

Article

Structure and Mechanical Properties of Porous TiNi Alloys with Ag Nanoparticles

Ekaterina Marchenko , Gulsharat Baigonakova * , Viktor Larikov, Aleksandr Monogenov and Yuri Yasenchuk 

Laboratory of Superelastic Biointerfaces, National Research Tomsk State University, 36 Lenin Ave.,
634045 Tomsk, Russia

* Correspondence: gat27@mail.ru

Abstract: The work studies the influence of the silver dopant (<0.5 at.%) on the structure and mechanical properties of porous TiNi alloys obtained by self-propagating high-temperature synthesis. These alloys are of high scientific and practical interest in medicine. The presence of silver in the TiNi alloy will ensure improved cytocompatibility and antibacterial properties. The TiNi porous alloys with 0.2 and 0.5 at.% Ag nanoparticles have multiphase composition. Quantitative X-ray diffraction analysis of the obtained alloys showed that an increase in the silver content is accompanied by a quantitative decrease in the austenite phase TiNi(B2) and an increase in the martensite phase TiNi(B19'), as well as in secondary phases Ti₂Ni, Ti₄Ni₂O. Evenly distributed silver nanoparticles up to 10 nm were found in the surface layer by transmission electron microscopy. The results of the scanning electron microscopy showed that inclusions containing silver are located mainly in the zones of Ti₂Ni peritectic crystallization. The mechanical characteristics were studied by means of compression tests and it was found that with an increase in the silver dopant, the elastic modulus and elastic limit decrease, but the maximum deformation to fracture increases significantly. It was found that with an increase in the volume fraction of silver, the plastic properties of the alloy increase. No dependency of the tensile strength on the amount of silver was found.

Keywords: mechanical characteristics; nanoparticles; porous alloy; silver; structure; TiNi



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1. Introduction

Currently, TiNi-based alloys are of high scientific and practical interest [1,2]. The unique properties of the TiNi alloys such as shape memory effect, superelasticity, strength, ductility, and corrosion resistance make them highly biocompatible compared to other alloys, which ensures their wide use in medicine. Various doping additives introduced into the TiNi composition give it various structure-phase states and effectively influence its physical and mechanical characteristics [3–5]. In work [3], aluminum was added into the porous TiNi alloy to improve the physical and mechanical properties and make it possible to use as an implantation material. In [4], the authors determined the range of silver content for the production of TiNi-Ag wires. It was found that the optimal balance between strength, ductility, and shape memory parameters was achieved at a silver concentration of 0.1 at.%. In a study of the silver effect on cell viability in cast TiNiAg alloys, results showed that silver in small amounts (0.1–0.2 at.%) is favorable for cell adhesion, and increases the cell viability level by more than 30% [6].

Porous TiNi alloys are well integrated into biological tissues and at the same time they remain permeable to biological fluids. Therefore, porous TiNi alloys are used as an effective osteoplastic material [7,8]. Nowadays, the implant industry pays special attention to materials with antimicrobial activity which prevent infection [9]. Among the metals with antimicrobial properties, silver has attracted the interest of many researchers due to its high biocidal activity. Silver has bactericidal activity at concentrations up to 35 parts per billion [9,10] without any toxic effect on mammalian cells. For the Ag particles in the range

of 20–30 nm, optimal characteristics of antibacterial activity, biocompatibility, and corrosion resistance were achieved [11,12]. In addition, the bacteria showed a low propensity to develop resistance to silver. But the results of studies on the antimicrobial efficacy of silver alloys are often inconclusive and conflicting.

Regarding the studies on TiNiAg alloys, there are mainly works on cast titanium nickelide alloys. TiNi alloys with the Ag concentration from 0.5 to 9 at.% are of particular interest in medicine. The presence of silver in the alloy ensures the improved cytocompatibility and antibacterial properties of TiNi [13–17] as well as increases the yield strength and tensile strength [18,19]. The shape memory effect of TiNi alloys was studied at the Ag concentration of 1.4 at.% [14]. Martensitic transformations, as well as microhardness, were mainly considered in the range of 0.6–1.9 at.% Ag [20–23]. The effect low silver content (<0.5 at.%) has on the structure, mechanical characteristics, and deformability of porous TiNiAg alloys has not been fully studied. No study was found on Ag addition during the production of porous TiNi alloys by self-propagating high-temperature synthesis. There are few studies on adding Ag during the sintering of porous TiNi alloys, as well as on modifying the surface of porous TiNi alloys using Ag. Ag addition reduces the Young's modulus of the porous TiNi alloy, which results in a greater similarity to the Young's modulus of the human bone, as well as an increase in the maximum deformation of the alloy [24].

The aim of this work is to study the effect silver dopant has on the structure and physical and mechanical properties of porous TiNi alloys obtained by self-propagating high-temperature synthesis (SHS).

The authors believe that the silver addition in the nanopowder form will provide antibacterial properties while maintaining the high functional characteristics of the porous-permeable NiTi. This will create a new material with a suitable microenvironment for osteogenesis and an antibacterial, anti-inflammatory effect in order to counteract the development of infection at the interface of the implant-biological tissue.

2. Materials and Methods

Two powder mixtures were prepared for the study, each containing the main part of nickel PNK OT-4, titanium PTOM-2, titanium nickelide PN45T55OM, and silver nanopowder dopant with an average particle size of 8 nm and the concentration of 0.2 at.% Ag and 0.5 at.% Ag. To distribute the dopant more evenly, silver nanopowder was mixed with nickel powder in equal amounts, then the main part of the nickel and titanium powders was added to the resulting mixture in small portions and mixed. The TiNiAg alloy samples were obtained by the SHS method in a flow reactor in the flowing argon atmosphere to prevent the mixture oxidation during heating and the oxidation of the synthesized alloy during cooling. The synthesis was initiated by an electric arc, after preheating the reactor to a stable temperature of 520 °C. After the synthesis reaction was passed, the reactor with the obtained porous alloys was cooled by immersion in water at room temperature.

