Cathodic arc low temperature separated ion deposition – new technique and equipment

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The findings of an investigation of characteristics of the developed wide-aperture electric arc plasma source that features flux separation from micro-particles and neutral component are described hereinafter. The source has been proved to form a highly ionized flux of gas and metal plasma with the ratio between the gas and metal component subject to control.

The coating deposition rate using the source can be as high as 40 mkm/h, whereas the etching rate - 8 mkm/h.

The influence of the substrate temperature on the deposited coating features has been examined. The possibility to deposit high quality coatings irrespective of the substrate temperature has been proved.

1. Introduction

Vacuum ion-plasma methods have found a extensive use in numerous industry fields during the last decades. These methods are used for surfaces etching, polishing, deposition of thin decorative, corrosion and wear resistant films, surface hardening and, as a whole, creating structures with distinct predefined characteristics at article surfaces.

Although all vacuum ion-plasma technologies are based on materials sputtering techniques aimed for production of ionized plasma, those of principal importance are cathode sputtering, high frequency sputtering, magnetron sputtering, electric beam sputtering and electric arc sputtering.

The electric arc method is advantageous in comparison with other ones by having the high degree of plasma ionization and high- energy potential of charged plasma particles, it is quite simple in use, and enables adequate technological process control. This is the reason for extensive use of the electric arc evaporation technique in deposition of hard wear resistant coatings. However, numerous drawbacks of this method set considerable limits on its technological capabilities.

One of these drawbacks is that at arc evaporation from the cathode, molten cathode metal drops enter to the plasma. These drops that settle on the article surface together with the coating cause coating defects, thus impairing its strength. Moreover, most of coatings deposite in this way are have typical for them columnar structures and contain micro-pores going through all the coatings, thus impairing the coating corrosion resistance.

Another drawback is that in order to obtain high quality coatings the treated products must be usually kept at a temperature of 450°C and more. Relatively high temperature does not allow treatment of products that change their physical and mechanical volumetric properties when subjected to heating.

This report describes the results of an investigation of characteristics of the developed electric arc plasma source [1] featuring flux separation form micro-particles and neutral component. The influence of temperature on the properties of the deposited coatings has been investigated and the technique of coating deposition at relatively low temperatures has been offered.

2. Separated plasma source SPS-1

Different filters for separation of electric arc plasma flow from micro-particles and neutral component were described (refer for example to [2-5]). However, most of these filters are inefficient (low plasma transmission coefficient) [6] and inapplicable for industrial use. The main reasons for the poor efficiency of known filters have been described in [1].

A highly effective wide aperture electric arc source featuring plasma flux separation and high plasma density at the output [1] was developed in IBT group. The schematic drawing of the source is illustrated in Fig. 1. The source consists of a plasma guide formed as a tore segment with the angle of 120°. The internal tore diameter is 200 mm. An electromagnetic coil is positioned at the outer side of the plasma guide. Cathode assembly at the plasma guide inlet includes a cathode fastened on it, which is offset from the plasma guide center in such a manner that relative to the tore center it is located on radius $R_0=\sqrt{r*R}$ where r and R are the small and the big radiuses of the plasma guide walls respectively. Arc discharge anode, with the vacuum chamber walls possibly serving its

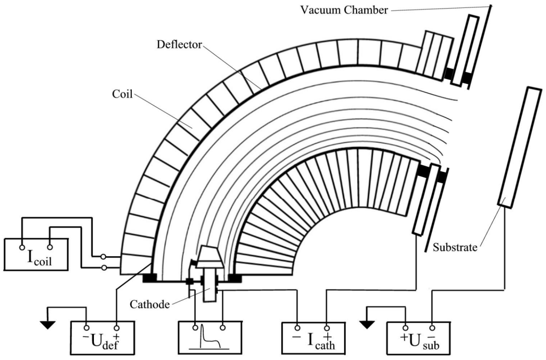

Fig. 1 . Schematic drawing of plasma source SPS-1

function, is located at the opposite end of the plasma guide. Positive or negative voltage is applied to the deflector body.

