Influence of ion treatment in the production of thin multilevel surface layers

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Abstract. The regularities of the formation of titanium and tantalum multilayers with the use of magnetron sputtering and ion bombardment were investigated depending on the varied technological parameters. Metallic composite materials had a multilayer structure. The surface morphology at low radiation doses in the course of preliminary ion etching corresponds to the substrate surface morphology. With a long duration/energy of ion bombardment, a thin surface structure in the form of point depressions is observed, smoothed by a layer deposited from above, and the length of the layer and its crystallinity also increase. The transition layer ensures high adhesion of the surface layer to the substrate.

1. Introduction
Layered composites, which are widely used in electronics, optics, medicine, in the creation of structural and other functional objects, can be efficiently obtained using vacuum ion-plasma methods. In this case, the parameters of the layers obtained are directly related to the process parameters, which can vary over a fairly wide range: sputtering time, the relative position of the sputtered target made of the material of the formed layer, and the substrate on which the layer is applied, in space, which determines the intensity of the effective flow equal to the power of the process, the nature of the sprayed material and the condition of the surface on which it is applied, incl. determined by the phase composition of this surface. And in the case of a multicomponent spraying system, the variability of the results obtained increases many times. At the same time, the formation of new materials with a complex structure contributes to the versatility of products made from them.

In [1-2] it was indicated that (110) is the lowest-energy lattice for bcc materials (α-Ta) and provokes the formation of the same structure on itself. Being the zone of nucleation of a new surface, the surface of the substrate determines the nature of the formation of its structure. It was shown that beta tantalum is formed on amorphous carbon-containing or oxide surfaces (the natural state of titanium and silicon in an oxygen atmosphere or glass), and for example, alpha forms on titanium without natural oxide or TaN [1-5].

For example, the formation of a two-layer system "Ta - Ti - substrate made of glass or silicon" was studied with and without intermediate vacuum interruption (placing freshly deposited titanium in an
oxygen-containing atmosphere) [4]. In the first case, titanium oxide was always formed and promoted the formation of beta tantalum. Without interrupting the vacuum, the beta (cubic lattice) and alpha (hexagonal) forms of titanium were formed on glass and silicon, respectively, and α-Ta on them. β-Ti and α-Ta have a similar type of crystal lattice (110); the lattice parameters of α-Ti coincide with the parameters of the hexagonal lattice composed of the atoms of the nearest α-Ta planes. In these two cases, titanium grains can serve as nucleation nuclei for alpha Ta crystallites. The amorphous oxide layer differs too much in structure from the crystal lattice of α-Ta and this difference leads to the formation of β-Ta. And although the presence of oxygen on the substrate surface did not always prevent the formation of α-Ta, it is still believed that it promotes the formation of β-Ta.

The work was aimed at investigating the regularity of the formation of titanium and tantalum multilayers using magnetron sputtering and ion bombardment, depending on the varied technological parameters, as well as determining the characteristics of the materials obtained.

2. Materials and methods

Glass plates were used as the basis (substrate) of the formed composite materials. To clean, activate and polish the surface of the substrate and the intermediate composition, bombardment with argon ions with discharge parameters $U_e = 900-1200$ V, $I_e = 70-150$ mA - preliminary ion etching was carried out. To determine the effect of the underlying surface on the structure of the formed layer, preliminary ion etching was carried out with an increase in the time and power of the irradiation.

Chemically pure titanium and tantalum were used as the material of the surface layer. Surface layers of tantalum were formed on a previously deposited titanium layer obtained under the same conditions on a glass plate substrate after ultrasonic cleaning in alcohol, distilled water, and drying.

The creation of metal composite materials was carried out by the formation of surface layers using a magnetron at a direct current (~ 865 mA) at a voltage of ~ 400 V in an argon gas atmosphere at an operating and residual pressure of ~ 0.4 and 4x10^-4 Pa, respectively, in spraying time of 30 min at a spraying distance of 250 mm. The points of analysis on the surface of the sample facing the sprayed flow were arranged in an arbitrary order so that both the middle and the edges of the formed plane were covered. The temperature on the surface of the substrates did not exceed 150 ° C.

The morphology and layer-by-layer elemental composition (including the use of cross-sectional sections) of the surface of the materials were investigated on a TESCAN VEGA II SBU scanning electron microscope (SEM) equipped with an INCA Energy attachment for energy dispersive analysis, an electronic Auger spectrometer JAMP-9500F from JEOL in combination with ion etching with argon bombardment at an angle of 30 ° and a GDS 850A atomic emission spectrometer with a high-frequency AC source. The X-ray diffraction spectra of the coating samples were recorded on an UltimaIV X-ray diffractometer (Rigaku, Japan) with a vertical goniometer and a D / teX high-speed semiconductor detector in CuKα radiation by the Breg-Brentano method, as well as oblique shooting with a fixed angle of rotation of the X-ray tube. Phase analysis of the coating samples was performed in the PDXL software package using the ICDD database.

