Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Composition, structure and mechanical properties of metal oxide coatings produced on titanium using plasma spraying and modified by micro-arc oxidation

Vladimir Koshuro, Aleksandr Fomin*, Igor Rodionov

Yuri Gagarin State Technical University of Saratov, Institute of Electronic Technology and Engineering, 77 Politechnicheskaya str., Saratov 410054, Russia

ARTICLE INFO

Keywords:
Alumina
Plasma spraying
Titania
Micro-arc oxidation

ABSTRACT

Metal oxide coatings on VT6 titanium alloy were formed by plasma spraying of aluminum oxide powder and subsequent microarc oxidation at a current density from 1 to 3 kA/m^2. As a result of combined treatment, metal oxide coatings consisting of a mixture of aluminum and titanium oxides were obtained on the surface of titanium samples. The most pronounced changes in the morphology of the plasma-sprayed coating were observed at the highest current density of 3 kA/m^2. The open porosity decreased from 56% to 38% due to the modification by micro-arc discharges, whereas the microhardness increased from 1013 ± 150 HV to 1639 ± 31 HV.

1. Introduction

Titanium and its alloys have found wide application in the aviation and space industries, engine building, shipbuilding, chemical and electronic industries, as well as in the manufacture of medical products [1–9]. The main disadvantage of titanium alloys is low wear resistance [10–12]. The required surface characteristics of titanium products, *e.g.* dental implants and metal components of endoprostheses, are usually increased by thermal, chemical-thermal and electrochemical treatment, as well as the formation of metal-ceramic coatings by various methods, including plasma spraying [13–15].

Plasma modification of the titanium surface is used to change its physical characteristics, in particular, to increase the wetting ability [16–18]. It is difficult to increase the mechanical properties of the surface of titanium products by thermal treatment and without changing the chemical and phase composition. Therefore, different types of chemical-thermal treatment of titanium are intensively developed, including carburization, nitridation and oxidation [13]. For example, carburization of titanium is performed in a gaseous medium [19]. Layers of TiC are formed on titanium by ion implantation using methane as the reaction medium [20].

The processes of titanium oxidation are conditionally divided into gas-thermal and electrochemical ones. During gas-thermal oxidation, titanium is heated in an oxygen-containing atmosphere to a temperature of 650–850 °C and then it is exposed for 6–14 h [21]. The resulting oxide film consists of rutile and has a hardness of about 21 GPa [22]. For high-temperature induction treatment (up to 1200 °C) the duration of the oxidation process can be reduced to 2–5 min [23,24]. At the given treatment high indicators of mechanical properties and the set parameters of morphology are retained. However, this treatment option is well suited for simple shape products (disks and cylinders).

In addition to thermal oxidation, methods of electrochemical oxidation of titanium and its alloys are widely used, *e.g.* anodizing and micro-arc oxidation (MAO), also known as plasma electrolytic oxidation (PEO) [25]. Anodizing of titanium is performed in aqueous alkaline/acid solutions or in anhydrous fluoride electrolytes. As a result of the treatment of titanium, wear-resistant coatings consisting of titanium oxides are formed [26,27]. MAO differs from anodizing in the formation of electrical discharges, as a result of which the structure, phase composition and mechanical properties of the oxide layers change [25,28,29]. The main parameters of MAO are the current density, duration of the process and electrolyte composition.

The surface characteristics of titanium products are increased by coating deposition, *e.g.* by sol-gel method, physical vapor deposition (PVD) and gas-thermal spraying [30,31]. Gas-thermal spraying is characterized by high productivity and the possibility of forming coatings from refractory materials. Corrosion- and wear-resistant coatings of carbides and oxides of aluminum and some transition metals (titanium, tantalum, *etc.*) are formed on titanium by plasma spraying [32,33]. Plasma spraying is also used to form calcium phosphate coatings on medical titanium implants [34–36]. Despite their widespread use, plasma-sprayed coatings are characterized by heterogeneity of the structure and low adhesion. To eliminate the defects, clad powders are used or subsequent thermal and thermomechanical treatment

* Corresponding author.
E-mail address: afominalex@rambler.ru (A. Fomin).

https://doi.org/10.1016/j.ceramint.2018.04.056
Received 16 January 2018; Received in revised form 6 April 2018; Accepted 7 April 2018

is performed [37,38].

In the course of plasma spraying, the coating is formed from a variety of fully or partially melted particles, between which the structural defects, *e.g.* pores, appear. Porosity and heterogeneity of the phase composition of plasma-sprayed coatings are minimized by complex and long modification. Previous studies confirmed the change in the structure and composition of the plasma-sprayed material after MAO [39], however, the effect of current density on the mechanical characteristics of composite coatings, in particular hardness, was not established. Therefore, in this study it is proposed to apply the effect of electric discharges arising at MAO to increase the hardness and change the structure of the plasma-sprayed coating.

2. Materials and methods

2.1. Preparation of coatings

In the current study, disk samples with a diameter of 6 mm and length of 1.5 mm were used. The samples were made of VT6 titanium alloy (analogue Ti-6Al-4V). The surfaces of titanium samples were grinded using sandpaper (grain size from P600 to P1000) and subsequent cleaning in an ultrasonic bath with ethanol.

Plasma spraying of an electrocorundum powder (Grade "25AF230") with a dispersion of 75 ± 25 μm was performed on the equipment "PSE-28" at a spraying distance of 130 mm, arc current of 450 A and voltage of 30 V. Argon was used as the carrier and working gas at a flow rate of 20 l/min.

