Main problems and perspectives of the synthesis of nanocomposite coatings on the surface of complex-shaped components

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Abstract. The main methods for composite coating synthesis in the surface layer of complex-shaped workpiece with dissipative properties have been investigated in this study. The problem of their application can be solved by using low-temperature plasma of combined discharge. The plasma is formed directly around the treated surface, which allows the use of the maximum amount of energy transmitted by its ions for the synthesis process itself. The main mechanism is the synthesis of three-body recombination, in which surface structures are heated to temperatures that change the phase of their constituent atoms. As a result, the original structure of the surface layer of the workpiece is transformed into a composite structure consisting of nanoclusters of ~ 50 ... 100 nm in size and an amorphous layer of particles which acts as binder, and gradient transition from the coating to the base material filling the microvoids.

1. Introduction
The current stage of production development in various industrial sectors is characterized by tighter operating conditions for items made of metals and alloys. This requires continuous refinement of existing methods and development of new manufacturing technologies to improve the product operational reliability in terms of abrasion and fatigue resistance.

Traditionally, increasing fatigue strength and abrasion resistance is ensured by protective coatings [1-7]; however, a promising approach is associated with the creation of technologies and equipment that allow formation of coating structures with dissipative properties due to the presence of the amorphous phase that performs the work of irreversible local movement of minimal number of minimum size particles (groups of atoms) in a minimum of time without momentum transfer. In conventional coatings, atoms do not have such freedom, so, any displacement leads to surface cracks and crystal lattice defects causing delamination and destruction of coating as well as reduced chemical activity and mechanical strength.

Special coatings obtained by ion-plasma deposition (IPD), as well as vapor deposition of nano-dispersed powder materials can act as dissipative structures [8-11]. Studies in this direction are carried out in many countries: Russia, Japan, the USA, Germany, France, Canada, South Korea, Switzerland, Israel, Liechtenstein, Ukraine and Belarus. Coatings produced by IPD methods are homogeneous, poreless and tight fit on the base layers of the workpiece of any configuration. In the course of IPD, plasma condenses on the metal surface with a possible simultaneous plasma chemical reaction to form a compound of the desired chemical composition.

There are several modifications of the IPD method:
1) activated evaporation with chemical reaction (ARE);
2) reactive electron-beam plasma deposition (REP);
3) condensation of matter with ion bombardment (CIB);
4) low pressure plasma deposition (LPPD);
5) hollow cathode deposition (HCD);
6) cathodic arc low temperature separated ion deposition (CALTSID) which lets you create:
   - multilayer nano-gradient coatings from separative plasma of arc discharge;
   - atomic layer coating by applying microlayers of various components of 1-100 nm thick;
   - self-lubricating and anti-friction diamond-like coatings (DLC coatings), i.e. "solid lubricant",
     which operate in a wide range of temperatures in vacuum, at high and low temperatures on the cutting
     tool, in ground power plants and aerospace engines;
   - wear and corrosion-resistant multilayer ion-plasma coatings for various applications, used in hard
     alloys working in heavy conditions of interrupted cuts on metal cutting machines.

2. Problems

It should be noted, however, that obtaining these coatings is associated with the solution of the whole
set of problems, complex from both technological and technical points of view, which include:
   - elimination of the droplet phase accompanying the ion-plasma deposition, which requires
     substantial modernization of technological equipment;
   - realization of a long and multi-stage process cycle which includes, for example, pumping - ionic
     surface cleaning - ion etching - ion-plasma nitriding - application of microlayer of titanium and
     aluminum nanolayers 1-100 nm thick - microlayer of titanium nitride and aluminum nitride 1-100 nm
     thick, with ionic surface cleaning after each microlayer;
   - creation of ultra-high vacuum (~ 10^-7 mm Hg) in the working chamber, which leads to lower
     coating speeds and hence a longer cycle time. The latter, in turn, determines the need for special
     preventive measures for maintaining the equipment in working condition.

In addition to the above, the absence of transition layer in the coatings is responsible for their low
adhesion to the base substrate and, as a result, it cannot be used at high temperatures and power loads.
The formation of ‘coating – substrate’ transition layers also requires ion implantation that needs
special equipment with high accelerating voltage (~ 50 kV). Finally, these technologies dictate the
transformation of the volume created by flaming workpiece and its delivery to the working surface. In
this case, most of the energy consumed is spent on the plasma creation, maintaining its generation
conditions and the delivery of active plasma particles with a given energy to the subject of treatment
with their subsequent scanning on the surface; while the same process of nanocoating formation
requires only a few percent of the total energy input.

The use of nano-dispersed powder materials also has a number of negative technological features
caused by the resulting powder as a fraction of 60-100 nm when grinding and the special conditions of
storage of such powders as well as difficulties of formation of structurally uniform coatings when
applying nanodisperse powders by gas-phase synthesis with vapour condensation method.

Thus, the objective difficulties of forming multi-layer nano-coatings make them exclusive, expensive
and only available for laboratory research, while their industrial use seem problematic. It
leads to the conclusion that the formation of geometrically complex products of chemically inactive
nanocomposite dissipative structures with high hardness and stability, especially when operating in
extreme conditions in the surface layers presents a critical scientific and practical problem.

3. Solution procedure

It is possible to generate dissipative structures in the workpiece surface layer by exposing it for 1.5 ... 15 min. to a low-temperature plasma formed by superimposed electrostatic microwave
electromagnetic field at a reduced level of microwave power (30 ... 90 W) at a pressure of about 300 Pa in a mixture of process gases at a total power consumption of 2.0 kW [12]. The plasma is formed
directly around the treated surface, which allows the use of the maximum amount of energy
transmitted by its ions for the modification process itself, rather than for maintaining the conditions for the generation and delivery of the active plasma species to the workpiece.

