INFLUENCE OF HEAT TREATMENT ON MICROSTRUCTURE PROPERTIES OF NiTi ALLOY

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Abstract

Thermal treatment of NiTi alloys allows influencing of superelastic behavior through microstructure changes significantly. The appropriate thermal regime is able to move austenite-martensite transformation temperatures. The aim of the work was the study of microstructure of NiTi specimens with 55.85 wt.% Ni of the wire shape before and after the thermal treatment. The heat regimes were performed at these conditions: solution treatment at 600 °C for 1 hour followed by water quenching; ageing at eight different temperatures (250, 270, 290, 300, 350, 400, 450 and 500 °C) for 30 minutes. Microstructures features were studied by means of optical and scanning electron microscopies, EDX microanalysis and microhardness measurement. Higher ageing temperatures led to an increase in microhardness and microstructure changes.

Keywords: NiTi, heat treatment, ageing, microstructure, SEM/EDX analyses

1. INTRODUCTION

The NiTi intermetallic compound, usually called Nitinol, belongs to a group of materials known as Shape Memory Alloys (SMA); sometimes it is also called a "Smart Alloy". Its chemical composition ranges between 49 to 51 at.% Ni [1]. Apart from the shape memory behavior, we should mention also very high corrosion resistance and biocompatibility that are caused by a naturally or artificially formed TiO_2 oxidic layer, similarly as on other Ti-based alloys.

The control of functional properties of NiTi alloys merely through chemical composition changes is insufficient in many cases and is not able to solve various problems for particular applications [2]. Heat treatment is a different, and in many regards preferable, alternative, which influences significantly a lot of resulting properties, such as a microstructure, a level of internal stresses, a homogenous distribution of alloying elements, a character of segregated phases or precipitates and many other characteristics. In a case of NiTi alloy, heat treatment has also a crucial effect on the shape memory behavior and superelasticity, therefore this issue is necessary to be dealt with closely. However, a general summary of a heat treatment effect on NiTi alloys is very complicated and strongly depends on a particular material composition. In NiTi alloys with a higher Ni concentration, precipitation processes occur during some thermal or thermo-mechanical processing in contrast to alloys with a higher Ti proportion.

Parameters of the primary or reverse phase transformation austenite ↔ martensite and transformation temperature values can be changed significantly through modifications of a heat treatment temperature, a holding period on the given temperature or a cooling rate and a cooling method. Various annealing and ageing variants, having an important influence particularly on types of structural phases in final products, can be concrete examples of the applied heat treatment for NiTi alloys [3]. However, it is not only the thermal regime and the above mentioned characteristics that make a difference; the heating procedure itself and the outer environment are important factors for heat treatment as well. It is important to avoid oxidation processes to occur on NiTi alloy surfaces at high temperatures during a defined thermal regime, therefore a determination of a furnace atmosphere is so important for the applied heat treatment [3].

For binary NiTi alloys containing < 50.4 at.% Ni (near equiatomic alloys), pseudoelasticity has been observed in specimens that were cold formed and subsequently annealed at temperatures below their recrystallization critical temperature. The annealing temperature for invoking the optimal pseudoelastic behavior ranges typically between 397 - 467 °C. In products annealed within this temperature interval a high dislocation density after the foregoing cold forming is maintained [4].

The influence of the thermo-mechanical processing on the stress-strain behavior (the stress-strain curve changes) was described by Otsuka [5], who found out that the best superelastic or shape memory characteristics were achieved after annealing of a NiTi specimen at 400 °C following a foregoing cold forming. This behavior was closely connected with the presence of dislocations in a structure and recrystallization phenomena.

During particular annealing processes various phenomena occur, such as internal stress relaxation, reorientation of dislocations or recrystallization, and naturally also changes of transformation temperatures which characterize transformations of austenite, martensite, possibly R-phase (if present in the given alloy). Meng et al. [6] detected temperatures of phase transformations of M_s, M_f martensite and A_s, A_f austenite through measuring electrical resistance changes. The authors [6] observed the R-phase transformation at 36 °C in a specimen annealed at 400 °C and found out occurrence of Ti_3Ni_4 precipitates. For alloys with a higher Ti proportion, which are commonly annealed after forming processes, dislocation hardening is applied in particular, while for Ni-rich alloys, which are subjected to ageing, precipitation hardening is applied more likely. Due to this hardening a common feature for both of the cases is an increase in yield strength, for example in comparison with only annealed materials [4, 7].

