Microstructure evolution of heat treated NiTi alloys

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Abstract. Superelastic behavior of off-stoichiometric NiTi alloys is significantly affected by microstructure changes due to heat treatment. Applying appropriate thermal treatments important effects on microstructural changes, transformation temperatures and thermomechanical properties of final NiTi products can be achieved. The experimental samples of NiTi alloy with 55.8 wt.% Ni were submitted to heat treatment and the microstructures before and after the treatment were observed. The thermal regimes consisted of annealing treatment at 600 °C for 1 hour followed by water quenching and of ageing at eight different temperatures (250, 270, 290, 300, 350, 400, 450 and 500 °C) for 30 minutes. Microstructure features studied by means of optical and scanning electron microscopies, EDX microanalyses, X-ray diffraction analyses and microhardness measurement, have shown that higher ageing temperatures led to microstructure changes and corresponding increase in microhardness.

Keywords: NiTi, annealing, ageing, XRD, martensite, Ni₄Ti₃.

1. Introduction

The intermetallic NiTi-based alloy, usually called Nitinol, belongs to a group of materials known as Shape Memory Alloys (SMA); sometimes also called as “Smart Materials”. Its chemical composition ranges between 49 and 51 at.% Ni. Beside shape memory behavior and superelasticity, very high corrosion resistance and good biocompatibility due to TiO₂ surface layer should be mentioned.

The control of functional properties of NiTi alloys only through chemical composition changes is insufficient in many cases and is not able to solve various problems for particular applications. 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 closely. However, a general summary of a heat treatment effect on NiTi alloys is very complicated and strongly depends on a particular material composition. Generally, with a higher Ni concentration in NiTi alloys, precipitation processes occur during thermal or thermo-mechanical treatments unlike Ti-rich compositions. Ageing treatment promotes the formation of various Ni-rich precipitates, such as Ni₄Ti₃, Ni₃Ti₂ or Ni₃Ti and the occurrence of multi-stage transformation behavior including the R phase transformation associated with the formation of fine and coherent Ni₄Ti₃ particles [1-4]. As the most commercial NiTi alloys...
belongs to Ni-rich alloys, their transformation and mechanical properties can be affected by developing Ni$_4$Ti$_3$ precipitates.

It is known, that the temperature of reverse phase transformation austenite ↔ martensite can be changed significantly through modifications of a heat treatment temperature, a time at the temperature or a cooling rate and a cooling method. Generally, increasing ageing temperature within range from 400 to 600 °C decreases the temperature of reverse transformation [3-6]. Thus, applying various annealing and ageing treatments important differences in structural phases and transformation behavior can be achieved in final products [6].

The work was focused on the study of microstructure changes in NiTi alloy occurring after application of thermal treatment at different temperatures.

2. Experimental

The experimental binary NiTi alloy was supplied by MEDIN, a.s. in form of a wire with a diameter of 1 mm. The chemical composition of the alloy corresponded to Ni content of 55.8 wt.% (which is equivalent to 50.7 at.%). Ten specimens of lengths within the range from 1.5 to 2 cm were taken from the as-received NiTi wire. One specimen was maintained in the as-received condition as reference sample, the others were heat treated in Linn HT-1800 chamber furnace with resistance heating. The heat treatment under argon atmosphere involved annealing at 600 °C for 1 hour with following water quenching and ageing at eight temperatures (250, 270, 290, 300, 350, 400, 450 and 500 °C) for 30 minutes with following water quenching, as seen in Figure 1.

![Figure 1. Schematic of heat treatment of NiTi samples.](image)

The microstructure was studied on metallographically prepared and chemically etched (solution of HF + HNO$_3$ + CH$_3$COOH) specimens using the optical microscopy on OLYMPUS GX51. The phase analysis was performed by means of scanning electron microscope (SEM) JEOL JSM-6490LV equipped with INCA x-act analyzer. The Vickers microhardness was measured by FUTURE-TECH FM-100 automatic microhardness tester with FM-ARS900 control unit. The microhardness values were determined by twelve indents in central line parallel with the sample edge at load of 0.1 kg.

