Modification of the surface layers with plasma of a vacuum-arc discharge by controlling the energy of precipitating particles

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Abstract. In this paper we consider one of the most effective ways to improve the performance properties of metals – their treatment by intense flows of metal plasma generated by a vacuum-arc discharge. The change in the thermal regime and the duration of the plasma treatment allows controlling both the thickness of a modified layer and the distribution of implanted ions into its depth. At the first stage of part processing the preliminary cleaning of the surface is carried out using a glow discharge in argon. In the second stage, vacuum-arc plasma sources are used, that provide surface treatment with ions of the sprayed material. To weaken and purify the plasma flow special separation systems were used to ensure the creation of an impassable barrier for the droplet fraction. Modification of the treated surface layer is achieved either due to the high energy of the deposited particles, or due to the implementation of the diffusion processes deep into the substrate. The presence of a modified surface layer allows improving the quality of the working coating that is deposited further.

1. Introduction
One of the most effective ways to improve the performance properties of metals is their treatment with intense streams of charged particles and, in particular, flows of metal plasma generated by a vacuum-arc discharge. The advantage of this method is that not only the high-energy ions, but also a high flux density has an impact on the conditions of interaction. The latter contributes to an increase of the target temperature to \(~1000~K\), which allows forming in the surface layer of compounds, the synthesis of which is impossible under ordinary conditions, and as well obtaining intermetallic compounds and solid solutions with a high concentration of nanosized phases of implementation [1].

The change in the thermal regime and the duration of the plasma treatment allows controlling both the thickness of a modified layer and the distribution of implanted ions into its depth, while the observed modification of the target volume is achieved to a sufficient depth with the absence of a sharp boundary of separation. For example, during the deposition of carbon the following sequence of generated layers is observed under certain conditions [2]: \((\text{Me}_{\text{base}} - \text{Me}_2\text{C} - \text{MeC}_{\text{sub}} - \text{C}_{\text{coat}})\), where “\text{Me}” denotes a metal, particularly molybdenum or tungsten; indexes “\text{sub}” and “\text{coat}” mean substrate and coating, respectively.

It should be noted that a significant part of the carbide phases of transition metals has a wide area of homogeneity, within which the change in the carbon content occurs without the restructurization of the crystal lattice \((\text{MeC}_{1-x} - \text{MeC})\) [3]. Carbides, having a close to stoichiometric composition, possess
the least resistance. With the increase of the imperfection degree for carbon of the carbide lattice the resistance increase, that is caused by a significant decrease of the mobility of conductivity electrons due to a strong scattering by vacancies in the carbon sublattice, which are in this case the centers of scattering. The microhardness of the resulting carbides is defined by the energy sustainability of the \( d^x\)-configurations that leads to the disruption of \( sp^3\)-configurations of carbon and strong delocalization of electrons.

2. Results and discussion

Technology of the processing of metal parts with a flow of plasmachemical synthesis of compounds includes the following technological operations (figure 1).

![Figure 1. Technological ion-plasma processes (\( I_{\text{dis}} \) – discharge current).](image_url)

The first stage is the pre-cleaning of a treated surface using a glow discharge in argon at a pressure of \( 10^{-1} \) Pa. At this stage, along with cleaning of the surface through its sputtering the heterogeneities (microscopic protrusions) are removed, capable of causing breakdowns in the system “plasma – device” during the high-energy treatment of the substrate by metal ions at the stage of formation of a pseudodivision layer. Smoothing of the microscopic irregularities at an average current density of ions from the gaseous medium of about 1 mA/cm\(^2\) and their energy of 600...700 eV takes few minutes.

At the second stage vacuum-arc plasma sources (figure 2), providing a surface treatment using ions of the sprayed material, are used [4, 5]. High energy of ions (several keV) is achieved under condition that on the treated surface a negative potential \(-U_{\text{bias}} = 1...2\) kV is set.

For the weakening and cleaning of a plasma flow a special separation system, ensuring the creation of an impenetrable barrier to droplet fraction, is used [6]. This unit allows to allocate the stream of charged particles and to control the density of the charged particles flow arriving at the treated part. In addition, it is possible to provide a high electric strength of the system, i.e. to exclude the possibility of breakouts.

