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Structural and tribological properties of wear resistant coatings obtained by electrospark deposition

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Abstract. In the present work, a new type of wear-resistant coatings obtained on steels by non-contact Electrical Spark Deposition (ESD), using a rotating electrode has been studied. Multicomponent electrodes for ESD containing WC-Co, Ni-Cr-B-Si semi-self-fluxing alloys and additives of superhard and refractory compounds of B_4C and TiB_2 have been obtained by the methods of mechanochemistry and powder metallurgy. The phase composition, microhardness and structural peculiarities of the coatings have been studied using methods of XRD, optical microscopy and SEM. The influence of the electrode composition and parameters of the deposition process on the structure, roughness, thickness, and abrasion wear of coatings have been studied. Tribological properties and wear resistance characteristics of coatings have also been examined. Coatings obtained using examined electrodes show higher friction and abrasion wear resistance than that obtained by conventionally used materials.

1. Introduction

The method of Electro Spark Deposition (ESD) is a progressive and dynamically developing direction of modern tribo technologies that meets modern requirements due to its unique set of advantages over the existing methods; high adhesion to the substrate, minor heating of the parts and lack of deformations, simplicity of the technology and equipment, low energy consumption, environmental safety. Selection of the composition of the electrode material is decisive for the complex of tribological and mechanical properties of coatings and for their service life. Traditional electrode materials for ESD are metals and their alloys - to increase the adhesion, the uniformity and the thickness of coatings [1,2,3], as well as carbide composites based mainly of tungsten [4,5] and titanium compounds [6,7] - to increase the hardness of the surface layers. Recently there has been a trend to used as electrodes composites based on non-metallic high melting super hard compounds such as B_4C, AlN, Al_2O_3 etc. [8,9,10] but its high brittleness limits their use.

In this connection, the aim of this work is to investigate and create suitable compositions for layering electrodes based on carbides, hard alloys, metals and additives from superhard and self-fluxing materials with which to obtain ESD coatings with improved wear resistance and triboefficiency.

The issue of improving adhesion of deposits and their wear resistance in the present work is solves by using of new composite materials with bonding components forming the unlimited solutions in the iron (Co, Ni, Cr). For maximally preserve the beneficial properties of the individual components of the coating material into the composition of the electrode material is introducing self-fluxing additives (B, Si, C,). The simultaneous introduction of the B_4C and the less fragile and high rigid components titanium diboride - TiB_2 and tungsten carbide - WC can reduces the brittles of B_4C, securing the necessary performance characteristics of the surface layer.

2. Materials and methods

The method of contactless Local Electro-Spark Deposition (LESD) [11] have been used to obtain layers on carbon steel with 0.45%C - (45) (ISO 683-1:2018) with hardness 160-180HB, and of 210Cr12 steel (ISO 4957:2018) heat treated to a hardness of HRC 59–61 and polished to a roughness Ra=0.63µm are used for substrate.

Depositing process has been performed on machine type "Elfa 541"[12] with single pulse energy up to 0.06 J. During the process, the substrate is moved with a controlled rate of axes X and Y. The high stability of the plasma spark discharges and the coating process is provided by an automatic regulation of the interelectrode distance.

During the experiments the following parameters of the regime for LESD have been used: current: 12.8÷32.0 A; voltage: 90 V; capacity: 0.22÷5.00 µF; impulse duration: 5, 8, 12, 20 µs; impulse fill factor: 0.1, 0.2 (impulse frequency - 5÷40 kHz); single impulse energy: 0.005÷0.06J; coating speed 0.5÷1.0 mm/s; number of passages of the electrode: 1÷4; rotation speed of the electrode 1500 rpm. Based on the literature analysis WC added Ni- and Co- based bonding electrode materials marked as NW and KW, respectively have been used (table 1).

Table 1. Chemical composition of the bonding metal mixtures

Designation/Element (%)	C	Si	Cr	Fe	B	Ni	Co	∑	WC
NW	0.6	2.9	12	3.9	3.6	balance	-	55	45
KW	1.5	1.5	23	0.5	1.5	30	42	45	55

The presence of self-fluxing additives (B, Si, C) and elements like Ni, Cr, Co forming unlimited solid solutions with Fe ensures obtaining of high-quality layers [8,10,13]. Different amounts of a hard alloy (WC-8%Co) and refractory and superhard B containing materials (TiB_2 and B_4C) have been added to the electrode materials designed as NW and KW to form composite materials with designations and compositions shown in table 2.

