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THE ELECTRO-SPARK DEPOSITED WC-Cu COATINGS MODIFIED BY LASER TREATMENT

POWŁOKI WC-Cu NANIESIONE ELEKTROISKROWO I MODYFIKOWANE OBRÓBKĄ LASEROWĄ

The main objective of the present work was to determine the influence of laser treatment on microstructure, X-ray diffraction, microhardness, surface geometric structure and roughness, corrosion resistance and tribological properties of coatings deposited on C45 carbon steel by the electro-spark deposition (ESD) process. The studies were conducted using WC-Cu electrodes produced by the powder metallurgy route. The tests show that the laser-treated electro-spark deposited WC-Cu coatings are characterized by higher corrosion resistance, surface roughness and seizure resistance which come at the expense of lower microhardness. The laser treatment process causes the homogenization of the chemical composition, structure refinement and healing of microcracks and pores of the electro-spark deposited coatings. Laser treated ESD coatings can be applied in sliding friction pairs and as protective coatings.

Keywords: electro-spark deposition, laser treatment, powder metallurgy, coating, properties

W pracy badano wpływ obróbki laserowej na mikrostrukturę, skład fazowy, mikrotwardość, topografię powierzchni, chropowatość, odporność na korozję oraz własności tribologiczne powłok nakładanych na stal C45 metodą elektroiskrową (ESD). W badaniach wykorzystano elektrody WC-Cu otrzymane metodą metalurgii proszków. Badania wykazały, że pomimo nieco niższej mikrotwardości, powłoki poddane obróbce laserowej posiadają wyższą odporność na korozję, chropowatość oraz odporność na zatarcie. Ponadto, obróbka laserowa przyczynia się do rozdrobnienia ziarna i ujednorodnienia składu chemicznego powłoki, a także do usunięcia porów i mikropęknięć. Z badań wynika, że obrabiane laserowo powłoki otrzymywane metodą ESD mogą być z powodzeniem wykorzystywane do pracy w węzłach tarcia oraz jako powłoki ochronne.

1. Introduction

There are many methods for producing surface coatings, such as electroplating, plasma spraying, etc. Very thin layers can be deposited by vapour deposition. Various surface treatment techniques have been developed to improve the desired properties of the deposited layers. Some of these methods are expensive and should only be used for special applications, where the high cost is justified. For most applications, however, there is a need for inexpensive coatings having good properties. This study attempts to improve a widely used low cost method of electro-spark deposition (ESD). It has been already recognized as an economically effective surface coating [1-5]. ESD is also widely used due to the low cost equipment required for this process. The coating deposition is performed by an electrical circuit, which generates sparks between the electrode and the work-piece. Electrical pulses of high frequency and high direct current between the electrode (anode) and work-piece (cathode) release very hot micro-particles of the electrode material to form a coating on the work-piece surface. This leads to energy savings because only the micro particles are heated, while the substrate remains cool.

Electro-spark deposited coatings have also some disadvantages but these can be easily eliminated by laser beam machining (LBM), which can be used for polishing the surface, sealing and modifying its topography, and chemical homogenization of coatings [6-7].

It is envisaged that the advantages of the laser-treated electro-spark coatings will include:

- lower roughness,
- lower porosity,
- better adhesion to the substrate,
- higher wear and seizure resistance,
- higher fatigue strength due to the occurrence of compressive stresses in the sub-surface zone,
- higher resistance to corrosion.

2. Materials and experimental procedures

The work discusses the properties of electro-spark deposited WC-Cu coatings subjected to laser treatment.

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The properties of the coatings after laser treatment were assessed by means of scanning electron microscopy, X-ray diffraction analysis, surface geometric structure and roughness measurement, resistance to corrosion, microhardness tests and tribological studies.

The coatings were deposited on the C45 grade plain-carbon steel by the ESD method. The electrodes containing 50% WC and 50% Cu were produced using the powder metallurgy hot press route [8]. The main characteristics of the powders used to prepare the electrodes are included in Table 1.

TABLE 1

Powders used to manufacture WC-Cu electrodes

Powder	Particle Size, µm	Surface Area (B.E.T.), m2/g	Producer
WC	~0.2 †	1.8	OMG
Cu	~0.4 †	-	NEOMAT

† measured using Fisher Sub-Sieve Sizer

The powders were mixed for 30 minutes in the chaotic motion Turbula-type mixer. The mixture was then poured into rectangular cavities of a graphite mould, each 6×40 mm in cross section, and consolidated by passing an electric current through the mould under uniaxial compressive load. A 3 minute hold at 950°C and under a pressure of 40 MPa permitted obtaining electrodes of porosity <10% and strength sufficient to maintain integrity when installed in the electrode holder.

