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Effect of the Composition and the Thermal Treatment on Corrosion Resistance of WC-Co-Al₂O₃ Ceramic Coatings

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The effect of the composition and thermal treatment of WC-Co-Al₂O₃ coatings (without and with of Al₂O₃) on the C45 mild steel surface on the corrosion resistance were examined. The aggressive acidic chloride (1.2 M Cl⁻) environment was used for the testing of corrosion resistance of the materials. The ceramic coatings (CC) on the steel surfaces were deposited by a electrospark (ESD) technique. The content of aluminum oxide (Al₂O₃) was varied between 5 and 15 wt.%. However, thermal treatment of the tested coatings were done for temperature which was changed between 25 and 1200 $^{\circ}$ C. The anticorrosion properties of the coatings without and after heat treatment were mainly investigated by electrochemical methods. Moreover, the scanning electron microscope (SEM) was employed for the observation the surface of materials. It was found that the structure of coatings were depended from the composition of electrospark electrodes. However, the corrosion rate of the substrate decreases about six times after applying the WC-5Co-15Al₂O₃ coating. Unfortunately, after thermal treatment at 800 $^{\circ}$ C the WC-Co and WC-Co-Al₂O₃ ceramic coatings lose their anti-corrosion properties.

Keywords: Mild steel; WC-Co-Al₂O₃ coating; Ceramic coating; Electrospark deposition; Corrosion rate

1. INTRODUCTION

Advanced coatings are in requirement in many industrial sectors to enhance the surface characteristics of structural elements or to functionalize a surface. In order to reduce the corrosion of metals, several types of coatings and various application techniques have been used [1,2]. Ceramic coatings (CC) as WC-Co-Al₂O₃ play a significant role in the cases where exceptional wear and erosion resistance are required [3-6]. The carbide phase imparts the coating high hardness and wear resistance, while the metal binder phase. Therefore, the CC are comparable with that of hard chrome coating,

suggesting their possibility of replacement for toxic hard chrome coating. Ceramic coatings produced by the electrospark deposition (ESD) technique are used for a broad range of industrial applications. As a result of ESD treatment the materials obtain greater hardness, abrasion resistance or improving the mechanical properties of the surface. Moreover, electrospark deposition is 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 the improvement of the operating life of different metal parts [7-9]. The deposition of coating by means of ESD involves the use of spark discharge energy to carry the mass of the material being eroded from the carefully selected electrode (anode), which provides the coating material, to negative electrode (the cathode) which constitutes a specially modified substrate. The quality of electrospark deposition mainly depends on the shape, the duration and the average value of current or pulse power. A series of chemical and electrochemical reactions accompany ESD coating formation, which usually degrades mechanical properties and the microgeometry of applied coatings [10]. In the case ceramic coatings the addition of Al₂O₃ in WC-Co coating enhanced its microhardness and wear properties. The microhardness gradually increased with the increase in Al_2O_3 content as Al_2O_3 is harder than WC [11]. Moreover, the WC-12Co coating is widely adopted as an alternative to hard chrome coating, particularly for the landing gears of an aircraft, petrochemical industry and marine applications, due to environmental reasons, low production costs and equal or better material properties [12,13]. On the other hand, the limitation of WC coating is that it usually suffers from decomposition or decarburization at high temperatures [14,15]. The decarburization process induced microstructure evolution of WC coatings during the production and thermal processing is still lacking. Even though intense research effort has been devoted to understanding the decarburization mechanism of WC coating at high temperature.

The aim of the current investigations concerned to the effect of the composition and thermal treatment on corrosion resistance of WC-Co coatings (without and with an addition of Al_2O_3) on the C45 mild steel surface. The coatings were produced by the electrospark deposition (ESD) technique. The aggressive acidic chloride (1.2 M Cl⁻) environment was used for the testing of corrosion resistance of the materials. For the study mainly of the electrochemical method was applied.

2. EXPERIMENTAL

2.1. Electrospark deposition

The WC-Co or WC-Co- Al_2O_3 coatings were produced by electrospark deposition. The scheme of the layer formation on the surface of metal is shown in Figure 1.