MAO of titanium samples with plasma-sprayed coatings was conducted at a current density j of 1, 2 and 3 kA/m^2 for 20 min using an aqueous electrolyte containing 3 g/l of NaOH.

2.2. Coating characterization

Elemental composition of the coatings was studied by the method of energy dispersive X-ray fluorescent analysis (EDX) on "MIRA II LMU" electron microscope with "INCA PentaFETx3" detector. Phase composition of metal oxide coatings was determined by X-ray diffraction (XRD) on "Gemini/Xcalibur" diffractometer using an X-ray tube with a copper anode (CuKα, λ = 1,541874 Å, 2Θ = 25–80°). To analyze the crystal structure of the coatings, "Crystallography Open Database" was applied. Morphology of the coatings was studied by the scanning electron microscopy (SEM) using "MIRA II LMU". The open porosity, distribution of linear grain sizes and coating defects were determined from SEM images obtained with magnifications of ×5000 and ×50,000 using "Metallograph" software [36]. The prepared microsections were used to define the thickness of coatings.

The stages of statistical evaluation of the morphological parameters included: 1. obtaining digital images of the morphology; 2. selection of rectangular areas (ratio width: height = 12: 9) for the subsequent analysis and statistical processing of morphological parameters (Fig. 1a); 3. entering data on the frame width of a rectangular image; 4. loading the image into "AGPM" software for analyzing the geometric parameters of micro-objects; 5. conversion of the original image into a black and white one (Fig. 1b); 6. calculation of porosity (black areas corresponded to open pores or cavities); 7. statistical analysis of the image and production of the output data, namely the average size of microparticles (or micropores in inverted images), the total number of microparticles (or micropores) and dispersion, and graphs showing the microparticles (or micropores) distribution in size.

The microhardness was measured using "PMT-3m" hardness tester with an indenter load of 200 gf (1.96 N). In addition, to assess the mechanical properties, a selective measurement of the strength of the coatings was performed by scratch testing using "NANOVEA Ergonomic Workstation" tester at a load not exceeding 1 N, which was applied to a conical diamond indenter (radius of rounding 20 μm, angle 60°) [23]. This method was chosen because the resulting coatings were characterized by small thickness (about 20–30 μm), which limited the use of other tests for adhesion strength. The obtained information was summarized in diagrams showing the change in the depth of indentation, force and friction coefficient depending on the length of the scratch. The strength of the coating was estimated from the ratio of the frictional force to the contact area of the indenter and the coating before its destruction (delamination).

3. Results and discussion

3.1. Thickness of coatings

According to SEM results of microsections, the thickness of the untreated plasma-sprayed coating was 41.7 ± 6.6 μm (Fig. 2a). In the structure of the plasma-sprayed coating, particles of the sprayed powder with different degrees of melting were present. The size of single non-melted microparticles was much less (about 20–25 μm) compared to the initial value of the dispersion (75 ± 25 μm) of the electrocorundum powder, which may be due to its fragmentation (crushing) in the plasma jet under the thermal stresses.

After MAO the thickness of plasma-sprayed coatings decreased with the growth of the current density and equaled: 30.2 ± 5.3 μm at j = 1 kA/m^2, 26.6 ± 3.8 at j = 2 kA/m^2, 19.5 ± 3.0 μm at j = 3 kA/m^2 (Fig. 2b–d). Thus, the structure of electrocorundum coatings was modified by electrical discharges, which caused a change in the parameters of porosity, in particular of open porosity.

The modification of the plasma-sprayed ceramic coating underwent several stages (Fig. 3). Initially, an oxide film of a metal substrate grew at the bottom of the through pores of the coating (Fig. 3a). A gas-vapor bubble consisting of electrolyte molecules appeared as a result of the electrolyte heating (Fig. 3b). Then an electric breakdown of the bubble occurred and a plasma-vapor area was formed, which started to expand (Fig. 3c). During the expansion, high temperature and pressure impulsively influenced the material of the sprayed coating. When the

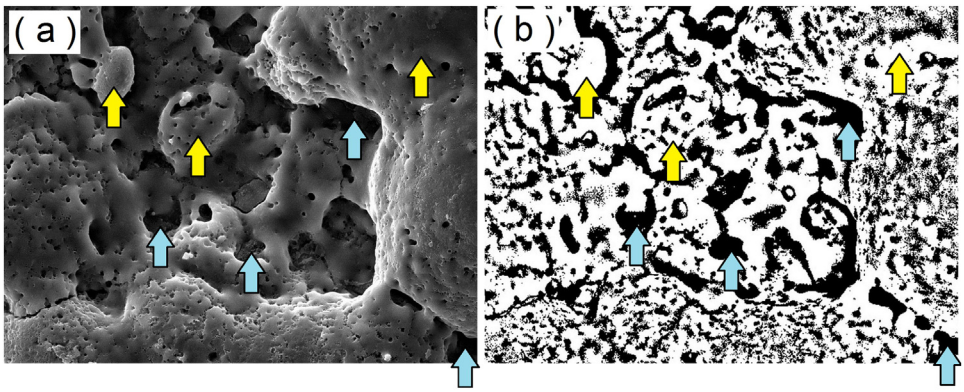

Fig. 1. Stages of the image processing of the coating morphology: a – selection of rectangular areas; b – conversion of the original image into a black and white one (the yellow arrows indicate the protrusions; the blue arrows mark pores and cavities). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)