APPLICATION OF N–O–C–H GAS SYSTEMS FOR SYNTHESIS OF STRENGTHENING COMPONENTS IN PLASMA COATINGS

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Possibility of strengthening component synthesis during plasma spraying with application of plasma-chemical reactor is considered. Thermodynamic analysis of systems based on bottled gases N_2, CO_2, C_3H_8–C_4H_{10}, CH_4, as well as air (N_2 and O_2 mixture) and a number of powder materials was performed. Iron-based materials and powders with sufficiently high titanium content were selected as model ones. Fundamental possibility of producing carbides, nitrides and oxides in the condensed state is demonstrated, ranges of thermodynamic parameters, in which they exist, dependence of synthesized compound content in the system on process temperature, pressure and quantity of initial solid product were established. It is found that organization of spraying process with concurrent synthesis of strengthening components is impossible without availability of objective data on energy capabilities of plasma equipment, consisting of plasmatron–plasma-chemical reactor complex. A series of experiments were performed on plasma coating spray-deposition and testing them for abrasive wear. 8 Ref., 6 Figures.

Keywords: *complex gas systems, plasmatrons, plasma-chemical reactor, plasma spraying, strengthening component synthesis*

Rising requirements to service properties of parts and structures necessitate application of more complex compositions of materials, from which the functional surface layers are formed. Traditionally, initial material chemical composition is made more complicated by introduction of alloying elements or composite material application [1, 2]. Combination of plasma spraying with purpose-oriented chemical transformations can be an alternative [3].

Application of complex plasma-forming mixtures provides a potential possibility for running of reactions of interaction of plasma active gas components with the initial material that may result in synthesis of strengthening components in the produced coating [4, 5]. For instance, in [6] ultrafine particles of titanium nitride were found in splats produced with plasma-chemical reactor application under the conditions of supersonic spraying in nitrogen atmosphere. A number of powders were selected, after analyzing the possible variants of formation of strengthening components, which can be synthesized in plasma-forming media of N–C–H–O, N–C–H or N–O system, and taking into account the condition of availability of initial materials, on the base of which synthesis will be performed. These materials are batch produced and are available in the market of Ukraine [7]. They can be conditionally subdivided into four main groups:

- iron-based materials (PZh R3, self-fluxing iron-based), in which iron carbides and, partially, silicon and chromium carbides (in the case of presence of these elements in the initial material) can form; alternatively, the initial material can be strengthened by synthesized iron oxides;
- nickel-based materials (PG-10N-03, PKh40N60, PG-SR3, PG-SR4, PG-19N-01), which have sufficiently high content of carbide-forming components — chromium, silicon, boron in their composition;
- materials, containing considerable amount of titanium (PT65Yu35, PN55T45), and in which nitride and carbide synthesis is possible;
- aluminium-based materials (PAD, ASD-T, PT65Yu35, PN70Yu30), in which strengthening components of aluminium oxide can form under certain conditions.

Thermodynamic calculations were conducted with application of TERRA software package. Systems, based on the above spraying materials and N_2, CO_2, C_3H_8–C_4H_{10}, CH bottled gases, as well as air (N_2 and O_2 mixtures), were studied. Fundamental possibility of producing carbides, nitrides and oxides in the condensed state was established, as well as the range of thermodynamic parameters, in which they exist, and dependence of these compounds content in the system on process temperature, pressure and quantity of initial solid product.

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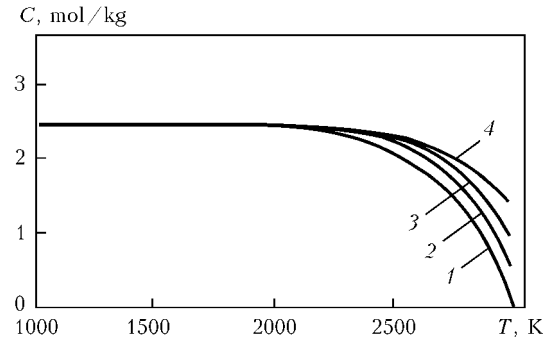

Figure 1. Dependence of target product (40.39 % Fe, 35.38 % N_2, 24.23 % C_3H_8) yield on process temperature: *1* — pressure of 0.1; *2* — 0.3; *3* — 0.3; *4* — 0.4 MPa