The output of the charged particles (ions and electrons) from the plasma flow is defined as by the above-mentioned conditions, and also by the design of the vacuum installation and parameters of the deposition process: bias voltage; value of the discharge current; distance between the substrate and the cathode; distribution of the magnetic field; degree of rarefaction (pressure is below \( 10^{-3} \) Pa) and the use of additional gases contributing to an increase in the degree of ionization of the plasma flow (Ar, He) and ensuring the flow of chemical reactions with the formation of chemical compounds (hydrocarbon compounds – \( C_nH_m \)).
Figure 2. Design of a coaxial vacuum-arc plasma source ($U_{\text{sup}}$ – supply voltage; $j_i$ – ion current density): 1 – anode; 2 – cathode; 3 – igniting electrode; 4 – screen; 5, 6 – stabilizing and focusing solenoids; 7 – working volume; 8 – workpiece; 9 – planetary gear.

The formation of the sublayer or, otherwise, the modification of the treated surface layer is achieved either due to a high energy of the deposited particles (directional velocity of the plasma flow is $10^4$ m/s), or due to the implementation of the diffusion processes into the depth of a substrate (figure 3).

Figure 3. Distribution of the concentration of the deposited material into the substrate material (Me$_{\text{sub}}$ – metal of the substrate; Me$_{\text{diff}}$ – metal diffusing into the substrate).

The conditions for the occurrence of diffusion processes between the deposited particles and atoms of the surface are determined by the energy and properties of the particles themselves, as well as the process conditions: substrate temperature and the composition of its surface.

Changing the nature of the flow of diffusion processes the quality and composition of the coating, and also its adhesion and structure can be varied [7].

The occurrence of the diffusion processes leads to a distribution of deposited atoms through the thickness of the substrate $n_{\text{diff}}(x, t)$. The diffusion coefficient $D(x) = D_\tau + D'(x)$ is represented as the sum of the thermal ($D_\tau$) and radiation-enhanced diffusion $D'(x)$. In accordance with the theory [8] $D'(x)$ is chosen proportional to the concentration of radiation defects $C(x)$:

$$D'(x) = [D_\tau D_\phi + D_\phi N_0]C(x),$$

where $D_\tau$, $D_\phi$ – self-diffusion and defects diffusion coefficients, respectively. The coefficient of the thermal diffusion of implanted atoms is estimated by the formula of Arrhenius [9]:

$$D_\tau = D_0 \exp\left(-\frac{E_a}{kT}\right),$$

where $D_0$ – pre-exponential factor; $E_a$ – activation energy; $k$ – Boltzmann constant; $T$ – temperature of the target. Due to the high diffusion mobility of the interacting components, provided by the thermal
conditions, the diffusion zone in the substrate reaches a significant size [10]. The diffusion coefficient along grain boundaries is much higher than the coefficient of volume diffusion, due to a large value of the energy of volume diffusion [11, 12].

3. Conclusions
Diffusion of carbon atoms into the substrate leads to the chemical reactions with the formation of chemical compounds of Me,C type, which in turn leads to the emergence of structural inhomogeneities and internal interface surfaces, complicating the modeling of further diffusion process. In addition, the saturation of the surface layer reduces the number of carbon atoms involved in diffusion processes and contributes to the subsequent growth of the coating formed from the plasma of the vacuum-arc discharge. It should be noted that the presence of a modified surface layer allows improving the quality of the working coating that is deposited further.

Parallel use of the hydrocarbon compounds introduced into the working volume with the simultaneous spraying of the graphite cathode leads to the fact that in the area of the treated part exists a zone with a temperature equal to or higher than the decomposition temperature for the hydrocarbon compounds. This condition changes the kinetics and mechanism of formation of the deposited coating based on carbon.

Thus, it is shown that the treatment of the substrate by an intense flow of charged particles allows controlling the temperature of the target and form compounds in the surface layer, the synthesis of which is impossible under normal conditions. The obtained results can be applied in the production technology of electrovacuum devices, where refractory metals molybdenum and tungsten are used as a structural material, and their processing is carried out by carbon-containing particles that change their emission and mechanical properties.

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