Structural characteristics of NiTi alloys after thermal treatment

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Abstract. The study of the effect of thermal treatment conditions on NiTi alloy used in biomedicine was carried out. The experimental samples of NiTi alloy with 55.8 wt% Ni were subjected to the heat treatment. The thermal regimes consisted of aging treatment at 300, 350 and 400 °C for 30 minutes followed by air cooling. The microstructures before and after the heat treatment were observed by optical microscopy. The study was completed by the microhardness measurement and XRD analysis. The obtained results show that the aging temperatures led to microstructural and microhardness changes for the investigated alloy.

1. Introduction

Shape memory alloys based on NiTi, commonly known as “Nitinols”, are nowadays successfully used in different areas of the medicine, as for instance plates and nails in traumatology, vascular stents, surgery catheters, root canal instruments or orthodontic braces. Other properties, in addition to the shape memory behaviour, are also very good corrosion resistance, biocompatibility, advantageous strength/density ratio or high damping capacity.

The shape memory effects and superelastic behavior of Ni-rich NiTi alloys, it means more than 50.6 at% Ni, are significantly dependent on microstructural modifications provided through the heat treatment [1-6]. It is generally known that thermal treatment of Ni-rich NiTi alloys induces diffusion processes that lead to precipitation of different phases: metastable Ni₄Ti₃, metastable Ni₃Ti₂ or stable Ni₃Ti [3-5]. The microstructural changes have a major impact on the austenite-martensite transformation temperatures and consequently on the martensitic transformation in NiTi alloys. Owing to an appropriate thermal regime the alloy behavior can be modified according to requirements [7]. Moreover, the precipitation of secondary phases can also contribute to a substantial increase in the strength of NiTi alloys. Farther critical factor influencing both transformation and microstructure characteristics of the NiTi material is the alloy composition.

The work is focused on the effect of heat treatment on NiTi alloy containing 55.8 wt% Ni (50.7 at% Ni). The microstructure of experimental specimens was observed by optical microscopy in the condition of as-received and heat treated. The microhardness measurement and X-Ray diffraction (XRD) analysis appeared as useful tool for the study of microstructure changes.
2. Experimental
Commercially available NiTi wire composed of 55.8 wt% Ni, ≤ 0.05 wt% O, ≤ 0.02 wt% C and balance of Ti (SE508 alloy) were subjected to heat treatment (aging). The LAC chamber furnace with resistance heating was used for annealing. The thermal regimes that consisted of holding at 300, 350 and 400 °C for 30 minutes followed by air cooling are shown in Figure 1.

Figure 1. Schematic of thermal treatment regimes applied for NiTi specimens.

For the microstructure study longitudinal cuts of the samples were cold mounted into LevoCit (Struers) resin, ground, polished and etched. The martensite microstructure was revealed by immersing into an etching solution of CH₃COOH:HF:HNO₃ (in ratio of 3:3:5) for 4–5 s. The microstructure features before (as-received) and after the aging were observed by optical microscopy (OLYMPUS GX51). The study was completed by Vickers microhardness measurement using FUTURE-TECH FM-100 automatic microhardness tester with FM-ARS900 control unit. XRD analysis was performed by means of Bruker-AXS D8 device equipped with Lynx-Eye PSD (CuKa source/Ni filter). As the samples were observed only in longitudinal sections, the microhardness was measured using five impacts performed in the central area parallel to the edge of the samples and by loading of 0.1 kg. The X-Ray diffraction was measured under following conditions: accelerating voltage 40 kV, anode current 40 mA, step mode – step 0.0147, range 5–80°, detailed measurement of the spectrum in the range from 38–47°, where appropriate conditions exist.

3. Results and discussion
The microstructure observed for all samples is given in Figure 2 and is formed of remaining austenite and needle/plate-like martensite with different space distribution and orientation, thickness or length. The abundance of both phases seems to be depending on the aging temperature. For the samples in as-received and at 400 °C heat treated conditions, it is possible to observe a microstructure formed by coarse martensitic needles and plates with remaining austenite (Figure 2a and 2d). Conversely, very fine martensitic needles that seem in principle to constitute all surface observed are seen for the sample after the aging at 350 °C (Figure 2c). The highest degree of arrangement of martensitic needles to particular packets is revealed in the sample heat treated at 300 °C.

