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Effect of Bias Voltage on Coating Homogeneity in Plasma Immersion Ion Implantation

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Abstract. The paper presents research results demonstrating the influence of bias on the homogeneity of plasma immersion ion implantation. The research results allow the conclusion that plasma immersion ion implantation can be used to advantage for surface modification of medical materials, e.g., nickel-titanium (NiTi) alloys. In particular, doing of NiTi with silicon at pulsed bias provides highly homogeneous surface treatment.

INTRODUCTION

Many, if not all, articles used in different branches of industry as well as in medicine have complex configurations, and the problem is to provide their homogeneous vacuum plasma treatment because the homogeneity greatly influences the quality of treatment, e.g., the corrosion resistance of an article as a whole.

Here we investigate the modes of vacuum plasma and plasma immersion surface modification of NiTi specimens (surface doping and coating deposition) depending on the parameters of their negative bias to provide highly homogeneous surface treatment. The material under study was chosen for the following reasons.

Now, more and more multifunctional materials, including alloys with shape memory effects and superelasticity, are used in medicine. These alloys are able to recover inelastic strains, behave in a rubber-like manner similar to living tissues, exhibit damping properties, generate considerable stresses, etc. The deformation behavior of such alloys makes them biocompatible with living tissues and most optimal for use in medical engineering [1]. It is generally recognized that the leader among the shape memory materials is nitinol (NiTi alloy). This material is used for manufacturing vascular stents and filters, valves, occluders, bone and dental implants, braces, clamps, clips, etc. [2, 3].

The main requirement on NiTi implants is their biocompatibility to provide the growth of endothelial cells on an implant and its successful implantation. The growth of cells and their adhesion to the implant surface is influenced by the chemical composition of this surface [4]. As has been shown [5], for increasing the anticorrosion properties of NiTi implants, their biocompatibility, and cell adhesion, the chemical composition of NiTi should be changed by doping its surface with Si atoms in amount of tens of atomic percent to a depth of tens of nanometers. These facts dictated the choice of NiTi substrates and Si coatings for our study.

EXPERIMENTAL EQUIPMENT, MATERIALS, AND RESEARCH TECHNIQUE

For plasma immersion doping and coating deposition, we used a SPRUT technological vacuum plasma setup (Tomsk state university, Tomsk, Russia); its design and technological capabilities are described elsewhere [6].

The NiTi specimens contains 50.9 at % of nickel, which meets the requirements on superelasticity and shape memory effect and on manufacturing implants, in particular vascular stents. The specimens were shaped as

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rectangular plates of dimensions 35×25 mm and thickness 0.8 mm to imitate sharp edges of articles of complex configuration. In essence, they as such were articles of complex configuration.

Before vacuum plasma doping and coating deposition, the specimen surface was polished to an average roughness R_a = 0.05 μm: mechanical polishing on a SAPHIR-550 machine with different abrasive grits and electrochemical polishing in a mixture of perchloric and acetic acids. For removal of electrolyte residues, the specimens were cleaned in an IL 100-4 ultrasonic bath with surfactants. According to optical interference profilometry, the average surface roughness of the specimens was 0.040 ± 0.010 μm. Before placing in the vacuum chamber of the setup for plasma immersion ion modification, the specimens were rinsed in ethanol.

In the vacuum chamber, the specimens were fixed in a holder representing a vertical segment of a steel hexahedron of dimensions S = 32 mm and L = 80 mm located on a working table to which a negative bias with respect to the vacuum chamber could be applied. For measuring the process temperature, a chromel-alumel thermocouple was inserted into the holder via a quartz glass to prevent the measuring equipment from bias exposure. The specimens were tightly pressed to the holder for accurate measurement of their temperature.

The treatment of the specimens on the SPRUT setup included ion plasma cleaning of their surface in the gas discharge plasma of high-purity argon (99.998%) at a discharge current of 20 A and operating pressure of 0.3 Pa. The specimen holder rotated about its axis with a rate of 2 rpm. For extraction of Ar ions to the specimen surface, the specimens were biased with respect to the anode (vacuum chamber) by applying a pulsed (pulse duration 17 μs, repetition frequency 30 kHz) [7, 8] or a constant (dc) negative bias of up to 450 V. In both cases, the ion current density at the specimen surface was 0.3 mA/cm^2, ensuring high-quality cleaning and heating of the specimens to T = 90°C in 30 min.

For surface modification at constant (dc) bias (450 V) and pulsed bias (450 V) [7, 8], the plasma generator was turned off and four magnetron sputtering systems with pure silicon (99.999%) targets were simultaneously turned on at the same Ar pressure in the vacuum chamber. The operation of four unbalanced magnetron sputtering systems with a dissipated power of 0.2 kW at each target ensured the generation of plasma containing mostly Ar atoms and ions and Si atoms. At the bias used, the ion current density from the plasma to the specimen surface was 0.4 mA/cm^2. In both experiments on modification, the specimen temperature increased to T = 190°C. Upon completion of plasma immersion modification, the specimens were cooled in high vacuum to a temperature of ≤100°C.

