

**CORROSION RESISTANCE OF ESD COATINGS BEFORE AND AFTER LASER PROCESSING**<sup>1</sup>Norbert RADEK, <sup>2</sup>Jacek PIETRASZEK, <sup>3</sup>Łukasz J. ORMAN<sup>1</sup>*Kielce University of Technology, Faculty of Mechatronics and Mechanical Engineering, Kielce, Poland, EU, [norrad@tu.kielce.pl](mailto:norrad@tu.kielce.pl)*<sup>2</sup>*Cracow University of Technology, Institute of Applied Informatics, Cracow, Poland, EU, [jacek.pietraszek@mech.pk.edu.pl](mailto:jacek.pietraszek@mech.pk.edu.pl)*<sup>3</sup>*Kielce University of Technology, Faculty of Environmental, Geomatic and Energy Engineering, Kielce, Poland, EU, [orman@tu.kielce.pl](mailto:orman@tu.kielce.pl)*<https://doi.org/10.37904/metal.2020.3575>**Abstract**

A number of modern surface processing methods use an energy flux. The examples include electro-spark deposition (ESD) and laser processing (LP). Electro-spark deposition is a cheap high-energy process. The method was first used in the USSR in the 1940s almost simultaneously with the destructive electrical discharge machining. The ESD technique was studied intensively in the 1960s. In the next decade, it was commonly applied to deposit hard-melting materials on selected metals and alloys, mainly steel. Polish scientists became interested in electro-spark alloying of coatings as early as in the 1980s. Electro-spark deposited coatings have some disadvantages but these can be easily eliminated. One of the methods is laser processing; a laser beam is used for surface polishing, surface geometry formation, surface sealing or for homogenizing the chemical composition of the deposited coatings. The corrosion resistance of C45 steel coated with WC-Cu electro-spark technique and the influence of the laser treatment process on the properties of the coatings were examined in a chloride environment. The coatings were deposited by means of an EIL-8A. The laser processing was performed with an Nd:YAG, BLS 720 system. The studies were conducted using WC-Cu electrodes produced by the powder metallurgy route. The potentiodynamic polarization technique was mainly used. Scanning electron microscope (SEM) was employed for the observation the surface of materials. The structure of coatings was dependent on the composition of electrospark electrodes. It is assumed that the use of laser-modified electro-spark deposited coatings will increase the applications of using relatively inexpensive materials in areas requiring special alloys, for example, sealing technology, precision products or surfaces in sliding contact.

**Keywords:** ESD coatings, laser processing, corrosion resistance, microstructure, surface topography**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.

A number of modern surface processing methods use an energy flux. The examples include electro-spark alloying (ESA) and laser beam machining (LBM).

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 to (a) to protect new elements or to (b) to recover the properties of worn elements. The electro-spark deposition coating is characterized by a non-etching structure. The surface layer is constituted in environment of local high temperature and high pressure. Electro-machining is characterized by [5]:

- shock wave pressure coming from electric spark is  $(2-7) \cdot 10^3$  GPa,
- temperature reaching  $(5-40) \cdot 10^3$  °C.

As electro-spark coatings are reported to be resistant to wear and corrosion, they can be applied to e.g. ship propeller components, casting moulds, fuel supply system components or exhaust system components.

Electro-spark deposited coatings have some disadvantages but these can be easily eliminated. One of the methods is laser beam machining; a laser beam is used for surface polishing, surface geometry formation, surface sealing or for homogenizing the chemical composition of the deposited coatings [6-8].

The work discusses the properties of electro-spark deposited WC-Cu coatings subjected to laser treatment. The properties were established basing on the results of a microstructure analysis, corrosion resistance tests and surface geometric structure measurements. In addition to similar issues (e.g. [9]), the results obtained may be of interest to other materials science researchers e.g. steel treatment [10], light alloys [11,12] or conductivity modifications [13]. It can also be inspiring to improve and develop theoretical methods, in the field of stress analysis in a modified surface layer [14] and also image analysis [15-17] of this layer.