When current flows through the coil, a magnetic field homogenous throughout the length is generated inside the plasma guide. The magnetic field intensity at the tore axis line is as high as 600 erg. The arc discharge is initiated between the cathode and the anode and it provides for the arc electron flow via the plasma formed inside the inside the plasma guide. Since the electron component of the plasma is magnetized, the magnetic field force lines crossing the cathode adjacent the plasma guide axis assume potential close to that of the cathode, whereas the force lines adjacent to the plasma guide walls – the walls potential. Hence, electric field perpendicular to the deflector walls is generated in the plasma. The electric field provides for ions drift from or towards the deflector walls, depending on the polarity and magnitude of the voltage applied to the walls. In this way the ionized plasma component is transported along the force lines of the magnetic field in the plasma guide to the outlet. At the same time the micro-particles and the neutral component of the plasma are deposited on the plasma guide walls.

3. Investigating the separated plasma source SPS-1 parameters

Industry standard coating device HHB-6.6 having its standard electric arc evaporator replaced by SPS-1 source was used in the experimental study of the developed electric arc plasma source. The cathode was made from titanium. At the ion current measurement the substrate was formed as a disc 200 mm in diameter located at a distance of 250 mm from the plasma guide end.

Figure 2 and 3 illustrate the ion current to the substrate and TiN coating deposition rate versus the

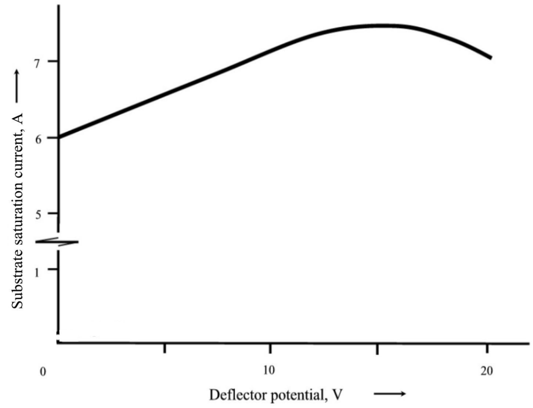

Fig. 2. Substrate saturation current versus the plasma guide walls potential.

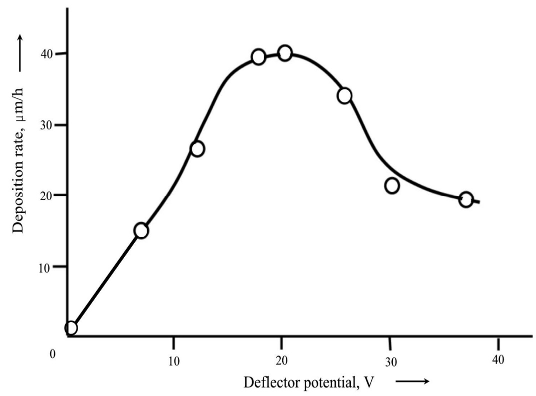

Fig. 3. Coating deposition rate versus plasma guide walls potential.

plasma guide walls potential. The measurements were conducted in nitrogen environment under a pressure of $2 \cdot 10^{-3}$ mm Hg in the vacuum chamber. The arc discharge current was equal to 200 A.

During the current measurement, negative potential of –500 V was applied to the substrate. During the deposition rate measurement, the substrate potential was –80V. One can recognize a similar nature of the substrate current and the coating deposition rate changes. Both curves have an apex point: the current change curve reaches the apex when the separator body voltage is ~ 16 V, whereas the deposition rate curve - at a voltage of 20 V. As the voltage is decreased or increased, the substrate current and the deposition rate are decreased. However, in the event of relatively slight substrate current decrease following slight voltage drop, the deposition rate virtually drops to zero.

