

## Structure of metal-oxide Ti-Ta-(Ti,Ta)<sub>x</sub>O<sub>y</sub> coatings during spark alloying and induction-thermal oxidation

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**Abstract.** The study focuses on combined spark alloying of titanium and titanium alloy surface and porous matrix structure oxidation. The metal-oxide coatings morphology is the result of melt drop transfer, heat treatment, and oxidation. The study establishes the influence of technological regimes of alloying and oxidation on morphological heterogeneity of metal-oxide system Ti-Ta-(Ti,Ta)<sub>x</sub>O<sub>y</sub>.

### 1. Introduction

Titanium and tantalum are applied in medicine due to their high biocompatibility. Previously, these metals were mainly used for the production of corrosion-resistant construction components operating at high temperatures. Particular attention was paid to the study of the oxidation kinetics, weight gain, chemical and phase transformations occurring in the microstructure [1]. The effect of prolonged (up to 16 hrs) heat treatment in oxygen, argon-oxygen and nitrogen-oxygen mixtures within the temperature range from 800 to 1400 °C was studied. It was concluded that a mixture of oxides of titania TiO<sub>2</sub>, tantalum pentoxide Ta<sub>2</sub>O<sub>5</sub>, etc. are formed on the surface.

The application of oxide ceramics based on Ta<sub>2</sub>O<sub>5</sub> in the form of coatings for endosseous implants, including the form of nanotubes, contributes significantly to the corrosion, biocompatible and osseointegrative qualities of these small metal items.

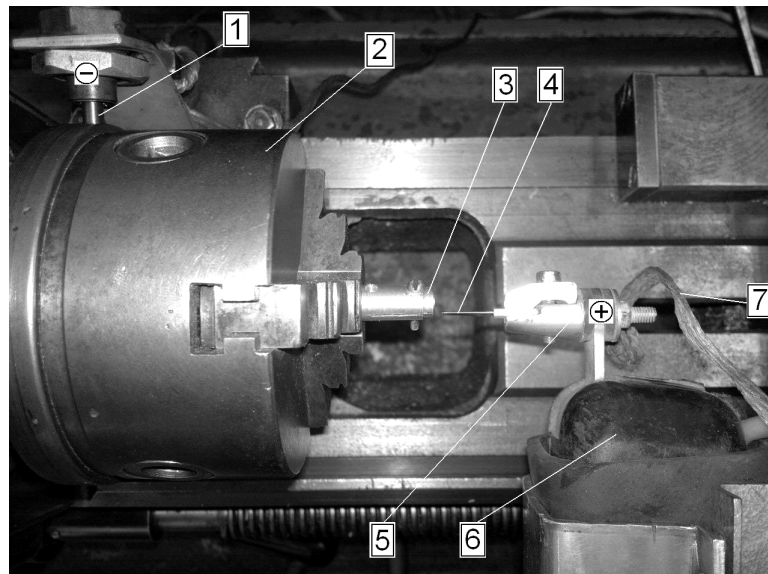
### 2. Methodology

Samples of commercially pure (cp) titanium VT1-0 and titanium alloy VT16 were subjected to electro-spark alloying with tantalum and subsequent oxidation with induction heat treatment (IHT).

Spark alloying is carried out in pulsed mode with the following parameters: pulse duration within 100 ms, current amplitude from 0.8 to 2.2 A, and pulse energy ranging from 0.01 to 0.1 J [2]. The technological regime is the current varying from 0.8 to 2.8 A. In this work the effect of 3 steps of current ranging was studied: 0.8, 1.5 и 2.2 A.

Main functional elements of the technological equipment for the production of metal heterogeneous coatings are shown on the screw-cutting lathe design and device for spark alloying surface modification "EFI-46A" (Figure 1).





**Figure 1.** Design of functional elements during spark alloying (top view).

The operating area includes 1 – slide bronze electrode; 2 – three-jaw chuck with the tool for sample attachment; 3 – titanium sample; 4 – tantalum electrode; 5 – electrode holder; 6 – cover of the electrode holder with low-frequency mechanical oscillator (100 Hz); 7 – copper conductor line.