Figure 1. Scheme of the layer formation on the surface of metal: 1 – substrate (cathode), 2 – cylindrical electrospark electrode (anode), 3 – coating, 4 – stream of plasma, 5 – zone of diffusion, 6 – protective zone

The cylindrical electrospark electrodes, 5 mm in diameter and 10 mm in height were used to deposit the coatings on the C45 mild steel surface. They were produced by the impulse-plasma sintering method in a graphite matrix of tungsten carbide (particle diameter ~0,2 μ m, OMG (USA)), metallic cobalt (particle diameter ~0.4 μ m, Umicore (Belgium)) and aluminum oxide (particle diameter ~0.15 μ m, SNI (USA)) nanopowders at the temperature of 1100 °C, under the pressure of 50 MPa. The nanopowders: WC, Co and Al₂O₃ were mixed in the appropriate proportions, which are listed in Table 1.

Electrospark electrode symbol	Mixture nanopowders wt.%	Elemental electrospark electrode/coating composition
EA	80% WC, 20% Co	WC-20Co
EB	80% WC, 15% Co, 5% Al ₂ O ₃	WC-15Co-5Al ₂ O ₃
EC	80% WC, 10% Co, 10% Al ₂ O ₃	WC-10Co-10Al ₂ O ₃
ED	80% WC, 5% Co, 15% Al ₂ O ₃	WC-5Co-15Al ₂ O ₃

Table 1. Mixture nanopowders and elemental composition of electrospark electrodes/coatings

Image of the electrospark electrodes of WC-20Co and WC-15Co- $5Al_2O_3$ respectively are shown in Figure 2.



Figure 2. Image of the electrospark electrodes: a) WC-20Co (EA), and b) WC-15Co-5Al₂O₃ (EB). Magnification $10\times$

An EIL-8A pulse spark generator was used to deposit coatings on the steel surface. The maximum output power of the electrospark deposition welder was 4 kW, with the voltage output of 250 V (50 Hz) continuously regulated and eight-step capacitance (470 μ F). The revolving electrospark electrode was held on the deposition gun that rotates round its own axis at the speed of 240 circles/minute during the work time.

2.2. Solutions

The following reagents were used to make solutions: FLUKA analytical grade sodium chloride (NaCl) and POCH analytical grade hydrochloric acid (HCl). Distilled and deionized water was used for the preparation of solutions. The corrosive environment (supporting electrolyte) was obtained by mixing sodium chloride (1 M) and hydrochloric acid (1 M), so the concentration of Cl⁻ ions was 1.2 M and pH 1.5.

2.3. Electrodes

Working electrodes (stationary) were made from C45 mild steel without and with of WC-Co or WC-Co-Al₂O₃ coatings. The elemental compositions of the steel were 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 geometric surface area of the working electrode (rectangle) which was in contact with the electrolyte was 2.5 cm^2 . Before every measurement each electrode was rinsed with double distilled water and degreased in ethanol. The working electrode prepared in such way was immediately immersed in the test solution.

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

A platinum foil (99.99% Pt) as an auxiliary electrode was used.

2.4. Potentiodynamic polarization curves

All electrochemical measurements were made using a potentiostat/galvanostat PGSTAT 128N, AutoLab, Netherlands with the NOVA 1.7 software of the same firm. The corrosion tests were performed with a conventional three-electrode cell. Potentiodynamic polarization curves were recorded in 1.2 M Cl⁻ acid solution. Measurements were carried out in the potential range from -800 to 100 mV vs. SCE. The potential scan rate in all experiments was 1 mV s⁻¹. Potentiodynamic polarization curves were used to designate the corrosion potential (E_{corr}), corrosion current density (j_{corr}) and the slope of the segments of the Tafel polarizing curves (i.e. $-b_c$ and b_a) which were used to calculate the polarization resistance of the electrode. Moreover, the corrosion rate of specimens were calculated using the following equation:

$$k_{corr} = 3.268 \times \frac{j_{corr} M}{n \rho} \tag{1}$$

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

All measurements were carried out at the temperature of 25 ± 0.5 ^oC which was maintained by an air thermostat of home production. The experiment was started 30 min. after immersing the electrode in the testing solution which was neither mixed and nor deoxidized.

