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Abstract. Structural features of porous TiNi-based materials with Ti additives produced by diffusion sintering have been studied. TiNi powder fraction with a size of 100–160 μm used for sintering provides highly porous material. It is found that increased concentrations of Ti additives decrease the porosity coefficient of the material and increase the volumetric content of the secondary Ti_2Ni and Ti_4Ni_2 (O, N, C) phases. It is shown that Ti powder additives can be used to improve the atomic composition of the TiNi compound.

INTRODUCTION

Biocompatible TiNi-based porous alloys exhibit unique functional and structural properties due to the combination of a developed three-dimensional structure and martensitic transformations. Various methods of powder metallurgy used to create porous TiNi alloys provided creation of implantable structures for various fields of medicine [1–5]. Small-sized implants with high porosity, permeability and a developed terrace-like structure of the pore wall surface are produced by sintering calcium hydride TiNi powder [6–8]. This technology for producing implants implies a porous body of the structure that consists of a set of individual powder particles with a new recrystallized rough surface due to wetting by the $Ti_2Ni + TiNi$ melt. The volume of the melt formed is controlled by the temperature-time sintering regime, and its amount should ensure formation of high-quality interparticle contacts with shrinkage of not more than 15–20%.

However, as is known, during high-temperature aging of TiNi-based alloys, titanium segregates onto free surfaces, and an oxide layer of complex composition and particles of secondary Ti_4Ni_2 (O, N, C) phases are formed [8–11]. The basic TiNi compound in TiNi powder produced by hydride-calcium reduction is found to be Ti-depleted under high sintering temperatures. This significantly decreases the characteristic temperatures of martensitic transformations, which causes deterioration of functional properties—shape memory effects and superelasticity. One of the solutions to this problem can be the use of titanium additives to improve the atomic composition in the TiNi compound during high-temperature aging.

In addition, the problem to be solved is preparation of highly porous TiNi-based materials by diffusion liquid phase sintering with a porosity exceeding 60%. During liquid-phase sintering, the particles are attracted to each other under the action of the melt and form inter-pore bridges. The higher the sintering temperature, the more amount of the $TiNi + Ti_2Ni$ melt is formed, and shrinkage increases. The porosity coefficient is found to reduce to 50%. An additional task posed was production of material with a higher value of the porosity coefficient by analyzing the particle size distribution to make the material maximally correspond to the macrostructure of the human body bone tissues, which could not be achieved earlier.

In this regard, this study is aimed at solving two problems and addresses the investigation of the effect of Ti additives on the structure and properties of porous TiNi–Ti alloys in order to produce a highly porous material with martensitic transformations.

MATERIALS AND METHODS

Structural features of porous TiNi-based alloys produced by single diffusion liquid phase sintering of a PV-N55T45 grade TiNi powder and PTEM-1 grade Ti powder additives with a concentration of (2.5, 5.0, 7.5, 10.0, 15.0 at % Ti above the TiNi quantity). The fraction of Ti and TiNi powder was in the range of 0–200 μm, with an average particle size of 140 μm. The range of Ti additive values was chosen wide due to a significant degree of alloy depletion in Ti after sintering without additives and minimal enthalpy of formation of particles based on the Ti_2Ni phase at sintering temperatures used, which primarily causes active formation of particles based on these additives [12]. The results of structural studies of TiNi materials with Ti additives (2.5–15.0 at % Ti) can be used to assess the effect of Ti powder additives on structural features.

Single sintering was carried out in a SNVE-1.31/16-I4 electric vacuum furnace for 15 min at 1250–1260°C, which was controlled using a thermocouple based on a tungsten–rhenium alloy. The indicated temperature-time regime was successfully tested in [8] to produce porous samples without Ti additives, which showed an optimal sintering degree with a high quality of interparticle contacts and a regular porous structure. Sintering was performed at a pressure of 6.65×10^{-4} Pa with an average heating rate of 10 °C/min. The initial porosity of the bulk was 60–65%. The powder was poured into quartz capsules with an internal diameter of 13–14 mm and a length of 65–80 mm (Fig. 1). The powder was poured through a side hole with a diameter of 3–4 mm on one of the edges of the quartz capsule. To prepare the powder mixture, TiNi powder with a fraction in the range of 100–160 μm was used. Ti powder additives had two fractions in equal proportions—160–200 μm and less than 100 μm. The Ti 160–200 μm fraction was used to increase porosity; the fraction of less than 100 μm was used to uniformly distribute Ti in the mixture and maximize dissolution in the $Ti_2Ni + TiNi$ melt. The value of the fractions was determined using a sieve analysis. The initial powders were pre-dried in a dry oven at 150°C for 2 h. The quantities were calculated using the A&D GH-200 analytical balance of accuracy class 1. Mixing was carried out in a V-shaped mixer for 8 h. The produced porous samples with Ti additives had a diameter of 11–13 mm and a length of 65–80 mm.

