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INVESTIGATIONS OF THE STRUCTURE OF POROUS TITANIUM NICKELIDE AFTER THERMAL TREATMENT

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Methods of optical metallography, scanning electron microscopy, and x-ray structural and spectral microanalyses are used to investigate the structural features of porous titanium nickelide produced by the method of self-propagating high-temperature synthesis (SHS) after its thermal treatment. It is demonstrated that the clearly expressed structural-phase inhomogeneity observed in porous titanium nickelide after SHS is retained after thermal treatment. During thermal treatment with increase in the annealing temperature, the volume fraction of the Ti_2Ni *phase enriched in titanium remains essentially unchanged; it is redistributed over the sample volume. The volume fraction of the* $TiNi_3$ *phase increases and nonuniformity in its density distribution over the sample volume, caused by the chemical inhomogeneity of the matrix, is observed.*

INTRODUCTION

High biochemical and biomechanical compatibility with living tissues of an organism of porous permeable titanium-nickelide–base alloys produced by the method of self-propagating high-temperature synthesis (SHS) as well as good physicomechanical and electrochemical properties of these materials allow them to be widely used in various fields of medicine and technology [1–3]. They are most often used in the form of plates, disks, rods, pins, and individual designs capable of fulfilling definite functions in the organism. In the process of manufacture of these designs, the material is thermally treated upon heating to temperature $T \sim 1000°\mathrm{C}$. Such treatment can essentially change the material structure and, as a consequence, its physicomechanical characteristics. It is well known that after thermal treatment of monolithic titanium nickelide, its structural and phase state changes significantly, resulting in a displacement of the temperature interval of phase transformations and a change in the sequence of martensitic transitions [4]. Thermal treatment will affect the properties of porous permeable titanium nickelide produced by the SHS method even greater than the properties of the monolithic alloy due to the special features of its macrostructure.

Porous titanium nickelide has a large specific surface due to the presence of a system of open pores. Sizes of interpore membranes in the alloy are comparable with pore sizes; in addition, the membranes comprise dead-end pores in which a large amount of oxygen is accumulated [5].

During thermal treatment, titanium in titanium nickelide is prone to segregation on free surfaces, which causes interaction with oxygen and formation of oxides [6]. In addition, upon heating, regions of the alloy with increased titanium content will sorb oxygen and form titanium oxides (on free surfaces of the alloy, grain boundaries, pores, and local regions of the matrix with increased titanium content). This phenomenon is of great importance for an analysis of special features of martensitic transformations in titanium nickelide, because enrichment of surfaces in titanium and formation of oxides change essentially the concentration composition of the matrix and its thermoelastic behavior. In this regard, deep and comprehensive investigations of the structure and properties of porous permeable titanium nickelide depending on thermal treatment are rather urgent.

The present work studies the influence of thermal treatment on the macro- and microstructures of porous permeable titanium nickelide produced by the SHS method.

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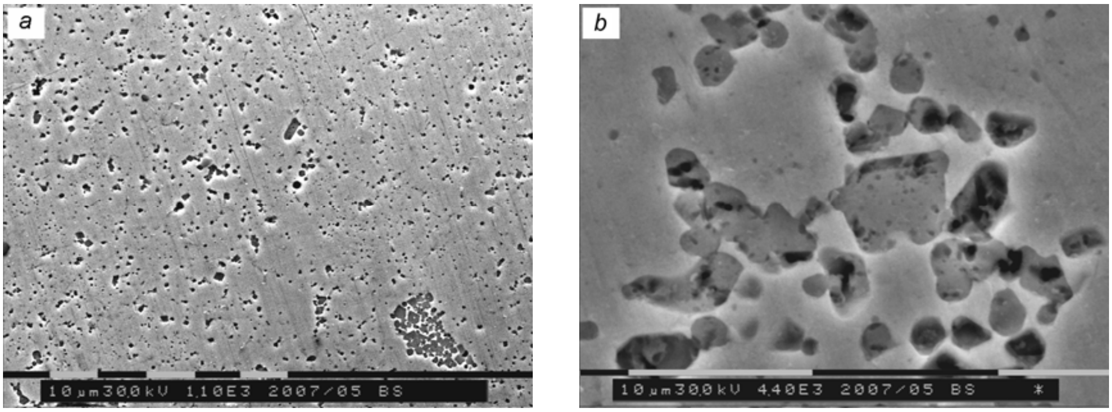

Fig. 1. Microstructure of porous titanium nickelide after SHS.

