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The influence of laser treatment on the properties of electro-spark deposited coatings

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Abstract

The aim of the study is to determine the influence of the laser treatment process on the properties of electro-spark deposited coatings. The properties were assessed by analysing the coating microstructure, microhardness, residual stresses, bonding strength and corrosion resistance. The tests were conducted for Mo, Ti and Cu coatings (the anode), which were electro-spark deposited over the C45 steel substrate (the cathode) and melted with a laser beam. The coatings were deposited by means of an ELFA-541. The laser processing was performed with an Nd:YAG, BLS 720 system. The tests show that the laser-treated electro-spark deposited Cu-Ti and Cu-Mo coatings are characterized by higher microhardness, higher adhesion and higher resistance corrosion. It is also reported that in laser-treated coatings tensile stresses occur deeper. The laser treatment process causes the homogenization of the chemical composition, the structure refinement and the healing of microcracks and pores of the electro-spark deposited coatings. The coatings, whether laser-treated or not, exhibit very good performance properties, and this makes them suitable for use in sliding friction pairs.

Key words: electro-spark deposition, laser treatment, coating, microstructure, corrosion resistance, residual stress, bonding strength

1. Introduction

By applying new engineering materials or protective coatings, it is possible to improve the functional properties of machine parts so that they are resistant to corrosion, abrasion and erosion, and possess high fatigue strength. The new materials, for instance, alloy steels, are usually costly, which is undesirable, because the higher the cost of the material, the higher the price of a finished product. However, if an element is to be subjected to high loads, then strength rather than cost is a primary factor.

Applying protective coatings to machine parts is economically justifiable if the wear is local or if the coating material is expected to display properties different from those of the substrate. Most surface layers are technological surface layers (TSLs) – they are produced before objects are used. Functional surface layers (FSLs), on the other hand, are applied during maintenance.

A number of modern surface processing methods use an energy flux. The examples include electro-spark deposition and laser treatment. Electro-spark deposition (ESD) is a cheap high-energy process. Developed in the post-war period, the technology has been frequently modified. Its main advantages are the ability to select precisely the area to be modified, the ability to select the coating thickness, which may range from several to several dozen micrometers, good adhesion of a coating to the substrate, and finally, cheap and simple equipment for coating deposition.

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]. Today, different electro-spark deposition techniques are used; they are suitable for coating formation and surface microgeometry formation [2–4].

Coatings produced by electro-spark deposition are applied:

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

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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.

Research on this technology is being conducted all over the world, and the companies interested in applying it include NASA and the US Navy [5–6].

As electro-spark coatings are reported to be resistant to wear and corrosion, they can be applied, for instance, to

- ship propeller components,
- casting moulds,
- fuel supply system components,
- exhaust system components.

Electro-spark deposited coatings have some 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,
- 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 based on the results of a microstructure analysis, corrosion resistance tests, microhardness tests, a residual stress analysis and adhesion tests.

2. Materials and treatment parameters

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). In this case, 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 in wt.% is 0.42–0.50 % of C, 0.50-0.80 % of Mn, 0.10–0.40 % of Si, $\leq$ 0.04 % of P, and $\leq$ 0.04 % of S.

The coating materials, i.e. molybdenum (99.8 % Mo), titanium (99.8 % Ti) and copper (99.2 % Cu) in the form of wire (ø = 1 mm) were purchased from BIBUS Metals Sp. z.o.o. (certificate included).

The heterogeneous coatings were electro-spark deposited on the C45 steel substrate by means of an 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, $I = 8$ A); table shift rate $V = 0.5\,\mathrm{mm\,s^{-1}}$; rotational speed of the head with electrode $n = 4200\,\mathrm{rev\,min^{-1}}$; number of coating passes $L = 2$; capacity of condenser system $C = 0.47$ μF; pulse duration $t_i = 8$ μs; interpulse period $T_p = 32$ μs; 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 $V = 250\,\mathrm{mm\,min^{-1}}$; nozzle-sample distance $h = 1$ mm; pulse duration $t_i = 0.4$ ms; frequency $f_l = 50$ Hz.

