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# FORMATION OF Cu-Mo ANTI-WEAR COATINGS AND THEIR TRIBOLOGICAL PROPERTIES BEFORE AND AFTER LASER TREATMENT

# FORMOWANIE I WŁAŚCIWOŚCI TRIBOLOGICZNE PRZECIWZUŻYCIOWYCH POWŁOK KOMPOZYTOWYCH Cu-Mo PRZED I PO OBRÓBCE LASEROWEJ

### Key words:

electro-spark deposition, laser treatment, coating, tribology

## Słowa kluczowe:

obróbka elektroiskrowa, obróbka laserowa, powłoka, tribologia

#### Summary

The paper is concered with determining the influence of the laser treatment process on the **exploitation** properties of electro spark coatings. The properties were assessed after laser treatment by analysising microstructure, measuring the microhardness, friction coefficient and corrosion resistance. The tests were carried out for Mo and Cu coatings (the anode) electro-spark deposited over the C45 steel substrate (the cathode)and

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molten with a laser beam. The coatings were deposited by means of an ELFA-541. The laser treatment was performed with an Nd:YAG, BLS 720 laser. The coatings, whether laser-treated or not, exhibit very good performance properties and high reliability, and this makes them suitable for use in sliding friction pairs.

# **INTRODUCTION**

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 electrospark deposition involve mass and energy transport accompanied by chemical, electrochemical and electrothermal reactions. Today, different electro-spark deposition techniques are used; they are suitable for coating formation and surface microgeometry formation [L. 1–5].

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

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

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 [L. 6-7].

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

## **EXPERIMENTAL**

The tests were conducted for Cu-Mo coatings produced by electro-spark deposition, which involved applying Cu and Mo 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. Molybdenum act as the reinforcing constituents. The coating materials, i.e. molybdenum (99.8% Mo) and copper (99.2% Cu) in the form of wire ( $\phi = 1$  mm) were purchased from BIBUS Metals Sp. z o.o. (certificate included).

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  $\mu$ F; pulse duration T<sub>i</sub> = 8  $\mu$ s; interpulse period T<sub>p</sub> = 32  $\mu$ s; 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  $f_1 = 50$  Hz.

#### **RESULTS AND DISCUSSION**

#### **Microstructure analysis**

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 show the microstructure of electro-spark deposited two-layer Cu-Mo coating. The layer thickness is approximately 8–10  $\mu$ m, and the range of the heat affected zone (HAZ) inside the (underlying) substrate material is about 10–15  $\mu$ m. In the photograph, 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-Mo coating shows that the distribution of elements is non-uniform; there are zones with greater concentrations of Cu, Mo 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-Mo coating (Fig. 1b). 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.



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

- liniowy pierwiastków (b) w powłoce Cu-Mo
- Fig. 2. Microstructure (a) and linear distribution of elements (b) in the Cu-Mo coating after laser treatment
- Rys. 1. Mikrostruktura (a) i rozkład Rys. 2. Mikrostruktura (a) i rozkład liniowy pierwiastków (b) w powłoce Cu-Mo po obróbce laserowej

radiation caused intensive convective flow of the liquid material in the pool and, in consequence, the homogenization of the chemical composition (**Fig. 2b**). It also led to the structure refinement and highly saturated phase crystallization (**Fig. 2a**) because of considerable gradients of temperature and high cooling rates. The technological surface layers, 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-Mo coating ranged 20–40  $\mu$ m. In the heat affected zone (HAZ), which was 20–50  $\mu$ m thick, there was an increase in the content of carbon (**Fig. 2b**).

# **Microhardness tests**

The material microhardness was assessed using the Vickers method and a Hanemann tester. The measurements were performed under a load of 40G. 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 electrospark deposited Cu-Mo coating before and after laser treatment are shown in Tables 1 and 2. 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<sub>0.04</sub>; the same value was reported for the substrate before the process. There was a considerable increase in microhardness after depositing the heterogeneous Cu-Mo coating. The microhardness of the Cu-Mo coating was approx. 587  $HV_{0.04}$  – a rise of 110%. The microhardness of the Cu-Mo coating in the heat affected zone (HAZ) after electro-spark treatment was 51% higher than that of the substrate material. Laser treatment had a favorable effect on the changes in the microhardness of the electro-spark deposited of the Cu-Mo coating. There was an increase of 161% in the microhardness of the Cu-Mo coating.

# Table 1. Results of the microhardness tests for the Cu-Mo coating before laser treatment

Tabela 1. Wyniki pomiarów mikrotwardości powłoki Cu-Mo przed obróbką laserową

Measured zones	Microhardness HV <sub>0,04</sub>			Mean value
	N			
	1	2	3	<b>I I V</b> 0,04
Coating	566	606	589	587
HAZ	428	437	401	422
Substrate	282	285	276	281

 Table 2. Results of the microhardness tests for the Cu-Mo coating after laser treatment

Measured zones	Microhardness HV <sub>0,04</sub>			Mean value
	N			
	1	2	3	I I V 0,04
Coating	714	742	734	730
HAZ	583	612	578	591
Substrate	289	274	280	281

Tabela 2. Wyniki pomiarów mikrotwardości powłoki Cu-Mo po obróbce laserowej

# **Tribological tests**

The friction coefficient of coatings was studied at the Laboratory of Tribology, Kielce University of Technology. The coefficient of friction for Cu-Mo coating before and after laser treatment was determined using a T-01M – pin on disc type tribological tester. The tester enables continuous measurement of the friction force at a set load. The pin of  $\phi 4 \times 20$  mm was made of medium-carbon steel with a hardness of 27 HRC.

