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Structure and tribological properties of detonation coatings based on Cr_3C_2-NiCr after pulse-plasmaine treatment

Cr_3C_2-NiCr metal-ceramic coatings have found wide application in the protection of machine parts and equipment operating under extreme conditions. In this study, Cr_3C_2-NiCr based detonation coatings which have been subjected to pulse-plasma treatment were studied. The study showed that IPO reduced the surface roughness by 48 %, reduced the coating friction coefficient by about 2 times, increased the hardness of the coatings from the original 12 GPa to 16.2 GPa and improved their wear resistance by 2 times compared to untreated coatings. Pulse-plasma treatment provides qualitative formation of coatings from metal-ceramic material of Cr_3C_2-NiCr system with complex heterogeneous structure-phase state, where the layered structure of areas of carbide particles and matrix metal in immediate proximity from "carbide-matrix" border with selections in matrix of dispersed secondary carbides is revealed.

Keywords: ceramic metal coatings, detonation spraying, pulse-plasma treatment, coating modification, hardness, wear resistance.

Introduction

Metalloceramic chromium carbide-nickel-chromium alloys are used as acid-resistant materials in the chemical industry and for the manufacture of wear-resistant parts. They compete in this respect with WC-Ni-Cr and TiC- Ni(Co)-Cr alloys. Due to the high melting point, hardness and chemical resistance the highest Cr_3C_2 chromium carbide is used as a component of cladding alloys, as well as alloys used for manufacturing nozzles, stamps, high-temperature bearings, press molds for pressing brass profiles, sandblaster tips, inserts in large-sized matrices for pipe broaching [1-4].

Cr_3C_2-NiCr based coatings are used for corrosion and wear protection of component surfaces working at high temperatures and in aggressive environments [5], which is provided by the possibility to bind a solid phase of Cr_3C_2 carbide with a NiCr matrix and create a high density coating material [6]. Various spraying technologies are used for coating deposition: atmospheric plasma spraying (APS), high-velocity oxy-fuel spraying, air-fuel spraying (HVOF, HVAF) and detonation spraying.

In the process of coating materials made of Cr_3C_2-NiCr powder by HVOF and HVAF methods, a change in the chemical composition of the material is observed due to a decrease in the carbide content in the coating due to elastic rebound [7] and also due to oxidation [8, 9] caused by the presence of oxygen and superheated water vapor in the combustion products [9, 10].

The coating materials obtained by detonation spraying are characterized by increased hardness and wear resistance compared to HVOF and atmospheric plasma spraying [11-13]. Detonation spraying does not cause a large change in the chemical composition of the material and it is possible to regulate the chemical composition of the coating by changing the technological regimes [14, 15].

The specifics of gas-thermal spraying methods of ceramic-metal materials on a carbide base is that under the influence of high temperature (several thousand degrees) and oxidizing atmosphere of gaseous combustion products of a combustible mixture the depletion of higher carbides to lower carbides, oxidation of carbide particles, as well as migration of products of carbide particles dissociation into the metal matrix takes place [16, 17]. Since the highest carbide Cr_3C_2 has the highest performance characteristics, the processes of significant decarbonization of carbide particles are undesirable.

Further improvement of the qualitative characteristics of carbide-based metal-ceramic coatings is possible by external high-energy impact [18, 19]. The most effective technology is a complex pulse-plasma treatment, including surface modification by: magnetic field, electric current (flow of charged elementary

particles), high gradient thermal stream (plasma), containing metallic and nonmetallic alloying elements [20].

Pulse-plasma treatment (PPT) provides a rapid heating (heating time 10^{-3} — 10^{-4} s) of a surface layer followed by its intense cooling by heat removal into the volume of a product. High speed (up to 10^7 K/s) of melting and crystallization of surface layers contribute to formation of nanodisperse crystal structure and high density of dislocations. Impulse heat influence, elastoplastic deformation of processed material structure in combination with electromagnetic influence are carried out. Due to pulse current (up to 10 kA/cm^2) flowing through the surface layers of the coating, physical and chemical processes as well as heat and mass transfer are intensified.

The purpose of this work is to study the possibility of increasing the complex of physical and mechanical properties of the coating material made of Cr_3C_2-NiCr powder with the use of modern methods of cumulative-detonation coating deposition and subsequent pulse-plasma treatment.

Materials and methods of research.

