

Structural phase states in nickel-titanium surface layers doped with silicon by plasma immersion ion implantation

Oleg A. Kashin, Aleksandr I. Lotkov, Andrey N. Kudryashov, Konstantin V. Krukovsky, Marina G. Ostapenko, Alexey A. Neiman, and Dmitry P. Borisov

Citation: [AIP Conference Proceedings](#) **1683**, 020078 (2015); doi: 10.1063/1.4932768

View online: <http://dx.doi.org/10.1063/1.4932768>

View Table of Contents: <http://scitation.aip.org/content/aip/proceeding/aipcp/1683?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Quenching of surface-exciton emission from ZnO nanocombs by plasma immersion ion implantation](#)
Appl. Phys. Lett. **91**, 071921 (2007); 10.1063/1.2772668

[Plasma immersion ion charge state and mass spectrometer](#)
Rev. Sci. Instrum. **77**, 03C303 (2006); 10.1063/1.2171756

[High-current vacuum-arc ion and plasma source “Raduga-5” application to intermetallic phase formation](#)
Rev. Sci. Instrum. **77**, 03C115 (2006); 10.1063/1.2170037

[Interfacial reactions in nickel/titanium ohmic contacts to n -type silicon carbide](#)
J. Vac. Sci. Technol. B **23**, 2530 (2005); 10.1116/1.2126677

[Ion Beam Synthesis Of Metal - Silicon Carbide - Si Multilayer Structures](#)
AIP Conf. Proc. **680**, 579 (2003); 10.1063/1.1619783

Structural Phase States in Nickel-Titanium Surface Layers Doped with Silicon by Plasma Immersion Ion Implantation

Oleg A. Kashin^{1, a)}, Aleksandr I. Lotkov^{1, b)}, Andrey N. Kudryashov^{2, c)},
Konstantin V. Krukovsky^{1, d)}, Marina G. Ostapenko^{1, e)},
Alexey A. Neiman^{1, f)}, and Dmitry P. Borisov^{1, g)}

¹ *Institute of Strength Physics and Materials Science SB RAS, Tomsk, 634055 Russia*

² *Angioline Interventional Device Ltd., Novosibirsk, 630090 Russia*

^{a)} Corresponding author: okashin@ispms.tsc.ru

^{b)} lotkov@ispms.tsc.ru

^{c)} kudryashov@angioline.ru

^{d)} kvk@ispms.tsc.ru

^{e)} artifakt@ispms.tsc.ru

^{f)} nasa@ispms.tsc.ru

^{g)} borengin@mail.ru

Abstract. The paper reports on a study of NiTi-based alloys used for manufacturing self-expanding intravascular stents to elucidate how the technological modes of plasma immersion ion implantation with silicon influence the chemical and phase composition of their surface layers. It is shown that two types of surface structure can be obtained depending on the mode of plasma immersion implantation: quasi-amorphous Si coating and Si-doped surface layer. The Si-doped surface layer contains new phases: a phase structured as the main B2 phase of NiTi but with a lower lattice parameter, R phase, and phase of highly dispersed SiO₂ precipitates.

INTRODUCTION

One of the promising ways to enhance the biocompatibility of medical implants is their surface modification by various ion plasma methods, in particular by plasma immersion ion implantation and deposition (PIII&D) [1–4]. By now it has been proven that the interaction of living cells with an implant is influenced by the chemical composition, phase state, and topography of its surface layer [5, 6]. The ion plasma methods allow chemical and structural phase modification of only thin surface layers without any changes in properties of base materials. This is particularly important for medical NiTi implants such as intravascular stents used to recover the lumen of blood vessels narrowed by atherosclerosis. Therefore, research in the mechanisms of structure and phase formation in NiTi surface layers during their modification is a necessary stage in developing medical implants with high biocompatibility.

MATERIALS AND RESEARCH TECHNIQUES

The test NiTi specimens contained 50.9 at % of nickel were shaped as square plates of dimensions 10×10 mm and thickness 1 mm. The specimens were subjected to mechanical grinding and polishing in a Saphir 550 machine with different abrasive grits, and then to electrochemical polishing in a mixture of perchloric and acetic acids. For removal of the electrolyte residue from the specimen surface, the specimen were washed with distilled water in an ultrasonic bath and dried in an oven.

Surface modification of the NiTi specimens by plasma immersion ion implantation was realized on a SPRUT technological vacuum complex developed at Tomsk State University.