The testing was performed at the following parameters:

- load Q = 10 N,
- rotational speed n = 382 rpm,
- test duration t = 500 s.

**Figure 3** shows friction coefficient in the function of time at a load of 10 N. This diagram illustrates the Cu-Mo coating before and after modification with a laser beam. Dry friction observed in the case of the coatings resulted in the transformation of the outer layer into a surface layer. This was mainly due to the sliding stresses and speed, and the interaction with the medium. The state stabilization of the antiwear surface layer was observed.

In **Fig. 3**, one can see stabilization of the friction coefficient after 80 sec., its value fluctuating at 0.16–0.18. In the case of a laser modified Cu-Mo coating, the friction coefficient stabilizes after 240 sec., and its value fluctuates at 0.35–0.37. The average friction coefficient of a Cu-Mo coating is lower than that of a laser-modified Cu-Mo coating (at the moment of stabilization).



**Fig. 3.** Relationship between friction coefficient and time Rys. 3. Zależność współczynnika tarcia od czasu

#### **Corrosion resistance tests**

The corrosion resistance of the Cu-Mo coating 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  $\pm 200$  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 ( $\pm 1^{\circ}$ C).

Material	Corrosion current density Ι <sub>κ</sub> [μΑ/cm²]	Corrosion potential Е <sub>кок</sub> [mV]
C45	112 ± 17.8%	-458
C45+laser	86.4 ± 16%	-522
Cu-Mo	42.9 ± 11.8%	-620
Cu-Mo+Laser	30.7 ± 2.6%	-629

 Table 3.
 Current density and corrosion potential of the materials tested

 Tabela 3.
 Wartości gestości pradu i potencjału korozyjnego badanych próbek

**Figure 4** shows example diagrams of the polarization curves of the surface layers. The characteristic electrochemical values of the materials under test are presented in **Table 3**. The electro-spark deposited coatings were reported to have similar corrosion resistance to that of the substrate material. 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. Resistance to wear and corrosion depends on the quality of coatings, particularly their sealing properties.



Fig. 4. Curves of the Cu-Mo coating polarization: a) before laser treatment, b) after laser treatment

Rys. 4. Krzywe polaryzacji powłoki Cu-Mo: a) przed obróbką laserową, b) po obróbce laserowej

The Cu-Mo coating was reported to have the highest corrosion resistance. The corrosion current density of the coating was  $42.9 \,\mu\text{A/cm}^2$ , while that of the C45 steel substrate was  $112 \,\mu\text{A/cm}^2$ . Applying the Cu-Mo coating improved the sample corrosion resistance by approx. 162%. 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 improved the surface smoothness and corrosion resistance; there was a decrease in the surface roughness, Ra, from 2.02  $\mu$ m to 1.75  $\mu$ m.

# CONCLUSIONS

- 1. A concentrated laser beam can effectively modify the state of the surface layer, i.e. the functional properties of electro-spark coatings.
- 2. 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.
- 3. The average value of the friction coefficient (at the moment of stabilization) obtained during the tribological tests for a Cu-Mo coating is approximately 54% lower than that obtained for the same coating after laser modification.
- 4. Laser treatment caused a 20% increase in the microhardness of the electrospark deposited Cu-Mo coatings.
- 5. Laser radiation causes an improvement in the functional properties of the two-layer electro-spark deposited Cu-Mo coating, i.e. they exhibit higher resistance to corrosion.
- 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.

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## Recenzent: Zbigniew GAWROŃSKI

#### Streszczenie

W pracy badano wpływ obróbki laserowej na właściwości powłok nanoszonych elektroiskrowo. Ocenę właściwości powłok po obróbce laserowej przeprowadzono na podstawie obserwacji mikrostruktury, pomiarów mikrotwardości i współczynnika tarcia oraz badań odporności korozyjnej. Badania przeprowadzono, wykorzystując Mo oraz Cu jako materiały powłokowe (anody) nakładane elektroiskrowo na próbki ze stali C45 (katody), a następnie przetapiane wiązką laserową. Do nanoszenia powłok elektroiskrowych użyto urządzenia produkcji bułgarskiej, model ELFA-541. Obróbkę laserową nałożonych powłok elektroiskrowych wykonano laserem Nd:YAG, model BLS 720. Powłoki tego typu zarówno przed, jak i po obróbce laserowej mają dobre własności i mogą znaleźć zastosowanie w ślizgowych węzłach tarcia.