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) × $10^6\,\mathrm{N\,mm^{-2}}$ and the temperature reaches values of the order of (5–40) × 10^3 ℃ (in grinding it does not exceed 1000 ℃).

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. 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 1a and 2a show the microstructure of electrospark deposited two-layer Cu-Ti and Cu-Mo coatings. The layer thickness is approximately 8–10 μm, and the

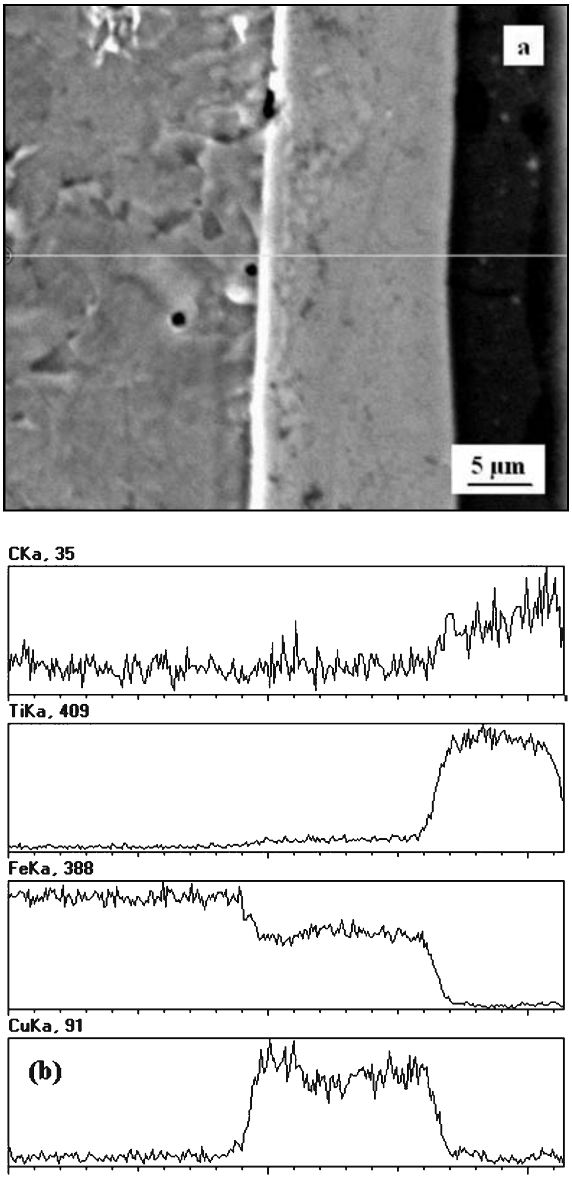

Fig. 1. Microstructure (a) and linear distribution of elements (b) in the Cu-Ti coating.

