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Effect of cold deformation to transformation temperatures of Ni-Ti shape memory alloys

C. Yildiz*, B.O. Kucukyildirim, A. Akdogan Eker
Department of Mechanical Engineering, Yildiz Technical University, Besiktas, Istanbul, 34349, Turkey
* Corresponding e-mail address: ceyildiz@yildiz.edu.tr

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ABSTRACT

Purpose: of this paper is to predict the effect of cold deformation to transformation temperatures of Ni–Ti SMA and clarify the relation between cold forming ratio and the parameters of thermo mechanical process.

Design/methodology/approach: 25% and 50% cold formed Ni–Ti wire specimens are investigated for defining the relation between the ratio and the parameters of thermo mechanical processes of without annealing and with annealing at 450°C for 30 minutes and 600°C for 30 minutes. Moreover, Differential Scanning Calorimeter (DSC) measurements are applied to the specimens for obtaining the transformation temperatures.

Findings: According to DSC measurements, start and finish temperatures of transformation of austenite, martensite and rhombohedral phases are calculated. Hence, their changes are related to deformation and annealing, so it can be implied that cold deformation process leads to increases in the temperature ranges, slow occurrences of transformation and also the shape memory property lowers.

Research limitations/implications: It is observed that some specimens exhibit rhombohedral phase transformation and this affects the martensite phase transformation temperatures and results. Thus, annealing time can be increased to determine both positive and negative effect to transformation properties for further research. Moreover, the grain-size and form may also be effective, so this case should be studied.

Practical implications: can be stated as suitable transformation temperatures must be paid attention to desired service temperatures of products those are made of Ni–Ti SMAs, otherwise they may exhibit unexpected shape change due to the affected transformation temperature.

Originality/value: is that Ni–Ti SMAs may be exposed to cold deformation when they are manufactured for being given any product shape, so with this research it can be determined that if their transformation temperatures change or not. Besides, it can be implied that they change and so this study presents the changes, the intervals of start and finish temperatures relevant to the cold forming ratio.

Keywords: Shape memory alloys (SMAs); Titanium-nickel alloys; Cold forming; Transformation temperatures

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MATERIALS MANUFACTURING AND PROCESSING

1. Introduction

Shape memory alloys (SMAs) can be implied as smart metals, especially alloys having the abilities of remembering and taking predetermined forms those are caused by thermodynamic properties of them. Nowadays, Ni-Ti alloys are researched intensively as functional materials for development of various fields and applications.

They are already used in the engineering and medical fields, due to the superior mechanical properties and corrosion resistance [1].

They were first discovered and studied as SMAs in the early 1960s by W.F. Buehler, a researcher studying on non-traditional alloys for the Naval Ordnance Laboratory in Silver Springs, Maryland, USA [2]. Because of name of the research laboratory, these sorts of alloys may also be called as "Nitinol". He noticed that they could produce shape memory effects with a controlled heat treatment.

Shape memory behaviour is based on the change from a low temperature phase of martensite to a high temperature phase of austenite by a predetermined shape by heating [3]. Thermomechanical behaviour of the material changes according to five main temperatures, which are: M_s and M_f at which martensitic phase formation occurs, A_s and A_f perform as austenite phase formation and M_d above which the material behaves as any ordinary material with no unique properties [3,4]. Moreover, mechanical and thermal effects such as thermal cycling, heat treatment, deformation, chemical composition, etc. may lead to an intermediate phase of rhombohedral, which is shown as R and may be detected between austenite phase transforming to martensite phase, in certain circumstance [5].

Researchers have paid more attention to Ni-Ti alloys against other SMAs since their discovery. They are much stronger and also tend to recover higher strains up to 8 or 10% in regard to other ones. Their properties of biocompatibility and high corrosion resistance lead to excessively use of them in medical applications in cardiovascular and orthopaedic devices and surgical instruments. For these applications, A_f temperature becomes a key optimization parameter influencing how a Ni-Ti alloy part or device behaves, since it affects the amount of stresses and strains [6].

It is known that SMAs are generally formed cold for industrial applications and if the effect of A_f temperature is considered, the related temperature values and also the hysteresis of the transformation temperatures become more important. Accordingly, cold deformation is one of the factors affecting the transformation temperatures of SMAs. In this study, 25% and 50% cold formed Ni-Ti wire specimens are investigated for defining the relation between the ratio and the parameters of thermo mechanical process.