To determine the phases present in the NiTi alloy after different heat treatments X-ray diffraction (XRD) was performed using a Bruker-AXS D8 Advance system with 2θ/θ geometry of measure operated at 40 kV and 40 mA and equipped with Lynx-Eye PSD (CuK$_\alpha$ source/Ni filter, step size of 0.014° 2θ, dwelling time of 46 s per step). Data refinement, fitting and background elimination was done using Diffrac.EVA, version 2 software and PDF-2 database or COD respectively. Phase identification by X-ray diffraction was performed on the surface of 0.6 x 12 mm approximately at 45 ° 2θ and verified by Rietveld method modeling using Bruker Topas, version 5. Input data were adapted
of COD database. Martensite phases presence on XRD spectra were verified using Le Bail method modeling where input data were adapted of PDF database.

3. Results and discussion

The microstructure of selected specimens in the as-received stage, after annealing at 600 °C for 1 hour and after ageing at various temperatures are presented in Figures 2 - 6. The SEM observation and EDX microanalyses of NiTi specimens in different heat treatment conditions showed that the matrix consists of a NiTi near-equiatomic phase, in which a minority NiTi$_2$ phase occurs in a form of broken particle clusters elongated in a direction along longitudinal axis of the wire, i.e. along the wire drawing direction (Figures 2, 3a and 5a). The specimens in as-received stage showed martensitic structure that was markedly changed after annealing at 600 °C. Ageing at temperatures of 250, 270, 290, 300, 350, 400, 450 and 500 °C resulted in precipitation of a high number of fine disk-shaped precipitates, unlike martensite needles and plates that with increasing annealing temperature seemed to coarsen.

On the base of the X-ray diffraction analysis (Figure 7) it is evident that the phase compositions of the specimens are complex and formed of structure similar phases. The XRD spectra contain more intensive and strongly superimposed intensities only in relatively narrow range from 38.5 to 45.5° 29 CuKα. The intensities are evidently extended that indicates limited size of diffraction areas. Although the phase compositions are very similar in all specimens, the differences in the ratio of intensities corresponding to martensite and austenite phases were observed.

The precipitates Ni$_4$Ti$_3$ and NiTi$_2$ were identified as minority phases. Several martensite types were revealed, it means martensites with space group P21/m and P21/c, as well as R phase NiTi. The as-received sample is formed of evidently monoclinic super-textures P21/m + P2/c and cubic NiTi that is evidently faulted or highly textured for (003) diffraction being is quite missing. According to XRD analysis and metallographic observation, the structure is formed of ledge-like martensite aggregates, in which the submicron cubic parent NiTi is overgrown. Relatively high abundance of austenite and high crystallinity is observed in the sample aged at 400 °C. The annealing at 600 °C led to lowest content of austenite phase.

![Figure 2. Microstructure of NiTi samples a) as-received and b) annealed at 600 °C for 1 h and water quenched.](image)

As it was mentioned above two precipitates types were observed in metallographic observation and proved by XRD spectra. Whereas the Ni$_4$Ti$_3$ precipitation processes can be observed mainly in Ni-rich alloys containing more than 50 at.% Ni [5], the disc-shaped precipitates revealed in our case using SEM (Figures 5b and 6) are of Ni$_4$Ti$_3$ type. Their length ranged approximately between 0.7-1.3 µm, the thickness within an interval of 0.1-0.25 µm.
Figure 3. Microstructure of NiTi samples annealed at 600 °C for 1 h, water quenched and aged for 30 minutes a) at 290 °C and b) at 350 °C.

Figure 4. Microstructure of NiTi samples annealed at 600 °C for 1 h, water quenched and aged for 30 minutes a) at 400 °C and b) at 450 °C.