3. Results and discussion

Composite materials were obtained: an oxide layer (an area at the very boundary of a solid with the surrounding gas medium, free from substrate elements, where the titanium or tantalum content is not at the maximum, about 10 nm thick) - a surface layer of the deposited substance 1 (usually tantalum) - transition layer containing both deposited elements - sublayer of deposited substance 2 (usually titanium) - transition layer containing elements of both the sublayer and the base - the base "(Figure 1). Figure 3 clearly shows the deposited thin surface area, there is high adhesion, because, with brittle fracture of the sample, no peeling of the new surface from the substrate is observed. When tantalum is deposited on a titanium sublayer, a smoothing of the surface relief is observed (Fig. 4). The results of energy dispersive analysis of samples of multilayer composite material are shown in Figure 5.

Regardless of the irradiation regime of the glass plate, titanium was deposited in the form of the beta phase. Figure 2 shows the X-ray diffraction patterns of a single-layer composite with a titanium
surface layer. Because thin films are obtained, the amorphous substrate makes a significant contribution, and the only crystal line at ~ 35° can be the (100) α-Ti line in the presence of the strongest texture (100) of the surface.

Figure 6 shows how the surface morphology of the deposited layer changes depending on the degree of ion irradiation during the preliminary etching of the surface to be deposited. At low power and duration, the surface layer externally repeats the substrate morphology (Figure 6, a). Prolonged ion bombardment provokes a uniform distribution of point depressions [6]. Unexpectedly, an increase in the fraction of deposited titanium was observed depending on the degree of irradiation of the glass substrate (Fig. 7).

During the deposition of tantalum on titanium, an increase in the degree of crystallinity of the film was observed with an increase in the dose/time of ion etching of the titanium sublayer. In the sample, after 10 minutes of etching at 63 W, an amorphous phase is observed with the 1st and 2nd halo maxima at ~ 40° and ~ 67°, and a barely distinguishable line at ~ 56°, possibly being the line (200) β-Ti (or Ta, or their alloy). It should be noted that for the samples under consideration, the total thickness of the deposited layers in which is about 200 nm.
crystalline lines of this sample in the sample become stronger after 45 minutes of etching, and after 80 minutes their strengthening continues and other lines appear, including a line above the 1st maximum of the halo at ~ 38°. Most of the lines are multiple orders of reflection of the first weak line by ~ 16°, which indicates a very strong texture of the initially precipitated phase crystals, which could be expected for epitaxial growth on a single crystal substrate.

Thus, we can observe that in the case of a sample with Ta the surface layer contains many α- and β-Ta peaks, which correspond to different crystal orientations - β (002), β (410), β (202), β (004), β (513), β (333), β (404), α (110), α (211) and α (220), etc., i.e. a highly textured complex structure is observed, which is insignificantly related to the initial structure of the substrate and the underlying layer, while the degree of crystallinity of the samples strongly depended on ion bombardment.

As in the case of the titanium layer, a slight increase in the thickness of the surface layer is observed as the duration/energy of ion irradiation of the surface of the underlying layer increases. This can be attributed to an increase in adhesion due to the activation of the surface by a high-energy flow.

![Figure 4](image4.png)

**Figure 4.** Surface morphology of a composite material with (a) titanium surface layer on a glass substrate and a tantalum (b) surface layer deposited on surface A

![Figure 5](image5.png)

**Figure 5.** Results of energy dispersive analysis of samples of multilayer composite material with tantalum and titanium surface layers
Figure 6. Surface morphology of a composite material with a titanium surface layer and a plate-like glass base after ion etching at a power of 63 W for: 2 min (a), 10 min (b), and 50 min (c)
Figure 7. Composition of the surface of a composite material with a titanium surface layer and a glass base after ion etching at a power of 63 W for: 2 min (a), 50 min (b).

4. Conclusions
The regularities of the formation of titanium and tantalum multilayers with the use of magnetron sputtering and ion bombardment are investigated depending on the varied technological parameters. Metallic composite materials had a multilayer structure "oxide layer - surface layer of the deposited substance 1 - transition layer containing both deposited elements - sublayer of deposited substance 2 - transition layer containing elements of both the sublayer and base - base".

The surface morphology at low radiation doses in the course of preliminary ion etching corresponds to the substrate surface morphology. With a long duration/energy of ion bombardment, a thin surface structure in the form of point depressions is observed, smoothed by a layer deposited from above, and the length of the layer and its crystallinity also increase. The transition layer ensures high adhesion of the surface layer to the substrate.

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