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Plasma Immersion Ion Implantation for the Efficient Surface Modification of Medical Materials

Vladimir A. Slabodchikov[1, a)], Dmitry P. Borisov[1, b)], and Vladimir M. Kuznetsov[1, c)]

[1] *National Research Tomsk State University, Tomsk, 634050 Russia*

[a)] Corresponding author: dipis1991@mail.ru
[b)] borengin@mail.ru
[c)] kuznetsov@rec.tsu.ru

Abstract. The paper reports on a new method of plasma immersion ion implantation for the surface modification of medical materials using the example of nickel-titanium (NiTi) alloys much used for manufacturing medical implants. The chemical composition and surface properties of NiTi alloys doped with silicon by conventional ion implantation and by the proposed plasma immersion method are compared. It is shown that the new plasma immersion method is more efficient than conventional ion beam treatment and provides Si implantation into NiTi surface layers through a depth of a hundred nanometers at low bias voltages (400 V) and temperatures (≤150°C) of the substrate. The research results suggest that the chemical composition and surface properties of materials required for medicine, e.g., NiTi alloys, can be successfully attained through modification by the proposed method of plasma immersion ion implantation and by other methods based on the proposed vacuum equipment without using any conventional ion beam treatment.

INTRODUCTION

Nowadays, metal implants are widely used in medicine for the treatment and correction of various types of trauma, defects, and other diseases. For manufacturing medical implants, titanium and its alloys have long been used to great advantage [1]. A promising implant material, for example, in the treatment of cardiovascular diseases is nickel-titanium (NiTi) alloy [2]. This material displays high strength and elastoplastic properties (shape memory effects or superelasticity) and is suitable 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 with a human organism to provide the growth of endothelial cells on an implant and its successful implantation. The growth and adhesion of endothelial cells are influenced by many factors, e.g., by the microrelief of the implant surface and particularly by its chemical composition [3, 4].

In efforts to improve the corrosion resistance of NiTi implants, their biocompatibility, and adhesion of cells to their surface, it was found that the chemical composition of NiTi should be changed by doping its surface layers with Si ions [5]. In order to improve the above properties, it was sufficient to modify a thin (tens of nanometers) NiTi surface layer by conventional implantation of Si ions with an ion source [5, 6]. It was shown that high-dose implantation of Si ions into the surface of NiTi-based alloys enhanced the proliferation of mesenchymal stem cells of rat bone marrow [5].

However, the thickness of a substrate surface layer implanted at moderate energies (≤200 keV) corresponds in order of magnitude to the projective range of ions in the substrate material and is normally no greater than 0.1 μm. A representative example that demonstrates the potentials of ion implantation as a tool of metal doping is an experiment in which Al ions were implanted into a Ni substrate at an energy of 180 keV [7] with the result that the concentration of implanted Al ions at an irradiation dose of 6×10^{17} ion/cm^2 was 25 at %, but in a surface layer of merely 100 nm.

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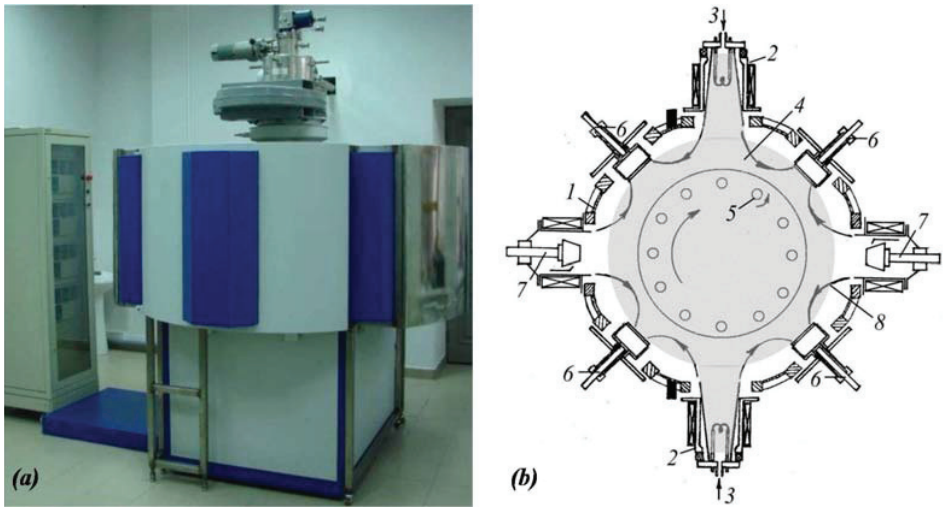

FIGURE 1. Photo (a) and schematic (b) of the SPRUT vacuum plasma setup: *1*—vacuum chamber; *2*—cathode units of the plasma generator; *3*—gas supply; *4*—bulk gas discharge plasma; *5*—treated objects; *6*—magnetron sputtering systems; *7*—arc evaporators; *8*—closed magnetic field lines (magnetic wall)

In view of the small depth of implanted surface layers required for biomedical applications and high complexity, high cost, and low efficiency of ion beam doping technologies, it is reasonable to use plasma treatment alone, e.g., through magnetron sputtering, to enable efficient surface doping. This paper presents modern vacuum plasma equipment designed by the authors and demonstrates the capabilities of plasma immersion ion implantation in comparison with ion beam treatment for the surface modification of medical materials.