The homogeneity of treatment in two modes was analyzed using a Shkhuna-2 Auger spectrometer (Tomsk Polytechnic University). We studied the chemical composition in depth of the modified layer at different surface sites of the specimens, including their sharp edges at which the probability of treatment inhomogeneity was high.

RESULTS AND DISCUSSION

The experiment on surface modification of the NiTi specimens with Si at a constant (dc) negative bias of 450 V revealed high inhomogeneity of such treatment. Figure 1 shows an image of the specimen treated in this mode with indication of its surface points at which the elemental composition was analyzed by Auger spectrometry.

It is seen from the image that the treatment is highly inhomogeneous. At the center of the specimen, there is a region with a deposited Si coating, whereas the edges of the specimens are etched by the ion flow. The inhomogeneity of treatment of this specimen is due to concentration of the field lines at the edges and amplification of the Ar flow from the plasma to the edges. As a result, the edges of the specimen are more etched by ions than its central part.

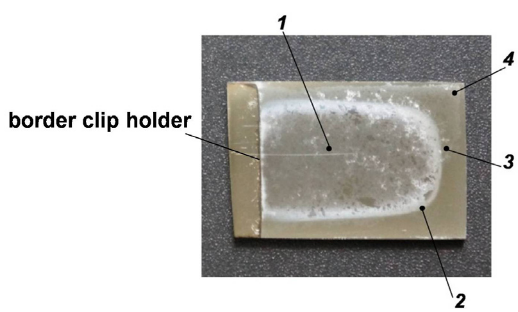


FIGURE 1. Image of the NiTi specimen with a Si surface layer formed by magnetron sputtering at constant (dc) negative bias with indication of points analyzed by Auger spectrometry

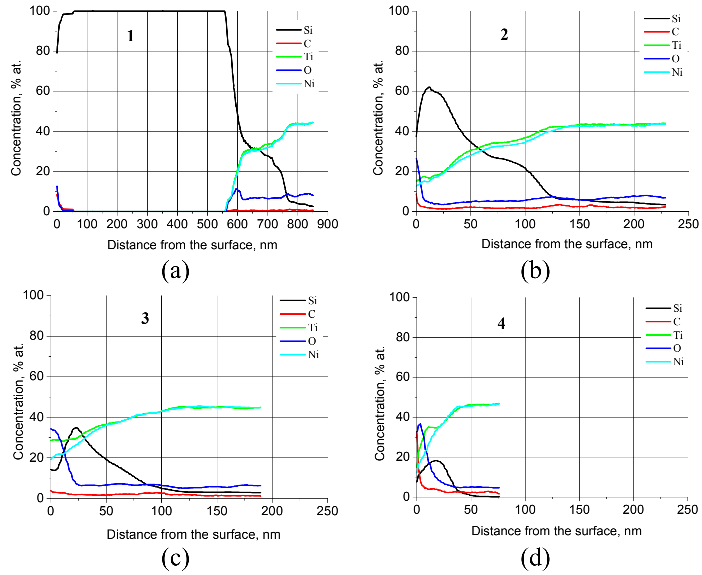


FIGURE 2. Auger profiles of the NiTi specimen modified at constant (dc) bias for the respective four points indicated in Fig. 1: *1* (a), *2* (b), *3* (c), *4* (d)

Because of the structure complexity of the modified layer obtained in this mode, the specimen surface was analyzed by Auger spectrometry at four points indicated in Fig. 1: in the central part where the specimen is coated (*1*); at the interface between the coating and the coating-free surface (*2*); in the central part of the etched surface (*3*); and at the specimen edges (*4*).

The data of Auger spectrometry revealed different profiles of the element distribution at four surface points, as can be seen in Fig. 2.

The data of Auger spectrometry confirmed the high inhomogeneity of ion plasma treatment at constant (dc) bias in the plasma produced by the magnetron sputtering systems of the SPRUT setup. At point *1* (Fig. 1), there is a coating of thickness 600 nm with penetration of Si deep into the material (to 300 nm). At point *2*, i.e., at the boundary between the coating and the coating-free surface, the coating is etched, but the penetration of Si into the material is rather deep (200–250 nm) with a maximum Si content of 60 at %. At point *3*, the penetration of Si is much lower and the Si content in the surface layer is 35 at %, suggesting more intense ion etching of this specimen region. Finally, at point *4*, the penetration of Si measures a mere 50 nm and its concentration in the surface layer is lower than 20 at %, suggesting highly intense ion etching of the specimen edges and catastrophic inefficiency of plasma immersion modification of articles with sharp edges at constant (dc) bias.

