

# Physico-Mechanical and Tribological Properties of Carbon-Containing Surface Nanocomposites Produced by Electrosark Alloying

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**Abstract**—Nanostructured composite surface layers of metal articles improve the operating characteristics of the work-piece. Under the conditions of electrosark alloying (ESA), both the material transfer to the treated surface and the change in its characteristics under the influence of an electric discharge occur. A possibility of surface modification during ESA with the use of electrodes containing carbide phases, as well as with the use of graphite electrodes in order to form such phases, has been investigated. In this case, the main purpose was to strengthen the surface and to increase its friction resistance. The electrodes of T15K6 and VK8 alloys, as well as of steel 45, tungsten, and graphite, were used. It is shown that the presence of carbides in the surface layers has a decisive influence on the wear resistance, in particular, when a steel 45 electrode is used. With an increase in the carbides' concentration in the substrate, the wear resistance of the obtained layers also increases. It is shown that the ESA treatment with tungsten and graphite electrodes with sequential deposition of a number of alternating layers allows the production of carbide-containing surface layers directly in the alloying process.

**Keywords:** electrosark alloying, microhardness, wear resistance, carbide-containing layers

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## INTRODUCTION

It has been more than 60 years since the electrosark modification of metal surfaces was developed [1, 2]; however, there still exists no established terminology that maximally corresponds to the peculiarities of this surface treatment method. Evidently, the best term is “electrosark alloying” [2], though “electrodischarge treatment” or “electrosark deposition”, etc. are used. Obviously, the cause consists in the fact that different technological methods based on the same physical process are used. In particular, the growth in the changed layer on the part surface can be necessary to recondition the working surface, and the strengthening of the surface or the increase in its corrosion resistance may require no growth in its thickness. Moreover, when seeking a solution of certain technological problems, one needs to prevent the increase in the thickness of the strengthened or corrosion-resistant layer.

Evidently, in the most general case under the conditions of electrosark alloying (ESA, the most fre-

quently used term), specifically the modification of the metal surface takes place, which can be performed both with the layer growth or without it. Under the application of ESA, it was shown many times that the resulting surface layer (strengthened, corrosion-resistant, or possessing some other properties) is a composite containing the substrate material in addition to the working electrode substance. Thus, not only the characteristics of the working electrode but also the substrate material should considerably affect the properties of the obtained surface layers.

At present, it appears evident that the nanostructuring of the surface layers and the deposition of nanostructured coatings is an effective method of strengthening the structural and tool materials [3, 4]. Using the notion of nanocrystalline materials [5], for which the volume of separate elements (grains) is less than the volume of interfaces between them, the methods to control the properties of surface layers based on the nanostructuring of them are possible [3, 4]. The realization of this process is performed due to the application of the corresponding technological processes:

magnetron deposition, ion-plasma treatment, vacuum-arc coatings, ultrasound machining, and different types of combined treatment [3].

ESA is classified as one of these methods. As is shown in [6–8], the formation of nanostructured surface layers is possible under the conditions of ESA with different working electrodes. When using the electrode being a mixture of a refractory matrix and a low melting component, an assembly of the low melting component nanofibers forms with a considerable increase in the coating wear resistance as a consequence [6, 7]. The possibilities of nanostructuring the surface layers are shown in a number of works [9–11] which describe the ESA process with the help of working electrodes produced with the SHS (self-propagating high-temperature synthesis) method, including the ultradispersed refractory oxides, carbides, and ultradispersed diamond. Furthermore, the hardness, wear resistance, and heat resistance are increased in the coatings, and there is possible decrease in the friction factor in comparison with the surface layers not containing the nanodispersed components. Apparently, the nanostructuring occurs not only in these cases, and the surface layers formed at the ESA are usually nanostructures (see, for instance, [6–8, 12]).

