Composite ion-plasma coatings with nanodisperse reinforced phase: scientific and practical aspects of synthesis

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Abstract. The article describes the main aspects of the synthesis of composite coatings in the surface layer of figurine-shaped product using low-temperature plasma of combined discharge. The example of cutting tools shows the benefits of using the coatings in extreme conditions that occur in machining of materials by cutting.

1. Introduction
During operation, changing the properties of the working surfaces of products for various purposes occurs at the contact areas under the active influence of the external environment. It is the most relevant for the products operating under extreme temperature and power loads, such as cutting tools of complex mechatronic machine tools, precision parts of aircraft drives and others. This results in a continuous change in the shape of the contact surfaces, which leads to a change in temperature and stress distribution in the area of actual contact, and as a consequence, to fatigue and abrasion strength/resistance outage.

A promising way to increase abrasion and fatigue resistance is the creation of technologies and equipment that allow forming structures characterized by dissipative properties in the product surface layer. Special protective coatings may serve as these structures; they are created with the use of single-layer coating deposition techniques (with ion assisting); multilayer coatings with layers of nanometer thickness; multiphase coatings and their combinations, produced by ion-plasma technology [1-4]. It should, however, be noted that the works on producing these coatings in most cases are in the stage of laboratory research and testing. The use of conventional coatings to create dissipative structures is not possible due to the absence of amorphous phase in their structure, and this phase works for permanent local moving of minimum number of particles of minimal size (groups of atoms) in a minimum time without momentum transfer.

In conventional coatings atoms do not have such freedom, so any displacement causes crack formation on the surface, and lattice defects causing delamination and destruction of the coating, reducing its reactivity and mechanical strength, especially during functioning under extreme conditions. In addition, practical implementation of these technologies is associated with the need to create plasma volume which is then transformed and delivered to the treated surface. In this case, most of the energy consumption is spent on the creation of plasma, maintaining its generation conditions and delivery of active plasma particles with a given energy to the object of processing and further scanning them on the surface. The process of forming nanocomposite structure takes only a few percents of the general energy input. In addition, most of the methods that create directional movement of charged particles through the use of various ion source and
accelerator systems, cannot modify the geometrically complex parts and products due to their limitations in the machined surface profile (planar and/or cylindrical with no protruding elements). Finally, the methods are expensive and have long processing cycles. The foregoing means that the formation of nano-composite dissipative non-reactive structures with high hardness and resistance in the operation in extreme conditions, and on this basis, providing higher efficiency of the surface layer is an acute scientific and practical problem.

2. The Scientific Basis
It is possible to increase the strength of the product surface layer by its modification with low temperature plasma combined discharge, the formation of which is a sequential flow of the following events [5]:

- application of electrostatic field (displacement potential + 65 ... 200) and microwave electromagnetic field at a reduced level of microwave power (30 ... 90 W) at a pressure of about 300 Pa in a process gas mixture;
- local gas breakdown at the outer boundary of the plasma cloud;
- electron drift to the inner boundary of the plasma cloud;
- formation of compensated flow of charged particles;
- emission of electrons and ions with the inner boundary of the plasma.

To improve the modification efficiency plasma should be formed immediately around the treated surface, which will make it possible to use the maximum amount of energy for proper execution of the synthesis process of the composite coating per se and not on maintaining the conditions of formation and delivery of active plasma particles (electrons and / or ions) to the treated surface as it is implemented in other technologies [6]-18.

Mathematical description and the analysis of its results, firstly, show that the decisive role in the formation of low-temperature plasma is played by ionization-recombination bulk processes and processes of ambipolar diffusion, and, secondly, allow determining the conditions that ensure plasma formation around the working portion of the article:

- efficient energy deposition in ionization processes under the gas breakdown in ionizing electromagnetic fields and collecting electrostatic field by reducing breakdown voltage using working pressure and easily ionized additives;
- formation of compensated stream of charged particles in the drift space, which results from the Coulomb interaction between charged particles in quasineutral space and prevents separation of charges in their joint motion with the same speed towards the surface of the product.

The validity of the conditions has been confirmed by research into their efficiency, including:

- Recording the emission spectra of the low-temperature plasma under different conditions of its formation, determined by the parameters of the electrostatic and electromagnetic fields;
- The study of the distribution of the spectral line intensities and their correlations, depending on changes in the level of input microwave power;
- Identification of the chemical composition of the gases involved in plasma formation;
- Comparison of the spectra with literature report.