Powder of Cr3C2-NiCr (75/25) (H.C. Starck: AMPERIT® 584.054) with a dispersion of 10-45 µm was used as the spraying material. The coatings were applied to 12Cr1MF steel samples by detonation spraying (DS) on a multichamber detonation apparatus [21]. To create high parameters (pressure, velocity) of the combustion products, a multichamber device design was used in which the detonation combustion regime of the gas mixture in specially profiled chambers and the subsequent accumulation of combustion energy from these chambers in a cylindrical bore are implemented [21]. The device provides formation of a jet of combustion products to accelerate and heat the sprayed powder and to apply high-quality metal and ceramic coatings [21, 24].

Figure 1 shows a general view of a multichamber detonation device [21, 24], which was developed at the E.O. Paton Institute of Electric Welding, National Academy of Sciences of Ukraine. The device has three chambers: 1 — prechamber for initiation of the detonation process; 2 — the main cylindrical chamber, where the detonation mode of combustion occurs; 3 — an annular hemispherical chamber with a slotted exit to the conoid chamber coaxial with the barrel. The powder dosage is accelerated and heated in the cylindrical barrel 4. The powder is metered and fed through an annular slot 5. Detonation is initiated by a spark plug 6. The pressure and velocity of the combustion products are measured by pressure sensors 7 and 8 mounted at the ends of the barrel. In the hemispherical chamber, the detonation mode in the corner concentrators is implemented, which significantly increases the rate and completeness of combustion of the combustible mixture components. The combustion products from the chambers are accumulated and provide them with high pressure and temperature. In the final result, this is realized in high velocity and sufficiently high temperature, providing the possibility of spraying ceramic coatings [25].
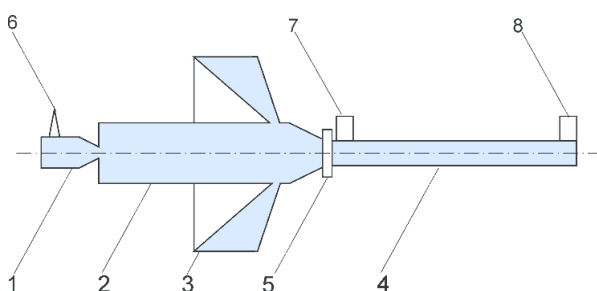

Figure 1. Scheme of the detonation apparatus. 1 — prechamber; 2 — cylindrical chamber; 3 — annular hemispherical chamber; 4 — barrel; 5 — annular slot; 6 — spark plug for initiation of detonation; 7, 8 — pressure sensors.

The design features of the multichamber detonation device provide the possibility of detonation combustion of poor combustible mixtures, which reduces the temperature of the combustion products, almost without reducing their velocity. For acceleration and heating, a dose of powder is fed into the barrel. The internal diameter of the barrel is 16/18 mm and its length is 300/500 mm, depending on the material properties of the sprayed powder. As a result of collapse of combustion products in front of the nozzle barrel from the annular hemispherical and cylindrical chambers, the pressure (up to 40 atm.) and their density increase significantly, which ensures effective acceleration and heating of the powder dose fed through the annular slot of a special gas dynamic dosing and pulse delivery unit of a compact dose of gas-powder

mixture. The detonation regime of combustion of the combustible mixture is initiated by an automotive spark plug.

The detonation repetition frequency is 20 Hz or higher. The supply of gases and powder to the detonation device is carried out continuously, from a standard powder feeder. Powder flow rate is 0.9 kg/hour and higher. Dosing of gases and powder and their release into the device is carried out by gas dynamic devices at the expense of the energy of combustion products. The flow rate of combustible mixture components of this device is shown in Table 1.

T a b l e 1

Consumption of combustible mixture components of the detonation apparatus

The components of the mixture:		Flow rate, m^3/hour
	O_2	2.92
Chamber 1	Air	1.33
	C_3H_8	0.66
	O_2	2.93
Chamber 2	Air	1.43
	C_3H_8	0.66
Transporting gas:		0.9

To modify the resulting detonation coating on the surface of the product, a pulsed plasma technology (PPT) was used. Pulsed plasma generation was carried out at the "Impulse-6" unit developed at the Institute of Electric Welding named after E.O. Paton of the National Academy of Sciences of Ukraine [21]. Paton Institute of Electric Welding of NAS of Ukraine [22]. The peculiarity of the technology is the possibility to commutate electric current up to 15 kA by ionized gas region behind the detonation wave front [23].