Each test was repeated three times to verify the reproducibility of data and the average values were reported.

2.5. Thermogravimetric measurements

Thermogravimetric measurements were carried out on an NETZSCH STA Jupiter 449 thermogravimetric analyzer (TGA). A specimens were prepared in the furnace of a thermobalance under controlled temperature to obtain the corresponding thermogravimetry (TG). The TG baselines were corrected by subtraction of predetermined baselines which are determined under identical conditions except for the absence of a specimens. The specimens in the furnace were heated up from 25 to 1200 °C with the heating rate of 5 °C min⁻¹. In order to eliminate the effects caused by the mass and heat transfer limitations, small quantities of specimens were put into a Al₂O₃ crucible for each run under non-isothermal conditions. In addition, the oxidizing atmosphere inside the furnace of a thermogravimetric analyzer during temperature – programmed measurements was provided by means of a continuous air flow of 70 cm³ min⁻¹. The geometric surface area of the specimen was 4.5 cm². Before every measurement each specimen was rinsed with double distilled water, degreased with ethanol, and was immediately immersed in the furnace of a thermobalance. The oxidation rate of materials at the high temperature can be estimated by the increase in the scale thickness (X_{scale}) with time or as change mass of materials versus exposition time:

$$k_{ox} = \frac{\Delta m}{A t}$$
(2)

where Δm is the change mass of specimen, A - surface area and t - exposition time. The oxidation rate of material was expressed as: mg cm⁻² h⁻¹.

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2.6. Additional measuring instruments

Surface topography of specimen was observed using a scanning electron microscope (SEM) Joel, type JSM-5400. The accelerating voltage was 20 kV. Figure 3 shows the SEM image of the top surface of C45 mild steel after mechanical treatment and WC-10Co-10Al₂O₃ coating on the steel surface. A similar surface was obtained for the remaining specimens of WC-Co-Al₂O₃ coatings.



Figure 3. SEM image of the top surface: a) C45 mild steel after mechanical treatment, and b) WC-10Co-10Al₂O₃ coating on the steel surface

The scratches visible on the steel surface are the result of mechanical treatment (Fig. 3a)). In this case the surface of the substrate was cleaned by sand blasting treatment. The splash appearance, micro-cracks and spattering particles can be seen (Fig. 3b)). 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 in different directions. Moreover, the elemental composition of the all coatings is very similar to the initial composition of the electrode used (Table 1).

An analysis of the phase composition of WC-Co or WC-Co-Al₂O₃ coating was carried out by means of the X-ray diffraction method (XRD) 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, with CuK α radiation of

wavelength $\lambda = 1.54$ Å. During the measurement the 2 Θ angle was changed in the range of $20 - 80^{\circ}$ and the scanning velocity of $0.05^{\circ}/3$ seconds.

Microhardness values of the studied specimens were determined by the Vickers (HV) method using a Microtech MX3 tester under the load of 0.4 N.

3. RESULTS and DISCUSSION

3.1. Production mechanism of electrospark coating

The electrospark of coating on the steel surface was formed according to [16]: $W + C \rightarrow WC$ (3) and: $2W + C \rightarrow W_2C.$ (4)

The C45 mild steel surface was covered with a heterogeneous of WC/W₂C coating which was held to the surface by metallic bonding. In conclusion of WC/W₂C coating does not protect against the oxidation of C45 mild steel surface, because numerous micro-cracks appear on the surface of coatings (Fig. 3). Moreover, an additional layer is formed on the specimen surface as a result of metallic bonding between iron and cobalt:

 $m Fe + n Co \rightarrow Fe_m Co_n.$ (5)

The layer of Fe_mCo_n as an intermetallic bond adheres well to the C45 mild steel surface. The similar intermetallic connections of iron with different metals were observed by Deevi and Sikka [17]. Moreover, in the case of Al_2O_3 the short duration of the electrical pulse leads to the extremely rapid solidification of deposited materials and results in an exceptionally fine-grained homogeneous of WC-Co-Al_2O_3 coatings that approaches the amorphous structure.