The phase composition and structure of the alloys were studied with a Shimadzu XRD-6000 diffractometer in $\text{CuK}\alpha$ radiation. X-ray diffraction patterns were indexed with the PowderCell 2.4 full-profile analysis program and compared with the PDF 4+ database. The volume fractions of the phases were estimated by full-profile analysis based on calculations in relation to the intensities ratio of diffraction reflections using the POWDER CELL 2.4 program and the PDF-4+ database. The lattice parameters and micro-stresses were calculated with precision using the POWDER CELL 2.4 software. SEM images of porous TiNiAg samples were obtained with a scanning electron microscope (TESCAN ORSAY HOLDING, Brno, Czech Republic) with a Tescan MIRA 3 LMU Schottky cathode equipped with an Oxford Instruments Ultim Max 40 energy dispersive X-ray spectrometer (Oxford Instruments, High Wycombe, UK).

The structure of the samples in cross-section geometry was studied using transmission electron microscopy at an accelerating voltage of 200 kV using the JEOL JEM-2100 (JEOL Ltd., Tokyo, Japan) electron microscope at the Center for Collective Use Nanotech, Institute

of Physics and Mathematics, Siberian Branch of the Russian Academy of Sciences. The study of mechanical properties was performed on an Instron 5969 (Instron, a division of Illinois Tool Works Inc., Norwood, IL, USA) setup using a compression loading scheme. Samples for compression with geometric dimensions $6 \text{ mm} \times 3 \text{ mm} \times 3 \text{ mm}$ were cut from the workpiece with an electric spark machine. Uniaxial compression loading was carried out at a room temperature of 24°C . When studying the mechanical properties of each composition, at least 5 samples were tested.

3. Results and Discussion

3.1. Results

3.1.1. XRD of Cross Sections TiNiAg Specimens

Figure 1 shows X-ray diffraction patterns of TiNi samples containing Ag. The phase composition of the studied alloys consists of $\text{Ti}_4\text{Ni}_2\text{O}$, Ti_2Ni , $\text{TiNi}(\text{B19}')$, and $\text{TiNi}(\text{B2})$ phases. Due to the small amount of silver, no Ag-based phases were found.

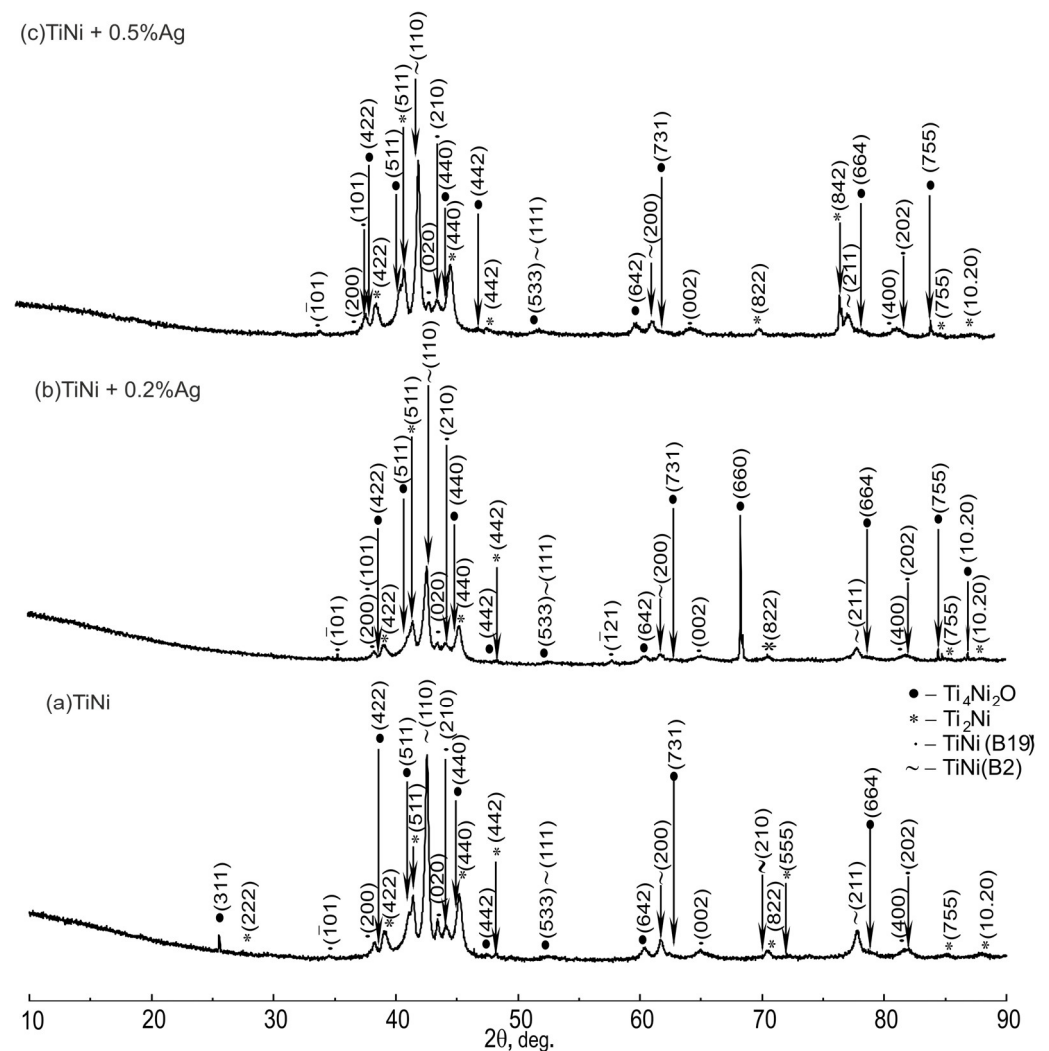
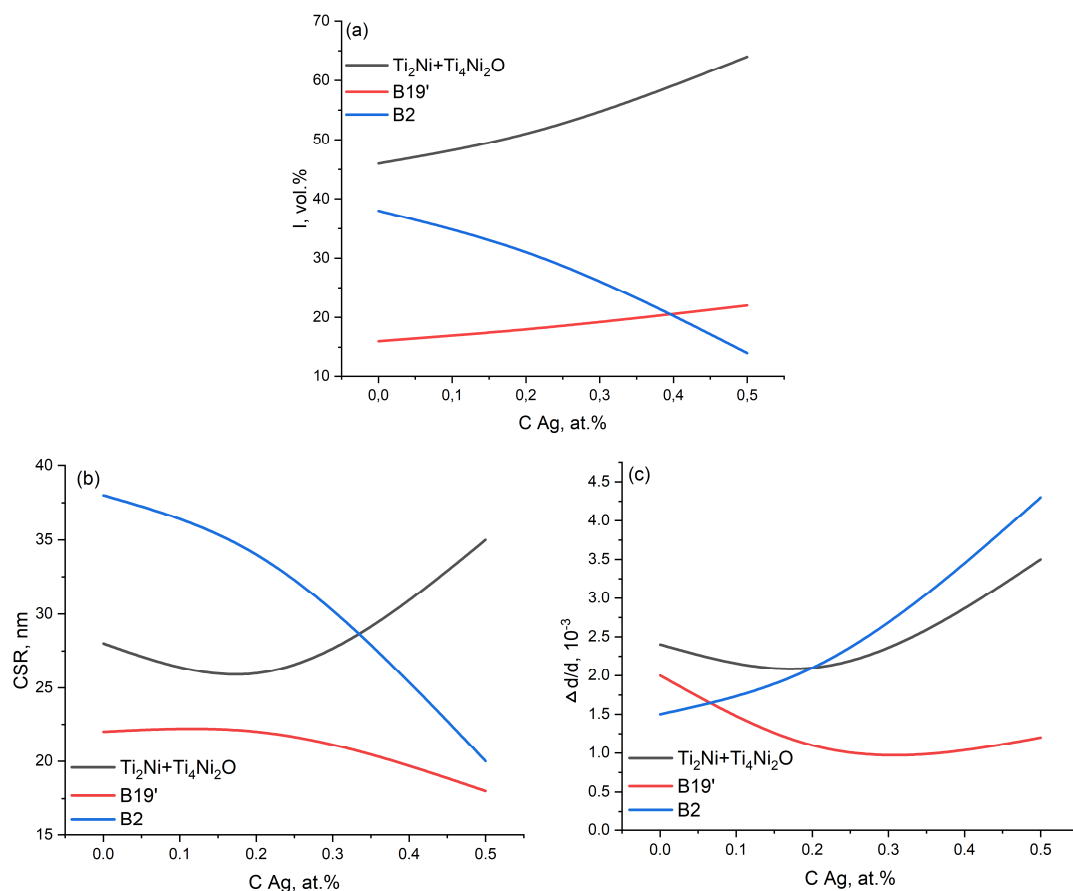