The research results led to the following conclusions:

- Near the boundary of plasma there is a thin layer in which, as a result of ionization, multiply charged ions are formed in a gas mixture of complex composition. The maximum energy of the incident electrons involved in the ionization does not exceed 42 eV;
- Multiply charged ions are formed;
- Changes in external conditions (in the level of input microwave power in particular) entail a change in the concentration of electrons and their temperature, which is accompanied by a change in plasma nonideality (electron and ion temperatures ratio);
- intensity of volumetric recombination processes affects the emission processes at the boundary of the plasma.

Another aspect of composite coating synthesis is connected with the transfer of plasma energy to surface atoms of the workpiece. The results of the mathematical description revealed that the transfer
can be performed most efficiently via the surface three-body recombination in which the neutralization of charge carriers by connecting the oppositely charged carriers into neutral molecules at a surface of the product takes place [19, 20[20]]. Unlike ionization, recombination is accompanied by the release of energy, contributing to intense local heating of the surface, with an arbitrarily small kinetic energy of the interacting particles. However, effective recombination process requires directing the energy of the particles in plasma flow to the formation of certain behavior in electrostatic field at its inner boundary: electron deceleration in order to reduce their kinetic energy and ion acceleration to increase their kinetic energy. The control is performed by changing the power input of the electromagnetic field and the placement of the product in the treatment chamber as well as by the value of positive potential, as the first two parameters are responsible for the concentration of charged particles at the outer boundary of plasma, the third is being responsible for the formation of compensated flow in quasineutral space.

Finally, the last aspect of synthesis is the need to form a gradient transition (sublayer) from the coating to the base material (matrix), which is a factor of increasing the adhesion characteristics of parts and products. In the formation of the underlayer, grains of matrix boundary layer must undergo changes similar to the changes occurring in the surface layer, i.e., change of shape. Under these conditions, the melted surface grain layer is able to flow and fill the microvoids, and subsequent cooling fixes a new modified shape working as a binder for unfused grains (Figure 1 a). In operating conditions it will provide additional environmental resistance of parts or products. Otherwise, the inevitable macrodefects, up to chips, occur due to the shift of grains in microcavities (Figure 1 b).

![Figure 1. The state of worn matrix of hard alloy products: a - with a sub-layer; b - without a sublayer.](image)

The results obtained in the study of these aspects became the basis for the creation of equipment and technology for the synthesis of composite coatings on figurine product surface.

The equipment design was carried out to ensure receiving combined discharge and reproducibility of the synthesis results[5]. The high efficiency of microwave energy deposition into the discharge when working at low levels of microwave power allowed simplifying the microwave path without additional protection of the magnetron from reflected power. The equipment power consumption generally does not exceed 2 kW. The positive results of prototype operation (installation ‘Chrome’) allowed to work out design principles that apply to equipment for both single- and multi-position processing without generality loss.
The main criterion for the technology development was creating identical synthesis conditions on the results of the following actions.

Pre-cleaned and degreased in hot trichlorethylene ClCH=CCl product is installed in a special mandrel fixed in the holder. The surface of the mandrel and a portion of the product surface that are not to be treated are insulated with two layers of thin fluoroplastic tape. Then, the product is placed in the treatment chamber at the coordinates corresponding to its type and size. The processing chamber is sealed and pressurized. The pressure in the camera is decreased to the ultimate level of 10 Pa, and then it is filled with the process gas to 100 Pa, the power supply turns on providing desired potential for the product; the power supply of the microwave energy generator is turned on as well.

By continuously adjusting the anode current of the magnetron microwave power for igniting plasma is fed into the treatment chamber.

Upon processing completion, the time of which ranges from 2 to 20 minutes depending on the size, the product cools in a protective environment, and is removed from the holder after processing chamber depressurization.

3. Practical Aspects

Let us consider practical aspects of the formation of composite coatings through the example of metal-cutting tools for different purposes as a typical figurine-shaped product functioning under extreme temperature and power loads.

