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Influence of Laser Treatment on the Corrosive Resistance of WC-Cu Coating Produced by Electrospark Deposition

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The corrosion resistance of C45 carbon steel coated with WC-Cu (at different composition) electrospark deposition (ESD), and the influence of the laser treatment on the properties of the coatings were examined in acid chloride environment. The potentiodynamic polarization technique was mainly used. The surface topography was assessed using a scanning electron microscope (SEM). The following layer structures were observed: homogeneous in the case of Cu and heterogeneous in the case of WC-Cu. The structure of the coatings depends on the composition of the electrodes. Steel coated with a nanopowders mixture containing 25% WC and 75% Cu proved to be the most resistant to corrosion. The laser treatment causes the homogenization of the chemical composition, the structure refinement and the healing of microcracks and pores of the ESD coatings. The corrosion rate in case laser treatment of WC25-Cu75 coating is about three times slower comparing to coating without laser irradiation.

Keywords: A, C45 carbon steel; B, Electrospark deposition; A, WC-Cu coating; B, Laser treatment; C, Corrosion rate

1. INTRODUCTION

The corrosion of metallic surfaces in acidic solutions causes considerable costs. In order to reduce the corrosion of metals, several techniques have been applied [1].

Carbon steel is very widely used, mainly as a construction material in a wide range of industries. It owes its popularity to its low price and excellent mechanical properties [2]. The disadvantage of carbon steel is its high susceptibility to corrosion, causing its users a great deal of problems [3]. Steel deteriorates as a result of corrosion in the course of normal operation and when exposed directly to an aggressive atmospheric or aqueous environment. For this reason, scientists are constantly searching for effective and affordable ways to prevent corrosion. An effective way to protect metals against corrosion is the use of various kinds of metal coatings.

Since early 1990s the electrospark deposition (ESD) process has drawn increasing concerns as a promising surface treatment technique [4]. Electrospark deposition is a low-cost and effective method for improving the performance characteristics of metal parts. Metal coatings deposited on the metal substrates improve the corrosion resistance of the latter contributing to an improvement in the operating life of different metal parts. The deposition of a coating by means of ESD involves the use of spark discharge energy to carry the mass of the material being eroded from an carefully selected electrode (anode), which provides the coating material, to a negative electrode (the cathode), which constitutes a specially modified substrate. As the electrodes approach each other, electrical field intensity rises, which is accompanied by an electrical discharge, gas ionization in the fissure, formation of a plasma channel, anode erosion, light radiation, thermal radiation and evaporation of the melted metals, followed by the formation of a coating, diffusion and solidification. This method makes it possible to deposit ultra thin (from a few μm) and slightly thicker (to tens of μm) coatings made of any metal. The high temperature ($5 - 10\times10^3$ ^{0}C) and high pressure induced by the pressure shock wave from the electrical discharge, determine the shape of the top layer of the coating. The coating is bonded to the substrate by means of diffusion. A series of chemical and electrochemical reactions accompany ESD coating formation, which usually degrade the mechanical properties and microgeometry of the applied coatings [5-7]. Electrospark deposition treatment is usually used in the automotive, aerospace and shipbuilding industries.

Electrospark deposition have some disadvantages, which can be easily eliminated. One of the methods is the laser treatment. The laser beam is used for the surface polishing, surface geometry formation, surface sealing or for homogenizing the chemical composition of the coatings deposited [8]. During the laser treatment, a high cooling rate often leads to the solubility extension of the solute atoms, thus producing novel metastable microstructures on the metal surface.

The purpose of the research was to determine of inhibition effect of WC-Cu coatings on the C45 carbon steel surface. The coatings were deposited by the electrospark method. Moreover, the influence on the corrosive resistance of laser treatment of WC25-Cu75 coating was tested. An aggressive acidic environment of chlorides was used for testing the corrosion resistance of coatings.

2. EXPERIMENTAL

2.1. Solutions

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 (1 M) and hydrochloric acid (1 M), so the concentration of Cl^- ions was 1.2 M and the pH was 1.5.

2.2. Electrodes

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.

The coatings were produced by electrospark technique. Cylindrical electrodes, 5 mm in diameter and 10 mm in height were used to deposit the coatings WC-Cu on the steel surface of working electrode. They were produced by means of the impulse-plasma sintering method in a graphite matrix of tungsten carbide (particle diameter ~0,2 μm) and metallic copper (particle diameter ~0.04 μm) 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 WC25-Cu75, Figure 1.

