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Structure and microhardness of bioinert coatings of Ti-Ta-N system

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Abstract. The coatings of Ti-Ta-N system have been obtained for the first time. Production of bioinert coatings of Ti-Ta-N system was realized by means of promising technique of electroexplosion spraying and subsequent electron-ion-plasma modification with nitrogen ions. Titanium of VT6 grade was used as a substrate for spraying of coatings. Electroexplosion spraying with use of tantalum foil leads to formation of tantalum coating on titanium substrate. Subsequent electron-ion-plasma modification with nitrogen ions results in synthesis of the following phases: TiN, Ta and β -Ti. Average microhardness values of the coatings formed vary from 449 kgf/mm² (E = 11.47 %) to 530 kgf/mm² (E = 10.02 %). Electroexplosion processing promotes the increase in titanium substrate microhardness near coating - substrate interface. In volume of titanium substrate the microhardness decreases to values corresponding to reference data. Irradiation of electroexplosive tantalum coating by electron beam with subsequent nitriding leads to homogenization of structure. Optimum mode of irradiation should be considered the one at powder density of electron beam of 0.5 MW/cm². At lower value of power density the electron beam melts the electroexplosion coating to insufficient depth. At higher values of power density the electron beam leads to boiling of the melted coating and formation of larger quantities of pores .These phenomena are caused by thermal and physical characteristics of titanium substrate.

1. Introduction

In modern medicine the metal implants for different purposes are widely used. Nowadays, metals and alloys free from toxic alloying elements of Al and V [1, 2] are employed as base materials for implants. About 70 - 80 % of medical implants are manufactured from bioinert metallic materials which are presented by stainless steels, cobalt alloys, commercially pure niobium, tantalum, titanium and their alloys [3, 4]. Metallic biomaterials are extremely important for recovery of damaged hard tissue, for improvement of patients' life quality [5, 6].

Material for bone implants should meet the requirements of biomechanical and biomedical compatibility with bone tissue [7, 8]. It is necessary for it that modulus of elasticity of the material being implanted to be approximate to that of bone tissue (30 GPa) that permits one to avoid a manifestation of so-called' stress-shielding effect' which shows itself in dissolution of bone in region of absence of mechanical load [9, 10]. Biomaterial should contain only safe components allowed for medical application and possess high corrosion resistance in organism's media [11, 12]. Among metallic biomaterials titanium and its alloys are the most preferable that is caused by their unique biocompatibility, weak toxicity, low coefficients of thermal expansion and heat conductivity, nonmagnetization and high specific strength relative to stainless steels [13, 14].

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Titanium and its alloys possess moderate modulus of elasticity (100 - 120 GPa) in contrast to steels (190 - 200 GPa) as well as low cost as compared to pure niobium and tantalum [15]. Disadvantage of titanium alloys is their corrosion in biological media being ac-companied by emission of heavy metals' ions which cause unfavourable electro-chemical reactions in organism and affect the compatibility of implant with surrounding tissues [16]. Applying the coatings to surface of metal implants allows this problem to be solved effectively [17]. Decrease in elastic modulus of products' surface made of titanium alloys is possible by means of coatings based on Ti-Ta-N system.

However, the attempts to synthesize the coatings of the system on titanium surface were not successful so far. In recent years the method of electroexplosion spraying of coatings with different systems is developed by Russian [18] and Chinese scientists [19]. To the present moment of time we have succeeded in obtaining the bioinert coatings of Ti-Zr system [20] by electroexplosion method. The search is concerned with electron-ion-plasma modification with nitrogen ions to strengthen surface layer of electroexplosive tantalum coating by formation of nitrides as well as supersaturated solid solutions.

2. Materials and methods

The object of the research was titanium pin for intramedullar osteosynthesis of ulna (elbow bone) on which electroexplosion coating from tantalum was formed by electroexplosion method [18]. Such implants with electroexplosion tantalum coating need a reliable protection from corrosion effect of biological liquids of living organism. Therefore, to protect the implants' surface it is enough to form coating of Ti-Ta-N system with thickness of not more than 300 μ m on their surface. Tantalum foil with mass of 500 mg was used as current-carrying exploded material. Time of plasma effect on sample's surface was ~ 100 μ s, absorbed power density on jet axis ~ 1.5 GW/m², pressure in shock compression layer near surface being irradiated ~ 12.5 MPa, residual pressure of gas in working chamber ~ 100 Pa; temperature of plasma on nozzle cut ~ 10⁴ K, thickness of thermal effect zone \approx 50 μ m.

After electroexplosion spraying the electron-ion-plasma modification with nitrogen ions was performed in order to strengthen the surface layer of electroexplosion tantalum coating by formation of nitrides as well as supersaturated solid solutions. Irradiation of electroexplosion tantalum coating by electron beam was carried out in atmosphere of nitrogen at the following values of power density of electron beam: 0.45, 0.5, 0.55 and 0.6 MW/cm². Structure and morphology of the coating were analyzed by methods of light microscopy (device OLYMPUS GX71 with digital camera DP70 and software Image Scope M) and X-ray structural analysis (X-ray diffractometer ARLX' TRA). Microhardness measurement was taken using microhardometer HVS-1000.