Figure 1. X-ray diffractograms of SHS-TiNi porous alloys specimens: (a) TiNi; (b) TiNi + 0.2% Ag; (c) TiNi + 0.5% Ag.

Quantitative X-ray diffraction analysis of TiNiAg alloys shows an increase in the volume fraction of the TiNi martensitic phase with the B19' structure, Ti_2Ni , $\text{Ti}_4\text{Ni}_2\text{O}$ secondary phases, and a decrease in the fraction of the TiNi austenite phase with the B2 structure with increasing silver content (Table 1 and Figure 2a).

Table 1. X-ray analysis of TiNiAg alloys.

Sample	Detected Phases	Volume Fraction, vol. %	Lattice Parameters $\text{\AA}$, and Unit Cell Volume, $\text{\AA}^3$	CSR Dimensions, nm	Microdistortions, $\Delta d/d, 10^{-3}$
TiNi	Ti ₂ Ni + Ti ₄ Ni ₂ O	46	a = 11.3414 V = 1458.8143	28	2.4
	B19'	16	-	22	2.0
	B2	38	a = 2.9969 V = 26.9164	38	1.5
TiNi + 0.2% Ag	Ti ₂ Ni + Ti ₄ Ni ₂ O	51	a = 11.1026 V = 1368.5923	26	2.1
	B19'	18	-	22	1.1
	B2	31	a = 3.0058 V = 27.1569	34	2.1
TiNi + 0.5% Ag	Ti ₂ Ni + Ti ₄ Ni ₂ O	64	a = 11.3065 V = 1445.3884	35	3.5
	B19'	22	-	18	1.2
	B2	14	a = 3.0039 V = 27.1054	20	4.3

**Figure 2.** Concentration dependence according to the results of X-ray diffraction analysis of TiNiAg: (a) volume fraction of the phases; (b) CSR values; (c) microdistortions.

Quantitative X-ray diffraction analysis showed microdistortions of all the phases in the TiNiAg alloy system. It can be assumed, and it follows from Table 1, that silver is

probably incorporated into the crystal lattice of both the B2 and Ti_2Ni phases, since the greatest microdistortion of these lattices is observed, especially in the B2 phase (Figure 2c).

3.1.2. SEM Study of Polished TiNiAg Samples

With an increase in the silver content, the porosity of the samples did not change and accounted for $62\% \pm 2\%$ (Figure 3).

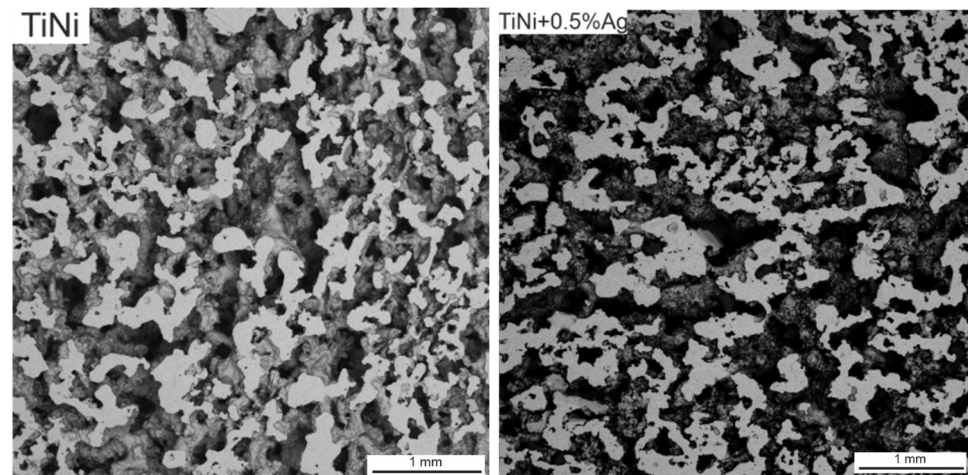


Figure 3. The cross-sectional SEM image of SHS–TiNi porous alloys specimens.

Apart from titanium and nickel powders, the mixture includes TiNi powder PN55T 45OM. It is not possible to distinguish the TiNi powder which does not participate in the synthesis reaction from the TiNi phase after SHS by X-ray diffraction. At the same time, the SEM study of the phase and elemental composition of porous alloys made it possible to do this. Phase 1 enriched with nickel forms a residual skeleton of the inert powder particles which partially dissolve in the reaction melt (Figure 4, Table 2).

