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INVESTIGATIONS OF THE CU-MO AND CU-TI ELECTRO-SPARK COATINGS AFTER LASER TREATMENT

The article focuses on the laser treatment impact on strength of electric-spark deposited coatings. The coating microstructure, microhardness, and corrosion resistance are analyzed to evaluate the coating properties. Experiments have been carried out with Mo and Ti coatings deposited onto the substrate of steel 45 followed with a laser fusion treatment carried out in BLS 720 installation with neodymium (ND) glass.

1 Introduction

The processes of coating formation on metal parts including electro-spark deposition involve mass and energy transport accompanied by chemical, electrochemical and electrothermal reactions [1÷3]. Today, different electro-spark deposition techniques are used; they are suitable for coating formation and surface microgeometry formation [4÷7].

The process of electrospark deposition is characterized as follows:

- the reinforcement effect is dependent on the sedimentation of the anode material on the cathode surface; the best results are obtained when the anode material is very hard and resistant to wear, e.g. tungsten, titanium, or chromium carbides;

- the hardened outer layer is a result of the interaction of the anode and cathode elements forming solid solutions, chemical compounds, oxides and nitrides;

- the transfer and interaction of electrode materials as well as the impulse action of high temperature and pressure are responsible for the hardening effect, and they lead to the formation of extremely unbalanced phases.

The electro-spark deposition coating is characterized by non etching structure. It is stay white after etching. The surface layer is constituted in environment of local high temperature and high pressure. The fundamental value parameters of electromachining are as following [8]:

- shock wave pressure comes from electric spark is (2-7)10^3 GPa,

- temperature rich (5-40)10^3 Celsius degree value.

How the surface layer was generating by electro-spark deposition process is depicted in details in Figure 1. To understand this scheme below is necessary to list accurate descriptions, i.e.: 1 – material of base (cathode), 2 – working electrode (anode), 3 – created coating with established operational features, 4 – plasma, 5 – diffusive or reactive-diffusive zone, 6 – nearer surrounding (shielding gas), 7 – further surrounding (air), 8 – electrode holder with channels supplying gas, IR - infrared radiation, UV ultraviolet radiation.

Coatings produced by electro-spark deposition are applied:

1. to protect new elements,
2. to recover the properties of worn elements.

Electro-spark alloying is becoming more and more popular as a surface processing technology. Electro-spark deposited coatings are frequently applied in industry, for example, to produce implants or cutting tool inserts. The coatings are deposited with manually operated equipment or robotized systems.

In the United States, the research on this technology has been sponsored, for instance, by NASA, AIR FORCE, and US NAVY [9].

Electro-spark deposited coatings are not free from disadvantages but these can be easily eliminated. One of the methods is laser treatment; a laser beam is used for surface polishing, surface geometry formation, surface sealing or for homogenizing the chemical composition of the coatings deposited.

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

– lower roughness,
– lower porosity,
– better adhesion to the substrate,

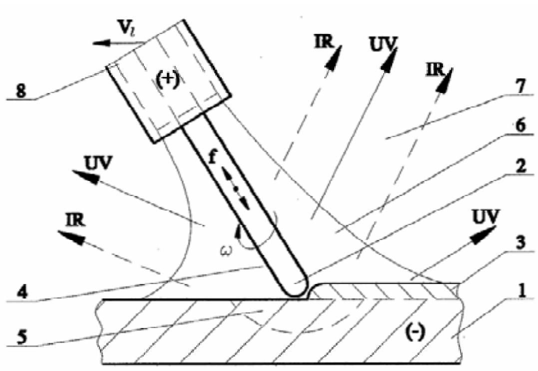

Fig. 1. Scheme of surface layer forming by electro-spark deposition method [3]

– higher wear and seizure resistance,

– higher fatigue strength due to the occurrence of compressive stresses on the surface,

– higher resistance to corrosion.

The work discusses the properties of electro-spark deposited Cu-Ti and Cu-Mo coatings subjected to laser treatment. The properties were established basing on the results of a microstructure analysis, corrosion resistance tests and microhardness tests.

2 Experiments

The tests were conducted for heterogeneous Ti-Cu and Cu-Mo coatings produced by electro-spark deposition, which involved applying Cu, Mo and Ti electrodes with a diameter of 1 mm (the anode) on the C45 steel substrate (the cathode). Here copper constitutes the core coating material in the formation of low-friction surface layers; it also compensates for the occurrence of residual stresses. Titanium and molybdenum act as the reinforcing constituents. The chemical composition of C45 carbon steel is presented in Table 1. The coating materials, i.e. molybdenum (99.8% Mo), titanium (99.8% Ti) and copper (99.2% Cu) in the form of wire (ϕ = 1 mm) were purchased from BIBUS Metals Sp. z.o.o. (certificate included).