MATERIALS AND METHODS OF RESEARCH

We investigated samples of porous titanium nickelide with porosity of 80% and average pore sizes of 200 μm. Thermal treatment (annealing) of samples was performed in vacuum at 10^{-4} Pa and temperatures in the interval 290–1000°C for 1 h with subsequent cooling together with a furnace. To investigate the microstructure, microsections of samples were prepared by the standard method, and then their surfaces were electropolished in a solution of electrolyte containing 5.6 mL of perchloric acid and 94.4 mL of glacial acetic acid. To reveal the microstructure, the samples were etched in a solution of nitric and fluoric acids and water. The sample macrostructure after thermal treatment was studied using on Olympus GX-71 optical microscope, and the sample microstructure was studied using a Philips SEM 515 scanning electron microscope. The phase composition was determined using x-ray structural and spectral microanalyses.

RESULTS AND THEIR DISCUSSION

The data of x-ray structural analysis demonstrated that mainly intermetallic compounds – TiNi (in $B2$ and $B19^1$ biphase states), Ti_2Ni, and $TiNi_3$ phases – were formed in porous titanium nickelide alloys produced by the SHS method without thermal treatment. The main feature of the porous alloy structure after SHS was clearly pronounced nonuniformity of phase precipitate distributions over the entire sample volumes. Regions with different precipitate density distributions were observed on the sample surface. A high density of small oval-like precipitates with sizes of 0.1–3 μm with nonuniform distributions both inside the grain body and on the grain and pore boundaries were observed (Fig. 1*a*).

The grain-boundary precipitates were enriched both in titanium and nickel, in good agreement with laws of primary crystallization according to the phase diagram for the TiNi system. In addition to single small equiaxial precipitates, chains comprising separate small and large precipitates of arbitrary geometrical shapes with larger sizes of 4–8 μm were observed (Fig. 1*a*).

The characteristic feature of the initial structure was the presence of local arbitrary localized clusters – conglomerates – consisting of many particles with arbitrary geometrical shapes and sizes enriched in titanium (Ti_2Ni). These phase clusters can be formed both on the pore boundaries and in any arbitrary regions of the matrix (Fig. 1*b*). It should be noted that smaller oval- or plate-like particles also enriched in titanium were most often observed on the surface of large precipitates having arbitrary shapes.

The local microanalysis of the detected precipitates demonstrated that small equiaxial particles represent phases enriched in titanium – Ti_2Ni. Judging by the state diagram for the TiNi system, these phases are formed during

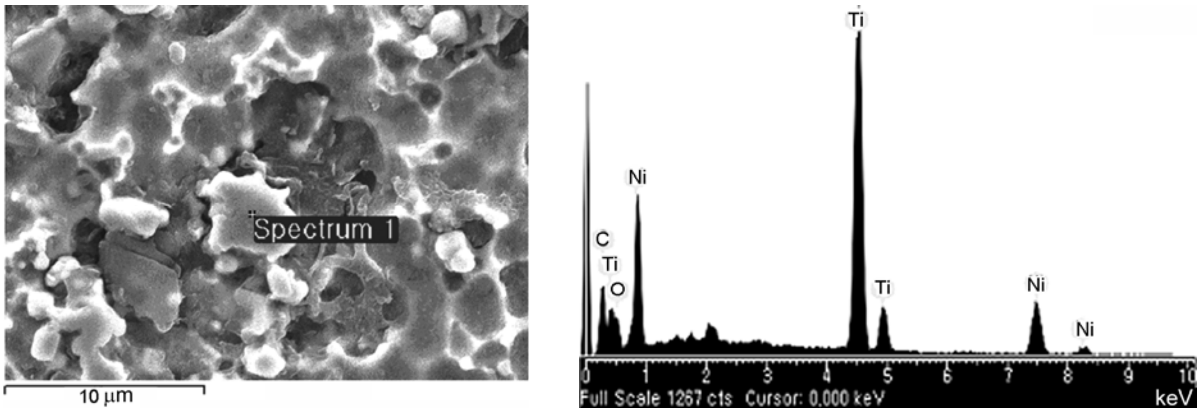

Fig. 2. X-ray spectral microanalysis of $Ti_4Ni_2(O,C)$ particles enriched in titanium.