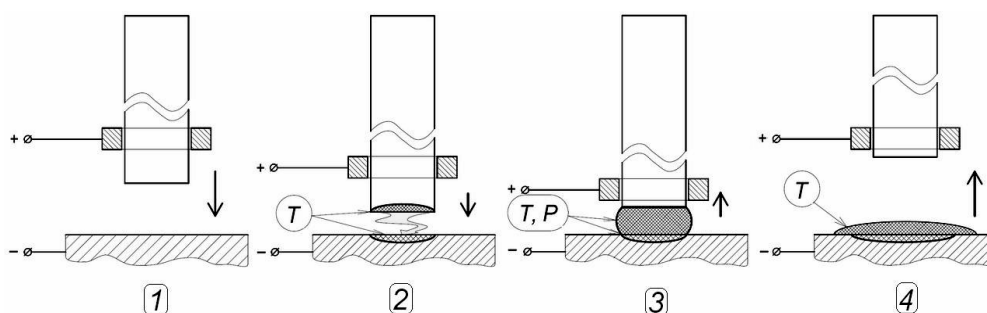
Further, the surface of the prepared samples is oxidized in the course of treatment with HFC. Maximum power consumption  $P_{\max}$  of the laboratory device for treatment with HFC during heating of the products with the geometry of this type is within 550 W, the frequency of the current in the inductor is  $90 \pm 2$  kHz; when it reaches a predetermined treatment temperature of 800 °C – power consumption  $P$  of the device equals 150 W. In the experiment the length of IHT was 30 and 300 s, which is associated with the probable appearance of nano-sized and submicron oxide crystals [3].

The surface morphology of the samples after the selected technological treatment is studied using scanning electron microscopy (SEM) in the micro- and nanoscale to understand the patterns of structure formation of the surface layer and coatings. SEM combined with energy-dispersive X-ray analysis (EDX) of chemical composition of samples is performed on "MIRA II LMU" with "INCA PentaFETx3" detector. Changes in tantalum and oxygen concentrations as well as other impurities measured in atomic percent (at.%) are studied in the areas of samples with various morphology.

### 3. Results

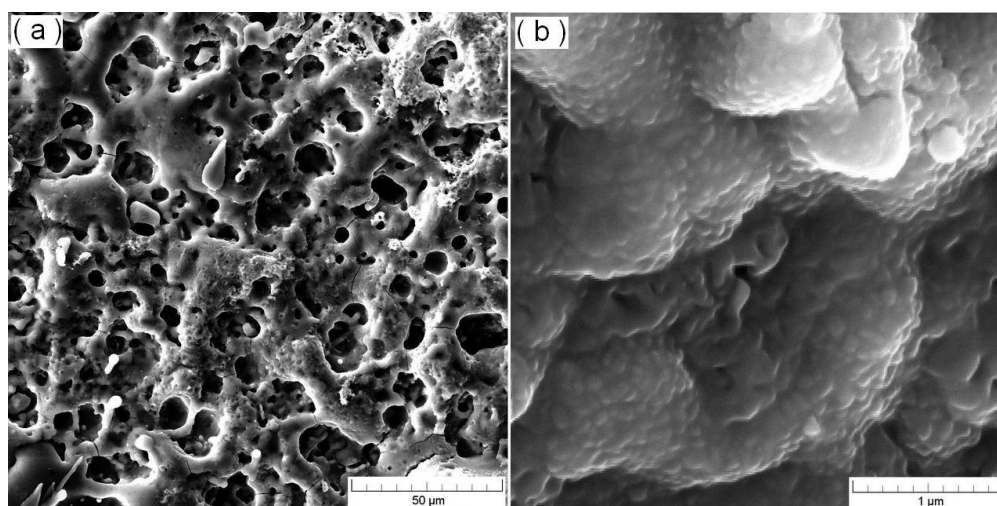
The deposition of the required conductive material (tantalum) on the surface of the metal substrate takes 4 main steps: 1 – convergence of the electrodes at a predetermined potential difference providing the interelectrode gap breakdown (IGB) in 5 to 300  $\mu\text{m}$ ; 2 – breakdown of the IGB and heat  $T$  required for melting of the contact parts of the electrodes; 3 – contact (short circuit mode) of the heated electrodes with the development of certain pressure  $P$  (impact); 4 – retraction of electrode-tool to form a single crystallized micro-ingot (drop) – coating splat (Figure 2).

The resulting tantalum coatings on titanium alloys are characterised by developed morphological heterogeneity of the surface, and their microstructure resembles the texture of plasma-sprayed thermal coatings [4]. When a current is 0.8 A the transfer of microdroplets occurs and a coating of splats with a large spread in size is formed as a result. This is associated with the fact that titanium surface has not enough time to warm up and contacting tantalum microdroplets start to splash across a colder titanium substrate.



**Figure 2.** The scheme of the formation of metallic coating during electro-spark alloying.

The increase in the current contributes to more efficient transfer of tantalum on the surface of titanium and more efficient heating of the titanium substrate to the visco-plastic state. As a result, the share of large splats of about 150–300  $\mu\text{m}$  increases in the coating. The best morphological parameters are formed at current of 2.2 A. During the interaction well heated materials of both electrodes are stirred intensively to form a homogeneous porous structure (Figure 3a).