2. Material and method

2.1. Material and sample properties

Due to the aim of studying two factors, cold deformation ratio and annealing conditions, with three different levels for each of them, nine samples are prepared for Differential Scanning Calorimeter (DSC, Perkin-Elmer Pyris-6) measurements. Details of the samples are shown in Table 1.They are annealed at different conditions (450°C for 30 minutes and 600°C for 30 minutes) in a muffle furnace and cooled to room temperature in air. Then, the samples are rolled cold at two different deformation ratios (25% and 50%).

Table 1.
Details of the samples properties

Sample	Annealing temperature, °C	Cold deformation ratio, %	Weight, mg
1	As received	0	14.5
2	450	0	15.5
3	600	0	16.6
4	As received	25	13.0
5	As received	50	13.1
6	450	25	16.5
7	450	50	15.2
8	600	25	16.9
9	600	50	17.4

2.2. DSC Measurements

At the beginning, the effect of heating/cooling rate on the melting temperatures of the standard indium and zinc are measured and these are used as calibration values. Then, the weighed samples are placed into standard aluminium sample pans and treated with a heating/cooling rate of 20°C/min under a constant nitrogen flow for 1st cycles and 10°C/min for 2nd cycles in the DSC device.

According to the DSC curves, start and finish temperatures of the transformation are determined by the

intersection of a base line and the tangent to a peak. The enthalpy change ΔH is calculated by dividing the area under the curve, which is related to the absorbed/released energy of the transformation process, to the mass of the sample.

A polycrystalline and near-equiatomic Ni-Ti SMA wire with a diameter of 1.000 mm, manufactured by Memory Metalle GmbH, Germany, is used.

3. Results and discussion

3.1. Results

The transformations start, peak and finish temperatures and ΔH amounts are obtained from the DSC Curves and shown in Table 2. The results of 1st and the 2nd cycle treatments are shown in Table 2. At first glance, samples 5, 7 and 9 have no R phase. According to the results, the comparative histograms are prepared, presented in Figs. 1-4 and then discussed.

When the start, peak and finish temperatures of austenitic transformations are observed in Fig. 1, it can be stated that the 1st cycle results are higher than the 2nd cycle ones and As temperature of the sample 5 is the highest. This can be reveal about the sample 5, which is drawn previously by the manufacturer and deformed cold for the study with no annealing, starts to transform A phase at the highest temperature according to the others.

Figure 2 shows that 50% cold deformed samples do not transform to R phases according to their DSC measurements and the R phase transformations of the samples annealed at 450°C start at higher temperatures relatively.

Figure 3 shows the start, peak and finish temperatures of martensitic transformations. Especially, the temperatures of M_s can be assumed as important, so the samples 5, 7 and 9 take attention.

In addition, sample 1 and 4 are not annealed and they response the transformation at different sub-zero temperatures. This character may be relevant with not being annealed and cold deformation ratio.

The histogram of ΔH amounts of samples is consistent with phase transitions by endothermic and exothermic processes. Austenite phase transformations are inherently endothermic and the other phases transformations are exothermic. ΔH amounts of austenite phase transformations lower by increasing the deformation ratios. According to the graph, it can also be mentioned that the cold deformed and not annealed samples exhibit the lowest ΔH amounts.