The equipment used for electro-spark deposited was an EIL-8A model. Basing on the results of previous research as well as instructions given by the producer, the following parameters were assumed to be optimal for ESA:

- voltage $U = 230$ V,
- capacitor volume $C = 150$ µF,
- current intensity $I = 0.7$ A.

Then, the coatings were treated with an Nd:YAG laser (impulse mode) model BLS 720. The samples with electro-spark deposited coatings were laser-modified using the following parameters:

- spot diameter d = 0.7 mm,
- power $P = 60$ W,
- laser beam velocity $v = 250$ mm/min,
- nozzle-workpiece distance $\Delta f = 6$ mm,
- pulse duration $t_i = 0.4$ ms,
- pulse repetition frequency $f = 50$ Hz,
- beam shift jump $S = 0.4$ mm,
- nitrogen gas shield $Q = 25$ l/min.

3. Results and Discussion

3.1. Measurements of the surface geometric structure and roughness

The surface geometric structure (SGS) substantially influences many processes that occur in the outer layer. A lot of publications deal with the measurement methods and the assessment of surface roughness and waviness [9-10].

Measurements of surface geometric structure were carried out at the Laboratory of Computer Measurements of Geometric Quantities of the Kielce University of Technology. They were performed using Talysurf CCI optical profiler that employed a coherence correlation algorithm patented by Taylor Hobson company. The algorithm makes it possible to take measurements with the resolution below 0.8 nm along the z axis. The result of measurements were recorded in 1024 x 1024 measurement point matrix, which yielded the 1.65 mm x 1.65 mm measured area and the horizontal resolution of 1.65 mm x 1.65 mm for the x10 lens.

Three-dimensional surfaces and their analysis with TalyMap Platinum software made it possible to precisely identify the geometric structure of the tested surfaces. Table 2 provides major parameters of the surface geometric structure of the examined specimens.

TABLE 2

Parameters of the surface geometric structure

SGS parameters	Coating	
	WC-Cu	WC-Cu + laser
Sa [µm]	4.02	6.95
Sq [µm]	5.24	8.48
Ssk	0.15	0.02
Sku	3.89	2.77
Sp [µm]	26.44	34.03
Sv [µm]	21.21	66.76
Sz [µm]	47.65	100.80

Figures 1-4 present images of surface topography, distribution of ordinates with bearing curves, isotropy diagrams and the specimen autocorrelation function before and after laser treatment.

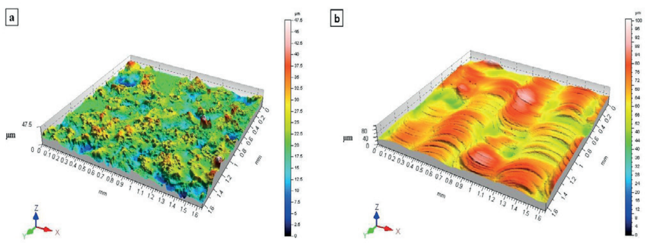

Fig. 1. Specimen surface topography: a) before laser treatment, b) after laser treatment

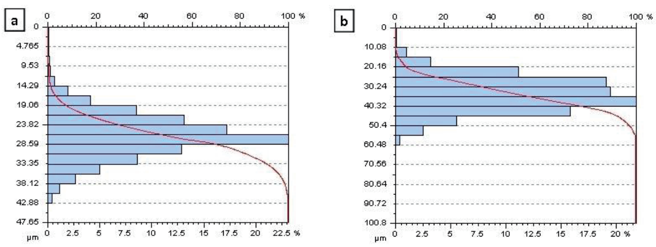

Fig. 2. Distribution of ordinates and specimen bearing curves: a) before laser treatment, b) after laser treatment

