

Structure, mechanical properties and martensitic transformations of porous material based on TiNi with reactive additive

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It is shown that the addition of a reaction additive of Ti and Ni powders in different proportions to the TiNi powder reduces the sintering temperatures and allows maintaining the regular porous structure of the TiNi-based material. With an increase in the proportion of the reaction additive, the sintering quality improves: the average pore size and pore bridges and the tensile strength increase. By X-ray diffraction analysis It is shown that the following intermetallic compounds are present in the material: phases TiNi ($B2$ and $B19'$), Ti_2Ni and $TiNi_3$.

Keywords: TiNi, porous, reactive additive, structure, martensitic transformations.

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The production of implants from porous alloys based on titanium nickelide (TiNi) is a pressing issue in current medical materials science. It is known that the correspondence between the mechanical characteristics of a TiNi alloy and biological tissues of the human body underlies its biomechanical compatibility [1,2]. The well-developed three-dimensional structure of the TiNi pore space is close to the anatomical structure of bone tissue and establishes favorable conditions for integration of implanted devices [3].

High strength characteristics under alternating loads are required in certain medical applications. A porous TiNi-based material may fail to meet these requirements. One possible alternative is a porous-monolithic material based on TiNi, which has already been used to design endoprostheses for reconstruction of resected fragments of ribs and defects of the lower jaw and to fabricate dental implants [1]. The above products share a similar composite structure of a monolithic TiNi plate surrounded by porous TiNi. The monolithic part of the structure improves the stress-strain performance of an implant. At the same time, the porous part increases the biocompatibility of an implanted structure by enabling the ingrowth of biological tissues [1].

The first models of rib endoprostheses were made from monolithic TiNi-based plates [1]. In the long term, such implants could cause damage to surrounding soft tissues and skin rupture. Therefore, they were superseded by porous-monolithic endoprostheses produced by coupling monolithic and porous plates mechanically with titanium rivets or thin threads. The porous parts could crumble around rivets, violating the integrity of an implant. To eliminate this drawback, the fabrication procedure was made more complex: a monolithic plate mounted vertically in a quartz tube was surrounded by a Ti–Ni charge mixture, and self-propagating high-temperature synthesis was initiated. The resulting cylindrical blanks were used

to machine a rib endoprosthesis. This procedure is labor-intensive and is characterized by a high percentage of waste during processing [1]. Thus, it may be concluded that an efficient method to produce rib endoprostheses has not been devised yet.

In the present study, we propose to use sintering of titanium nickelide powder onto the surface of monolithic TiNi plates to solve this problem and form a high-quality interface between porous and monolithic parts [1]. The porous implant part may be fabricated by sintering at a temperature of 1250 °C. Since this temperature may have a negative effect on the stress-strain performance of the monolithic plate, it needs to be reduced. Diffusion sintering of powdered TiNi with activating additives of titanium and nickel is a way to solve the posed problem. Sintering in the powder system is activated due to the exothermic reaction between titanium and nickel. In view of this, the aim of the study is to examine the influence of a reactive Ti and Ni additive on the structural features (macrostructure, phase composition), mechanical properties, and martensitic transformations of a porous material based on titanium nickelide.

Powdered TiNi (PV-N55T45, fraction (f) 100–160 μm) prepared by the calcium hydride reduction method was used to produce experimental porous samples. The reactive additive was a mixture of Ti (PTEM-1, $f = 0$ –100 μm) and Ni (PNK-OT4, $f = 20$ –63 μm) powders. The initial TiNi, Ti, and Ni powders were dried in a dry-heat oven at a temperature of 90 °C for 60 min. To distribute the reactive additive evenly, Ti and Ni powders were mixed first, and the resulting mixture was added to the TiNi powder. Mixing was carried out in a V-shaped mixer over 8 h.