3.2. X-ray spectra

Figure 4 shows the X-ray diffractogram (XRD) pattern of as-received WC, Co, Al₂O₃ powders and WC-Co or WC-Co-Al₂O₃ electrospark coatings respectively.

The diffraction peaks observed for powders in Figures 4A and 4B clearly indicate the phases corresponding to WC, Co and Al₂O₃, whereas in the WC-20Co or WC-5Co-15Al₂O₃ coatings W₂C phases were also observed. The W₂C phase shows strong peak intensity, suggest slightly enhanced decarburization of WC coating. Decarburization of WC dissolved in the liquid cobalt was caused by the oxidation of C to CO or CO₂ with the precipitation of W₂C on the surface of WC crystals [18]. Moreover, in the case of WC-5Co-15Al₂O₃ coating (Fig. 4B) in addition a phase of Al₂O₃ was appeared.



Figure 4. XRD spectra of WC, Co, Al₂O₃ powders and: A - WC-20Co, B - WC-5Co-15Al₂O₃ coatings on C45 mild steel surface. The numbers were marked: 1 - WC, 2 - W₂C, 3 - Co, 4 - Al₂O₃

3.3. Cross - section of electrospark coating

The Figure 5 shows the cross-section of WC-Co and WC-Co-Al₂O₃ electrospark coatings on the C45 mild steel surface which were observed by a scanning electron microscope.

The average thickness of the coatings was determined using image analysis performed across the cross - section. It was appeared that the coatings are having an almost equal thickness about 100 μ m. The cross – section of WC-20Co coating is characterized by uneven structure, numerous craters and cracks are visible. (Fig. 5 a).



Figure 5. Cross – section of coatings on C45 mild steel surface: A, a) WC-20Co, B, b) WC-15Co-5Al₂O₃, C ,c) WC-10Co-10Al₂O₃, D, d) WC-5Co-15Al₂O₃



Figure 6. Element distribution (along the black line) face map of WC-Co-Al₂O₃ on C45 mild steel substrate: a) WC-5Co-15Al₂O₃, b) W, c) C, d) Co, e) Al

On the other hand, the WC-Co coatings with addition of Al_2O_3 appear to have stable structures, low porosity and are macrocrack free (Fig. 5 b) – d)) because of higher Al_2O_3 content which covers most of the surface. Therefore, aluminum oxide modifies the structure of WC-Co coatings.

The elements distribution of the face map of WC-5Co-15Al₂O₃ coating on the C45 mild steel surface (along the depth, as indicated by the black line) were shown in Figure 6. The homogeneous

distribution of elements can be observed indicating that the alloying process of the element was fully performed between the base and the substrate. In addition of Co and Al_2O_3 transfer to the substrate so easily that it is difficult to recognize the interface between the substrate and the coating according to both elements face distribution map.

3.4. Microhardness of the materials

The microhardness values of the materials were listed in Table 2. The average microhardness of the materials were analyzed using the Vickers (HV) method.

Materials	Average microhardness HV0.4		
C45	278 ± 11		
WC-20Co	794 ± 26		
WC-15Co-5Al ₂ O ₃	883 ± 54		
WC-10Co-10Al ₂ O ₃	938 ± 37		
WC-5Co-15Al ₂ O ₃	1042 ± 41		

 Table 2. Average microhardness for the materials

The microhardness HV were measured at fifteen points of the materials tested. It turned out that the average microhardness of the C45 mild steel was 278 HV0.4. If the surface of C45 steel was covered with WC-20Co coating then microhardness increased more than three times (794 HV0.4). If the WC-Co coatings were enriched with aluminum oxide, the average microhardness of the materials systematically increased (Table 2). However, average microhardness for the WC-5Co-15Al₂O₃ coating was about 38% higher compared to the microhardness of the substrate.

