Effect of plasma ion immersion treatment on the structure and phase state of the TiNi alloy for medical implantants

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Abstract. In this paper we present the results of studying the structure and phase composition of the medical alloy Ti-50.9 at. % Ni processed by method of plasma ion-immersion implantation (PIIID) by Si ions. TEM\EDS\XPS analyses were used. After ion-plasma treatment, a separate amorphous layer is formed on the TiNi sample surface, containing Si. It is found that diffusion transformations in TiNi during PIID occur. The aging in the bulk of samples takes place with the separation of coherent Ti₃Ni₄ precipitation. After cooling in the alloy a B₂→R martensitic transformation is realized.

1. Introduction
Peculiar mechanical properties of TiNi – alloys like the shape memory effect and the superelasticity which arise from various martensitic transformations ensure the use of these alloys in medicines [1]. Near stoichiometric TiNi alloys are used in modern medical devices, for example intravascular self-expanding stents [2, 3]. The creation modified layers can improve performance characteristics and prevent the Ni release. The method of plasma-immersion ion implantation with deposition (PIIID) allows creating thin layers with excellent adhesion on the difficult-branched shape product like the stent [4]. In PIIID technological modes used for TiNi, a treatment time varies from 20 minutes to 3 hours, with samples being heated from 473 K to 1023 K. Often, preliminary surface cleaning in argon plasma, up to 1.5 hours, is used [5]. The elevated temperature of samples facilitates penetration of the doping element into the interior of the sample due to thermally activated diffusion [6]. At the same time, stimulation of diffusion processes creates conditions for the decomposition of the solid solution in TiNi alloys, which can lead to a change in a phase transformation behaviour and, consequently, the functional properties of the products [1]. However, in the articles on the plasma-immersion ion implantation of TiNi these questions are not discussed. The nature and mechanisms of these processes in the ion-modified TiNi layers remain unclear, due to a lack of structural studies in this direction. The purpose of this work is to investigate the effect of surface plasma-immersion ion processing on structural-phase transformations in a TiNi substrate.

2. Experimental setup
PIIID was performed on a setup «SPRUT» developed at Tomsk State University [7]. Magnetrons with a pure silicon cathode and a plasma generator with a distributed thermionic cathode to generate high-purity (99.998) argon gas discharge plasma were used. The inhomogeneity of the distribution of the generated gas discharge plasma within the working volume of the vacuum chamber, measured with
the help of the Langmuir probe, was ±4% of the mean value. The technological mode parameters of PIID: pulsed negative bias voltage on samples $U_s=1000$ V with $f=30$ kHz; total power of magnetrons $P=0.8$ kW, plasma generator was turned on at the same time (magnetron sputtering of a Si target in argon plasma). A working pressure was about $7.1\times10^{-2}$ Pa.

Ab-initio samples cut from the rolling plates had a size of $10\times10\times1$ mm and an electrochemical polished surface. The samples were placed on a special holder on a work-table of the vacuum-plasma complex. The work-table and the holder were rotated independently at speeds of 2 turn per minute during PIIID. The preliminary surface cleaning by argon gas plasma was used in the standard mode (stepwise increase in $U_s$ from 50 to 1000 V, $f=30$ kHz) for 90 minutes.

The following surface treatments were used: (i) preliminary surface cleaning with Ar ions in standard mode for 90 minutes; (ii) surface cleaning with Ar ions in standard mode and subsequent treatment with Si ions for 40 min in one vacuum cycle. The temperature was measured with a thermocouple on the surface of the sample holder. In the process of ion-plasma treatment, samples were heated to 573 K when treated with Ar ions and up to 703 K when Si was processed, respectively.

The microstructure was examined by the transmission electron microscopy method (TEM) using the "JEM 2100" (JEOL) microscope with energy dispersive spectrometer (EDS) "Inca Energy" (Oxford Inst.). Thin foils in a cross sections were prepared by the ion slicer "EM 09100IS" (JEOL) with accelerating voltage 4-6 eV and angle of incidence of ions 1-3°. To study the chemical composition of the surface, X-ray photoelectron spectroscopy (XPS) was used by the "Nanoscan 50". It was used Al Kα radiation; the width of the emission line is ~0.8 eV; the diameter of the spot on the surface is ~5×5 mm; the energy resolution of the spectrometer when the spectrum is 1.5 eV; step 0.5 eV; preliminary surface cleaning Ar, 600eV.

3. Results

3.1. Preliminary surface cleaning by argon gas plasma

The initial samples at room temperature (figure 1a) were in an austenite (B2-phase) state with a high dislocation density and rare stress-induced martensitic plates B19′. Temperatures of martensitic transformations: $M_s=290$ K, $M_f=270$ K, $A_s=303$ K, $A_f=330$ K. Average grain size was 15 µm. An amorphous film of titanium oxide with a thickness of 5-7 nm was present on the surface samples.

It was established that in the process of cleaning the surface of a sample with Ar ions, diffusion transformations take place in the TiNi sample. Low-temperature aging of the TiNi alloy is observed, with the Ti$_3$Ni$_4$ particles deposited from the supersaturated Ni solid solution, preferably by a homogeneous nucleation and growth mechanism [1]. The mean size of the particles is 50 nm, standard deviation is 19.5 nm. The dark-field image in the Ti$_3$Ni$_4$ reflex is shown in figure 1c. Figure 1b demonstrates the SAED pattern taken from this region. One can see the reciprocal lattices sections of B2 austenite, R-martensite, and Ti$_3$Ni$_4$ particles connected by orientation relationships. Simultaneously two crystallographic variants of the particles with a plane of habit of type {111} are observed. Changes in the distribution and particle sizes in depth from the surface were not detected.

