Effect of different methods of preliminary surface treatment
and magnetron sputtering on the adhesion of Si coatings

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Abstract. The paper presents research results on the adhesion of Si coatings deposited by magnetron sputtering on NiTi substrates after preliminary surface treatment (cleaning and activation) with low-energy ion beams and gas discharge plasma. The adhesion properties of the coatings obtained by two methods are analyzed and compared using data of scratch and spherical abrasion tests.

1. Introduction
One of the promising implant materials for medicine, e.g. for treatment of vascular diseases, is nickel-titanium (NiTi) alloy [1], featuring high strength and elastoplastic properties (shape memory effect and superelasticity) and applicable for manufacturing self-expanding intravascular stents, including peripheral, occluders, cava filters, cardiac valves, clips, and clamps.

The main requirement on such implants is their biocompatibility to provide the growth of endothelial cells on an implant and its successful implantation. The anticorrosion properties of NiTi implants, their biocompatibility, and the cell adhesion to their surface can be increased through surface modification with Si atoms [2] either by Si doping to a depth of tens of nanometers or by deposition of a Si coating of tens of nanometers [3,4].

When depositing a Si coating on a NiTi implant, it is required to provide its high adhesion to the implant surface, thus precluding its separation during the operation of the implant in a body, for which the implant surface should be chemically clean and free of any impurities (adsorbed residual gases, residues of organic and inorganic solvents) that can form intermediate layers between the coating and the implant surface and affect the coating adhesion up to its loss. There are different methods of preliminary surface treatment or cleaning: for example, with ion beams and with gas discharge plasma which provide, in addition to efficient desorption of contaminants, a large number of point defects in surface layers, enhanced diffusion, and hence, better coating adhesion.

Here we report on a comparative study to assess how the coating adhesion is influenced by two widely used types of preliminary surface cleaning: with ion beams and with gas discharge plasma at a negative bias.

2. Experimental equipment and research technique
The test material was NiTi with a Ni content of 50.9 at% applicable for manufacturing intravascular implants. The NiTi specimens were square plates of dimensions 10×10 mm and thickness 1 mm polished to an average surface roughness $R_s = 0.05 \mu m$ and deposited with Si coatings $\approx 600 \text{ nm}$ thick by magnetron sputtering of Si targets. Before coating deposition, the specimens were treated with ion beams and gas discharge plasma to compare the effect of two methods on the coating adhesion.
The experiments with ion beam pretreatment were performed on a Kvant ion-magnetron setup with a vacuum chamber of dimensions 600×600×600 mm at the Laboratory of Nanotechnology and Materials Science of Coatings of the Institute of Strength Physics and Materials Science SB RAS (Russia). On the upper flange at the center of the chamber, there was a resistance heater (molybdenum). The setup comprised a vacuum arc ion source and a circular planar magnetron sputtering system located on the side flanges of the vacuum chamber at an angle of 120° to each other.

Before placing in the vacuum chamber, the specimens were cleaned in an ultrasonic bath successively with benzine and ethanol for 20 mins and were dried. Then, the specimens were placed in the vacuum chamber and the chamber was pumped by a cryogenic pump to an ultimate residual pressure of 0.003 Pa.

The ion source operating in continuous mode produced a Ni ion flow (Ni⁺) at an accelerating voltage of 900 V with an ion current density to a substrate of 6 mA/cm². The substrates were located perpendicular to the ion source and were spaced from it by 220 mm. The time of ion beam pretreatment was 2 mins during which the radiation dose at the NiTi substrates reached 4.5·10¹⁵ ion/cm². Simultaneously, the Mo heater heated the substrates to 300 °C.

After ion beam pretreatment, the substrates were deposited with a Si coating on the magnetron sputtering system with a Si target of diameter 100 mm located parallel to the substrates at a distance of 60 mm. The time interval between ion beam irradiation and coating deposition was 1–2 min. The average power of the magnetron sputtering system was 1 kW at a pulse frequency of 50 kHz and pulse duration of 16 μs. The working gas was argon at a pressure of 0.3 Pa; the negative bias applied to the substrate was 100 V, and the substrate temperature was 300 °C.

The experiments with gas discharge plasma pretreatment were performed on a SPRUT technological vacuum plasma setup developed at Tomsk State University (Russia) [5].

The main plasma device of the setup is its plasma generator with thermionic (hot) cathode units located on the diametrically opposite flanges of a cylindrical vacuum chamber measuring 0.7 m³ in volume. Applying a voltage between the hot cathodes and grounded vacuum chamber with gas supply to the cathode cavities at the same flow rate causes the ignition of a non-self-sustained arc discharge the operation of which is ensured by thermionic emission from the hot cathodes. The working volume of the chamber is thus uniformly filled with “shadow-free” bulk gas plasma (e.g., Ar plasma) which provides efficient treatment (cleaning, etching, heating, etc.) of all sides of articles immersed in the plasma. The density of the gas discharge plasma produced by the generator can be varied from 10⁸ to 10¹¹ cm⁻³ over wide operating pressure range (0.13–0.67 Pa) by varying the discharge current from 10 to 250 A. The setup includes four magnetron sputtering systems equally spaced over the lateral surface of the vacuum chamber pumped with a cryogenic pump rated at 5000 l/s.

Once the NiTi specimens were placed in the vacuum chamber of the SPRUT setup, the chamber was pumped to an ultimate residual vacuum of 6·10⁻⁴ Pa and was checked for possible air leak-in. The leak-in permissible for vacuum plasma treatment was no more than 3.4·10⁻⁵ Pa·m³/s (0.02 sccm); this value is determined by specifications of the setup and excludes the presence of excess gas impurities (oxygen, carbon, etc.) in the vacuum chamber. The specimens were subjected to finish surface cleaning in the argon plasma in which they were heated to the desired temperature by varying both their negative bias and the plasma density. The gas discharge plasma produced in the setup provides highly efficient ion cleaning such that the only preliminary treatment of the specimens outside the vacuum was their rinsing in benzine and ethanol. In the vacuum chamber of the SPRUT setup, the specimens were arranged on special holders, allowing accurate measurements of their temperature with a chromel-alumel thermocouple.