Table 2.
Results of the DSC measurements

Sample Number	Cycle Number	A_s, ºC	A_p, ºC	A_f, ºC	ΔHA, J/g	R_s, ºC	R_p, ºC	R_f, ºC	ΔHR, J/g	M_s, ºC	M_p, ºC	M_f, ºC	ΔHM, J/g
1	1	105.61	125.26	158.51	6.4916	31.82	17.05	3.39	-3	-1.82	-4.21	-6.56	-0.03
1	2	37.31	53.52	63 89	4.6752	39.14	22.86	4.98	-4.4045	-1.82	-4.21	-6.56	-0.032
2	1	52.65	58.47	65.06	8.3265	52.65	45.01	34.56	-3.0751	25.59	7.51	-14.07	-4.5155
2	2	49.49	60.25	64 85	13.3344	52.65	45.01	34.56	-3.0751	25.59	7.51	-14.07	-4.5155
3	1	52.35	57.88	63 89	12.9455	31.72	29.24	26.99	-4.4362	19.32	16.09	10.72	-8.995
3	2	49.89	56.21	60 18	17.3563	31.66	29.24	27.01	-4.1227	19.31	16.09	10.71	-8.9897
4	1	87.97	138.5	176.64	2.8871	41.86	29.81	-0.55	-0.236	-17.35	-20.13	-22.72	-0.0696
4	2	25.69	48.57	64.25	3.0936	46.43	26.34	-0.55	-0.236	-17.35	-20.13	-22.72	-0.0696
5	1	140.81	144.08	173.42	0.19	-	-	-	-	42.35	26.02	10.28	-0.9851
5	2	21.65	42.84	58 71	1.0341	-	-	-	-	43.7	24.51	1.47	-0.5995
6	1	101.72	108.07	146.34	3.5907	60.33	47.36	34.92	-2.1753	25.61	8.03	-10.43	-2.192
6	2	45.47	58.7	69.28	10.7742	60.66	47.86	34.35	-2.0846	27.2	12.86	-0.29	-0.8372
7	1	98.01	132.52	168.86	1.8302	-	-	-	-	69.54	18.51	-5.2	-10.4374
7	2	43.96	59.53	73.99	2.0674	-	-	-	-	65.78	49.65	31.03	-1.8916
8	1	82.69	106.32	135.02	13.3164	38.81	29.71	23.18	-0.9607	21.06	13.51	5.03	-0.3255
8	2	43.72	54.4	61.31	9.71	40.27	31.37	25.67	-1.4493	22.71	14.54	4.31	-1.392
9	1	101.56	123.68	158.22	4.2819	-	-	-	-	55.9	28.75	-8.02	-9.6124
9	2	36.84	50.05	60.49	3.5003	-	-	-	-	44.94	31.69	24.35	-0.7321

