Decomposition of the hydrocarbon compounds in the vacuum arc discharge plasma

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Abstract. Vacuum arc discharge, maintained in the vapors of the cathode material, is used for the implementation of plasmachemical synthesis. For the formation of compounds into the plasma flux a working gas is injected. In this work the principle of decomposition of the carbon containing compounds in the low temperature vacuum arc discharge plasma is considered.

One of the commonly used methods of coating deposition is a vacuum arc discharge, existing in the vapors of a cathode material [1]. Prospect of application of the directed flows of charged particles belonging to the plasma flux is associated with the ability to control the process of their deposition during the coating formation, and also high density of the energy released by the substrate, and possibility to regulate its temperature. Despite all these advantages of the technological process, it should be noted their complex relationship shown in figure 1 [2, 3].

Figure 1. Relationship and influence of the parameters of the plasma flux on the formed coating.
Technology using vacuum arc plasma sources allows both to create clean coatings and to carry out the plasmachemical synthesis of the compounds [4]. To obtain carbide compounds, possessing high melting temperature and wear resistance, into the flux of metal plasma the hydrocarbon compounds are introduced.

Introduction of a carbon containing compound into the vacuum chamber from the side of the sputtered cathode (figure 2) ensures mixing of the plasma flux and gas atoms, and also the active dissociation of the gas molecules into the excited molecules, molecular ion formations, individual atoms and particles of different valences (radicals).

**Figure 2.** Plasmachemical process of the carbon based compounds formation.

The ground state of a molecule is a condition with the most stable electronic configuration. In this case, the molecule is in an energy minimum and has fairly high activation barriers for the changes in its structure. In the periodic table for carbon (C – $1s^2\ 2s^2\ 2p^2$) and hydrogen (H – $1s^1$) the number of the valence electrons corresponds to the number of the valence orbitals, which explains the high stability of the chemical bonds C–C (351.8 kJ/mol) and H–H (432.1 kJ/mol). Compounds of carbon with hydrogen differ in the nature of bonds, number of atoms in the molecules and their structure. Hydrocarbons constitute a homologous series, in which two consecutive hydrocarbons differ in exactly one same group of atoms. With increasing number of carbon atoms in homological series of hydrocarbons or with an increase in molecular weight generally grows their melting and boiling point and also their state changes.

As the working carbon containing compound commonly used is benzene ($C_6H_6$) – aromatic hydrocarbon ($C_nH_{2n-6}$, $n \geq 6$) with the first ionization potential 9.24 eV. Benzene contains the stable cyclic group of atoms (benzene nucleus) with a closed system of conjugated bonds. The bond length between the carbon atoms in benzene is 0.139 nm, which is an intermediate value between the length of a single bond in the alkanes ($C_nH_{2n+2}$, 0.154 nm) and a length of double bonds in alkenes ($C_nH_{2n}$, 0.133 nm). Circular conjugation allows gaining energy 150 kJ/mol, what is the magnitude of the conjugation energy – the amount of energy required for the destruction of the aromatic system $C_6H_6$.

Noticeable decomposition of the aromatic hydrocarbons in the gas phase with long bonds into molecules of shorter length is observed already at temperatures around 800 K, under these conditions the molecule becomes thermodynamically unstable.

The process of decomposition of the hydrocarbons is a complex process, consisting of the consecutive and parallel chemical reactions. Forming intermediate particles are characterized by altered electronic structure of an atom or molecule, and because of the continuous participation in the occurring chemical reactions have a short life time. Molecules and intermediate particles decay into...
the fragments with sequential transformation of one free radical into the other: $\mathbf{\hat{R}_1} \rightarrow \mathbf{\hat{R}_2} \rightarrow \mathbf{\hat{R}_3} \rightarrow \ldots$. and also into separate atoms of hydrogen and carbon, as well as into excited states of molecules and molecular ion formations [5].

In the gas discharge plasma to the chemical processes of pyrolysis is added the decomposition reaction of hydrocarbons due to the interaction with the plasma flux components: the formation of CH radicals is in the process of direct dissociation by an electron impact. The structure of the formed radicals depends on the rate of separation of the hydrogen atoms, while the less hydrogen atoms are contained in the molecule, the easier is the decomposition of the hydrocarbon. The speed of course of the chemical reactions is proportional to the multiplication of the current concentrations of the reactants (law of Guldberg and Vahe).