Table 1. Chemical composition of C45 carbon steel

Elements	C	Mn	Si	P	S
Content %	0,42…0,50	0,50…0,80	0,10…0,40	0,04	0,04

The heterogeneous coatings were electro-spark deposited on C45 steel substrate by means of the ELFA-541 made by a Bulgarian manufacturer. Basing on the analyses of the current characteristics as well as the manufacturer's recommendations, it was assumed that the parameters of the ESD operation should be as follows: current intensity I = 16 A (for Cu I = 8A); table shift rate V = 0.5 mm/s; rotational speed of the head with electrode n = 4200 rev/min; number of coating passes L = 2; capacity of condenser system C = 0.47 мF; pulse duration T_i = 8 мs; interpulse period T_p = 32 мs; frequency f = 25 kHz.

The subsequent laser treatment was performed with the aid of a BLS 720 laser system employing the Nd:YAG type laser operating in the pulse mode. The following parameters were assumed for the laser treatment: laser spot diameter d = 0.7 mm; laser power P = 20 W; beam shift rate V = 250 mm/min; nozzle-sample distance h = 1 mm; pulse duration t_i = 0.4 ms; frequency f_l = 50 Hz.

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3 Results and discussion

3.1 Microstructure analysis

A characteristic feature of any electro-spark deposited coating is that the new layer has a difficult-to-etch structure – it remains white. Similar layers are produced by grinding and lapping. What the processes have in common is high temperature and high loads applied locally. Electro-spark deposition differs from grinding and lapping in the process intensity: the pressure of the shock wave from an electric spark discharge is (2÷7)*10^6 N/mm^2 and the temperature reaches values of the order of (5÷40)*10^3 °C (in grinding it does not exceed 1000 °C) [10].

The temperature during an electro-spark discharge increases locally and it is much higher than the boiling point of the materials the electrodes are made of. A high heat transfer rate causes that the temperature within the layer falls rapidly to the solidifying point, the thickness of the coating being of the order of several micrometers. According to Ref. [11], the processes of crystallization, phase transition and chemical interaction occur in the solid phase. Electro-spark deposited coatings are fine-grain non-equilibrium structures, which are heterogeneous in composition, structure and properties. They are characterized by very high adhesion to the underlying substrate, which is a result of the diffusion or reaction-diffusion processes.

A Joel JSM-5400 scanning microscope equipped with an Oxford Instruments ISIS-300 X-ray microanalyzer was used to test the coating microstructure. Figures 2a and 3a show the microstructure of electro-spark deposited two-layer Cu-Ti and Cu-Mo coatings. The layer thickness is approximately 8÷10 mm, and the range of the heat affected zone (HAZ) inside the (underlying) substrate material is about 10÷15 mm. In the photographs, the boundary line between the two-layer coating and the substrate is clear. There are microcracks running across and along the coating. A linear analysis of the

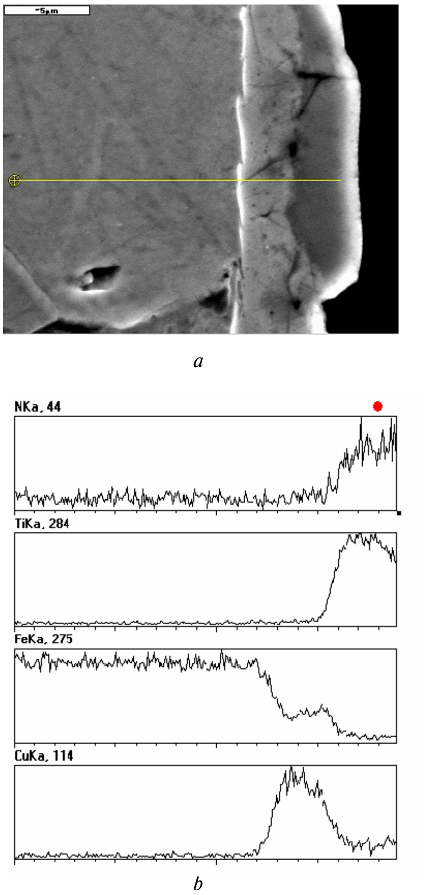


Fig. 2. Microstructure (*a*) and linear distribution of elements in the Cu-Ti coating (*b*)