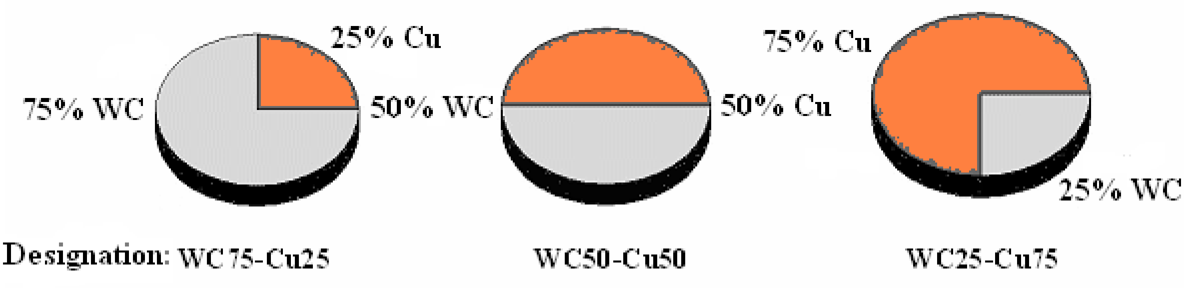

Figure 1. Composition of nanopowders mixture containing tungsten carbide and copper

An EIL-8A pulse spark generator was used to deposit the coatings on the steel surface. The maximum output power of the electrospark deposition welder was 4 KW, with output of voltage 250 V (50 Hz) continuously regulating, and eight-step capacitance (470 μF). The revolving electrode was held on the deposition gun that rotates round its own axis at the speed of 2400 circles/minute during the work time. Scheme of formation the layer on the surface of metal (electrode) is shown in Figure 2 [5]. The quality of electrospark deposition depends mainly on the shape, duration, and average value of current or pulse power. An average value of current is directly proportional to the number of generators operating in parallel. Figure 2a shows the SEM image of the top surface of the WC50-Cu50 coating on the C45 carbon steel surface. The splash appearance and spattering particles can be seen. The molten droplets formed on the electrode tip during the heating process. The droplets are accelerated by high current plasma, and impinge on the substrate surface, resulting in the splash at different directions. The SEM image of the top surface of the single-pulse deposition is illustrated in Figure 2b, which appears as one of the units of the coating. The countless single-pulse points overlap with each other and make up the coating on the surface of metal.

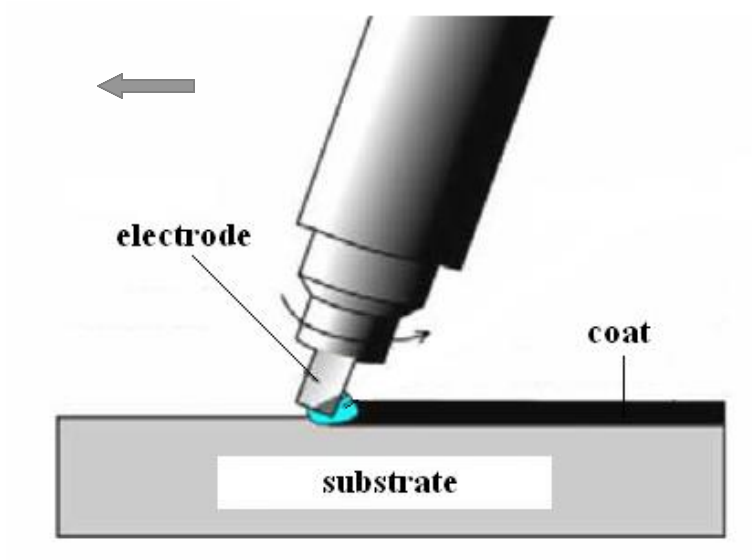

Figure 2. Scheme of formation the layer on the surface of working electrode

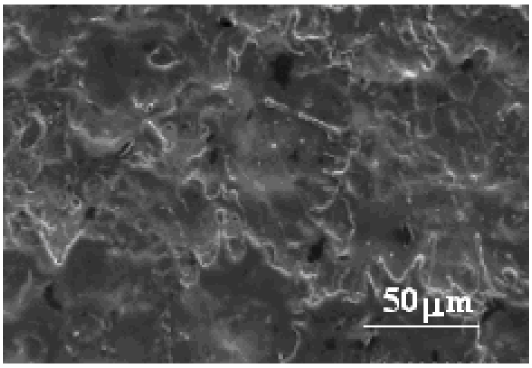

Figure 2a. SEM image of the top surface of WC50-Cu50 coating on the C45 carbon steel surface. Magnification 100×