3. The results and discussion

Structural studies of transverse metallographic section of electroexplosion coating based on tantalum after electron-ion-plasma modification with nitrogen ions (figures 1 and 2) were performed by light microscopy method. Characteristic images of general view of transverse sections' structure of Ti-Ta-N system samples are shown in figure 1. These images demonstrate clearly the structure obtained with metallographic microscope. According to data in figure 1 the thickness of coating and characteristic constituents of structure are well recognized.

Coatings' thickness of Ti-Ta-N system formed after electron-ion-plasma modification with nitrogen ions at values of power density of electron beam 0.45 (figure 1, a), 0.5 (figure 1,b), 0.55 (figure 1,c) and 0.6 MW/cm² (Figure 1, d) amounts to 128 - 232, 94 - 166, 81 - 161 and 279 - 375 µm, respectively. Such a broad distinction in coating thickness, on the one hand, may be explained by choice of corresponding power density of electron beam and on the other hand, by the fact that with growth of internal mechanical stresses the increase in thickness of coatings and pore dimensions takes place. The coating obtained under irradiation in the mode of 0.45 MW/cm² is characterized by weak homogenization of structure. In this mode the thickness of melting by electron beam reaches less than 50 µm. The most homogeneous pore-free coating is that obtained in mode of 0.5 MW/cm².

This mode of electron-ion-plasma modification with nitrogen ions provides melting of coating throughout thickness of $94 - 166\mu m$, homogenization of structure and saturation with nitrogen ions. With increase in power density of electron beam to 0.55 MW/cm² the melt of coating begins to boil and pores are formed in it. Low values of temperature conductivity ($9.3 \cdot 10^6 m^2/s$ at temperature 300 K) and heat conductivity ($22.3 W/(m \cdot K)$ at temperature 300 K) of titanium substrate [21] contribute to slow heat removal into volume of integrally cold sample. With temperature growth the temperature and heat conductivities of titanium substrate decrease [22] that induces even greater overheating of coating's melt and its boiling. It is the explanation for increase in quantity of pores (dark areas in figure c, d) in coatings obtained in modes of 0.55 and 0.6 MW/cm². The coatings obtained in all modes of processing have highly dispersed structure.



Figure 1. General view of electroexplosion coatings of Ti-Ta-N system after electron-ion-plasma modification with nitrogen ions at values of power density of electron beam 0.45 (a), 0.5 (b), 0.55 (c) and 0.6 (d) MW/cm². Coating of Ti-Ta-N system is designated by arrow.

In spite of described features of structure, and relying on the examination results of figure 1 the boundary between coating and substrate (figure 2) contains no pores. The boundary has a wave-like character with wavelength of about 10 μ m. It is in good agreement with obtained results of electroexplosion spraying of bioinert coatings of Ti-Zr system [20]. Scientists of Lanzhou University of Technology [19] note the analogous features in structure at boundary of coaling with substrate at electroexplosion spraying of high-melting Ta10W and non refractory Ni60A coatings. It is explained by general feature of electroexplosion methods of applying the coatings. At coating-substrate boundary the thickness of diffusion zone is less than 10⁻³ mm with diffusion coefficient D = 10⁻⁵ cm/s and pulse action time of $10^{-2} - 10^{-7}$ s. At coating-substrate interface the initiation of mechanical is inescapable and their stresses whose value is the higher the stronger is the difference of coating properties from those of substrate material.

Low adhesion strength of coatings obtained by conventional methods of spraying [23–25] is caused, first, by jump of properties at interface because of absence or weakly expressed diffusion zone. Interface, essentially, is a macroscopic defect-source of stresses of the first kind. Therefore, features of structure at boundary of electroexplosion coatings with substrate contribute to greater

adhesion compared with coatings being obtained by traditional method of spraying. The increase in quality of coatings by forming the broad diffusion zone at coating-substrate interface and rise in efficiency of coating's formation process is possible due to use of electroexplosion spraying technique.





Analysis of metastable state diagram of titamium alloys indicates that increase in quantity of betaisomorphous stabilizer should result in the following evolution in phase composition of material [26]: $\alpha \rightarrow \alpha \rightarrow \alpha \rightarrow \alpha \rightarrow \beta$ (ω) $\rightarrow \beta$ (ω) $\rightarrow \beta$. In initial state VT6 alloy is a binary alloy containing $\alpha + \beta$ phases. Polycrystalline and homogeneous, in lattice parameter, material gives narrow diffraction peaks while amorphous or noncrystalline inhomogeneous material-wide and low ones. X-ray diffraction patterns of coatings under study (X-ray structural analysis was done from surface layer of coatings formed) are shown in figure 3. Analysis of X-ray diffraction patterns of electroexplosion tantalum coatings after electron-ion-plasma modification with nitrogen ions (figure3) has shown that principal phases being present in the coating are β -titanium with cubic lattice and lattice parameter a = 0.3311nm, tantalum (lattice parameter a = 0.3302nm) and titanium nitride with cubic lattice and lattice parameter a = 0.4241 nm.