When a single-component TiNi powder charge is sintered, the atomic composition of TiNi shifts towards enrichment in Ni (up to 52 at.%) [4]. The obtained material undergoes martensitic transformations within the range

Mass of the initial components (TiNi, Ti, and Ni powders) and sintering temperature (T_{sint}) of the porous material based on TiNi with different fractions of the reactive additive

| Sample | $m(A)$, g | $m(B)$, g | $m(\text{TiNi})$, g | $m(\text{Ti})$, g | $m(\text{Ni})$, g | T_{sint} , °C |
|--------|------------|------------|----------------------|--------------------|--------------------|-----------------|
| 1:0.5 | 50.00 | 25.00 | 47.61 | 14.64 | 12.75 | 1050 |
| 1:0.75 | 50.00 | 37.50 | 47.61 | 20.89 | 19.00 | 1000 |
| 1:1 | 50.00 | 50.00 | 47.61 | 27.14 | 25.25 | 1000 |

of $-150-0^{\circ}\text{C}$ [2], but it is important for the practical application of porous TiNi-based materials that the martensitic transformation occurs at a temperature above 20°C . According to the results of our research [5], a charge with the addition of Ti of the TiNi–5Ti composition should be used for sintering. Since the obtained material undergoes martensitic transformations within the range of $25-40^{\circ}\text{C}$, it serves as a base for the mixture for use with a reactive additive. To ensure an exothermic reaction, Ti+Ni powders in an equiatomic ratio in various proportions are added to the discussed powder mixture. The obtained mixtures A (TiNi–5Ti) and B (Ti+Ni) were mixed in proportions of 1:1, 1:0.75, and 1:0.5. Thus, three types of experimental samples (see the table) were prepared.

In preparation for sintering, the powder mixture was introduced into quartz vessels with an internal diameter of 13–14 mm and a length of 65–80 mm. The initial porosity of the charge was 60–65%. Single-step sintering was performed for 15 min in an SNVE-1.31/16-I4 electric vacuum furnace at a pressure of $6.65 \cdot 10^{-3}$ Pa with an average heating rate of $10^{\circ}\text{C}/\text{min}$. The temperature level within the range of $950-1100^{\circ}\text{C}$ was chosen for each proportion of the reactive additive experimentally. Sintering temperature T_{sint} is indicated in the table.

The obtained porous TiNi-based blanks were cut by electrical discharge machining into experimental samples $4 \times 4 \times 8$ mm in size for mechanical compression tests and plates $1 \times 4 \times 30$ mm in size for investigating the temperature dependence of specific electrical resistance.

To study the macro- and microstructure of the porous TiNi alloy samples, metallographic sections were also prepared in accordance with the standard procedure [6]. The structure of the metal matrix of the samples was examined by optical and scanning electron microscopy using Axiovert-40 MAT and Quanta 200 3D microscopes, respectively. The concentration composition of phases was determined using an EDAX ECON IV energy-dispersive spectrometer. The phase composition was examined by X-ray structural analysis with a Shimadzu XRD-6000 diffractometer ($\text{CuK}\alpha$ -radiation with a wavelength of 1.541 \AA) at 40 kV and 30 mA. Measurements were carried out within the $10-80^{\circ}$ range of diffraction angles at a scanning rate of $1^{\circ}/\text{min}$. The phase composition was analyzed using PDF 4+ databases and the POWDER CELL 2.4 full-profile analysis program. The parameters of macrostructure of porous samples were determined using stereometric techniques in ImageJ. The sample porosity was

measured as

$$P = \left(1 - \frac{\rho_{por}}{\rho_{mon}}\right) \cdot 100\%,$$

where ρ_{por} and ρ_{mon} are the porosities of porous and monolithic samples, respectively.

Mechanical compression tests were performed using an INSTRON 3369 machine at 25 and 150°C . The strain rate was 6% per minute. The test temperature was chosen so that the porous material assumed different structure-phase states. The temperature dependence of specific electrical resistance was determined using a SIES-30 setup at temperatures ranging from -150 to $+150^{\circ}\text{C}$ with a variation rate of $5^{\circ}\text{C}/\text{min}$. The characteristic temperatures of martensitic transformations were determined by the method of tangents to the $\rho(T)$ function plot.