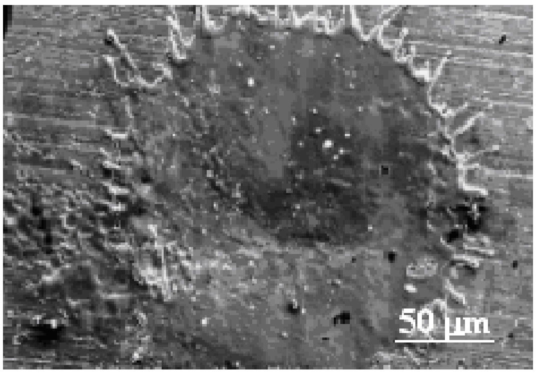

Figure 2b. SEM image of the top surface of WC50-Cu50 single-pulse deposition on the C45 carbon steel surface. Magnification 150×

The geometric surface area of the working electrode was 4.5 cm^2. Before every measurement, each electrode was carefully polished with emery paper 2500 grade. Then the electrode was rinsed with double distilled water and degreased in ethanol. The working electrode prepared in such a way was immediately immersed in the test solution.

A saturated calomel electrode (SCE) was used as the reference. It was connected with the solution using a Luggin capillary. The capillary tip was opposite to the end of working electrode about 3 mm from it.

The counter electrode (1 cm^2) was made from platinum foil (99.99% Pt).

2.3. Measuring instruments

All electrochemical measurements were made using a potentiostat/galvanostat PGSTAT 128N, AutoLab, Netherlands with NOVA 1.7 software the same firm.

The coatings WC-Cu were treated with an Nd:YAG laser (impulse mode) model BLS 720. Nitrogen as protective gas was applied. The samples with electrospark alloyed coatings were lased modified with the following parameters: laser spot diameter 0.7 mm, laser power was changed in range from 50 to 70 W, traverse speed 250 mm/min, pulse duration 0.4 ms, pulse repetition frequency 50 Hz, and laser beam shift jump 0.4 mm.

Surface topography was observed using a scanning electron microscope (SEM) Joel, type JSM-5400. The accelerating voltage was 20 kV.

An analysis of the phase composition of the WC-Cu coatings was carried out by means of the X-ray diffraction method using a Philips PW 1830 spectrometer, equipped with a copper anode tube powered with a voltage of 40 kV, and a current of 30 mA. During the measurement, the 2 Θ angle was changed in range 30 – 60^0, the scan rate was 0.05^0/3 seconds.

The microhardness values of WC-Cu coatings were determined by means of the Vickers hardness test using a Microtech MX3 microhardness tester set to a load of 0.4 N.

All measurements were carried out at a temperature of 25±0.5 ^{0}C, which were maintained using an air thermostat. The experiment was started after 30 min of immersion of the electrode in the testing solution, which was not mixed, and not deoxidized.

2.4. Potentiodynamic polarization curves

The potentiodynamic polarization curves were recorded in a 1.2 M Cl^- acid solution. Measurements were carried out under a potential range from -800 to -200 mV vs. SCE whereas the potential change rate was 1 mV s^{-1}. Potentiodynamic polarization curves were used to designate the corrosion potential (E_{corr}) and corrosion current density (j_{corr}). The corrosion rate was calculated using the following equation [9-11]:

$$k_{corr} = 3.268 \times \frac{j_{corr}\ M}{n\ \rho} \qquad (1)$$

where j_{corr} is the corrosion current density, M - molecular weight of iron, n - number of electrons exchanged, ρ - iron density.

3. RESULTS AND DISCUSION

3.1. Influence of coating type

Figure 3 shows the potentiodynamic polarization curves (as Tafel plots) for C45 carbon steel in a 1.2 M solution of chlorides. Curve (a) depicts the uncoated electrode, while curves (b) and (c) correspond to the electrodes with coatings of WC and Cu respectively.

