Equipment and Methods for Hybrid Technologies of Ion Beam and Plasma Surface Materials Modification

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Abstract – An installation for realization of hybrid technologies of the ion-beam and plasma material treatment includes vacuum-arc generators of gaseous and metal plasma with the devices for microparticles filtering, medium frequency dual magnetron, high current ion and plasma source, high voltage generator for short-pulsed, high-frequency, plasma-immersion ion implantation or coating deposition. With the use of the complex installation equipment, an intermetallide Al → Ti system was formed in a target surface layer to a depth of 2600 nm with a dopants concentration up to 60%. The abilities of improvement of the main physical and mechanical characteristics of coatings in comparison with conventional PVD technologies have been demonstrated on the example of formation of monolayer TiSiB coating and multilayer TiAlN/TiN coatings with the thickness of each separate layer varied from 2 to 10 nm.

1. Introduction

The latest tendencies of hybrid ion-beam and plasma technologies development are connected with the formation of multi-phase including multilayer functionally-gradient nanostructure systems in the surface layers of materials or in the form of coatings. Such systems can be created under the regime of high concentration (HCII) including plasma immersion ion implantation and ion-assisted deposition of multilayer functionally-gradient coatings, containing up to several thousands of separate layers with thickness from several units to several tens or even hundreds of nanometers [1, 2].

Taking into account the diversity of ion beam and plasma influence methods, now there is an acute need in creation of multi-purpose equipment, which can provide an efficient choice of a treatment regime. The example of such equipment can serve the new generation complex installation (CI) created at Nuclear Physics Institute (Tomsk) [3].

2. Equipment

CI was designed in the form of the single technological module, the external view of which is shown in Fig. 1. CI equipment is located on the basis of a vacuum chamber with a volume of 0.6 m^3, planetary mechanism of samples rotation with a heating device.

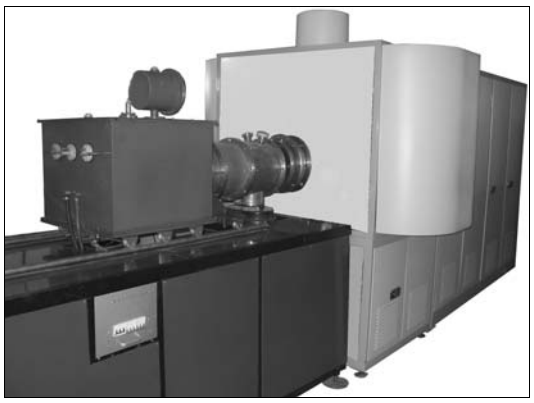


Fig. 1. External view of the complex installation

The chamber is equipped with a turbo-molecular pump of high throughput, gas puffing device, and sensors for temperature measurements. The configuration of CI equipment can be easily changed thanks to application of removable walls in the vacuum chamber.

Up to eight axial-symmetric vacuum-arc evaporators (VAE) based on dc vacuum arc discharge (VAD) and those, adapted for operation with heat-resistant materials can be used in CI as the main plasma generator. VAE are equipped with axial-symmetric electromagnetic shutter-type plasma filters (PF). The given data [4, 5] demonstrate a possibility of decreasing MPF on the coating surface by more than 10^2–10^4 times.

Plasma distribution in the interelectrode gaps of PF is defined in $E \times B$ fields, which were formed by current through shutter electrodes and a positive bias potential application to PF electrode. PF opacity for the charged plasma component depends on geometric parameters and electrodes orientation, reactive gas pressure, bias potential amplitude and magnetic field topography. As a result of optimization of the specified parameters, the relation of ion saturation current from plasma at the PF input and output can reach 0.58 [5].

A middle frequency extended dual magnetrons are used in CI as plasma generators for a uniform processing of extended products [3]. The magnetron sputtering system (MSS) presents a planar dual magnetron with direct target cooling by running water. Magnetrons insulated from each other were connected to the supply source with an output power up to 25 kW that generates bipolar voltage pulses with duration of 12 μs and frequency up to 40 kHz. The application of a dual system enables to take away the substrate from the current flow area. In combination with the pulsed re-

gime of plasma generation, it provides high stability of the discharge, practically complete absence of MPF, without application of expensive schemes of arc quench and retention of high rate of coating deposition for a wide range of reactionary gases.

