Formation of alpha and beta tantalum at the variation of magnetron sputtering conditions

E O Nasakina¹, M A Sevostyanov, A B Mikhaylova, A S Baikin, K V Sergienko, A V Leonov and A G Kolmakov

Institution of Russian Academy of Sciences A.A. Baikov Institute of Metallurgy and Material Science, Leninsky Avenue, Moscow, Russia

E-mail: nacakina@mail.ru

Abstract. Nano- and microdimensional surface layers of α and β tantalum on flat NiTi, Ti, glass, etc. substrates were created. Structure and composition of samples were defined by SEM, AES and x-ray diffractometry. With increase in deposition time surface layer thickness not linearly increases. The transitional layer providе high adhesion of a surface layer to a substrate. Irrespective of summary sputtering time the β phase is formed in the beginning and at sputtering time more than 20 min on it α tantalum is deposited, while temperature remains below 150 °C. Keywords: composite materials, surface layer, tantalum, alpha and beta phase, nitinol, corrosion resistance.

1. Introduction
Development of the composite materials allowing to effectively combine desirable operational characteristics of the modified surface layers and the main material at the present time is perspective in many areas of human activity: in optics (filtering, reflecting, absorbing, etc. environments), electronics (conductors, semiconductors, dielectrics), mechanical engineering, building and household (tribological, durable, functional, protective, resistant to action of aggressive environment, decorative and other coatings), medicine (biocompatible), etc. An effective method for layered composites formation is physical vapor deposition, including magnetron sputtering, since at relatively small expenditure of time and resources it allow to receive qualitative products of various nature and geometry and control properties of the created materials. In particular as a new surface on a substrate from other material tantalum is interesting due to high corrosion resistance, radiopacity, conductivity, wear resistance, etc. Thus in case of thin films of tantalum, according to literary data, formation of both alpha and beta phases, which differ in properties, is possible [1-19].

2. Materials and methods
Creation of layered composites was carried out by formation of tantalum surface layers on nitinol, glass, titanium and copper substrates (basis) with use of a magnetron sputtering method. Working and residual pressure in the vacuum chamber was 0.4 and 4×10⁻⁴ Pa, respectively. For cleaning, activation and polishing of a substrate surface bombarding by argon ions was carried out. The magnetron worked at a direct current at ~ 850 mA, ~ 700 V, deposition distance 200 mm and various time. Phase structure

¹ To whom any correspondence should be addressed.
of the deposited films was characterized by the x-ray diffractometer "Ultima IV" of Rigaku firm with Cu Kα radiation. The surface morphology and layer-by-layer element structure research was investigated by the TESCAN VEGA II SBU scanning electronic microscope with an INCA Energy energy dispersive spectrometer system and JEOL JAMP-9500F Auger spectrometer in combination with ion etching through argon ion bombardment at 30°.

3. Results and discussion

Figure 1 shows dependence of tantalum surface layer thickness from time of magnetron sputtering on a nitinol substrate. Increasing the sputtering time to 20 min increased the thickness of both the surface layer (consisting only of the deposited substance) and the transition layer (containing elements of both the substrate and deposited substance). Further increasing the sputtering time caused an increase only in the thickness of the surface layer and up to 30 minutes more intensively, than at bigger time. This situation remains at all used materials. It occurs, most likely, because at the beginning of layers formation atoms and ions of deposited substance, overcoming a sputtering distance, collides with particles of working gas, with each other and with substrate surface and don't appear at each site of its surface in equal volume and at the beginning interact with it chaotically and unevenly (including with the sites which are already was formed by the previous deposited particles). And further (at increase of sputtering time, and so of the time of influence on a surface) particles continue to collide, mixing up, try to reach thermodynamically more advantageous position and state, and more uniform distribution of the deposited substance at the surfaces takes place. By consideration of cross section of samples it is visible that at smaller time of a sputtering the surface shows big heterogeneity.