At the same time, the mode of surface modification of the NiTi specimens with Si by magnetron sputtering at pulsed bias [7, 8] provides a highly homogeneous modified surface layer (coating).

Figure 3 shows an image of the specimen after treatment in this mode with indication of its surface points analyzed by Auger spectrometry.

As can be seen from the figure, the surface is uniformly colored, suggesting homogeneity of treatment in this mode. The data of visual observations are confirmed by Auger spectrometry at points *1* and *2* (Fig. 3) [7, 8], corresponding to the central part of the specimen and its edges most critical in terms of ion etching.

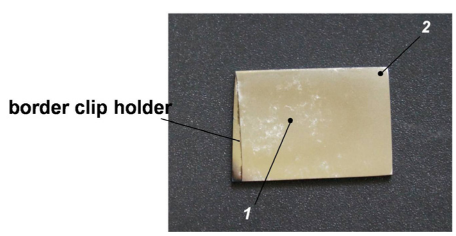
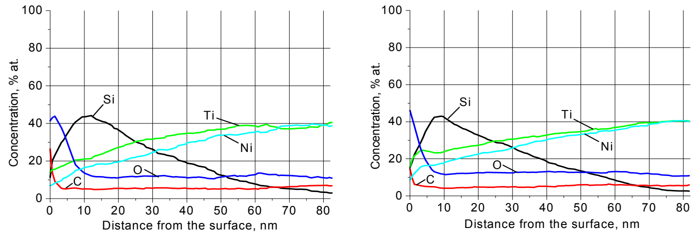


FIGURE 3. Image of the NiTi specimen with a Si surface layer formed by magnetron sputtering at pulsed bias [7, 8] with indication of its surface points analyzed by Auger spectrometry



(a) (b)

FIGURE 4. Auger profiles in depth from the NiTi surface modified at pulsed bias [7, 8] for the points indicted in Fig. 3: point *1* (a), *2* (b)

Figure 4 shows Auger profiles of the chemical elements in depth of the modified (doped) layer of the specimen at its center (point *1*) and edges (point *2*), respectively [7, 8].

As can be seen form the profiles of the chemical elements in the surface layers of the NiTi specimen, its central region (a) and edges (b) reveal highly homogeneous ion plasma treatment. The chemical composition in depth of the doped layers is almost the same in both regions. The maximum content of penetrated Si atoms in both regions is ≈ 43 at %. This means that this mode of vacuum plasma immersion treatment provides homogeneity of the process not only in the central region but at the edges of the specimen: the intensity of ion bombardment is almost the same in both regions. The cause for this is that at pulsed negative bias, the plasma at pulse-to-pulse intervals is closely attached to the specimen surface, ensuring smooth treatment of the entire surface, including the sharp edges. During the pulses of negative bias, the plasma is moved from the specimen surface with the formation of a positive space charge layer of ions bombarding the surface. For homogeneous treatment of articles of complex configuration, it is required to choose the pulse duration so that the plasma would move from the treated surface to a small distance to exclude the concentration of field lines at the edges, which is what we managed to do in the latter experiment.

CONCLUSION

The performed experiments allowed us to determine one of the modes of homogeneous (uniform) plasma immersion treatment of articles of complex configuration by using pulsed negative bias in magnetron sputtering. The formed homogeneous Si layer meets the requirements imposed on the corrosion resistance of the NiTi material and on its use for biomedical purposes. After ion plasma treatment in the specified mode, the surface roughness of the specimen increased slightly to 0.060 ± 0.010 μm [7, 8], which only little decreased the surface quality. By and large, the results evidence that plasma immersion ion modification holds much promise for treatment of medicine articles.

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REFERENCES

1. K. Otsura and X. Ren, Prog. Mater. Sci. **5**(50), 511 (2005).
2. D. Stoeckel, A. Pelton, and T. Duerig, Eur. Radiol. **2**(14), 292 (2004).
3. J. Van Humbeeck. Scripta Mater. **50**, 179 (2004).
4. T. Ziebart, A. Schnell, C. Walter, et al., Clin. Oral Investig. **17**(1), 301 (2013).
5. L. L. Meisner, A. I. Lotkov, V. A. Matveeva, et al., Adv. Mater. Sci. Eng. (2012). doi 10.1155/2012/706094.
6. D. P. Borisov, N. N. Koval, V. M. Kuznetsov, et al., IEEE Trans. Plasma Sci. **41**, 2183 (2013).
7. O. A. Kashin, A. I. Lotkov, A. N. Kudryashov, et al., AIP Conf. Proc. **1683**, 020078 (2015).
8. A. I. Lotkov, O. A. Kashin, Yu. A. Kudryavtseva, et al., AIP Conf. Proc. **1683**, 020126 (2015).