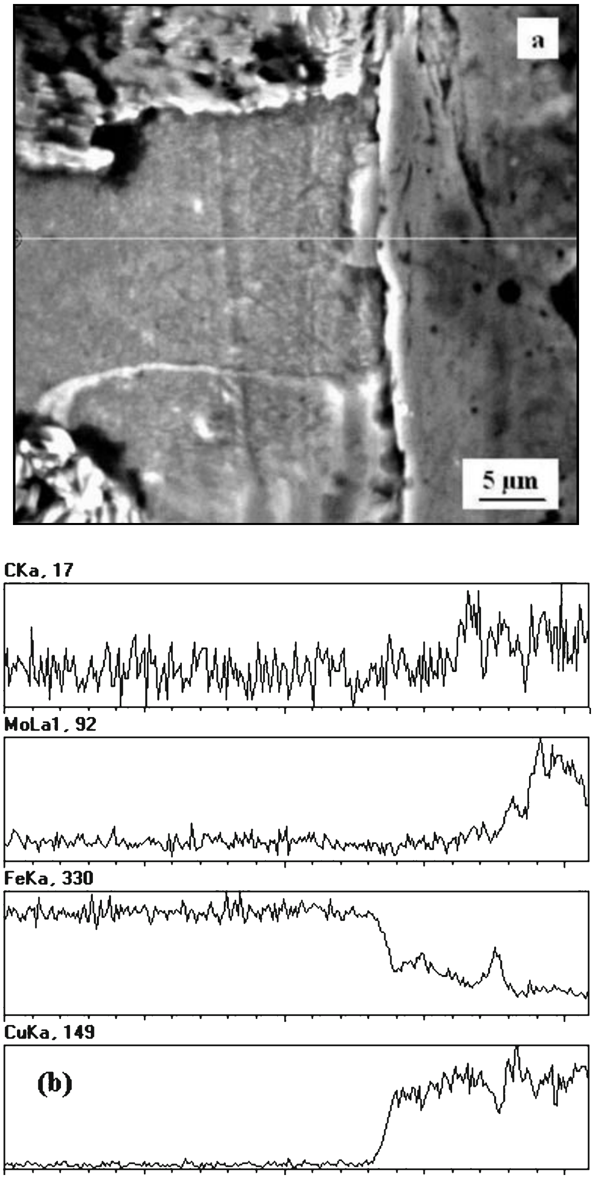

Fig. 2. Microstructure (a) and linear distribution of elements (b) in the Cu-Mo coating.

range of the heat affected zone (HAZ) inside the (underlying) substrate material is about 10–15 µm. 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 elements (Fig. 1b) 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. Analysing 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. 2b). 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 TSL because of thermal interaction. Another observation is the diffusion of copper into the molybdenum layer (Fig. 2b).

An SEM/EDS analysis of the samples shows that there is some nitrogen in the Cu-Ti layer (Fig. 1b). 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 analysed 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

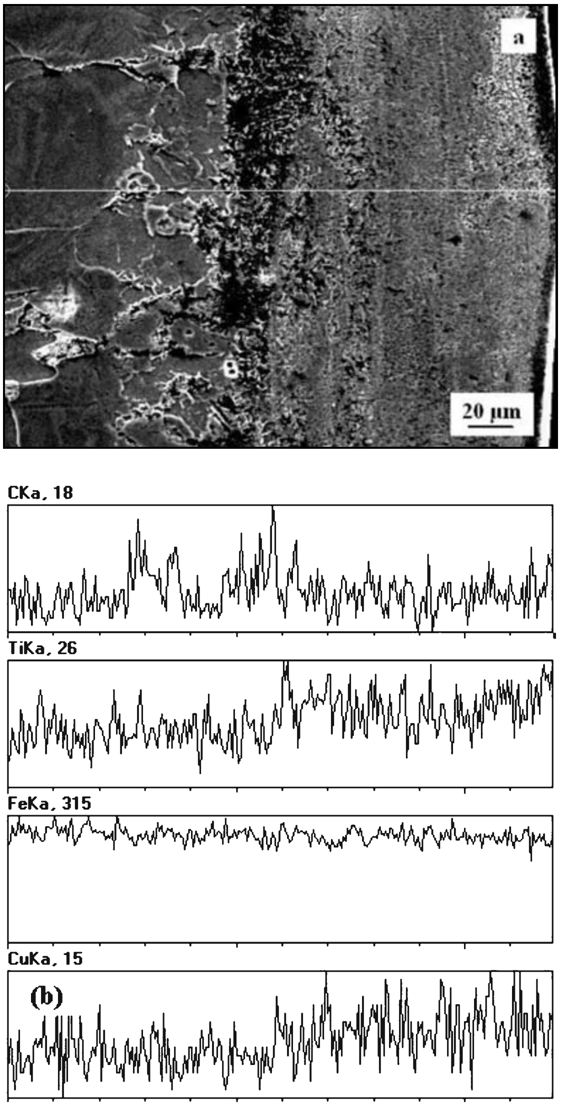

Fig. 3. Microstructure (a) and linear distribution of elements (b) in the Cu-Ti coating after laser treatment.