Table 2. Compositions and abbreviations of electrode materials

Abbrev./Comp.(%)	NW	KW	WC-8%Co	TiB_2	B_4C
NWW15T20	65	-	15	20	-
NWW15B10T20	55	-	15	20	10
NWW10T10B10	70	-	10	10	10
KWB10T20	-	70	-	20	10
KWB10T10	-	80	-	10	10

The electrodes have been produced by powder metallurgy methods including grinding, mixing, pressing and vacuum sintering at 1400 ˚C, and thereafter electrically discharge cutting with form and dimensions suitable for LESD. For comparison, a carbide electrodes with a composition of 2.8% (Ta, Nb) C + 9% CO + WC and indications WK9 [7] was used.

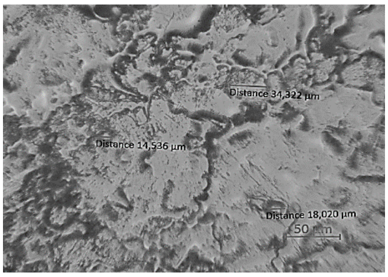
The surface roughness (Ra), and thickness (δ) of the resulting coatings were measured by using a Profilometer AR-132B and Leptoskop 2021 Fe (Germany). Density, uniformity, and morphology of the coatings have been monitored by a VT-300 digital microscope. The microstructure and microhardness of the coatings have been studied by optical microscopy metallographic microscope Neophot 22 (Germany) under indentation load of 5 and 10 g. The phase identification has been performed using X-ray diffractometer Bruker D8 Advance operating with Cu radiation tube. SEM methods (Bruker) have been used for structural investigations of coatings and detection the elemental distribution. The tribological properties and wear resistance of the coatings have been investigated by comparative tests of friction with tribotester type Thumb-disk under dry surface friction with hard-fixed abrasive particles. The fooling experimental conditions are used: Normal load – 5N, Nominal contact area - 2.25 cm^2 , Speed of rotation-212 min^{-1}, The friction path of the center of the contact site- 42.68 m, Abrasive surface - Corund P 320.

3. Results and discussion

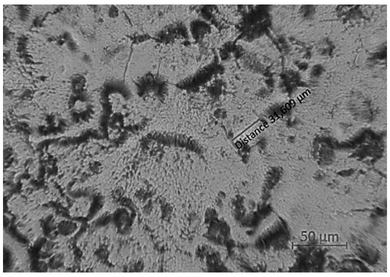
3.1. Characterization of coatings

The obtained coatings have improved geometrical characteristics - higher density, uniformity, low porosity, acceptable repeatability, and lower roughness, which in most cases do not require further processing. Figure 1 shows the morphology of typical coatings from both cobalt and nickel based electrode materials. It can be seen that the surface of the coatings is mainly formed by a melt. The pictures show that the coatings have small in size structural components, with no visible cracks and pores. The morphology of coatings both cobalt and nickel-based electrodes onto the two steels is similar. Separated protuberances resulting from the fragile destruction of electrodes, whose quantity at the coatings from "NW" electrodes is bigger, can be seen. This indicates that the anode materials are eroded in both solid and liquid phases.

The minimal and maximal values of the thickness (δ), surface roughness (Ra), and microhardness (HV) of coatings, obtained from the used electrodes at different parameters of the LESD are shown in table 3. The higher amount of bonding metal in the compositions of electrodes leads to higher thickness of layers in both types of steel substrates. From the results obtained it is found that the specific values of the roughness and the thickness of coatings are different for the different electrodes but they are similar in value.The energy increase of pulses leads to increase of the roughness and thickness of the layers. The presence of B and Si slows down the formation of oxide films and has a favourable efect on the thickness of layers. The presence of B also reduces the erosion resistance of the electrode, thus increasing the transport of electrode material to the substrate surfaces [10].



a) electrode NWW15B10T20



b) electrode KWB10T20

Figure 1. Microphotography of coating surface obtained by LESD on 45 steel with E=0.05J