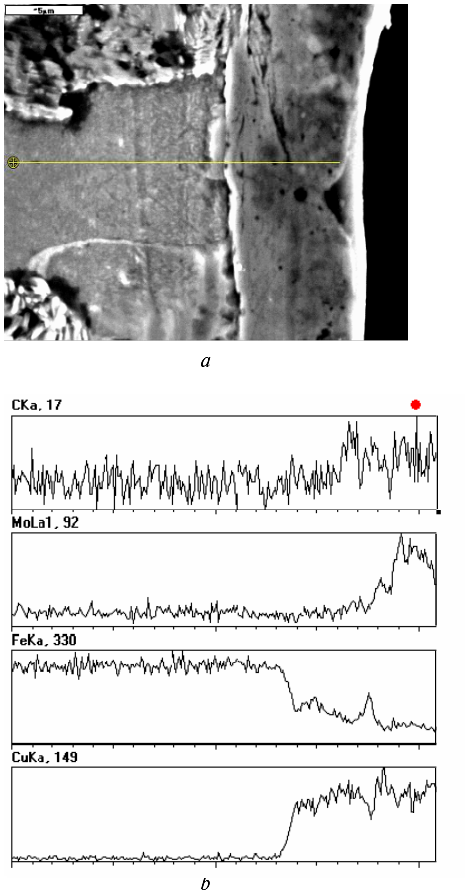


Fig. 3. Microstructure (*a*) and linear distribution of elements in the Cu-Mo coating (*b*)

elements (Fig. 2*b*) of the Cu-Ti coating shows that the distribution of elements is non-uniform; there are zones with greater concentrations of Cu, Ti and Fe. Analyzing the linear distribution of elements, one can see that the adhesion of the coating to the substrate is of diffusive type. There is no clear separation of components either in the Cu-Ti or Cu-Mo coating (Fig. 3*b*). A higher content of carbon reported in the electro-spark deposited Cu-Mo coating is a result of ascending diffusion. Carbon from the C45 steel substrate travels to the electro-spark deposited technological surface layer (TSL) because of thermal interaction. Another observation is the diffusion of copper into the molybdenum layer (Fig. 3*b*).

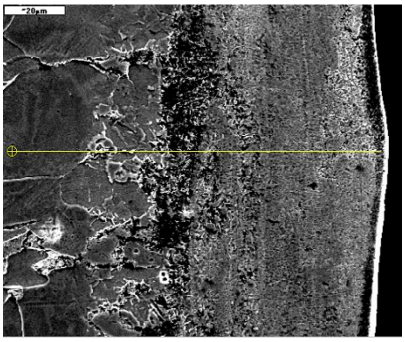
An SEM/EDS analysis of the samples shows that there is some nitrogen in the Cu-Ti layer (Fig. 2*b*). It is assumed that the high-energy process accompanied by plasma formation results in the occurrence of a thin-layer phase of titanium nitride. The problem will be analyzed in detail at a later stage of the investigation.

The melting and solidifying processes during laser treatment resulted in the migration of elements across the coating-substrate interface. Laser radiation caused intensive convective flow of the liquid material in the pool and, in consequence, the homogenization of the chemical composition (Figs. 4*b* and 5*b*). It also led to the structure refinement and highly saturated phase crystallization (Figs. 4*a* and 5*a*) because of considerable gradients of temperature and high cooling rates. The technological surface layers, TSLs, produced by laser alloying, were free from microcracks and pores – an effect of surface sealing, and non-continuities across the coating-substrate interface. There was practically no change in the chemical composition of the substrate. The thickness of the fused two-layer Cu-Ti and Cu-Mo coatings ranged 20÷40 mm. In the heat affected zone (HAZ), which was 20÷50 mm thick, there was an increase in the content of carbon (Figs. 4b and 5*b*).

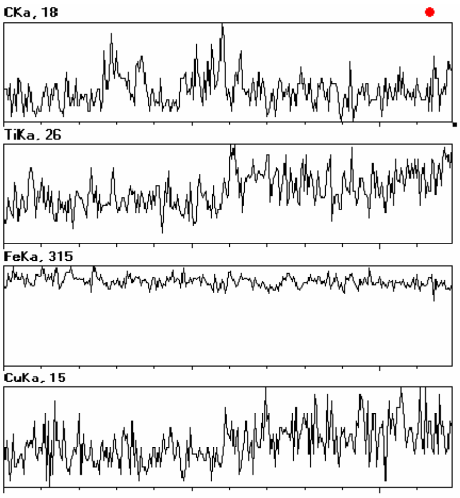
The point analysis conducted for the outer surface of the technological surface layers (TSLs) (Figs. 6a and 7*a*) shows high intensity of peaks of the elements present in the coating. In the Cu-Ti coating the contents of Ti and Cu are 73.96% at. and 15.43% at., respectively. The Cu-Mo coating contained 66.07% at.

of Cu and 10.98% at. of Mo, which may testify to the mixing of the two elements and the formation of a multi-component alloy (Fig. 7*a*).