Figure 5. SEM microstructure of NiTi samples a) as-received (red indexes: 1 - NiTi$_2$, 2 - NiTi matrix, 3 - fractured NiTi$_2$); b) after annealing at 600 °C for 1 h and water quenching.
Figure 6. SEM microstructure after annealing at 600 °C for 1 h, quenching and ageing for 30 minutes
a) at 290 °C and b) at 300 °C.

Owing to their very small size the determination of chemical composition by EDX analyses was not possible to perform. The morphology and the structure properties of very fine Ni$_4$Ti$_3$ precipitates were confirmed in [6].

Unlike the as-received NiTi wire with martensitic microstructure, at 600 °C heat treated specimen developed the transformation into austenite structure that after water quenching passed to multiphase composition in accordance with XRD analyses in the Figure 7b. Martensite needles were very fine and only exceptionally in the neighborhood of the NiTi$_2$ particles reached the well detectable sizes, as seen in the Figure 2b.

An influence of ageing on a change of the NiTi$_2$ phase particles was not observed. However, with an increasing temperature of ageing a coarsening of the martensitic structure occurred (Figure 3). 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.

Figure 7. XRD charts for a) as-received wire, b) annealed at 600 °C and c) annealed at 600 °C and aged at 400 °C.

1 – measured and calculated model, 2 – NiTi austenite, 3 – P21/m martensite (B19), 4 – Ni$_4$Ti$_3$ hexagonal phase,
5 – NiTi$_2$ cubic phase, 6 – NiTi R phase, 7 – P21/c martensite (B19’), 8 – difference profile model
The average results of HV0.1 microhardness are summarized in Table 1. Comparing the as-received specimen and the specimens after annealing at 600 °C, an appreciable drop in HV0.1 microhardness was caused by the transformations from coarse martensite structure into fine martensite one. Afterwards a well evident increase in the microhardness values was noted with increasing ageing temperatures that corresponded to changes in the martensite and austenite proportion in the structure as well as to the Ni$_4$Ti$_3$ precipitation.

Table 1. Microhardness HV0.1 of NiTi samples after various conditions of heat treatments.

| Heat treatment | As-received | Annealed (°C) | Temperature (°C) of ageing for 30 minutes |
|----------------|-------------|---------------|------------------------------------------|
| Microhardness  | 357         | ± 19          | 600                                       |
|                 |             | ± 18          | 250                                       |
|                 |             | ± 17          | 270                                       |
|                 |             | ± 19          | 290                                       |
|                 |             | ± 22          | 300                                       |
|                 |             | ± 36          | 350                                       |
|                 |             | ± 23          | 400                                       |
|                 |             | ± 18          | 450                                       |
|                 |             | ± 25          | 500                                       |

The above mentioned results imply that the phase composition is critical parameter for requirements to influence the superelastic behavior of NiTi applications. It is clear, that the choice of a particular heat treatment affects strongly above all the transformation temperature values ($A_s$, $A_f$, $M_s$ and $M_f$) and precipitation processes.

5. Conclusion

Based on the study of microstructure changes in NiTi alloy occurring after thermal treatment at different temperatures several conclusions can be drawn:

1. It was proved by means the optical microscopy, SEM/EDX and XRD methods that applying heat treatment (annealing at 600 °C and following ageing) can affect precipitation processes in the NiTi alloy in favor of very small Ni$_4$Ti$_3$ particles.

2. No essential changes in the morphology and size of NiTi$_2$ precipitates in the matrix were observed.

3. The tiny disk-shaped morphology implies that these ones are of Ni$_4$Ti$_3$ type even the EDX analyses couldn’t confirm the stoichiometric composition of the particles.

4. The following ageing regimes led to the change in proportional abundance of martensite/austenite.

5. The decrease in microhardness values after annealing at 600 °C and their slow increasing with growing ageing temperature attached the changes in microstructure.

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