With ESA utilized to strengthen the surface, the working electrodes containing the tungsten carbides and other elements (Ti, Cr, Mo, Zr, Ta) are mainly used. However, considering the ESA conditions, the formation of carbide phases in the coatings is possible not only due to the usage of working electrodes containing them but also due to the process itself if a graphite electrode is applied as a working one. Thus, for instance, during the ESA of iron alloys with graphite, a strengthened layer containing a viscous austenite and hard carbide is formed. A high rate of cooling at the formation of the surface strengthened layer leads to the formation of a phase composition with the generation of metastable phases, including carbides [14–16]. ESA with a graphite electrode is not accompanied with an increase in the part dimensions, which allows for comparing it with a kind of chemico-thermal treatment—carbonization [14]. When the depth of carbonization is greater, then the content of carbon in steel is greater [16]. The ESA treatment with the working electrode of a certain type with the following processing with a graphite electrode was used to improve the wear and corrosion resistance of parts [16, 17].

The purpose of this investigation is to estimate the possibilities of modification of the surface during ESA using the working electrodes containing carbide phases as well as formation of similar phases with application of graphite electrodes. Since the main aim of modification in this case is the surface strengthening, we supposed to estimate the possibility of control based on determining the wear resistance of the produced layers under different conditions of friction. It was intended to study the obtained modified layers not

only in the form of the coatings with a finite thickness but also the strengthening of the modified surface with no change in its dimension.

The complexity of the quantitative estimation of the wear resistance of the produced surface layers consists in that (a) they have a high roughness and (b) they are drastically nonuniform both in composition and properties. Thus, the main method to estimate the tribological properties of these coatings is the evaluation of the wear resistance of the modified surface in comparison with the wear resistance of the substrate (see review [18]). However, the generalization of the investigation results performed in [18] show that it is far from always possible to make firm conclusions on the basis of the carried out experiments since many of the most important parameters influencing the wear resistance, such as the counterbody material properties, the roughness degree effect, and the pattern of mechanical tests, were essentially different. This fact did not allow any correct analysis of the results and fairly wide generalizations.

A similar method of comparative tests is also used in this work; however, we will try to estimate

(1) the influence of the substrate material (steels with different content of carbides) on the wear resistance of the modified layer;

(2) the possibility to receive carbide phases during the treatment process with the purpose to improve the wear resistance;

(3) the peculiarities of the effect of surface microhardness and roughness on the wear rate.

## RESEARCH PROCEDURE

The treatment of the surface of steel specimens with a different content (st20, st35, and st45) was performed using the ALIER-31 (Scinti, Moldova) and the EFI-10a (Moldova) devices with the discharge energies 0.3 and 1 J. Furthermore, we used the working electrodes of T15K6 and VK8 alloys containing tungsten and titanium carbides as well as St45 and tungsten. The specimens with coatings of T15K6 and VK8 of two types were received: with and without the subsequent treatment with the graphite electrode for modification of the surface. The latter kind of treatment was performed by different methods described in the corresponding sections of the paper. When applying a coating, the treatment time was 1, 3, and 5 min/cm<sup>2</sup>. Modifying the surface, we applied the coating at a treatment time of 2 min/cm<sup>2</sup> with the subsequent treatment with graphite for 1 min/cm<sup>2</sup>.

The microhardness was determined using the PMT-3 instrument at a load of 100 g. Considering that the results of the microhardness determination can greatly vary due to the surface nonuniformity, we calculated the average value and standard deviation. The microhardness at a load of 50 g was also measured on

**Table 1.** Composition of the composite made with electrode of hard alloy T15K6 in different modes of treatment

No.	Discharge energy, J	Concentration of elements in composite, wt %			
		Fe	W	Ti	Co
1	0.3	69.1	22.2	3.8	4.9
2	1.0	62.2	26.6	4.7	5.3

the coating section with a much higher accuracy and less quantity of the standard deviation.

The wear tests were carried out in two variants. "Ball on plate" friction conditions were used in the first of them. A corundum ball 6.35 mm in diameter (microhardness ~2500 HV) was used as a counterbody. The linear friction rate was 0.4 m/s, and the sliding path was 240 m at a load of 10 N. The sliding path diameter was 8.4 mm. The mass wear was measured with the help of the Vibra 225DRCE weighing scales with an accuracy of 0.01 mg. The wear resistance quantity  $I$  was calculated on the basis of the specimen weight loss in the form of  $\Delta/Hm$ , where  $\Delta$  is the change in the specimen weight (ng) and  $m$  is the length of the sliding path in meters.