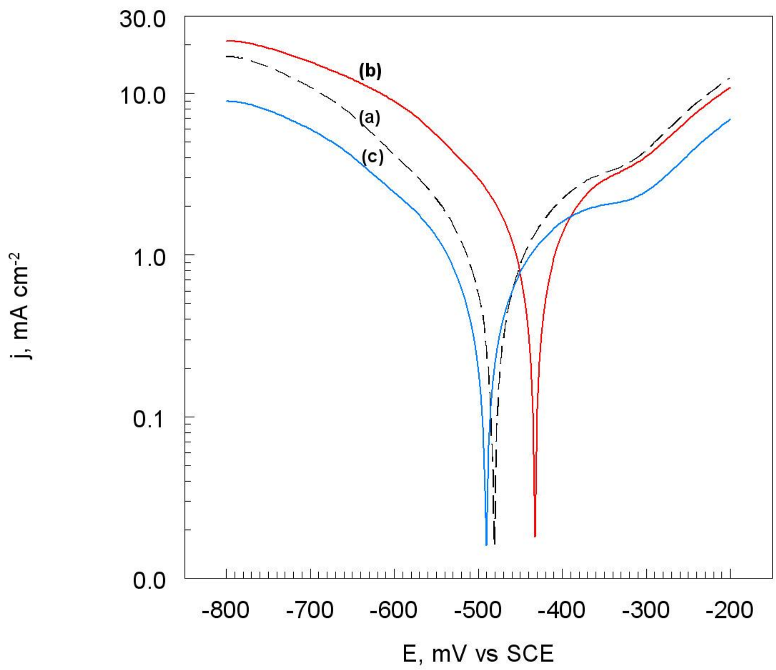

Figure 3. Tafel plots for C45 carbon steel. Solution containing 1.2 M Cl^-. Appearance surface of electrode: (a) absence of coating, (b) carbide coating (WC), (c) copper coating (Cu), dE/dt 1 mV s^{-1}

In an acidic environment of chlorides, the cathode branches correspond to the reduction reaction of hydrogen:

$$Fe + H^+ = (FeH^+)_{ads}, \quad (2)$$
$$(FeH^+)_{ads} + e^- = (FeH)_{ads}, \quad (3)$$
$$(FeH)_{ads} + H^+ + e^- = Fe + H_2, \quad (4)$$

whereas the anode process can be described as follows:

$$Fe + Cl^- = (FeCl^-)_{ads}, \quad (5)$$
$$(FeCl^-)_{ads} = (FeCl)_{ads} + e^-. \quad (6)$$

In the area of more positive potentials, the adsorbed intermediate is dissolved:

$$(FeCl)_{ads} = (FeCl^+) + e^-, \quad (7)$$
$$(FeCl^+) = Fe^{2+} + Cl^-. \quad (8)$$

The authors of work [12,13] proposed the similar mechanism corrosion of steel.

In the electrospark process of coating deposition using a tungsten carbide electrode, a layer was formed on the steel surface [4]:

$$W + C = WC \quad (9)$$
$$2\,W + C = W_2C. \quad (10)$$

The surface of C45 carbon steel was covered with a heterogeneous WC/W_2C coating which was held to the surface by metallic bonding. A small decrease in the anode current density (compared to the electrode without a coating, curve (a)) is observed on the polarisation curve (b), resulting from iron oxidation (reactions (5) - (8)). In conclusion, the WC/W_2C coating does not protect against oxidation steel surface. It is thus clear that numerous micro-cracks are present on the surface, through which the electrolyte easily reaches the surface of the metal.

If the electrode surface is ESD coated with a layer of copper, then a layer is formed as a result of metallic bonding between iron and copper:

$$m\,Fe + n\,Cu = Fe_mCu_n. \quad (11)$$

The layer of Fe_mCu_n as the intermetallic bond adheres well to surface of C45 carbon steel. The similar intermetallic connections of iron with of different metals were observed [14].

The short duration of the electrical pulse allows an extremely rapid solidification of the deposited material and results in an exceptionally fine-grained homogeneous coating that approaches an amorphous structure.