A source based on low-pressure arc discharge with heated cathode of PINK series is used in CI to form the gaseous plasma flow [6]. Plasma generator provides the formation of uniform plasma with concentration of 10^9–10^{10} cm^{-3} in the volume exceeding 1 m^3. Plasma is not polluted by the cathode material, because the discharge burns diffusely, without the cathode spot formation. PINK proved to be very good in regimes of surface clearing and heating, additional ionization of reactionary gases, nitriding, etc. [7].

Ion-beam influence on materials is provided by two systems of accelerated ions formation. In particular, a regime of generation of short (0.5–2 μs) pulsed ion flows under conditions of high frequency (up to $4.4 \cdot 10^5$ pps) negative bias potential supply on the samples immersed into plasma is realized.

Alongside with traditional advantages of a plasma-immersion scheme of ion flow formation, transition to high-frequency, short-pulse, plasma-immersion ion implantation and (or) coating deposition (HFSP^{2}I^{3}D) enables to sufficiently increase bias potential on the samples without initiating micro-arc processes on the surface being processed [8].

The principal advantage of HFSPPI^{3}D method is connected with an opportunity of effective treatment of dielectric materials, located on conductive holder. In this case, the bias potential pulse duration will be determined by charge time of capacitor. The electric field arising at the dielectric surface is determined by its thickness, dielectric permittivity, dynamics of ion accumulation on the surface, plasma parameters and bias potential amplitude and duration. Estimations presented in [8] show that HFSP^{2}I^{3}D method can be realized as with the ion current density from plasma of tens and hundreds of A/cm^2, with pulse duration of tens or hundreds nanoseconds, as well as with the current density of units and parts of milliamper, with pulse duration of tens and hundreds of microseconds.

CI includes based on dc VAD “Raduga-5” source for the formation of ion beams of conductive materials with energies varying from 20 to 160 keV [9]. The source combines dc mode of microparticle filtered plasma generation with repetitively pulsed or dc ion beam formation with a pulsed ion beam current up to 2.5 A. The diode of the source is formed by PF electrodes and “grounded” grid electrode.

An additional grid under negative potential is provided for the cut-off of secondary and plasma electrons from the accelerating gap. The average ion beam power as well as the sequence of ion and plasma material treatment can be varied by changing the vacuum arc current, accelerating voltage pulse amplitude and pulse repetition rate.

3. Conditions of joint operation of equipment in the CI

Hybrid technologies of ion beam and plasma treatment can be realized both with low pressure and in the ambient of reactionary gases. It can be seen on the diagram (Fig. 2) that the pressure range for the CI equipment ranges from 10^{-5} to 1 Pa. Joint operation of the all CI equipment is realized under the pressure of 10^{-3}–10^{-1} Pa.

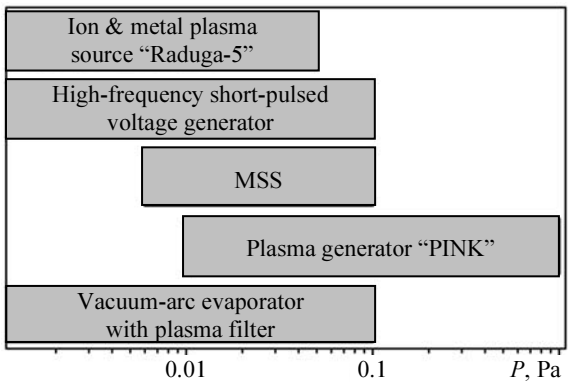


Fig. 2. Working pressure range of the CI equipment

Investigations in nitrogen show that with pressure less than 0.1 Pa, PF operation is stable. When pressure increases the frequency of electrons collision with gas atoms increases which decreases the conditions of electron “magnetization” and causes ion losses on the PF walls. In the pressure range of 0.1–1 Pa, ion current from plasma decreased by 2.6 times without PF and by 3 time with PF. Consequently in the pressure range under consideration, the areas of the PF and VAE application coincide [8].