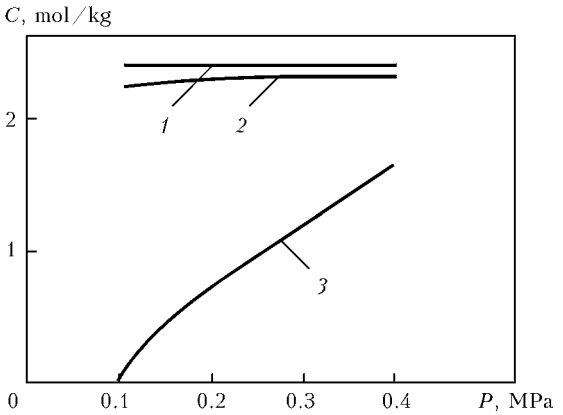

Figure 2. Dependence of target product (40.39 % Fe, 35.38 % N_2, 24.23 % C_3H_8) yield on pressure in reaction space: *1* — T = 1000–2000; *2* — 2500; *3* — 3000 K

Special attention was given to two materials, which had been selected as model ones: iron and nickel–titanium. We will assign Fe_3C iron carbide as the target product, which will be synthesized at spraying of iron-based powder. Fe_3C synthesis is possible in the presence of a sufficient amount of carbon in the system and prevention of its binding by plasma medium oxygen. Among the possible variants of reaction medium composition, which were studied, the composition formed by plasma-forming nitrogen and propane turned out to be the most effective. Propane was fed into pre-formed gas-powder flow within the plasma-chemical reactor.

Figures 1 and 2 show the dependencies of the yield of iron carbide condensed phase on process temperature and pressure in the reaction volume. Presented dependencies reveal that the temperature range of target product (Fe_3C condensed phase) yield depends on the content of hydrocarbon gas in the reaction medium. Within this temperature range, the level of target product yield practically does not change.

Temperature range is maximum wide in the case of hydrocarbon gas content of 19–25 wt.% and becomes narrower in the case of going beyond this interval with appearance of explicit maximum of product yield at 1800–1900 K. Exceeding 2500 K temperature level markedly reduces the product yield. It is found that pressure in the zone of plasma-chemical reaction running practically does not influence the target product yield within the process working temperature range, and has a significant influence on temperature range boundaries. Figure 3 shows the dependencies of target product yield on the quantity of loaded initial material under the condition of unchanged quantity of the gaseous phase, and of target product yield on the quantity of hydrocarbon gas, fed into the reaction zone.

Increase of hydrocarbon component content from 8.6 to 12.4 wt.% increases the carbide yield practically 2 times, but further increase of hydrocarbon gas quantity in the system practically does not lead to increase of synthesis process efficiency.

Increase of the quantity of loaded initial material, proceeding from calculation results, reduces the quantity of synthesized product (provided the values of other mode parameters remain unchanged).

Presence of a small (up to 45 wt.%) quantity of titanium in PN55T45 alloy composition creates the prerequisites for possible synthesis of tita-

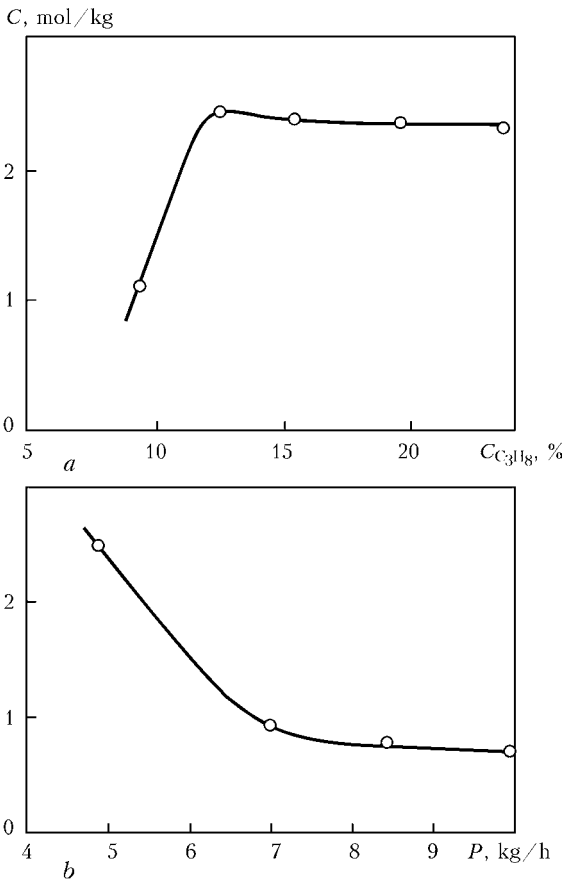

Figure 3. Dependence of synthesized carbide quantity on propane content in reaction medium (*a*) and quantity of loaded dispersion material (*b*)