The sintering temperature specifies the structural features, phase composition, mechanical properties, and martensitic transformations of the material based on titanium nickelide with a reactive additive [3]. The temperature and temporal parameters of sintering enabling the production of a porous material with a porosity range of 50–55%, which corresponds to the structure of bone tissue of the human body [1,3], were determined experimentally for each proportion of the reactive additive. The sintering temperature for the samples with the highest and lowest proportions of the reactive additive was 1000°C and 1050°C , respectively. According to literature data [7], the amount of heat released in the exothermic reaction between Ti and Ni is 16.96–32.45 kJ, which makes it possible to reduce the sintering temperature by $200-250^{\circ}\text{C}$.

Figure 1 presents the typical structure of the obtained porous material based on TiNi with the reactive additive. It was found that all samples had a similar macrostructure; therefore, the 1:1 sample is characterized below. The porous material with the reactive additive consists of a matrix based on TiNi with particles of secondary phases enriched in both titanium and nickel that are distributed unevenly within the material volume. Owing to chemical heterogeneity, phases enriched in titanium, such as Ti_2Ni , form during sintering at the sites where titanium particles are located. The size, shape, and positioning of titanium-rich particles in the TiNi matrix are non-uniform. Particles $0.5-5 \mu\text{m}$ in size are seen alongside with larger ones (up to $25 \mu\text{m}$) of an arbitrary geometric shape. They are located both on the periphery and inside the pore bridges. Phases enriched in nickel, such as TiNi_3 , form at the sites where nickel particles

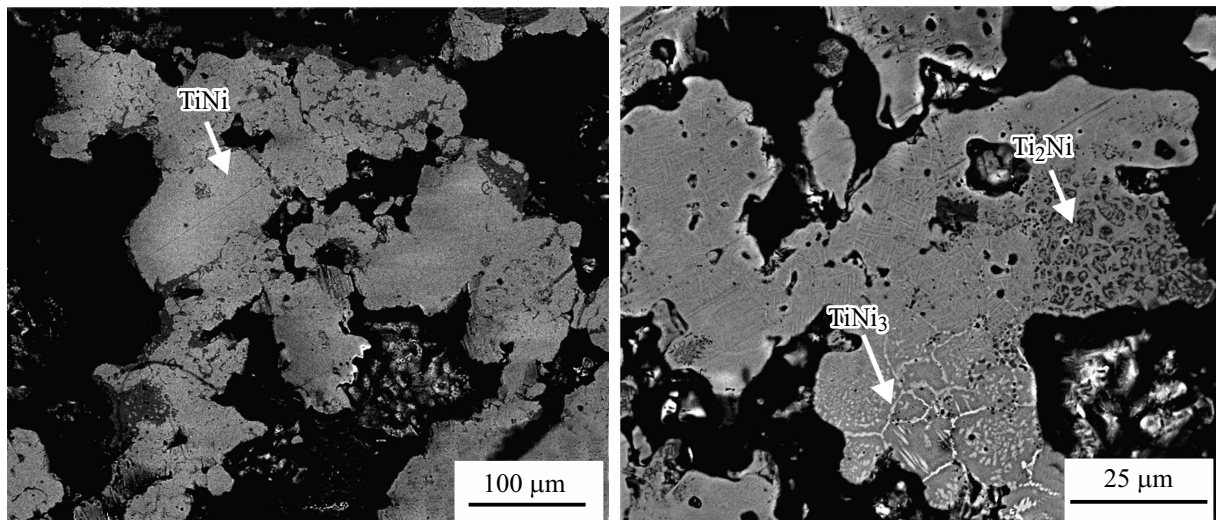


Figure 1. Microstructure of the porous TiNi-based material mixed in a proportion of 1:1 with the reactive additive.