Table 3. Properties of coatings obtained on 210Cr12 and 45 steel

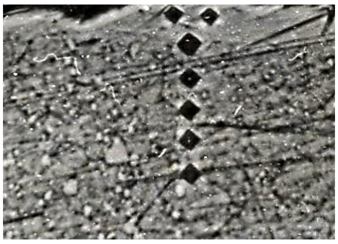
Electrode	Coatings on 210Cr12 steel (E_i=0.005-0.05J)				Coatings on 45 steel (E_i=0.005-0.05J)			
	Ra (µm)	δ (µm)	HV (GPa)	Coeff. of hardening	Ra (µm)	δ (µm)	HV (GPa)	Coeff. of hardening
WK9	0.95÷2.5	4.5÷14	11÷14	1.2÷1.65	1.0÷ 2.6	4÷14	6÷11	2.6÷5
NWW15T20	1.3÷3.6	3.5÷20	12÷16	1.4÷1.75	1.3÷3.5	4÷20	7÷12	3÷5.4
NWW10B10T10	1.3÷3.5	3.5÷20	12÷16	1.4÷1.75	1.35÷3.7	4÷20	7÷14	3÷6.3
NWW15B10T20	1.3÷3.5	3.5÷18	12÷18	1.4÷1.75	1.35÷3.7	4÷16	7÷14	3÷6.3
KWB10 T10	1.1÷2.8	4÷18	11÷18	1.2÷1.85	1.0÷2.65	4÷18	6÷15	2.6÷5.4
KWB10T20	1.1÷3.2	4÷16	11÷17	1.2÷1.75	1.0÷2.65	4÷16	6÷15	2.6÷5.4
Substrate 210Cr12/ 45 steels	0.63	-	8.6	1.0	0.63	-	2.2	1.0

3.2. Structure and Microhardness of Coatings

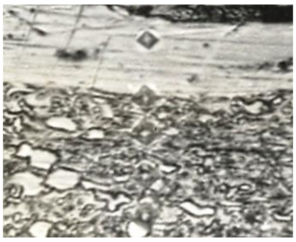
Figure 2 represents the typical microstructure of some of the studied coatings. The coatings have a compact and uniform structure with hardness varing within the range 5÷18 GPa, depending on the electrode material and pulse energy of the LESD process. The initial hardness values of the hard compounds B_4C, TiB_2 and WC are 34, 33 and 25 GPa, respectively [13]. Due to the structural inhomogeneity of the coatings and the presence of a matrix of lower hardness and hard carbide phases, the microhardness of the surface layers widely varies. The maximal hardenss value of 18 GPa on 210Cr12 steel is achieved with KWB10T20 and NWW15B10T20 electrodes. The highest coefficient of increase, (K=3.8÷6 times) of the hardness, however, has been observed on 45steel, while the values of the same coefficient of tool 210Cr12 steel are 1.4÷2. Results indicate that the LESD method and the new electrodes are more effective for application to unhardened carbon steels. The observed results could be explained by the hindering influence of the alloying elements in the substrate composition.

3.3. Phase composition of coatings

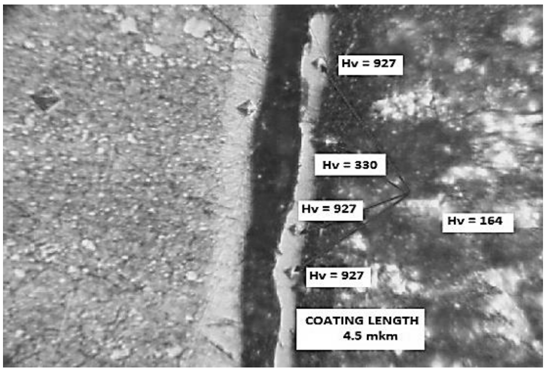
Figure 3 shows the X-ray diffraction patterns of coatings deposited with NWW15B10T20 and NWW15T20 electrodes. The results show that the phase composition of layers is a mixture of disequilibrium heterogeneous finely grained martensitic-austenitic structures, ultra-disperse carbides and borides, solid solutions, intermetallic compounds and amorphous phases, whose part increases with increasing energy of deposition.



