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EFFECT OF IMPULSE BIAS POTENTIAL TO FORMATION OF WEAR-PROOF COATING DEPOSITED FROM PLASMA FLUXES

Summary. Plasma-based technology is used to deposit a wear-proof nanostructured coating on plunger tappets of pump of aviation oil system block, which allows increasing the life of the parts up to 3–5 times. For the nanostructured coatings, which are formed at the impulse bias supply, the electric field strength is 10^3-10^4 times greater than for the microstructured coatings. It results in significant change of activation energy of the process of strong bond formation in the growing coating, which makes it possible to obtain high qualitative characteristics of the coating.
Keywords: plasma-based deposition; nanostructured coatings; impulse bias

1. INTRODUCTION

Nowadays new technologies and materials are widely applied for transport quality improvement and increasing of its service life [1]. Ion-plasma technologies have been used for the last 50 years to change the surface properties for various applications [2-5]. The method of plasma immersed ion implantation and deposition (PIII&D) has become especially widespread [6, 7]. The essence of this method is that the work piece, located on

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the substrate, is under negative potential, which makes it possible to accelerate the ions in the electrostatic layer, which is formed between the work piece and plasma. The energy supplied by ions to the growing coating, allows activating a range of processes, simultaneously avoiding the significant increase of the work piece temperature. When the coating is deposited without plasma and PIII&D method, the typical temperature of the work piece should reach the value of more than $0.6T_m$ (where T_m is melting temperature) to obtain the coating with proper characteristics. PIII&D methods allow increasing the work piece temperature only to the value of about $0.4T_m$, which make it possible to prevent recrystallization and loss of positive characteristics obtained at preliminary heat treatment. However, the temperature of $0.4T_m$ allows obtaining microstructured coatings, thus limiting the work piece service properties. To overcome this limit, a transition from “traditional” microstructured coatings to nanostructured coatings with grain size of about 10^{-9} m should occur. The temperature should be lowered to the values of about $(0.2…0.3)T_m$ to obtain such coatings; a big number of crystallization grains appears at such condition, which facilitates the formation of fine-grained structure. However, the speed of strong bonds formation is very low in the coating due to the low temperature; the mechanical characteristics of obtained coatings are not adequate because of big number of pores.

To obtain nanostructured coatings we can apply the impulse high negative potential to the substrate coupled with the background constant (floating) negative potential. We used the technique to deposit wear-proof coating to the plunger tappets of pump of aviation oil system block, and the life of the part was increased up to 3–5 times comparing to the un-treated samples. Microscopic investigation shown that a nanostructured coating is formed under the influence of the impulse bias supply. The purpose of this paper is to describe the possible mechanism of coating formation under such conditions.

2. EXPERIMENTAL RESULTS

The experimental setup is shown schematically in Fig. 1 (left); the work pieces are shown in Fig. 1 (right).