The treatment of the NiTi specimens on the SPRUT setup included ion plasma cleaning of their surface in the gas discharge plasma of high-purity argon (99.999%) at a discharge current of 20 A and operating pressure of 0.3 Pa. For extraction of Ar ions to the specimen surface, the specimens were biased with respect to the anode (vacuum chamber) by applying a negative pulsed bias with a pulse duration of 17 μs, pulse repetition frequency of 30 kHz, and amplitude of up to 400 V. Thus, the ion
current density at the specimen surface during the pulses was 0.3 mA/cm², ensuring efficient surface cleaning and heating of the specimens by Ar ions to \( T = 90 ^\circ C \) in 30 min.

The same bias parameters but with an amplitude of 200 V were used for deposition of Si for which the plasma generator was turned off and four magnetron sputtering systems with pure silicon targets were simultaneously turned on at the same Ar pressure in the vacuum chamber. The operation of four unbalanced magnetron sputtering systems with a diffused power of 0.2 kW at each target ensured the generation of plasma containing Ar and Si ions in the specimen region at a distance of 440 mm from the systems. At the bias used, the ion current density from the plasma to the specimen surface was 0.4 mA/cm². During deposition for 90 min, the specimen temperature increased to \( T = 150 ^\circ C \).

The properties of the coatings deposited after two types of preliminary surface treatment were studied on analytical equipment of the Material Properties Measurements Centre of the Institute of Physics and Technology at Tomsk Polytechnic University (Russia). The adhesion properties of the coatings were studied in scratch tests on a CSEM micro scratch tester with increasing load on an indenter with a rounding-off radius of 100 μm throughout its motion (track). The critical load in newtons (adhesion strength) at which the coating was separated from the substrate was determined from no less than six scratch tracks for each of the specimen by visual observation in an optical microscope. The coating thickness was measured using a rotating sphere on a Calotest device (CSM Instruments) with a Nikon microscope. The same method was used to analyze the character of fracture and the quality of coating adhesion.

3. Results and discussion
Figures 1 and 2 show images of the tracks produced by the scratch tester in studying the adhesion strength of the coatings deposited after pretreatment with ion beams and gas discharge plasma, respectively. It is seen that the critical load for coating separation (adhesion strength) in two cases is almost the same. The onset of fracture and separation of the coatings in the form of islands (Figure 1a) and bands (Figure 2a) is observed at an indenter load of 16 N.

The indenter load at which the coatings are fully separated (critical load) is equal, on average, to 19 N for ion beam treatment (Figure 1b) and to 20 N for discharge plasma treatment (Figure 2b). The results of scratch testing demonstrate that the coatings deposited after gas discharge plasma treatment on the SPRUT setup have higher adhesion than the coatings deposited after ion beam treatment, though the difference is very slight. By and large, the coatings of both types feature high adhesion properties compared, e.g., to antifriction coatings [6] whose adhesion estimated with the same device is no greater than 10 N.

It is seen from Figures 1 and 2 that the coatings obtained by two methods differ in their fracture (separation). The coatings deposited after gas discharge plasma treatment are separated from the substrates as such (Figure 2). In the specimens coated after ion beam treatment, there is a film between the substrate and the coating (Figure 1). The film has likely the same thickness throughout the interface and is separated in portions baring the substrate surface.

The foregoing allows the conclusion that the substrate surface is strongly activated by high-dose Ni ion implantation, and this, together with the high substrate temperature after the process (300 °C), time interval between ion activation and deposition, and uncontrollable composition of the gas atmosphere, can lead to the formation of an oxide film. The adhesion of the oxide film to the substrate is higher than the adhesion of the Si coating to the film. As can be understood from Figure 1, the Si coating was stripped at lower indenter loads before the film was detected, and the critical load 16 and 19 N determines the adhesion strength of the intermediate oxide film to the substrate in view of its successive separation in portions of equal thickness. The above conclusion is confirmed by spherical abrasion tests demonstrating different patterns of abrasion for two coating types at the same coating thickness (0.6 μm). Figure 3a shows an image of the abraded Si coating which was deposited after Ni ion implantation. It is seen that the abrasion reveals a dark layer with a “ragged” boundary between the Si coating and the substrate.
At the same time, the coating deposited after preliminary plasma treatment on the SPRUT setup (Figure 3b) reveals a perfectly smooth abraded crater of uniform color and regular circular shape with tight attachment of the coating to the substrate.

The results of spherical abrasion tests also demonstrate that of the two methods of coating deposition, the SPRUT setup provides higher adhesion at the same surface roughness of the specimens.
before pretreatment and coating deposition. The most probable cause of the high adhesion of the ion plasma coatings deposited on the SPRUT setup consist in stringent requirements on vacuum plasma processes, low residual pressures in the vacuum chamber, and low leak-in for operation with high-purity argon, and these factors provide highly efficient surface cleaning without any contamination by oxygen, carbon, and their compounds.

4. Conclusion

By and large, both methods of deposition of Si coatings on NiTi substrates demonstrate high coating adhesion. The higher quality and the higher adhesion of the coatings deposited with preliminary plasma cleaning and surface activation of the substrates suggests efficiency of this method of coating deposition. In particular, the plasma method offers advantages over ion beam irradiation for treatment of articles of complex configuration, and this opens up great opportunities for its use in developing efficient technologies of treatment, including treatment of medical materials.

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