The point analysis of the electro-spark coatings treated with a laser beam (Figs. 6*b* and 7*b*) shows high intensity of iron peaks in the alloyed layers. The content of iron in the laser-treated technological surface layers was between 88% at. and 97% at. After laser treatment, the intensity of peaks of Ti, Mo, Cu in the electro-spark deposited coatings was lower.

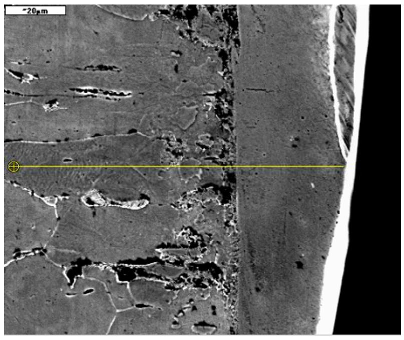


a



b

Fig. 4. Microstructure (*a*) and linear distribution of elements in the Cu-Ti coating after laser treatment (*b*)



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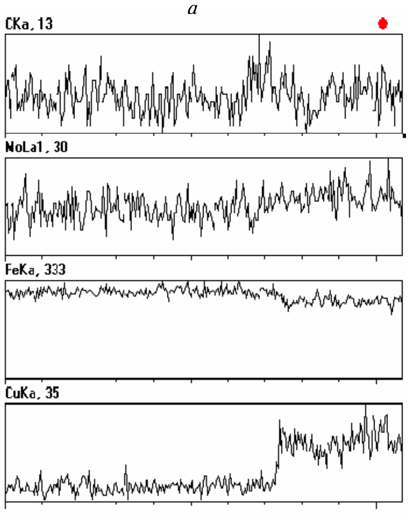
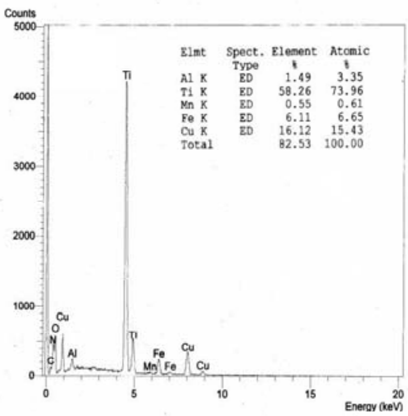


b

Fig. 5. Microstructure (*a*) and linear distribution of elements in the Cu-Mo coating after laser treatment (*b*)



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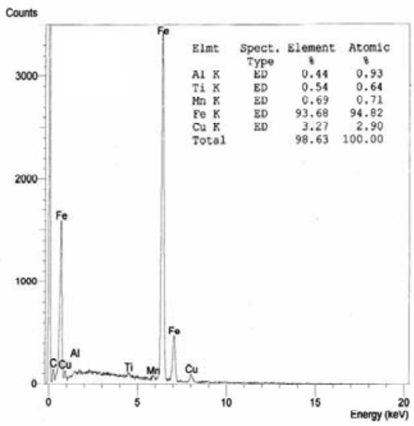
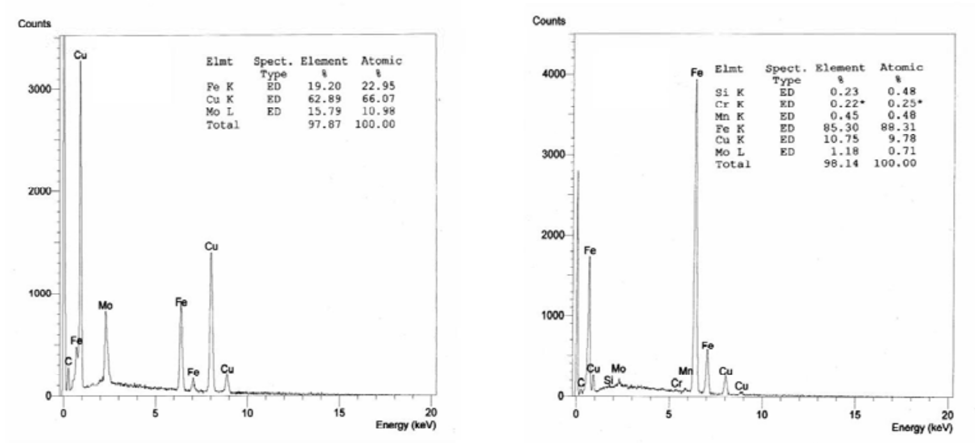