Fig. 4 illustrates the substrate current change versus the substrate voltage applied to the substrate,

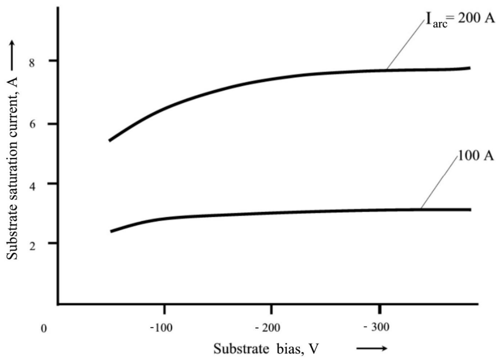

Fig. 4. Substrate current versus accelerating potential

for two different arc discharge current values. One can see, that the substrate current practically reaches saturation at about –100V and then remains almost unchanged.

Fig. 5 illustrates the coating deposition / substrate etching rate – versus substrate potential at zero voltage at the plasma guide body. The

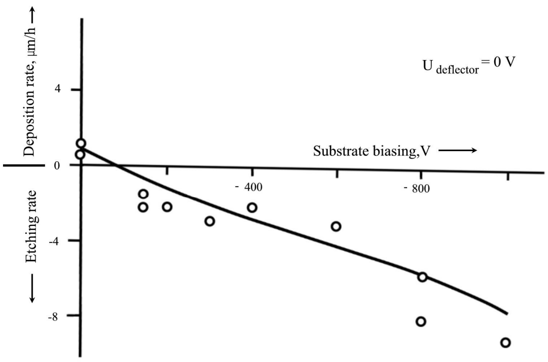

Fig. 5. Substrate deposition – etching rate versus the substrate voltage.

measurements were conducted in argon environment under a pressure of $2{\cdot}10^{-3}$ mm Hg and arc discharge current of 200 A. As substrate material tool-grade steel P6M5 was used. At a zero substrate potential slow coating growth at a rate of 0.5 mkm/h can be observed. As the voltage is increased over 150 V, the substrate sputtering occurs and the etching rate goes as high as 8 mkm/h at the substrate voltage of 1000 V.

Fig. 6 illustrates the pressure at the plasma guide inlet (close to the cathode assembly) and the TiN coating deposition rate versus the arc discharge current. The measurements were taken with nitrogen pressure in the chamber equal to $2{\cdot}10^{-3}$ Hg mm.

It can be seen that at the absence of the arc discharge the pressure at the plasma guide inlet is

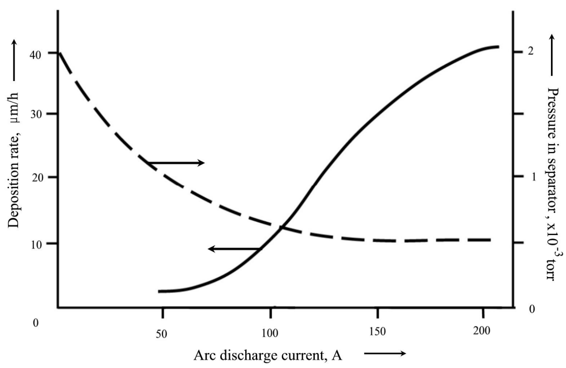

Fig. 6. Pressure at the deflector inlet and deposition rate versus arc discharge current.

equal to the pressure in the chamber. As the current is increased the pressure is reduced and when the current goes beyond 100 A, it becomes much lower *than in* the system chamber. When the current is beyond 100 A, the deposition rate increase becomes remarkable and reaches 40mkm/h when the current is 200 A

From the results it might be suggested that the plasma source generates a highly ionized flux of gas and metal plasma. The ratio between the gas and metal components depends on the deflector bias voltage. At zero bias potential the gas component is dominant. This is evidenced by nearly zero coating deposition rate at a sufficiently high substrate current, whereas at negative substrate voltage the substrate etching is quite fast. The increase of the deflector potential results in higher metal component share in the plasma flux and the beginning of coating generation. The deposition rate reaches 40 mkm/h when the plasma guide body potential is equal to 20 V. The substrate current drop and the coating growth rate decrease at further bias increase are likely to occur because of generating of instabilities inside the plasma guide and partial plasma settling on the walls.

