Effect of heat treatments on the structure and properties of a small-diameter thin-walled tube of a medical nickel titanium alloy

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Abstract. The present study examines the effect of annealing at temperatures of 300-500°C on the structure and properties of a thin-walled nitinol tube of composition Ti49.1Ni50.9 used for the manufacture of intravascular stents. Annealing temperature dependences are obtained for the martensitic transformation temperatures, the size of the structural elements of the grain-subgrain structure, phase composition, pseudo-yield stress, and ultimate strength. The effect of the Ti3Ni4 particle precipitation in aging during annealing at different temperatures on the obtained dependences is analyzed.

1. Introduction
Starting from 1997, cardiovascular surgery has been using self-expanding stents made of NiTi-based alloys with shape memory and superelasticity to restore the blood vessel lumen for atherosclerosis treatment [1]. In endovascular repair, a compressed stent placed into a small-diameter catheter is delivered to the narrow segment of the blood vessel and then released from the catheter to restore its initial shape, due to which the vessel expands. The starting material for the manufacture of stents is a thin-walled nickel titanium tube of small diameter. A stent is produced from the tube by laser cutting. Then, the stent is adapted to the required diameter by heat treatments using special mandrels (figure 1). For proper functioning, the stent must have necessary functional and mechanical characteristic at the human body temperature. Heat treatments can change these characteristics compared with the properties of the original tube, which can adversely affect the stent properties. In order to obtain optimal performance characteristics, we should know the effect of various heat treatments on the structure and properties of the stent material. Here we study the changes in the phase transformation temperatures, microstructure, and mechanical properties of a thin-walled nitinol tube of composition Ti49.1Ni50.9 with a diameter of 1.63 mm during heat treatments in the temperature range from 300 to 500°C. The structure and properties of an alloy of composition Ti-50.9 at. % Ni were studied by other authors [2-5] on wire samples. Thin-walled tubes of Ti-50.8 at.% Ni alloy were examined in [6]. The main attention is paid to changes in the martensitic transformation temperatures and functional properties.

2. Materials and experimental procedures
The investigation was performed on a thin-walled nitinol tube with a 50.9 at.% nickel content produced by VASCOTUBE GmbH (Germany). The outer tube diameter was 1.63 ± 0.01 mm; the wall thickness was 0.23 ± 0.01 mm. The martensitic transformation temperatures were determined by
thermoresistometry. Specimens with a length of 20 mm were cut longitudinally into two halves by electric spark machining. Heat treatment of the specimens was carried out according to the scheme used in the manufacture of stents at the stage of forming. Heat treatment was performed in a molten salt bath with automatic temperature control. After holding for a certain time, the specimens were quenched in water at room temperature. Microstructural studies were conducted on a JEOL JEM-2100 transmission electron microscope (Tokyo Boeki Ltd., Japan). Foils were prepared using an EM-09100 IS ion slicer (JEOL, Japan).

Figure 1. Stent sample on a forming mandrel.

Tensile tests were carried out on 25-mm long tube segments. The specimens were fixed in a specially designed system of self-adjusting grips and installed into a Walter + Bai testing machine (Series LFM-125) with DionPro software. The gage length of the specimens was 10 mm. To firmly grip the specimen, a hardened steel rod with a diameter corresponding to the inner diameter of the tube was inserted into the tube at both ends, and then the specimen was clamped with screws. The tests were conducted at room temperature with an initial strain rate of $10^{-3}$ s$^{-1}$.

3. Results and discussion

Figure 2 and Table 1 show the measurement results for the martensitic transformation temperatures of the tube material after various heat treatments.

Martensitic transformations both in the as-received and heat-treated material during cooling occur according to the B2→R→B19′ sequence, which is clearly seen from the temperature dependence of the electrical resistivity (figure 2a). These data suggest that the tube material in the as-received state at room temperature is in the high-temperature B2 phase. As a result of annealing for 1 hour with increasing annealing temperature $T_{\text{ann}}$, the martensitic transformation temperatures change differently. Upon annealing at 350°C, all martensitic transformation temperatures increase with the smallest increase observed for the finish temperature of the direct martensitic transformation $M_f$. With annealing temperature increase to 400°C, all martensitic transformation temperatures also increase, with the exception of $T_R$, which decreases. A further increase in the annealing temperature leads to a gradual decrease in $T_R$, $A_s$, and $A_f$, and upon annealing at $T_{\text{ann}} = 500^\circ$C $T_R$ and $A_f$ become close (15 and 10°C respectively).