The pulsed electric current releases thermal energy on the weakened areas of the coating material that have an increased resistivity. It heats them, up to melting, activates diffusion processes and, eventually, "heals" defects (microcracks, pores), increasing the adhesion and cohesion characteristics [26, 27].

Pulse-plasma generator (Fig. 2) consists of a detonation chamber — 1, where the initiation of combustion of combustible gas mixture (C_3H_8, O_2, air) and coaxial electrodes — 2, 3. If it is necessary to introduce dopant elements into plasma in the form of vapor phase, erodible electrode — 4 is used. When electric current flows behind the detonation wave — 5 in the interelectrode gap, joule heat is released, thereby increasing the electromagnetic and gas dynamic components of the force, which accelerates the plasma flowing on the surface on the products -6. The energy characteristics of plasma jets at the outlet of the pulse-plasma device depend on the geometry of the coaxial electrodes and the electric field strength in the interelectrode gap.
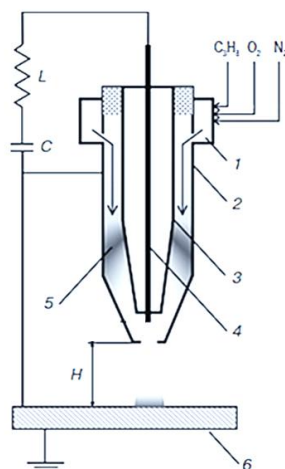

Figure2. Schematic diagram of the pulse-plasma device. 1 — detonation chamber; 2,3 — coaxial electrodes; 4 — eroding electrode; 5 — interelectrode gap; 6 — product; H — distance to product surface.

The parameters of the pulse-plasma treatment are shown in Table 2.

T a b l e 2

Consumption of combustible mixture components of the detonation device

Parameter	Value
Capacitor battery voltage (V)	3200
Capacitor bank capacity (μF)	960
Discharge circuit inductance (μH)	30
Plasma pulse frequency (Hz)	1.2
Displacement speed (mm/s)	5
Distance to surface (mm)	50

At electric field strength between the electrodes 3.5×10^5 V/m the plasma velocity at the exit from the plasma torch reaches 4 km/s, and the temperature is 12000 K. At the moment of interaction of the plasma pulse with the surface of the product — 6 an area of shock-compressed plasma layer is formed in the contact zone.

The electric circuit between the electrode being eroded and the item is closed. The current density reaches 10 kA/cm^2. As a result, the surface is subjected to multiple pulses of electric current, magnetic field and plasma heat. Heat flux power density is 10^4-10^6 W/cm^2. It is possible to generate pulsed plasma with a frequency of 1-4 Hz and energy up to 7 kJ.

The phase composition of DS and DS/PPT coatings was studied using X-ray diffractometer X'PertPRO with Cu-Kα radiation (λ = 2.2897 Å), voltage 40 kV and current 30 mA. The diffractograms were interpreted using HighScore software, and measurements were made in the 2θ range equal to 20°-90° with a step of 0.02 and a counting time of 0.5 s/step. The surface morphology was investigated by scanning electron microscopy (SEM) using backscattered electrons (BSE) on a JSM-6390LV scanning electron microscope. Micrographs of the coating surface were obtained using an Altami MET 5S metallographic microscope. The surface roughness of the coatings Ra was evaluated using a profilometer model 130. Microhardness of cross-section of samples was measured according to GOST 9450-76 (ASTM E384-11) on Metolab 502 microtest meter at loads on indenter P=1 N and exposure time 10 s.

Tribological tests for sliding friction were performed on a TRB[3] Anton PaarSrl tribometer, using the standard "ball-on-disk" technique (international standards ASTM G 133-95 and ASTM G99), where a ball 6.0 mm in diameter, SiC coated steel, with a load of 6 N and a linear speed of 15 cm/s, a curvature radius of 5 mm, a friction path of 1200 m was used as a counterbody.

Results and discussion.