Joint operation of VAE and MSS, enabled to decrease the working gas pressure in magnetron more than by an order. In this case, vacuum arc plasma performed the function of the additional gas.

The range of changing the intensity of ion and plasma influence on the materials surface using CI equipment is presented in Fig. 3.

The CI provides formation of ion beam and flows with the energy from 100 eV to 160 keV with average power density up to 100 W/cm^2. The pulse duty factor during HFSPPI^{3}D regime varies from 0.08 to ~ 1. Relation of ion current density on the target from plasma and in the form of ion beams can vary from 0 to 100%. The coating deposition rate including in the medium of reactionary gas reaches several tens of micrometers per hour.

In conditions of joint or successive ion beam and plasma influence on materials, CI enables to realize regimes of the surface clearing and activation, “conventional” and HCII, formation of transition layers between the substrate and coating, coating deposition under intense ion mixing.

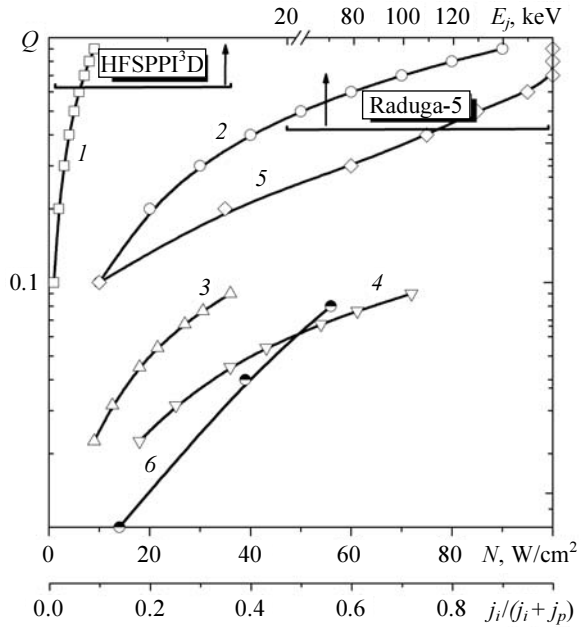


Fig. 3. Variation range: average ion energy for HFSPPI^{3}D and Raduga-5 source, average ion power density (*1–4)* for j_i = 10 mA/cm^2 and ratio of accelerating ion current density (j_i) to plasma ion current density (j_p) (*5*, *6*) of the duty factor (Q), HFSPPI^{3}D: *1* – E_i = 1 keV; *2* – E_i = 10 keV, Raduga-5; *3* – E_i = 40 keV; *4* – E_i = 80 keV; *5* – HFSPPI^{3}D; *6* – Raduga-5 (E_i = 80 keV at a distance of 50 cm from the ion source)

4. Technological application

Joint application of "Raduga-5" ion beam source and short high-frequency bias potential allows realizing various variants of ion implantation.

Thus, for example, the regime of "conventional" ion implantation, in the absence of coating deposition between the pulses of ion beam accelerating voltage can be realized provided that the gaps between the bias potential pulses are less than the time of plasma flowing, formed near the target surface of an accelerating gap [10]. Conventional ion implantation can also be executed in case of ion beam dc generation by "Raduga-5" [9].

The transition to HCII regime is realized with compensation of a layer sputtered from the target surface, deposition from plasma of the same material that the implanted ions have, between the pulses of accelerating voltage [1]. At the expense of introduction of implanted material atoms as recoil ones from the surface deeper into the target, the concentration of the dopants can exceed the irradiation doze and reach 100 at.% near the surface.

In paper [11] the HCII regime has been realized at Al ion (j_i = 1.2 mA · cm^{-2}, E_i = 40 keV) processing of a Ti target placed on the distance of 40 cm from the output of ion source. During 125 min, a Ti–Al intermetallic system having the concentration of dopants up to 60 at % was formed. Radiation-stimulation diffusion processes, contributed to the doped layer formation at a depth of about 3 μm. The average size of the formed phases constituted 24–65 nm.