To study the macro- and microstructure of the porous TiNi alloy samples, metallographic sections were prepared using the standard technique. To reveal the structural features of the test samples, the surface of the metallographic sections was treated in aqueous solution of nitric and hydrofluoric acids (2 parts HNO_3, 1 part HF, 3 parts H_2O) at a solution temperature of 55–60°C for 2–3 s. The structure of the metal matrix of the prepared samples was studied 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 X-ray diffraction analysis was performed using a Shimadzu XRD 6000 X-ray diffractometer with Cu radiation equipped with semiconductor detector. The phase composition was analyzed using PDF 4+ databases and the full-profile analysis program POWDER CELL 2.4. A quantitative description of the pore structure was performed – porosity was determined by the weighing method, and the pore size distribution was constructed by the secant method. Quantitative analysis of the content of the Ti_2Ni and $Ti_4Ni_2(O, N, C)$ phases was carried out by the stereographic method using ImageJ software. The characteristic temperatures of martensitic transformations were determined with regard to temperature dependence of electrical resistivity.

RESULTS AND DISCUSSION

It was found that TiNi powder with the maximum size fraction of 160–200 μm provides the initial porosity of the bulk of about 60%, which, taking into account the shrinkage after sintering, does not solve the problem of producing high porous ($P > 60\%$) material. The porosity of the remaining fractions of 100–160 and <100 μm was about 70%. The analysis of the powder material of various fractions by scanning microscopy provided interpretation of the results obtained. It was found that the particles of the powder fraction of 160–200 μm exhibit compact morphology and have traces of deformation (Fig. 1). On the contrary, the initial porosity of the bulk consisting of powder particles of medium and small fractions was about 70%, since the particles had a spongy morphology. The particle shape in this case is close to a flattened body in a plane with the maximum area. Thus, TiNi powder fractions were found for production of porous materials with increased porosity. However, for implantable TiNi-based devices, only the average TiNi powder fraction of 100–160 μm was used, since a decreased powder particle size provides the growth of the average pore size and a decrease in the porous material permeability.
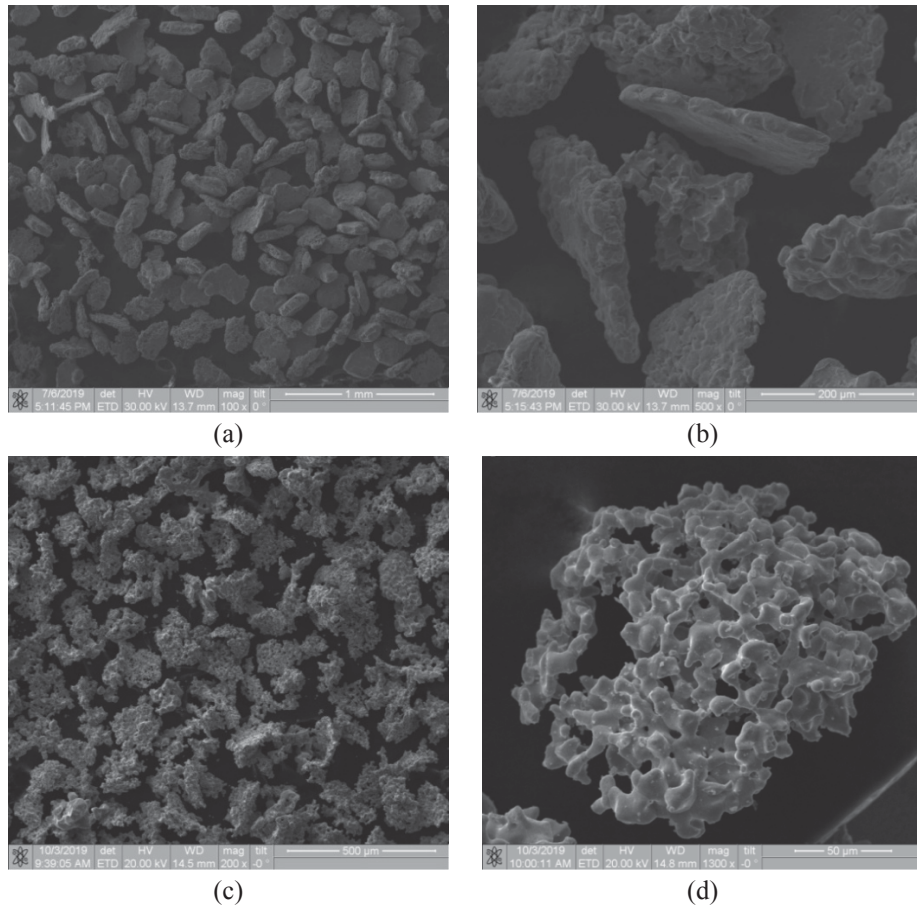
FIGURE 1. Macrostructure of TiNi powder particles of fractions: (a, b) 160–200 μm, (c, d) 100–160 μm.