Figure 3 shows the results of measuring the surface roughness of the Cr$_3$C$_2$-NiCrbased coating material, according to which it was found that the surface has a non-uniform structure with the presence of pores. The Ra value, which is the arithmetic mean deviation of the profile, was chosen as the main parameter for assessing the surface roughness of the coatings. The roughness parameter of the coatings obtained before the PPT has a value of Ra = 11.2 (Fig. 3a), and after the PPT has a value of Ra = 5.31 (Fig. 3b). The twofold decrease in the roughness parameter is caused by pulse plasma melting of the protruding fragments and pores of the coating roughness, which contributed to a decrease in the surface roughness value by ≈ 48 % as compared to the coating roughness parameters before PPT.
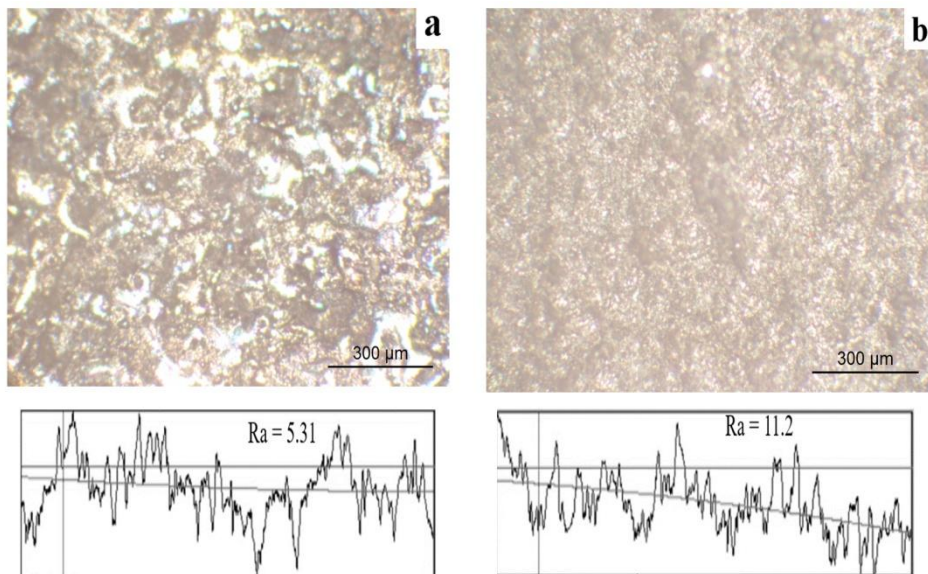
Figure 3. Micrograph of topography and surface roughness of Cr_3C_2 coatings before (a) and after the PPT

Figure 4 shows the diffractograms of the coating surface before and after the pulsed plasma treatment (PPT). The following phase components were detected in the coatings before the pulse-plasma treatment: Ni-Cr-Fe, Cr_3C_2, Ni-Cr-Fe/ Cr_7C_3 and Cr_7C_3 phases (Fig. 4a). Cr_2O_3 chromium oxide phases were found on the surface after PPT (Fig. 4b). Thus, after an PPT on the diffractogram it is observed growth of intensity of peaks of chrome carbide Cr_3C_2, (Fig. 4b), the reason for which is short-term activization of a surface of a covering from behind a pulse plasma where the plasma containing active carbon and oxygen causes course of two mutually exclusive chemically thermal processes of oxidation and carburization. The combination of solid phases of chromium oxide and carbide in the hardened metal matrix significantly increases the durability of the resulting material in conditions of abrasive wear.
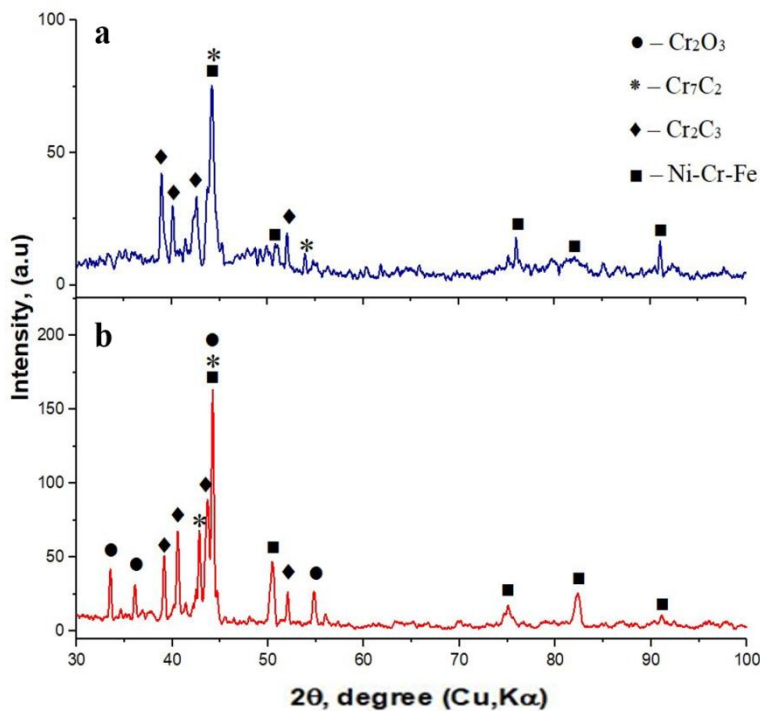