In this case, a clear reduction of anode and cathode current density occurs, as depicted by curve (c). The copper coating inhibits the hydrogen reduction process (reactions (2) - (4)) and iron oxidation (reactions (5) - (8)) to a much better extent. Furthermore, the inhibition of the steel corrosion process is also associated with the sealing of the copper coating due to the adsorption of the reaction product [9-10,15,16]:

$$Cu + Cl^- = CuCl_{ads} + e^-, \quad (12)$$

a further increase in the potential of the electrode causes $CuCl_{ads}$ to dissolve [17,18].

For C45 carbon steel corrosion rate constants were determined both in the presence and absence of the coatings (Equation (1), and the results have been presented in Table 1.

Table 1. Corrosion rate of C45 carbon steel in absence and presence of tungsten carbide or copper coating. Solution containing 1.2 M Cl^-

Coating	Absence	WC	Cu
k_{corr}, mm/year	12.8	12.2	8.7

The corrosion rate of steel coated with WC and Cu corrodes is only about 1.5 times slower in the case of copper than compared to the sample without the coating.

The WC coating does not protect the steel against corrosion. Copper coating clearly improves the resistance of C45 carbon steel against electrochemical corrosion.

3.2. Influence of coating composition

The potentiodynamic polarization curves for C45 carbon steel, coated by means of ESD using tungsten carbide (WC) and copper (Cu) mixed in various proportions (Figure 1) are shown in Figure 4 as Tafel plots.

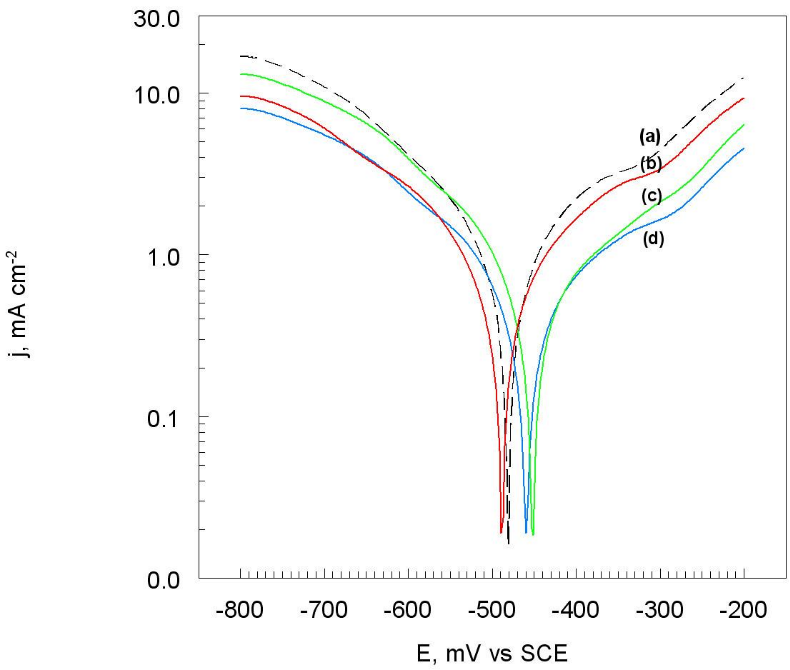

Figure 4. Tafel plots for C45 carbon steel. Solution containing 1.2 M Cl^-. Appearance surface of electrode: (a) absence of coating, (b) WC75-Cu25, (c) WC50-Cu50, and (d) WC25-Cu75 of coatings, dE/dt 1 mV s^{-1}

Potentiodynamic polarization curves were used to determine the various parameters of steel corrosion, which have been summarized in Table 2. As the copper content in the nanopowders mixture used in the deposition of WC-Cu coatings onto the surface of steel increased, the corrosion potential shifted slightly (about 20 mV) towards positive values, while the corrosion current density decreased. Alloying process between molten electrode and substrate fully performed during deposition process. Due to physical and chemical processing in the interelectrode gap initial structure of an electrode material changed and modified surface layer. Consequently, in the case of WC25-Cu75 coating, the corrosion rate is approx three times slower as compared to steel, which has not been coated with WC-Cu at all.

Table 2. Chosen corrosion parameters and corrosion rate of C45 carbon steel in absence and presence of WC-Cu coatings. Solution containing 1.2 M Cl^-

Coating	E_{corr} mV	j_{corr} mA cm^{-2}	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

An addition of copper to the nanopowders 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.