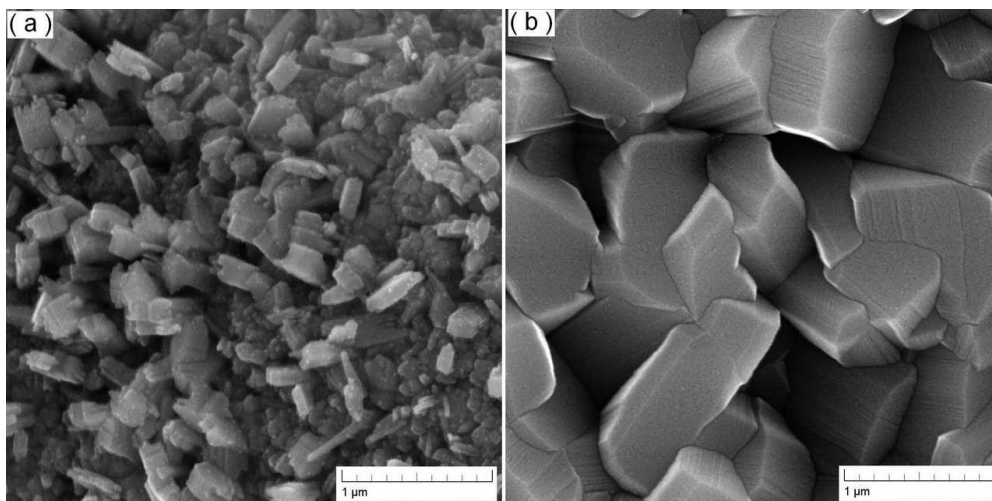
**Figure 3(a, b).** Morphology of a tantalum coating produced on titanium (a); nanostructure (b).

Crystallization processes of splats having different sizes are not the same. This contributes to significant differences in morphology in the nanoscale. Surface morphology of splats is characterized by the grains of 90 to 120 nm and their agglomeration of particles of about 200–300 nm (Figure 3b).

To change the structure and surface properties of titanium substrate alloyed with tantalum induction heat treatment (IHT) can be effectively used. Significant changes in the morphology of a titanium-tantalum system start at the temperature of 800  $^{\circ}\text{C}$ . During the short IHT of 30 s the splat surface is uniformly covered with oxide crystals (Figure 4a). Longer IHT within 300 s contributes to a significant increase in oxide crystals (Figure 4a).

To determine the probable phase state of the resulting metal-oxide  $\text{Ti-Ta}-(\text{Ti,Ta})_x\text{O}_y$  systems chemical elemental analysis has also been performed. Most detailed study has been given to the concentration of introduced alloying tantalum and oxygen saturation of the system with the formation of oxide crystals. The content of tantalum on the surface of titanium substrate ranges from 10 to 12 at.%, which corresponds to a monolayer of splats. When coatings of greater thickness (2–3 alloying cycles) are formed the tantalum concentration can reach 18–25 at.%. Further IHT contributes to

intensification of oxidation and oxygen concentration increases to 57–65 at.% at the short treatment of 30 s. Longer IHT within 300 s contributes to a slight increase in oxygen concentration and equals 65–69 at.%.



**Figure 4(a, b).** Nanostructure of Ti-Ta-(Ti,Ta)<sub>x</sub>O<sub>y</sub> system obtained after IHT on cp-titanium at different durations of treatment: 30 s (a); 300 s (b).

#### 4. Conclusions

Thus, the surface structure of samples of titanium after electric-spark alloying with tantalum and subsequent IHT is characterized by the formation of the coatings of Ti-Ta-(Ti,Ta)<sub>x</sub>O<sub>y</sub> system. These functional coatings are formed of nano-sized and submicron oxide crystals. The most pronounced nanostructure is formed at the short duration of IHT of about 30 s and is characterized by the size of nanograins of 60–90 nm, the concentration of tantalum is about 1.1–1.5 at.% and oxygen is at least 60–65 at.%.

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#### References

- [1] Park Y S and Butt D P 1999 *Oxidation of Metals* **51** 383
- [2] Koshuro V A and Fomin A A 2014 Proc. 10th Int. Vacuum Electron Sources Conf. and 2nd Int. Conf. on Emission Electronics (Saint-Petersburg) (Saint-Petersburg: IEEE) p 145
- [3] Fomin A, Dorozhkin S, Fomina M, Koshuro V, Rodionov I, Zakharevich A, Petrova N and Skaptsov A 2016 *Ceramics International* **42** 10838
- [4] Fomin A A 2015 *Handbook of Nanoceramic and Nanocomposite Coatings and Materials* (Oxford: Butterworth-Heinemann) p 293