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Effect of Preliminary Vacuum Plasma Treatment on Coating Adhesion

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Abstract. The paper presents research results on the adhesion properties of Si coatings synthesized by different methods and under different conditions of preliminary vacuum ion plasma treatment of substrates with subsequent magnetron sputtering. The substrate surface was pretreated with low-energy ion beams, high-energy ion beams, gas discharge plasma, and plasma produced by a magnetron sputtering system. The vacuum conditions (pump type, pressure, etc.), the ion current density, and the bias parameters (pulse repetition frequency and duration) were varied. The research results demonstrate a considerable effect of plasma immersion ion implantation on the adhesion of Si coatings to NiTi substrates.

INTRODUCTION

Among the promising materials for medical implants, e.g., for treatment of blood vascular systems, is nickel-titanium (NiTi) alloy [1]. This material features high strength and elastoplastic characteristics (shape memory effects or superelasticity) and is applicable for manufacturing self-expanding intravascular stents, including peripheral, occluders, cava filters, cardiac valves, and clamps.

The main requirement imposed on such implants is their biocompatibility to provide the growth of endothelial cells on an implant and its successful implantation. As has been shown [2], for increasing the anticorrosion properties of NiTi implants, their biocompatibility, and the cell adhesion to their surface, the chemical composition of NiTi should be changed by surface modification with silicon (Si) atoms. For this purpose, it is possible to use Si doping of a thin (tens of nanometers) surface layer and deposition of a thin (tens of nanometers) Si coating [3, 4].

If a Si coating is deposited on a TiNi implant, it is required to preclude its separation during the operation of the implant in a body, and hence, the coating adhesion to the implant should be high. To provide high coating adhesion, the substrate surface should be chemically clean because adsorbed residual gases in a vacuum chamber and residues of organic and inorganic solvents after cleaning the specimen outside the chamber create intermediate layers between the coating and the substrate surface. These contaminated layers affect the coating adhesion up to its complete loss. The adhesion of coatings is increased by different methods of surface pretreatment (cleaning). An efficient way of surface cleaning is ion beam irradiation or gas discharge plasma treatment. During such treatment, contaminants are desorbed and a large number of point defects are formed in surface layers, amplifying the diffusion and increasing the coating adhesion.

The paper presents research results on the adhesion of coatings deposited on substrates after their preliminary surface treatment by two vacuum plasma methods: ion beam treatment and treatment in gas discharge plasma with negative bias applied to the substrates.

EXPERIMENTAL EQUIPMENT, MATERIALS, AND RESEARCH TECHNIQUE

In our experiments, we used NiTi specimens with a Ni content of 50.9 at %, which meets the requirements for manufacturing intravascular implants. The specimens were shaped as square plates of dimensions 10×10 mm and

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thickness 1 mm. Before vacuum plasma treatment and coating deposition, the specimen surface was polished to an average roughness $R_a = 0.05$ μm. The NiTi substrates were deposited with Si coatings of thickness 250–300 nm by magnetron sputtering of Si targets.

The specimens were subjected to ion beam treatment on a multi-aperture ion source [5] at the Laboratory of Applied Electronics of the Institute of High Current Electronics SB RAS (Russia). Before placing in the vacuum chamber, the specimens were cleaned in an ultrasonic bath successively with acetone, isopropyl alcohol, and distilled water. Then, the specimens were placed in the vacuum chamber and the chamber was pumped by a turbomolecular pump to an ultimate residual pressure of 2.5×10^{-3} Pa. The operation of the ion source was continuous; the working gas was argon at a pressure of 3.6×10^{-2} Pa. The accelerating voltage of the ion flow was kept at 1.75 kV, and the ion current density to the substrates was 0.5 mA/cm^2. The specimen surface was treated for 3 min, whereupon Si coatings were deposited using a round planar magnetron sputtering system with a Si target of diameter 95 mm. The specimens were arranged on the axis of the sputtering system at a distance of 10 cm from the target. The coatings were deposited for 13 min at an argon pressure of 9.6×10^{-2} Pa. The negative bias to the substrates with respect to the vacuum chamber was 100 V with a frequency of 100 kHz and pulse duration of 2.5 μs. The power of the magnetron sputtering system was 160 W at a discharge voltage of 655 V.

Experiments on preliminary surface treatment of NiTi specimens in gas discharge plasma [6, 7] were performed using a SPRUT technological vacuum plasma setup developed at Tomsk State University (Russia) [8].