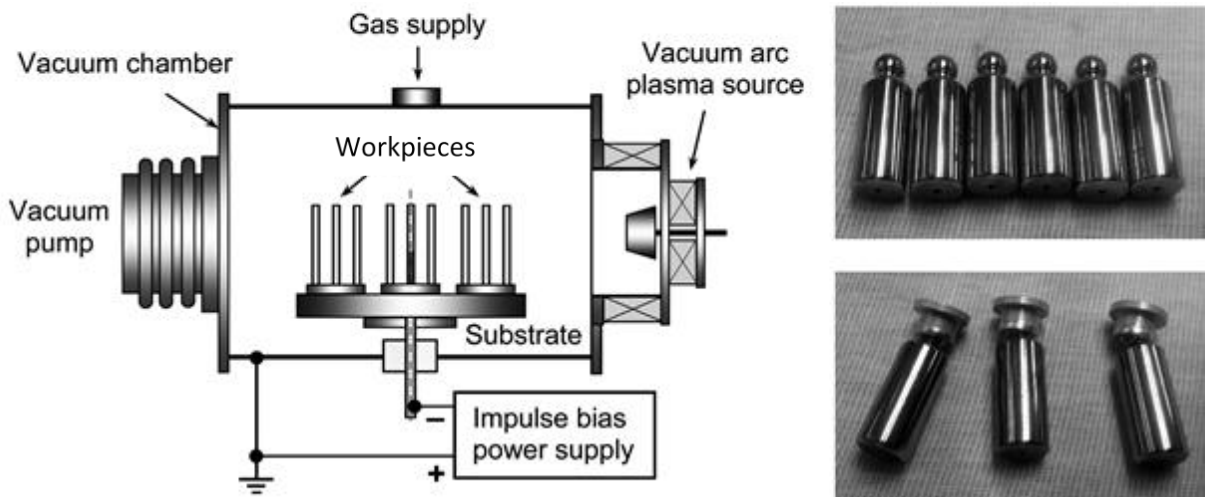

Fig. 1. Experimental setup and work pieces

The setup includes vacuum chamber with a vacuum arc plasma source mounted on a flange of the chamber. An evaporated cathode was made of titanium. A rotating substrate with fixtures for work pieces installation was located in the chamber. When operating the plasma source, the dc arc current was applied between the cathode and the grounded walls of the vacuum chamber, which served as anode. A source of impulse bias (2 kV, 1 μs, 1 kHz) was used to supply power to the substrate. An automated gas-handling system maintained a nitrogen pressure of 0.1 Pa. The time of the work pieces exposure to the plasma was 20 min. TiN coatings with columnar structure with diameter of about 30 nm and microhardness of 20 GPa were obtained on the surfaces of the work pieces as a result of the plasma treatment; the temperature of the samples did not exceed 450 K at the experiment. The coatings with the diameter of the columnar structure of about 200–400 nm and the same microhardness can be obtained at constant bias potential of 100 V and the temperature of the samples of 750 K, which is not allowed by the specifications for the work pieces. To describe the experimental results, the following theoretical model was developed.

3. THEORETICAL MODEL

The model is based on the fact that electrical field strength is higher in those areas of conductor where the radius of curvature is smaller. We apply the known assumptions [8] to the model, when the grain of the growing coating with radius R_{nano} rests on the grain of the substrate (work piece) with radius of R_{micro}. The electrostatic potential can be calculated by use of formula for spherical charge q_i:

$$\varphi_i = \frac{1}{4\pi\varepsilon_0}\frac{q_i}{R_i}. \qquad (1)$$

For charges equilibrium we need the equality of potentials $\varphi_{nano} = \varphi_{micro}$, which results in:

$$\frac{q_{nano}}{R_{nano}} = \frac{q_{micro}}{R_{micro}}. \qquad (2)$$

Since the field at the outer surface of the conductor is:

$$E = \frac{\sigma}{\varepsilon_0}, \qquad (3)$$

where σ is the local surface charge density, which is proportional to the total charge divided by radius squared, we can state that:

$$\frac{E_{nano}}{E_{micro}} = \frac{q_{nano}/R_{nano}^2}{q_{micro}/R_{micro}^2} = \frac{R_{micro}}{R_{nano}}. \qquad (4)$$

The ratio between the strength E_{micro} and the value of the bias potential U_s applied to the substrate can be determined by use of the cathode layer thickness *s*:

$$E_{micro} = \frac{U_s}{s} \tag{5}$$

$$E_{nano} = \frac{U_s}{s}\frac{R_{micro}}{R_{nano}}. \tag{6}$$

The presence of electric field on the grain surface results in changing the rate of formation of strong bonds between the deposited ions and grains of coating on the substrate surface. This rate is proportional to the probability described by factor $exp(-\varepsilon_a/kT)$, where ε_a is the energy of bond formation, *T* is the substrate temperature [9]. Considering the influence of the additional electric field to the probability of the strong bond formation, we can write:

$$P_a = \exp\left(-\frac{\varepsilon_a - \Delta\varepsilon_a}{kT}\right) \tag{7}$$

where $\Delta\varepsilon_a$ is the work, carried out by electric field E_{nano} to overcome the repulsive force between the ion and the grain at the distance of around lattice parameter a_0:

$$\Delta\varepsilon_a = E_{nano} a_0 \tag{8}$$

Then finally, we can write:

$$P_a = \exp\left[-\frac{\varepsilon_a}{kT}\left(1 - \frac{U_s}{\varepsilon_a}\frac{a_0}{s}\frac{R_{micro}}{R_{nano}}\right)\right]. \tag{9}$$

High negative potential supplied to the grain surface, results in generation of strong electric field, which can reduce significantly the activation energy of the process of strong bond formation according to formula (9), thus compensating low temperature *T* of the growing surface.

The need to supply the high potential at specifically pulse mode is conditioned by two constraints. The first is the requirement to sustain a relatively low temperature of the work piece thus lowering the heat current supplied by ions to the substrate after acceleration in the cathode layer. The second constraint is imposed by the rate of change of work piece geometry, which becomes negative (the work piece coating and surface layer are predominantly sputtered), when the energy of ions exceeds the value of approximately 500 eV. Hence, to deposit a wear-proof coating at low temperatures, we need to supply the high impulse negative potential, when the ratio of the impulse duration to the impulse period is significantly smaller than one.

