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THE INFLUENCE OF REPEATED HEATING AND COOLING PROCESS ON THE TRANSFORMATION CHARACTERISTICS IN Ni-Ti ALLOY

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K e y w o r d s: Ni-Ti alloy, heating and cooling cycles, DSC, transformation behaviour.

A b s t r a c t

The transformation characteristics of a near-equiatomic polycrystalline Ni-Ti alloy in an annealed state (600°C/30 min/air-cooling) were determined by DSC measurements in order to investigate the effect of repeated heating and cooling process through the martensitic transformation region. It was observed that transformation profiles exhibited qualitative differences depending on the number of executed heating and cooling cycles. Due to the increasing number of thermal cycles, the forward transformation changed from a one-stage (B2→B19') to a two-stage (B2→R→B19') reaction while the reverse martensitic transformation showed the one-stage character (B19'→B2), independently of the number of achieved cycles. The other thermal properties were also found to change with thermal transformation cycles. Based on the calorimetric results and literature studied, it is thought that observed changes in transformation characteristics can be attributed to the modifications of the alloy microstructure. In this case the introduced defects which are accumulated during the thermal cycles play an important role.

WPŁYW PROCESU WIELOKROTNEGO NAGRZEWANIA I CHŁODZENIA NA CHARAKTERYSTYKI PRZEMIAN W STOPIE Ni-Ti

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S ł o w a k l u c z o w e: stop Ni-Ti, wielokrotne nagrzewanie i chłodzenie, metoda DSC, zachowanie się stopu w zakresie przemiany.

Abstrakt

Metodą pomiarów DSC wyznaczano charakterystyki cieplne przemian fazowych w stopie polikrystlicznym Ni-Ti o składzie bliskim równoatomowemu, w stanie po wyżarzaniu (600°C/30 min/chłodzenie w powietrzu) w celu zbadania wpływu procesu wielokrotnego nagrzewania i chłodzenia w obszarze występowania przemiany martenzytycznej. Stwierdzono, że rejestrowane profile DSC przemian przejawiały jakościowe zmiany w zależności od liczby wykonanych cykli cieplnych. Wraz ze wzrostem liczby cykli przemiana z ang. „wprost" zmieniła się od jednostopniowej (B2→B19') do dwustopniowej (B2→R→B19'), podczas gdy przemiana odwrotna wykazywała sekwencję jednostopniową (B19'→B2), niezależnie od zrealizowanej liczby cykli. Poza tym ustalono, że inne właściwości cieplne również się zmieniają. Na podstawie uzyskanych wyników kalorymetrycznych oraz przeglądu literatury można sądzić, że obserwowane zmiany w charakterystykach cieplnych mogą być spowodowane modyfikacją mikrostruktury stopu. W tym przypadku defekty oraz ich nagromadzenie się wskutek wielokrotnego nagrzewania i chłodzenia odgrywają główną rolę.

Introduction

From among many "smart/interactive" materials (WEI et al. 1998, MACKERLE 2001, MONNER 2005, WILSON at al. 2007), shape memory alloys (SMAs) still have strong interest in scientific and commercial areas. From the wide range of alloys with the reversible effect of shape memory (FREMOND, MIYAZAKI 1996, SCHWARTZ 2002, SHAW et al. 2008), it is commonly accepted that near-equiatomic Ni-Ti alloy (designated as Nitinol) exhibits the best shape memory and structural properties. In the studies of SMAs, for example, with regard to their cyclic applications, it is important to know the material response to the various thermal/mechanical treatments. There are many factors having an influence on the transformation characteristics in NiTi alloys (NURVEREN et al. 2008, PAULA et al. 2004, MEHRABI et al. 2009). One of them is the repeated heating↔cooling, i.e. thermal cycling which can lead to changes in sequences of the forward and reverse transformations (MATSUMOTO 1993, MCCORMICK, LIU 1994, WU et al. 1999, MATSUMOTO 2003). The transformation behaviour in SMAs is mostly examined using differential scanning calorimetry (DSC) method. In such experiments different types of transformations depending on the above indicated factors, therefore, can be revealed. According to (EGGELER et al. 2005), one-step transformation means that only one DSC peak is observed on cooling from the high temperature to the low temperature phase. In two- and multiple-step transformations two and multiple peaks appear. Two-step transformations, in turn, are explained by the R-phase, which forms first (B2→R), followed by the formation of B19' (R→B19').

The present paper gives the DSC results of the repetition of the forward and reverse martensitic transformation during stress-free thermal cycling process, and its influence on the thermal transformation properties in an annealed Ni-Ti alloy is considered.