nium nitride (TiN). High activity of titanium makes higher requirements to reaction medium composition. Preliminary estimates show the rationality of application of plasma-forming nitrogen, in order to create the conditions for titanium nitride synthesis, with subsequent addition of reaction nitrogen into the pre-formed gas-powder flow within the plasma-chemical reactor.

According to calculations, temperature range of target product (TiN condensed phase) yield depends on the ratio of interacting solid and gaseous phases, and in the studied range of this ratio change it becomes narrower at lowering of gaseous phase content. Increase of nitrogen content from 75.77 to 86.22 wt.% widens the temperature range by 100 K. In this case, absolute quantity of synthesized nitride will rise.

Pressure increase in the reaction space widens the temperature range of existence of titanium nitride condensed phase. Thus, it is rational to conduct the process of heating of dispersed nickel–titanium material within the plasma-chemical reactor at nitrogen content of 75–85 wt.%, in the temperature range of 2000–2400 K and about 0.1 MPa pressure in the reaction medium. Under these conditions, required fixing of synthesized product is performed by feeding hardening nitrogen into the reactor end part.

Process of coating deposition with simultaneous synthesis of strengthening components is implemented in a special spraying device, which consists of plasma sprayer and plasma-chemical reactor, tightly and rigidly combined in one unit.

Initial material together with carrier gas is fed into plasmatron arc channel. A jet of high-temperature gas flows out through outlet electrode orifice into reaction space (within the plasma-chemical reactor), in which the dispersed material is heated and accelerated.

During heating the material of initial particle surface layer evaporates with temperature rise with formation of a vapour cloud around the liquid or ductile core. Additional gas is fed into reaction space behind plasmatron nozzle edge. As a result of interaction with it, synthesis of appropriate chemical compound begins in the vapour phase surrounding the particles. Part of synthesized strengthening component can condense on the surface of carrier-particles, and the other part is in the gaseous phase around the core.

At reaction zone outlet hardening gas is fed into the unit, which, while lowering system temperature, creates the conditions for condensation of formed refractory compound on the surface of carrier-particles. Here, the particle proper remains in the liquid or ductile state, that promotes the process of mixing of the particle liquid surface layer with the condensed compound and coagulation of synthesized ultrafine particles with those of initial material.

Strengthening component composition depends on chemical composition of initial material, plasma, carrier, reaction and hardening gases.

Process of synthesis of coating strengthening components during heating and acceleration of initial material envisages application of plasma generators, capable of creating flows of low-temperature plasma from complex, reactive gaseous plasma-forming mixtures in a broad range of variation of energy parameters, and, in particular, of specific enthalpy. Plasma flow components should take an active part in synthesis, or, at least, not hinder its running.

Successful practical implementation of the process is possible in the case of availability of sufficiently complete data on energy characteristics of the used plasmatron and their interrelation with plasma generation mode parameters. Comprehensive studies of the above characteristics of plasmatrons, generating plasma of N–O–C–H system [8], allowed application of exactly this gas system for producing strengthened plasma coatings. In the specific case, straight polarity two-electrode plasmatron with stepped anode of up to 35 kW total power was used, which is capable of stable operation in nitrogen, air and mixtures of air with hydrocarbon gases (methane, propane, butane).

Proceeding from the results of these studies, criterial dependence of specific enthalpy on mode and geometrical parameters of plasma sprayer operation was established. This dependence is the basis for preliminary calculation of mode parameters of the process, at which strengthening components synthesis is possible with maximum yield of synthesized product during coating deposition.

In the simplified variant (for the applied design) in the case of air application, the criterial dependence has the following form:

$$\varepsilon = 3.984 I^{0.648} Q_{\text{air}}^{-0.33} d_1^{0.092} d_2^{-0.035} p^{0.357}, \quad (1)$$

where I is the arc current, A; Q is the plasma gas flow rate, m^3/h; d_1 and d_2 are the diameters of the narrow and wide part of outlet electrode arc channel, mm; p is the pressure at plasmatron inlet, N/m^2.

