STRUCTURE AND PROPERTIES OF TiO_x AND TiN_xO_y COATINGS FORMED IN VACUUM ARC PLASMA FLUXES

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The structure, microhardness and protective properties of titanium oxide and titanium oxynitride coatings formed in vacuum arc plasma fluxes depending on the negative potential on the substrate and the oxygen pressure, and also on the oxygen content in the gas mixture (N_2+ O_2) were studied. It is shown that titanium coatings deposited in a pure oxygen atmosphere at the pressure of 0.03 Pa represent a dispersed system of oxides in composition depends on the bias potential of the substrate. Unlike titanium oxide coatings, TiN_xO_y coatings are single-phase, which lattice parameter varies within the oxygen partial pressure. TiN_xO_y system has high microhardness (34 GPa), corrosion resistance and decorative properties of the coating deposition at optimal technological parameters.

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INTRODUCTION

Now, attention is paid to the three-component compounds of MeN_xO_y type [1] transition metals. This is explained by the fact that such coatings have high operational and decorative properties [1-3]. From the impurities effect point, the three-component phases synthesis is carried out under less stringent conditions, which do not require special purity of the starting materials. In a number of cases the question arises of the expediency of replacing oxides and nitrides with oxynitrides.

The most studied class of high-hard coatings formed by ion-plasma methods are nitrides and titanium carbides [4]. Problems in the oxides of various metals synthesis by a vacuum arc method has been fully consecrated in the review [5]. We have developed vacuum-arc nanostructured coatings based on TiO_2 (structure-anatase) with controlled bactericidal activity for orthopedic implants [6] earlier. The information in the technological aspects literature of obtaining oxynitrides within vacuum-arc method is insufficient. Thus, in the structure [7] and decorative properties of oxide-titanium coatings deposited from separated streams of arc discharge plasma were studied. Variable parameters of the process were: arc current and oxygen pressure. Depending on the gas pressure, the coating was either monophase (TiO, Ti_2O_3, TiO_2) and composition of these phases. The influence of the negative potential on the substrate was not investigated by the authors [7]. One of the titanium oxynitrides possible applications is improvement of the biological compatibility of implants. Platelet adhesion and fibrinogen adsorption are lower for TiNxOy than for TiO_2, and the best hemocompatibility was found in $TiN_{0,4}O_{1,6}$ coatings [7].

The aim of this work was to study the effect of negative potential on the substrate, oxygen pressure, oxygen content in the mixture (N_2+O_2) on the structure, microhardness and corrosion properties of the oxide and oxynitride titanium coatings.

1. EXPERIMENTAL TECHNIQUE

The deposition of the coatings was carried out in a "Bulat-6" system [8]. Titanium of the VT-1-0 grade (99.9 %) was used as the cathode. The arc discharge current was ~ 100 A. The polished substrates (Ra ~ 0.03 μm) of steel 3 and stainless steel 12X18N10T were placed parallel to the cathode plane at the distance of 250 mm from it. Prior to the deposition, the substrates were sputtered at a pressure of 0.005 Pa using titanium plasma under 1200 V negative substrate bias voltage for 3 min. Variable parameters of the deposition process were the negative potential on the substrate U_b = -30...-300 V, the pressure of the gas mixture (P = 0.03...2.5 Pa), which was prepared in advance with different oxygen content (0...100 %). The thickness of the obtained coatings was determined by the method of shadow knives using the interference microscope MII-4 and we have received ~ 6 and 12 μm. The temperature of the samples was measured with a chromel-alumel thermocouple and increased as the substrate potential increased from 350°C (at U_b = -30 V) to 750 °C (at U_b = -300 V). Chemical composition of the coatings was performed using energy dispersive X-ray spectroscopy – EDS (Oxford Link ISIS 300) at 20 kV. The structure of the condensates and the phase composition was studied by X-ray diffraction analysis using a DRON-3M system in monochromatic CuKα radiation. The microhardness of the coatings was measured on a PMT-3 microhardnesser at 50 and 100 g loads. Corrosion properties of coatings were determined by electrochemical method using potentiostat PI-50-1 in a 3 % NaCl + 3 % H_2SO_4 solution.

2. RESULTS AND DISCUSSION

Coatings of the TiO_x system obtained at a fixed oxygen pressure P_{O2} = 0.03 Pa in the range of potentials U_b = -30...-300 V are a dispersed system of titanium oxides.

Fig. 1 shows the change in the oxygen concentration and the phase composition of the TiO_x coatings as a function of the potential on the substrate.