Experimental

A polycrystalline Ni-Ti SMA in sheet form was utilized in this study, and its composition was 50.08 nickel in atomic percent. Owing to the fact that the thermo-mechanical history of the as-received material was unknown, the alloy sample was initially annealed at 600°C for 30 minutes prior to the proper DSC measurements. It should be noted that the Ni-Ti alloy exhibited in the as-received state the presence of the R-phase, as shown elsewhere (KUŚ 2007, KUŚ, BRECZKO 2010). The annealing process of a rectangular sample with dimensions of 3x1.7x0.5 mm was carried out in a muffle furnace, followed by air-cooling to room temperature (about 22°C). In order to reduce the oxidation of the sample during heat-treatment, a continuous flow of argon gas through the furnace chamber was applied. The annealing conditions selected for this study ensured a one-step of the B2↔B19' reaction, i.e. without revealing the intermediate R-phase. After the annealing, the sample surface was carefully cleaned by fine abrasive paper, washed in distilled water and alcohol, and etched with a $5H_2O+4HNO_3+1HF$ solution for 30 s. Following that, the sample was again washed in water and alcohol. These operations were aimed at removing the surface layer that might be slightly oxidized during heat-treatment.

A differential scanning calorimeter (DSC 204, Netzsch) system was used to characterize the transformation properties of the thermally cycled alloy. After an initial heating the sample from room temperature to +70°C, it was cooled (10 K/min) to -40°C (first cooling cycle) and kept for 2 min to obtain thermal equilibrium. Then the specimen was heated (10 K/min) to +70°C (second heating cycle) and held again for 2 min. The repeated stress-free heating and cooling was carried out up to 60 cycles.

Results and discussion

Figs. 1-2 show a set of DSC graphs of the thermally cycled Ni-Ti sample, illustrating the courses for the forward and reverse transformation, respectively. The numbers on the curves indicate the number of thermal cycles.

The repeated heating and cooling process caused that transformation behaviour of the sample tested demonstrated qualitative differences depending on the number of accomplished thermal cycles. In the early stage of thermal cycling, both the forward and reverse transitions occurred as the one-step sequence from austenite to martensite, and vice versa (B2↔B19'). However, after achieving the first full 10 cycles, the DSC courses on cooling began to show interesting changes. With effect from an appearing small shoulder on the

