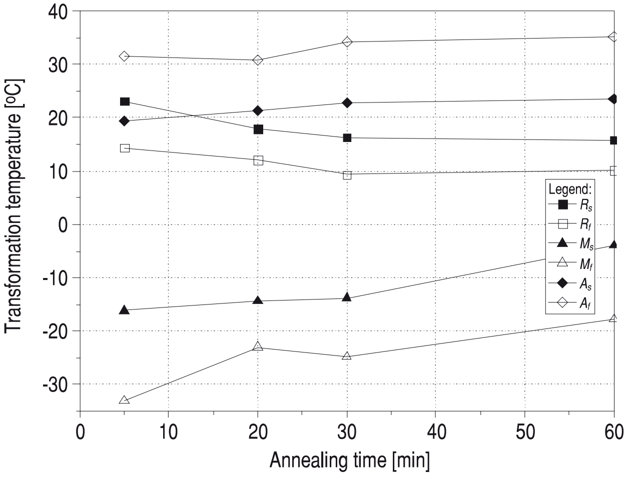

Fig. 7. Transformation temperatures vs. annealing time for the samples annealed at 550°C

high, the prolonging of annealing time did not cause the qualitative variations in phase transformation behaviour. For the samples being annealed at the highest temperature (600°C), the measured transformation temperatures exhibited initially a strong upward trend, as shown in Fig. 8. When the time of annealing was more than 20 min, they stayed at an almost constant level showing that longer annealing times have no effect on the transformation temperatures. To clarify, in all cases, when the two-stage transition was identified on cooling, the M_s temperature was always associated with the R-phase→martensite reaction as opposed to the one-stage behaviour where it directly resulted from the cooling of the austenite phase. According to the present study, annealing at 600°C for 20 min was found to be a critical thermal condition to eliminate completely the intermediate structure from the as-received material (Fig. 3). Regardless of the used different annealing conditions for Ni-Ti SMA which was used here, the M_s temperature was below room temperature.

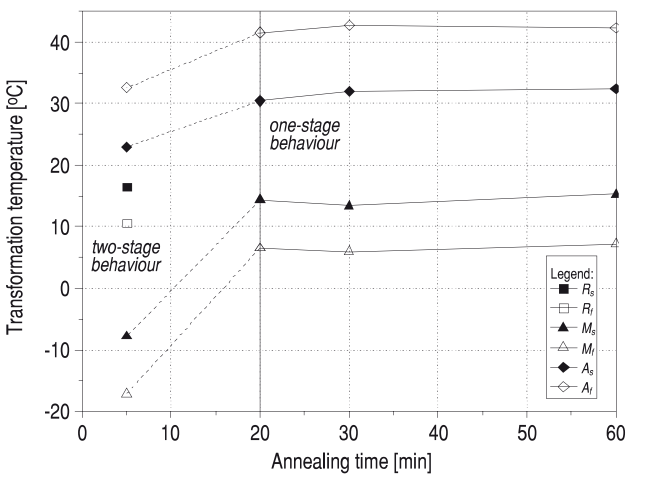

Fig. 8. Transformation temperatures vs. annealing time for the samples annealed at 600°C

From the data collected in Figs. 4-8, it can be also perceived that with simultaneous increasing annealing temperature and annealing time, both the R_s and R_f temperatures decreased whereas the A_s and M_f ones increased. Other temperatures, including M_s and A_f were observed to decrease after annealing at temperatures till 550°C. Above this temperature, the trend reversed and an increase was stated to take place.

In general, it is known that heat treatment in the previously cold deformed SMAs is a way to reduce the structural defects and by exceeding some critical temperature the recrystallization process appears [2, 13]. Furthermore, annealing treatment is a final process of Ti-Ni SMA fabrication to memorize the shape [14], as well as a simple method for setting a new defined shape or size into the material

[15]. Since the alloy used for the present study had precisely unknown thermo-mechanical processing history, the presence in the as-delivered condition of the two-stage transformation both on heating (here less clear) and cooling indicates that it could somehow be treated before. In fact, each technological step in the material history is important with respect to its final characteristics [15, 16]; therefore in the case of the as-received SMA, an earlier treatment will definitely affect the response to the subsequent heat treatment. DSC runs, similar in appearance to those obtained from the as-received material, can be found in Refs. [17, 18], where a TiNi alloy with the approximate composition in atomic percentage was analysed calorimetrically after cold working and subsequent heat treatment. Such a specific thermo-mechanical processing for these alloys, in which thermal stage is executed within certain temperatures, is known to promote the R-phase transformation [7, 19-21]. Hence, on the basis of the cited reports [17, 18] and from the results in the present study, it is concluded that the last processing stage for the as-received alloy was probably annealing at relatively low temperatures, i.e. well below its recrystallization temperature. On the other hand, it is also known that thermal treatment not exceeding this critical temperature following the cold-working is used to obtain a desirable functional behaviour, mainly for improving the pseudoelastic effect in equiatomic Ni-Ti SMAs or with lower Ni-content [13, 18, 21-23].