3.6. Potentiodynamic polarization curves

The generation of polarization curves continues to be important in aqueous corrosion research. The time consuming potentiostatic method has been largely replaced by the potentiodynamic approach where the potential of the corroding metal is automatically varied with time. Moreover, the current need to maintain the metal at each applied potential is ascertained and the potential/current data is plotted to give the experimental polarization curve. Figure 7 shows a typical example of potentiodynamic polarization curves for the C45 mild steel without and with WC-Co or WC-Co-Al₂O₃ ceramic coatings in 1.2 M solution of chlorides. Figure 7, curve (a) depicts the uncoated of C45 mild

steel electrode, while curves (b) - (e) correspond to the electrodes with the WC-Co or WC-Co- Al_2O_3 coatings, respectively.



Figure 7. Potentiodynamic polarization curves for C45 mild steel: (a) without and with: (b) WC-20Co, (c) WC-15Co-5Al₂O₃, (d) WC-10Co-10Al₂O₃, and (e) WC-5Co-15Al₂O₃ coatings. Solution contained 1.2 M Cl⁻, d*E*/d*t* 1mV s⁻¹ at 25 ⁰C

For the C45 mild steel in the acidic chloride environment the cathode of branch correspond to the reduction reaction of hydrogen. When the potential of the electrode was changed in the anodic direction iron oxidation was observed (Fig. 7, curve (a)). Moreover, the adsorption layer as $(FeClOH)_{ads}$ on the electrode surface was appeared and the electrode surface was coated with a porous iron oxide layer (Fe₂O₃). The mechanism of mild steel corrosion in the acidic chloride environment has been discussed many times in detail [19-21].

Inhibition of corrosion of the C45 mild steel surface with the WC-Co coating involves sealing of WC-20Co coating through the cobalt layer as a product of reaction:

$$Co + Cl^{-} \rightarrow (CoCl)_{ads} + e^{-}.$$
(6)

Hovewer, for the more positive potentials of the working electrode (Fig. 7, curve (b)) follows dissolving of (CoCl)_{ads} layer:

$$(\text{CoCl})_{\text{ads}} \rightarrow \text{Co}^+ + \text{Cl}^-.$$
 (7)

Potentiodynamic polarization curves for the WC-Co-Al₂O₃ ceramic coatings are presented in Fig. 7, curves (c) – (e). The cathodic and anodic current density decreases as the Al₂O₃ content on the WC-Co coatings increases. Probably, in the acidic chloride environments a simple chemical reaction occurs:

$$Al_2O_3 + 4 H^+ + 2 Cl^- \rightarrow 2 [Al(OH)Cl_2]_{ads} + H_2O.$$
(8)

The $[Al(OH)Cl_2]_{ads}$ layer additionally protects of the C45 mild steel surface against corrosion in the aggressive chloride environment.

On the other hand, of potentiodynamic polarization curves (Fig. 7) were used to determine various parameters of metal corrosion and polarization resistance of the electrodes, which were summarized in Table 3.

Table 3. Corrosion parameters and polarization resistance for the C45 mild steel in the absence and with presence of WC-Co or WC-Co-Al₂O₃ coatings in 1.2 M Cl⁻ at 25 ⁰C

	E _{corr}	j _{corr}	-b _c	b _a	R _p
Coating	mV mA cm ⁻²		mV dec ⁻¹		Ω cm ²
Absence	-440	1.50	175	231	30
WC-20Co	-427	1.12	190	275	41
WC-15Co-5Al ₂ O ₃	-424	0.71	185	270	69
WC-10Co-10Al ₂ O ₃	-421	0.41	180	265	122
WC-5Co-15Al ₂ O ₃	-416	0.24	175	265	169

In the case of WC-Co or WC-Co-Al₂O₃ ceramic coatings the corrosion potential shifted slightly towards positive values. The corrosion current density decreased due to the increase in Al_2O_3 content in the mixture of the nanopowders (Table 1). In addition, the slope of the anodic and cathodic

segments of the potentiodynamic polarization curves has not changed. Thus, the increase in Al_2O_3 content in the tested coatings did not change the mechanism of corrosion process for the substrate. Moreover, an increase of the polarization resistance values for the WC-Co and WC-Co-Al_2O_3 coatings means that Al_2O_3 addition to the WC-Co coating (Table 3) significantly reduces the exchange of the mass and electric charge between the electrode and the electrolyte solutions.