It can be seen from the figure that at U_b = -200 V, TiO monoxide with an oxygen concentration of ~50 at%, A crystallite size of ~ 14 nm, and a sufficiently strong preferential orientation (100) is formed in the coating. With a decrease in the potential of the substrate to -30 V, the formation of oxides shifts toward the formation of a series of intermediate oxides (with different weight composition), up to the formation of a higher oxide of β-TiO_2 (anatase). This is due to an increase of the oxygen content around the coatings to 65 at %. It should be noted that for anatase the size of the crystallites increases to ~ 50 nm, and the texture is rather weakly expressed (orientation (101) and the formation of the Ti_2O_3 compound.

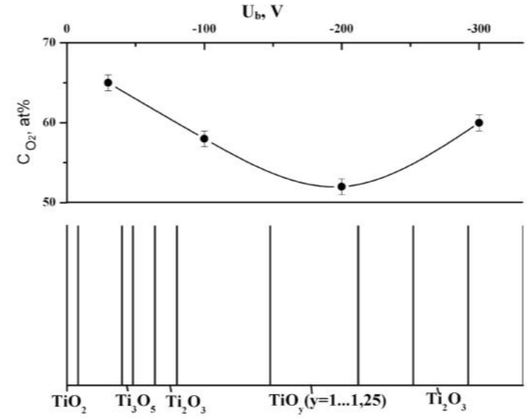

Fig. 1. Estimate diagram of the phase composition of Ti coatings deposited in the oxygen medium, depending on the potential on the substrate (P_{O2} = 0.03 Pa)

A decrease of the oxygen concentration from 65 to 50 at % in coatings with an increase of the bias potential from -30 to -200 V seems to be due to its selective sputtering. A similar picture is also observed in the vacuum-arc deposition of nitride coatings, for example, CrN [9]. The relative increase of the oxygen concentration to 60 at % at U_b = -300 V can be associated with an increase in the temperature of the samples to 750 °C, which leads to an additional oxidation of the condensation surface and the formation of the Ti_2O_3 compound. Oxinitride coatings of titanium, obtained in the pressure range P_{O2+N2} = 0.3...2.5 Pa, are a single-phase system with a face-centered cubic structure. The dependence of the lattice parameter and the microhardness of the coatings on the pressure and the percentage ratio of nitrogen and oxygen in the gas mixture is presented in Table.

With increasing nitrogen content in TiN_xO_y coatings, the lattice parameter increases sharply and then decreases insignificantly, which corresponds to the literature data [10]. However, the coatings lattice calculated parameters under investigation throughout the concentration range are much higher than in the literature data, which is due to the presence of macrostresses of structural-phase origin.

Dependence of lattice parameter (a), microhardness (H) and deposition rate (v) TiN_xO_y coatings under the pressure of the mixture of nitrogen and oxygen (U_b = -200 V)

P_{N2+O2}, Pa	O_2, %	a, nm	H_v, GPa	*v*, µm/h
0.5	0	0.4266	24	6.2
0.3	10	0.4277	21	6.2
0.7	10	0.4277	20	6.1
1.4	10	0.4283	28	7.5
2.5	10	0.4287	34	8.4
2.5	20	0.4275	34	8.4
2.5	50	0.4207	24	9.5
0.03	100	–	18	10.5

The estimation of microstresses, carried out from the lattice parameters maximum value of TiN_xO_y (P_{O2+N2} = 2.5 Pa) and TiN (P_{N2} = 0.5 Pa), is ε = 0.87 % and ε = 0.66 %, respectively, which correlates with the microhardness changes. The crystallite sizes contribution to the changes in values of microhardness is not decisive, since the average crystallite size for TiN_xO_y corresponds to ~15 nm, and for TiN ~ 19 nm.

Coatings are highly textured with a texture plane (111). As the oxygen content increases, the texture (111) decreases and becomes (200) at P_{O2+N2} = 1 Pa. The deposition rate of TiN_xO_y coatings in the pressure range of the gas mixture P_{O2+N2} = 0.3 ... 0.7 Pa practically does not change and is ~ 6 µm / h (see Table). At P> 1 Pa, for the N_2/O_2 = 1/1 mixture, it increases and reaches ~ 9.5 µm/h, which corresponds to a deposition rate in pure oxygen of ~ 10 µm / h at P_{O2} = 0.03 Pa. This may be due to an increase in the molar volume of the phases formed.

Electrochemical measurements analysis results shows that the current density characterizing the steel dissolution with a coating of nitride and titanium oxynitrides of thickness ~ 6 µm is 0.5 ... 1 order lower than for uncoated in the range of potentials of corrosion -0.5...0 V (Fig. 2). When the coating thickness is increased to 12 µm, the samples corroded much slower, what corellates with a decrease of the coatings through porosity. The density of the corrosive current decreases by 2.5…3 exponents of the magnitude.