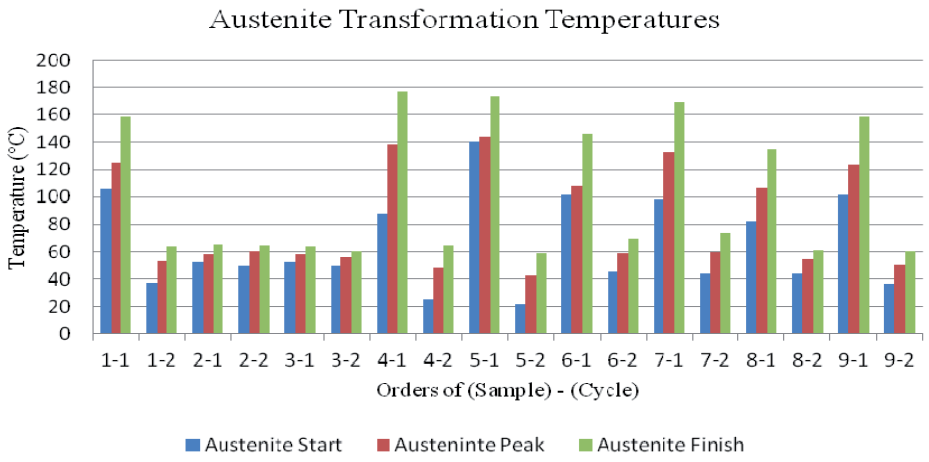

Fig. 1. A_s, A_p and A_f temperatures of samples and cycles

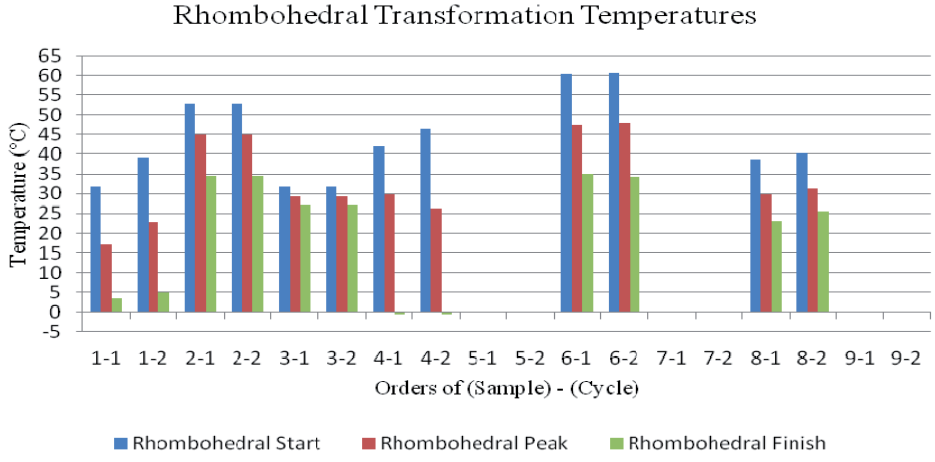

Fig. 2. R_s, R_p and R_f temperatures of samples and cycles

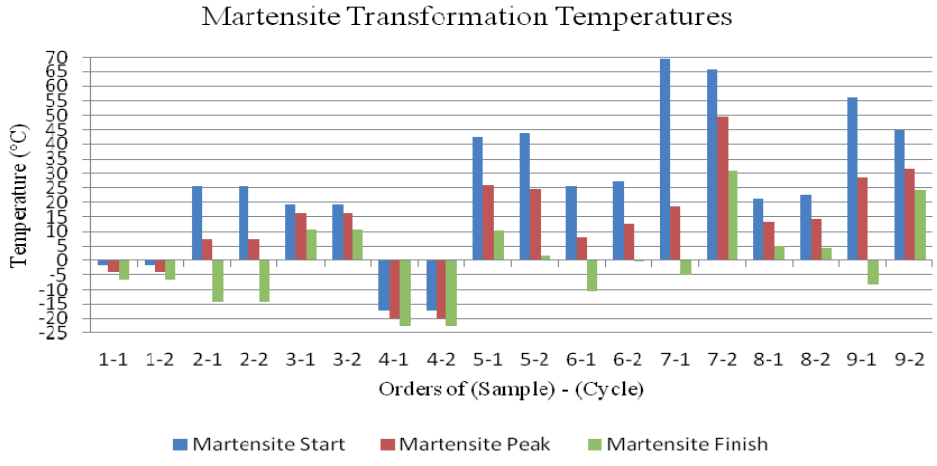

Fig. 3. M_s, M_p and M_f temperatures of samples and cycles

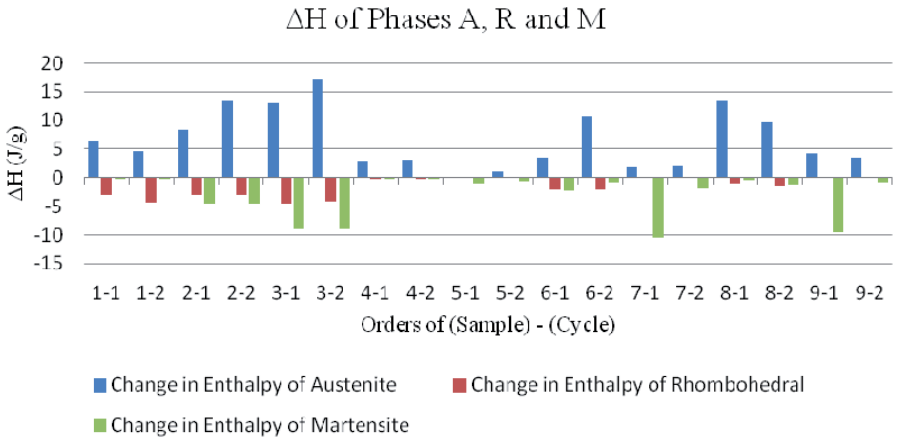

Fig. 4. *ΔH* amounts of samples and cycles

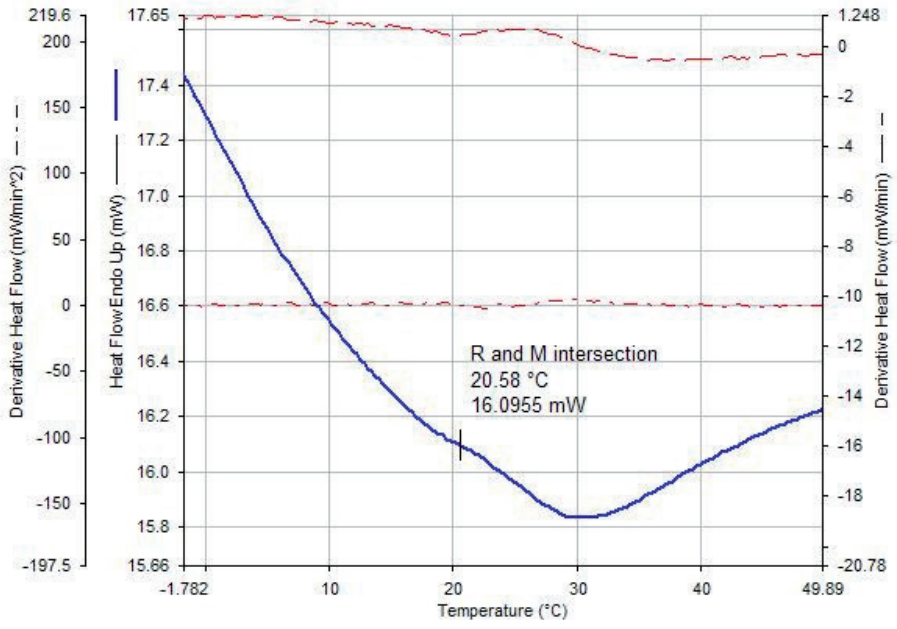

Fig. 5. Cooling section of the DSC curve of the first cycle of sample 9

3.2. Discussion

Classifying the samples makes comparing them with each other easier. Such as the group of 4-6-8 can be assumed as 25% cold deformed samples where 5-7-9 are 50% and if 50% cold deformed samples are evaluated, R phases are not observed obviously according to their DSC measurements.

These results can be obtained by studying the DSC thermal cycle curves and Fig. 5 can be given as an example.

An intersection of R and M phases can be noticed and it can also be verified by its 2nd order derivation, so the R phase can be neglected.