The analysis of the initial porosity of the PTEM-1 Ti powder of various fractions of 160–200, 100–160 and <100 μm showed values of about 60–70%. Therefore, initially, fractions of 160–200 μm were used for Ti additive to increase porosity due to formation of a frame structure in the volume of the TiNi–Ti mixture, and the Ti fraction with a particle size of <100 μm was used for a more uniform distribution of Ti in the TiNi powder volume.

To study the effect of Ti powder additives on the properties of TiNi powder intermetallic compound, porous TiNi–Ti samples with TiNi powder additives in the range of 2.5–15.0 at % Ti were fabricated. The phase-chemical composition of the material was improved to show different effects of Ti additive on the material. We produced porous TiNi–Ti alloy with 2.5–7.0 at % Ti additive with high-quality interparticle contacts in the entire volume of the material with porosity of about 60–62%. A significant degree of shrinkage is found in the transverse direction in the alloy with 10 at % Ti additive due to the large volume of the melt formed during liquid phase sintering. In alloys with 10 at % Ti additive, a larger amount of melt is formed, which causes small pores coalescence and decrease in the porosity to 27%. Production of the alloy with 15 at % Ti with a regular porous structure is impossible due to an excess melt volume formed in sintering. A high concentration of Ti powder results in formation of an almost monolithic material with porosity of 6%. The analysis of the results obtained showed that the volume of the $Ti_2Ni + TiNi$ melt is different for porous TiNi–Ti alloys obtained under similar temperature and time conditions, which is confirmed by different values of the porosity coefficient compared to the initial value.

Data on the X-ray diffraction analysis of TiNi-based porous alloys show that the alloy contains an austenitic TiNi (B2) phase, martensitic TiNi (B19′), Ti_2Ni and Ti_3Ni_4 secondary phases and traces of the $TiNi_3$ phase. It was impossible to interpret the quantitative parameters of the volumetric content of the phases detected due to inhomogeneous macrostructure of the porous TiNi alloy. However, the quantitative parameters of the volumetric content of large Ti_2Ni and Ti_4Ni_2 phases (O, N, C) could be interpreted using stereographic techniques. This analysis is required due to a significant effect of the Ti-rich phases on the properties of the resulting TiNi material. The volumetric content of the phases was 8.3% for TiNi alloys with 2.5 at % Ti, 12.7% for alloys with 5 at % Ti, 16.3%

for alloys with 7.5 at % Ti, and 25.3% for alloys with 10 at % Ti. When the Ti additive concentration increases, the fraction of the Ti_2Ni phase grows. The sintering temperatures of the porous material are in the range that promotes formation of the secondary Ti_2Ni phase particles, which are formed as a result of the liquid-phase interaction of the TiNi melt and Ti particles according to the equation $TiNi + Ti \rightarrow Ti_2Ni$.

When the concentration of Ti additive increases, the Ti_2Ni phase acquires distinctive morphological features. In alloys with small and moderate concentration of Ti (2.5–7.5), the Ti_2Ni phase has the form of separate precipitates of round, pyramidal and rectangular shapes, or their combination (Fig. 2a). The chemical composition of the particles analyzed was 66.13 at % Ti and 33.87 at % Ni. The observed particles are inherited from the initial TiNi powders with a compact and spongy morphology and are additionally formed under the impact of Ti powder additives. Interstitial impurities based on O, C, and N, which are always present in TiNi powder, actively interact at high temperatures. Based on the Ti_2Ni phase particles, large particles of Ti_4Ni_2 (O, N, C) oxycarbonitrides of various shapes and sizes are formed, which are predominantly located along the boundaries of grains and pores, and less commonly in the grain body (Fig. 2). An increase in the Ti concentration to 10 at. % increases the amount of Ti_2Ni melt, which involves individual large and small Ti-rich particles. The interlayers of the Ti_2Ni phase with a composition of 65.89 at % Ti and 34.11 at % Ni (Fig. 2b, phase 3) are formed around individual grains. In addition, individual particles of the Ti_2Ni phase could be observed (Fig. 2b, phase 2). The interlayers based on the Ti_2Ni phase are formed only at the primary stage of the process, since according to [13] a further increase in the Ti concentration leads to formation of the dendritic structure Ti_2Ni–TiNi.

Various concentrations of Ti additives allow improvement of the TiNi compound composition. The use of 5.0 at % Ti additive resulted in the chemical composition of the TiNi compound with 49.14 ± 0.24 at % Ti, while the double amount of Ti additive made it possible to increase the amount of Ti in the TiNi phase only to 49.73 ± 0.17 at %. This can be due to the fact that in the alloy with 10.0 at % Ti a large amount of Ti is spent on the formation of interlayers based on the Ti_2Ni and Ti_4Ni_2 (O, N, C) phases with a minimum formation enthalpy in the Ti–Ni system under study.