As a part of the study the quantitative analysis of X-ray diffraction patterns was carried out and percentage of phases in coatings under examination was determined. Table 1 shows phase composition of samples under study. Diffraction patterns contains reflections at 18.50° , 23.00° , 32.55° , 39.90° , 48.52° corresponding to titanium nitride. Reflections at 35.50° , 45.50° , 48.55° , 55.60° correspond to β -titanium phase, and reflections at 24.85° , 27.00° , 35.90° , 52.00° belong to tantalum (figure 3).



Figure 3. Portions of X-ray diffraction patterns of electroexplosion coatings of Ti-Ta-N system after electron-ion-plasma modification with nitrogen ions at values of power density of electron beam of 0.45 (1), 0.5 (2), 0.55 (3) and 0.6 (4) MW/cm².

Table 1. Phase composition of bioinert coatings of Ti-Ta system formed by electroexplosion spraying method.

Value of powerdensity of electron beam, MW/cm ²	Phase composition
0.45	0.34 vol.%TiN; 47.24 vol.%Ta; 52.41 vol.%β-Ti
0.5	75.77 vol.%TiN; 7.42 vol.%Ta; 16.80 vol.%β-Ti
0.55	10.15 vol.%TiN; 42.14 vol.%Ta; 47.71 vol.%β-Ti
0.6	21.03 vol.%TiN; 52.65 vol.%Ta; 26.32 vol.%β-Ti

When performing a series of tests for microhardness measurements (figure 4) the microhardness values of electroexplosion tantalum coating after electron-ion-plasma modification with nitrogen ions at different thickness of coating were obtained. Microhardness of coating amounts to 532.24 ± 53.25 kgf/mm² (E = 10.02 %), 499.56 ± 28.33 kgf/mm² (E = 5.68 %), 466.47 ± 49.77kgf/mm² (E = 10.55 %), and 439.26 ± 50.44 kgf/mm² (E = 11.47 %) for samples irradiated in modes of 0.45, 0.5, 0.55 and 0.6MW/cm², respectively. Average microhardness value of coating adjacent to substrate is 466.47 ± 77.89 kgf/mm² (E = 13.08 %), 400.23 ± 37.22 kgf/mm² (E = 9.30%), 466.47 ± 32.52 kgf/mm² (E =

6.97 %), and 363.40 \pm 29.22 kgf/mm² (E = 8.04 %) for samples irradiated in modes of 0.45, 0.5, 0.55 and 0.6MW/cm², respectively.



Figure 4. Dependences of change in microhardness on coating's thickness of Ti-Ta-N system after electron-ion-plasma modification with nitrogen ions at values of power density of electron beam 0.45, 0.5, 0.55 and 0.6 MW/cm².

Average microhardness values of substrate adjacent to electroexplosion coatings were determined as well. According to studies performed these amounted to $270.81 \pm 24.38 \text{ kgf/mm}^2$ (E = 9.00 %), $363.34 \pm 53.74 \text{ kgf/mm}^2$ (E = 14.79 %), $370.35 \pm 46.23 \text{kgf/mm}^2$ (E = 12.48 %), $258.76 \pm 21.24 \text{ kgf/mm}^2$ (E = 8.21 %). According to reference data the microhardness of VT6 titanium amounts to 81 kgf/mm^2 [27]. Thus, electroexplosion processing promotes the increase in microhardness amounts to 81 kgf/mm^2 .

4. Conclusion

At surface of titanium pin for intramedullar osteosynthesis of elbow bone the bioinert coatings of Ti-Ta-N system were obtained for the first time. Formation of Ti-Ta-N system coating was performed by means of processing of tantalum foil. Subsequent to it, electron-ion-plasma modification of electroexplosion tantalum coating with nitrogen ions was carried out. Combined processing results in formation of coating from 94 to 375 μ m in thickness depending on mode parameters of processing. Coatings have highly dispersed structure .The most homogeneous pores-free coating is that obtained in mode of 0.5 MW/cm². At lower value of power density of electron beam the coating's structure homogenizes weakly but at higher one –pores form in coating. Wave-like boundary of coating with substrate (wavelength is about 10 μ m) contributes to greater adhesion compared to coatings obtained by traditional techniques of spraying. Phase composition of coating is presented by the following phases: TiN, Ta and β -Ti. Combined processing promotes the increase in microhardness of coatings to values of 439 – 532 kgf/mm². In total, the studies performed showed prospects for formation of bioinert coatings of Ti-Ta-N system by combined method.

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