3.7. Corrosion rate

The potentiodynamic polarization technique is a powerful tool for the monitoring corrosion rate of metal [7-9]. The corrosion rates (Eq. (1)) were determined for the C45 mild steel in the absence and with presence of WC-Co or WC-Co-Al₂O₃ ceramic coatings, which are presented in Table 4.

Table 4. Corrosion rate for the C45 mild steel in the absence and with presence of WC-Co or WC-Co-Al₂O₃ coatings in 1.2 M Cl⁻ at 25 0 C

Coating	Absence	WC-20Co	WC-15Co- 5Al ₂ O ₃	WC-10Co- 10Al ₂ O ₃	WC-5Co- 15Al ₂ O ₃
k _{corr} , mm y ⁻¹	17.38	12.98	8.23	4.75	2.78

The value of the corrosion rate for the C45 mild steel was 17.38 mm y⁻¹ and for the substrate with WC-5Co-15Al₂O₃ coating was 2.78 mm y⁻¹ (Table 4). These results revealed that with increasing of Al₂O₃ content the corrosion rate for the tested coatings significantly decreased (about six times) in the relation to the mild steel without coating (Table 4). Therefore, the WC-Co-Al₂O₃ coatings effectively protects the C45 mild steel surface against electrochemical corrosion process in acid chloride solution. The high content of Al₂O₃ (15%) in the electrospark nanopowders mixture (ED) Table 1 clearly improves the anti-corrosion properties of WC-Co coating. This is obvious that the Al₂O₃ improves the tight of WC-Co layer making difficult contact of the substrate surface with the aggressive environment [7,8].

3.8. Thermogravimetric measurements

Thermogravimetric measurements in the air atmosphere were carried out in the range temperature from 25 to 1200 0 C. The clear increase of mass specimens were observed after crossing the so-called the critical temperature of conversion. The critical temperature of conversion for the C45 mild steel, WC-Co and WC-Co-Al₂O₃ coatings are listed in Table 5.

Materials	Critical temperature conversion ⁰ C		
C45	610		
WC-20Co	615		
WC-15Co-5Al₂O₃	620		
WC-10Co-10Al ₂ O ₃	625		
WC-5Co-15Al ₂ O ₃	630		

Table 5. Critical temperature of conversion for the C45 mild steel, WC-Co and WC-Co-Al₂O₃coatings

It was found that the critical temperature of conversion tested materials increases with increasing content of aluminum oxide in the coatings. Therefore, the further thermogravimetric measurements were carried out for the temperatures higher than critical temperature of conversion for the tested materials. However, the change mass of C45 mild steel, WC-Co and WC-Co-Al₂O₃ ceramic coatings in referring to the time of exposition at 800 0 C are presented in Figure 8.

The significant increase in the mass of the tested materials were observed after eight hours of exposition in the air atmosphere at 800 0 C. The largest increase in mass (about 46.39 mg cm⁻²) was noted for the C45 mild steel and the smallest (about 27.89 mg cm⁻²) for the WC-5Co-15Al₂O₃ ceramic coating (Fig. 8). The oxidation mechanism of steel in the air atmosphere and the high temperature can be considered as electrochemical process, which we discussed in detail in the earlier article [22]. It turned out that a multi-layer oxide: Fe₂O₃ / Fe₃O₄ / FeO was formed on the steel surface in the ratio: 1/4/95%. Moreover, for the WC-Co and WC-Co-Al₂O₃ coatings the surface was coated with cobalt oxide:

$$2 \operatorname{Co} + \operatorname{O}_2 \to 2 \operatorname{CoO}, \tag{9}$$

which additionally completes the composition of the oxide layer on the surface of the tested coatings. Probably, as a result of oxidation of cobalt the anti-corrosion properties of WC-Co-Al₂O₃ coatings were getting worse. On the other hand, at 800 $^{\circ}$ C the other coating ingredients i.e. WC and Al₂O₃ do not take part in the oxidation reaction in the atmosphere of hot air.



