

Application of a vacuum-arc discharge for the production of biocompatible coatings

D K Kostrin and A A Lisenkov

Department of electronic instruments and devices, Saint Petersburg Electrotechnical University "LETI", 197376, Saint Petersburg, Russia

E-mail: dkkostrin@mail.ru

Abstract. Vacuum-arc discharge is an effective method of forming pure metal and metal-like coatings of complex composition. In this paper, the possibility of its use for the production of biocompatible coatings on the example of synthesis of titanium nitride and titanium carbide on metal substrates is evaluated.

1. Introduction

Biomedical coatings are used to change the properties of contact between implants and the human body, to achieve the desired properties, such as wear resistance in moving parts of the prosthesis and corrosion protection under the influence of biological fluids of the body, as well as to reduce the diffusion of the implant material into the living tissue. Titanium nitride and carbide coatings received special attention [1], the advantage of their biomedical application is due to the properties of biological compatibility, which depend on their composition and structural properties, such as stoichiometry, surface morphology, microhardness, corrosion and wear resistance. Such coatings are used in the manufacture of prostheses hip and knee joints, as well as screws and nails for bone synthesis (figure 1) [2, 3].



Figure 1. Examples of medical devices with applied protective biocompatible coating.

Biomedical materials must meet a number of often mutually exclusive requirements, and different structural elements may require different properties of the materials used. The use of metal coatings is possible if the surface material is extremely hard and durable. The manufacture of implants entirely from materials that meet these requirements is not possible, as such hard materials will be too fragile to use. Thus, the implant is made of available materials with the required characteristics, and the



surface properties are achieved by applying biocompatible metal or metal-like coatings. The main requirements for the applied coatings are that they should not be brittle or prone to cracking, should be sufficiently rigid and durable, and their material should be compatible with the substrate material [4].

In turn, the requirements for the coating technology are the possibility of obtaining not only simple metal, but also dense composite coatings, ensuring a stable connection between the coating and the substrate material, minimal heat dissipation, so as not to cause excessive microstructure damage to the substrate material, as well as adjustable and sufficient deposition rate of the material, capable of achieving the required coating thickness in a reasonable time.

2. Technology of obtaining coatings

The flow of the process in vacuum at a pressure of not more than 10^{-3} Pa, provides both purity and high adhesion of the coatings to materials with different physicochemical characteristics. The vacuum-plasma technology is based on the formation of coatings due to the deposition of ions with high kinetic energy. Changing the accelerating potential U_{bias} allows to regulate the energy of precipitating ions, and, therefore, to control the flow of the technological process. In this regard, the vacuum coating process consists of two stages.

At the first stage, the surface is prepared for processing: external pollution, adsorbed gases and oxide films are removed from it [5]. At the same time, the ions of the applied material are introduced into the substance of the treated surface, which leads to the formation of a pseudo-diffusion layer, which is of great importance in improving the adhesive properties of the resulting coating. At the second stage, the coating is formed, the properties of which on different substrates are determined by the heating temperature of the treated surface. Vacuum-arc plasma sources make it possible to perform plasmachemical synthesis of nitride and carbide compounds [6, 7], for which the reaction-capable working gas is introduced into the generated plasma flow (figure 2).

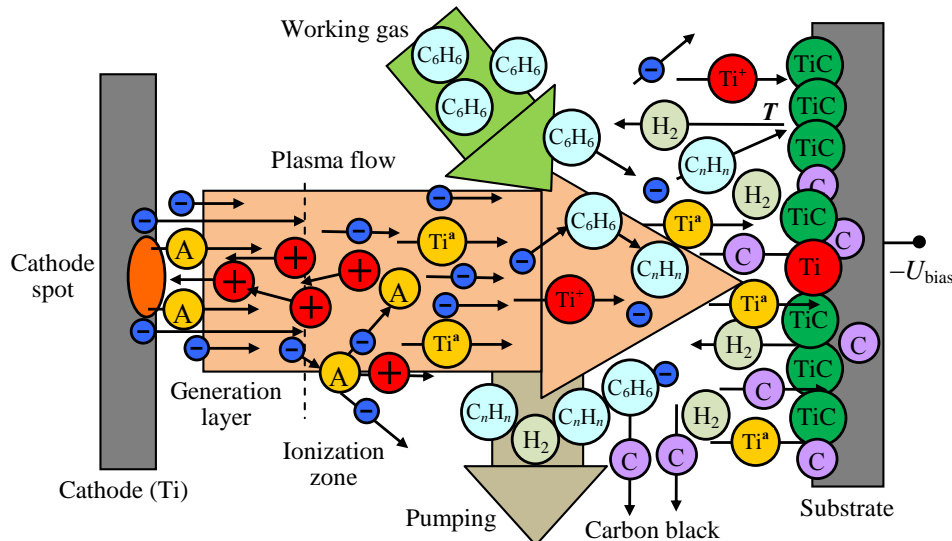


Figure 2. Schematic representation of the processes in the plasma flow of vacuum-arc discharge during deposition of titanium carbide.