For nitrogen:

$$\varepsilon = 3.684 I^{0.66} Q_{\text{N}}^{-0.318} d_1^{0.092} d_2^{-0.058} p^{0.357}. \quad (2)$$

For a mixture of hydrocarbon gases with air (without combustion within the plasma-chemical reactor):

$$\varepsilon = 0.273 I^{0.6} Q_{\Sigma}^{-0.214} d_1^{-0.297} \times \times d_2^{0.303} p^{0.633} (l/l_1)^{-0.034} n^{0.099}. \quad (3)$$

For a mixture of hydrocarbon gases with air (with running of the process of mixture component combustion within the plasma-chemical reactor):

$$\varepsilon = [0.273 I^{0.6} Q_{\Sigma}^{-0.214} d_1^{-0.297} \times \times d_2^{0.303} p^{0.633} (l/l_1)^{-0.034} n^{0.099}] + + [0.0895 a Q_{a.g} I^{-0.132} Q_{\Sigma}^{-0.69} d_1^{-0.119} \times \times d_2^{-0.059} p^{0.241} (l/l_1)^{0.079} n^{0.064}]. \quad (4)$$

Plasma-chemical reactor is a system of individual sections sequentially and tightly connected to each other. Two kinds of sections were used: sections for feeding reaction gases and feed-through sections, the purpose of which is creation of a certain reaction volume. Each feed-through section has individual water cooling. Sections for gas feeding are cooled by those gases, which are fed through them. Geometrical dimensions and configuration of all the sections (except for the first one) are unified, that allows changing the reactor overall length by increasing the number of feed-through sections. Accordingly, location of sections for gas feeding within the reactor can be also changed, depending on process requirements.

Longitudinal geometrical size of reactor inner space (time of material particles staying in the reaction zone) is determined by number of sections, used in the structure.

Reaction zone diameter was selected constant, proceeding from preliminary information about the angle of opening of the heterogeneous flow during spraying with the plasmatron of the used design (proceeding from the condition of elimination of dispersed material deposition on the reactor inner wall during the process). Overall schematic of the technological process of spraying practically does not differ from the traditional process of plasma spraying, although its individual stages have certain specific behavioural features.

Typical preparation of initial material usually envisages powder drying and its sieving to remove possible contamination and separation of fractions of a certain range, suitable for forming the coating. The proposed process envisages application of essentially narrower range of possible dimensions of individual particles. Range narrowing improves the stability and predictability of the process of strengthening component synthesis, as it runs in the vapour cloud around the particles. Reduction of initial powder particle size can lead to complete evaporation of the particle, and its increase — to its insufficient heating and slowing down of the process of surface layer evaporation.

Requirements to temperature mode of the base become more stringent. Thermal insulation of the plasma jet from the environment by reactor walls promotes preservation of high level of heat flows to the base at spraying distances. This leads to base overheating, acceleration of the processes of oxide film growing on item surface and, consequently, to lowering of the strength of coating adhesion with the base. In the case of application of gas mixture hydrocarbon components, the fragments of which burn down at reactor outlet during sucking of oxygen from the air, additional measures are required for more intensive cooling of the item as natural cooling becomes insufficient. Here, higher requirements are made to stability of parameters of plasma sprayer and initial material feed system. Random change of carrier gas flow rate and dispersed material quantity disturbs the spatial arrangement of gas-powder flow within the plasma-chemical reactor, leading to powder particle deposition on reactor walls, and destabilizes the process of plasma-chemical synthesis.

The synthesis process is also sensitive to change of working medium energy level and it can be disturbed as a result of instability of sprayer input parameters and electrode fracture because of erosion. The required nominal mode parameters of heterogeneous flow generation (arc current, plasma gas flow rate and its chemical composition, gas pressure, arc channel geometrical dimensions, reaction and hardening gas flow rates) are calculated beforehand.

The main thermodynamic parameters, determining the probability of running of plasma-chemical reaction of strengthening component synthesis (in the condensed form), are pressure and weight-average temperature in the reaction space. Temperature, in its turn, is the derivative of the amount of energy, applied to a unit of volume (mass) of reaction medium (specific enthalpy).