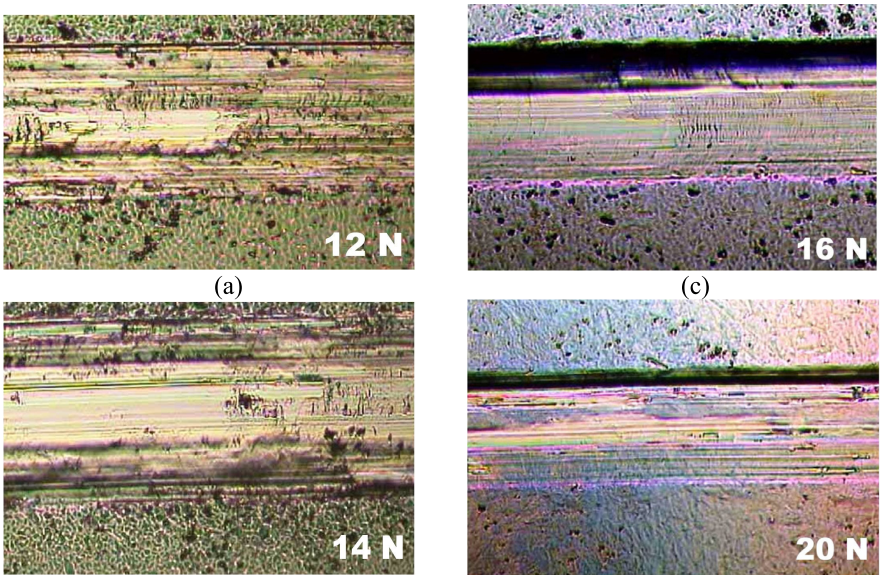
The main plasma device of the setup is its plasma generator based on thermionic or so-called hot cathodes. The cathode units are located on the diametrically opposite flanges of a cylindrical vacuum chamber measuring 0.7 m^3 in volume. The voltage applied between the hot cathodes and grounded vacuum 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., argon plasma) with 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 10^8 to 10^{11} cm^{-3} over a 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 which is pumped a cryogenic pump rated at 5000 l/s.

Once specimens for treatment are placed in the vacuum chamber of the SPRUT setup, the chamber is pumped to an ultimate residual vacuum of 6×10^{-4} Pa and is checked for possible air leak-in and gas desorption from its walls and other elements. For this check, the control system of the setup closes the high-voltage valve, records the current pressure in the vacuum chamber, and starts its timer. Within 30 s after start of the timer, the control system again records the pressure and calculates the leak-in from two pressure values in Pa$\times$m^3/s or sccm. The leak-in permissible for further vacuum plasma treatment is determined by specifications of the setup and is no more than 3.4×10^{-5} Pa$\times$m^3/s (0.02 sccm). If the leak-in exceeds this value, the vacuum conditions are considered to be an emergency requiring routine and preventive repair to eliminate the excess leak-in for further operation of the setup. Under trouble-free vacuum conditions, the technological processes are continued and the specimens are subjected to finish surface cleaning in the argon plasma in which they can be heated to the desired temperature by varying both their negative bias and plasma density. Due to the high ion cleaning efficiency in the gas discharge plasma of the setup, the only preliminary treatment of the specimens outside the vacuum is their rinsing in benzine and ethanol.

In the vacuum chamber of the SPRUT setup, the specimens were arranged on special holder which allowed accurate measurement of the specimen temperature with a chromel-alumel thermocouple.

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. 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. As a result, the ion current density at the specimen surface during the pulses was 0.3 mA/cm^2, ensuring efficient ion cleaning and heating of the specimens to $T = 90°C$ 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 dissipated 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/cm^2. During deposition for 90 min, the specimen temperature increased to $T = 150°C$.



(a) (c)

(b) (d)

FIGURE 1. Images of the indenter tracks for the Si coatings deposited after preliminary treatment of the substrates with an ion beam (a, b) and gas discharge plasma (c, d)

The properties of the coatings were studied using 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 testing on a CSEM micro scratch tester. The coated surface was scratched using an indenter with a rounding-off radius of 100 μm; the load on the indenter was increased during its motion (along its 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 specimens by visual observation in an optical microscope. The chemical composition in depth form the specimen surface modified by ion plasma deposition was analyzed on a Shkhuna-2 Auger spectrometer with an energy resolution of 0.7%.