Figure 4. Surface diffractograms of Cr_3C_2-NiCr coating material before (a) and after (b) pulse plasma treatment

Figure 5 shows SEM images of the cross section of the coating material before (Fig. 5a) and after the pulse-plasma treatment (Fig. 5b). According to the image obtained with SEM before the pulse-plasma treatment (Fig. 5a), one can observe the porous structure characteristic of detonation spraying with large open defects of medium size localized closer to the surface layer of the coating. After pulse-plasma treatment in a subsurface layer of the coating pores are reduced to the minimum indicators, see Fig. 5b., which is associated with melting of the boundaries of large defects, as well as melting by pulse plasma of the protruding fragments and pores of coating that is caused by subsequent "healing" of defects during the passage of pulses of electric current.
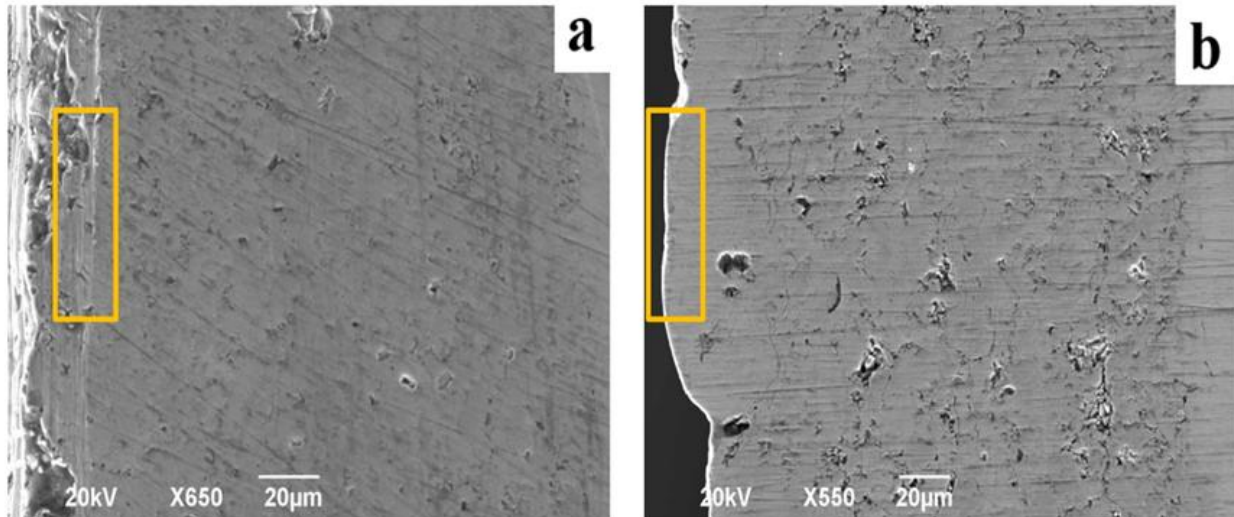

Figure 5. SEM image of the coating material before (a) and after PPT (b).