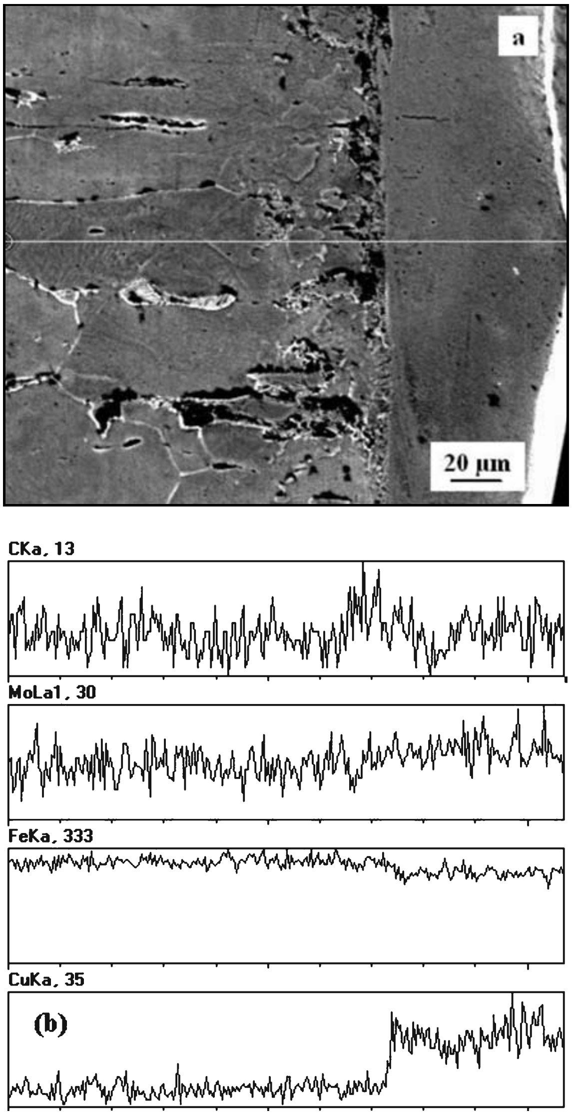

Fig. 4. Microstructure (a) and linear distribution of elements (b) in the Cu-Mo coating after laser treatment.

chemical composition (Figs. 3b and 4b). It also led to the structure refinement and highly saturated phase crystallization (Figs. 3a and 4a) because of considerable gradients of temperature and high cooling rates. The 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 μm. In the HAZ, which was 20–50 μm thick, there was an increase in the content of carbon (Figs. 3b and 4b).

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 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. 5. 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

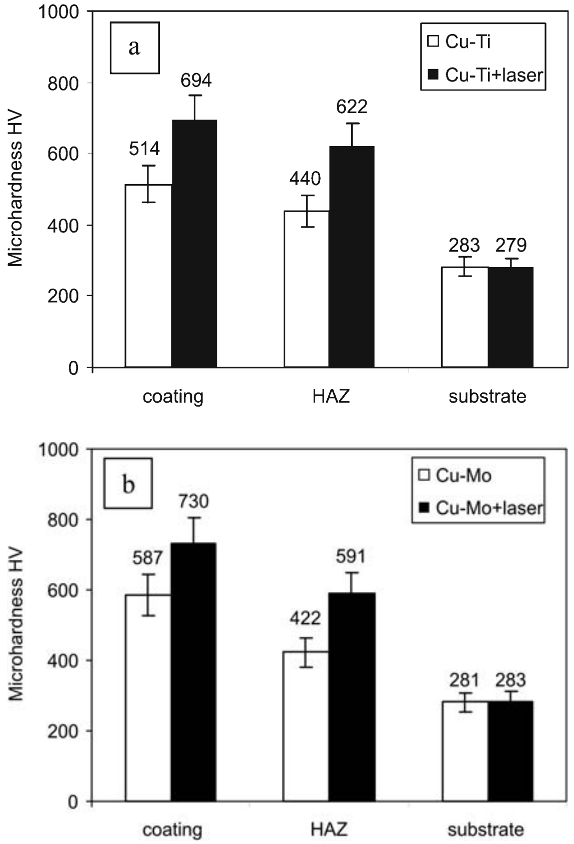

Fig. 5. Results of the microhardness tests for: a) the Cu-Ti coating before and after laser treatment, b) the Cu-Mo coating before and after laser treatment.

