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Metal oxide (Ti,Ta)-(TiO_2,TaO) coatings produced on titanium using electrospark alloying and modified by induction heat treatment

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Metal oxide coatings (Ti,Ta)-(TiO_2,TaO) on VT1-00 cp-titanium and VT16 titanium alloy (Ti-3Al-4.5 V-5.0Mo) were formed by electrospark alloying (ESA) at an operating current from 1 to 2.5 A and subsequent induction heat treatment (IHT) with the duration from 30 to 300 s at the temperature of 800 °C. ESA at a high operating current $I = 2.5$ A and subsequent IHT with a long exposure time $t = 300$ s ensured the formation of coatings with a high content of tantalum (about 4.5–5%) and tantalum oxide TaO (about 7–8%). The resulting coatings were characterized by high hardness of 9.5–15 GPa and elastic modulus E of 450–700 GPa.

1. Introduction

In order to improve the wear resistance of metal products, methods of thermal and chemical-thermal treatment of the surface, as well as the deposition of coatings, are highly efficient. To change the properties of the surface of products and to restore the worn parts of the processing tools (forming rolls, dies, punchers), gas-thermal methods are used, *e.g.* plasma spraying of powder and wire materials [1,2], as well as electrospark treatment [3]. Products after strengthening treatment of the working surfaces have improved characteristics of wear resistance, the parameters of roughness, porosity and functional properties necessary for ensuring biocompatibility (cell adhesion, proliferation, etc.).

Electrospark treatment, in particular electrospark alloying (ESA) and electrospark deposition (ESD), differs from the conventional methods of strengthening treatment of the surface with lower productivity, but the characteristics of the resulting coatings and alloyed layers have high values of hardness and wear resistance. The electrospark processes of alloying and coating deposition are characterized by the pulse effect of an electric current, as a result of which the interelectrode gap is heated to an extremely high temperature $(8–25) \times 10^3$ K. The materials of the tool electrode (anode) and the treated surface (cathode) are intensively heated and melted, whereas the particles of the deposited material are rapid cooled on the surface of the product at a rate of about 10^5–10^6 K/s. These cooling conditions lead to the formation of a nanoscale structure of the near-surface layer of the product or coating particles [4].

During the formation of the coatings on the surfaces of steel products, metals with a lower melting point, *e.g.* copper, can be used, which provide the required structural changes [4]. A protective atmosphere of argon can be used to prevent oxidation. The surface morphology parameters are controlled by the use of electrodes of various types of action (vibrating or rotating) and changes in the main technological parameters, including the operating current, operating voltage, anode diameter, anode displacement speed relative to the treated product surface and anode oscillation [5]. After the coating or alloyed layer is obtained, the final machining, *e.g.* grinding, is performed.

As a result of ESA with metal ceramics based on tungsten carbide (WC–79%, W–15%, Co–6%), the hardness of structural steel (C–0.45%) increases from 400 HV to 840 HV [4]. Various cermets are used as coatings on tool steels, *e.g.* Mo_2FeB_2-based cermet coating (Fe-6B-48Mo-2.5Cr-2.9Ni-0.5C, wt%) is obtained by ESA of the high speed steel [6]. As a result of rapid crystallization, the cermet changes its structure and much amorphous phase (up to 82%) and martensite appear in the coating. The cermet coating obtained by this method has a hardness of about 1100–1300 HV, which is almost 2.5 times higher than the steel base (550 HV). The coating of hard alloy T15K6 (79% WC, 15% TiC and 6% Co) with an antifriction additive, *e.g.* bronze BrOF6.5–0.15 (0.05% Fe, 0.2% Ni, 0.15% P, 0.02% Pb, 0.3% Zn, 6% Sn, and Cu – balance), is deposited on steel using ESD method [7]. Another material, metal-ceramic coating WC-Co-Al_2O_3 (85% WC, 10% Co, 5% Al_2O_3), is also used as a wear-resistant element on the product surface [8]. This coating is obtained due to the combined effect of ESD and subsequent laser processing (Nd:YAG) in the pulsed mode. After ESD, the roughness parameter Ra reaches 6.16–7.79 µm with a coating thickness of 60–70 µm and a depth of the thermal effect zone of 30–40 µm. Laser modification leads to a reduction in the number of cracks in the resulting coating, which enables the production of