The aim of this work was the study of microstructure of NiTi alloy specimens with 55.85 wt.% Ni of the wire shape with a diameter of 1 mm before and after the thermal treatment using annealing and subsequent various ageing regimes.

2. EXPERIMENT

The initial material for the experiments was a NiTi alloy wire delivered by MEDIN, a.s., a manufacturer of the original material was Nitinol Devices & Components (Fremont, California). The production designation of the material is SE508. The chemical composition is shown in **Table 1**.

Table 1 Chemical composition of the initial NiTi material [8]

Element	**Ni**	**Ti**	**O**	**C**
Wt.%	55.8	rest	≤ 0.05	≤ 0.02

10 specimens with lengths from 1.5 to 2 cm were taken from the initial NiTi wire with a diameter of 1 mm. Nine specimens were heat treated in Linn HT-1800 chamber furnace with resistance heating. One specimen was maintained in the initial condition for a comparison. The heat treatment involved solution treatment and ageing - see **Figure 1**. The solution treatment (ST) was performed at 600 °C temperature for a period of 1 h, the specimens were subsequently quenched in water. In order to avoid or maximally eliminate the high-temperature oxidation, to which Ti and its alloys are strongly susceptible, the heat treatment process was performed in the argon atmosphere. The ageing process was performed for a period of 30 minutes at temperatures: 250, 270, 290, 300, 350, 400, 450 and 500 °C. Immediately upon ageing the specimens were quenched in the aqueous medium.

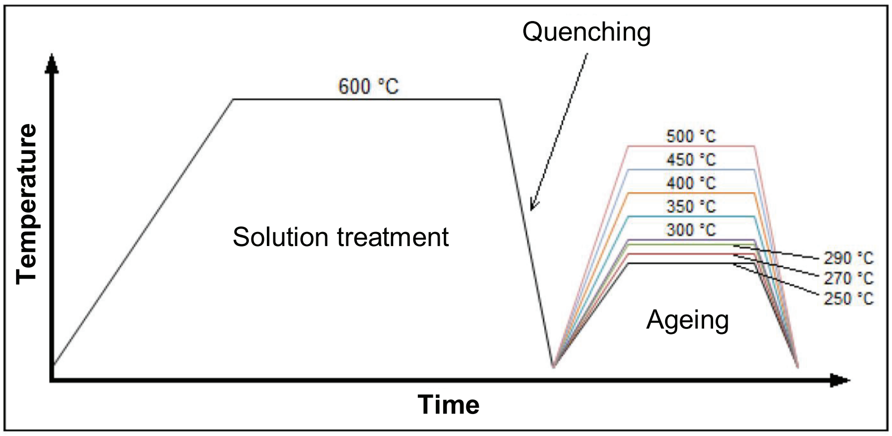


Figure 1 Heat treatment of NiTi wires

The prepared metallographic specimens were studied using the optical method (OLYMPUS GX51 inverted metallographic microscope equipped with OLYMPUS DP12 digital camera). The microstructure and phase analysis was performed using the SEM/EDX method (a scanning electron microscope, JEOL JSM-6490LV type equipped with INCA x-act analyzer). FUTURE-TECH FM-100 automatic microhardness tester with FM-ARS900 control unit was used to determine the Vickers microhardness. The microhardness was measured through 12 indents in the central part in parallel with the edge of the specimen at 0.1 kg load.

3. RESULTS

3.1. Microstructure analyses

Figure 2 shows images of the selected specimens after different heat treatment regimes, both in the initial condition and after high-temperature annealing 600 °C/1h, as well as after ageing in various conditions. The structure was developed using chemical etching in a solution of HF + HNO_3 + CH_3COOH acids.

3.2. SEM/EDX analyses

Figure 3 shows SEM microstructure images and EDX microanalyses of NiTi specimens after different heat treatment conditions. The matrix consists of a NiTi stoichiometric phase (50:50 at.%), in which a minor Ti_2Ni phase (67:33 at.%) occurs in a form of formations elongated in a direction along a longitudinal axis of the wire, i.e. along the wire deformation direction during drawing through dies. In **Figure 2,** the dark tiny formations being in a contact with the Ti_2Ni phase are oxides.