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 favourable 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.

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 analysed 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.

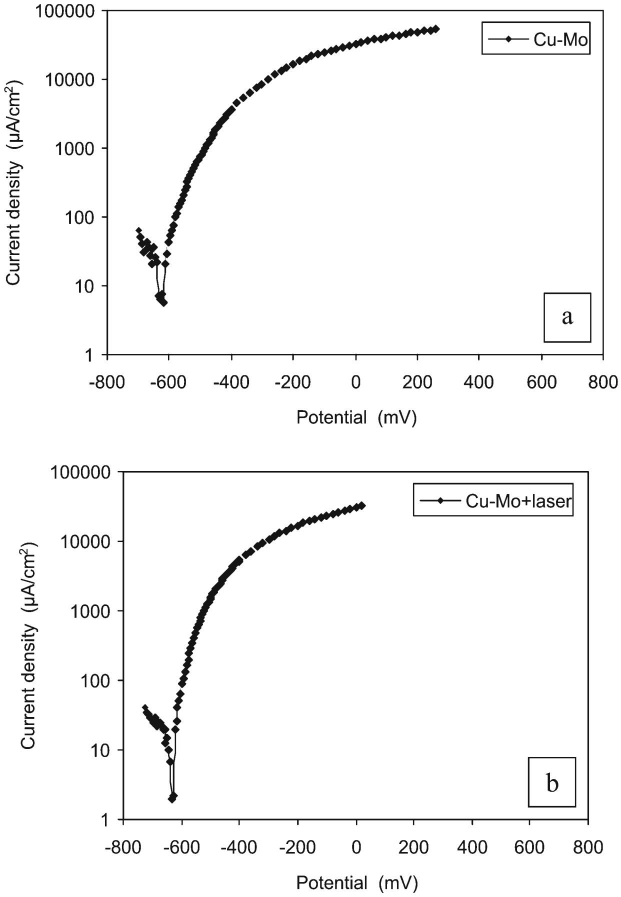

Fig. 6. Curves of the Cu-Mo coating polarization: a) before laser treatment, b) after laser treatment.

Table 1. Current density and corrosion potential of the materials tested

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

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^{-1} in the range of ±200 mV of the corrosive potential, and with 0.4 mV s^{-1} 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 ℃ (±1 ℃).

Figure 6 shows example diagrams of the polarization curves of the surface layers. The characteristic electrochemical values of the materials under test are