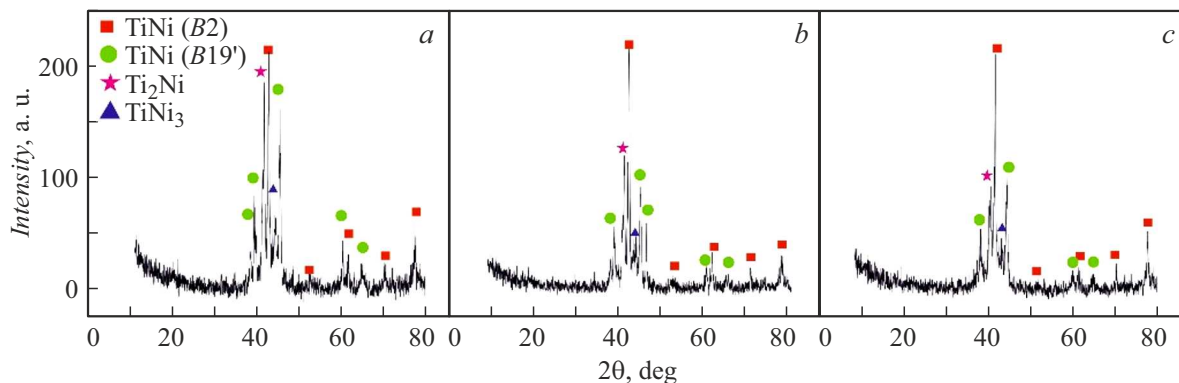


Figure 2. X-ray diffraction analysis of the porous TiNi-based material with different proportions of the reactive additive: *a* — sample 1:0.5, *b* — sample 1:0.75, and *c* — sample 1:1.

are located. The results of energy-dispersive microanalysis revealed that the primary compound (TiNi) in the obtained samples contains 49.5–50 at.% Ni.

It was found that the average size of pores and pore bridges in the samples prepared by diffusion sintering with the reactive additive was 120–140 and 90–120 μm, respectively. As the reactive additive amount increases, the pore bridges grow larger due to mass transfer processes and the activation of alloy formation processes under the influence of activating Ti and Ni additives.

Figure 2 shows the X-ray diffraction patterns of the obtained porous materials based on TiNi with different proportions of the reactive additive. It is evident that the primary TiNi compound is in a two-phase state (*B2* and *B19'*), and the following secondary phases were also detected: Ti_2Ni and TiNi_3 . The overall content of austenitic and martensitic TiNi phases (*B2* and *B19'*) is as high as 65–70%. The volume fraction of phase *B19'* decreases from 38 to 27% as the reactive additive amount increases. The volume fractions of secondary phases enriched in

titanium (Ti_2Ni) and nickel (TiNi_3) are as high as 30 and 10%, respectively. Pure Ti and Ni were not detected.

Strength properties are among the most important characteristics of porous TiNi-based alloys. Since materials with a similar macrostructure have a high degree of similarity in mechanical behavior, Fig. 3, *a* presents the stress-strain diagram obtained by compressing the 1:1 sample. It was found that the tensile strength increases from 40 to 135 MPa at a test temperature of 25 °C and from 45 to 160 MPa at 150 °C as the reactive additive amount increases (Fig. 3, *b*). This tensile strength enhancement is attributable to an improved sintering quality due to an increase in average size of pore bridges. The difference in fracture stress is indicative of different deformation mechanisms in the martensitic and austenitic states. At a temperature of 25 °C, the porous alloy is deformed by the formation and reorientation of martensite and by dislocation slip. At a test temperature of 150 °C, strain accumulation may proceed via the formation of stress-induced martensite and dislocation slip, which agrees with the data reported in [8]. These mechanisms are