3.3. Microhardness

The resulting average $HV_{0.1}$ microhardness values obtained from 12 measurements are summarized in **Table 2**.

Table 2 Microhardness $HV_{0.1}$ of NiTi after various heat treatments (average value from 12 measurements)

Annealing 1 hour & quenching	No	600 °C								
Ageing 30 minutes & quenching	No	No	250 °C	270 °C	290 °C	300 °C	350 °C	400 °C	450 °C	500 °C
Microhardness $HV_{0.1}$	357	246	253	291	301	349	323	315	320	320
Standard deviation σ_o	18.6	17.9	16.5	18.8	22.3	36.3	22.6	17.5	24.9	13.5

3.4. X-ray diffraction analysis

On the base of the x-ray diffraction analysis the sample (initial material - see **Figure 2 A**) is formed with the martensitic TiNi (evidently monoclinic super-textures P21/m + P2/c) and with the cubic TiNi - **Figure 4**. The TiNi cubic phase is evidently defective or high textured, (003) diffraction is quite missing. According to analysis by means of SEM, the specimen is formed with ledgelike aggregate of the martensite, in which the submicron cubic crystals (cubic TiNi) are overgrown.

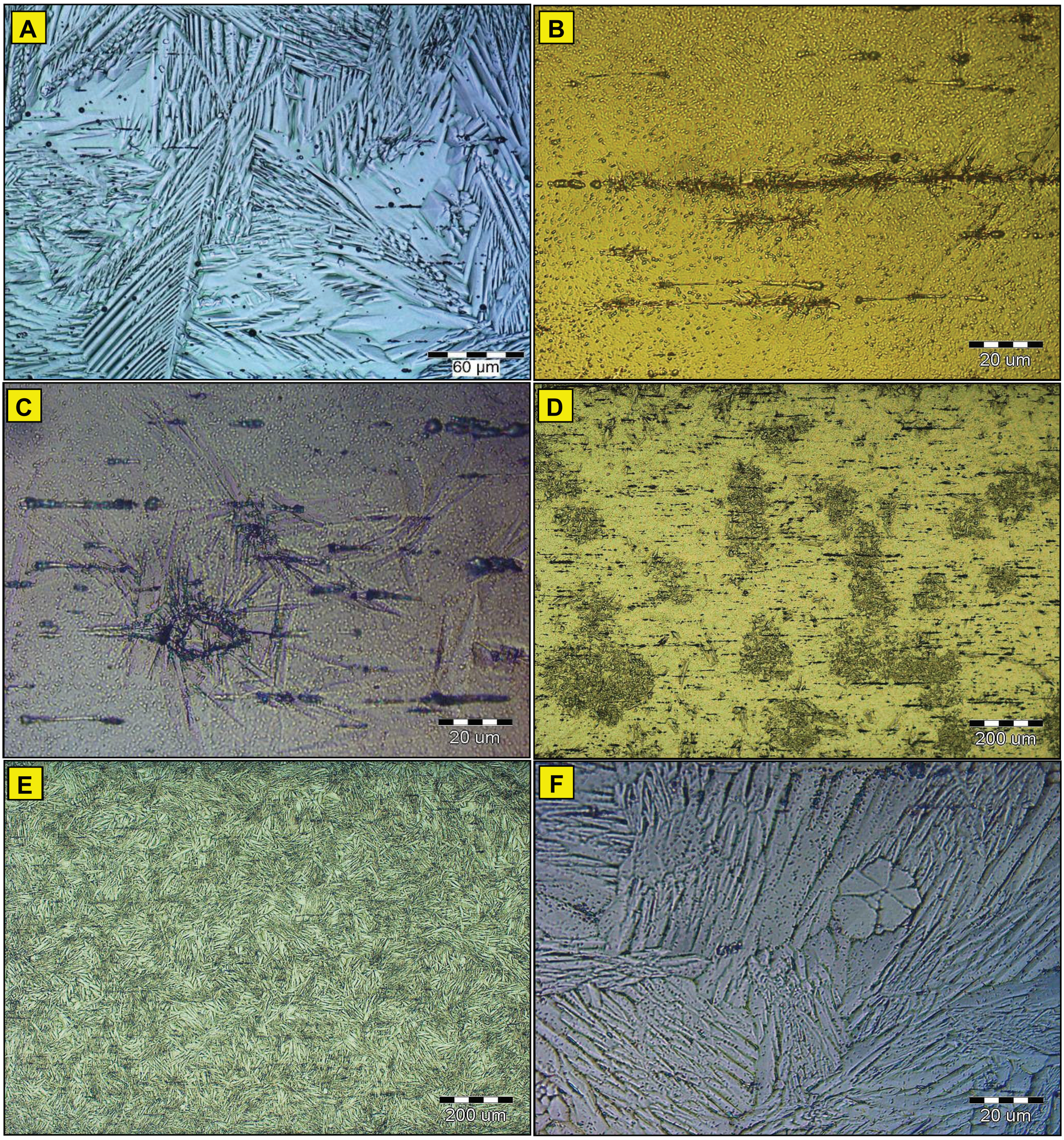
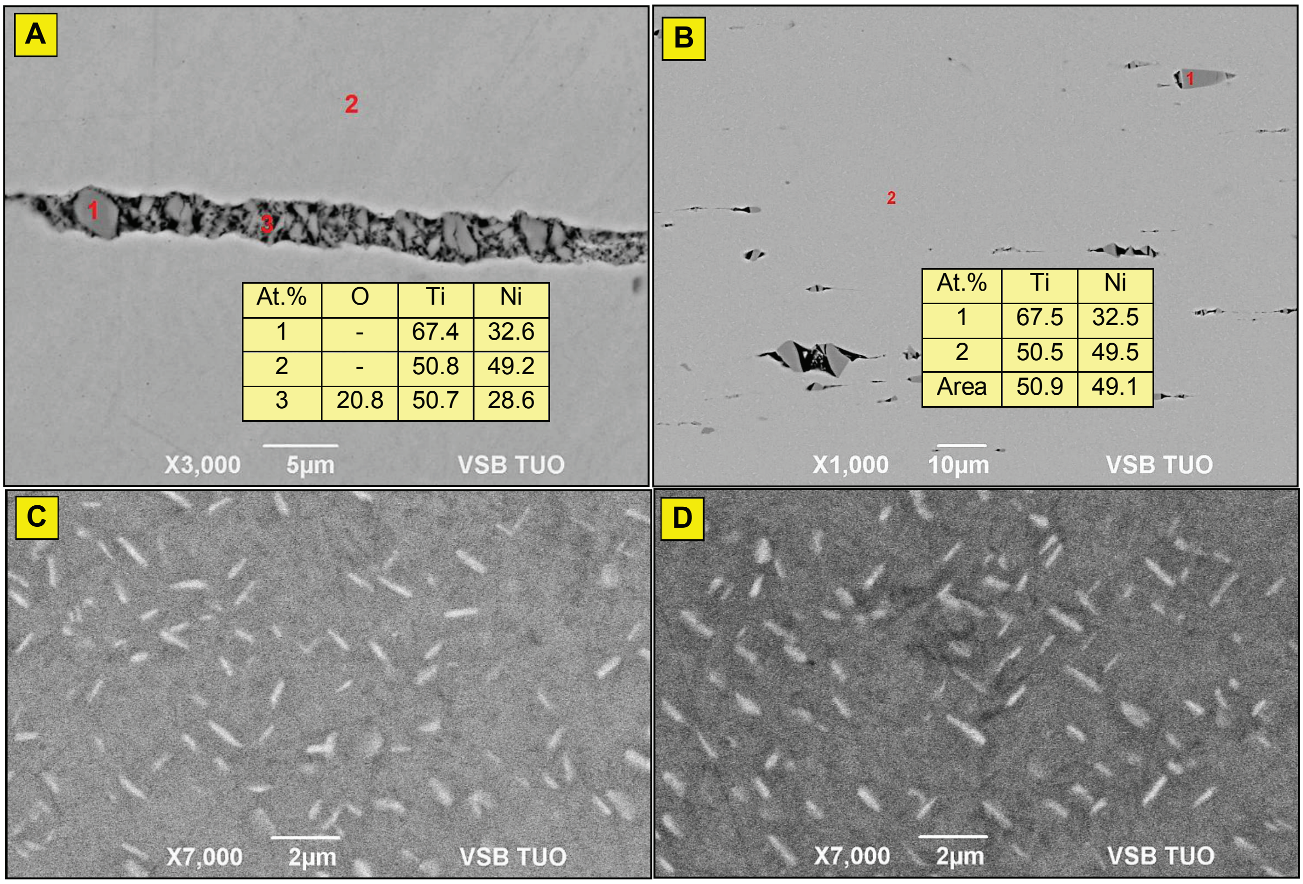