The highest corrosion resistance is observed in samples with coatings of thickness ~ 12 µm deposited from the oxygen and nitrogen mixture at P_{O2+N2} = 1.4 Pa and at an oxygen pressure $P_{O2} = 3\times10^{-2}$ Pa (Fig. 2, curves 4, 8). These coatings provide corrosion resistance of steel close to the strength of a pure coating of titanium nitride in a 3 % aqueous solution of NaCl (see Fig. 2, curve 9), measured in [11].

The color characteristics of TiN_xO_y coatings were assessed visually. It was found that titanium oxide coating color varies depending on the bias potential on the substrate. With an increase of the negative potential, the dominant color of the oxide coatings changes (in accordance with the change of the phase composition of the coatings) from black with a weak violet hue at U_b = -30 V to a superposition of blue and violet tones at U_b = -300 V. Oxynitride coatings are golden.

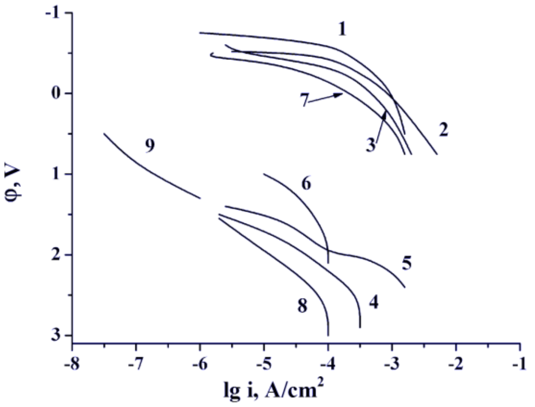

Fig. 2. Anodic potentiodynamic curves of TiN_xO_y coatings on St.3 in a 3 % NaCl + 3 % H_2SO_4 solution at thicknesses of ~ 6 µm (1…3.7) and ~ 12 µm (4…6.8): 1 – St.3; 2, 3 – P_{O2} = 0.03; 0.07 Pa; 4, 5, 6 – P_{O2+N2} = 1.4; 2.5; 0.7 Pa; 7 – TiN (P_{N2} = 0.5 Pa); 8 – TiO_y (P_{O2} = 0.03 Pa); 9 – TiN [11]

CONCLUSIONS

The effect of deposition parameters of oxynitride titanium coatings on their structural-phase state and service characteristics-microhardness, corrosion and decorative properties was studied.

It is shown that titanium coatings deposited in an oxygen medium under pressure of 0.03 Pa represent a dispersed system of oxides whose composition depends on the magnitude of the bias potential on the substrate. TiN_xO_y coatings which lattice parameter varies within the oxygen partial pressure are single-phase.

TiN_xO_y coatings have high microhardness (34 GPa), corrosion resistance and decorative properties at optimal technological parameters.

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СТРУКТУРА И СВОЙСТВА ПОКРЫТИЙ TiO_x И TiN_xO_y, СФОРМИРОВАННЫХ В ПОТОКАХ ВАКУУМНО-ДУГОВОЙ ПЛАЗМЫ

В.А. Белоус, В.М. Лунев, А.С. Куприн, М.А. Бортницкая

Изучены структура, микротвердость и защитные свойства оксидных и оксинитридных титановых покрытий, образующихся в потоках плазмы вакуумной дуги, в зависимости от отрицательного потенциала на подложке и давления кислорода, а также от содержания кислорода в газовой смеси (N_2+O_2). Показано, что титановые покрытия, осажденные в атмосфере чистого кислорода при давлении 3×10^{-2} Па, представляют собой дисперсную систему оксидов, состав которых зависит от потенциала смещения подложки. В отличие от покрытий из оксида титана покрытия TiN_xO_y являются однофазными, параметр решетки которых зависит от парциального давления кислорода. При оптимальных технологических параметрах нанесения покрытия система TiN_xO_y имеет высокую микротвердость (34 ГПа), коррозионную стойкость и декоративные свойства.

СТРУКТУРА ТА ВЛАСТИВОСТІ ПОКРИТТІВ TiO_x ТА TiN_xO_y, ЩО СФОРМОВАНІ В ПОТОКАХ ВАКУУМНО-ДУГОВОЇ ПЛАЗМИ

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Вивчено структура, мікротвердість та захисні властивості оксидних та оксинітридних титанових покриттів, що утворюються в потоках плазми вакуумної дуги, в залежності від негативного потенціалу на підкладці та тиску кисню, а також від вмісту кисню в газовій суміші (N_2+O_2). Показано, що титанові покриття, осаджені в атмосфері чистого кисню під тиском 3×10^{-2} Па, являють собою дисперсну систему оксидів, склад яких залежить від потенціалу зміщення підкладки. На відміну від покриттів з оксиду титану покриття TiN_xO_y є однофазними, параметр решітки яких залежить від парціального тиску кисню. При оптимальних технологічних параметрах нанесення покриття система TiN_xO_y має високі мікротвердість (34 ГПа), корозійну стійкість та декоративні властивості.