It is known that precipitation of fine lenticular Ti$_3$Ni$_4$ particles leads to a change in temperatures and sequence of martensitic transformations when transition occurs a two or three stages through the rhombohedral R phase $B2\rightarrow R\rightarrow B19′$ [1, 8, 9]. When samples are cooled after PIIID, fine-dispersed R-martensite is formed and at room temperature the samples are in the B2+R state. The heterogeneous character of nucleation of R-martensite crystals in local stress fields near the precipitates [1] predominates.

3.2. PIIID of Si: surface and near surface layers structure

A separate modified layer with a thickness of 5÷10 nm is formed on the samples surface after PIIID with Si ions (inset in figure 2a). It is seen, there are two sublayers in it: an outer amorphous oxide film (2÷3 nm) and a lower ion-modified defect sublayer having a darker contrast on the bright-field image. Figure 2c shows survey spectra from surface of samples doped Si that acquired in the range from 0 to
1200 eV. A calculation of an elemental composition was based on the measured areas under peaks of the core levels, taking into account the theoretical values of the Scofield photoionization cross sections for the selected line (Ti, Ni, O, C and Si) and the spectrometer transmission function. Thus, the modified layer is an oxide layer containing 20.4 at. % titanium and up to 7.3 at. % silicon. EDS analysis (a beam diameter on a foil surface was about 10 nm) showed a rapid decrease in the concentration of silicon and oxygen with increasing distance inward from the surface of the sample: 6.6 at. % Si on the surface, 1.7 at. % Si at a depth of 10 nm (figure 2d). The content of 0.5 at. % Si and oxygen in a bulk of the sample (labeled in figure 2d as "in matrix") corresponds to contamination of the foil surface and can be taken as zero level. The EDS/XPS data show a significant depletion of Ni in the outer oxide layer, where the content of Ni atoms does not exceed 3 at. %. The depletion of nickel in the surface modification of TiNi alloys is associated with weaker Ni-O interatomic bonding as compared to Ti-O, Si-O and a higher nickel oxide formation energy [2, 3]. As a result nickel atoms diffuse from a surface to regions with a lower O content. In our samples, the Ni content with depth increases gradually, there is no maximum indicating the accumulation of Ni atoms under the oxide layer, as in the case of oxidation or ion implantation. The absence of such nickel-reach area is the advantage of the treatment we use.

It was shown that in the process of PIIID of TiNi aging takes place with the release of excess phases of Ti$_3$Ni$_4$ predominantly by the homogeneous mechanism of decomposition and the formation of the B2+R structural state [8, 9]. The size of Ti$_3$Ni$_4$ particles did not change compared to it after the argon treatment (we used the paired t-test, α=0.05). Two crystallographic variants of Ti$_3$Ni$_4$ are observed simultaneously, as before (figure 2b). The particle density increases, but its distribution remains homogeneous. It was reported that the Ni$_4$Ti$_3$ precipitation rate achieves a maximum at 673-723 K [10], so the heat-treatment at this temperature range increases the volume fraction of Ni$_4$Ti$_3$ phase significantly.

The heterogeneous character of nucleation of R – martensite crystals near particles and structural defects predominates. The morphology of the R phase is changing. In the near-surface layer 80÷100 nm thick there is a fine-dispersed R phase similar to that in samples after Ar ions treatment, as seen from figure 2a. Deep from the surface, a size of plates of R – martensite increases. The change in the intensity of the reflections of the R phase on the SAED pattern taken from the region C in figure 2a
indicates exist of favourable variants of the orientation relationship between the B2 and R phases. The bulk of the sample is dominated by coarser packets of lamellar morphology. Martensitic phase B19' was not detected.

![Image](image_url)

### Figure 2. The microstructure of sample subjected to the PIIID of Si: (a) cross-sectional TEM bright-field image of the surface layer, the insets shows a two-layer structure of the outer surface layer; SAED patterns taken from the area B and C, \( B = [111]_{B2} \); (b) bright-field image of precipitates Ti₃Ni₄, the grain in figure 2a with another diffraction condition; (c) XPS survey spectra from surface and the surface composition in at.%; (d) the dependence of the content of Si and O on the distance \( h \) to the surface, EDS.

### 4. Conclusion
It has been shown that after treatment of the alloy surface with Si ions using the PIIID method, a thin amorphous oxide layer containing Si is formed. Significant depletion of the surface modified TiNi layer by Ni atoms is an important factor when using TiNi in medicine as implants. It has been found that low-temperature aging occurs already during surface purification with Ar ions, as a result of which Ti₃Ni₄ particles are released. Precipitation leads to a change in the temperatures and sequence of martensitic transformations. As a result, the multistage character of the martensitic transformations...
B2→R→B19' is realized in the alloy. The obtained data on thermally activated processes in TiNi alloys with surface modification should be taken into account when choosing the ion-plasma treatment regime, since the mechanical and functional properties can be changed simultaneously. The results obtained in this paper can be extended to other technological regimes in which samples of TiNi alloys are heated to temperatures of low-temperature aging.

Acknowledgments
The investigation were supported by the Russian Academy of Sciences in the framework of the Program of Basic Research for 2013-2020, project No. 23.2.2. The TEM examinations were carried out using the equipment of the Shared Use Centre “Nanotech” of the ISPMS SB RAS in Tomsk; the XPS analysis was performed at the “Nanostructures” Shared Use Centre in ISP SB RAS in Novosibirsk.

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