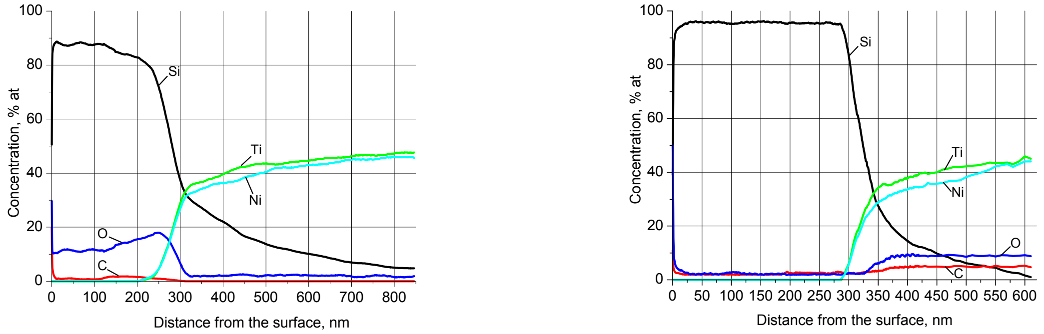
RESULTS AND DISCUSSION

Figure 1 shows images of the tracks produced by the scratch tester in studying the adhesion strength of the coatings with indication of average loads. The images in Figs. 1a and 1b correspond to the coatings obtained with preliminary ion beam surface treatment of the NiTi specimens. It is seen from Fig. 1a that the onset of fracture and separation of the coating occurs at an indenter load of 12 N, and its full separation at a load equal, on average, to 14 N (critical load). Figures 1c and 1d show images of the tracks for the coatings deposited after preliminary treatment of the NiTi substrates in gas discharge plasma: the onset of buckling and fracture (Fig. 1c) and separation of the coatings (Fig. 1d).

The data of scratch testing demonstrate that the coatings deposited after preliminary treatment of the specimens in gas discharge plasma on the SPRUT setup have higher adhesion strength than the coatings deposited after their ion beam pretreatment. For analyzing the cause of this, the coatings were examined Auger spectrometry.

Figure 2 shows Auger profiles of the chemical compositions for the coatings deposited after preliminary ion beam treatment (Fig. 2a) and discharge plasma treatment (Fig. 2b) [6, 7]. It is seen from the profiles that during deposition of the coatings after both types of treatment, silicon is implanted into the NiTi surface. For gas discharge plasma treatment, the depth of Si penetration into the substrate material is 300 nm, and for ion beam treatment, it is more than 600 nm

The cause for the observed phenomenon can be intense Ar ion bombardment during preliminary surface cleaning of the specimens, resulting in the formation of crystalline defects in the substrate material and in amplified diffusion processes. For ion beam surface cleaning, this effect is stronger and likely due to more intense action of Ar ion flows on the surface and higher energies of bombarding ions.



(a) (b)

FIGURE 2. Auger profiles of the Si coatings and NiTi substrate surface for preliminary ion beam treatment (a) and gas discharge plasma treatment (b) [6, 7]

However, as can be seen from the profiles in Fig. 2, the coatings deposited after ion beam surface cleaning contains oxygen in amount of almost up to 20 at %, whereas the oxygen and carbon content in the coatings deposited after plasma cleaning on the SPRUT setup [6, 7] is, in total, no greater 5 at %. This fact is likely due to poorer vacuum conditions in the first method compared to the method using the SPRUT setup, and the presence of oxygen is likely to be the cause for the lower adhesion properties of the Si coatings deposited after ion beam cleaning compared to those deposited after discharge plasma cleaning.

The most probable cause for the high adhesion of the ion plasma coatings obtained on the SPRUT setup is stringent requirements on vacuum plasma processes with low residual pressures in the vacuum chamber and low leak-in for high-purity argon which provide clean treated surfaces with no contamination by oxygen, carbon, and their compounds.

CONCLUSION

By and large, both methods of deposition of Si coatings on NiTi substrates demonstrate high adhesion properties. The higher adhesion of the coatings with plasma cleaning evidences the efficiency of plasma immersion doping and deposition. In particular, the plasma method is advantageous over ion beam doping and deposition for treatment of articles of complex configurations, and this opens up great opportunities for its use in developing technologies for medicine of the future.

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