Thermal transformations of benzene occur in a wide range of temperatures. At low temperatures (800...1100 K), is observed a breakage of C–H bond, accompanied by the formation of biphenyl (C_{12}H_{10} – twin phenyl radical) and to a lesser extent of polyphenyls. Radical C_6H_2 is formed by attaching the atomic hydrogen to benzene. At higher temperatures the flow of complex and nonselective processes of splitting of the phenyl nucleus are observed. The decay rate of C_6H_2 and C_6H_3 is so great that the kinetics of the decay of C_6H_6 in these terms and conditions and in the assumption of the direct reactions of dissolution can be written as:

$$C_6H_6 \rightarrow C_2H_2 + C_4H_2 + 2H.$$  

In the plasma chemical synthesis the sputtered flux of metal ions of the cathode material $dn/dt$ reaching the substrate is calculated using the current of the vacuum arc discharge $I_{av}$ selectable from the conditions for stable burning of the discharge and the operating temperature of the cathode. A balanced flow of the gas molecules $dn_{cath} / dt$ is determined based on the ratio of a chemical reaction between the metal and reactive gas and the size of the receiving surface [6].

The formation of a coating on a solid surface follows simultaneously with the process of carbon black formation occurring in the working volume. These reactions proceed in parallel.

Chemical conversion processes of the different carbon compounds into the solid particulate carbon are accompanied by the physical processes of the emergence of new dispersed phase. Carbon black is formed during nonequilibrium spontaneous condensation of carbon due to the inelastic collisions of particles. At the initial stage occurs decomposition of the carbon substances and formation of the clusters in a form of a radical mesh with torn bonds, after which on the condensation nuclei there is an intensive buildup of the carbon particles.

The formation of the compound flowing on the surface of condensation may occur according to the following scheme of splitting of hydrocarbons with long bonds into the molecules of a shorter length:

$$C_6H_6^w \rightarrow C_2H_2^{\tau} + C_4H_2^{\tau} + H_2^{\tau};$$

$$Me_{\text{substrate}} + (\text{Me}_{\text{plasma}} + C_6H_6)_{\nu} \rightarrow (Me_{\text{substrate}} + Me_{\text{plasma}} + C + C + C) + C_{\text{carbon black}} \downarrow + C_2H_2^{\tau}.$$  

Using as the processed substrate the transition metal with unpaired electrons [7], allows to additionally apply it as a catalyst, which increases the rate of decomposition of the hydrocarbon and influences the structure of the formed carbonaceous material. The catalytic reaction proceeds on the surface and is caused by the activation of molecules of the reagents in the interaction with the surface. The evolved carbon is adsorbed on the surface and enters into a chemical reaction with it.

The advantage of using vacuum arc plasma sources is the formation of the coating by deposition of the ions with high kinetic energy. The speed of the plasma flux is mainly formed in the cathode region [8], and in the area of transportation it does not change and is about $10^4$ m/s. The plasma flux is moving in a diverging magnetic field. It has significant spatial heterogeneity due to the presence of actuators with different geometry, and motion of charged particles is performed at a substantial distance from the axis of the system.

Analysis of the plasma flux composition was carried out using emission spectral analyzer ISM3600 [9]. Figure 3 shows emission spectra of a vacuum arc discharge in the visible range, obtained in a
substrate region at a current of 80 A during sputtering of a titanium cathode in vacuum at a pressure of 7.8·10^{-3} Pa and in benzene vapors at a pressure of 8.7·10^{-2} Pa. On spectra lines corresponding to excited neutral titanium atoms (Ti I), singly (Ti II) and doubly (Ti III) charged titanium ions and singly charged carbon ions (C II) are marked.

**Figure 3.** Radiation spectra in the process of titanium (a) and titanium carbide (b) deposition.

Introduction of a benzene vapor into the plasma flux significantly modifies the emission spectrum, affects the charge composition of the titanium plasma and the concentration of titanium in the implementation of the plasmachemical synthesis. The resulting titanium carbide has a well formed crystalline structure with all the lines of maximum intensity recorded on X-ray diffraction patterns.

Changing the value of the accelerating potential \( U \), defined on the workpiece, makes possible to regulate the energy of the deposited ions and hence to control the flow of the process of the coating formation. Preliminary condensation of the sprayed cathode material (Mo, W) to a face of a similar metal contributes to obtaining of a structural based coating, which in a subsequent diffusion reaction reduces the interfacial tensions related to the difference of the crystal lattices, and improves the strength of the adhesive bond. Plasmachemical synthesis of carbide compounds in the flux of a metal plasma of a vacuum arc discharge was carried out in the vapors of benzene (C\(_6\)H\(_6\)).

Because of the peculiarities of the electronic structure and complex covalent-ionic-metallic nature of the interatomic interactions the phase diagram of the carbide systems for Mo and W have several structural modifications, stable in different temperature and concentration intervals [10]. Under the chosen conditions of the coatings formation have been produced layers composed, respectively, of the phases of molybdenum carbide – MoC or tungsten carbide, formed from the inner layer of W\(_2\)C and polyamide monocarbide surface layer WC with a hexagonal structure.

It is thus shown that the composition of the original carbon containing gas determines the yield of carbon and the nature of course of the chemical reaction of formation of the carbide compounds.

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