a) electrode KWB10T20/210Cr12 steel, E≈0.02J



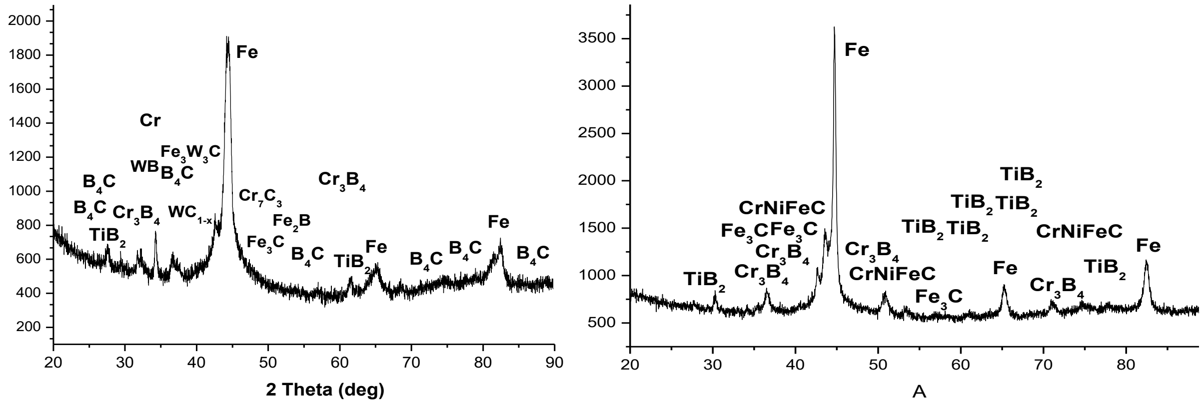
в) electrode NWW15B10T20/ 45 steel, E≈0,05J



c) electrode KWB10T20: left - 210Cr12 steel, E≈ 0.05 J; right - 45 steel, E≈ 0.02 J

Figure 2. Cros sectional images of coatings from KW and NWW electrodes applied by LESD on 210Cr12 and 45 steels

The type and the number of the phases are determined by the anode and cathode composition and the energy of deposition. The following main phases arranged sequentially in the intensity of the characteristic lines have been registered in coatings deposited on steel 210Cr12: martensite (γ-Fe) and modified multi-component matrix of alloyed austenite (γ-Fe) - Cr-Ni-Fe-C, or Co- Cr-Ni-Fe-C when "KW" electrodes have been used. Modified carbides and borides: WC1-x, Cr_3B_4, TiB_2, TiB, B_4C, Fe_3W_3C and carbides of the basic material - $(Cr\ Fe)_7C_3$, Cr_3C_2, Fe_3C Fe_2C with a low intensity of peaks have also been registered. Traces of Co_3W_3C, CrNiW, WB, Fe_2B, WB as well as intermetallics and nitrides of Fe and Cr: - CrFe, $FeNi_3$ Cr_2N, Fe_2N, Ti_2Fe have been detected. On the samples of 45 steel martensite (γ-Fe) and multicomponent matrix of alloyed austenite (γ-Fe), modified carbides of type: WC1-x, and refractory borides and carbides: Cr_3B_4, TiB_2, TiB, B_4C, Cr_3C_2 have been registered. Traces of intermetallic compounds of Fe with W, Ti and Cr have also been observed. The short contact time of the particles with oxygen from the environment and the presence of self-flushing additives, create favorable conditions to prevent the coating from oxidation, which is of essential importance of the wear resistance.



a) LESD coating from electrode NWW15B10T20 on 210Cr12 steel

b) LESD coating from electrode NWW15T20 on 45 steel

Figure 3. X-ray diffraction patterns of multi-component compositions coatings applied on 210Cr12 and 45 steels

New carbide and boride phases have been obtained by the reaction between the electrode bonding metals with boron and carbon. LESD process with electrodes NWW15B10T20, KW15B10T20 and KWB10T10 in addition to the upper shown phases leads to formation of high wear-resistant phase of the superhard compound B_4C. It indicates that B_4C has partially retained its original form during the transfer process, or which is also possible in the process of deposition secondary B_4C is synthesized. Volatilization of B leads to sytnesis of high wear resistant borides of Cr and W. It has been established that, although B_4C does not belong to the electrically conductive materials, the presence of titanium borides and tungsten carbides in the composition of electrodes make this material suitable for modifying the surface layers on steels by the method of LESD.

3.4. SEM analysis of coatings

Figure 4 shows a typical picture of the microrelief and the elemental distribution on 45 steel coated with NWW15B10T20 electrode.