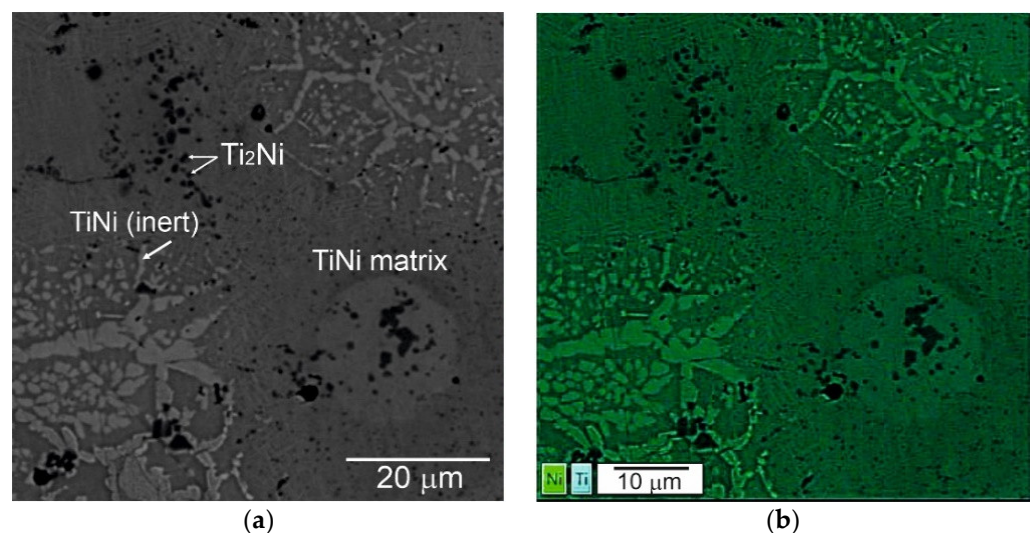


Figure 4. SEM image (a) and EDS elemental mapping (b) of initial porous TiNi alloy.

Table 2. Elemental composition of phases in TiNi SHS alloys.

Identification	Ti, at. %	Ni, at. %	O, at. %
TiNi (inert)	40.57	59.43	0
TiNi matrix	49.36	50.64	0
Ti_2Ni	56.2	36.87	6.93

The presence of silver in the form of light inclusions up to $0.1\ \mu\text{m}$ was detected on the SEM–EDS maps of element distribution in porous SHS alloys $\text{TiNi} + 0.2\% \text{Ag}$, $\text{TiNi} + 0.5\% \text{Ag}$ (Figures 5 and 6, Tables 3 and 4). The localization of silver particles is predominantly on the particles of the Ti_2Ni or $\text{Ti}_4\text{Ni}_2\text{O}$ phases.

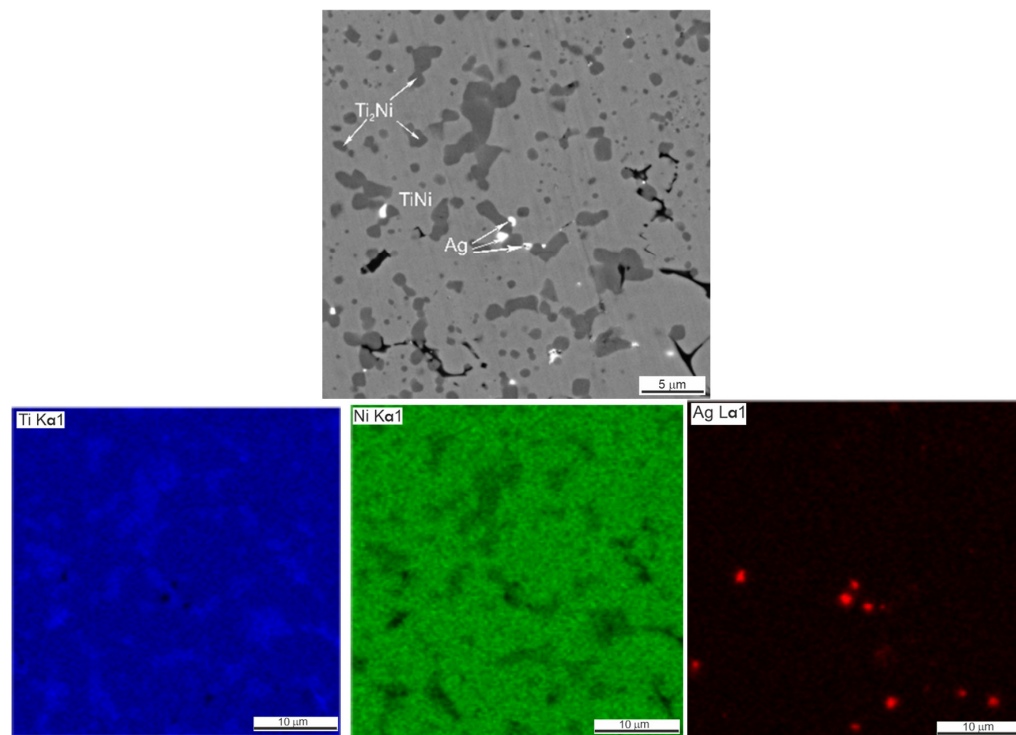


Figure 5. SEM image and EDS elemental mapping of porous SHS $\text{TiNi} + 0.2\% \text{Ag}$.

