Formation of biocompatible surface layers depending on the sputtering distance

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Abstract. Nano- and micro-dimensional surface layers of silver and tantalum on flat and wire NiTi substrates by the method of magnetron sputtering in vacuum were produced. The structure and composition of the samples were determined using SEM and Auger spectroscopy. With an increase in the sputtering distance, the thickness of the surface layers decreases, and the thickness of the transition layer and the dependence of the thickness change as a whole depend on the nature of the sputtered substance.

1. Introduction

Methods of physical vapor deposition make it possible to quickly and efficiently produce thin films of a diverse nature in a short time on virtually any substrate. Among other things this technology can be successfully used in the formation of medical composite materials that need to have complex properties, combining only the required characteristics of classical materials – for example, for the production of noninvasive stent implants designed to restore the patency of hollow parts of the cardiovascular, excretory, digestive and respiratory systems [1]: biomechanical compatibility and shape memory effect of titanium nickelide [2] with high resistance to dissolution in aggressive media, radiopaque and nontoxicity of tantalum [3–4] and silver (also exhibiting antitumor and antibacterial action) [5]. At the same time, the parameters of the resulting composites depend on a number of process conditions that can be conveniently varied over a wide range. And the purpose of this work was to determine the influence of the sputtering distance on the parameters of the layers being formed.

2. Materials and methods

Layered composites were produced by magnetron sputtering in argon at residual and working pressures of $\sim 4 \cdot 10^{-4}$ and $\sim 0.4$ Pa, respectively. The substrates were ion etched: surface cleaning, activation, and polishing through argon ion bombardment. Under any conditions, the substrate surface temperature did not reach 150 °C.

The surface layers were produced in the following conditions: direct current magnetron, $I \sim 865$ mA, in the case of silver layers $U \sim 830$ V, in the case of tantalum layers $U \sim 400$ V; sputtering time $t = 30$ min, the distance from the target to the substrate was 40–160 mm. To examine surface morphology and obtain composition–depth profiles, we used a TESCAN VEGA II SBU scanning electron microscope equipped with an INCA Energy energy-dispersive spectrometer system, and a
JEOL JAMP_9500F Auger electron spectrometer in combination with ion etching through argon ion bombardment at 30°.

3. Results and discussion
Externally, the surface layer repeats the substrate morphology. At small distances surface micro-defects appear as point depressions (figure 1), recalling effect of high bias voltage and ion implantation [6–7], which is correlated with a more intense flow of the sprayed material reaching the surface of the substrate, in comparison with larger distances.

![Figure 1](image1.png)

**Figure 1.** Morphology of the silver surface layer at a distance of 40 mm.

Researches of regularity of structure change of surface layers have shown, in general, identical results (figure 2): to 20 nm in depth from a surface the layer is enriched with oxygen, surface layer only of tantalum or silver, a transition layer (where the oxygen content is also increased and elements of the deposited layer and the substrate are contained) and the volume of the substrate itself lie deeply.

![Figure 2](image2.png)

**Figure 2.** Composition of the composite with a silver surface layer on a titanium nickelide substrate obtained at a distance of 150 mm.
On the one hand, with distance increasing at other equal conditions the thickness of the surface layer naturally decreases (figure 3) because larger volume of the sputtered substance is scattered away from the substrate; on the other hand, the thickness of the transition layer increases, which can be explained by a more intense flow of the sputtered substance at a shorter distance, uniformly but faster filling the surface and less diffusing into the substrate; and the total thickness of the layers eventually reaches a certain plateau, practically unchanged when the distance is more than 80–90 mm. Since the presence of a substantial transition layer is a presumable reason for the good adhesion of a new surface to the substrate [3, 4, 6], the surface layer must be adjusted to the mechanical properties of the substrate, and also considering the microdefects of the surface at small distances, the distances from the target to the substrate in the range of 100–150 mm are more optimum.

![Figure 3. Change in the tantalum surface layers thickness as a function of the distance between the target and the substrate.](image)

In contrast to tantalum, where the appearance of the surface layer thickness curve completely corresponds to the calculated models [7], in the case of a silver layer two plateaus are observed (figure 4): almost constant thicknesses at small sputtering distances can be attributed to saturation of the surface at high intensities of flux falling on the substrate. Also, unlike the previous case, both the surface layer and the transition layer are thinned with increasing distance, because a smaller volume of substance reached its goal, but the intensity of the flow did not affect the formation of the transition layer.

Formation of layers on the side that is opposite to the sputtered flow was noted. In this case, the structure and patterns of these layers changes are analogous to the straight side, but every 10–15 times thinner (figure 5).

4. Conclusions
Nanoscale and microscale layered composites with surface layers of silver and tantalum on flat and wire NiTi substrates were produced by vacuum magnetron sputtering. The presence of the transition layer that contains both substrate and target elements and presumably provides high adhesion of the surface layer to the substrate has been demonstrated.
The morphology of a new surface repeats the substrate state regardless of the sputtering conditions. Our results demonstrate a nonlinear increase in the thickness of the growing surface layers with decreasing sputtering distance under otherwise equal conditions. But the thickness of the transition layer and the dependence of the thickness change as a whole depend on the nature of the sputtered substance.
It has been shown that, at distances of 40–160 mm, insignificant deposition on the substrate side that is opposite to the sputtered flow is observed, with the thickness of formed layers also depending on the distance between the target and the substrate.

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