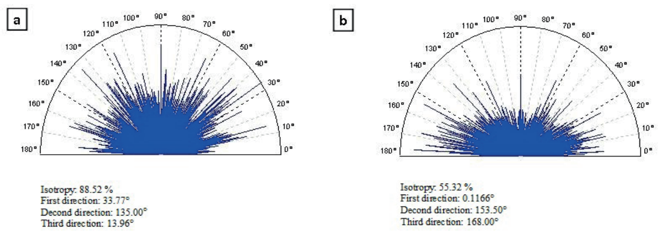

Fig. 3. Specimen isotropy: a) before laser treatment, b) after laser treatment

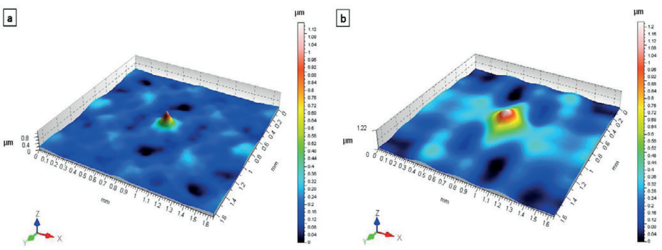

Fig. 4. Specimen autocorrelation function: a) before laser treatment, b) after laser treatment

A greater value of the mean arithmetic deviation of surface roughness Sa, a basic amplitude parameter in the quantitative assessment of the state of the surface under analysis, was recorded for the specimen after the laser treatment, for the specimen before the laser treatment the value of this parameter was by almost 50% smaller.

A similar tendency is observed for the mean square root deviation of surface roughness *Sq*. Complementary information on how the surface of examined elements is shaped is provided by amplitude parameters, namely the coefficient of skewness (asymmetry) *Sku* and the coefficient of concentration (kurtosis) *Ssk*. Those parameters are sensitive to the occurrence of local hills or valleys, and other surface defects. The parameter *Ssk* has a positive value for both specimens, the value is close to zero for the untreated specimen, which indicates the symmetrical location of the distribution of ordinates with respect to the mean plane. The obtained values of kurtosis were close to *Sku* = 3. This indicates that the distribution of ordinates for both specimens is close to normal.

Before the laser treatment, the specimen had random isotropic structure (Iz = 88.52%), whereas after the treatment, that became a periodic structure, located in the transient area between isotropic and anisotropic structures (*Iz* = 55.32%). That is confirmed by the shape of the autocorrelation function of both surfaces, for the surface before treatment, the shape is circular and symmetrical, whereas for the surface after treatment, it is asymmetrical and elongated.

The roughness of the WC-Cu coatings was assessed quantitatively using the Talysurf CCI optical profiler. Roughness profiles are routinely measured by dragging a stylus along the laser beam path whereas the maximum values of the arithmetic average departure from the plain surface are reported to occur in the perpendicular direction. Therefore in this study an average value of *Ra* was calculated for each coating from the readings taken on evenly divided sampling lengths running parallel to the electrode/laser beam motion path and on similar lengths at 90º. It was found that the employed surface treatments increased the average roughness value (*Ra*) from 0.41¸0.44 µm for the C45 steel substrate up to 2.37-3.67 µm and 3.05¸4.26 µm for the WC-Cu coatings in as-deposited and laser treated condition, respectively.

3.2. Seizure resistance tests

Seizure resistance tests were carried out using the T-09 tribotester, in which the friction pair consisted of a cylinder and two prisms (Fig. 5). The prisms with deposited WC-Cu coatings and C45 steel (laser treated and untreated) were used as the specimens, whereas a roller of hardened carbon steel, 6.3 mm in diameter, was used as a counter-specimen. In order to investigate different material combinations, three kinematic pairs were employed with paraffin used as a lubricant.

Figure 6 presents cumulative information on average values of seizure load for specimens before and after the laser treatment. The results indicate that the laser treatment resulted in an increase in the load that produced seizure both for electro-spark deposited coatings and for the C45 steel as well.

Figure 7 shows the dependence of load and friction forces as a function of time. The patterns are typical of seizure tests conducted with the T-09 instrument. An increase in the normal force is accompanied by a respective increase in the friction force. Consequently, the increasing load applied to the sliding pair leads to such an increase in the friction force that the copper pin fails and the test is terminated. The maximum value of the load, at which seizure occurs and the time that elapsed from the beginning of the test, can be read from the recorded graphs.