Under conditions of Al introduction in the form of ions and recoil atoms, the retained dopant dose reached 3.6 · 10^{18} ion · cm^{-2}, which is 1.6 times more than the irradiation dose.

The possibility of varying the density of the ion flow power enables to expand sufficiently the range of the realized regimes of material treatment using CI equipment. A possibility of an efficient clearing of a sample surface of a titanium alloy VT-9 in HFSP^{2}I^{3}D regime before an application of a multicomponent TiSiB coating has been demonstrated in paper [10]. At bias potential –4 kV, and the pulse duty factor of 0.66, density of the Ar ion flow power was 40 W/cm^2. Efficient ion etching contributed not only to the surface clearing but also to its roughness decrease. The transition from surface cleaning to formation of a transition layer and coating deposition was realized by changing of the amplitude and (or) bias potential pulse repetition rate on the samples.

The coating was deposited under HFSPPI^{3}D regime with the use of additional vacuum arc generators with PF equipped with composite TiSiB cathodes. At the pulse duty factor of 0.3, the primary coating deposition was realized under ion mixing conditions. The radiation-stimulated diffusion mechanism of forming a transition layer (in conditions of high average power density in the ion flow) caused a smooth character of dopants concentration distribution from the surface to target depth up to 1 μm.

During investigation of a coating structure with a thickness of 6 μm, the formation of an amorphous layer was observed in the surface layer at depths up to 25 μm. It promoted an increase of the ultimate strength under cyclic sample loading by two orders of magnitude. The ion-assisted increase in the coating density resulted in a 20-fold increase in the resistance to salt corrosion of samples in the presence of the chlorine ion at elevated temperatures under conditions of thermal cycling [10].

At the formation of a multilayer, nanostructure coating based on TiAlN/TiN system, CI comprised the gaseous plasma generator, four VAE with PF with the cathodes of Ti and four VAE with PF with composite TiAl (50/50 at%) cathodes.

The formation of a multilayer coating was carried out in the nitrogen plasma during the rotation of holders with the samples from one VAE to another one. Thickness of the separate layers was controlled by vacuum arc current and the rate of the samples rotation and changed from 2 nm for TiN layer to 10 nm for TiAlN layer. Thus, the size of the phases being formed did not exceed the thickness of separate layers of a coating. With a total thickness of a coating 4 μm, more than 333 separate double TiAlN/TiN systems were formed.

The process of the coating formation included four main stages: surface clearing by Ar ions, formation of

a transitional layer and saturation of a surface by N_2 atoms, sample heating and coating deposition. It follows from the data presented in Fig. 4 that the processes of a transition layer formation and coating deposition are accompanied by a decrease in temperature of a condensation surface.

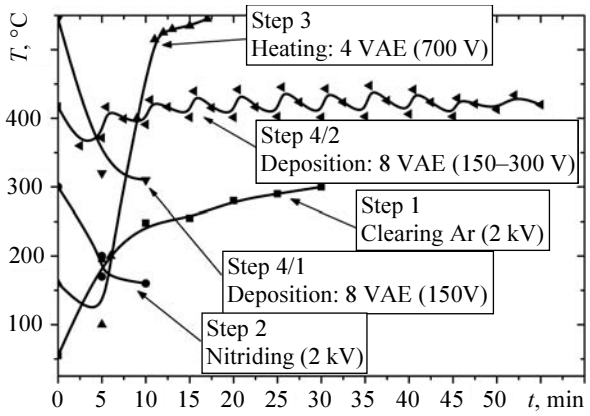


Fig. 4. Temperature of the sample surface on various stages of a technological cycle

The coating deposition was realized in conditions of a periodic change of a bias potential in the process of ion assisting with the purpose of maintaining the constant temperature. The short-term varying of the ion energy enabled to maintain the optimal temperature of the process on the level of 430 °C. The variant of a dynamic bias potential change seems more preferable in comparison with an application of a higher constant bias potential. The results of comparative measurements of an adhesive strength and hardness of a monolayer TiN and TiAlN coating deposited in the regime of dc bias potential, monolayer structurally-gradient TiAlN coating and multilayer nanostructure TiAlN/TiN coating presented in Fig. 5 are the evidence of this.