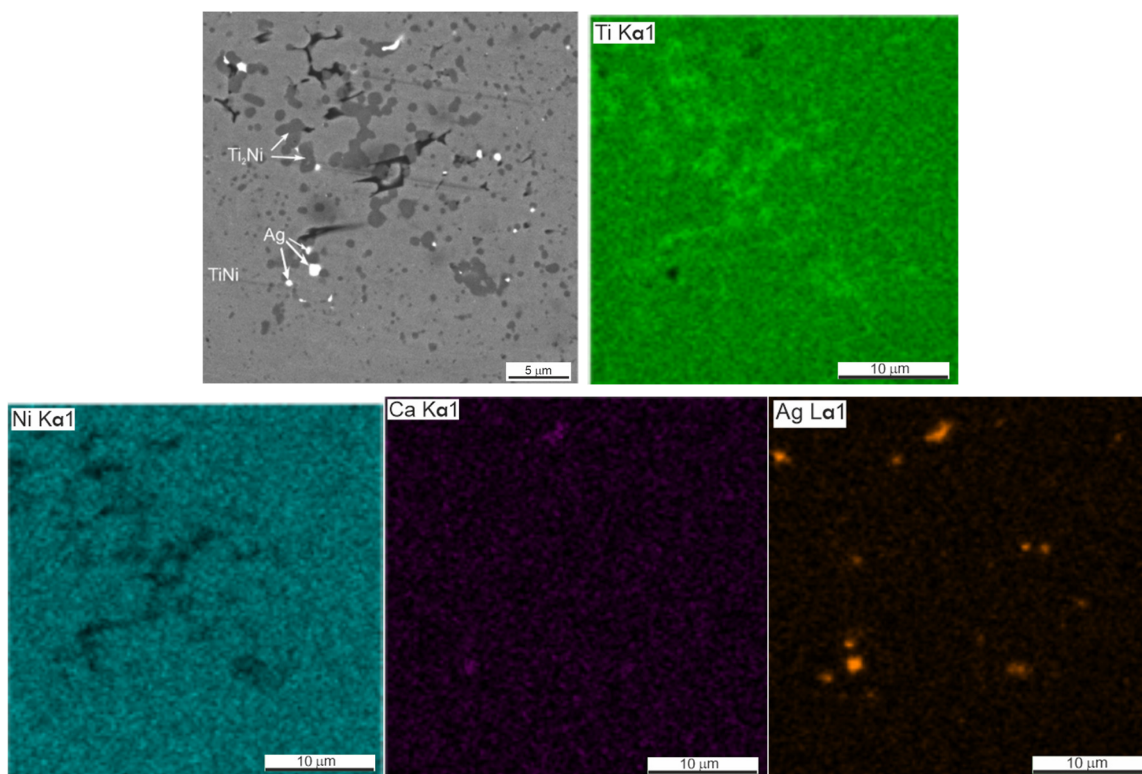


Figure 6. SEM image and EDS elemental mapping of porous SHS alloy $\text{TiNi} + 0.5\% \text{Ag}$.

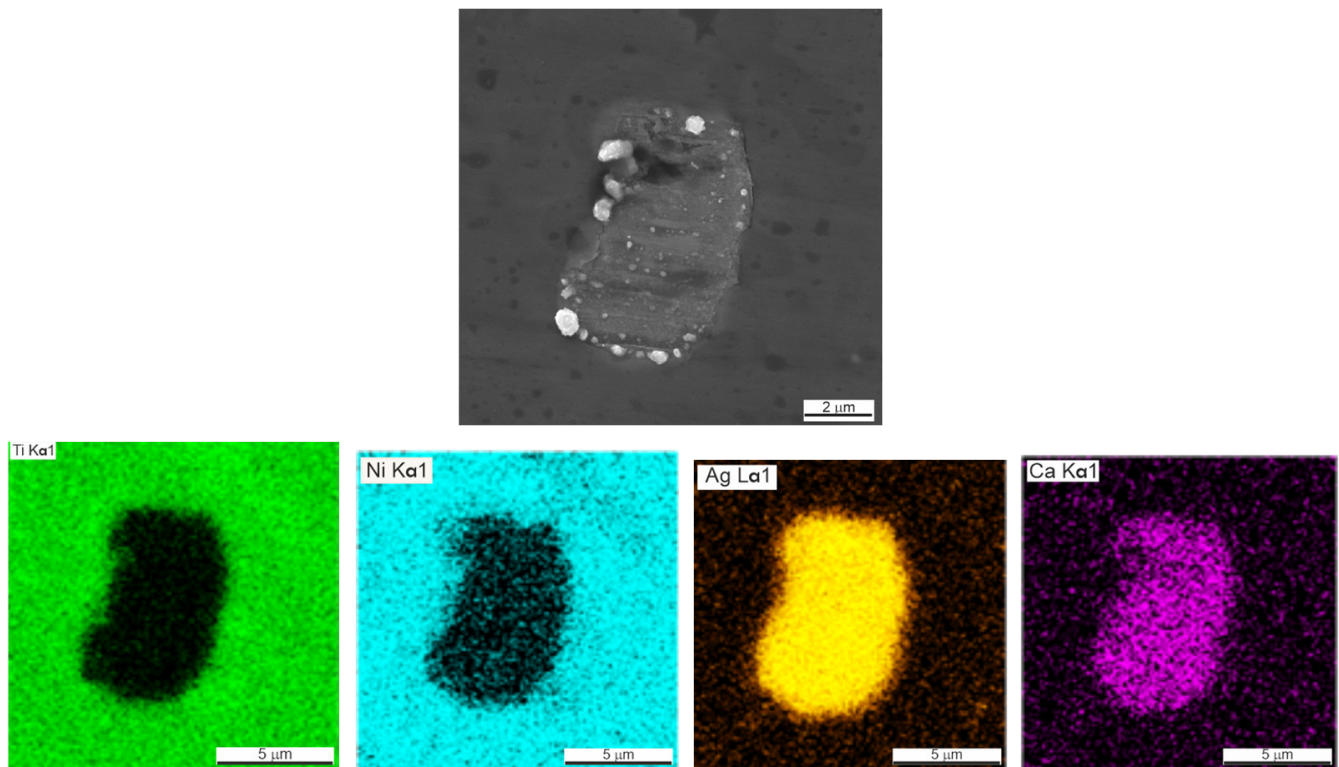
Table 3. Elemental composition of phases in SHS alloys TiNi + 0.2% Ag.

Identification	Ti, at. %	Ni, at. %	O, at. %	Ag, at. %	Ca, at. %
TiNi matrix	51.18	48.82	-	-	-
Ti ₂ Ni	59.55	29.84	10.09	0.52	-
Ag	0.41	0.29	4.23	89.06	6.01

Table 4. Elemental composition of phases in SHS alloys TiNi + 0.5% Ag.