However, the WC92-Co8 coating produced by electrospark deposition was studied by Wang and Ruijum et al. [4,5]. The WC92-Co8 as the electrode material has been deposited on titanium alloy. Titanium alloys are now the most attractive metallic materials mainly for biomedical applications. However, their poor resistance to wear and corrosive wear limit their applying [19,20]. The WC92-Co8 coating effectively improves the surface performance of the substrate. The metallurgical bond between the coating and substrate was established, which is accredited to the intermixing of the WC92-Co8 and Ti alloy at localized melt pool and the interface. The phases, such as TiC, W_2C and W were stable in the coating. Unfortunately, authors [4,5] did not examine the corrosive resistance of WC92-Co8 coating.

The average microhardness of the substrate material, namely that of C45 carbon steel was 278 HV0.04 while following ESD using the WC75-Cu25 electrode, the average microhardness of the coating reached a value 692 HV0.04. After using the WC25-Cu75 electrode, there was a clear decrease of average microhardness to a level of 398 HV0.04. It is worth noting that the high content of copper in a WC-Cu coating leads to a reduction of coating hardness, but at the same time it increases its flexibility, which is essential in improving the strength of some machine parts.

However, the best anticorrosive properties possessed of WC25-Cu75 coat on the C45 carbon steel in aggressive chloride environment. Therefore, next experiments will concern to WC25-Cu75 coat on the investigate carbon steel surface

3.3. Influence of laser treatment

The microstructure of electrospark coating is much finer and less micro-segregation (Fig. 2a). The substrates are irradiated often under a protective gas argon or nitrogen a surface modified layer with ultra-fine structure and good surface properties will be produced under proper laser parameters [21-23]. If irradiated in air atmosphere, many different oxides will be formed on surface of material. The electrospark of WC-Cu coating outer surface layer were modified via Nd:YAG focused laser beam, which has significant impact on the coating surface properties.

Figure 5 shows the potentiodynamic polarization curves (as Tafel plots) for WC25-Cu75 coating on the C45 carbon steel surface: (a) without, (b) with laser treatment.

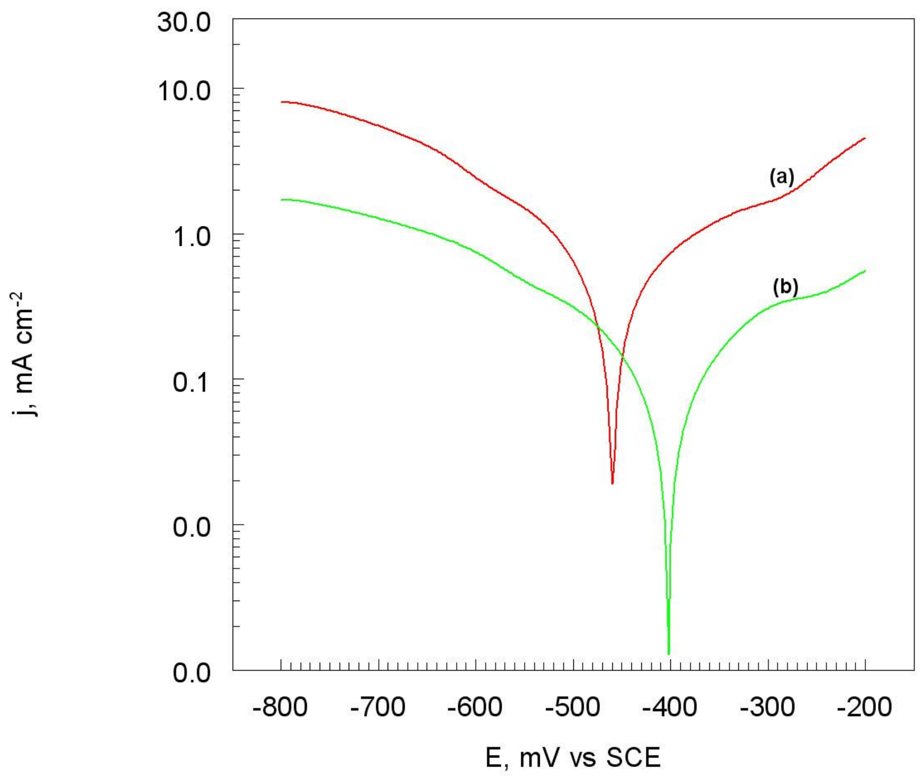

Figure 5. Tafel plots for C45 carbon steel. Solution containing 1.2 M Cl^-. The WC25-Cu75 coating of electrode: (a) without, (b) with laser treatment, dE/dt 1 mV s^{-1}