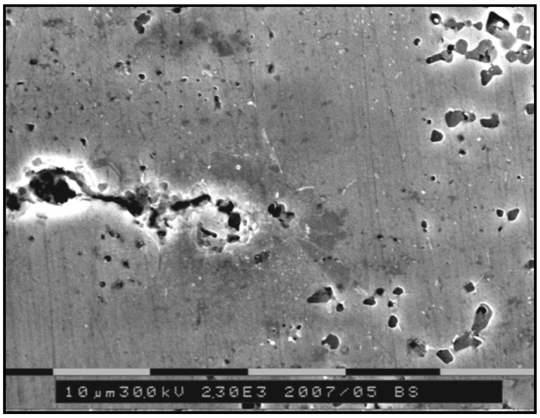

Fig. 3. Microstructure of porous titanium nickelide after SHS: finely dispersed white precipitates are $TiNi_3$ phases enriched in nickel.

crystallization in the course of a peritectic reaction. A large role in the phase formation is played by oxygen and other interstitial impurities – C, H, and N – that are always present in the lattice of the TiNi alloys produced by the SHS method. Because of the presence of vacancies in the lattice, it can dissolve O, N, and C, thereby causing the formation of $Ti_4Ni_2(O,N,C)$ oxicarbonitrides [6, 7]. These precipitates differ only slightly from Ti_2Ni because of close similarity of their crystal lattices. The data of x-ray spectral analysis demonstrate that the observed precipitates are enriched in titanium, have irregular geometric shapes, and represent most often complex $Ti_4Ni_2(O,C)$-type oxicarbides (Fig. 2).

Among a wide variety of inhomogeneities, large precipitates comprising Ti, Ni, Ca, Fe, Si, and Al in various proportions can be distinguished in arbitrary regions of the matrix. They are formed through the interaction of titanium with metal and nonmetal impurities.

In addition to small equiaxial precipitates, large particles of arbitrary geometric shapes, and particle conglomerates, rare finely dispersed white oval- and plate-like precipitates with sizes of 0.1–0.2 µm were observed in some regions of the matrix and sometimes on the grain boundaries (Fig. 3).

The x-ray spectral analysis demonstrated that they represented the $TiNi_3$ phases enriched in nickel. The data of x-ray structural analysis also confirmed the presence of small volume fraction of the $TiNi_3$ phase. The volume fraction of phases enriched in nickel was much less than of phases enriched in titanium.

After thermal treatment, the TiNi, Ti_2Ni, $Ti_4Ni_2(O,C)$, and $TiNi_3$ phases observed in the initial material were retained at all annealing temperatures. In addition, aging with precipitation of the finely dispersed $TiNi_3$ phase enriched in nickel occurred during annealing and subsequent slow cooling of the alloy with the furnace (see Fig. 4).

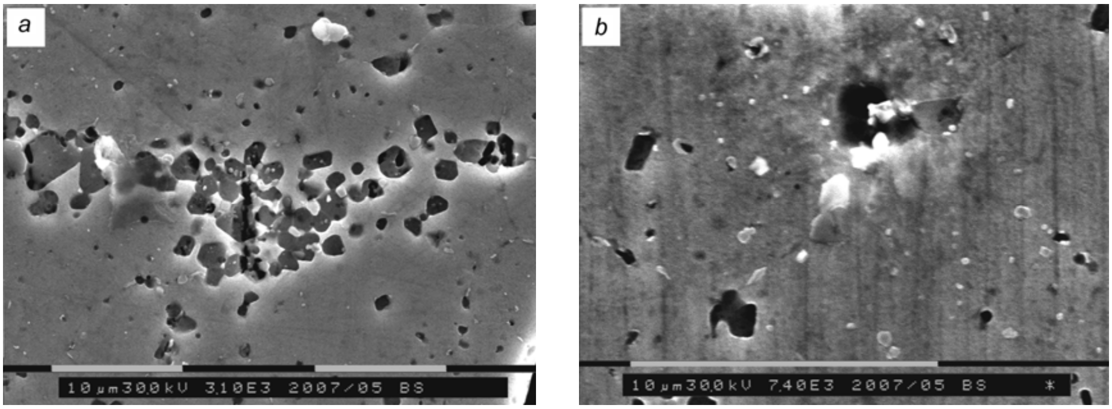

Fig. 4. Microstructure of porous titanium nickelide after annealing at $T = 290°C$ for $t = 1$ h: *a*) black precipitates of the phase enriched in titanium and *b*) white precipitates of the phase enriched in nickel.