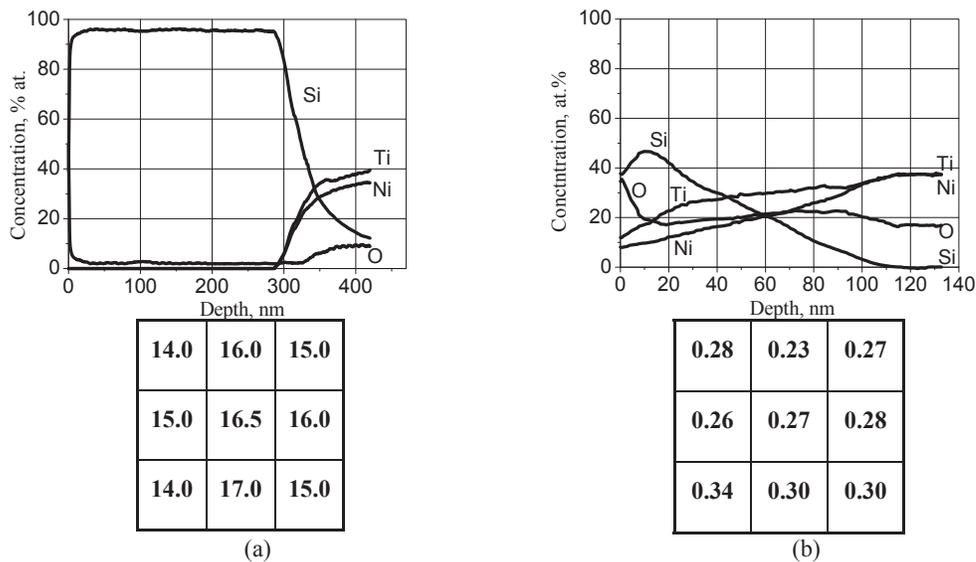


FIGURE 1. In-depth distribution of the chemical elements in the surface layer (upper diagrams, Auger spectroscopy) and Si distribution over the specimen surface (lower diagrams, XRD) after PIII&D in modes 1 (a) and 2 (b)

In the vacuum chamber of the complex, there are two plasma generators, four magnetrons, and two arc evaporators. In our study, the specimens were treated using four unbalanced magnetrons with pure-silicon cathodes and one plasma generator with a distributed thermionic cathode to produce gas discharge plasma of high-purity argon (99.998). The technology of plasma immersion ion implantation, unlike classical ion implantation, allows doping of various elements into surface layers of complex-shaped articles, e.g., vascular stents. For the formation of different structural phase states in the treated NiTi surface layer, we varied the number of magnetrons and their total power (P_m), substrate bias voltage (U_s) and its pulse repetition frequency (f), treatment time (t), and used either simultaneous or sequential operation of the plasma generator and magnetrons.

In a large series of experiments, two radically different surface structures were observed depending on the PIII&D mode: (1) Si coating of thickness variable by varying the PIII&D parameters and (2) surface layer doped with Si atoms. The in-depth distribution of Si atoms also depended on the PIII&D parameters. The observed difference in surface layer structure is explained as follows. During the process of PIII&D in the plasma containing Si ions, silicon deposition on the specimen surface and surface layer sputtering occur at a time. Moreover, the accelerated Si ions penetrate into the NiTi lattice and diffuse deep into the specimen. The rate ratio of these processes depends on the technological parameters of PIII&D and defines the way in which the specimen surface is modified.

We studied the microstructure and properties of the NiTi specimens treated in two characteristic technological modes. Mode 1 ensured coating formation and mode 2 ensured surface layer doping with Si atoms. The main difference in modes 1 and 2 was in the negative substrate bias which was $U_s = 160$ V in mode 1 and $U_s = 1000$ V in mode 2. The structure of the NiTi specimens before and after plasma immersion ion implantation was examined by X-ray diffraction analysis at room temperature on a DRON-7 diffractometer in Co- K_α radiation. The imaging was in symmetric (Bragg-Brentano) and asymmetric geometry. The in-depth elemental composition of the NiTi specimens was analyzed by Auger electron spectroscopy. The structure and chemical composition of the material was analyzed on an EVO 50 scanning electron microscope with a Wave 500 wavelength dispersive spectrometer (Oxford Instruments), AXIOVERT-200 optical microscope, and JEOL JEM 2100 transmission electron microscope. The adhesion of the modified surface layers to the base material was estimated in scratch testing with a Revetest micro scratch tester.