To justify the proposed mechanism of influence of the impulse bias supply to the substrate at the coating growth, we calculated the probability $P_a(U_s, R_{nano}, T)$ of the strong bond formation of the system “nanostructured coating – microstructured work piece” with respect to the probability $P_a(0, R_{micro}, T)$ of the strong bond formation of the system "microstructured coating – microstructured work piece".

Fig. 2a shows the results of calculations of electric field strength on the surface of a grain of a coating at dependence on the grain radius R_{nano}, when the radius of the grain of the substrate material is R_{micro} = 10 μm. The amplitude of the impulse bias of U_s = 2000 V and the plasma sheath thickness of s = 0.1 mm are considered as parameters. Then we considered the growth of a nano-sized grain of a coating with radius of R_{nano} = 50 nm on a surface of a micro-sized grain of substrate with radius of R_{micro} = 10 μm. The results of calculation of ratio P_a(2000 V, 50 nm, 450 K)/P_a(0, 10 μm, 750 K) are shown in Fig. 2b. These results allows comparing the growth of the wear-proof coating when the substrate temperature is low (T = 450 K) but high bias potential is supplied (U_s = 2000 V) which corresponds to conditions in our experiment, with the deposition of the wear-proof coating when the substrate temperature is high (T = 750 K) and the bias potential is not supplied (U_s = 0) that is close to a conventional process of growth in plasma.

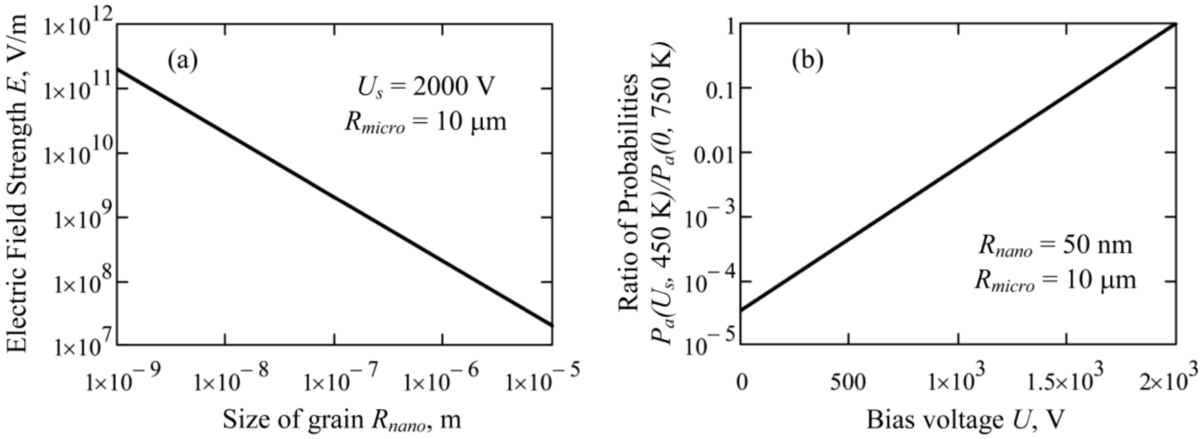

Fig. 2. Electric field strength E at dependence on radius R_{nano} of a grain of coating at interaction with a grain of work piece (substrate) of radius R_{nano} = 10 μm (a), and ratio of probabilities P_a(2000 V, 50 nm, 450 K)/P_a(0, 10 μm, 750 K) at dependence on voltage U (b)

According to the calculations, the electric field strength for the nanostructured coatings exceeds 10^3-10^4 times the strength obtained for microstructured coatings, when the impulse of high bias potential is applied to the substrate. At the potential of 2000 V and coating with grain sizes of 50 nm deposited on the surface with grain size of 10 μm, the probability P_a(2000 V, 50 nm, 450 K) of strong bonds formation at the substrate temperature of 450 K equals the probability P_a(0, 10 μm, 750 K) of strong bonds formation at the substrate temperature of 750 K. Thus, impulses of high negative potential allows changing significantly the activation energy of the process of strong bonds formation in the growing coating, which makes it possible to obtain high quality characteristics of coating at growth temperature of about 450 K.

4. CONCLUSION

The developed model allows describing adequately the effect of high negative impulse potential applied to the substrate for deposition of wear-proof nanostructured coating. The model can be useful to describe the changes in quality characteristics of a surface layer, which depend on bonding energy between the atoms of growing coating such as microhardness, adhesion, inherent stress, reflecting power, friction factor, durability, etc.

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