Investigations of the alloy structure demonstrated that after low-temperature annealing (at $T = 290°C$ for $t = 1$ h), the nonuniformity in distribution of precipitates enriched in titanium was retained. An insignificant increase in sizes of small Ti_2Ni particles and a tendency toward their formation on grain boundaries were observed. An insignificant increase in the volume fraction of the $TiNi_3$-type precipitated phases enriched in nickel was observed both inside the grain body and on the grain boundaries in arbitrary regions of the matrix. In this case, their highly nonuniform distribution over the sample was retained. It seems likely that because of the inhomogeneous chemical composition of the matrix, the maximum particle density was observed in regions with increased nickel content. Three particle types were identified: small equiaxial, lens-like, and plate-like particles (Fig. 4*b*). The x-ray spectral microanalysis confirmed that these phases were enriched in nickel. The data obtained are in good agreement with the data presented in [8, 9] where it was pointed out that during low-temperature thermal treatment of the quenched TiNi alloy enriched in nickel (50–52 at%) at $T < 400°C$, nucleation and growth of finely dispersed coherent particles enriched in nickel occurred. In this case, the process of aging of the TiNi alloy had two stages – high-temperature ($T > 400°C$) and low-temperature aging ($T < 400°C$) – during which $Ti_{11}Ni_{14}$, Ti_3Ni_4, Ti_2Ni_3, and $TiNi_3$ were precipitated in a definite sequence. The initial stages of decomposition of TiNi alloy enriched in nickel at temperatures ≥250°C were caused mainly by uniform precipitation of Ti_3Ni_4 or $Ti_{11}Ni_{14}$ particles. In the initial stage, these particles had structures isomorphic to the *B*2-matrix and coherent to it, equiaxial shape, and high degree of dispersion (sizes smaller than 3–5 nm). During further aging from 250 to 400°C, lens-like and then plate-like particles were precipitated, first finely dispersed and then coarsely dispersed particles. During high-temperature aging ($T > 400°C$), the Ti_3Ni_4 phase precipitated homogeneously had the rhombohedral structure. After short aging, it was shaped as thin plates, and after long aging, lens-like particles were formed [8, 9].

With increase in the annealing temperature ($T = 400°C$ and higher), the matrix volume purification from small precipitates of the Ti_2Ni phases was observed. Regions without particles arose, and the grain boundaries became sharper because of the increased density of precipitates (Fig. 5). Enlargement of both individual Ti_2Ni particles enriched in titanium and their conglomerates comprising large precipitates – complex $Ti_4Ni_2(O,C)$ oxicarbides – was observed. It seems likely that such enlargement of particles with increasing annealing temperature is due to the processes of dissolution and partial coagulation of particles as well as due to additional oxides formed on the surface of these phases because of additional dissolution of oxygen in the Ti_2Ni lattice. In addition, further aging with precipitation of the finely dispersed coherent $TiNi_3$ phase enriched in nickel occurred in the alloy with increasing temperature ($T > 600°C$) during annealing and subsequent cooling with the furnace. With increase in the annealing temperature, the volume fraction of finely dispersed phase increased, but the nonuniformity of its distribution over the sample surface was retained. Regions with uniform particle distributions over the surface and zones without precipitates were observed together with precipitates on the grain boundaries. The $TiNi_3$ phases of two types, namely, oval- and plate-like precipitates were observed (Fig. 6).