Figure 6 shows the plots of microhardness distribution by coating thickness before and after pulse-plasma treatment. The graph of dependence of microhardness on thickness of the Cr_3C_2-NiCr coating material (Fig. 6) shows non-uniform distribution of hardness: the coating material near the transition layer to the part base has a lower value of microhardness in contrast to the near-surface layers. The microhardness of the coating material deposited after the PPT (Fig. 6b) is rather higher than before the pulsed plasma treatment (Fig. 6a).
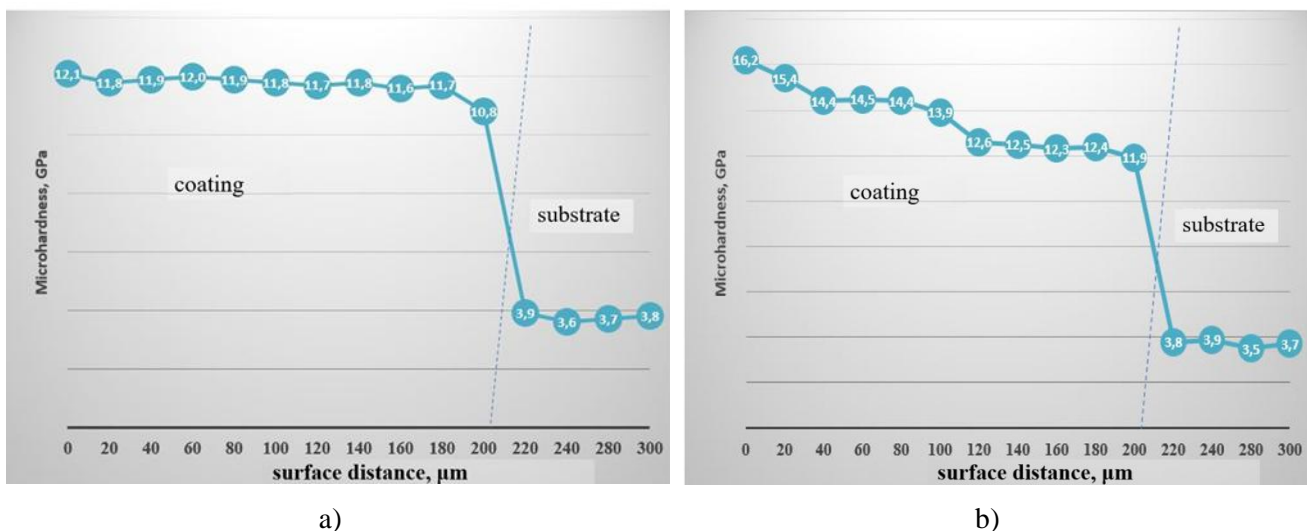

Figure 6. Graph of the depth hardness distribution of Cr_3C_2-NiCr coatings before (a) and after the PPT (b)

One of the main properties responsible for the durability of products is the tribological parameters, which in this work were evaluated by the value of the wear volume of coatings before and after the PPT according to the scheme "ball-on-disk" (Fig. 7a). Profilograms were built using the obtained values of the

profilometer, and values for calculating the wear volume before and after the PPT were obtained using a special program. The test results showed that after PPT the coating has increased wear resistance according to the confirmation of the XRD this is most likely due to the increased proportion of Cr_3C_2 carbide phase, which has a high resistance to wear. According to the study of tribological characteristics of the coating surface it was found that the pulsed plasma treatment had a significant impact on the friction coefficient of the coating surface (decreased by 2 times) and wear resistance (increased by 2 times compared with the values before the PPT).
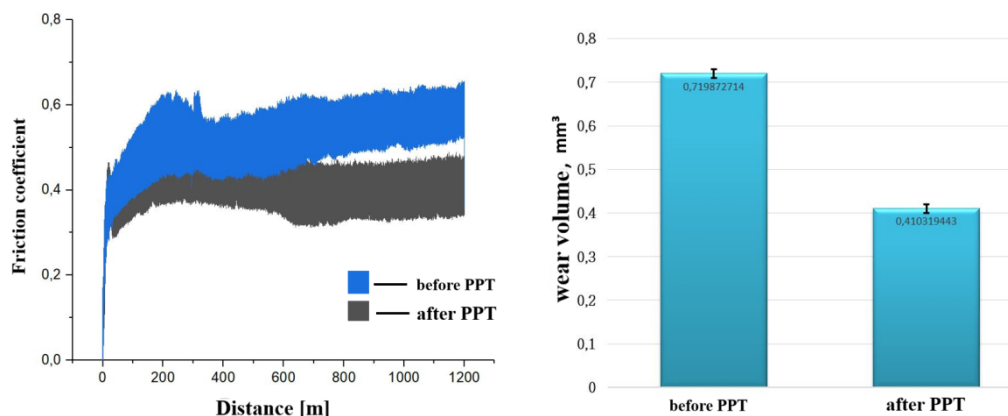