Similarly, Fig. 6 shows another intersection of R and M phases, but their inflection points are more distinct than Fig. 5. The intersections are also common for the samples those are annealed at 600°C, so it may be interpreted that annealing at this condition leads to significant effect on the transformation tendency, changes in micro structures of the samples and extinctive effect to R phase.

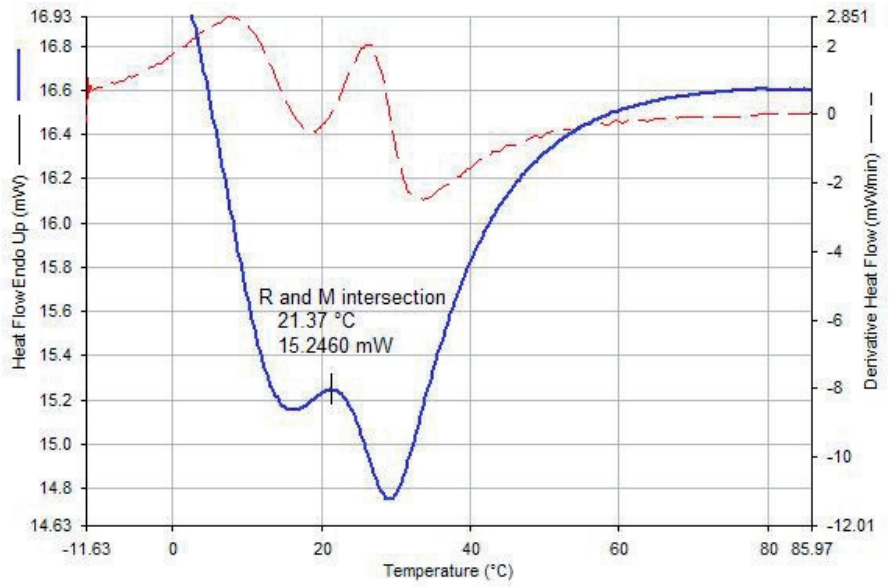

Fig. 6. Cooling section of the DSC curve of the first cycle of sample 8

This circumstance accords with Uchil et al., where they imply that internal stress disappear as the heat treatment temperature increases and the possibility of forming R phase decreases hence, this leads to moving of M_s towards higher values [7].

Several studies reveal that the temperature range of 550-600°C is assumed as the critical annealing temperature range, so this influences the transformation characteristics [5] and this consideration is consistent with the present results, because as received and at 450°C annealed samples have different microstructures from ones annealed at 600°C.