Schematic of preliminary determination of mode parameters for conducting the process can be as follows:

- proceeding from analysis of chemical composition of spraying material and assigned strengthening component, element composition

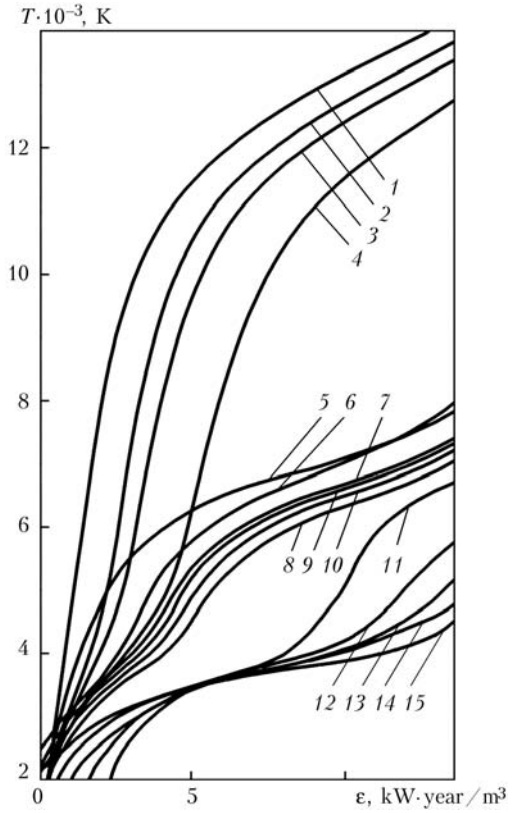

Figure 4. Dependence of plasma jet weight-averaged temperature on specific energy input into plasma gas: *1* — Ar; *2* — Ar + 15 % H_2; *3* — Ar + 25 % H_2; *4* — Ar + 50 % H_2; *5* — N_2; *6* — air; *7* — air + CH_2, α = 1; *8* — air + CH_4, α = 0.4; *9* — air + CH_4, α = 0.8; *10* — air + CH_4, α = 0.6; *11* — CO_2; *12* — products of carbon dioxide conversion of natural gas; *13* — NH_3; *14* — products of steam conversion of natural gas; *15* — H_2O

of gas system, in which the process is to be implemented, is determined;

• element composition of gas system is provided with application of the respective plasma gas, which contains the chemical elements from the required list, and reaction gas, which with its chemical composition complements the system as to chemical element list and their content;

• thermodynamic calculations of created systems (allowing for solid phase presence) are conducted in a broad range of thermodynamic parameters variation — process pressure and temperature;

• complete range of the above parameter values, in which formation of target product is possible, and values, at which product yield will be maximum, are established;

• required value of considered gas system specific enthalpy is determined (by dependencies similar to those given in Figure 4), which provides the required process temperature level (in case of ensuring appropriate pressure in reaction space);

• equations of (1)–(4) type are used to determine the required values of mode and geometrical characteristics of the process.

The process of coating spray-deposition begins from starting the plasma sprayer with complete plasma gas mixture or with its main component, at arc current, usually, below the nominal value. After the plasma sprayer has reached the working mode in terms of current, composition and flow rate of plasma gas, feeding of dispersed material into the reaction space begins.

Appearance of heated particle flow at the outlet of plasmatron–reactor system is the signal to start feeding reaction and hardening gases into the reactor. Here, the dimensions and shape of gas flow at reactor outlet change visually (Figure 5).

Functional properties of coatings from iron powder, which at this moment is the cheapest initial material for plasma spraying, can be essentially improved, by adding to coating composition iron carbides or its oxides synthesized during spraying. Selection of reaction medium chemical composition is performed, depending on chemical composition of target product. Thermodynamic calculations confirm the theoretical possibility of carbide synthesis during spraying in a mixture of carbon-containing gases.