It was found that 2.5 at % Ti additive is insufficient to improve the atomic composition, as the produced material showed the Ti concentration equal to 47.3 ± 0.35 at %. The temperature dependence of electrical resistivity was experimentally determined to study the possibility of martensitic transformations in the obtained porous TiNi–Ti materials. An integral characteristic of the porous alloy with an estimated implementation of martensitic transformations was obtained. It is established that the material with 2.5 at % Ti additive exhibits an extremely wide temperature hysteresis of phase transformations ($T_R = 24°C$, $M_s = -120°C$, M_f is not found), which indicates the inhomogeneous chemical composition of the TiNi compound that is responsible for martensitic transformations. According to the obtained dependence $\rho(T)$, the sequence of phase transformations corresponds to the two-stage transformation $B2 \rightarrow R + B19' \rightarrow B19'$. The analysis of the temperature dependence of specific electrical resistivity showed that 5.0–10.0 at % Ti additives enabled fabrication of the material with almost equal intervals for implementation of martensitic transformations, which indicates almost similar composition of the TiNi compound. A porous TiNi–Ti alloy with martensitic transformation interval of $T_R = 50°C$, $M_s = 30°C$, $M_f = 0°C$, $A_s = 5°C$, $A_f = 70°C$ was produced.
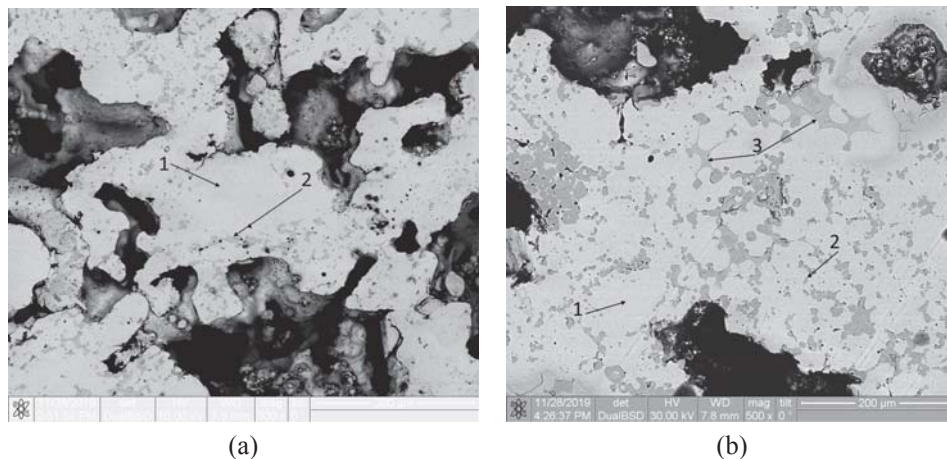
FIGURE 2. Microstructure of porous TiNi-based materials with 2.5–7.5 at % Ti (a) and 10 at % Ti (b) additives:
1—TiNi phase, *2*—individual Ti_2Ni and Ti_4Ni_2 (O, N, C) phases, *3*—interlayers of the Ti_2Ni phase.

Various concentrations of Ti additives make it possible to improve the composition of the TiNi compound for implementation of martensitic transformations. The use of 5 at % Ti additive resulted in the chemical composition of the TiNi compound with 49.14 ± 0.24 at % Ti, while the double amount of Ti allowed increasing the amount of titanium in the TiNi phase only to 49.73 ± 0.17 at %. The noted feature can be explained by the fact that in the alloy with 10 at % Ti, a large amount of titanium is spent on the formation of interlayers based on the Ti_2Ni and $Ti_4Ni_2(O, N, C)$ phases, since they have a minimum formation enthalpy in the Ti–Ni system under study.

CONCLUSIONS

Thus, the study revealed the effect of various concentrations of Ti additives on the macro- and microstructural features of porous TiNi-based alloys. The use of the TiNi fraction with a size of 100–160 μm allows fabrication of high porous material. The increased concentration of Ti additives decreases the porosity coefficient and increases the interval of pore sizes and average pore size. It is shown that Ti additives of more than 10.0 at % cause formation of a completely monolithic structure due to excessive melt formed during sintering. A change in the concentration of Ti additive causes morphological changes in the Ti_2Ni phase. The interlayers of the Ti_2Ni phase were formed along the grain and pore boundaries after the addition of 10.0 at % Ti, except for individual particles based on Ti_2Ni and $Ti_4Ni_2(O, N, C)$. The Ti additives used to produce high porous materials enabled improvement of the atomic composition of the TiNi compound and creation of the conditions for martensitic transformations.

ACKNOWLEDGMENTS

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