Identification	Ti, at. %	Ni, at. %	O, at. %	Ag, at. %	Ca, at. %
TiNi matrix	28.75	71.19	-	0.05	-
Ti ₂ Ni	51.2	48.73	-	0.1	-
Ag	0.41	0.29	4.23	89.06	6.01
Ag _x Ca _y	-	-	-	x	y
Ag (Ag ₉ Ca ₂ , Ag ₇ Ca ₂)	-	-	-	96.03	3.97

Silver was found not only in the form of subnanocrystalline particles but also in the composition of larger, up to 7 μm , intermetallic inclusions of the Ca–Ag system (Figures 7 and 8). Calcium is a residual technological impurity, which is used in the production of titanium powder by calcium hydride reduction. Elemental EDS mapping showed the presence of Ca and Ag in the form of inclusions of 5–10 μm . Most of the inclusions are in the form of the chemical compound Ag_xCa_y containing Ag less than 1 μm .

**Figure 7.** SEM image of the microstructure and EDS mapping of the element composition of the pure silver phase in the porous TiNi + 0.5% Ag alloy.

Ag and Ca form a number of chemical compounds [25] which contain some of the detected Ag in a dissolved state. Some amount of the unreacted Ag was found in a free state or in the compound with the predominant content of silver, Ag₉Ca₂, Ag₇Ca₂.

The results of the EDS mapping of TiNiAg (0.2–0.5) samples showed that inclusions containing silver are located mainly in the zones of Ti_2Ni peritectic crystallization. The temperature of Ti_2Ni peritectic crystallization is about 950 °C, while the crystallization of all Ag–Ca system compounds occurs in the range of 750–910 °C. With an increase in the Ag concentration in the alloy from 0.2% to 0.5%, the size of agglomerates from inclusions containing Ag increases from 0.2 to 6 μm (Table 5 and Figure 8).

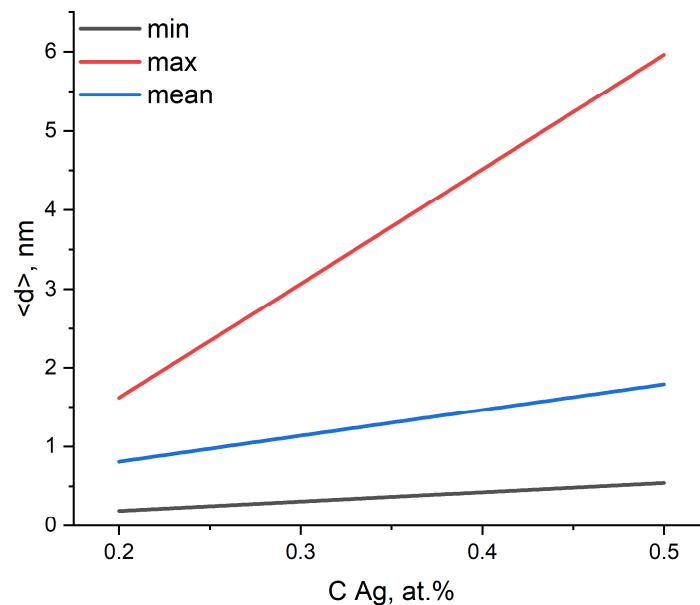


Figure 8. The dependence of the particle size containing silver on the Ag dopant concentration.

Table 5. The size of agglomerates of inclusions with silver.

Sample	Min, μm	Max, μm	Average, μm
TiNi + 0.2% Ag	0.19	1.619	0.81
TiNi + 0.5% Ag	0.542	5.962	1.79

3.1.3. TEM Image and EDS Elemental Mapping of Cross-Section of TiNiAg Alloy

According to the results of transmission electron microscopy of TiNiAg(0.2–0.5) samples in the cross-section geometry, silver was found in the form of nanoparticles up to 10 nm in the surface layer of $\text{Ti}_4\text{Ni}_2\text{O}$ (Figure 9). Moreover, they were found not in agglomerates, but in the form of isolated particles evenly distributed over the entire surface layer. Importantly, silver was found in the matrix in large inclusions up to 2 μm . Other authors have found Ag in the form of dispersed particles on the surface of ternary TiNiAg alloys [13,14], and also [4,26] showed the solubility limit of silver in a TiNi solid solution up to 0.26 wt.%.

The mechanical properties of porous alloys were studied under a compression loading scheme. The stress–strain dependence of the TiNiAg system alloys is characterized by the absence of a martensitic plateau, and the porous alloy deforms elastoplastically. With an increase in the silver content, the strength properties do not change and the ultimate strength is 70 ± 4 MPa (Figure 10 and Table 6). The elastic limit decreases from 26 to 11.5 MPa, the elastic modulus decreases from 1700 to 950 MPa. The maximum strain to fracture in compression of porous TiNiAg alloys increased from 7% to 27% with increasing silver concentration. SEM images of fracture surfaces taken after compression testing showed that the alloy with the silver content 0.2 at.% and 0.5 at.% is partially in a martensitic state, which can be proved by the presence of the areas of quasi-cleavage and plastic shear traces.