Table 3. Chosen corrosion parameters and corrosion rate of C45 carbon steel in presence of WC25-Cu75 coating without and with laser treatment. Solution containing 1.2 M Cl^-

Laser treatment	E_{corr} mV	j_{corr} mA cm^{-2}	k_{corr} mm/year
Without	-459	0.40	4.6
With	-402	0.15	1.7

Potentiodynamic polarization curves (Fig. 5) were used to determine the chosen parameters of steel corrosion, which have been summarized in Table 3. It can be seen that in case of coating after laser treatment corrosion potential shift (about 50 mV) to more positive values, and corrosion current density is greatly decreased (about three times) in relation to coating without laser treatment. It suggests that the corrosion resistance of WC25-Cu75 on C45 carbon steel surface has been clearly improved after laser treatment. This can be attributed mainly to the improvement of the WC-Cu conditions after laser irradiation. In result of laser treatment different oxides and fine grains form on the surface of coating, which leads to different corrosion characteristics. However, the compact oxide layer can serve as a more effective barrier to protect of coating on the carbon steel against the corrosion attacks in aggressive environment of chlorides.

Another parameter, the corrosion rate (Equation (1)) can also be used to compare the corrosion resistance of WC25-Cu75 coating carbon steel without and with laser treatment (Fig. 5). The corrosion rate in mm/year values are presented in Table 3. The corrosion rate in case laser treatment of WC25-Cu75 coating is approximately three times slower comparing to coating without laser treatment.

The microstructure using a scanning electron microscope ware conduced for WC-Cu coatings without and with laser treatment. The thickness the obtained layers was 36 - 60 μm. Moreover, the heat affected zone ranged approximately from 20 to 30 μm into the studied carbon steel (substrate).

In Figure 6a selected view of the surface microstructure of an electrospark allowed of WC25-Cu75 coating is illustrated. There it is visible clearly boundary between the coating and the substrate, where pores within microcracks are observed. The electrospark alloyed of WC25-Cu75 coating was modified via laser treatment which caused their composition changes, Figure 6b. The laser irradiation leads to the homogenization of the coating, chemical composition, structure refinement, and crystallization of supersaturated phases due to the occurrence of temperature gradients and high cooling rate. However, the laser-modified outer layer does not possess microcracks or pores. Moreover, the laser treatment causes that does not change the thickness of coating, and enlarged imperceptibly range of the heat affected zone of the substrate.

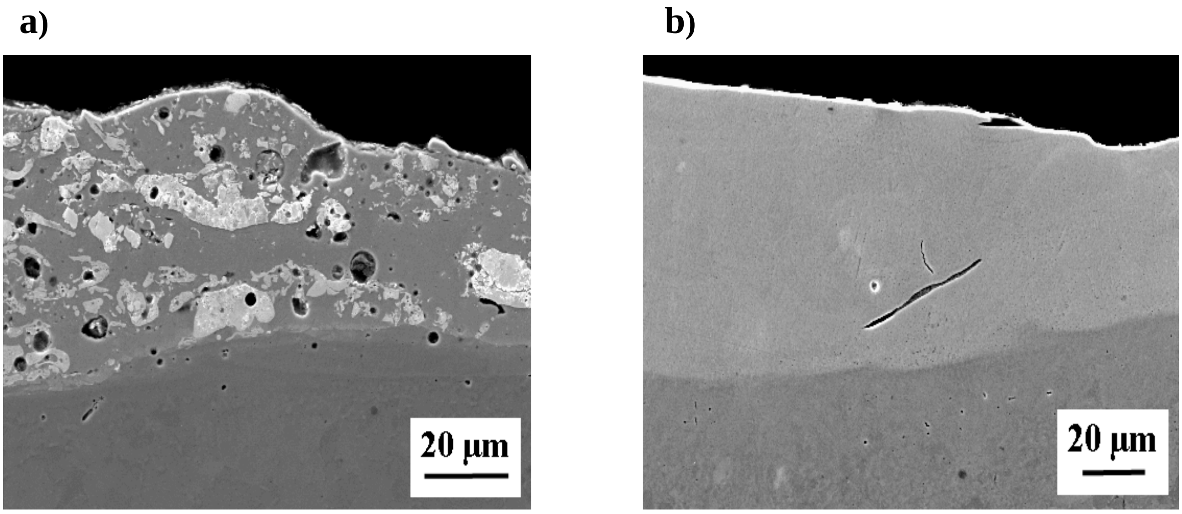

Figure 6. Microstructure of WC25-Cu75 coating: a) without, b) with laser treatment. Magnification 800×

The X-ray diffraction spectrum for WC25-Cu75 coating on the C45 carbon steel surface is shown in Figure 7.