b

Fig. 6. Spectrum of the characteristic X-ray radiation for an electro-spark deposited Cu-Ti coating on a C45 steel substrate: *a* — before laser treatment; *b* — after laser treatment



a *b*

Fig. 7. Spectrum of an X-ray radiation for an electro-spark deposited Cu-Mo coating on a C45 steel substrate

a – before laser treatment; *b* – after laser treatment

3.2 Microhardness tests

The material microhardness was assessed using the Vickers method and a Hanemann tester. 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 electro-spark deposited Cu-Ti and Cu-Mo coatings before and after laser treatment are shown in diagrams in Fig. 8. Electro-spark deposition caused changes in the microhardness of the material. The microhardness of the substrate after electro-spark deposition was on average 280 $HV_{0.04}$; the same value was reported for the substrate before the process. There was a considerable increase in microhardness after depositing the heterogeneous Cu-Ti and Cu-Mo coatings. The microhardness of the Cu-Ti coating was 514 $HV_{0.04}$ – an increase of 84%. The microhardness of the Cu-Mo coating was approx. 587 $HV_{0.04}$ – a rise of 110%. The microhardness of the Cu-Ti coating in the heat affected zone (HAZ) after electro-spark treatment was 57% higher than that of the substrate material. In the Cu-Mo coating, it increased by 51%. The higher microhardness of the Cu-Ti coating in the HAZ may have been due to the formation of titanium carbides. Laser treatment had a favorable effect on the changes in the microhardness of the electro-spark deposited coatings. There was an increase of 161% in the microhardness of the Cu-Mo coating and an increase of 144% in microhardness of the Cu-Ti coating.

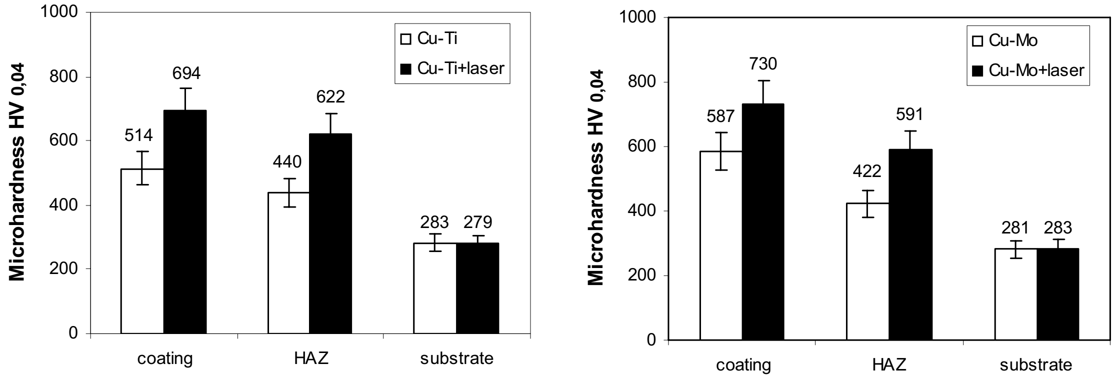


Fig. 8. Results of the microhardness tests for:

a – the Cu-Ti coating before and after laser treatment, *b* – the Cu-Mo coating before and after laser treatment

3.3 Corrosion resistance tests

The corrosion resistance of the Cu-Ti and Cu-Mo coatings and the underlying substrate before and after laser treatment was analyzed using a computerized system for electrochemical tests, Atlas'99, produced by Atlas-Sollich. The potentiodynamic method was applied, because it is reported to be one of the most effective methods of electrochemical testing.

The cathode polarization curve and the anode polarization curve were determined by polarizing the samples with a potential shift rate of 0.2 mV/s in the range of ±200 mV of the corrosive potential, and with 0.4 mV/s in the range of higher potentials. Samples with a marked area of 10 mm in diameter were polarized up to a potential of 500 mV. The polarization curves were drawn for samples exposed for 24 hours to a 3.5% NaCl solution so that the corrosive potential could be established. The tests were performed at a room temperature of 21 °C (±1 °C).