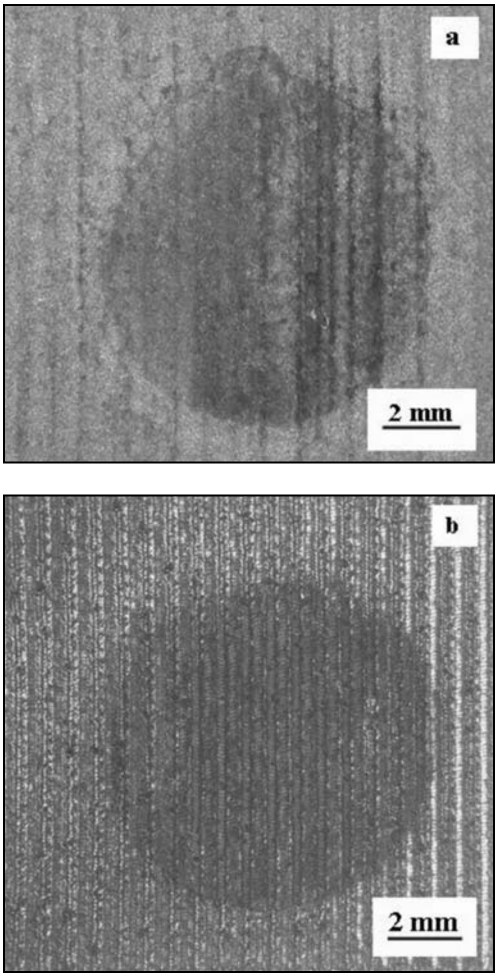

Fig. 7. Stereoscopic photographs of the Cu-Mo coating after the corrosion resistance test (magnification × 6.3): a) before laser treatment, b) after laser treatment.

presented in Table 1. In Fig. 7, we can see example stereoscopic photographs of the sample surfaces after the corrosion resistance test. The 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. 1a) sometimes followed by the coating unsealing and loss of corrosion resistance. A system with a two-layer coating is assumed to fulfil 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.

The Cu-Mo coating was reported to have the highest corrosion resistance. The corrosion current density of the coating was $42.9\,\mu A\,cm^{-2}$, while that of the C45 steel substrate was $112\,\mu A\,cm^{-2}$. 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 (Π°) 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 ($I_k = 30.7\,\mu A\ cm^{-2}$). For the C45 steel substrate, I_k was $6.4\,\mu A\,cm^{-2}$. 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. 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 μm to 1.75 μm.

3.4. Residual stress analysis

A residual stress analysis for the Cu-Mo and Cu-Ti coatings before and after laser treatment was conducted using the Waisman-Phillips method. A computerized test facility enabled registration and visualization of the measurement data.

The electrolyte solution was a mixture of concentrated acids: 850 ml of H_3PO_4 and 150 ml of H_2SO_4 per litre. The current density on the surface being etched was $1\,A\,cm^{-2}$. In order to eliminate the initial stresses in the C45 carbon steel substrate resulting, for example, from rod rolling in a steelworks or sample cutting with a wire electro discharge machine (WEDM), the samples were subjected to etching at a temperature of 300 ℃ for 12 hours.

Laser treatment of the Cu-Mo and Cu-Ti coatings first led to the occurrence of tensile stresses in the surface layer, but these decreased with depth. The tensile stresses in the surface layer were unfavourable

Table 2. Results of the adhesion test

Coating	Critical force (N)				
	Measurement number			Mean value (N)	Standard deviation (N)
	1	2	3		
Cu-Mo	4.34	4.59	2.82	3.91	0.95
Cu-Mo + laser	5.91	4.78	5.15	5.28	0.57
Cu-Ti	2.18	1.66	1.98	1.94	0.26
Cu-Ti + laser	3.14	3.07	2.24	2.81	0.50