## 2. MATERIALS AND TREATMENT PARAMETERS

The working electrode (a stationary) was made from C45 carbon steel. The elemental composition of the steel was as follows (wt.%): C: 0.42 – 0.50, Mn: 0.50 – 0.80, Si: 0.10 – 0.40, P: 0.04, S: 0.04.

An EIL-8A pulse spark generator was used to deposit the coatings on the steel surface. The operating parameters of the generator were determined experimentally: 0.7 A, 230 V and 150  $\mu$ F capacitors. Cylindrical electrodes, 5 mm in diameter and 10 mm in height were used. They were produced by means of the impulse-plasma sintering method in a graphite matrix of tungsten carbide (particle diameter  $\sim 0.2$   $\mu$ m) and metallic copper (particle diameter  $\sim 0.04$   $\mu$ m) nanopowders at a temperature of 950 °C, under a pressure of 40 MPa. The nanopowders were mixed in the following proportions: 75 % WC and 25% Cu, 50% WC and 50% Cu, 25% WC and 75% Cu. The following designations were given to the particular electrodes: WC25-Cu75, WC50-Cu50 and WC75-Cu25. 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.

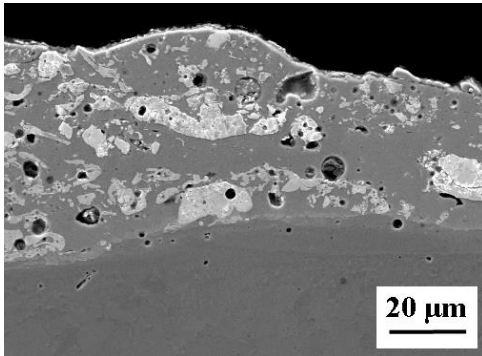
## 3. EXPERIMENTAL RESULTS AND DISCUSSIONS

### 3.1. Microstructure analysis

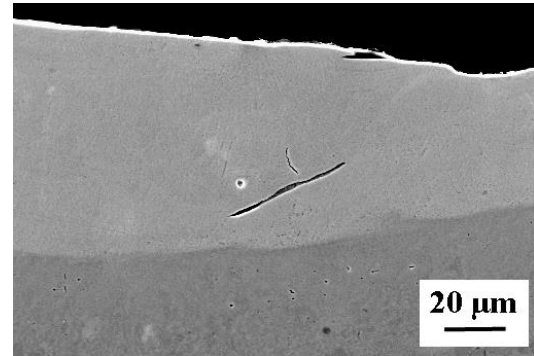
A microstructure analysis was conducted for WC-Cu coatings before and after laser treatment using a scanning electron microscope Joel JSM-5400.

**Figure 1** shows the microstructure of an ESD WC-Cu coating. It is clear that the thickness of the obtained layer varied from 36 to 60  $\mu$ m, whereas the heat affected zone (HAZ) ranged from 20 to 30  $\mu$ m into the substrate. **Figure 1** also reveals a clear boundary between the coating and the substrate and pores within the

coating. The ESD WC-Cu coatings were modified by the laser treatment, which caused changes in their composition. The laser treatment homogenizes the coating chemical composition, causes structure refinement, and crystallization of non-equilibrium phases due to the occurrence of temperature gradients and high cooling rates.



**Figure 1** WC50-Cu50 coating microstructure after electro-spark alloying



**Figure 2** Microstructure of the electro-spark alloying WC50-Cu50 coating after treatment with an Nd:YAG laser

The laser-modified outer layer does not possess microcracks or pores (**Figure 2**). There is no discontinuity of the coating-substrate boundary. The thickness of the laser-treated WC-Cu coatings ranges from 40 to 62  $\mu\text{m}$ . Moreover, the heat affected zone (HAZ) is in the range of 25 to 35  $\mu\text{m}$ , and the content of carbon in the zone is higher.