The study of the impact of low-temperature plasma on the surface of the product revealed that its main mechanism is the three-body surface recombination (Figure 1) at which neutralization of charge carriers by combining oppositely charged carriers into the neutral molecules on the surface of the product takes place. Unlike ionization, recombination occurs with the release of potential energy at arbitrarily low kinetic energy of the interacting particles. Mathematically, this process is described by the following relationships:

\[
J_{\text{emis}} = \frac{I_e + I_{p_1^+} + I_{p_2^+} + I_{p_2^-}}{S_{bd}},
\]

\[
Q = n_e n_{p_1^+} \frac{N_B}{S} \gamma_{p_1^+} \langle U_i + U_a \rangle + n_e n_{p_2^+} \frac{N_B}{S} \gamma_{p_2^+} \langle U_j + U_a \rangle,
\]

where \( J_{\text{emis}} \) is the compensated flow emitted from the unit surface area of the lower boundary of plasma \( S_{bd} \), which consists of low-energy electrons \( (I_e) \), singly charged ions \( (I_{p_1^+}, I_{p_2^+}, I_{p_2^-}) \); type \( p_1, p_2 \) particles and negative ions \( p_1^- \), falling on unit surface area of the product \( S \); \( Q \) is the amount of heat transferred to the surface atoms per unit time in the process of recombination of positive and negative monovalent ion; \( \langle U_i + U_a \rangle \) and \( \langle U_j + U_a \rangle \) are averaged energies. The value \( \langle U_i + U_a \rangle \) is greater than or equal to the potential of \( p_1 \) atoms ionization, and \( \langle U_j + U_a \rangle \) is greater than or equal to the energy of formation of negative and positive ions.

Figure 1. Steps (I-III) of the three-body recombination: 1 - incident electron, 2 - adsorbed ion, 3 - surface atom (dipole), 4, 5 - subsurface atoms, 6 - neutral atom resulting from recombination (during and after transmission of the stored energy), 7 - surface atom displaced as a result of recombination.

The main result of the recombination process is the heating of the surface structures to temperatures changing the phase of their constituent atoms and leading to their displacement in the nature of thermal vibrations. In other words, a layer of the liquid phase (melt) is formed that contains unstable groups of individual disordered atoms and dense metastable atom groupings with higher local resistance and ordering symmetry different from that of the crystal one. Subsequent quenching of the surface under reduced pressure gives fixation (solidifying) of the formed melt. As a result, the original
structure of the surface layer of the workpiece is transformed into a nanocomposite structure consisting of (Figure 2):
- nanoclusters of ~ 50 ... 100 nm in size and high strength, and an amorphous layer of particles of the same chemical composition with the size of ≤10 nm, which acts as a binder (coating);
- gradient transition from the coating to the base material (sublayer) filling the microvoids.

4. Results and discussion
The results of the structure microhardness measurement and their analysis showed [13] that, firstly, the microhardness increases (Figure 3), and secondly, it is achieved by consolidation of the surface layer (Figure 4), which affects the structure behavior under working conditions. Above all, this applies to operation under conditions of intense temperature and power loads, including alternating stress, for example, of the tool during mechanical or ultrasonic machining. Therefore, to assess the prospects for the practical use of products with nanocomposite coatings it is necessary to study their operation process.

**Figure 2.** The structure of the working part of the product: 1 - synthetic composite coating; 2 - matrix; 3 – sublayer.

**Figure 3.** Imprints of the diamond pyramid on the surface of the carbide article at the same load before (a) and after (b) plasma treatment.

Research would be appropriate from the standpoint of the following provisions:
- in an elementary volume of the coating containing some free space in the form of voids between the atoms of the amorphous phase coating and some free space in the form of grain voids of adjacent underlayer, local deformation will be accompanied by an increase in the free volume both in the coating and in the underlayer;
- the coating is exposed to typical for amorphous materials processes of local tension and compression which lead to local surface micro volumes displacement determined by the direction and nature of the applied load;
- the presence of nanoclusters enhances the coating capacity for structural adjustment in the narrow spatial scale;
- underlayer of a high density and, therefore, hardness and having a structure with a minimum of microvoids decreases mobility of the grains of the base material and increases its resistance under external temperature and force pressure.

Figure 4. A typical example of the distribution of microhardness in depth of the surface layer of the carbide product before (1) and after (2) composite coating formation: arrow shows the consolidation of surface layer structure.

Taken together, these provisions determine the ability of the nanocomposite coating to perform the dissipative function in the operation of the product.
5. Conclusions

The preliminary results show (Figure 5) that the dissipative functions are carried out by a composite coating structure according to multi-stage scheme, since with the loss of stability of the structures of ~ 200 nm, the structures of ~ 40-70 nm maintain the contact with the amorphous binder, flexibility, the ability to migrate and can be transformed, i.e. form a stable streamlined contact surface. This gives reason to hope that, based on the study, we will be able:

![Image](image.png)

**Figure 5.** The result of the composite coating structure dissipation functions during operation of the solid alloy workpiece:
1 - voids of submicron structures (~200 nm).

- to establish the interrelations between the physical-mechanical, chemical characteristics of the ‘cover – sublayer’ structure and the conditions of its synthesis;
- to solve the problems of optimizing the process of synthesis of the nanocomposite coating according to the criteria of intensity and uniformity of the impact of low-temperature plasma on the surface of the workpiece, and the process of use of the product by the criterion of composite coating guaranteed performance of its dissipative functions.

Acknowledgement

The authors would like to acknowledge the assistance of the Russian Science Foundation. The present study was supported by the Russian Science Foundation grant (Project No 15-19-00030).

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