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coatings with the thickness of 90–110 µm and a depth of the thermal effect zone of 50–60 µm. As a result of laser modification, the hardness of the coating decreases from 843 to 784 $HV_{0.04}$, while the wear resistance increases by almost 41%. Steel products with high characteristics of the surface wear resistance are also produced by ESA with metallic materials, *e.g.* copper and molybdenum [9]. As a result of ESA and subsequent laser modification, the hardness of Cu-Mo coating reaches 587 $HV_{0.04}$ and 730 $HV_{0.04}$, respectively. The friction coefficient of the coatings after modification is reduced by almost 54% and the corrosion resistance grows. Corrosion resistance also increases when WC-Cu mixture (50–50%) is applied in order to produce the coatings using a combination of ESD technology and laser modification [10]. In the case of production of a metal-ceramic coating of VK8 hard alloy with an addition of 1–5% Al_2O_3, the hardness of steel products increases by 2.6–3.9 times [11].

As a result of ESA, an oriented microstructure of the coating is formed, *e.g.* from aerospace nickel-based IN718 superalloy (composition of (wt%) 0.5% Al, 0.1% Si, 0.9% Ti, 17.5% Cr, 19.0% Fe, 49.0% Ni, 5.1% Nb, 3.0% Mo) [12]. In a thin near-surface layer, the stresses caused by a decrease in the grain size are accumulated. After high-temperature heat treatment (annealing at a temperature of about 1100 °C), recrystallization occurs. With this combined treatment, it is possible to maintain a high hardness of the coating of about 300–350 HV, while the hardness of the substrate is reduced from 240 to 170 HV. Directional solidification using ESD is used in the preparation of the coatings of complex composition, *e.g.* NiCoCrAlYTa (Co 25%, Cr 20%, Al 8%, Y 0.6%, Ta 4%, Ni – balance), on the surface of DS DZ22 nickel superalloy [13]. The resulting coating of NiCoCrAlYTa can have a thickness of up to 8 mm, its structure is characterized by the dendritic composition of nanoscale (about 500 nm) clusters, and the hardness has a small variation in depth from 450 to 480 $HV_{0.05}$. Amorphous coatings with the thickness of about 30 µm on an iron base, *e.g.* $Fe_{48}Cr_{15}Mo_{14}Gd_2C_{15}B_6$, are also produced by ESD method [14]. A similar approach is also used to produce the coatings on zirconium base, *e.g.* $Zr_{41.2}Ti_{13.8}Ni_{10}Cu_{12.5}Be_{22.5}$ [15]. High-quality welded joint of AISI 410 stainless steel with niobium is obtained by depositing nickel Alloy 82 using ESD on the surface of niobium plate and subsequent laser welding [16]. As a result of the complex treatment, a high strength of the welded joint (about 285 MPa) is ensured.

ESA has found application in the surface treatment of titanium products, *e.g.* using graphite anodes in silicone oil (mainly composed of C, H, Si, and O) [4]. Depending on the environment (air, nitrogen or silicone oil) for ESA structural, physical and chemical properties change, in particular there is an almost 1.5-fold decrease in the roughness parameter Ra, an almost 15–20-fold increase in wear resistance (compared to the untreated titanium alloy Ti-Al-4V), Knoop hardness of the near-surface layer (5–10 µm thick) reaches 1200–1400 HK, the corrosion potential shifts to a positive area from −0.3 to −0.1 mV (there is an almost double reduction in corrosion rate). As a result of ESA, a modified layer with high biocompatible characteristics is formed on the surface of Ti-Al-4V titanium alloy. Biocompatible coatings with the thickness within 30 µm and having a multicomponent chemical and phase composition, high roughness parameters (Ra = 3.7–6.1 µm) and hardness 7–11 GPa are produced by pulsed electrospark deposition [17]. The electrodes used are a composite of various ceramic materials $TiC\text{-}CaO\text{-}Ti_3PO_{(x)}$ and $TiC\text{-}CaO\text{-}Ti_3PO_{(x)}\text{-}Ag_2Ca$ [18]. The addition of silver in the electrode material composition provides antibacterial properties of the coatings obtained on the surface of titanium medical products. The oxygen and nitrogen content in the coatings varies due to the choice of the reaction atmosphere, *e.g.* argon, air or distilled water.