The rate of the reaction gas supply is based on the coordination of the flows of the interacting metal ion particles with the gas molecules. Gas pressure, discharge current and the distance between the cathode and the substrate lead to a change in the ratio of chemical elements in the coating and its phase-structural composition, allowing obtaining coatings with desired properties [8].

The peculiarity of the generated metal plasma flow is the presence in it of a noticeable number of cathode material particles: droplets having rectilinear trajectories and leading to a decrease in the quality of the coating due to the deterioration of microrelief and the appearance of porosity in the

formed structure. This disadvantage is the root cause of premature failure, corrosion and decrease in the performance properties of coatings. By lowering the discharge current the total number of droplets in the plasma flow cannot be significantly reduced.

For cleaning the plasma flow from the droplet fraction is used a separation system of the “jalousie” type creating a solid, impenetrable barrier to droplet formation, having the straight path of movement and deposited on the separator surface facing the working surface of the cathode or a special plasmaoptical system for transporting the plasma flow providing a reversal of the flow by 90°. By changing the magnetic field in time, it is possible to control the thickness of the formed coating with a predictable degree of unevenness not exceeding one percent, and in addition to obtain the required thickness at any point on the surface of the processed parts.

3. Synthesis of nitride compounds

For the synthesis of nitride compounds – metal-like formations with high hardness chemically active molecular nitrogen N_2 with a strong triple bond $d(N-N)$ is used as a reaction gas. The destruction of the triple bond is hindered by the unusually strong first of the disrupted bonds in the N_2 molecule. Dissociation of nitrogen leads to the reaction of interaction of nitrogen atoms with the sprayed metal ions (Me) with the subsequent formation of a compound Me_xN_y :



Nitrogen atom in nitrides having an isolated state s^2p^6 -configuration of valence electrons can be both a donor and acceptor. In the formation of compounds, depending on the electronic structure of the elements, the system can be transformed both into a stable s^2p^6 - and decomposed sp^3 -configuration.

Efficiency of the plasmachemical reactions of compounds synthesis depends both on the degree and nature of molecules excitation and on the kinetic energy of ions. The increase in the energy of charged particles bombarding the condensation surface leads to an increase in the surface diffusion mobility of adatoms, thereby causing a predominant growth of crystallites in the condensation plane. Chemical bond in metal-like nitrides is very strong due to participation in bonds between metal atoms and nitrogen not only of external electrons, but also of deep-seated electrons of unfinished shells. As a result, the nitrides of transition metals are very refractory and have high hardness and chemical resistance.

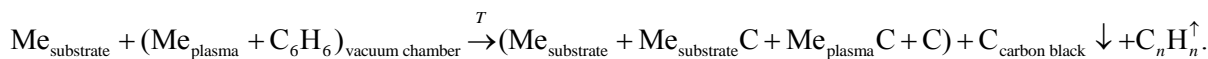
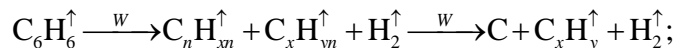
The area of homogeneity of TiN is very wide and therefore the properties of the compound strongly depend on the amount of nitrogen in the nitride, which affects the microhardness of the resulting films, which varies widely from 20 to 40 GPa. High hardness of the condensed TiN is a consequence of the high level of internal stresses. The dependence of the microhardness on the pressure is nonmonotonic. For stoichiometric TiN films, the main phase is the phase with a face-centered cubic lattice. The value of the lattice parameter is determined by a number of factors: nitrogen content, film thickness, as well as the presence of internal stresses.

4. Synthesis of carbide compounds

To carry out the plasma chemical synthesis of carbide compounds, a carbon-containing working gas is introduced into the plasma flow. In this case, the decomposition of hydrocarbon compounds is carried out both by their collisions with particles of the plasma flow and by thermal decomposition, which is a complex process consisting of a set of elementary reactions occurring both simultaneously and sequentially, with the formation of a large number of intermediate products [9]. In practice, benzene C_6H_6 , an aromatic hydrocarbon, whose molecules contain stable cyclic groups of atoms (benzene nuclei) with a closed system of conjugated bonds, is often used as a working substance.