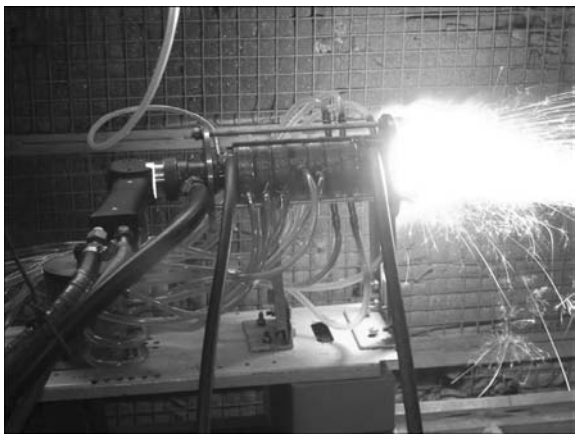

Figure 5. Process of coating spray-deposition

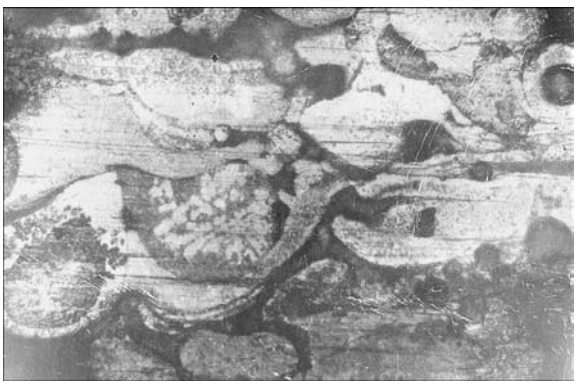

Figure 6. Microstructure (×1000) of coating, spray-deposited with PZh R3 material in a complex gas system using plasma-chemical reactor

Similar calculations show the theoretical possibility of oxide synthesis in the case of the change of spraying conditions.

In order to produce coating with synthesized iron carbide in iron matrix, the spraying process was conducted in nitrogen plasma with feeding of carbide-forming propane-butane into the reaction space.

Plasma gas flow rate was equal to 3.5 m^3/h, reaction gas flow rate was 0.7 and 1.5 m^3/h, arc current was 150 A. At these parameters voltage did not exceed 105–110 V. Coating material spraying efficiency was 5 kg/h, main size of dispersed material fraction was 63–100 μm.

Samples for spraying were mounted practically at the edge of plasma reactor last section. Spraying distance was equal to 230–250 mm, that is essentially greater than the optimum value in spraying by the traditional schematic. Increase of the distance during plasma-chemical spraying practically does not influence the value of particle velocity at the moment of colliding with the base surface and greatly increases particle temperature, as a result of limiting the air suction from the environment.

Figure 6 shows the microstructure of the produced coating. Coating has a characteristic laminated structure, which forms from molten particles. Presence of a certain quantity of particles of a globular shape, which have passed into the coating from unmolten state, is observed at the same time. All kinds of boundaries and pores are visible.

In addition to compounds, which were synthesized in the gas phase during gas medium interaction with material vapour phase and which coagulate with carrier-particles, intensive gas absorption by molten particle material occurs during spraying. Under the conditions of high cooling rates (about 10^5 K/s) gases dissolved in particles are fixed in the solid solution with formation of oversaturated solid solutions. Relaxation of metastable state leads to precipitation of ultrafine, nanosized excess phases in the cooling particles.

Quantitative microanalysis of sample microsection reveals considerable increase of carbon content: from 0.05 % in the initial material up to 5.0–5.6 % in the coating. Samples with identical coating were studied in parallel under the conditions of abrasive wear in LKI-3 instrument. The load was 150 N; fused corundum with main particle size of 300–400 μm was used as abrasive.

It is found that resistance of a sample with coating, containing a strengthening component, under identical test conditions is 7–7.5 times higher than that of a sample, sprayed without running of plasma-chemical reaction (mass loss was equal to 0.02583 g/m compared to 0.00343 g/m in a sample with strengthening component).

Conclusions

1. Use of plasma-forming media of N–O–C–H system creates prerequisites for synthesis of strengthening components (carbides, nitrides and oxides) during plasma spraying of protective coatings. Thermodynamic analysis of the respective systems allows evaluation of quantitative characteristics of target product yield and energy conditions of the process.

2. Practical realization of the technology of spray-deposition of coatings with concurrent synthesis of strengthening components is possible in case of availability of objective data on energy characteristics of applied plasma equipment and regularities of these characteristics connection to process mode parameters.

3. Results of studying coatings from PZh R3 powder reveal an abrupt (by 2 orders of magnitude) increase of carbon content in the coating, compared to initial material, and respective wear resistance increase (by more than 7 times) under conditions of abrasive wear.

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