Figure 8. Thermogravimetry curves at 800 0 C for: (a) C45 mild steel, (b) WC-20Co, (c) WC-15Co-5Al₂O₃, (d) WC-10Co-10Al₂O₃, and (e) WC-5Co-15Al₂O₃. Heating rate of 5 0 C min $^{-1}$

3.9. Oxidation rate

The results of thermogravimetric measurements for the C45 mild steel in the absence and with presence of WC-Co and WC-Co-Al₂O₃ ceramic coatings in the air atmosphere at 800 0 C were used to calculate the oxidation rate (Eq. (2)) of the tested materials. The calculation results are summarized in Table 6.

Table 6.	Oxidation rate	in the air a	tmosphere of	f tested materials	at 800 °C
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Coating	Absence	WC-20Co	WC-15Co- 5Al ₂ O ₃	WC-10Co- 10Al ₂ O ₃	WC-5Co- 15Al ₂ O ₃
k _{ox} , mg cm ⁻² h ⁻¹	0.74	0.69	0.51	0.47	0.44

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It was found that along with the increase in the proportion of aluminum oxide in the coating the oxidation rate of the tested materials significantly decreases. However, in the case of WC-Co-Al₂O₃ coating which contains of 15% Al₂O₃ the oxidation rate decreases slightly (only 1.6 times) compared to the C45 mild steel without coating (Table 6). Moreover, along with the increase in the cobalt content in the coatings the oxidation rate increases. Thus, cobalt only acts as a substance that glues the components of the coating.

3.10. Surface image



Figure 9. Top surface of C45 mild steel with the coatings: a) without, b) WC-20Co, c) WC-15Co-5Al₂O₃, d) WC-10Co-10Al₂O₃, and e) WC-5Co-15Al₂O₃ after exposition for fourteen hours in the atmosphere of air at 800 ⁰C

Figure 9 shows the images of the top surface of C45 mild steel with the WC-20Co, WC-15Co-5Al₂O₃, WC-10Co-10Al₂O₃ and WC-5Co-15Al₂O₃ coatings after exposition for fourteen hours in the atmosphere of air at 800 ⁰C. Fig. 9a) shows of the top surface of C45 mild steel. It can be observed that the surface of mild steel was partially damaged and the surface was covered with a porous multilayer of oxides as: Fe_2O_3 / Fe_3O_4 / FeO. However, the oxide layer adheres well to the surface of the substrate. In the case of WC-20Co coating (Fig. 9b)) the destruction of the surface is clearly visible as a result of hot air action on it. The cobalt, which connected the coating components under these conditions was oxidized according to the reaction (9). Therefore, the surface of WC-20Co coating partially covered with dark spots in the form of cobalt oxide. It should be assumed that the anticorrosion properties of WC-20Co coating have deteriorated significantly. The WC-20Co coating has been enriched by adding aluminum oxide to it. Figures 9c) - 9e) relate to the WC-Co coatings for which the aluminum oxide content has been varied between 5 and 15%. The surface of the observed coatings shows cavities, pores and numerous cracks that appeared as a result of thermal treatment of materials at a temperature of 800 ⁰C. It should be supposed that the diffusion of iron cations towards the oxide layer breaks the structure of WC-Co-Al₂O₃ layer on the C45 substrate. Therefore, the addition of Al₂O₃ to the WC-20Co coating does not improve of anti-corrosive properties of WC-Co coatings under high temperature conditions. The problem will be discussed later in this article.

3.11. Potentiodynamic polarization curves for the materials after heat treatment at 800 ^{0}C



Figure 10. Potentiodynamic polarization curves for C45 mild steel: (a) without and with: (b) WC-20Co, (c) WC-15Co-5Al₂O₃, (d) WC-10Co-10Al₂O₃, and (e) WC-5Co-15Al₂O₃ coatings after heat treatment at 800 ^oC. Solution contained 1.2 M Cl⁻, d*E*/d*t* 1mV s⁻¹

Figure 10 shows of potentiodynamic polarization curves for the C45 mild steel without and with WC-Co or WC-Co-Al₂O₃ ceramic coatings after heat treatment at 800 0 C in 1.2 M solution of chlorides. Figure 10, curve (a) depicts the uncoated of C45 mild steel electrode, while curves (b) - (e) correspond to the electrodes with the WC-Co or WC-Co-Al₂O₃ coatings, respectively.