EXPERIMENTAL EQUIPMENT, MATERIALS, AND RESEARCH TECHNIQUE

Plasma immersion ion implantation of NiTi specimens was conducted on new technological vacuum plasma equipment—SPRUT setup—developed at Tomsk State University [8]. A photo and schematic of the setup is shown in Fig. 1.

In the electrophysical scheme of the vacuum plasma setup the authors realized the theory on the possibility of obtaining necessary high surface properties of metal products by means of only plasma action onto their surface due to the functioning of effective volume electrical discharges of different types in the reaction vacuum volume. The choice of solely plasma ways of treatment and plasma sources corresponding to them is conditioned by high efficiency, similarity in the ranges of the working pressures of all these sources, their energy efficiency, simple realization and reliability of their operation in industry production. Besides, due to the possibility of changing the relation of the working parameters of the applied charges in a flexible manner there is a possibility of wide adjustment of intensity of diverse plasma action onto the surface, which in combination with the bias voltage of displacement of the treated items will allow to increase control of the formation of necessary phase-structure states of material of the base and deposited coatings.

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 a 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 plasma (e.g., argon) which provides for efficient treatment (cleaning, etching, heating, etc.) of all sides of articles immersed in the plasma. By varying the discharge current from 10 to 250 A, the density of the gas discharge plasma can be varied from 10^8 to 10^{11} cm^{-3} over a wide pressure range of 0.13–0.67 Pa. The setup also comprises four magnetron sputtering systems and two arc evaporators equally spaced over the lateral surface of the vacuum chamber. The vacuum chamber is pumped by a cryogenic pump rated at 5000 l/s.

A special feature of the system of vacuum pumping is the fact that the cryogenic pump is mounted on top of the vacuum chamber. Given this vacuum-pumping design, the cryopump is effectively protected from contamination with the products of plasma processes: evaporation and sputtering by marcoparticles (droplets, debris, clusters, etc.), since under the force of gravity the flow of these particles to the upper part of the chamber is considerably reduced.

The location of equally-spaced plasma sources along the side of the vacuum chamber ensures that the workpieces treated are continuously (without any breaks) present in the zone of concentrated plasma flows of these plasma sources or others (i.e., in the process zone). In addition, this configuration appears to improve the course of plasma-chemical reactions on the workpiece surfaces.

The use of unbalanced magnetron-sputtering systems and special coupling schematics of all magnetic systems with respect to each other, creates a region in the volume of the SPRUT facility, which is confined by closed magnetic-field lines (a "magnetic wall"), involving the space with the treated workpiece. It was discovered experimentally that the rate of coating deposition with an unbalanced magnetron sputtering system in the presence of this "magnetic wall" is by a factor of 1.4 higher than that of a balanced sputterer, given the same power of magnetron sputtering systems. This is probably due to the "magnetic wall" preventing the departure of fast plasma electrons from the discharge space. It should be noted that fast electrons oscillate in the vacuum chamber and increase the ionization of the sputtered material atoms, which, together with the negative bias voltage on the substrate always used in the experiments, would result in an increased coating deposition rate.

During the technological processes of plasma treatment the products are placed in the manipulator of product rotation and positioning. The manipulator is a rotary table located in the bottom part of the vacuum chamber. The rotary table has up to 36 positions (places) to set the products and a "planetary" mechanism of their displacement that allows each item to revolve on its axis in the working position during simultaneous revolution on its axis of the manipulator and the vacuum chamber.

Temperature control of the items during the technological process is performed using the thermocouples injected into the working volume and the pyrometer of infrared radiation.

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-vacuum valve, records the current pressure in the vacuum chamber, and starts its timer. Within 30 s after the start of the timer, the control system again records the pressure and calculates the leak-in from two pressure values in Pa×m^3/s or sccm. The leak-in acceptable for further vacuum plasma treatment is defined by specifications of the setup and is no more than 3.4×10^{-5} Pa×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 final surface cleaning in the argon plasma in which the specimens 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.

The NiTi specimens contained 50.9 at % of nickel, as per requirements for manufacturing cardiovascular implants, and were shaped as square plates of dimensions 10×10 mm and thickness 1 mm. Before doping, the surface of the specimens was polished to an average roughness of R_a = 0.05 μm. In the vacuum chamber of the SPRUT setup, the specimens were arranged on special holders which rotated with a rate of 2 rpm and allowed accurate measurements 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 (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, including the pulse amplitude 400 V, were used in surface doping of the specimens with Si ions 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. At the bias used, the ion current density from the plasma to the specimen surface was 0.4 mA/cm^2. During ion doping for 90 min, the specimen temperature increased to no more than T = 150°C.