![Figure 1. Dependence of surface layer thickness on time of magnetron sputtering on a nitinol substrate](image)

The X-ray diffraction patterns of our samples with nitinol basis (figure 2) demonstrate that depending on sputtering time tantalum is formed in two various crystal states – an alpha (a cubic crystal lattice) and a beta (a tetragonal lattice with the small content of oxygen) [3 – 14].

In the case of a sample with a Ta surface layer obtained by sputtering for 5 min, the major phase was nitinol, but many peaks β-Ta in the 2-theta range from 33 to 81 degrees were observed that also corresponds to various crystal orientation. In the composites formed after sputtering for 10 and 20 min, β-Ta with O were a major phase, and only 2 main peaks were observed, but nitinol was also present. After 29 min, the strongest peak was that from α-Ta, and there were β-Ta with O and nitinol, due to the averaging of results over the entire probing depth; at further increase in time α-Ta dominated, and very weak peaks of β-Ta and nitinol were observed. Thus it turns out that irrespective of summary sputtering time the beta phase is formed in the beginning and at sputtering time more than
20 min on it alpha tantalum is deposited. The same regularities are observed in case of other substrates which are united by availability of oxygen in a surface.

Several theories of tantalum formation in α or β phase is developed which are generally connected with working temperature and pressure (defining mobility and energy of atoms) and the substrate nature. However different authors achieve often contradictory results.

It is noted that the alpha phase is formed at temperatures more than 400 °C promoting deposited atoms mobility increase: initially at heating of a substrate or as a result of the annealing following sedimentation (then deposited β-Ta transforms in α-Ta) [1, 3, 6, 11]. However at a temperature about 400-500 °C also β phase received (for example, in the form of the particles distributed in α) [3, 6], and α is also formed without heating [9, 12]. It is specified that with growth of temperature the size of grains, impurity amount in a surface layer (for example, the dissociation of oxides enhanced, i.e. the O contents lowered) and its amorphousness decreases.

Presence at the working atmosphere of the high oxygen content according to [13] leads to fast formation of oxides and, therefore, promotes formation of a tantalic layer in a beta state whereas in [12] oxygen environment did not prevent the formation of alpha tantalum. At a deposition on silicon and glass substrates in [10, 13, 14] 0.5 - 0.7 Pa sputtering pressure led to α-Ta formation and smaller or bigger pressure - β-Ta, but in [12] already at 0.28 Pa α phase was formed.

In [14] also alpha tantalum formed at 0.3 and 1.4 Pa pressure, but at sputtering on earlier deposited α-Ta (110) layer. Also it was specified that (110) is the most low-energy lattice for BCC materials and provokes formation on itself of the same structure. Being a zone of a new surface nucleation the substrate surface specifies the character of its structure formation. It was shown that on amorphous carboniferous or oxidic surfaces the beta tantalum is formed, for example, on titanium without natural oxide or TaN substrates the α-Ta is formed [7, 9, 11, 14].

And though availability of oxygen on a substrate surface not always prevented the formation of α-Ta, nevertheless it is considered that it promotes formation of β-Ta. Therefore its creation in this work in an initial time period on all substrates is quite expected, despite ionic etching.

In [11], as well as in this research, it was shown that longer time promotes layering of α-Ta on earlier formed β-Ta, but authors connected it with a considerable warming up of a surface (more than
350 °C) whereas in this work temperature of a substrate didn't rise higher than 150 °C and so couldn't influence formation of alpha phase. Thus it is noted that α-Ta is thermodynamically more stable phase. Therefore it is possible to assume that the alpha phase is formed in this work with increase in time as a result of more uniform filling of a surface (since with growth of sputtering time possibility of particle choice of more suitable state and position increases) and also because of a possible local surface heating and absence on the surface of an oxygen which is already expended for formation of an underlayer β-Ta.

4. Conclusion
Nano- and microdimensional surface layers of α and β tantalum on flat NiTi, Ti, glass, etc. substrates were created. With increase in deposition time surface layer thickness not linearly increases. The transitional layer provide high adhesion of a surface layer to a substrate. Irrespective of summary sputtering time the β phase is formed in the beginning and at sputtering time more than 20 min on it α tantalum is deposited, while temperature remains below 150 °C.

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