Considering the above-mentioned issues, samples annealed at temperatures in the range of 500-600°C showed the obvious changes in transformation behaviour in comparison to those annealed at lower temperatures. However, with reference to the as-received material, the latter samples demonstrated already noticeable but small variations in the characteristic temperatures in spite of similar DSC diagrams. Simultaneously with the increase in annealing time, the evolution of transformation properties may suggest that microstructural changes caused by heat treatment at higher temperatures are more and more deepened. For a previously deformed material, for example, these variations are related to the rearranged lattice defects which disappear continuously. In this study, the annealing condition of 600°C/20 min seems to be sufficient to occur the recrystallization process (with reference to the as-received alloy and its prior deformed structure), as indicated by the appearance of a one-stage transformation during the DSC measurement and stable critical temperatures with further increasing annealing time.

Besides the findings presented here, it is believed that this type of studies can be also helpful in experiments concerning the influence of thermo-mechanical cycling conducted under different loading profiles on the shape memory behaviour in Ni-Ti alloys heat-treated at various conditions. To the authors' information, there are not rather many reports dealing with similar problems, and as known they are of great importance from a practical point of view because various applications of SMAs are sensitive to processing procedures [24]. This is now under an intensive study by the present authors and will be reported in due course.

4. Summary

This work, as a continuation of the previous research [1], shows the effect of different annealing conditions on the thermal transformation properties of near-equiatomic Ni-Ti alloy. Annealing temperatures of 400, 450, 500, 550 and 600°C and four various times of 5, 20, 30, and 60 min were selected for this purpose. As indicated by the DSC measurements, two-stage transformation behaviour was observed in the as-received alloy and for annealing up to 550°C. A qualitative change, after which the tested samples were free from R-phase (a one-stage transformation), appeared as a result of annealing at 600°C, except for the one annealed for the shortest duration (5 min), demonstrating still the two-stage transformation on cooling. Considering the effect of annealing time, there was no obvious change in the DSC profiles for annealing at 400 and 450°C. When the annealing temperature was further raised, the peak shapes on the calorimetric curves varied as the annealing time increased. Different annealing times were also found to affect the phase transformation temperatures where the most distinct alterations occurred for the M_s and M_f temperatures in comparison with the other ones. In the absence of the intermediate R-phase after thermal treatment at 600°C, the measured critical temperatures were found to be almost independent of annealing times above 20 min, suggesting that the recrystallization process occurred.

Although microstructural study was not carried out here, it may be concluded that evolution of transformation characteristics due to annealing under different parameters is attributed to some modifications that occur inside the material structure. In this context, a possible thermo-mechanical treatment of the as-received alloy is essentially important; however, its historical aspects were unknown in details before the experiments.

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Badanie charakterystyk cieplnych przemian fazowych w stopie Ni-Ti z pamięcią kształtu poddanemu wyżarzaniu przy różnych parametrach

Streszczenie. Za pomocą różnicowej kalorymetrii skaningowej (DSC) zbadano wpływ różnych parametrów wyżarzania na charakterystyki cieplne w zakresie występowania przemiany fazowej w stopie niklowo-tytanowym (Ni-Ti) o składzie chemicznym bliskim równoatomowemu. Próbki do badań pobrano z materiału o nieznanej historii uprzednich obróbek cieplno-mechanicznych, a następnie wyżarzano w temperaturach 400-600°C co 50°C przy czasach 5, 20, 30 i 60 min. Wykazano, że charakterystyki cieplne przemian badanego stopu są czułe na wyżarzanie prowadzone przy różnych parametrach. Wzrost temperatury wyżarzania spowodował zmianę sekwencji przemian od dwustopniowej (tj. poprzez fazę pośrednią R) do jednostopniowej, obserwowaną przy 600°C. Pomimo najwyższej temperatury obróbki wyjątek jedynie stanowił najkrótszy jej czas, gdzie wciąż rejestrowano sekwencję dwustopniową przemiany podczas chłodzenia stopu. Najniższe temperatury wyżarzania (400 i 450°C) nie spowodowały istotnych zmian w profilach DSC w przeciwieństwie do wyższych temperatur, gdzie obserwowano zmiany ich kształtów. Ustalono, że różne czasy wyżarzania mają wpływ na temperatury krytyczne przemian, spośród których M_s i M_f wykazały największe zmiany. Uważa się, że tego typu badania mogą być użyteczne z praktycznego punktu widzenia, zwłaszcza do zmian i kontroli charakterystyk cieplnych stopów z pamięcią kształtu (SMAs).

Słowa kluczowe: stop z pamięcią kształtu Ni-Ti, wyżarzanie, charakterystyki przemian DSC