Investigation of the thermal stability of titanium nickelide tantalum coating using photometric analysis of structural images

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Abstract. The paper considers the thermal stability of tantalum coatings on TiNi (titanium nickelide or nitinol) used in medicine (especially in endovascular surgery) and having their own characteristics. A method is proposed to control magnetron sputtered tantalum film coatings on titanium nickelide — a method of photometric analysis of structural images (PASI).

1. Introduction
The paper considers the thermal stability of Ta coatings on TiNi alloy (titanium nickelide or nitinol), used in medical devices for endovascular surgery. Nowadays titanium nickelide is widely adopted in medicine as material for producing stents of various purposes. Tantalum coatings, that have their own thermo physical properties different from that of TiNi, are used to prevent the release of toxic Ni-ions from the bare titanium nickelide stents into human being tissues [1], thus improving biocompatibility of stents and other medical devices. Anyhow the problem of stability of such Ta-coatings has not yet fully explored. The paper proposed a new method to control magnetron sputtered Ta-film coatings on TiNi — a method of photometric analysis of structural images (PASI). This method has been successfully applied in examining the thermo physical properties of different materials [2-4].

2. Materials and methods
Titanium nickelide (49.5 at.% Ti - 50.5 at.% Ni) with magnetron sputtered tantalum coating was investigated. Previous to sputtering the TiNi flat bar was subjected to mechanical and ion-beam processing. The Ta surface layer was manufactured by magnetron sputtering using a Torr International facility (USA) [5] in an argon atmosphere at a residual pressure of about 6·10⁻³ Pa. The magnetron with a chemically pure tantalum target operated on power of 70% of the maximum possible (DC) at a sputtering distance of 150 mm from the substrate, maximum voltage was 1 kV, and a sputtering time of 30 min.

After sputtering Ta coatings on the TiNi sample were studied using high-temperature “Reichert” microscope in the vacuum of ~10⁻⁵ Pa; microstructure and state of the coatings was examined when heated step wise in situ from 20 to 500°C. When reaching the fixed temperature the surface coatings pictures were taken using a special digital-camera adaptor with ×200 magnification.
All the captured photographs were examined using a PASI developed in IMET RAS. The principle of operation, analytical capabilities and application examples were previously considered in [2-4]. It is significant that PASI compares the photographic images of the fragments of the surfaces under study and the spectra of the brightness of the reflection of visible light from them in a differential pattern. One of the images is a reference of the surface in the initial state, i.e. the image of a fragment of the surface of the object under study prior to exposure to an external factor capable of changing its structural state. The external factor is physical fields of different nature, intensity and duration of exposure. In this paper, the external influence is the temperature field.

3. Results and discussion

Figure 1 shows a typical comparison result — fragments of the surface of the investigated coating and the brightness spectra of the reflection $I$ from them at 20 and 500°C.

The spectra of the brightness of the visible light reflection is presented in the coordinates “spectral density $p(I)$ at the brightness of the reflection $I$ — the brightness of the reflection of visible light $I’$.” The spectral density of the reflection brightness $p(I)$ is the ratio of the number of pixels in a selected interval of the spectrum $n$ to the total number of pixels into which the image of a fragment of the surface of the object under study $N$ is split, i.e.

$$p(I) = \frac{n(I)}{N}.$$

The spectral density $p(I)$ varies from 0 to 1. The abscissa axis shows the luminance values of the reflection of visible light (reflection intensity) $I$ in arbitrary units measured on a scale in which the limiting cases of total light absorption are taken to be zero, and the case of total reflection of light from the surface taken as a unit. On the brightness spectrum of the reflection of visible light, you can select up to five intervals with different colors. The colors of the intervals can be transferred to the image of the fragment, thereby obtaining a picture of the distribution of areas that contribute to the reflection in the interval highlighted by the corresponding color. In figure 1 it can be seen that the heating of the coating leads to the shift in the maximum of the spectrum towards an increase in the reflection brightness.

Figure 2 shows the histograms of the distribution of relative areas $S(n)$ painted in the corresponding colors of the selected intervals $n(I)$ by their relative shares in the total surface of the fragment at 20 and 500°C. The change in the distribution of colored areas on the surface of the coating with increasing temperature is associated with the reduction of its roughness and with the change in the orientation of the surface fragments with respect to the incident beam of visible light as a result of the activation of diffusion processes. This is also evidenced by the change in the average size of structural fragments and their dispersion with increasing temperature (Table 1).

Table 1. Average sizes of structural fragments of the coating and their dispersion at 20 and 500°C.

| $T$, °C | Average size of fragments, µm | Dispersion of fragment sizes, µm |
|---------|-----------------------------|---------------------------------|
| 20      | 48.94                       | 31.42                           |
| 500     | 92.90                       | 44.63                           |

When heated, the very nature of the distribution of the structural fragments of the coating over its surface significantly changes due to an increase in the relative proportion of small fragments and the grinding of larger ones. This can be seen by considering figure 3a and 3b which shows the size distribution ($r$, pixels) of the coating fragments at 20 and 500°C.

Figures 4a, b show the change in spectral densities in the selected intervals of the spectrum in the temperature range of 20-500°C. From figure 4 it can be seen that in the intervals highlighted in red and blue in a number of temperature intervals there are sharp changes in the spectral densities, which are apparently associated with phase transitions.
Figure 1. Comparison of the surface fragments of the investigated coating and the brightness spectra from them at 20 (left) and 500°C (right).

Figure 2. Histograms of the distribution of colored areas surface coatings at 20 (a) and 500°C (b).

Figure 3. Size distribution of coating fragments at 20 (a) and 500°C (b).
Figure 4. Temperature dependences of the spectral density in selected intervals of the spectrum of the brightness of the reflection (the colors of the curves correspond to the color of the intervals); the dotted line shows the curves corresponding to the stage of cooling.

Figure 5. Microstructures of the Ta coating on TiNi under study at 20 (a), 40 (b), 60 (c), 100 (d) and 400°C (e). ×200.
Figure 5 shows the microstructures of the Ta coating on the titanium nickelide at the temperatures from 20 to 400°C; the images were taken in-situ in the working chamber of the metallographic microscope “Reichert” in vacuum. Neither cracking nor blistering (peeling and separation) of Ta coating can be observed even at 400°C (figure 5e).

4. Conclusions
A method for controlling stent coatings with a Ta film deposited by magnetron sputtering is proposed — a method of photometric analysis of structural images.

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