As is seen from the presented data the optimal value of characteristics being measured is observed at middle bias potential of 100–200 V.

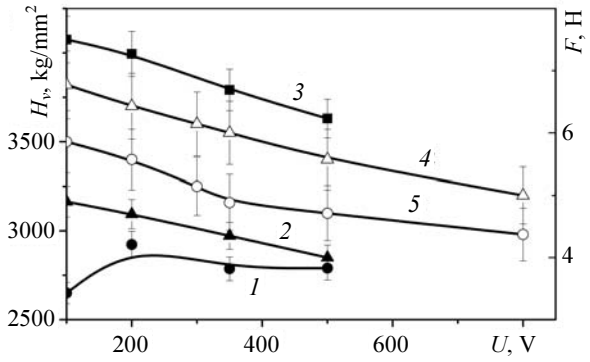
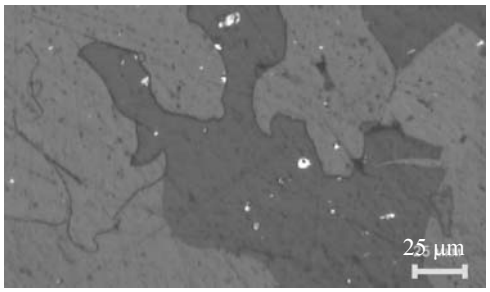


Fig. 5. Measurement of a critical load of delamination (*1–3*) and coating hardness (*4*, *5*) depending on the bias potential amplitude: *1* – (TiN) and *2* – (TiAlN) monolayer coating at DC bias potential; *3*, *5* – (TiAlN) and *4* – (TiAlN/TiN) coating at changing by amplitude short-pulse, high frequency bias potential

The coatings with nanosize layers showed the greatest sensibility to the change of ion energy. The micropicture of a multilayer (TiAl)N/TiN coating presented in Fig. 6, *a* shows that at bias potential of 300 V, high inner tensions, stimulating delamination of separate coating layers, are formed in the coating structure.



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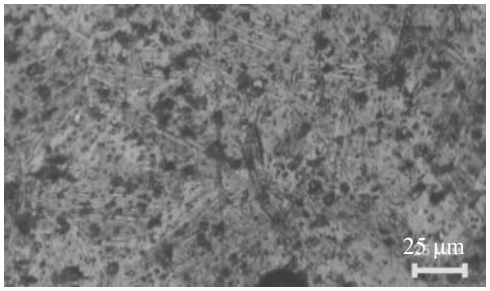

b

Fig. 6. Picture of a multilayer (TiAl)N/TiN coating with the thickness of separate layers of 5 nm: *a* – U = 300; *b* – 100 V

At the same time, the multilayer character of a coating prevents from the formation of deep cracks and cross delamination of a coating. Decrease in middle bias potential up to 100 V causes the reduction of compressive stresses and formation of a more homogeneous coating (Fig. 6, *b*).

5. Conclusions

The developed CI provides the formation of plasma flows of conductive materials and gases with concentration up to 10^{11} cm^{-3} and ion beams with energy from 100 to 160 keV with an average power density to 100 W/cm^2. The pulse duty factor at the ion flow formation varies from 0.08 to 1. Relation of ion current density on the target from plasma and in the form of ion beams can vary from 0 to 100%. The coating deposition rate, including in the reactionary gas medium, reaches several tens of micrometers per hour.

The possibility of forming deep (> 2 μm) modified layers with concentration of dopants to 60%, creation of wide transition layers between the substrate and coating, deposition of mono- and multilayer nanostructure coatings with improved physical and exploitation properties in comparison with traditional PVD technologies has been demonstrated with the use of CI equipment and the suggested methods of material treatment (HCII, HFSP^{2}I^{3}D).

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