Figure 7. Graph of the depth hardness distribution of Cr_3C_2-NiCr coatings before (a) and after PPT (b)

Conclusion

According to the evaluation and analysis of all obtained results, we can draw the following main conclusions on the present research work:

- Detonation coating technology and subsequent pulse-plasma processing provide formation of quality coatings from ceramic-metal powder on the basis of Cr_3C_2-NiCr with complex heterogeneous structural-phase state, where the layered structure of carbide particles and matrix metal areas in the immediate vicinity of the "carbide-matrix" border with allocation of dispersed secondary carbides in the matrix is revealed;

- Pulse-plasma treatment of coatings provides increase of hardness of matrix without significant degradation of primary carbide particles and formation of high values of local internal stresses that is caused by healing of defects, as well as accelerated mass transfer of carbon, oxygen, increase of carbide particles quantity and creation of chrome oxides in near-surface layer;

- Pulse-plasma treatment contributes to a 48 % decrease in surface roughness value and coating friction coefficient, an increase in material microhardness of Cr_3C_2-NiCr coatings from ~12 GPa (initial) to ~16.2 GPa and a 2-fold increase in wear resistance compared to untreated coating;

Detonation spraying and subsequent pulse-plasma treatment, can be recommended as an optimal way to protect the surfaces of parts operating in extreme wear conditions.

Acknowledgment

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Импульсті-плазмалық өңдеуден кейін Cr₃C₂-NiCr негізіндегі детонациялық жабынның құрылымы мен трибологиялық қасиеттері

Cr₃C₂-NiCr металл керамикалық жабындары экстремалды жағдайларда жұмыс істейтін машина бөлшектері мен жабдықтарын қорғауда кеңінен қолданылады. Бұл зерттеу импульсті-плазмалық өңдеуден өткен Cr₃C₂-NiCr негізіндегі детонациялық жабындарды зерттеуге арналған. Зерттеу нәтижелері көрсеткендей, импульсті-плазмалық өңдеу (ИПӨ) бетінің кедір-бұдырлығын 48 %–ға төмендетеді, жабынның үйкеліс коэффициентін шамамен 2 есе азайтады, жабындардың қаттылығын бастапқы 12 ГПа-дан 16,2 ГПа-ға дейін арттырады және өңделмеген жабындармен салыстырғанда олардың тозуға төзімділігін 2 есе жақсартады. Импульстік-плазмалық өңдеу күрделі гетерогенді құрылымдық-фазалық күйі бар Cr₃C₂-NiCr жүйесінің металл-керамикалық материалынан жасалған жабындардың сапалы қалыптасуын қамтамасыз етеді, мұнда дисперсті қайталама карбидтер матрицасындағы секрециялармен «карбид-матрица» шекарасына жақын карбид бөлшектері мен матрицалық металл аймақтарының қабатты құрылымы анықталады.

Кілт сөздер: металл-керамикалық жабындар, детонациялық бүрку, импульсті-плазмалық өңдеу, жабынды өзгерту, қаттылық, тозуға төзімділік.

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Структура и трибологические свойства детонационного покрытия на основе Cr₃C₂–NiCr после импульсно-плазменной обработки

Металлокерамические покрытия Cr₃C₂–NiCr нашли широкое применение в защите машинных деталей и оборудования, работающих в экстремальных условиях. В данном исследовании были изучены детонационные покрытия на основе Cr₃C₂–NiCr, которые были подвергнуты импульсно-плазменной обработке. Исследование показало, что ИПО снижает шероховатость поверхности на 48 %, уменьшает коэффициент трения покрытия примерно в 2 раза, увеличивает твердость покрытий от исходных 12 до 16,2 ГПа и улучшает их износостойкость в 2 раза по сравнению с необработанными покрытиями. Также было выявлено, что после ИПО повышается стойкость покрытий Cr₃C₂–NiCr к абразивному износу и эрозии. Импульсно-плазменная обработка обеспечивает качественное формирование покрытий из металлокерамического материала системы Cr₃C₂–NiCr со сложным гетерогенным структурно-фазовым состоянием, где обнаруживается слоистая структура областей карбидных частиц и матричного металла в непосредственной близости от границы «карбид–матрица» с выделениями в матрице дисперсных вторичных карбидов.

Ключевые слова: металлокерамические покрытия, детонационное напыление, импульсно-плазменная обработка, модифицирование покрытия, твердость, износостойкость.

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