The characteristic electrochemical values of the materials under test are presented in Table 2. Electro-spark deposited coatings were reported to have similar corrosion resistance to that of the substrate material.

There was a slight migration of elements between the coating and the substrate, which resulted in the occurrence of microcracks (Fig. 2a) sometimes followed by the coating unsealing and loss of corrosion resistance. A system with a two-layer coating is assumed to fulfill two functions: increase corrosion resistance and wear resistance. The coatings which contained Cu acted as cathodes. The coatings oxidized for instance with Ti (Cu/Ti, TiO_x), which are resistant to wear, acted as anodes. Resistance to wear and corrosion depends on the quality of coatings, particularly their sealing properties.

Table 2. Current density and corrosion potential of the materials tested

Material	Corrosion current density I_k [мA/cm^2]	Corrosion potential E_{KOR} [mV]
C45	112 ± 17.8%	-458
C45+Laser	86.4 ± 16%	-522
C45+Cu+Ti	97.8 ± 5.4%	-555
C45+Cu+Ti+Laser	89.3 ± 19.1%	-527
C45+Cu+Mo	42.9 ± 11.8%	-620
C45+Cu+Mo+Laser	30.7 ± 2.6%	-629

The Cu-Mo coating was reported to have the highest corrosion resistance. The corrosion current density of the coating was 42.9 мA/cm^2, while that of the C45 steel substrate was 112 мA/cm^2. Applying the Cu-Mo coating improved the sample corrosion resistance by approx. 162%. There was, however, no significant increase in the corrosion resistance when the Cu-Ti coating was applied. This is due to a considerable difference in the values of normal potentials (P^0) between copper and titanium, and the formation of galvanic microcells. The fusion of the coating and the substrate resulted in a considerable heterogeneity of electrochemical potentials on the coating surface. The microcracks in the surface layer also contributed to the intensification of the corrosion processes.

There was some improvement in the corrosion resistance of the electro-spark deposited coatings after laser treatment. The healing of microcracks resulted in higher density and therefore better sealing properties.

The highest corrosion resistance after laser treatment was reported for the Cu-Mo coating (I_k = 30.7 мA/cm^2). For the C45 steel substrate, I_k was 6.4 мA/cm^2. Thus, the corrosion resistance increased by about 30% after laser treatment.

Laser treatment caused a decrease in the corrosion current and in two out of three cases a decrease in the corrosion potential.

The C45 steel substrate after laser treatment had a martensitic structure, while in the normalized state it possessed a ferrite-pearlite structure. It can be assumed that martensite had higher corrosion resistance than ferrite and pearlite. A similar case was described in Ref. [11]. The martensite observed in 38HMJ steel modified with a laser beam had higher corrosion resistance, compared to that of the non-modified material.

Laser treatment improved the surface smoothness and corrosion resistance; there was a decrease in the surface roughness, Ra, from 2.02 mm to 1.75 mm.

Conclusions

The following conclusions can be drawn from the analysis and test results.

1. A concentrated laser beam can effectively modify the state of the surface layer, i.e. the functional properties of electro-spark coatings.

2. After laser radiation, two-layer electro-spark deposited Cu-Ti and Cu-Mo coatings are characterized by better functional properties, i.e. higher microhardness and higher resistance to corrosion.

3. There is no change in the chemical composition of electro-spark deposited coatings after laser treatment in spite of their melting and solidification. The results of laser radiation are the homogenization of the chemical composition, structure refinement and the healing of microcracks and pores.

4. The favorable changes in the properties of electro-spark coatings after laser treatment lead to the improvement of the abrasive wear resistance when the coatings are in contact with a neutral or aggressive medium.

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В статье рассматривается влияние лазерной обработки на прочностные свойства электроискровых покрытий. Свойства были оценены с помощью микроструктурного анализа, определения микротвердости и коррозионной стойкости. Эксперименты проводились для покрытий из молибдена, титана, нанесенных на сталь 45, с последующей лазерной обработкой с оплавлением. Лазерная обработка выполнена на установке BLS 720 с неодимовым стеклом.

У статті розглядається вплив лазерної обробки на міцністні властивості електроіскрових покриттів. Властивості були оцінені за допомогою мікроструктурного аналізу, визначення мікротвердості й корозійної стійкості. Експерименти проводилися для покриттів з молібдену, титану, нанесених на сталь 45, наступною лазерною обробкою з оплавленням. Лазерна обробка виконана на установці BLS 720 з неодимовим склом.