Thermal transformations of benzene can proceed both at 800...1100 K, and at higher temperatures. At low temperatures, there is a rupture of the C–H bond and the formation of diphenyl $C_{12}H_{10}$ and, to a lesser extent, polyphenols. C_6H_7 radical reactions play a significant role, which occurs both in the initiation processes and as a result of the addition of atomic hydrogen to benzene. At higher temperatures there are complex and non-selective processes of splitting the phenyl nucleus. The decay rate of C_6H_5 and C_4H_3 is so high that the kinetics of benzene decomposition under these conditions can

be described under the assumption of direct decay reactions, such as $C_6H_6 \rightarrow C_2H_2 + C_4H_2 + 2H$. The formation of a compound that occurs on the condensation surface can occur according to the following scheme of splitting hydrocarbons with long bonds into molecules of smaller length:



Titanium carbide TiC_{1-x} belongs to the group of non-stoichiometric compounds and has a wide area of homogeneity within which the carbon content ($TiC_{0.48} \dots TiC_{0.95}$) changes without rebuilding the crystal lattice. It is experimentally established that trigonal and cubic ordered phases of Ti_2C type are observed in TiC_x carbide in the region of $0.5 < x < 0.7$.

5. Results and discussion

The phase composition of the formed coatings was studied by X-ray phase analysis on the X-ray diffractometer DRON-3 in the filtered $Cu_{K\alpha}$ radiation. The thickness of the coatings was controlled by means of metallographic sections. For the analysis of coatings was used scanning electron microscope JSM-35CF. Figure 3 shows the surface of titanium carbide coatings with and without the use of plasma cleaning system, and also the metallographic section of the obtained coating.

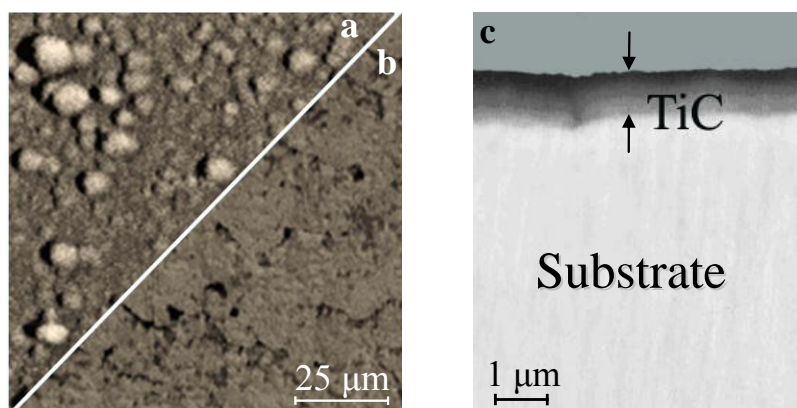


Figure 3. Surface of titanium carbide coatings without the use of a plasma cleaning system (a) and with the use of a plasma cleaning system (b), metallographic section of the obtained coating (c).

Improving the quality of formed coatings can be achieved not only due to the technological conditions of deposition, but also by reducing the thickness of the applied layers. It is known that the hardness of nanometer films is several times higher than the hardness of conventional films with micrometer thicknesses. The effects of hardening of thin surface films at the present time have not received an unambiguous physical interpretation and this explains the interest in research in the field of strength physics of composite materials.

When forming multilayer coatings, the determining factor is the correct choice of materials that make up the composite layer – in case of unsuccessful choice of materials, the disintegration of individual layers in the coating and the reduction of its mechanical characteristics occurs. Double and triple systems of carbides, nitrides, and carbonitrides of transition materials can be used as multilayer coatings [10]. High thermodynamic stability, hardness and strength of these compounds are due to the similarity of structures and the close size of atoms.

6. Conclusion

The developed technology of plasmachemical synthesis of titanium-based compounds in the flow of metallic plasma generated by a vacuum-arc discharge allows regulating the characteristics of the resulting compounds. Studies have shown that the main parameters affecting the structure and

properties of coatings are: gas pressure responsible for the elemental and phase composition of the coating; discharge current, which determines the composition of the plasma flow and the growth rate of the coating; bias potential, which determines the growth rate of the coating, microstructure and hardness; substrate temperature, which determines adhesion, microstructure and residual stresses.

It is shown that in the presence of droplet formations, coatings with a developed surface are obtained, and when cleaning the plasma flow, it is possible to effectively control the composition and structure of the formed coating.

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