Microstructure and properties of a silicon coating deposited on a titanium nickelide substrate using molecular-beam epitaxy equipment

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Abstract. The microstructure and properties of a silicon coating on a titanium nickelide substrate were studied to assess the possibility of using such a coating to improve the biocompatibility of medical implants. The silicon coating with thickness of 4.0±0.5 microns was applied to the TiNi substrate on a molecular beam epitaxy unit. The coating had a submicrocrystalline structure with a crystallite size of 0.1...0.2 microns, a developed surface, and high crack resistance.

1. Introduction
The most widely used shape memory alloys based on titanium nickelide have been found in medicine as implants. The use of alloys based on titanium nickelide makes it possible to simplify the design of implants, increase their service life, and facilitate operations to install such implants in the human body. However, the high content of toxic nickel ions is a reason for limiting the use of titanium nickelide implants. Various coatings such as metal, oxide, and nitride are applied to the implants to solve this problem. Some progress has been made on this path, and research in this direction continues [1–3]. For the successful application of such coatings, they must respond to a number of requirements for both medical and mechanical characteristics. In this regard, the development of new medical coatings and methods for their production is a relevant task.

One of the possible coating materials on titanium nickelide implants is silicon. Silicon has high biocompatibility, does not cause immune rejection, inflammatory, toxic and allergic reactions, and exhibits bioactive properties. There is a potential opportunity to make a silicon coating with nanoporous structure, which will allow it to be used as a container material for the placement of drugs [4].

Alloys based on titanium nickelide as a substrate were used in a limited number of studies [5, 6], where silicon coatings were created by magnetron sputtering, plasma-immersion ion implantation, deposition methods. In this paper, the idea of obtaining a silicon coating on titanium nickelide using molecular beam epitaxy equipment was implemented. The main advantages of using molecular beam epitaxy equipment are the production of coatings under very clean conditions of ultra-high vacuum, as well as the possibility of controlled heating of the substrate. Studying of their structure and properties to assess the possibilities of using the obtaining coatings in medical practice is a necessary step.
2. Materials and methods of research

Samples of electropolished polycrystalline alloy Ti49.2Ni50.8 (at. %) in the form of a square plate 35x35 mm with a thickness of 1 mm with an average grain size of d ≈ 20 microns without a pronounced texture were used as a substrate.

Silicon deposition was carried out on a high-vacuum two-chamber molecular-beam epitaxy unit "KATUN-100" [7].

A sample of titanium nickelide was placed on a silicon plate, which had a hole with a diameter of 20 mm in the center (figure 1).

![Diagram of silicon coating deposition on a Ti$_{49.2}$Ni$_{50.8}$ alloy substrate.](image)

**Figure 1.** Scheme of silicon coating deposition on a Ti$_{49.2}$Ni$_{50.8}$ alloy substrate.

The silicon plate in this case served as a mask. The silicon plate with a sample of titanium nickelide was placed in an epitaxy chamber and vacuum pumped to a pressure of about 10$^{-9}$ torr. Before deposition, the sample was heated to $T_{\text{heat}} = 500$ °C. The molecular beam of Si atoms was created by an electron beam vaporizer in the autocrucible mode. For this purpose, a target made of silicon with a purity of 99.999% was used. The deposition time was 240 minutes.

The studies were performed using optical microscopy (Axiovert-200MAT, Zeiss, Germany), scanning electron microscopy (LEO EVO 50 XVP, Zeiss, Germany), DM8 microhardness meter (AFFRI, Italy), interference profilometer New View 6200 (Zyga, Germany), and diffractometer Dron-7.

3. Experimental results and discussion

The resulting coating is a continuous film with a thickness of $h=(4\pm0.5)$ microns with complex protrusions located on it (figure 2 a). The average surface roughness of the coating was $R_a = 0.083$ microns. At the same time, the average height of the protrusions was quite large – about 0.5 microns.

The results of X-ray studies (figure 2 b) suggest that the coating has a polycrystalline structure with a crystallite size of 0.1...0.2 microns.

Figure 3 shows the dependences of microhardness on the load on the indenter for a sample of titanium nickelide with a silicon coating and without a coating. It can be seen that in the presence of the coating, the microhardness is higher than the microhardness of the titanium nickelide substrate.

At the same time, even at a load of 300 g, the coating does not crack along the diagonals of the indenter print (figure 4 a), only Hertz cracks are observed (figure 4 b).

The SEM-image of indenter track via scratch test of coating under load from 0 to 70 N is presented in figure 5. The estimations show that the first signs of delamination are observed when the load on indentor is 25-30 N. It indicates pretty high adhesion of the coating to a substrate. It is also indicated by the fact that there are the significant areas with non-delaminated coating on the track surface. Moreover, EDS show the presence of more than 10 at.% of Si even in areas that appear visually to be free from the
coating. It can be suggested that there is the diffusion of Si into NiTi lattice while the process of coating. The shape of delaminating flakes allows us to surmise about brittle fracture of the coating.

Figure 2. SEM-images of the surface of a silicon layer on a TiNi substrate (a) and a fragment of the X-ray spectrum of a TiNi sample with Si coating (b).

Figure 3. Dependence of the microhardness on the load on the indenter of a titanium nickelide sample with or without a silicon coating.

Figure 4. SEM-image of the indenter print at a load of 200 g (a) and the Hertz cracks (b).
4. Conclusions
Using molecular beam epitaxy equipment, a continuous silicon coating with a thickness of up to (4±0.5) microns on a polycrystalline TiNi substrate was obtained. The silicon coating has a submicrocrystalline structure with a crystallite size of 0.1-0.2 microns and has high crack resistance.

The obtained results allow us to express confidence about the possibility of using such coatings on medical implants.

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