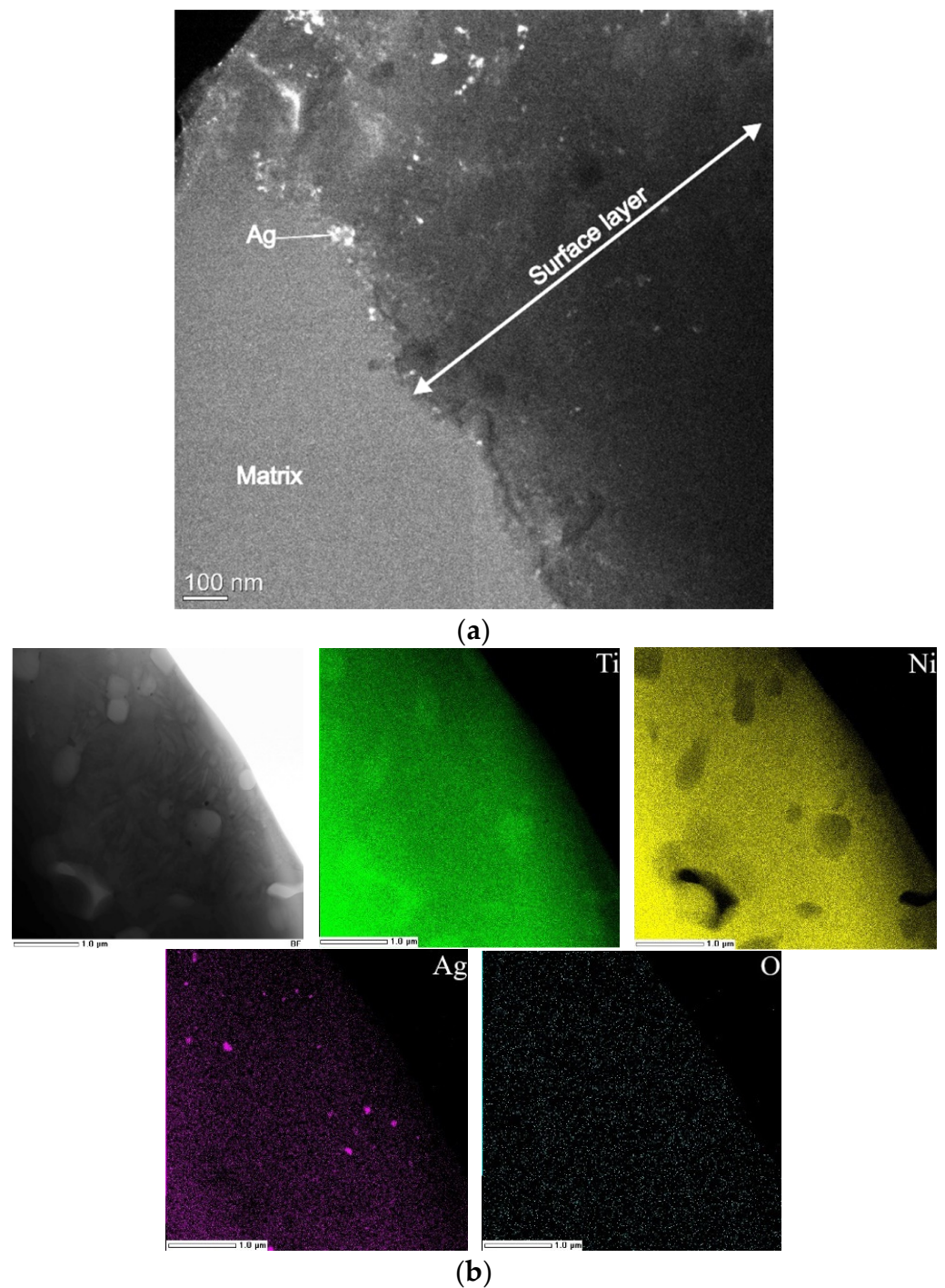


Figure 9. TEM image of TiNiAg sample in the cross-section geometry (a); TEM-EDS elemental mapping of TiNiAg matrix (b).

3.2. Discussion

Silver dissolves in the TiNi(B2) phase of the porous alloy to a limited extent, up to 0.1 at.%, although other authors found that the solubility of silver in the cast alloy does not exceed 0.26 at.% [13,14]. Silver crystallizes in its pure form. Silver particles were found in the matrix in the zones of peritectic crystallization of the Ti_2Ni phase in the form of large particles. In the surface Ti_4Ni_2O layer, silver particles crystallized in the nanocrystalline state evenly over the entire surface layer.

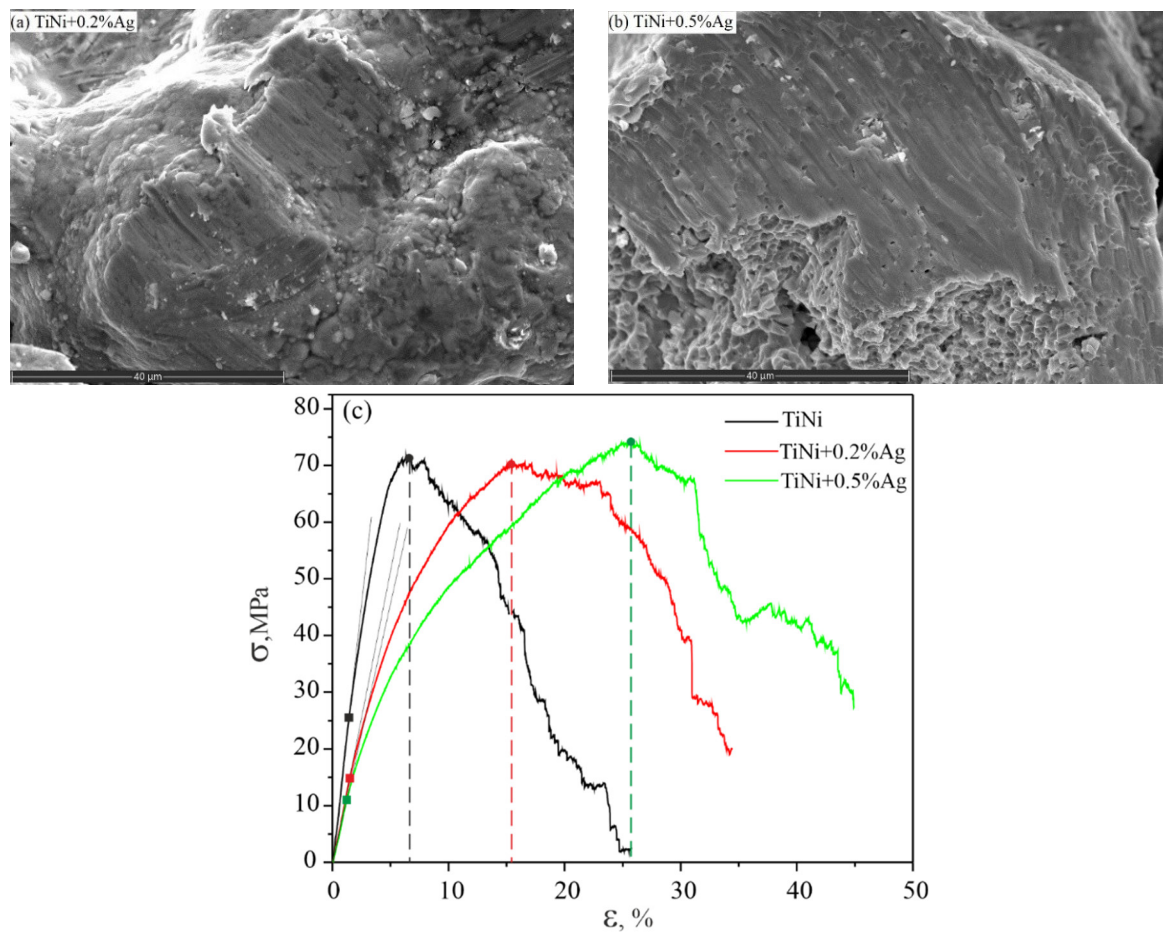


Figure 10. The fracture surface of the alloy sample for TiNi + 0.2% Ag (a); TiNi + 0.5% Ag (b); σ - ϵ dependence for the alloys of the TiNiAg system (c).