The pressure drop at the plasma guide inlet with arc discharge increase might be associated with the ions acceleration mechanism in the direction towards the plasma guide outlet. It might be a result of magnetic-plasma-dynamic effects occurring at the plasma guide outlet, where the plasma flux interacts with the diverging magnetic field having a radial component, as well as because of electrons flow (arc discharge current) through the plasma.

Hence the plasma source efficiency might depend be on the one hand - that the plasma is emitted from the cathode directly to the areas of homogenous magnetic field and transported along the magnetic field force lines without crossing them. Such configuration rules out appearance of “magnetic plugs”, as well as electrostatic barriers when applying voltage to the plasma guide body.

On the other hand, it can be a result of the arc discharge electron flow through the plasma in the plasma guide. The directional electrons motion results in the gas ionizing in the entire plasma guide volume, resulting in reduced energy losses of ions emitted by the arc discharge that stem from dissipation on gas particles. Moreover, electrons flows along the plasma guide axis are likely to interfere with the ions reaching the plasma guide walls and to produce the ions acceleration in the same direction.

4. Special features of coatings generated with the separated plasma source SPS-1

Some of the TiN coating features obtained with the source with plasma flux separation were investigated (refer also to [7]). Substrates made from tool steel P5M5 were used for coating. The coatings examination under an electronic microscope showed the total absence of drops phase. The coating has columnar structure with disperse columnar crystals size smaller than 0.1mkm. It is worth mentioning that the columnar crystallites in the coatings obtained with traditional electric arc evaporators measure 1.0 by 3.0 mkm. Fig. 7 illustrates the coatings micro hardness and

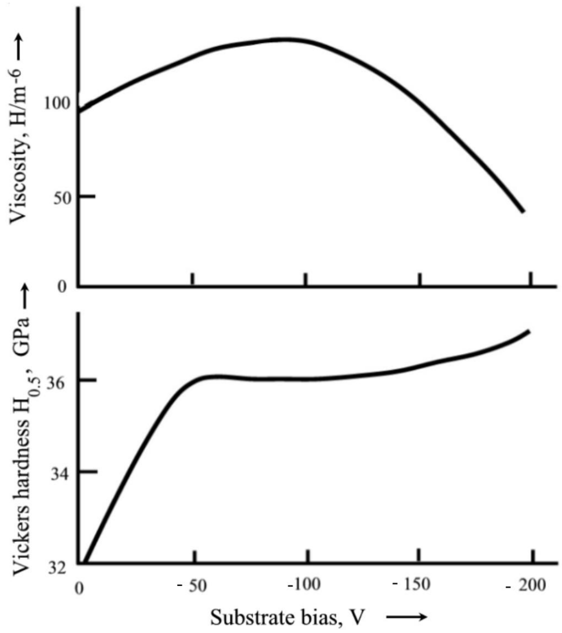

Fig. 7. Palmquist viscosity and micro-hardness of the coating versus substrate bias voltage.

viscosity (Palmquist) versus the substrate bias voltage. It can be seen that the coatings micro-hardness reaches 36-37 GPa at a viscosity of up to 150H/m^{-6}. The measurements indicated residual macro-tensions of about –3000 ÷ –3500 MPa. It is worth mentioning that usually the micro-hardness of coatings obtained using traditional electric arc.evaporators is of the order of 25 GPa, the viscosity of the order of 25 H/m^{-6} and internal compressing intensity of the order of –1700 MPa.

It may be suggested that high plasticity of coatings obtained with plasma sources using flux separation at high micro-hardness and compression macro-tensions, results from highly dispersed structure of the coating. Hence, overall structural parameters and physical / chemical features of the coatings obtained using the new plasma source might compare favorably with the coatings obtained using the traditional electric arc sources.

5. Low temperature coatings deposition

As already mentioned, in order to obtain coatings with improved functional properties, the substrate temperature during the deposition usually shall be maintained at 450°C and more.

At the same time some reports [8,9] describe electric arc method deposition at relatively low temperatures (about 200°C).

