Silicon coating deposition on NiTi substrate by plasma immersion ion implantation and deposition

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Abstract. This paper studies the deposition of a silicon coating on a substrate of a nickel-titanium based alloy using plasma immersion ion implantation and deposition (PIII&D). It is shown that the PIII&D technique allows a nickel titanium substrate to be coated with an up to 3 μm thick amorphous silicon coating. The PIII&D time is found to have a decisive influence on the coating thickness. The magnitude of the bias voltage $U_s$ has a much smaller effect on the thickness of the sputtered coating. To ensure a high adhesion of the coating to the substrate, the substrate must be preheated before PIII&D to a temperature of $\approx 300^\circ$C.

1. Introduction

Depending on the purpose and working conditions, various characteristics of coatings are required, such as thickness, wear resistance, hardness, and corrosion resistance in aggressive environments (including biological ones). For example, coatings for medical devices must have good biocompatibility. In any case, a necessary condition for the applicability of coatings is the high strength of the coating adhesion to the substrate surface. Adhesive characteristics depend on the coating technology, the interaction mechanisms between the substrate and coating materials, as well as on the geometric and physico-mechanical properties of the substrate and coating, such as coating thickness, surface roughness of the coating and interface, strength, Young’s modulus, Poisson’s ratio, hardness, ductility, and thermal expansion coefficients [1, 2].

Here we propose the idea of depositing porous silicon coatings on the surface of medical implants made of nickel-titanium based alloys [3]. The silicon coating is bioactive and can be used on bone implants to accelerate osseointegration. In addition, such coatings can be used as container materials for the encapsulation of therapeutic drugs in their porous structure. Earlier [3, 4] we showed that a silicon coating can be deposited on a nickel titanium substrate using the PIII&D technique. In the present work, we study the formation mechanisms of silicon coatings depending on the PIII&D parameters.

2. Materials and experimental techniques

The substrate material was a nickel titanium alloy with a nickel content of 50.9 at.%. Specimens for investigation were cut out by spark erosion in the form of square plates with the dimensions 10×10 mm and thickness 1 mm, which were then mechanically ground and electrolytically polished. Targets of silicon of 99.999% purity were used for the deposition of a silicon coating.
The deposition of silicon coatings on the surface of model nickel titanium specimens was carried out on a plasma-magnetron-arc setup for the deposition of gradient composite nanocoatings, which incorporates a plasma source with a thermionic cathode and an unbalanced magnetron sputtering system [5]. The setup is equipped with a round platform, on the periphery of which the nickel titanium specimens were placed in special holders. The platform can perform planetary rotation, owing to which it can rotate about its center and the specimens in the holder can rotate about their own axes. The rotating configuration allows the coating to be applied to objects with a complex geometric shape, such as for example intravascular stents. The distance from the specimens to the magnetron was 200 mm. Argon was used as an inert gas at a pressure of 1 Pa.

The main technological parameters that determine the thickness of the sputtered coating are the magnitude of the negative bias voltage $U_s$ on the specimen and the time of deposition. Based on previous studies, we chose the following values of $U_s$: 150, 200, 300, 400, and 600 V. At higher $U_s$ values, the sputtering process becomes dominant and the coating does not form. The deposition times were varied by performing experiments with and without rotating the platform. The time of coating deposition was effectively increased without platform rotation. In addition, we varied the preheating temperature of the specimens $T_{heating}$ before coating deposition.

There were 6 deposition modes chosen:

- $U_s = 150$ V, $T_{heating} = 200^\circ$C, without rotation;
- $U_s = 300$ V, $T_{heating} = 180^\circ$C, without rotation;
- $U_s = 600$ V, $T_{heating} = 75^\circ$C, without rotation;
- $U_s = 200$ V, $T_{heating} = 300^\circ$C, with rotation;
- $U_s = 400$ V, $T_{heating} = 303^\circ$C, with rotation;
- $U_s = 600$ V, $T_{heating} = 292^\circ$C, with rotation.

The surface morphology and chemical composition of the surface layer was examined using an EVO 50 scanning electron microscope (Zeiss, Germany) with an Oxford Instruments Wave 500 wavelength dispersive spectrometer, and a JEOL JEM 2100 transmission electron microscope (Shared Use Center of TSC SB RAS). The surface roughness of the deposited coatings was determined using a New View 6200 interference profilometer (Zyga, Germany) and a Solver HV atomic force microscope (Russia). The adhesive characteristics were studied using a Revetest RST scratch tester (CSM Instruments, USA). The microhardness of the coated specimens was determined on a Digital Micro Hardness Tester DM8 (AFFRI, Italia) depending on the indentation load.

In some cases, it is quite difficult to determine experimentally the coating thickness, which necessitates the use of various methods. The results of X-ray microanalysis, Auger spectroscopy, scanning and transmission electron microscopy, and X-ray diffraction showed that the silicon concentration values obtained by X-ray microanalysis are proportional to the coating thickness. The obtained data were used to plot a calibration curve of coating thickness vs. silicon concentrations, which turned out to be close to linear (figure 1). This dependence allowed us to determine the coating thickness only by X-ray microanalysis data, which significantly reduced the amount of studies for the coating thickness determination.