El	AN	Series	unn. C (wt.%)	norm. C (wt.%)	Atom. C (at.%)	Error (1Sigma) (wt.%)
Fe	26	K-series	16.48	23.22	14.10	0.49
Ni	28	K-series	11.91	16.78	9.69	0.39
Ti	22	K-series	11.63	16.38	11.60	0.37
B	5	K-series	8.80	12.40	38.89	3.15
Cr	24	K-series	8.70	12.25	7.99	0.28
W	74	L-series	7.25	10.22	1.88	0.31
Si	14	K-series	3.27	4.60	5.55	0.18
C	6	K-series	2.50	3.52	9.92	0.85
Co	27	K-series	0.45	0.64	0.37	0.06
		Total:	71.00	100.00	100.00	

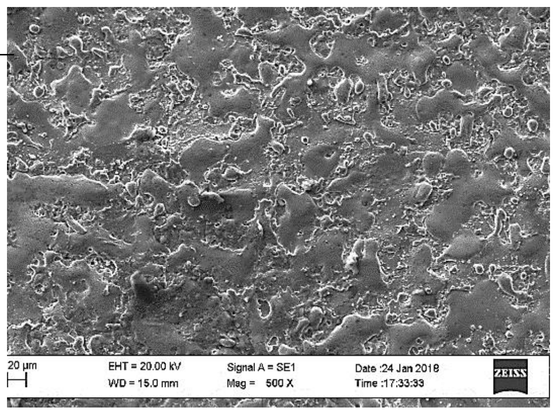


Figure 4. Microrelief and elemental composition of the coating of electrode NWW15B10T20 applied on 45 steel by vibration ESD in mode, Ee≈0.05J

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The elemental analysis showed the presence of Fe, W, Ni, Co, Cr, Si, B, and C in the layer surface. Based on the data obtained, it can be concluded that the elements, which are not involved in the formation of carbides and borides form a solid solution with the iron. The microrelief of the obtained coatings is uneven and heterogeneous both in structure and in composition. The reverse diffusion of iron from substrate in direction of the coatings could be a reason for observed picture.

3.5. Wear of coatings

The results of the comparative studies of the influence of the electrode compositions and the LESD regimes on the tribo-technical properties of the coatings are summarized in table 4 and figures 5-7.

Table 4. Parameters of wear of test samples at 200 friction cycles

Pattern, Electrode / Designation, regime	Mass loss (mg)	Wear rate (gmin^{-1})	Intensity (mgm^{-1})	Wear resistance (mmg^{-1})
NWW15T20/45 steel, E≈0.03J	12.3	12.8	29 x 10^{-2}	3.45
NWW15T20/45 steel E≈0.05J	7.5	7.81	17.6 x 10^{-2}	5.68
NWW15B10T20/45 steel, E≈0.03 J	8.7	9.1	20.4 x 10^{-2}	4.9
NWW15B10T20 /45 steel, E≈0.05J	6.2	6.5	15.0 x 10^{-2}	6.87
KWB10T20 /45 steel, E≈0.03 J	5.8	6.0	13.6 x 10^{-2}	7.34
KWB10T20/45 steel, E ≈0.05 J	5.4	5.6	12.7 x 10^{-2}	7.87
KWB10T10/45 steel, E≈0.03 J	5.5	5.7	12.9 x 10^{-2}	7.75
KWB10T10 /45 steel, E≈0.05 J	5.6	5.8	13.1 x 10^{-2}	7.61
WK9/st.45 E≈0.05 J	11.7	12.2	27.4 x10^{-2}	3.64
NWW10B10T20 / 210Cr12 steel, E≈0.05 J	5.1	5.3	12 x 10^{-2}	8.35
NWW15T20/210Cr12 steel, E≈0.05J	6.2	6.5	15.0 x 10^{-2}	6.87
KWB10T20 /210Cr12 steel, I=22A, C=5µF, Ti=12 µs	4.6	4.8	10.8 x 10^{-2}	9.26
WK9/210Cr12 steel, E≈0.05 J	9.5	9.9	22.3 x 10^{-2}	4.48
Substrate 210Cr12 steel	17.8	18.5	41.7 x 10^{-2}	2.4
Substrate 45 steel	26.6	27.71	62.4x 10^{-2}	1.6