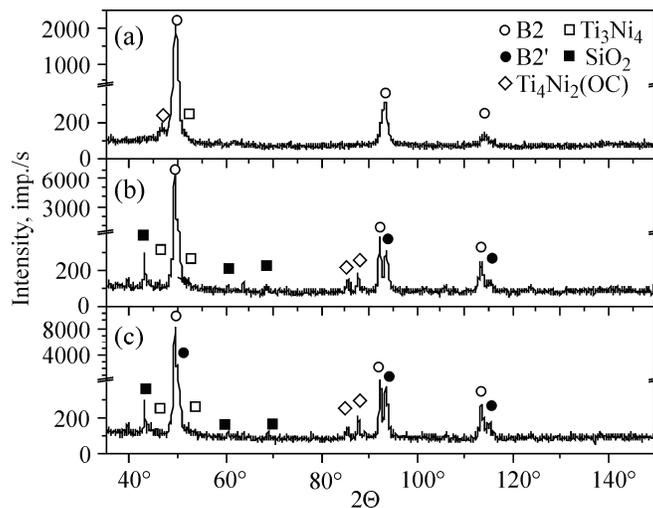


FIGURE 2. X-ray diffraction patterns of the initial specimen (a) and specimens treated in mode 1 (b) and 2 (c)

RESULTS AND DISCUSSION

Figure 1 shows Auger profiles of the main chemical elements in the NiTi surface layers modified by plasma immersion ion implantation in modes 1 and 2 (upper diagrams in Figs. 1a and 1b, respectively). It is seen that in mode 1, a layer of almost pure silicon with a thickness of ~ 300 nm is formed on the specimen surface. Between the coating and base material there is a transition layer of thickness ~ 100 nm with a gradual variation in the concentrations of Si, Ni, and Ti atoms.

In mode 2, no Si coating is formed on the specimen surface and the chemical elements reveal a distribution varying in depth. The maximum Si concentration is observed at a depth of ~ 10 nm and then it gradually decreases such that at ~ 110 nm no silicon is present. Note that surface modification by PIII&D greatly decreases the content of toxic Ni ions which is important for biocompatibility of medical implants.

The uniformity of the Si distribution over the specimen surface was analyzed by the X-ray diffraction (XRD) method, allowing one to quickly obtain a large body of data on element concentrations in different surface regions. For this purpose, the specimen surface was divided into nine regions (lower diagrams in Fig. 1) and in each region the Si atom concentration at five points was determined. Figure 1 presents the average Si concentrations over five points. For each mode, several specimens were analyzed. A certain spread in measured element concentrations was observed from specimen to specimen but this spread was no greater than 10%. The maximum concentrations of Si atoms were found in mode 1, and this is quite natural because the mode provides the formation of a rather thick Si coating on the specimen surface. The Si distribution over the specimen surface in mode 2 is uniform.

The XRD analysis shows that the phase composition of the NiTi surface layers after PIII&D, compared to the initial specimen before modification, was changed but was almost identical in both technological modes (Fig. 2). On the X-ray diffraction patterns taken for mode 1, no peaks of the Si lattice were observed. Such peaks were absent even on diffraction patterns taken in asymmetric geometry at low beam incidence angles when the volume fraction of silicon in the analyzed specimen region was high. This effect can be due to the X-ray amorphous structure of the coating.

The main volume of the initial material (Fig. 2a) represents a high-temperature NiTi phase with B2 structure (bcc, ordered as CsCl, lattice parameter $a = 3.0161 \pm 0.0005$ Å) and also contains 6–7 vol % of Ti_3Ni_4 and $\text{Ti}_4\text{Ni}_2(\text{OC})$. After plasma immersion implantation in modes 1 and 2, the phase composition of the NiTi surface layers is changed considerably, as evidenced by the presence of new peaks on the X-ray diffraction patterns (Figs. 2a and 2b). First, it should be noted that all peaks of the B2 phase is split and additional peaks at high angles appear. We suppose that these high-angle peaks belong to a new phase which preserves the structural type of the initial high-temperature B2 phase. This phase is denoted as B2' in Fig. 2. The lattice parameter of the new phase is $a = 2.9959 \pm 0.0005$ Å and its location, according to grazing incidence X-ray diffraction, falls mostly on the region near the specimen surface.

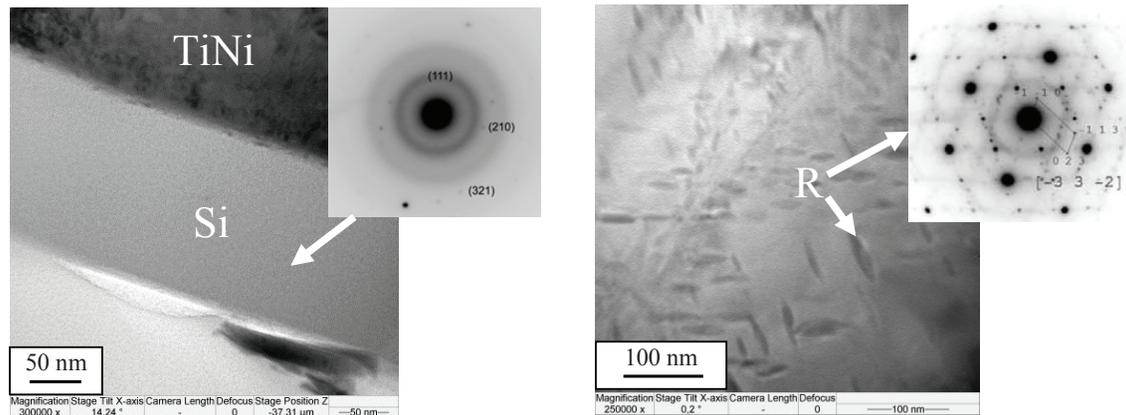


FIGURE 3. Lateral section near the specimen surface after treatment in mode 1 and corresponding microdiffraction pattern (a); image of the layer beneath the coating with R phase and corresponding microdiffraction pattern (b), TEM