Moreover, peak heights of DSC curves are interrelated with the scanning rates and the reaction rates. It is known that the scanning rates are constant and same as one another for this study, so the reaction rates specify the peak heights characters. Fig. 7 and Fig. 8 show the low peak heights of the second cycle of sample 5. It is convergent to sample 4.

Thus, it can also be stated that rates of reaction or transformation are slow and energy release is low for the samples those are cold deformed and not annealed. It is also known that stopping the movement of dislocations causes phase hardening in the alloy and this case exhibits thermoelastic martensitic transformation that bases a change in the range of transformation temperatures [5]. Due to the cold deformation of the samples, they are hardened and in the views of this situation and information, their martensitic transformation temperatures and the differences of M_f -M_s become higher than the other samples values. For instance, the ranges of martensitic transformation temperatures of 50% cold deformed samples are more than 25% cold deformed ones and the ranges of not deformed ones are the least according to their annealing clusters, so this result supports the approach.

In addition, the ranges of martensitic transformation temperatures of samples annealed at 450°C are more than the ones annealed at 600°C and the ranges of not annealed ones are the least. This may be based on term of the critical annealing temperature range.

If it is considered that annealing above the range has an extinctive effect to R phase and leads to moving of M_s towards higher values, samples annealed at 600°C would have tighter martensitic transformation temperatures ranges than the ones annealed at 450°C. In the meantime, ΔH amounts of austenite lower by increasing the deformation ratios. Nurveren et al. state that the dislocations those are based on internal stresses are associated with the transformation and for a given temperature, the amount of heat is proportional to the volume fraction of the transformed material, so when the samples are exposed to cold deformation, their dislocations amount gets much more and tries to block transformation, thus the ΔH amounts lower. This claim is explanatory of the decrease of shape memory property of the alloy when increasing the cold deformation.