Figure 2 Microstructure of NiTi wires after various conditions of heat treatment
A) Initial state. B) After annealing 600 °C/1 h + quenching. C) to F) After annealing 600 °C/1 h + quenching + ageing (30 min) + quenching. C) Ageing temperature 250 °C. D) 290 °C, E) 350 °C, F) 450 °C



At.%	O	Ti	Ni
1	-	67.4	32.6
2	-	50.8	49.2
3	20.8	50.7	28.6

At.%	Ti	Ni
1	67.5	32.5
2	50.5	49.5
Area	50.9	49.1

Figure 3 SEM/EDX analysis of NiTi wire after various heat treatment
A) Initial material. B) After ageing 290 °C/30 min. C) After annealing 600 °C/1h + quenching.
D) After annealing 600 °C/1h + quenching + ageing 300 °C/30 min + quenching

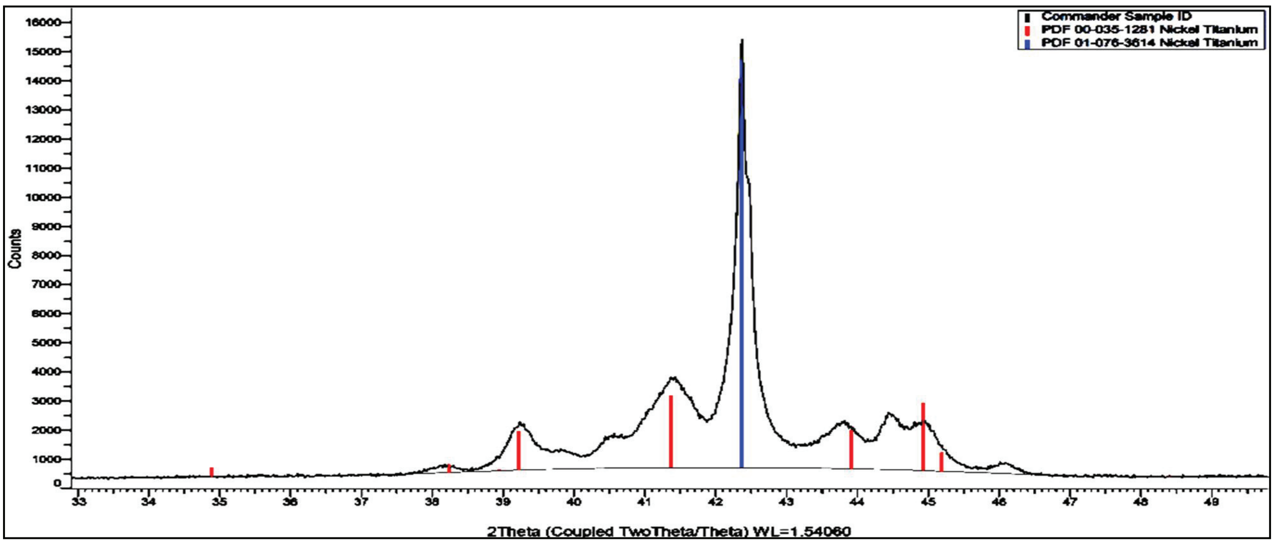


Figure 4 X-ray diffraction spectrum of TiNi alloy (wire diameter 1 mm, initial material

4. DISCUSSION

The EDX analysis showed that the Ni proportion in the chemical composition of the initial material used for the experiment made by NDC, Remont, from which the NiTi wire was manufactured, was 49.2 at.% Ni in contrast to expected 50.7 at.% Ni.

The SEM images as well as the EDX analysis results for all the specimens proved the presence of the minor Ti_2Ni phase in a form of individual particles or clusters of broken particles on oxide inclusions, which were formed into elongated formations parallel along the wire axis. According to [9] we can assume that Ti_2Ni phase particles have been formed just during manufacturing of the original material, which was used for the manufacture of the wire subsequently. This presupposition is proven also in the SEM images of the particular specimens (**Figure 3**). The occurrence of Ti_2Ni particles arranged in elongated forms was invoked by forming processes during manufacturing of the wire.