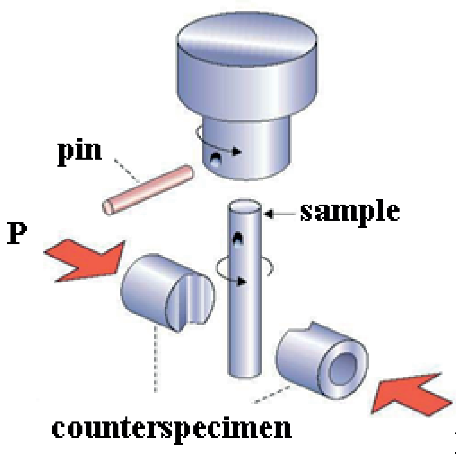

Fig. 5. Diagram of friction pair in a Falex T-09-type tribological tester

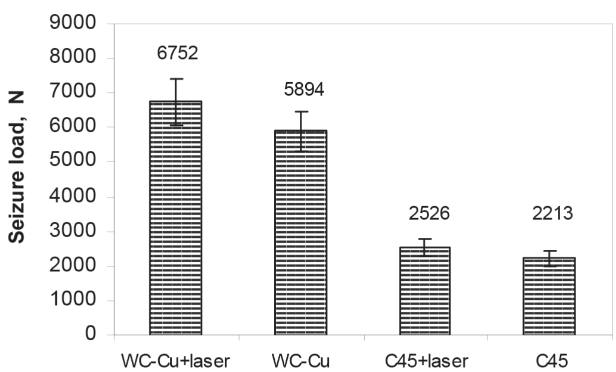

Fig. 6. Average values of seizure load

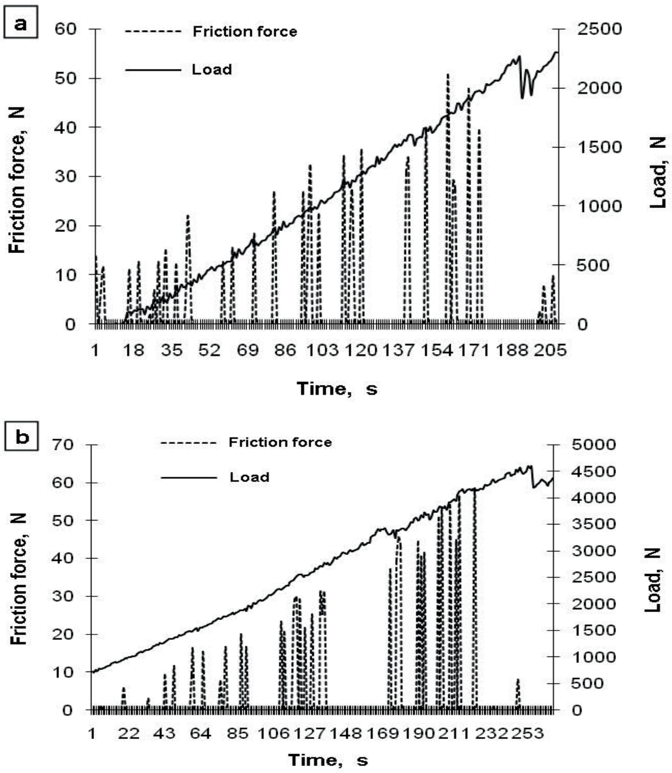

Fig. 7. Dependence of friction force and load as a function of time: a) C45 steel, b) WC-Cu coating

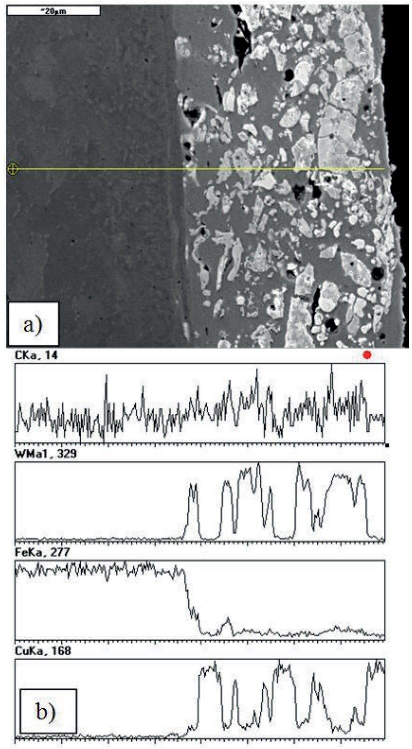

Fig. 8. Microstructure (a) and linear distribution of elements (b) in the WC-Cu coating.