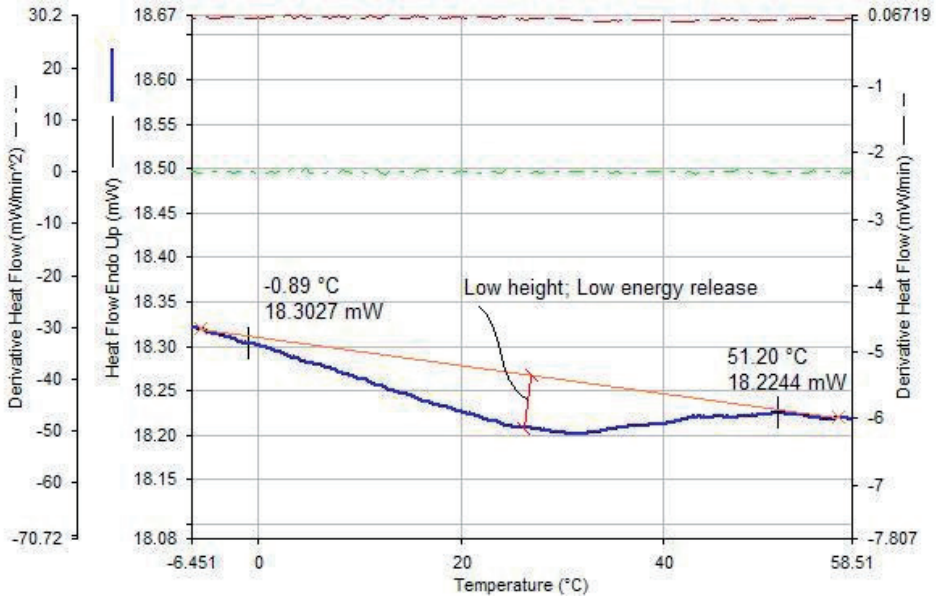

Fig. 7. Low peak height of martensite of the second cycle of sample 5

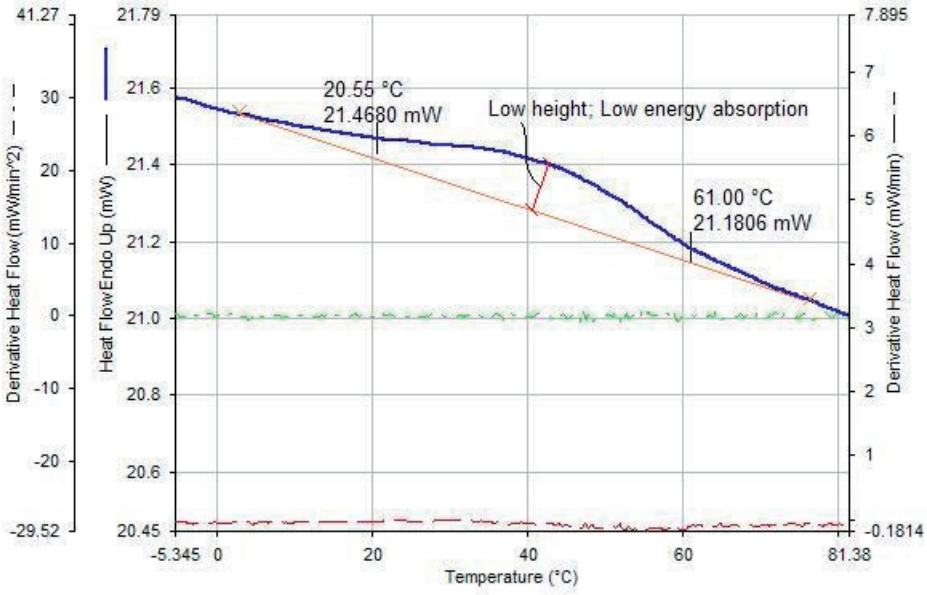

Fig. 8. Low peak height of austenite of the second cycle of sample 5

On the other hand, it is observed that as-received Ni-Ti alloy samples absorb less recovery energy hence, they lower the shape memory property and they get much more lower by increase of the additional cold deformation ratio. This result may take its source from the facts of not being annealed and the probability of deformed previously of the samples, since they have been drawn by the manufacturer.

4. Conclusions

The effect of cold deformation to transformation temperatures is studied by DSC measurements for Ni-Ti SMA samples, some of which are 25% and 50% cold formed and annealed at 450°C and 600°C. Consequently, the conclusions can be summarized as follows:

- The shape memory property lowers and the probability of encounter the martensitic transformation in room temperatures increases with the increasing cold deformation ratio, so post-heat treatment may be suggested for cold deformed SMAs.
- Cold deformation process leads to increases in the temperature ranges and slow occurrences of transformation, so it can be specified that process of cold deformation after training and promotion of shape memory effect provides convenience to the applications, which are demanded to have slow reaction rates.
- Suitable transformation temperatures must be prepared with regard to the certain use temperatures for the applications like robotics, surgery and military. Especially, it must be paid attention to desired service temperatures of products those are made of Ni-Ti SMAs during the manufacture of them.

References

[1] T. Sakuma, Y. Mihara, H. Toyama, Y. Ochi, K. Yamauchi, Effect of cold working on transformation and deformation behavior after pre-deforming in Ti-50 at %Ni shape memory alloy, Materials Transactions 47 (2006) 787-791.

[2] S.A. Thompson, An overview of nickel-titanium alloys used in dentistry, International Endodontic Journal 33 (2000) 297-310.

[3] D.E. Hodgson, M.H. Wu, R.J. Biermann, Shape memory alloys, Metals Handbook: Properties and Selection, Nonferrous Alloys and Special-Purpose Materials 2, 1990, 897-902.

[4] T.W. Duerig, A.R. Pelton, Ti-Ni Shape Memory Alloys, Materials Properties Handbook, Titanium Alloys 2, 1994, 1035-1048.

[5] K. Nurveren, A. Akdoğan, W.M. Huang, Evolution of transformation characteristics with heating/cooling rate in Ni-Ti shape memory alloys, Journal of Materials Processing Technology 196 (2008) 129-134.

[6] M.E. Mitwally, M. Farag, Effect of cold work and annealing on the structure and characteristics of Ni-Ti alloy, Materials Science and Engineering A 519 (2009) 155-166.

[7] J. Uchil, K.P. Mohanchandra, K.K. Mahesh, K. Ganesh Kumara, Thermal and Electrical Characterization of R-Phase Dependence on Heat Treat Temperature in Nitinol, Physica B: Condensed Matter 253/1-2 (1998) 83-89.