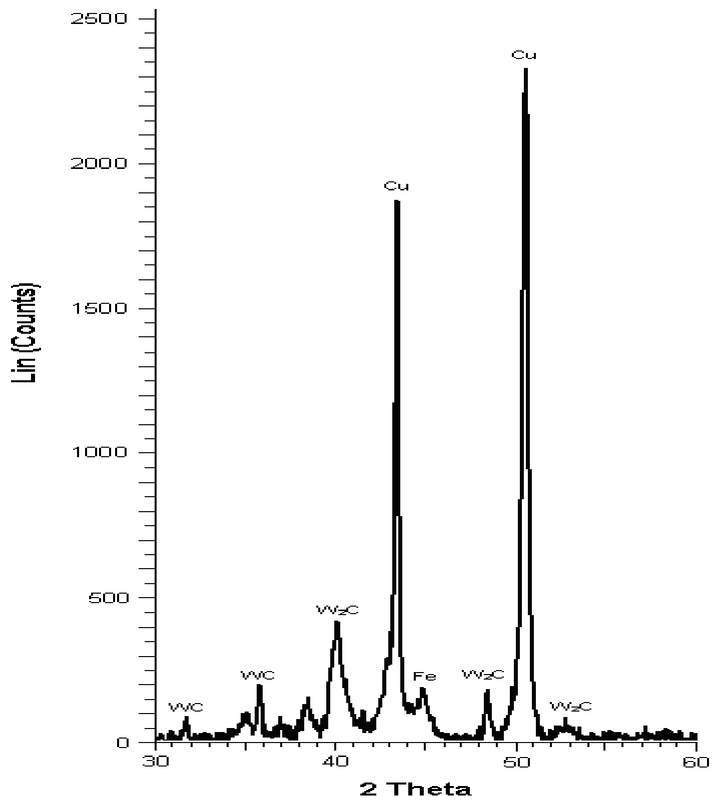

Figure 7. X-ray diffraction spectrum for WC25-Cu75 coating on the C45 carbon steel surface

This confirms the presumption that the top layer of the coating is mainly composed of Cu and WC_2 and small admixture of WC and iron.

However, after laser treatment the average microhardness of WC25-Cu75 coating was 362 HV0.04. The laser irradiation leads to the decrease (about 9%) of average microhardness of coating in comparison to sample without laser treatment. In the other hand, the decrease the hardness of coat influences on improvement of flexibility properties of sample.

The higher adhesion of coatings subjected after laser treatment was probably due to their lower porosity related to higher sealing properties of layer on the metal surface.

4. CONCLUSION

On the basis of the study, it was found that:

1. The surface of C45 carbon steel can be modified by means of electrospark deposition using of WC-Cu electrodes composed of various proportions of its two main constituents.
2. A coating made of tungsten carbide is heterogeneous and provides the steel with poor protection against oxidation in an aggressive environment of chlorides. A copper layer effectively inhibits the corrosion process of carbon steel.
3. The corrosion resistance of the surface of C45 carbon steel improves as the copper content in the mixture of WC and Cu nanopowders increases.
4. The microstructure analysis revealed that the coating thickness was 36-60 μm, whereas the heat affected zone ranged about 20-30 μm. The coatings possessed microcracks and pores.
5. The laser treatment causes the homogenization of the chemical composition, the structure refinement and the healing of microcracks and pores of the ESD coatings.
6. The corrosion rate in case laser treatment of WC25-Cu75 coating is approximately three times slower comparing to coating without laser irradiation.
7. The top layer of WC25-Cu75 coating is not homogeneous and consists of copper, WC_2, tungsten carbide and iron.
8. The laser irradiation leads to the decrease (about 9%) of average microhardness of WC25-Cu75 coating in comparison to sample without laser treatment.

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