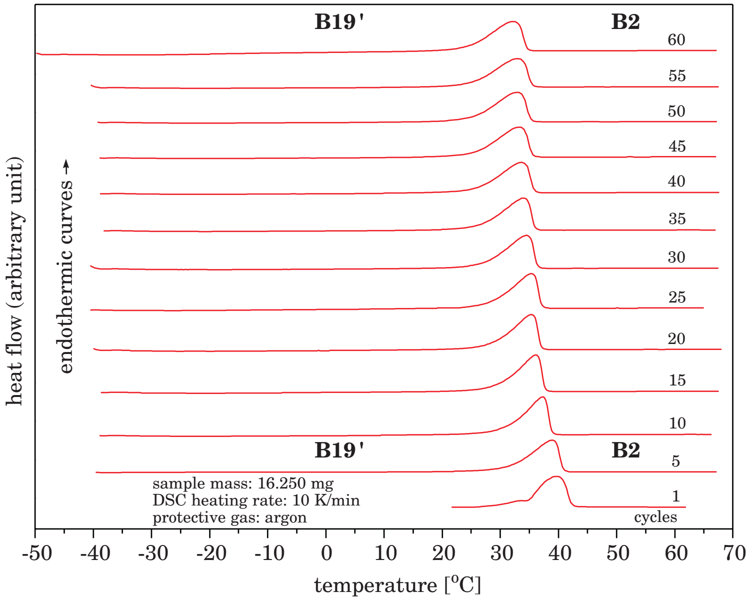

Fig. 1. DSC curves for the reverse transformation against thermal cycles

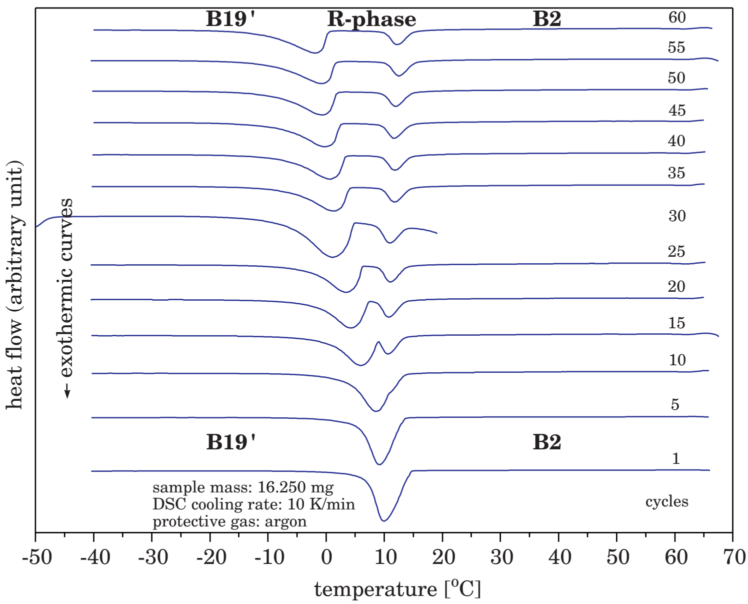

Fig. 2. DSC curves for the forward transformation against thermal cycles

exothermic peaks, two overlapping peaks were recorded in consecutive thermal cycles. It proves that the intermediate R-phase started to form prior to martensite. These heat flow peaks tended to be more distinct and separated as the number of thermal cycles increased, implying unequivocally that the forward transformation occurred in two successive steps (B2→R→B19'). The B2→R transformation was found to emerge clearly after eighteenth forward transformation cycles, not shown in Fig. 2. The endothermic DSC curves in Fig. 1 revealed only a single peak indicating that the reverse transformation still remained as the one-step sequence (B19'→B2). It follows that the repeated heating and cooling process has a significant effect on the transformation behaviour.

The changes in other thermal properties, which can be extracted from DSC thermograms, were observed simultaneously along with the variations in peak shapes, as illustrated in Figs. 3–4. The M_p, R_p, M^*_p and A_p are defined as the temperatures of the maximum DSC peaks for the B2→B19', B2→R, R→B19' and B19'→B2 transformations, respectively. The symbols ΔH_M, ΔH_R, ΔH_{M^*} and ΔH_A mean the transformations heats corresponding to the individual transformations in order as mentioned just above. The latter parameters were estimated from the areas between the heat flow peak and the base line by means of DSC equipment software.

There was a gradual decrease in the combined values of M_p+M^*_p, and A_p with the repetition of the transformation by thermal cycling, as shown in Fig. 3. The temperature difference between the first and the final cycle was measured to be about 11.5 and 7°C for the (M_p+M^*_p) and A_p, respectively.

By observing the curve shapes during cooling, it was found the height and width of the B2→B19' peak decreased and broadened resulting in gradually split into two separate ones (the first formed peak is due to B2→R transition), as the number of thermal cycles increased. From the twelfth cycle, there were no distinct changes in the peak temperature of the R-phase (R_p) during the thermal cycling, though a slight tendency to increase in the value outlined. The experimental results illustrated in Fig. 3 indicate that the thermal hysteresis, defined here as the difference between the calorimetric peak temperatures of the forward and the reverse transformations, enlarged with successive thermal cycles. It was varied from ca. 30 to 34°C. It is necessary to point out that after executing a dozen cycles the thermal hysteresis was only measured between the peak temperatures of the R→B19' and B19'→B2 (due to the introduction of intermediate phase).

With reference to the results presented in Figs. 1–3, it can be stated that the transformation behaviour and related thermal characteristics of the studied Ni-Ti alloy are influenced by the repeated thermal cycling. It is known that the presence of the R-phase can be revealed in Ni-Ti alloys only