Annealing significantly changes the alloy microstructure. The as-received tube material at room temperature has a polygonized nanocrystalline grain-subgrain structure with an average size of structural elements ~70 nm (figure 3a).

The nanocrystalline structure determines the ring-shaped reflections from the high-temperature B2 phase (figure 3b). The reflections are clearly distinguishable, indicating a high degree of perfection of the microstructure. Another indication is well-defined grain boundaries. Apparently, recovery occurs when the tube is cooled from the manufacturing temperature.

As a result of annealing at 450°C, the average size of structural elements increased to 80 nm (figure 4a). The microdiffraction pattern (figure 4b) shows, along with the reflections from the main B2 phase, well-defined R-phase reflections. R-martensite plates are observed mainly in subgrains and
large (up to 100 nm) grains. The microdiffraction pattern also has weak reflections, which can be identified as belonging to the $\text{Ti}_3\text{Ni}_4$ phase.

**Figure 2.** Temperature dependence of the electrical resistivity of the as-received tube material (a) and annealing temperature dependence of the martensitic transformation temperature change (b).

**Table 1.** Martensitic transformation temperatures of the nitinol tube with a 50.9 at.% nickel content after heat treatment

| Heat treatment | $T_R$, °C | $M_S$, °C | $M_F$, °C | $A_S$, °C | $A_F$, °C |
|----------------|-----------|-----------|-----------|-----------|-----------|
| As-received state | 6 | -62 | -130 | -41 | -15 |
| 350 1 hour | 41 | -33 | -124 | -13 | 15 |
| 400 1 hour | 39 | -29 | -78 | 6 | 27 |
| 450 1 hour | 29 | -30 | -77 | 3 | 20 |
| 500 1 hour | 15 | -29 | -69 | -1 | 10 |

**Figure 3.** Microstructure of the tube material of composition Ti-50.9 at.% Ni in the as-received state (a) and corresponding microdiffraction pattern (b).

Annealing at $T_{\text{ann}} = 500^\circ$C triggers recrystallization processes in the material (figure 5). The average size of grain-subgrain structure elements increases up to 160 nm. At room temperature, the heat-treated alloy is in the B2+R two-phase state. The microdiffraction pattern also shows weak reflections of the $\text{Ti}_3\text{Ni}_4$ phase.
Nitinol alloy with 50.9 at.% nickel content refers to aging alloys. At annealing temperatures starting from 300°C, finely dispersed Ti₃Ni₄ precipitates are formed in it [7], which naturally leads to the appearance of the Ti₃Ni₄ phase reflections. Unfortunately, particles of this phase are not visible in TEM images and therefore their size and volume fraction cannot be determined. Elementary estimates show that if we neglect the small volume change between the TiNi and Ti₃Ni₄ phases, then the segregation of 1 vol.% Ti₃Ni₄ precipitates causes a change in the nickel concentration in the remaining volume by about 0.7 at.%. According to Ref. [8], this concentration change in quenched Ti₄9.1Ni₅0.9 alloy leads to an increase in the martensitic transformation temperatures: by ~6°C for $T_R$ and by ~4°C for $A_s$ and $A_f$. Of course, for ultrafine-grained material these values may differ. Grain size reduction to the nanocrystalline state stabilizes the high-temperature B2 phase, causing a decrease in the phase transformation temperatures. At the same time, the segregation of ultrafine Ti₃Ni₄ particles promotes the formation of the R phase and an increase in $T_R$. The predominant segregation of Ti₃Ni₄ particles at grain boundaries and crystal lattice defects inhibits the M→B2 martensitic transformation, due to which $A_s$ and $A_f$ increase. The martensitic transformation temperatures can also change upon annealing as a result of changes in the dislocation substructure and grain boundary structure.