For example, [8] describe TiN coating deposition method with negative voltage pulses between tenths of second and several seconds. However, in this case a relatively thin coating as small as 1.5 mkm can be obtained. The thickness increase results in impairment of the operational features of the coating.

The study reported in [9] suggested to superimpose high voltage pulses of amplitude not over 20kV, frequency 1-2 kHz, and pulse duration 1-3 μsec to the DC accelerating voltage applied to the substrate. Such high pulsed accelerating voltage results in ions implantation in the near-surface layers along with mixing of surface layers and forming of stable coating structure. Wear-resistant coatings with adequate thickness and additional operational features were generated. This method was named “Hyper Ion”.

The method has the following drawbacks. Accelerated ion energies as high as these lead to considerable ions sputtering. Deposition of complex multi-component coatings results in preferential sputtering of certain components on the others, thus forcing out of the coating structure stoichiometry. In addition, the use of voltages as high as these makes the deposition process and the needed equipment more complex. High voltages are likely to lead to arc breakdowns in the vacuum chamber and discharge contraction. Special high-voltage electric inputs must be used for application of high voltage to the products. The mentioned problems become even more complicated because of different devices for products rotation and displacement normally used in vacuum chambers designed for coating deposition. These devices contain rotating, friction and contacting parts.

Most of the coating deposition equipment used in the industry is not designed for voltages as high as that, and is not applicable for the method implementation without fundamental changes.

Hence, in spite of the existing studies on coating deposition, yet highly efficient industrial technique of low-temperature deposition of wear-resistant coatings with additional operational features is to be developed. Such technique will widen the scope of work, and not only extend the highly efficient PVD technologies to new industry fields, but sometimes improve their performance in the traditional fields of such coatings application.

In this connection in the present work the substrate temperature influence at deposition on TiN coating features was investigated at the first stage. In different experiments the temperature of the specimens was changed from 200° to 600°C. The coatings structure was examined by X-ray analysis using difractometer "Dron-3.0" in filtered Co_k-radiation.

It has been found that at temperatures beyond 400° a homogenous coating gold-yellow in color is generated on the substrate surface. As the temperature is decreased spots of dark color emerge in the homogenous coating. At a temperature lower than 250°C the deposited coating consists of two layers: the lower ≤1mkm thick layer gold-yellow in color and the upper dark colored porous layer. The dark colored upper layer is easy removable from the surface.

Fig. 8 shows a difractogram of coatings generated at two different temperatures along with the difractogram of standard TiN powder. It can be seen that the coatings obtained at different temperatures are virtually single-phased and consist of TiN. However, the coating structures are different. Coating generated at high temperature shows expressed axial texture (111) in the direction normal to the surface. The coating generated at a low temperature does not have any expressed texture and its difractogram is quite similar to that of the standard powder.

Fig. 9 and 10 illustrate the half - width of diffraction lines and the lattice parameters for different lines versus temperature. It can be seen that the temperature decrease results in the line half-width increase. The lattice parameter depends

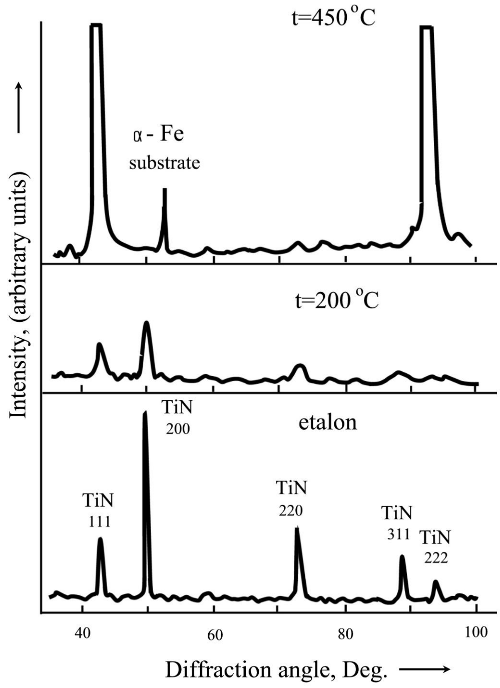

Fig. 8. Difractograms of coatings at different temperatures.