The coatings obtained reduced the wear intensity to a greater extent than these obtained using conventional tungsten hard alloys, slow down the development of wear over time, and can be used to increase the durability of friction steel surfaces as well as of parts subjected to abrasion wear. The level of wear of coated samples was 2-5 times lower than those of uncoated, and 2 times smaller than the deposited samples with WC-Co electrode. Comparing the influence of the electrode material it is found that at LESD with electrodes KWB10T20 and KWB10T10 the wear of the samples is up to 1.6 times lower than that of samples coated with the rest of electrodes shown in Table 4. Apparently, the combination of TiB_2, B_4C and WC in the composition of the Co-based electrodes allowed to use the full advantages of each of the individual component and to receive higher wear resistance of the layered surfaces compared to that obtained with WC - TiB_2 or with WC-Co electrodes. The fine-grained structure of the electrical-spark LESD coatings also contributes to the high wear resistance. Due to the lower roughness, better uniformity and the absence of thermal impact on the substrate the LESD with new electrodes is suitable for the initial layering of parts and tools with high demands on surface accuracy and quality.

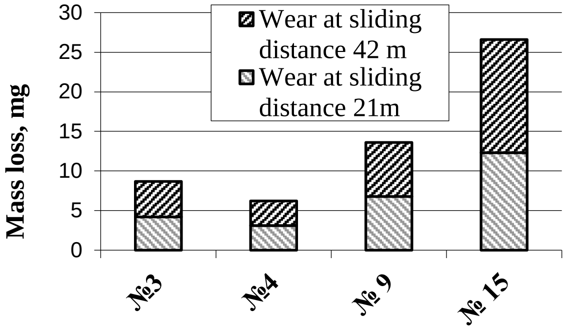

Figure 5. Mass loss as a function of sliding distance and puls energy for coatings from NWW15B10T20 electrode- table 4 on 45 steel

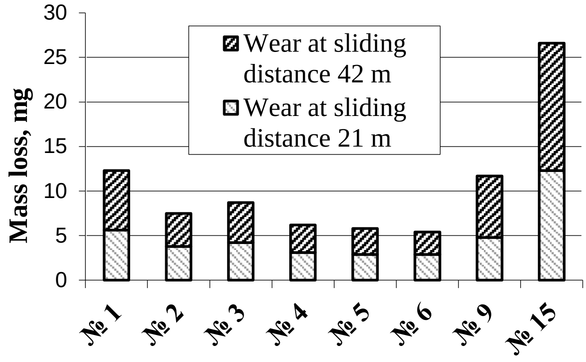

Figure 6. Mass loss as a function of sliding distance and puls energy for coatings from "NW"and "KW" electrodes - table 4 on 45 steel

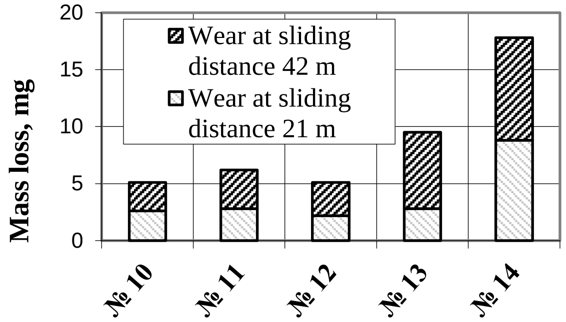

Figure 7. Mass loss as a function of sliding distance for coatings from "NW"and "KW" electrodes- table 4 on 210Cr12 steel

4. Conclusions

Multiphase electrodes based on mixtures of Ni-Cr-B-Si and Co-Ni-Cr-B-Si with additives of WC, TiB_2 and B_4C have been produced by the methods of powder metallurgy. Dense coatings with low roughness, thickness up to 20 μm and wear resistance over five times higher than that of non-coated surfaces have been obtained using LESD process.

The influence of the electrode composition and parameters of the LESD on the structure, roughness, thickness, and abrasion wear of coatings has been studied. The X-ray and SEM data show that the phase composition of coatings on steel 45 and alloyed tool steel 210Cr12 is enriched more significantly in carbide and boride phases than when conventional carbide electrodes have been used.

The optimal conditions and processing parameters to obtain the lowest wear of coated steels have been determined. The coatings obtained with KW10B20T20 electrode and the pulse energy of 0.05 J show the best wear properties.

The layers obtained may be efficiently used to strengthen rapidly wearing machine parts and tools of steels 45 and 210Cr12.

Acknowledgments

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