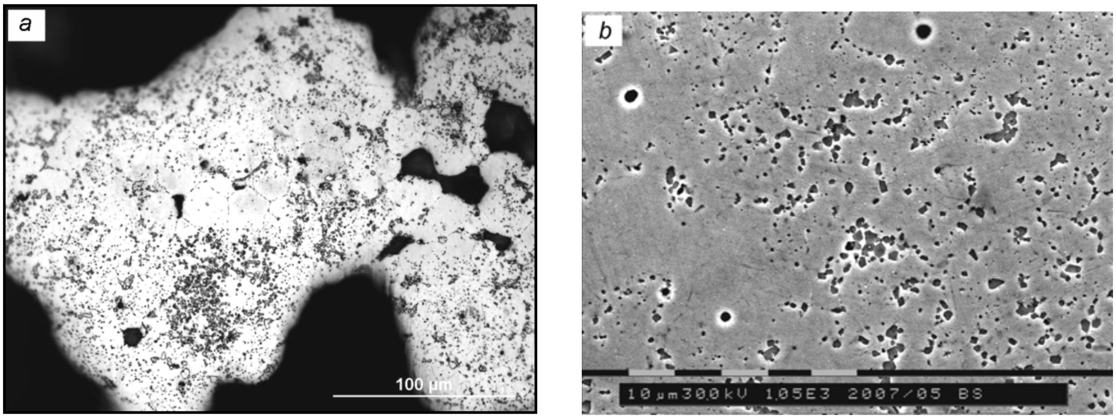

Fig. 5. Macrostructure (*a*) and microstructure (*b*) of porous titanium nickelide after annealing at $T = 400°C$ for $t = 1$ h; zones without precipitates can be seen.

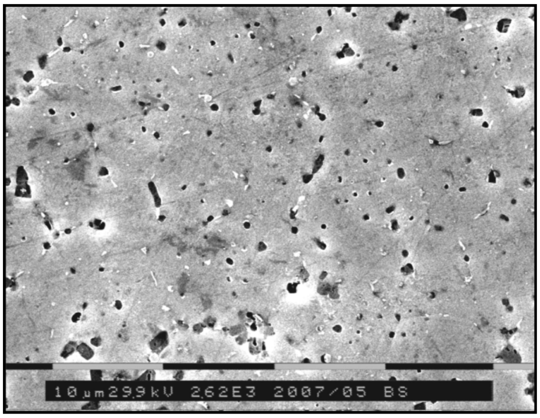

Fig. 6. Microstructure of porous titanium nickelide after annealing at $T = 600°C$ for $t = 1$ h.

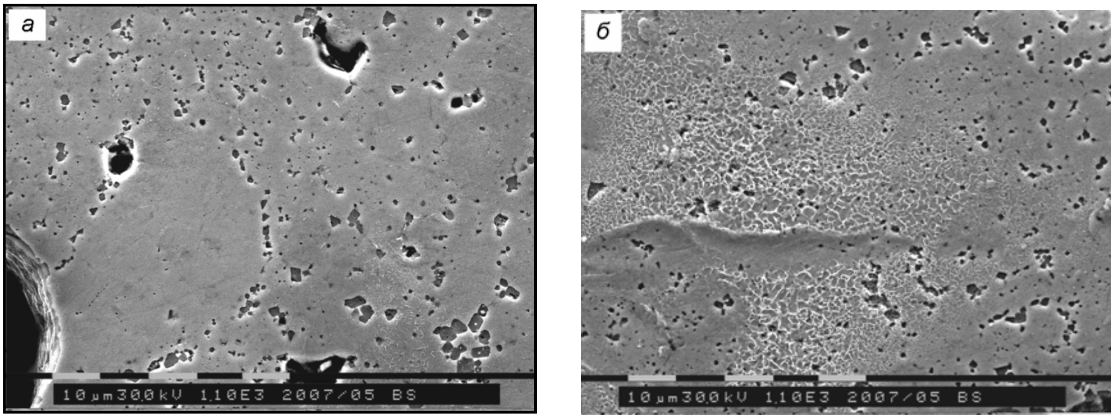

Fig. 7. Microstructure of porous titanium nickelide after annealing at $T = 1000°C$ for $t = 1$ h: *a*) matrix volume purification and *b*) network of the $TiNi_3$ precipitates.