It was found that compared to the substrate (i.e. C45 mild steel) the cathodic and anodic current densities decrease slightly for the WC-Co and WC-Co-Al₂O₃ coatings. The corrosion parameters for the C45 mild steel in the absence and with presence of WC-Co or WC-Co-Al₂O₃ ceramic coatings are listed in Table 7. For the WC-Co or WC-Co-Al₂O₃ ceramic coatings the corrosion potential shifted slightly towards negative values. Moreover, the corrosion current density for the WC-5Co-15Al₂O₃ slightly decreases by about of 0.35 mA cm⁻² compared to the corrosion current density for the substrate (Table 7). In the absence of heat treatment the difference in the corrosion current density was around of 1.26 mA cm⁻² (Table 3). This means that as a result of thermal treatment at 800 0 C the tested coatings have significantly lost their anti-corrosive properties. On the other hand, the slope of the anodic and cathodic segments of the potentiodynamic polarization curves has not changed, it means that did not change the mechanism of corrosion process [8] despite thermal treatment of the tested materials.

Table 7. Corrosion parameters and polarization resistance for the C45 mild steel in the absence and with presence of WC-Co or WC-Co-Al₂O₃ coatings in 1.2 M Cl⁻ after heat treatment at 800 ⁰C

Coating	E _{corr}	j _{corr}	-b _c	b _a	R _p
	mv	mA cm [–]	mV	dec -	$\Omega \text{ cm}^-$
Absence	-359	1.20	110	110	20
WC-20Co	-411	1.20	108	108	27
WC-15Co-5Al ₂ O ₃	-406	1.10	123	135	25
WC-10Co-10Al ₂ O ₃	-414	1.00	120	130	27
WC-5Co-15Al ₂ O ₃	-416	0.85	114	128	31

Moreover, slight increase in the value of the polarization resistance for the WC-Co and WC-Co-Al₂O₃ ceramic coatings (Table 7) means that as a result of heat treatment the surface of the materials was destroyed and the exchange of the mass and electric charge between the electrode and the electrolyte solutions is not difficult.

3.12. Corrosion rate for the materials after heat treatment at 800 ^{0}C

The corrosion rate (Eq. (1)) were determined for the tested materials, which are presented in Table 8.

Table 8. Corrosion rate for the C45 mild steel in the absence and with presence of WC-Co or WC-Co-Al₂O₃ coatings in 1.2 M Cl⁻ after heat treatment at 800 0 C

Coating	Absence	WC-20Co	WC-15Co- 5Al ₂ O ₃	WC-10Co- 10Al ₂ O ₃	WC-5Co- 15Al ₂ O ₃
k _{corr} , mm y ⁻¹	24.33	23.76	23.18	23.18	23.18

The corrosion rate values for the C45 mild steel in the absence and with presence of WC-Co or WC-Co-Al₂O₃ coatings after heat treatment at 800 0 C are comparable. Therefore, as a result of heat treatment the WC-Co and WC-Co-Al₂O₃ ceramic coatings lost their anti-corrosion properties in the acidic chloride environment.

4. CONCLUSIONS

On the basis of the studies were found that:

1. The surface of C45 mild steel was modified by electrospark deposition (ESD) using of WC-Co or WC-Co-Al₂O₃ electrospark electrodes. The coatings are having an almost equal thickness about 100 μ m.

2. The aluminum oxide modifies the structure of WC-Co coatings. However, the average microhardness (HV) of the materials increases as the aluminum oxide content in the coating increases.

3. Along with the increase in the content of aluminum oxide in coatings the corrosion rate of the tested materials in the acidic chloride environment is systematically decreasing.

4. The high content of Al_2O_3 in the electrospark nanopowders mixture clearly improves the anti-corrosion properties of WC-Co coatings.

5. The oxidation mechanism of C45 mild steel in the air atmosphere and the high temperature can be considered as electrochemical process. However, along with the increase in the cobalt content in the coatings the oxidation rate increases.

6. After heat treatment at 800 0 C the WC-Co and WC-Co-Al₂O₃ ceramic coatings lost their anti-corrosion properties in the acidic chloride environment.

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