The particles NiTi₂ of various sharp-edged shapes, fractured and aligned into parallel lines, as seen in Figure 2, are present in the samples as consequence of wire processing technology. The length of the particles alignment achieves up to several tens of micrometers in some cases. Moreover, the presence of NiTi₂ phase is observed in the microstructure of all samples, regardless of thermal treatment conditions, as it was confirmed in our previous SEM observation and EDX analysis [8]. As the NiTi wires serve as starting material for endodontic instruments producing the existence of sharp-edged NiTi₂ particles can be generally considered as negative for the mechanical behavior of the material. In practical use, NiTi instruments can be damaged by fatigue cracks initiated at the particle edges when subjected to significant rotation stresses.
Figure 2. Microstructure of NiTi wires in the conditions: a) as-received and heat treated, b) at 300 °C, c) 350 °C and d) 400 °C.

The average values of microhardness HV0.1 that are summarized in Table 1 range from 373 to 406. The changes in the microhardness due to the heat treatment are very small but can be related with the martensite morphology and distribution. The highest average value of 406 HV0.1 was measured for the sample heat treated at 350 °C (HT350) and corresponds to the very fine but not especially arranged martensitic needles (Figure 2c). The lowest microhardness (373 HV0.1) for the sample heat treated at 400 °C (HT400) is related with the different character of the microstructure composed of coarse martensite needles and laths. Nevertheless, the sample aged at 300 °C with highly arranged martensite needles reaches of 390 HV0.1 that is close to the value of the as-received stage but with quite different microstructure morphology.

Table 1. Microhardness HV0.1 of NiTi samples in conditions: as-received, heat treated at 300 °C (HT300), 350 °C (HT350) and 400 °C (HT400).

| Specimen     | HV0.1   |
|--------------|---------|
| As-received  | 395 ± 47|
| HT300        | 390 ± 14|
| HT350        | 406 ± 29|
| HT400        | 373 ± 29|

Unlike microstructures, the XRD patterns are very similar for the samples in the conditions as-received and heat treated at 300 and 350 °C (Figure 3a, 3b and 3c). In the XRD charts two principal peaks corresponding for austenite phase (parent B2 structure of NiTi) and R-phase NiTi (rhombohedral distortion of B2 phase) were only detected.
Figure 3. XRD patterns of the NiTi samples in the conditions: a) as received; heat treated at b) 300 °C, c) 350 °C and d) 400 °C.

Figure 4. Comparison of XRD patterns for the samples in four heat treatment conditions.
The evolution of the XRD chart of the sample aged at 400 °C shows differences in the presence of three spectra, where the monoclinic martensitic phase is appearing together with B2 and R-phase. The formation of monoclinic martensite (B19') corresponds to the lowest microhardness measured (Table 1). Due to inhomogeneous distribution of NiTi2 phase and most probably nanometric sizes of metastable Ni4Ti3 or Ni3Ti2 particles, no other evident peaks than that ones for austenite and martensite phases were detected.

4. Conclusion
The evolution of the microstructure after the heat treatment at the temperatures 300, 350 and 400 °C for 30 minutes followed by air cooling was investigated for NiTi (SE508 alloy) wires. Following conclusions were found by means of optical microscopy observation, XRD analysis and microhardness measurement:

1) The microstructure of all samples differed in morphology and was composed of needle/plate-like martensitic phase with different space distribution, thickness and length and remaining austenitic NiTi phase.
2) The heat treatment showed any influence on the occurrence or distribution of the NiTi2 particles that remained aligned in parallel to the wire axis.
3) The microhardness of the samples in different heat treatment conditions differed very slightly and ranged from 373 to 406 HV0.1.
4) XRD analysis proved the existence of austenite NiTi and R-phase in all heat treatment conditions of the specimens. Only for the sample aged at 400 °C the monoclinic martensite was detected.

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