The main result of low-temperature plasma impact in the working part of the tool is a significant change in the morphology and physico-mechanical properties of the surface layer (Figure 2): small stripes are virtually absent, scar edges are melted, all microasperities are smoothed. Layer microhardness increases 2-2.5 times, the roughness decreases 1.5-3.0 times, the ohmic resistance is reduced by 6 times. Additionally, the surface is brightened which indicates a change in the chemical composition of the material as a result of its saturation with alloying agents of higher atomic numbers, namely, close to or included into the carbide phase as well as with interstitial atoms of the process gas (nitrogen in this case). The study of the section surface showed the presence of a dislocation structure in the surface layer at a depth of 1.2-1.5 μm to 5 μm, and its absence at a depth of 1.2-1.5 μm. There has been recorded significant reduction in the size and concentration of carbide phase grains in the surface layer (1.8 and 1.74 times, respectively), which is possible only in case of their dissolution, and the change of their shape from a rounded (before) to elliptical (after plasma processing).

![Figure 2](https://example.com/figure2.png)

**Figure 2.** Surface layer of the drill made of steel R6M5 before (a) and after (b) plasma treatment.
Metallographic analysis and electron microscopic examination of the surface showed the presence of structure and phase changes in the surface layer of the tool working part that are not typical for usual thermal processes. The result was the formation of high strength nanoclusters of ~ 50...100 Nm and an amorphous interlayer of ≤10 Nm particles of the same chemical composition as a binder, i.e. composite structure, in the subsurface (to the depth up to 5 μm) (Figure 3). The total depth of the modified layer is 40 μm, while the tool core does not undergo any change, the values of its basic geometric parameters are not changed, distortion is not recorded.

![Figure 3](image)

**Figure 3.** The structure of the modified surface layer:
- 1 - synthesized composite coating;
- 2 - matrix;
- 3 - nanoclusters in amorphous bunch.

The results of the pilot operation of the tool with synthesized composite coating in manufacturing parts from different materials revealed that the average increase in high speed steel tool life time was 3.13 times, the hardmetal tool - 2.35 times, with maximum increase in both types up to 5.0 times. There was also recorded a significant reduction in roughness of the machined surface in AARH parameter: from 2.5-3.5 μm for uncoated tools to 0.80-2.0 μm for coated tools.

The study of the state of the coated tool working surfaces revealed the following. In the cutting process the impact of the cutting waste on the transformed subsurface layers of the tool material causes complex responses associated with both the local surface extension and with its local compression.

The stretching processes are concentrated in the micron surface layers and may have different local areas, determined by the direction of separated material and chips movement. Resistance of the formed coating is determined by the resistance of its nanodispersed reinforced amorphous phase to the tensile stress. The alternation of stretching and compressive effects leads to local changes in the geometry of the cutting edge. The role of the ion-plasma treatment in these conditions is determined by the increasing ability of the coating and gradient sublayer to restructure in the narrow spatial volumes without creating destructive defects. In other words, the synthesized structure acquires the property of self-organization, the mechanism of which is associated with the local transformation of its surface microvolumes as a result of contact processes of interaction with detachable plastic material under the influence and in the direction of the external forces and temperature, particularly at the cutting edge. The result is the formation of a stable streamlined shape of the cutting edge, providing a decrease in friction forces and, consequently, heat generation in the cutting process. Therefore, the structure...
remains stable and independent of local changes in the surrounding areas even if defects appear on the surface or the cutting edge.

4. Conclusions
The analysis of the materials presented in this paper leads to the following conclusions.

1. The main scientific and practical aspects of the change in the initial properties of the surface layer of figurine-shaped products in low-temperature ion-plasma treatment are associated with the creation of conditions that cause a controlled change in the layer structure and reducing the size of the grain, but in a way that it acquires the properties of increased hardness and ductility that ensure long-term efficiency under temperature exposure or force action during operation.

2. The stability of ion-plasma coating is determined by the ability of its nanodisperse reinforced amorphous phase in the overall situation of growing stress, on the one hand, to resist the tensile stresses on the other - to take compressive stress (ie to perform the dissipative function), since the loss of this ability leads the formation of defects increasing the load on gradient underlayer and further on the matrix.

3. Formation of the composite coating causes a change in the mechanism of wear of working surfaces of figurine-shaped products during their operation: the wear gradually abrades the coating to a state in which defects are formed. Coating self-organization based on the nanodisperse reinforced amorphous phase performance of its dissipative function allows to stabilize the coating purposefully changing the degree and direction of the defect impact and to provide on this basis the most complete performance of their protective functions in relation to the base material of the product without provoking its destruction.

Acknowledgement
The authors express their gratitude to the Russian Science Foundation, through a grant of which (Project No 15-19-00030) the present study was carried out.

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