The presented data indicate that the annealing-induced increase in the martensitic transformation temperatures in the range 300-400°C result from the segregation of Ti₃Ni₄ particles and associated changes in the concentration of nickel atoms in the material volume and triggering of the B2→R transformation.

Figure 6a shows examples of engineering stress-strain curves for tensile tubular specimens in the as-received state and after heat treatments. At the initial (elastic) stage of deformation, the curves for
all the studied materials almost coincide. At higher stresses, the curves differ noticeably from each other.

![Figure 6](image)

**Figure 6.** Engineering stress-strain curves of tube specimens in the as-received state and after heat treatments (a); annealing temperature dependences of the mechanical properties of tube specimens (see details in the text) (b).

Figure 6b illustrates the annealing temperature dependences of the stress at the beginning of the pseudo-yield plateau $\sigma_m$ and tensile strength $\sigma_B$ for the studied samples. For convenience of analysis, the figure also shows the annealing temperature dependences of the $A_s$ and $A_f$ temperatures. The dotted line indicates the test temperature $T_{test}$.

For the as-received material, $\sigma_m$ is rather high and amounts to about 460 MPa. After annealing in the temperature range 300-400°C, this value gradually decreases, being approximately equal to 310 MPa after annealing at 400°C. Annealing at higher temperatures does not significantly change the value of $\sigma_m$. The as-received tube material is in the B2 phase. Applied load induces the B2→B19' martensitic transformation in it. Annealing leads to the formation of the R phase in the material, which is preserved at room temperature, as can be seen from figure 6b and TEM results. The induced R→B19' martensitic transformation occurs at lower stresses. Apparently, the volume fraction of the R phase increases with increasing annealing temperature, due to which $\sigma_m$ gradually decreases.

The tensile strength $\sigma_B$ after annealing at 300 and 400°C gradually increases and after annealing at 400°C it increases by approximately 150 MPa (or by ~12%) compared to the initial state, reaching a maximum value of 1400 MPa. Note that, as can be seen from figure 6a for this type of treatment, the strain hardening coefficient at the stage above $\sigma_m$ also has a maximum value. A further increase in the annealing temperature causes a decrease in $\sigma_B$, and after annealing at 500°C the tensile strength almost coincides with that of the as-received material.

The increase in the tensile strength $\sigma_B$ of tube specimens after annealing at temperatures up to 400°C is obviously caused by hardening due to the formation of ultrafine Ti$_3$Ni$_4$ particles. Apparently, annealing at $T_{anneal} = 400°C$ provides an optimal combination of the size, volume fraction and distribution of particles over the material volume, leading to maximum hardening. With increasing annealing temperature, the tensile strength $\sigma_B$ decreases due to the formation of larger Ti$_3$Ni$_4$ particles and the beginning of recrystallization, which leads to an increase in the average grain size.

4. Conclusions

The performed investigation of changes in the structure and properties of a thin-walled nitinol tube of composition Ti$_{49.1}$Ni$_{50.9}$, used for the manufacture of intravascular stents, caused by annealing at temperatures of 300-500°C led to the following conclusions:
• Changes in the martensitic transformation temperatures during annealing are due to a change in the concentration of nickel atoms in the bulk of the material as a result of aging and formation of Ti$_3$Ni$_4$ particles;

• The segregation of Ti$_3$Ni$_4$ particles promotes the B2→R martensitic transformation, which allows the R phase to exist at room temperature. This fact, in turn, leads to a decrease in the stresses at the beginning of the pseudo-yield plateau due to the formation of the B19' martensitic phase under applied external load.

• The tensile strength $\sigma_B$ of the tubes is determined by the characteristic features of Ti$_3$Ni$_4$ particles formed during annealing, such as the size, volume fraction, and distribution of particles in the material volume. An optimal combination of these factors provides the maximum tensile strength values of up to 1400 MPa.

The obtained results can be used in the development of technology for the manufacture of self-expanding intravascular stents.

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