The surface layer of the modified specimens contains an R martensite the amount of which is no greater than 10 vol %. The volume fraction of Ti_3Ni_4 and $Ti_4Ni_2(OC)$ is increased. The X-ray diffraction patterns reveal additional peaks corresponding to SiO_2 (cubic, $Fd3m$). Approximate estimates of the phase volume fractions from the total intensity of SiO_2 peaks show that after modification in mode 1 (Si coating deposition), the SiO_2 content is ~5 vol %, and after modification in mode 2, it is less than 5 vol %.

The results of XRD studies were confirmed by data of transmission electron microscopy (TEM). Figure 3a shows the lateral section near the specimen surface modified in mode 1, demonstrating the presence of a coating sharply differing in contrast from the base material. According to microanalysis directly in the column of the transmission electron microscope, the chemical composition of the coating is represented by silicon, and this agrees with the data of Auger spectroscopy. The microdiffraction pattern taken for the coating (Fig. 3a) reveals halos, suggesting that the coating has a quasi-amorphous structure. Interpretation of the peaks present on the microdiffraction pattern shows that they are reflections from cubic SiO_2 . The surface layer immediately beneath the coating, like the initial specimens, contains $Ti_4Ni_2(OC)$ and Ti_3Ni_4 . Additionally, this layer contains SiO_2 and also an R phase covering a depth of more than 1 μm . A similar phase composition was found in the NiTi surface layers treated in mode 2. The R phase covered a depth of up to 5 μm which is an order of magnitude larger than the depth to which the chemical composition of the NiTi surface layer was modified. Probably, the formation of the R phase owes to the fact that the volume fraction of disperse Ti_3Ni_4 precipitates in the modified surface layer increases, changing somewhat the ratio of Ni and Ti in the layer and also assisting the increase in internal stresses.

The change in the chemical and phase composition of the NiTi surface layers did not affect the NiTi superelasticity which provides shape recovery of an implant inserted into a human. Both the Si coating and the Si-doped surface layer have high adhesion to the base material, are not cracked and not delaminated at a strain of up to 5–7%.

CONCLUSION

By varying the technological parameters of plasma immersion implantation of Si ions into the surface of NiTi-based alloys it is possible to form a Si coating of different thickness as well as Si-doped surface layers with a complex distribution of chemical elements. In technological modes which provide the formation of a Si coating, the silicon structure is quasi-amorphous; the coating contains highly dispersed SiO_2 precipitates. Modification by PIII&D in the plasma containing Si ions changes the phase composition and phase volume fractions both in the surface layer immediately beneath the coating and in the doped layer with no coating. In the doped surface layer, the volume fraction of $Ti_4Ni_2(OC)$ and Ti_3Ni_4 increases and a phase with B2 superstructure and decreased lattice parameter as well as an R phase and cubic SiO_2 are formed. The change in the chemical and phase composition of the NiTi surface layers does not change the functional properties of the material and this allows the use of Si-modified NiTi alloys as a material for manufacturing medical implants.

ACKNOWLEDGMENTS

The work was supported by Federal Target Program under grant agreement No. 14.604.21.0031 (unique project identifier: RFMEFI 60414X0031).

REFERENCES

1. E. J. D. M. Pillaca, M. Ueda, K. G. Kostov, et al., *Appl. Surf. Sci.* **258**, 9564–9569 (2012).
2. D. Xie, G. Wan, M. F. Maitz, et al., *Nucl. Instrum. Meth. Phys. Res. B* **289**, 91–96 (2012)
3. F. Hempel, B. Finke, C. Zietz, et al., *Surf. Coat. Tech.* **256**, 54–61 (2014).
4. Y. Zhou, M. Li, Y. Cheng, et al., *Surf. Coat. Tech.* **228**, S2–S6 (2013).
5. T. Ziebart, A. Schnell, C. Walter, et al., *Clin. Oral Investig.* **17**(1), 301–309 (2013)
6. Y. Shen, G. Wang, X. Huang, et al., *J. R. Soc. Interface* **9**, 313–327 (2012).