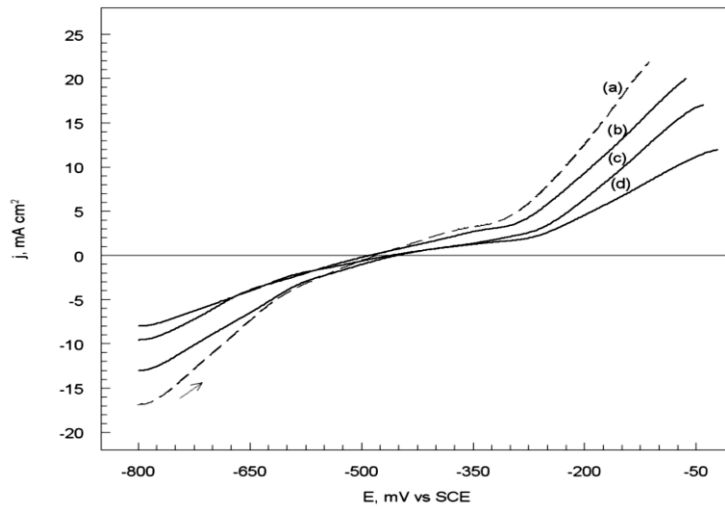
### 3.2. Corrosion resistance tests

Polarization measurements were made using a potentiostat/galvanostat PGSTAT 128N (AutoLab) equipment to investigate the influence of the composition of the coating (WC-Cu) on the electrochemical corrosion of C45 steel. The polarization curves were recorded in a 1 M  $\text{Cl}^-$  acid solution. The following reagents were used to make the solutions: FLUKA analytical grade sodium chloride (NaCl) and POCH analytical grade hydrochloric acid (HCl). Water, which was distilled three times, was used as a solvent. The corrosive environment (supporting electrolyte) was obtained by mixing the sodium chloride (0.8 M) and hydrochloric acid (0.2 M), so the concentration of  $\text{Cl}^-$  ions was 1 M and the pH was 1.5. Measurements were carried out under a potential range between -800 and -50 mV whereas the potential change rate was 1 mV  $\text{s}^{-1}$ . Polarization curves were used to designate the corrosion potential ( $E_{\text{corr}}$ ) and corrosion current density ( $j_{\text{corr}}$ ).

The polarization curves for C45 steel, coated by means of ESD using tungsten carbide (WC) and copper (Cu) mixed in various proportions are shown in **Figure 3**.

Polarization curves were used to determine the various parameters of steel corrosion, which have been summarized in **Table 1**. As the copper content in the nanopowder mixture used in the deposition of WC-Cu coatings onto the surface of steel increased, the corrosion potential shifted slightly (ca. 20 mV) towards positive values, while the corrosion current density decreased. Consequently, in the case of the WC25-Cu75 coating, the corrosion rate is approximately three times slower as compared to steel, which has not been coated with WC-Cu at all. An addition of copper to the nanopowder mixture clearly increases the corrosion resistance of steel. It seems that copper improves the tightness of the tungsten carbide layer, making it difficult for the aggressive chloride solution to contact the steel surface.

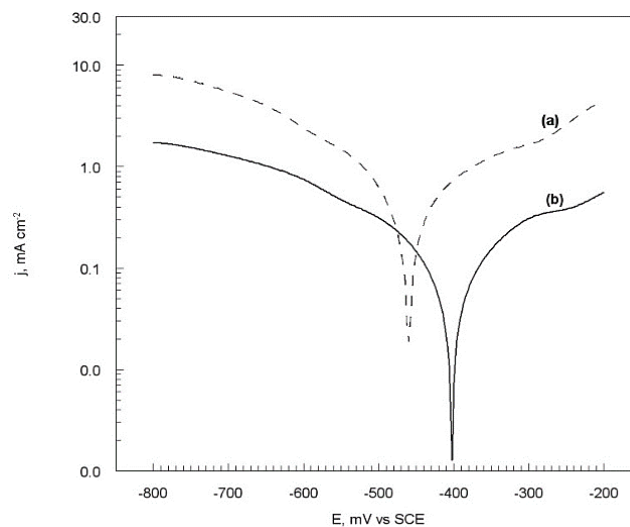
**Figure 4** shows the Tafel plots for the WC50-Cu50 coating on the C45 steel surface prior to (a) and after the laser treatment (b). Potentiodynamic polarization curves were used to determine selected corrosion parameters, which have been summarized in **Table 1**.