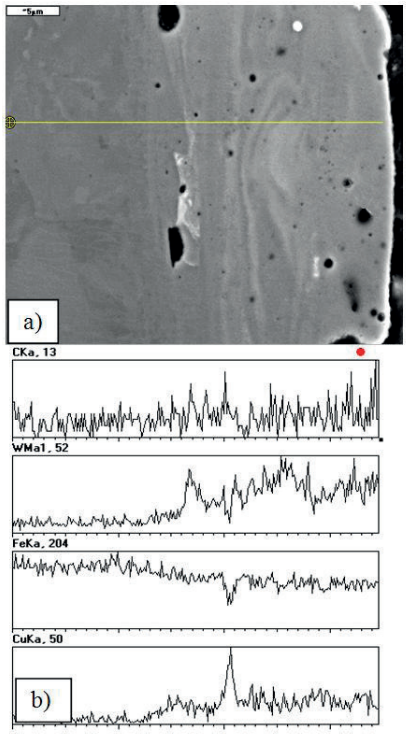

Fig. 9. Microstructure (a) and linear distribution of elements (b) in the WC-Cu coating after laser treatment

3.3. Metallographic examination and X-ray diffraction analysis

A microstructure analysis was conducted for the WC-Cu coatings before and after laser treatment using a scanning electron microscope Joel JSM-5400. Figure 8a shows the microstructure of an EDS WC-Cu coating. The thickness of the obtained layers was estimated at 38÷62 mm, whereas the heat affected zone ranged from 20 to 30 mm into the substrate. The micrograph in Figure 8a shows a clear boundary between the coating and the substrate as well as pores and microcracks.

The linear chemical analysis of the WC-Cu coating (Fig. 8b) shows that the distribution of elements is inhomogeneous. It is possible to distinguish zones with considerable amounts of W, Cu, and Fe. Moreover, in the diagram of the linear distribution of the WC-Cu coating, one can notice the traces of diffusive interaction between the coating and the substrate. In the coating, there is no clear segregation of components.

As seen in Figure 9b, laser treatment of the EDS WC-Co coatings leads to their homogenization, structure refinement, and crystallization of supersaturated phases due to the occurrence of temperature gradients and high cooling rates. The laser-modified outer layer does not contain microcracks, pores and discontinuities at the coating-substrate boundary (Fig. 9a). The thickness of the laser-treated WC-Cu coatings ranges from 41 to 64 mm. Moreover, the heat affected zone is in the range of between 25 and 35 mm, and contains more carbon.

The X-ray diffraction phase analysis of the examined coatings was performed using a filtered Cu Ka radiation.

The phase composition analysis of theWC-Cu coating (Fig. 10a) revealed that the surface layer of the coating consisted mainly of Cu and W_2C with a small amount of WC and Fe. Laser treatment did not cause the WC-Cu melt to penetrate into the substrate material (Fig. 10b). The surface layer of the WC-Cu coating after laser treatment has the same composition as that of the untreated coating with the most intense Cu peaks (Fig. 10a and 10b).

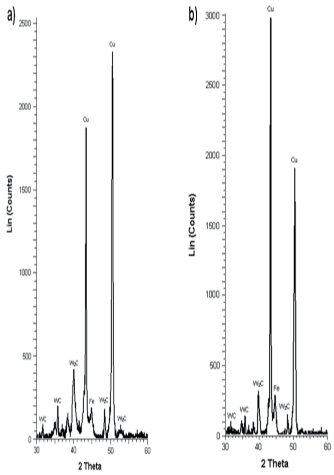

Fig. 10. X-ray diffraction pattern of the WC-Cu coating: a) before laser treatment, b) after laser treatment

3.4. Microhardness testing

The microhardness was determined using the Vickers method. The measurements were performed under a load of 0.4 N. The indentations were made in perpendicular microsections in three zones: the white homogeneous difficult-to-etch coating, the heat affected zone (HAZ) and the substrate. The test results for the ESD WC-Cu coating before and after laser treatment are shown in Tables 3. The laser treatment of the ESD coating caused a slight decrease in microhardness of both the coating and heat affected zone.