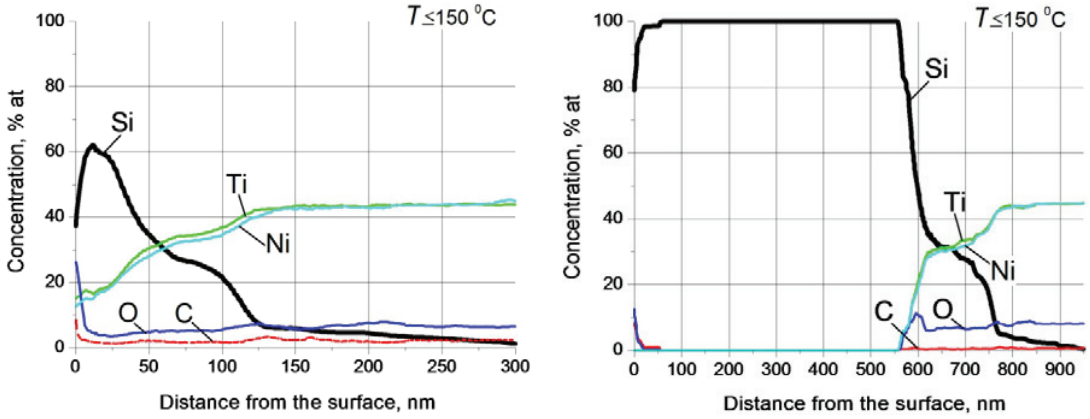

FIGURE 2. Auger profiles of the elements in the NiTi surface layer doped with Si by plasma immersion ion implantation at a negative bias of 400 (a) and 200 V (b)

The chemical composition in depth of the specimen surface modified by plasma immersion ion implantation was analyzed by Auger spectrometry with an energy resolution of 0.7%.

RESULTS AND DISCUSSION

Fig. 2a shows an Auger profile of the chemical elements in the NiTi surface layer doped with Si by plasma immersion ion implantation. It is seen that the process provides penetration of Si ions into the NiTi surface up to a depth of 300 nm. The profile of in-depth Si distribution is stepwise, which is probably due to different mechanisms of dopant accumulation with their inherent concentration peaks and doping rates. So, near the surface, the profile reveals a hump with a maximum Si concentration of 60 at % at a depth of ≈25 nm. The hump is followed by a relatively gentle slope and the Si concentration decreases to 30 at % at ≈60 nm. Further, the Si concentration reaches a plateau and its level at a depth of 60–80 nm is about 25 at %. Then, the Si concentration begins to decrease and reaches 7 at % at 130 nm, whereupon its profile represents a tail in which the Si concentration decreases from the latter value down to <1 at % at 300 nm.

The uniqueness of the result becomes obvious if we compare it with data on conventional ion implantation, e.g., with data on Si implantation into a NiTi alloy of the same composition by using accelerated ion beams [5, 6]. In the cited papers, to provide the desired NiTi biocompatibility, a pulsed ion source with an accelerating voltage of 60 kV was used to dope the NiTi surface with Si ions. At an ion current density of 0.43 mA/cm^2 in a pulse, accelerating pulse duration of 250 μs, and pulse repetition frequency of 50 Hz, the dose rate equal to 2×10^{17} ion/cm^2 was attained in 100 min. The NiTi temperature during the treatment, like in our experiment, was no greater than T = 150°C. The Auger profile of Si implanted into the NiTi surface revealed a maximum concentration of 30 at % at a depth of 30 nm from the surface and the maximum depth to which silicon penetrated was a mere 70–80 nm.

Comparison of our results with the data on Si implantation reported above [5, 6] does not favor the ion beam doping technologies; in our experiments, the profile of implanted silicon is more extended and higher in concentration with the same substrate material and at nearly the same temperature and treatment time. From this comparison it follows that the profile of implanted silicon (70–80 nm) required to provide biocompatibility [5, 6] can be attained by the proposed method of plasma immersion ion implantation at a low substrate bias of 400 V in a time two times shorter than that used in convention ion beam doping [5, 6].

The most probable cause for the high efficiency of vacuum plasma immersion ion implantation 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 other compounds. The foregoing is indirectly confirmed by the Auger profile of the NiTi surface coated with silicon at a lower negative bias of 200 V (Fig. 2), compared to 400 V, showing that the coating and the process itself are almost free from oxygen, carbon, etc.

CONCLUSION

The high efficiency of vacuum plasma immersion ion implantation, which can even greatly exceed the efficiency of conventional ion beam implantation in dopant penetration and concentration under certain conditions, offers great opportunities for the use of this method in developing surface modification technologies. It is expected in particular that plasma immersion ion implantation will find wide applications in advanced technologies for the medicine of the future.

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