The initial wire was subjected to annealing at 600 °C and follow-up ageing at temperatures of 250, 270, 290, 300, 350, 400, 450 and 500 °C. The resulting SEM analyses show precipitation of a high number of fine disk-shaped precipitates after the performed annealing. However, the precipitation processes can be observed mainly in Ni-rich alloys containing more than 50 at.% Ni. By segregation of the Ti_2Ni phase a decrease of Ti atoms in the matrix occurs, leading to enriching the matrix by Ni atoms subsequently. This situation is advantageous at elevated temperatures for the precipitation processes observed in the studied alloy.

Determination of the actual chemical composition and thus also the exact type of the fine precipitates observed in all of the specimens, which were subjected to annealing or ageing, was not possible due to their very small size. Their length ranged approximately between 0.7-1.3 µm, the thickness within an interval of 0.1-0.25 µm, which cannot be chemically analyzed using SEM equipped with EDX probe.

There are several kinds of precipitates that occur during heat treatment of NiTi alloys. These are in particular Ti_3Ni_4, Ti_2Ni_3 and $TiNi_3$ [10]. Most probably, in our case these are Ti_3Ni_4 type precipitates. The morphology of the precipitates observed in the SEM images is of a disk shape, similarly as the morphology of Ti_3Ni_4 precipitates, as confirmed in [11].

The first heat treatment regime (annealing followed by water-quenching) developed in the material the martensitic structure transformation into austenite (see **Figure 2**). The initial NiTi wire was in the martensitic condition, nevertheless, after the performed annealing the austenitic matrix in the wire structure prevailed, only exceptionally with local martensitic needles in the neighbourhood of the Ti_2Ni particles.

An influence of ageing on a change of the Ti_2Ni phase particles was not observed. However, along with an increasing temperature of ageing an increase in a volume proportion of the martensitic phase in the structure occurred (**Figure 2**). The increasing temperature gradient (along with the increasing temperature of ageing), which was then a driving force for the martensitic transformations during the following quenching of the specimens, can be considered the main factor enabling an occurrence and development of martensite.

Comparing the initial condition and the condition after annealing, a rapid drop in *HV* microhardness (**Table 2**) was caused by the structure transformation from purely martensitic into austenitic, and also, of course, due to relaxation of internal stresses that were induced in the initial condition by forming processes during the manufacture of the wire. Afterwards a well visible increase in the microhardness values followed, caused particularly by an increasing proportion of the martensitic phase in the structure.

The above mentioned results imply that the alloy composition is a critical parameter for a choice of a particular heat treatment. This affects strongly above all the transformation temperature values (A_s, A_f, M_s and M_f) and precipitation processes. Generally, it has been known [5] that a high critical stress value needed for slip needs to be ensured in order to reach a good superelastic behavior. This can be achieved for instance by application of forming processes in a combination with annealing or ageing at medium temperatures, when in particular annealing causes stress relaxation while maintaining an adequate dislocation density and then ageing can initiate a precipitation activity in a case of Ni-rich alloys.

5. CONCLUSION

The aim of the work was the study of microstructure changes in NiTi alloy occurring after application of thermal treatment at different temperatures and their potential influence on the shape memory and mechanical properties. Through optical microscopy and SEM/EDX methods it was found out that application of an appropriate heat treatment (annealing at 600 °C and following ageing) can affect precipitation processes in the used NiTi alloy, thus segregation of secondary phases in a form of very small particles in shapes of tiny disks. The morphology and size of these precipitates imply that these ones are Ti_3Ni_4 particles. The following stage of heat treatment was ageing, however, in this case no essential changes in the morphology, size or number of precipitates in the matrix was observed. However, an increase in a volume proportion of the martensitic phase was observed at conditions of ageing at temperatures above 300 °C and following water-quenching of specimens, which is also exhibited by an increase in *HV* microhardness along with temperature. The drop in microhardness comparing the initial condition and the condition after annealing was caused by internal stress relaxation, which was a result of forming processes during the manufacture of the initial NiTi wire.

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