3. Results and discussions

The coating thickness depends on the PIII&D parameters (figure 2). The greatest effect was observed when using the modes with and without rotation of specimens. In the mode without rotation, the coating thickness was about 2.5 µm at $U_s = 150$ V, almost linearly decreasing to ~ 1.5 µm with increasing $U_s$ to 600 V (curve 1, figure 2). A similar dependence was obtained for the mode with rotation (curve 2, figure 2), but the coating thickness was about an order of magnitude smaller than that in the mode without rotation. The preheating temperature did not influence significantly the thickness of the sputtered coating.

The investigation of coating microstructure by transmission electron microscopy and X-ray diffraction analysis revealed that the coating is amorphous irrespective of the deposition mode. Microdiffraction patterns taken from the coating show blurry halos (inset in figure 3a).
In all the modes used, the coating consists of silicon with a small concentration of argon (figure 3b). Apparently, a limited amount of argon ions or atoms were implanted into the silicon coating during plasma immersion ion implantation. No argon was detected in the substrate surface layer adjacent to the coating. The substrate structure did not change noticeably after coating deposition. As in the original material, the substrate structure was represented mainly by the high-temperature B2 phase with a small amount of the B19' phase.

Figure 3 shows, as an example, an AFM image of the coating surface formed in the mode with rotation at $U_s = 150$ V. Figure 5 illustrates how the surface roughness varied depending on the coating deposition modes (b). Compared to the initial roughness of substrates ($R_a \sim 0.03$ µm), the roughness of all specimens decreased after implantation and ranged from 7 to 15 nm, with less roughness on specimens with thicker coatings.

Figure 6 shows the dependences of the microhardness of the studied specimens on the indentation load. The microhardness of the specimens implanted in the modes without rotation was from 7 to 15 GPa at low loads (up to 10 g). According to the data from [6], the microhardness of silicon single crystals is about 10 GPa. Therefore, we can assume that the obtained values characterize the
microhardness of the silicon coating. The higher values obtained are evidently due to the amorphous structure of the coating. At higher loads, the indenter penetration depth is larger than the coating thickness and hence the microhardness values are the sum of the substrate and coating microhardness values. When the load was increased to 50 g, the microhardness of all specimens was close and equal to (4.0±0.2) GPa, which is slightly higher than the microhardness of the original uncoated nickel titanium substrates (2.65 GPa).

Figure 4. AFM image of the coating surface formed in the mode with rotation at $U_s = 150$ V.

Figure 5. The roughness variation depending on the coating deposition modes.

Figure 6. Curves of microhardness vs. indentation load for specimens coated in the mode without at different values of $U_s$.

Figure 7. Curves of microhardness vs. indentation load for specimens coated in the mode with rotation at different values of $U_s$.

For specimens implanted in the mode with rotation (figure 7), the coating thickness is much smaller, due to which the indenter penetration depth is larger than the coating thickness even at low loads (up to 10 g). The microhardness of these specimens ranged from 3.8 to 4.4 GPa. The microhardness measurement results suggest that the implanted specimens represent a system of a hard coating on a soft substrate.

Scratch tests revealed that the preheating temperature had the greatest influence on the adhesion characteristics of the sputtered coatings. At $T_{heating} \geq 200°C$, the first cracks in the coating of specimens implanted in the modes with rotation appeared at the indentation load of ~ 20 N (figure 8). The first
delamination areas were observed at a load of ~ 25 N. Noteworthy is that the coating was not separated from the substrate, but the coating material delaminated, which indicated good adhesion between the coating and the substrate. Probably, the delamination of more than 1 µm thick coating was promoted by internal stresses that arise during cooling from the coating formation temperature. At $T_{\text{heating}} = 75^\circ\text{C}$, the coating delaminated as early as at the initial stage of loading (figure 9).

Figure 8. SEM images of the indentation track on scratched specimens implanted in the modes without rotation at $U_s = 150$ V and $T_{\text{heating}} = 200^\circ\text{C}$. The arrow shows the indentation direction.

Figure 9. SEM images of the indentation track on scratched specimens implanted in the modes without rotation at $U_s = 600$ V and $T_{\text{heating}} = 75^\circ\text{C}$.

Thinner coatings sputtered in the modes with rotation at $T_{\text{heating}} \sim 300^\circ\text{C}$ had no visible traces of delamination, but they cracked under sufficiently high loads (more than 30 N).

4. Conclusion

- Using the PIII&D technique, it is possible to coat a nickel titanium substrate with an up to 3 µm thick amorphous silicon coating with a microhardness of 10–15 GPa.
- The main technological parameter affecting the coating thickness is the time of deposition. The magnitude of the bias voltage $U_s$ also affects the coating thickness: with increasing $U_s$ the coating thickness decreases, but its effect is by an order of magnitude lower than that of the deposition time.
- The main technological parameter that determines the coating adhesion is the preheating temperature of the nickel titanium substrate. When the preheating temperature is below 200°C, the sputtered coating has low adhesion and delaminates during cooling after PIII&D.
- The obtained results can be useful in selecting appropriate technological parameters to provide the necessary properties of silicon coated products, in particular, medical implants.

Acknowledgments
This work was supported by Russian Foundation for Basic Research and the government of the Tomsk region of the Russian Federation (grant No. 18-48-700013), and the Fundamental Research Program of the State Academies of Sciences, line of research III.23.2.2.

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