Bioactive coatings, *e.g.* hydroxyapatite, on the surface of St35 steel are obtained by the combination of ESD and MAO methods [19]. For this purpose, a layer of Ti-6Al-4 V titanium alloy is deposited on the surface of steel products in the first stage of the combined process using ESD method. The subsequent MAO is conducted in the aqueous electrolyte containing calcium acetate and β-calcium glycerophosphate-based electrolyte during 30 min. ESD + MAO combination provides the formation of highly porous coatings. This approach also allows the production of a metal-ceramic coating on St35 steel, which consists of titanium, aluminum and intermetallide oxides [20].

To impart high wear resistance to titanium products, their surface is treated by ESA in a nitrogen medium to produce a TiN nitride layer [21]. As a result of this treatment, the friction coefficient is about 0.3, the thickness of the modified layer is 52–77 µm at the roughness *Ra* = 32–56 µm. Commercially pure titanium (cp-Ti Grade 2) is also subjected to ESA with aluminum, which increases the hardness up to 800–1150 HV [22].

To improve the functional qualities of metal medical products, tantalum is added to their composition, *e.g.* in the form of an alloying additive. Multicomponent biocompatible films alloyed with tantalum are obtained by DC-magnetron sputtering of composite targets of the composition $(Ti,Ta)C + Ca_3(PO_4)_2$ and $(Ti,Ta)C + CaO$ [23]. The resulting films are characterized by high hardness of 38–44 GPa and elastic modulus of 310–350 GPa, which were determined with a low load on the indentor of 4–30 mN. The structure of these films is represented by grains with an average size of 20–60 nm and roughness of about 4 nm. At the same time the wetting contact angle was 37–47°, which is somewhat less than that in case of pure titanium (50°). Increased hydrophilicity of the surface is important when interacting with biological structures, *e.g.* cells.

Additive synthesis methods, *e.g.* using laser technologies for forming laser powdered materials for the production of frameworks (laser engineered net shaping or laser powder forming), allow the production of porous structures from tantalum [24,25]. For laser sintering, powders with the size of 45–75 µm are used. The resulting samples have an elastic modulus of 2–20 GPa, which is associated with a porosity of 27–55% and an offset yield strength of 100–746 MPa, respectively. The obtained samples of porous materials are subjected to chemical polishing and etching. The hardness of the resulting coatings reaches 400 HV, which is almost twice higher compared to that of titanium. Commercial versions of porous materials are also known, in particular tantalum grade “Trabecular metal” (Zimmer Inc.) with a porosity of 75–85%, pore size of about 550 µm and an elastic modulus of 2.5–3.9 GPa. These structural elements are used in hip and knee surgery. However, when using this technology, it is impossible to produce an integral implant design [26].

There are data on the results of the biocompatibility study of Ti–Nb, Ti–Nb–Zr, Ti–Nb–Hf alloys (with the shape memory effect), but their use in medicine is still limited [27]. The direction of obtaining alloys with a shape memory effect, the chemical composition of which differs from the conventional TiNi nitinol (50%/50%), is also developing. One of the variants of the biocompatible alloy is an alloy of titanium and tantalum, in which the percentage of components corresponds to the formula Ti–(30–40)Ta [28].

There are preliminary data on the formation of tantalum coatings by ESA method and their subsequent induction-thermal treatment (IHT) [3,29], according to which the recommended IHT temperature should not exceed 800 °C. Previously, the changes in the crystalline structure (phase composition) of the resulting metal oxide coatings were not investigated, and the comprehensive studies of the mechanical properties were not described. Therefore, in this study it is proposed to apply ESA at operating current from 1 to 2.5 A and further IHT with the duration from 30 to 300 s at the temperature of 800 °C to increase the hardness, elastic modulus and to change the chemical and phase composition, surface morphology of the tantalum coatings.

2. Materials and methods

2.1. Preparation of coatings

The experimental samples had disk shape (diameter 8–14 mm,