Formation of the silicon coating on the NiTi substrate by magnetron sputtering

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Abstract. The paper studies the regularities of silicon coatings formation on a substrate of an alloy based on nickel titanium using the radio-frequency (RF) magnetron sputtering method. It is shown that the use of the RF magnetron sputtering method allows making a silicon coating with a thickness more than 6 μm. It is determined that treatment time has the main influence on the thickness of a coating. The magnitude of the RF-power level of magnetron sputtering has a smaller effect on the thickness of the emerging coating.

1. Introduction
There are many reasons of death in the world and atherosclerosis is one of the main. Atherosclerosis is a chronic disease of blood vessels. There is deposition of lipids and growth of fibrous fibers. This triggers narrowing of vessels lumen and circulatory disturbance as a result. The main way of lumen recovery for stenotic (narrowing) vessel is stenting. Stenting is a surgical operation, which deals with placement of stent inside the area of narrowing. Stent is special construction with frame and its role is to regain lumen vessel. Several generations of stents are invented and applied. For today, the primary efforts are aimed at making stents, which can not only recover the lumen but also prevent possible complications, for example, restenosis (repetitive narrowing of vessels). The decision of this problem is gradual immersion of drugs into the area of stenting. This type of stents is called drug-eluting stent (DES) [1]. At this time, the stents are covered with biodegradable polymer with drug, which dissolves gradually in vessel therefore the drug releases. Although there are some problems with this method. Degradation speed of polymers is not constant and depends on many factors; because of that drug releasing is hard to control. In addition, during decaying polymers accumulate decomposition products, which can trigger immune response and restenosis [2]. Therefore, there is increasing interest in the development of a new type of stents that can provide the desired release time of the drug, but do not contain a polymer. One possible solution is to create a container material based on silicon. Porous silicon particles are considered as a promising tool for the delivery of drugs to various organs and tissues [3, 4]. The authors of this work consider the possibility of creating a container material for medicines on the surface of stents in the form of a porous silicon layer [5].

This paper considers silicon cover creation on model samples surface for the next formation of porous structure. Radio-frequency (RF) magnetron sputtering was chosen for making covers. The method has wide application for obtaining diverse coatings and allows to sputtered dielectrics.
2. Experimental equipment and research technique

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 mm² and thickness 1 mm, which were then mechanically ground and electrolytically polished. X-ray diffraction studies were carried out at room temperature on a DRON-7 diffractometer using CoKα radiation (Fe filter) and symmetric (Bragg-Brentano) and asymmetric schemes. Deposition of Si on the surface of model nickel titanium specimens was performed by RF magnetron sputtering. The distance between substrate and target was 70 mm. During the coating deposition, the working argon gas pressure was 0.7 Pa. Targets of silicon of 99.999% purity were used for the deposition of a silicon coating. To determine the possibility of controlling the thickness of coatings based on silicon, the following modes of the RF magnetron sputtering were chosen (table 1).

| Modes (№) | RF-power level, P (W) | Time, t (min) |
|-----------|----------------------|--------------|
| I         | 250                  | 120          |
| II        | 250                  | 15           |
| III       | 150                  | 15           |
| IV        | 100                  | 15           |

The surface morphology and chemical composition of the surface layer was examined using an EVO 50 scanning electron microscope (Zeiss, Germany) with an INCA energy dispersive spectrometer. The surface roughness of the deposited coatings was determined using a New View 6200 interference profilometer (Zyga, Germany).

3. Results and discussions

Surface morphology after application of silicon has some differences for the modes (figure 1). The results show (figure 2a) that islet structures are formed on the surface of the samples treated under mode I, uniformly distributed over the entire surface of the sample. The rest of the surface remains relatively smooth. The surface of the samples processed by modes III and IV has a morphology similar to the morphology of the initial samples (figure 2b). The samples obtained by mode II have a morphology similar to both the samples obtained by mode I and the samples obtained by modes III and IV.

The results of electron micro probe analysis showed the presence of titanium, nickel and silicon. Depending on the deposition mode, the concentration of silicon differed due to the thickness of the sprayed coating. The results of electron micro probe analysis depending on the deposition mode are shown in table 2. The thickness of the layer (h) for all samples was measured on the cross section of the samples. Figure 3 shows the dependence of the silicon concentration on the deposition mode and, accordingly, the thickness of a coating. The x-ray generation zone in the electron micro probe analysis has a depth of 5–7 µm, in the case where the thickness of the coating is less than these values, the contribution to the results of electron micro probe analysis will be given by the substrate elements, in our case titanium and nickel. Therefore, the smaller the thickness of coating, the greater the concentration of substrate elements.

The roughness of obtained coatings was measured in dependence on sputtering mode (figure 4). The results show that roughness has closed values in spite of difference in surface morphology (figure 1). In all probability, this is because of that if coating thickness is more 6 µm, sputtered silicon morphology dominates initial samples morphology completely and roughness corresponds to formed coating. The layer thickness of III and IV modes samples is comparable to geometric parameters of initial samples and because of that repeats their morphology.
The mode I samples diffractogram show very blurred peak (figure 5). The peak location correspond the reflex location (331) for silicon. The calculation of interplanar distance for the maximum of this pick was a little more than tabular value for silicon lattice. This may be due to amorphous structure. X-ray diffraction analysis of samples obtained by II–IV modes did not reveal any reflexes even with the use the method of the small-angle grazing incidence. This is due to the small thickness of the coatings.

Figure 1. SEM images of samples surface morphology after silicon sputtering: mode I (a), mode II (b), mode III (c), mode IV (d).

Figure 2. SEM images of samples surface morphology after silicon sputtering: mode I (a), mode IV (b).
Table 2. The elemental composition of the TiNi samples surface sample after Si deposition.

| Modes (№) | $h$ (μm) | Si (at.%) | Ti (at.%) | Ni (at.%) |
|------------|----------|-----------|-----------|-----------|
| I          | 6.7      | 98.7      | 0.5       | 0.8       |
| II         | 1.2      | 38.3      | 28.2      | 33.5      |
| III        | 0.63     | 17.2      | 37.3      | 45.5      |
| IV         | 0.47     | 11.2      | 39.5      | 49.3      |

Figure 3. The dependence between silicon concentration and a sputtering mode and obtained coating thickness ($h$).

Figure 4. Images of samples surface morphology after silicon deposition: mode I (a), mode II (b), mode III (c), mode IV (d).
4. Conclusion

- Using the RF magnetron sputtering method allows forming an amorphous silicon coating with thickness more than 6 μm on the NiTi substrate.
- The main technological parameter is the treatment time. The coating thickness increases when the power value increases, but this influence is minor in comparison with the treatment time.
- The obtained results allow formulating the requirement for technological modes, which will ensure needed properties of silicon coatings for the next porous structure formation.

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 program of fundamental scientific researches of the state academies of science, the branch III.23.2.2.

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Figure 5. The diffractograms obtained after silicon deposition with different modes.