**Figure 3** Polarization curves for C45 steel. Solution containing 1 M Cl<sup>-</sup>. Electrode surface: (a) absence of coating, (b) WC75-Cu25, (c) WC50-Cu50, and (d) WC25-Cu75,  $dE/dt$  1 mV s<sup>-1</sup>

**Table 1** Corrosion parameters and corrosion rate of C45 steel in absence and presence of WC-Cu coating in a solution containing 1M Cl<sup>-</sup>

Material	$E_{corr}$ (mV)	$j_{corr}$ (mA·cm <sup>-2</sup> )	$k_{corr}$ (mm/year)
Absence	-480	1.10	12.8
WC75-Cu25	-487	0.80	9.3
WC50-Cu50	-451	0.53	6.1
WC25-Cu75	-459	0.40	4.6
WC75-Cu25+laser	-360	0.23	5.8
WC50-Cu50+laser	-402	0.17	3.7
WC25-Cu75+laser	-410	0.15	1.4



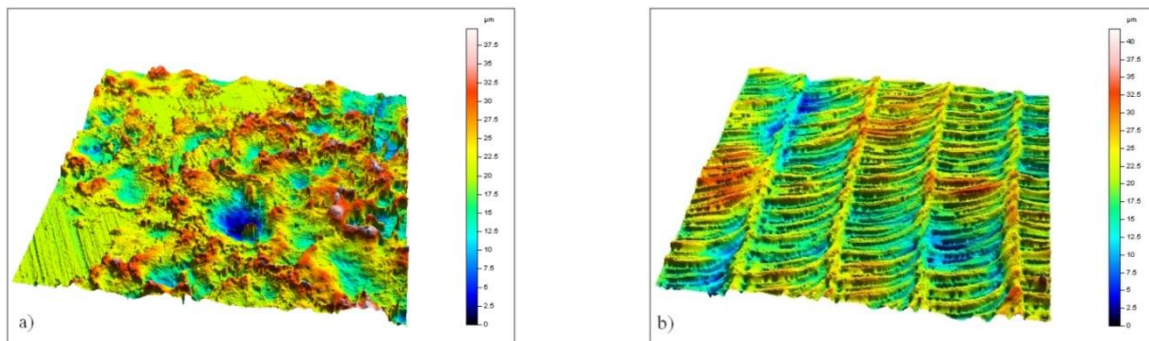
**Figure 4** Tafel plots for the C45 carbon steel in 1 M Cl<sup>-</sup>. The WC50-Cu50 coating: (a) before, (b) after laser treatment

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 by a factor of three compared to the untreated coating. It implies that the corrosion resistance of WC-Cu coatings on steel has been markedly improved by the laser treatment (**Table 1**). 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.

### 3.3. Measurements of the surface geometric structure

Surface geometric structure (SGS) of the WC-Cu coatings was measured at the Laboratory for Measurement of Geometric Quantities of the Kielce University of Technology using a TALYSURF CCI equipment. Three-dimensional surfaces and their analysis using the software TalyMap Platinum allowed to thoroughly know the geometric structure of the surface tested. **Figure 5** presents an example three-dimensional surface topography measurement of the WC50-Cu50 coatings after and before laser treatment.



**Figure 5** Specimen surface topography: a) before laser treatment, b) after laser treatment

A greater value of the mean arithmetic deviation of surface roughness  $S_a = 3.98 \mu\text{m}$ , 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 almost 5 % higher. Laser processing caused a slight decrease in the  $S_a = 3.80 \mu\text{m}$  parameter, which is very beneficial for surface quality.

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

## 4. CONCLUSIONS

Finally, it can be concluded that:

- A concentrated laser beam can be effective in modifying the state of the outer layer of electro-spark coatings and thus can modify their functional properties.
- Laser irradiation of coatings resulted in the healing of micro-cracks and pores.



- Parameters of surface geometric structure of electro-spark coatings have lower values when compared with SGS parameters of coatings after laser treatment.
- Laser radiation causes an improvement in the functional properties of the electro-spark deposited WC-Cu coating, i.e. they exhibit higher resistance to corrosion.
- Coatings of that type can be applied to sliding friction pairs and can operate as protective coatings.

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