Table 6. Mechanical properties of porous TiNiAg alloys.

Alloys	E, MPa	σ_y , MPa	σ_b , MPa	ϵ_b , %	P, %
TiNi	1733	26	71.5	6.8	62
TiNi + 0.2% Ag	1000	15	70	16	63
TiNi + 0.5% Ag	958.3	11.5	74	27	62

Where E—modulus of elasticity; σ_y —elastic limit; σ_b —compressive strength; ϵ_b —maximum deformation during compression up to fracture; P—porosity.

Out of the three alloying elements, Ag is known to have a significantly different electronic structure compared to Ni and Ti. Moreover, Ag atoms significantly differ in size in comparison with Ni atoms. Thus, different electron shell structures of the Ag, Ni, and Ti atoms cause the difference in the structure of the binary state diagrams of the Ag-Ni, Ag-Ti, and Ni-Ti systems. The behavior of the electronic subsystem correlates with the phase diagrams of the binary Ti-Ag alloy state, in which Ti and Ag in the Ti-Ag system can form solid solutions based on the initial components (Ag), (α Ti), (β Ti) and two intermetallic compounds AgTi and AgTi₂ at 1020 ± 5 and 940 °C. In the Ni-Ag system with a simple monotectic system, Ni and Ag are practically insoluble in each other on the state diagram. The maximum solubility of Ni in Ag is 0.102 at.%, and the maximum solubility of Ag in Ni is about 1 at.% and decreases with decreasing temperature [4,6,27–29].

In the Ag-Ti system, there are solid solutions based on alloy-forming elements (Ag), (α Ti), and (β Ti) with wide areas of homogeneity (Figure 1) [27,28]. Moreover, the solubility of Ag in (β Ti) reaches 15 at.% at 1020 °C. The solubility of Ti in (Ag) is much lower and corresponds to 5 at.%. In the area of stoichiometric compositions Ag₂Ti and AgTi,

peritectic reactions form compounds with tetragonal syngonies with space symmetry groups $I4/mmm$ and $P4/ptt$, respectively. In the Ag-Ti system, the eutectoid transformation $(\beta\text{Ti}) \leftrightarrow (\alpha\text{Ti}) + \text{AgTi}_2$ takes place on the Ti side. On the Ag side, a eutectic transformation is observed.

The phase diagram of Ag-Ni is characterized by the presence of monotectic and eutectic equilibria [29] (Figure 1). The eutectic point is located at a composition of 99.679 at.% Ag at 960 °C. Ni in Ag dissolves very slightly (on the order of 0.1 at.%). The maximum solubility of Ag in Ni is not high and amounts to ~1 at.%, and it decreases with decreasing temperature.

The state diagram of the Ti-Ni binary system is characterized by the formation of three intermetallic compounds Ti_2Ni , TiNi , and TiNi_3 . Three compounds are formed in the system: Ti_2Ni , TiNi , and TiNi_3 . The Ti_2Ni compound is formed by a peritectic reaction. The TiNi and TiNi_3 compounds crystallize from the melt with an open maximum. The TiNi compound has a homogeneity area which has a width range from 49.5 to 57 at.% Ni at 1118 °C and with decreasing temperature the area width narrows. There are three eutectic, one peritectic, and one eutectoid transformations in the Ni-Ti system. The solubility of Ni in Ti depends on the crystal structure and reaches 8 at.% in (βTi) . Whereas in (αTi) the solubility of Ni is not high and is equal to 0.2 at.%. The (Ni) based solid solution region is quite wide and reaches a maximum value of 13.9 at.% at a temperature of 1304 °C and narrows with decreasing temperature.

According to the results of mechanical testing of porous TiNiAg alloys, a similar effect on mechanical characteristics was found in the study of the effect silver has on TiNiAg wires [4]. The study revealed an improvement in the mechanical characteristics of alloys in TiNiAg wires with an increase in the silver content [21]. In the studied case, an increase in plasticity can be associated with the change in the ratio of titanium and nickel in the B2 phase. The change in the matrix composition results in martensite formation, which causes plastic strain when the alloy is deformed at room temperature. The increase in plasticity is apparently caused by the appearance of a secondary Ag phase in the alloy matrix, which is softer and more plastic.

Studies of the structure and mechanical properties of porous NiTi alloys doped with silver have shown positive prerequisites for further research. Moreover, in the future, studies of physical properties, superelasticity effect, biocompatibility, and antibacterial effect of porous TiNiAg alloys will be carried out, which are important characteristics for the use of the alloy for medical purposes.

4. Conclusions

Quantitative X-ray diffraction analysis of the obtained alloys showed that an increase in the silver content is accompanied by a quantitative decrease in the austenite phase TiNi(B2) and an increase in the martensite phase TiNi(B19') , as well as in secondary phases Ti_2Ni , $\text{Ti}_4\text{Ni}_2\text{O}$. Microdistortions of all the phases in the TiNiAg alloy system indicate that silver is incorporated into the crystal lattice of both the B2 and Ti_2Ni phases. EDS analysis showed that silver dissolves in the TiNi(B2) phase of the porous alloy to a limited extent, up to 0.1 at.%.

The results of the EDS mapping of TiNiAg samples with 0.2 and 0.5 at.% Ag showed that inclusions containing silver are located mainly in the zones of Ti_2Ni peritectic crystallization. With an increase in the Ag concentration in the alloy from 0.2% to 0.5%, the size of agglomerates from inclusions containing Ag increases from 0.2 to 6 μm . In the surface layer of the $\text{Ti}_4\text{Ni}_2\text{O}$ phase, evenly distributed silver nanoparticles up to 10 nm were found.

It was found that with an increase in the volume fraction of silver, the plastic properties of the alloy increase, while the compressive strength does not change and accounts for 70 ± 4 MPa. Obviously, the increase in the plasticity of the porous TiNi alloy from 7% to 27% is caused by the formation of soft and plastic inclusions with silver in the matrix of the TiNi alloy.

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