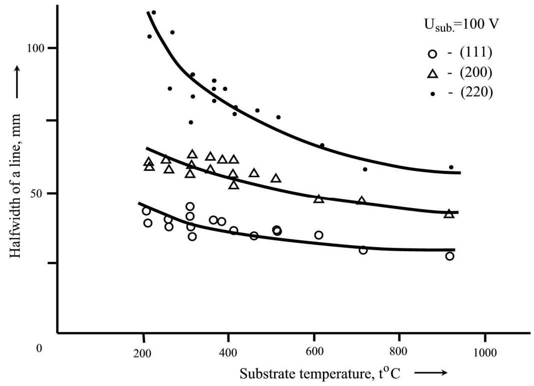

Fig. 9. Half-width of diffraction lines versus temperature.

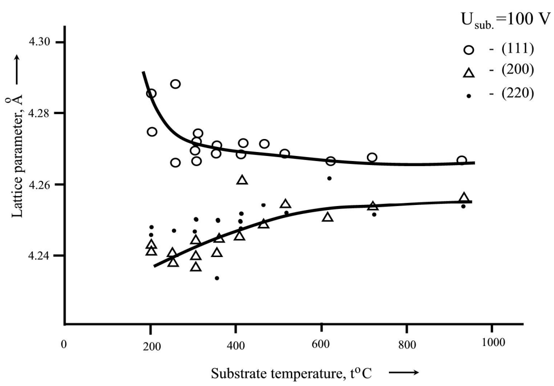

Fig. 10. Lattice parameter along different diffraction lines versus temperature.

on the temperature too. One can see on Fig. 10

different behaviors of the lattice parameter determined by the maximal values of different diffraction lines: that determined by the (111) line is increased, whereas that determined by (200) and (220) is decreased with the temperature decrease.

It is believed that annealing of thermal coatings occurs when the substrate temperature is high. As a result of diffusion processes occurring inside and at the coating surface the atoms occupy thermodynamically equilibrium states. At low temperatures with no diffusion a coating is formed as a result of random settling of atoms, and the structure may be far from thermodynamic equilibrium and exhibits high defects density and internal tensions.

Hence, the conclusion is that excitation of atoms settled at the target surface with their further relaxation to thermodynamic equilibrium state is likely to enable forming of a required coating structure regardless of the substrate temperature. The settled atoms can be excited by bombarding with accelerated ions. Since the plasma flux in electric arc deposition technique is highly ionized, bombarding with accelerated ions can be concurrent with deposition by application of acceleration voltage to the substrate.

For testing of such deposition pattern, a high-voltage pulse power supply was designed with the pulse voltage parameters such as pulses voltage amplitude, duration and frequency adjustable in a wide range.

At coating deposition the pulse parameters were selected on the following grounds. The pulse-repetition period shall be shorter than the time of settling of a single coating monolayer, i. e. $t_p \leq \delta/C$, where t_p – pulse-repetition period, δ - monolayer thickness, C- coating deposition rate. The pulses amplitude and duration shall be that which provide for energy transferred to the substrate by accelerated ions during the pulse period higher than the total threshold energy of displacement of all the particles settled between the pulses from the crystal lattice point. On the other hand, the parameters of pulse voltage shall be adjusted to prevent notable substrate heating.

The typical parameters were as follows: pulse duration from 50 to 150 mksec, pulses amplitude from 300 to 1000 V, pulse repetition period from 600 to 1200 mksec.

TiN and TiAIN coatings were deposited on a substrate made from tool steel P6M5 heated to the temperature of 200°C. The coating thickness was 6 mkm. The coating micro-hardness and adhesion measurements indicated that these characteristics were close and in some cases might compare favorably with similar coatings obtained at a temperature of 450°C.

Hence, theoretical (conceptual) possibility of generating of relatively thick high- performance coatings regardless of the substrate temperatures was proved.

Based on the conducted investigation a method of deposition of low-temperature ion-plasma hardening corrosion and wear resistant coatings was developed [10].

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