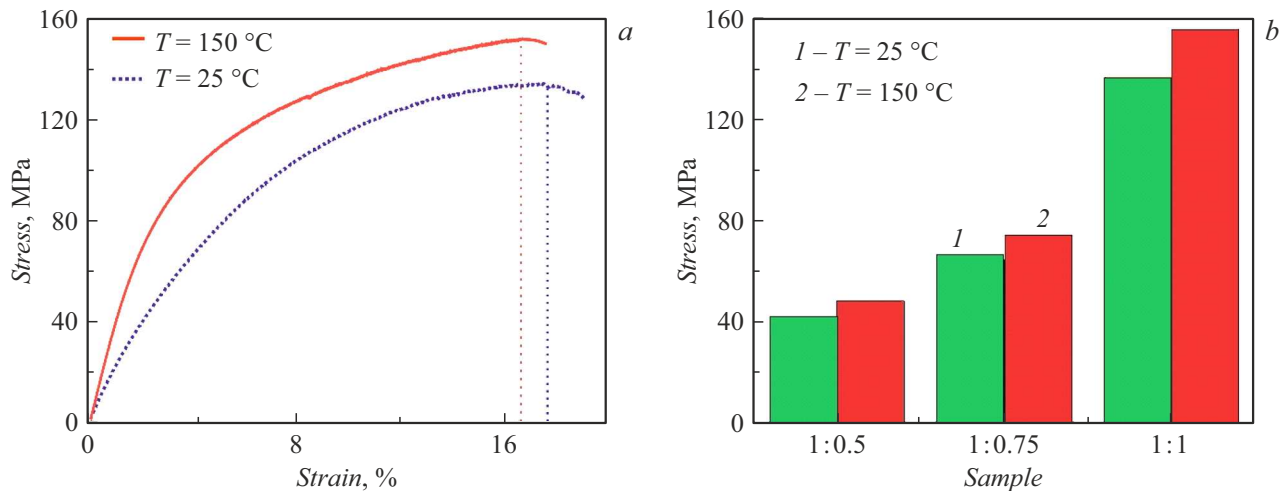


Figure 3. Mechanical properties of the porous material based on TiNi with different proportions of the reactive additive: *a* — dependences $\sigma(\epsilon)$ for the 1:1 sample at 25 and 150 °C; *b* — histogram with tensile strength values.

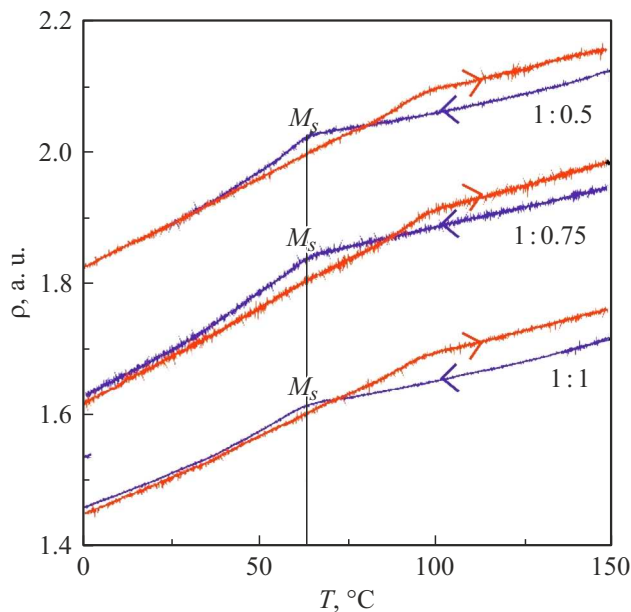


Figure 4. Temperature dependence of the specific electrical resistance of the porous material based on TiNi with different proportions of the reactive additive.

interconnected and specified by the test temperature and the nature of phase transitions of porous alloys based on titanium nickelide.

Figure 4 shows the temperature dependence of the specific electrical resistance of the porous material based on TiNi. The nature of dependence $\rho(T)$ is indicative of a single-stage martensitic transition from the initial $B2$ -phase to the martensitic $B19'$ phase in the examined alloys. The obtained dependences suggest that temperature M_s is approximately 62 °C. According to [2,9], temperature M_s corresponds to the temperature of the onset of martensitic transformation of TiNi with a nickel concentration of

49.5–50 at.%, which is consistent with the experimental results.

Thus, it was established that the introduction of a reactive additive of Ti and Ni in different proportions to powdered TiNi reduces the sintering temperature while preserving a regular porous structure and martensitic transformations. As the reactive additive amount increases, the quality of sintering improves (the average size of pores and pore bridges increases) and the tensile strength increases. It was demonstrated that the TiNi compound is in a two-phase state ($B2$ and $B19'$); secondary phases enriched in titanium and nickel were also detected.

The reactive additive proportion of 1:1 is the optimum one, since it provides the maximum temperature reduction (250 °C). The corresponding porous material has the highest tensile strength (135 MPa at 25 °C and 160 MPa at 150 °C) and optimum values of macrostructure parameters, such as porosity and average size of pores and pore bridges.

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Conflict of interest

The authors declare that they have no conflict of interest.

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