Further increase in the annealing temperature ($T = 800–1000°C$ for $t = 1$ h) intensified matrix volume purification from small precipitates due to gradual redistribution of the Ti_2Ni phase (Fig. 7*a*). In addition, the finely

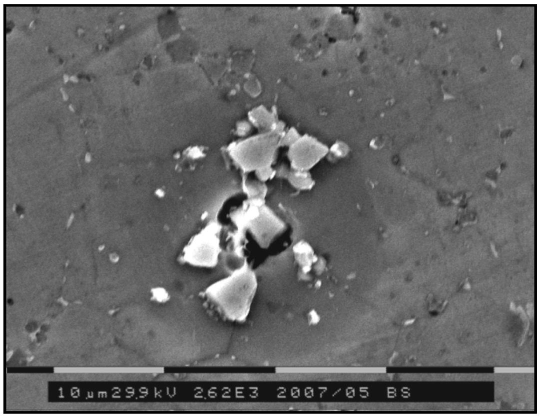

Fig. 8. Microstructure of porous titanium nickelide after annealing at $T = 1000°C$ for $t = 1$ h. Here white precipitates represent the $TiNi_3$ phase precipitated on grain and oxide boundaries.

dispersed coherent $TiNi_3$ particles enriched in nickel were homogeneously nucleated in the alloy during high-temperature aging. The density of finely dispersed precipitates in local matrix regions was so high that large regions with ripples (highly excited matrix state) were observed. In some regions, the network of $TiNi_3$ precipitates was also observed (Fig. 7*b*). In addition to the homogeneous precipitation of particles in the matrix during high-temperature aging, their heterogeneous nucleation on grain boundaries and inclusions of oxides were observed (Fig. 8).

It seems likely that the largest $TiNi_3$ particles are formed during annealing of the alloy (high-temperature aging), and finely dispersed Ti_3Ni_4 and $TiNi_3$ particles are formed during cooling from high annealing to room temperature. The network of the $TiNi_3$ phase precipitates is most probably formed in the regions most enriched in nickel. The nonuniform surface distribution of particles and different precipitation densities are caused by the clearly expressed inhomogeneous chemical structure of porous titanium nickelide.

We can conclude that in porous titanium nickelide produced by the SHS method and characterized by clearly pronounced chemical inhomogeneity of its structure, the intermediate metastable phases enriched in nickel – larger plate-like Ti_2Ni_3 precipitates and small plate- and lens-like $Ti_{11}Ni_{14}$ and Ti_3Ni_4 particles and finely dispersed stable $TiNi_3$ particles – can be formed in the matrix phase as a result of annealing at temperatures $T = 290–1000$ in regions with variable chemical composition.

The quantitative x-ray structural analysis of the precipitated phases demonstrated that the volume fraction of the Ti_2Ni phase enriched in titanium remained essentially unchanged during thermal treatment at temperatures in the range 290–1000°C. The volume fraction of the phase enriched in nickel increased with the annealing temperature. However, we failed to establish a law of its change. This is most probably due to its clearly pronounced nonuniform density distribution over the sample volume which, in turn, is caused by the chemical inhomogeneity of the matrix. Larger volume of statistical data is necessary to establish a law.

The established laws of changing the microstructure of porous titanium nickelide during thermal treatment, by analogy with monolithic titanium nickelide, can displace the characteristic temperatures of martensitic transitions, change their sequence, and influence the yield stress.

CONCLUSIONS

The analysis of structural features of porous titanium nickelide has demonstrated that the clearly pronounced structural phase inhomogeneity established in porous titanium nickelide after SHS is retained in the material after thermal treatment. The TiNi, Ti_2Ni, $Ti_4Ni_2(O,C)$, and $TiNi_3$ phases were observed in the porous titanium nickelide structure at all annealing temperatures. The Ti_2Ni phase was redistributed over the sample volume during thermal treatment with increase in the annealing temperature, that is, matrix purification from small precipitates of this phase occurred, and matrix regions without particles were observed. In this case, the volume fraction of the $TiNi_3$ phase increased, and its nonuniform distribution over the sample surface, caused by the clearly pronounced chemical inhomogeneity of the porous titanium nickelide composition, was retained. The established laws of changing the porous nickelide microstructure during thermal treatment can lead to a displacement of the characteristic temperatures of martensitic transitions, change their sequence, and influence the yield stress value.

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