TABLE 3

Results of the microhardness tests

Coating condition	HV0.4 †		
	Coating	HAZ	Substrate
WC-Cu	643 ± 54	438 ± 23	278 ± 18
WC-Cu+laser	617 ± 21	407 ± 22	279 ± 8

† scatter intervals estimated at 90% confidence level

3.5. Corrosion resistance testing

The corrosive environment was obtained by mixing the sodium chloride (NaCl) and hydrochloric acid (HCl), in which the concentration of Cl^- ions and pH were 1 M and 1.5, respectively. All electrochemical measurements were carried out using a potentiostat/galvanostat PGSTAT 128N (AutoLab, Netherlands) with NOVA 1.7 software.

The polarization curves were recorded in order to establish the effect of the coating (WC-Cu) on electrochemical corrosion of the C45 carbon steel in a 1 M Cl^- solution. Measurements were carried out within the potential range from -800 to -200 mV with the scan rate of 1 mV s^{-1}. The acquired polarization curves were used to evaluate the corrosion potential (E_{corr}) and corrosion current density (j_{corr}). The corrosion rate was calculated using the following equation [11-12]:

$$k_{corr} = 3.268 \times \frac{j_{corr}\ M}{n\ \rho} \tag{1}$$

where:

j_{corr} – corrosion current density
M – molecular weight of iron
n – number of electrons exchanged
ρ – iron density.

Figure 11 shows the Tafel plots for the WC-Cu coating on the C45 steel surface prior to (a) and after the laser treatment (b). Potentiodynamic polarization curves were used to determine selected corrosion parameters, which have been summarized in Table 4. The obtained results indicate that in the case of the laser treated coating the corrosion potential was shifted by about 50 mV whereas the corrosion current density was decreased be a factor of three compared to the untreated coating. It implies that the corrosion resistance of WC-Cu on steel has been markedly improved by the laser treatment. This can be attributed mainly to the improvement of the WC-Cu condition after laser irradiation. As a result of the laser treatment different oxides and fine grains form on the surface of coating, which leads to different corrosion characteristics. The compact oxide layer provides an effective barrier to protect the coating on the carbon steel against corrosion in an aggressive environment of chlorides.

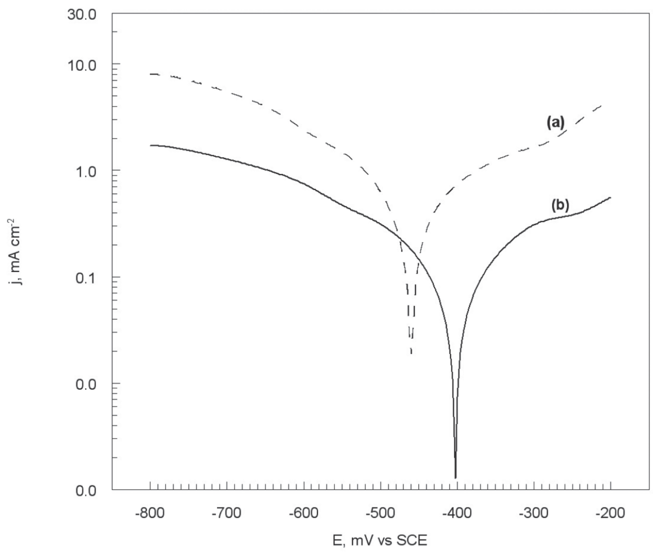

Fig. 11. Tafel plots for the C45 carbon steel in 1 M Cl-. The WC-Cu coating: (a) before, (b) after laser treatment

TABLE 4

Corrosion parameters for WC-Cu ESD coated C45 steel in solution containing 1 M Cl^-

Material	E_{corr} [mV]	j_{corr} [mA/cm²]	k_{corr} [mm/year]
C45	-480	1.10	12.8
WC-Cu	-451	0.53	6.1
WC-Cu+laser	-402	0.15	1.7

4. Conclusions

1. A concentrated laser beam can effectively modifying the state of the outer layer of ESD coatings thus changing their functional properties.
2. Laser irradiation of coatings assists in healing of micro-cracks and pores.
3. Parameters of surface geometric structure of ESD coatings have lower values when compared with those characterising coatings after laser treatment.
4. The subsurface layer of the WC-Cu coating before and after laser treatment consists of mainly Cu and W_2C and a small amounts of WC and Fe.
5. Laser treatment of WC-Cu coatings increases by approximately 13% the load at which seizure occurs.
6. Laser treatment of ESD WC-Cu coatings decreases its microhardness by 9%.
7. The corrosion resistance of the C45 plain carbon steel surface improves with the increase of copper content in the WC-Cu coating.

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