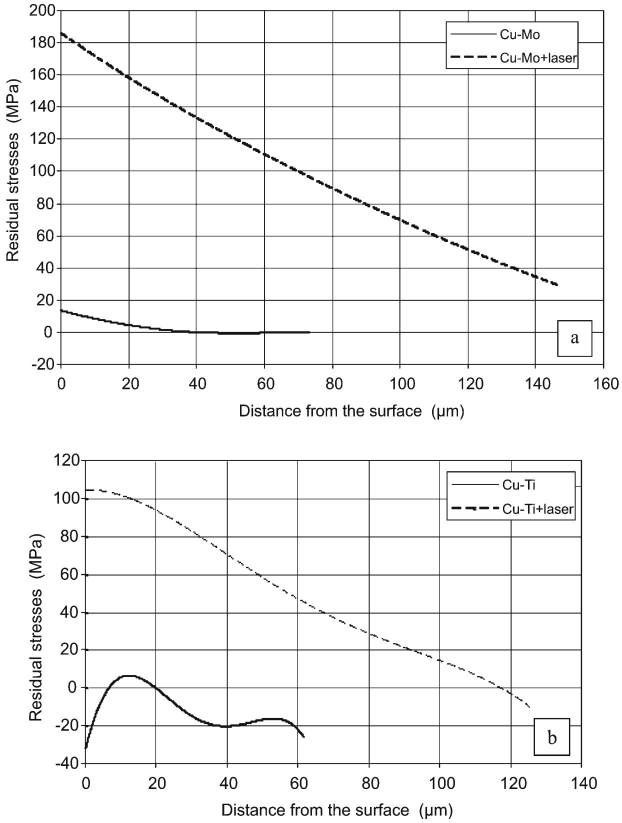

Fig. 8. Distribution of residual stress in the surface layer: a) the Cu-Mo coating, b) the Cu-Ti coating.

because they caused a decrease in the material fatigue strength. The occurrence of tensile stresses could be due to the melting of the coating surface, while the compressive stresses were a result of martensitic transition. Of importance was also the material used for the substrate.

The example responses of the residual stresses measured in the coating are shown in the diagrams in Figs. 8a,b. There is a fall in the stresses with depth. The stresses in the laser-treated Cu-Mo coating are tensile and they decrease to zero with depth. The residual stresses in the Cu-Ti coating subjected to laser radiation are different; they occur at a depth of about 118 µm; they are of compressive type and their maximum value is −10 MPa at a distance of 126 µm from the surface. The maximum tensile stresses in the laser-treated Cu-Mo and Cu-Ti coatings are different: +185 MPa and +104 MPa, respectively.

3.5. Adhesion test

A scratch test was conducted to measure the adhesion of the Cu-Mo and Cu-Ti coatings before and after laser treatment. A CSEM REVETEST scratch tester was used. The measurements were performed at a load increase rate of 103.2 N min^{-1}, a table feed rate of 9.77 mm min^{-1} and a scratch length of 9.5 mm.

A special indenter – the Rockwell diamond cone with a corner radius of 200 µm, was used to scratch the samples at a gradually increasing normal force (load). The information about the cracking or peeling of layers was obtained based on the measurements of the material resistance (tangential force) and the registration of acoustic emission signals. The lowest normal force causing a loss of adhesion of the coating to the substrate is called critical force and is assumed to be the measure of adhesion.

The critical force was determined based on the records of changes in the acoustic emission signals and the tangential force as well as on the results of observations with an optical microscope fitted in the REVETEST tester. The values of the critical force were established by comparing the scratches left by the indenter with the responses of acoustic emission signals. Table 2 shows the values of the critical force obtained from three measurements of a given sample, the force mean values and standard deviations.

Laser-treated coatings produced by electro-spark alloying are reported to possess adhesion higher than untreated coatings. The mean value of the critical force of the Cu-Mo coating calculated from three measurements was 3.91 N; after laser treatment, it increased to 5.28 N. The treatment caused a 26 % improvement in the adhesion of the Cu-Mo coating. For the Cu-Ti coating, the increase in the adhesion following laser radiation was 31 %. The higher adhesion of coatings subjected to laser treatment was probably due to their lower porosity related to higher sealing properties. Further details, however, will be established in the next stage of the research.

4. 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. Laser radiation causes an improvement in the functional properties of the two-layer electro-spark deposited Cu-Ti and Cu-Mo coatings, i.e. they exhibit higher microhardness and higher resistance to adhesion and corrosion.

3. The residual stresses in the electro-spark coatings are reported to be more or less the same before and after laser treatment. The stresses in the surface layer are of tensile type. With depth, they change to compressive. In laser-treated coatings, however, tensile stresses are found deeper.

4. 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 the laser radiation are the homogenization of the chemical composition, structure refinement and the healing of microcracks and pores.

5. The favourable 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.

6. In the next phase of the research, it is essential to determine the phase composition and porosity of the coatings before and after laser treatment.

7. It seems of significance to perform tribological tests for the electro-spark deposited coatings before and after modification with a laser beam.

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