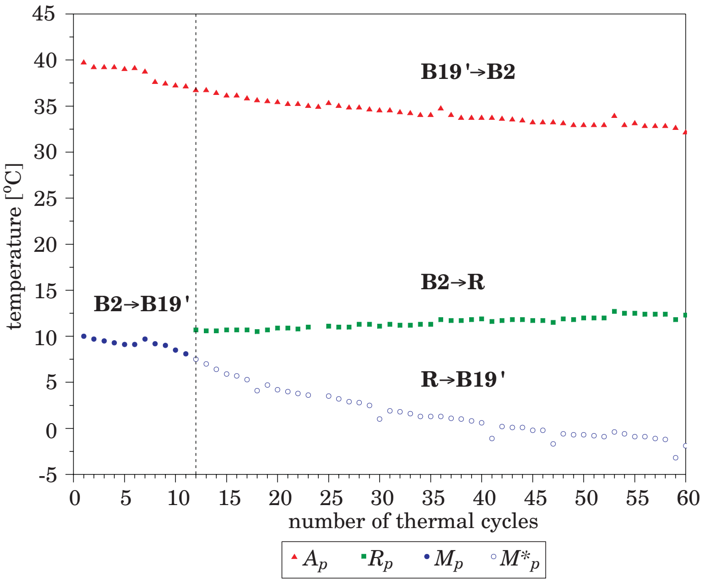

Fig. 3. Phase transformation peak temperatures against thermal cycles

if the M_s temperature is sufficiently low, so as to avoid direct A→M transformation (PAULA et al. 2004). Although the phase transformation starting and finishing temperatures were not quoted in the present paper, the changes in the DSC exothermic curves in Fig. 2 clearly show that there was a progressive fall in the M_s temperature by increasing the number of transformation cycles. Such a tendency in the critical temperature may be related to the decrease in stability of the martensite phase, thereby facilitating the formation of the R-phase (UCHIL et al. 2002). The decrease in M_s before the appearance of intermediate transition symptoms (as observed at ninth cooling cycle), was estimated to be about 3°C. The DSC results in Fig. 2 also show that the R-phase was stabilized during the repeated heating and cooling process but, only its temperature range was expanded as the number of thermal cycles increased.

The absorbed heat during reverse transformation and the released heats during forward transformation with respect to the number of thermal cycles are gathered in Fig. 4. From these data it can be seen that the heats measured for both the reverse and martensitic transformations shifted rather smoothly with increasing thermal cycles. The trend in the values of ΔH_A and ΔH_M (as absolute data) was decreasing and increasing, respectively. Basically, ΔH_M was calculated in the early stage of thermal cycling, although at the end of this range the two separate forward transitions on cooling were still combined

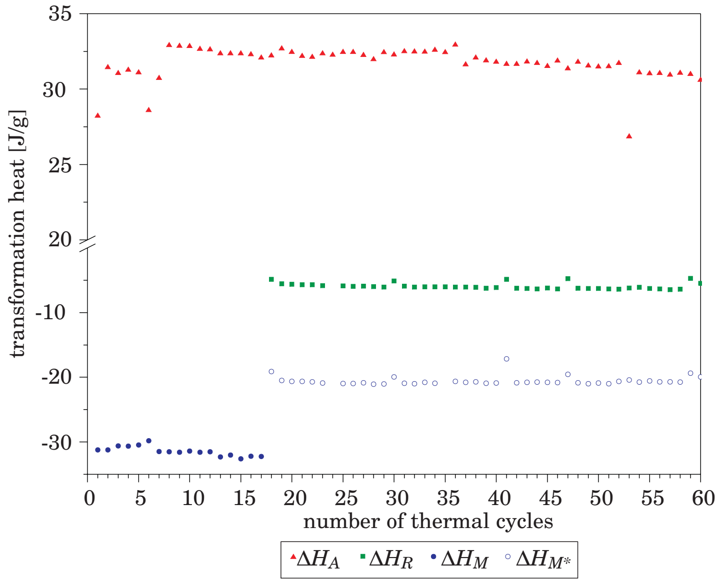

Fig. 4. Heats measured for the forward and reverse transformations against thermal cycles

together for the measurement due to the partial overlapping of the B2→R and R→B19' heat peaks. Once the two exothermic peaks were clearly separated, the values corresponding to the ΔH_R and ΔH_{M*} were estimated. It is evident from Fig. 4 that they appeared to stay almost unchanged with respect to the number of thermal cycling.

The presented calorimetric results in this paper, showing the influence of repeated heating and cooling process on the transformation behaviour in the near-equiatomic Ni-Ti alloy, are in agreement with other studies (MATSUMOTO 1993, MCCORMICK, LIU 1994, MATSUMOTO 2003). According to them, and also Refs. (UCHIL et al. 2002, MIYAZAKI et al. 1986), observed changes in the thermal transformation characteristics can be attributed to the modifications of the alloy microstructure. In this case the introduced structural defects (dislocations) which are accumulated by the thermal cycling process are of crucial importance consequently affecting the martensitic transformation behaviour.

Summary and conclusions

The effect of repeated heating and cooling process on the transformation characteristics in Ni-Ti alloy after annealing heat-treatment was analysed thermally using the DSC technique, and the main results received were as follows:

1. In the early stage of thermal cycling, which covered the twelfth first cycles, the specimen experienced a one-stage transformation behaviour (B2↔B19'). With further increasing thermal cycles, it already demonstrated a two-stage (B2→R→B19') transformation on cooling and a single-stage (B19'→B2) on heating, implying that the repeated thermal cycling has a strong influence on the transformation behaviour.

2. There was a gradual decrease in the critical transition temperatures during the thermal cycling, whereas not very discernible changes were found in the peak temperature of the intermediate R-phase. Due to the increasing number of thermal cycles, the R-phase manifested itself in stabilization although its temperature range was expanded progressively.

3. Obtained calorimetric results and literature analysed allow to think that changes in the thermal transformation properties can be related to the fact that some modifications to the alloy microstructure (mainly dislocations) are introduced and then accumulated due to the repeated heating and cooling process.

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