The pattern of another type provides the estimation of the mass wear of the flat specimen which executes reciprocal movement at a frequency of 180 double strokes per minute (3 Hz) and a stroke length of 40 mm with the over-mounted counterbody of the heat-treated steel 45 with a load of 20 N. The microhardness of the counterbody was 500 HV. The dimensional contact in the friction couple was  $10 \times 2$  mm. The wear rate was determined measuring the weight loss of both the counterbody and the specimens in ng/Nm. Furthermore, since the measurements were comparative in nature, the wear resistance of both the counterbody ( $I_{cb}$ ) and the composite ( $I_c$ ) were determined. In some cases, the wear rate was a negative value because the transfer of the counterbody mass to the specimen under study took place. The wear resistance of the surface under investigation was determined according to the sliding path (800, 1600, and 2400 m) by periodic measurements of the loss (growth) in the specimen weight after each stage of 10 000 cycles, which corresponds to a sliding path of 800 m. The ratio  $I_{cb}/I_c$  is indicative of the influence of the working electrode material, the discharge energy, the surface microhardness, and roughness on the wear resistance of the modified surface.

The measurements of the surface roughness (according to the criteria  $R_z$  and  $R_a$ ) were performed using the Surtronic 25 profilograph/profilometer (Taylor Hobson, Great Britain) both before the tribological tests and after them. The elemental composition of the composites after the surface modification and wear tests was determined using the method of X-ray fluorescence analysis (Xenometrix, Israel). The content of heavy elements in the surface layer are pre-

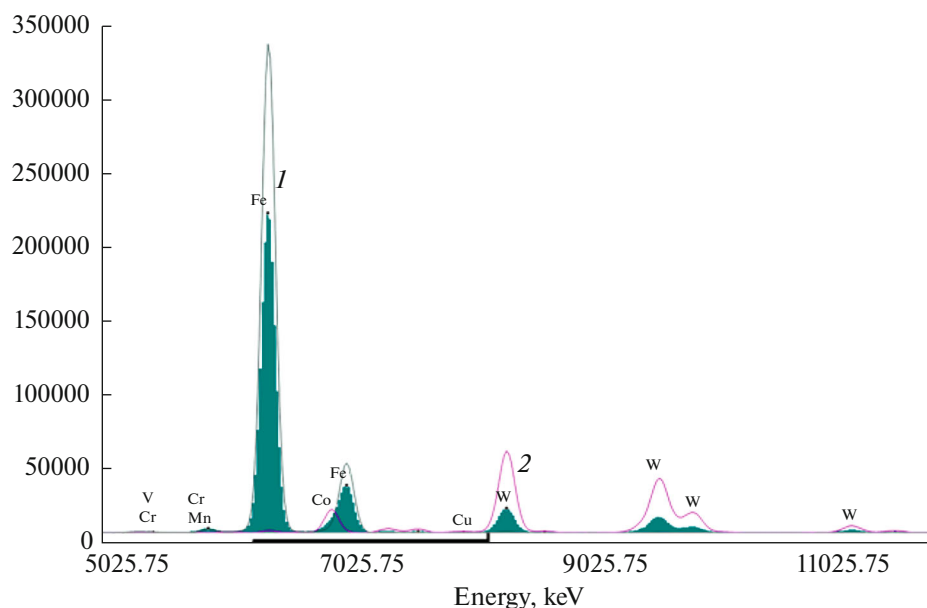
sented in the weight percentage. Light elements (carbon, oxygen, nitrogen) were not determined in the used method. The studied surface layer was 3–5  $\mu\text{m}$  in thickness.

## RESULTS AND DISCUSSION

### *Influence of Substrate Material on the Composition and Wear Resistance of Surface Layers*

The X-ray fluorescence analysis of the surface  $T_0$  obviously demonstrates that a composite, including the material of not only the working electrode but also of the substrate, is obtained due to the electrospark modification of the surface (Fig. 1). This is also confirmed by the results of the quantitative analysis of the surface layer components presented in Table 1. It is apparent that up to two thirds (in weight) of the surface layer consists of the substrate material. The increase in the discharge energy leads to the growth in the concentrations of the components contained in the working electrode and the decrease in the concentration of the substrate material (Table 1).

The increase in the carbide phase concentration in the substrate must affect the properties of the surface layer and, first of all, of wear resistance, which must grow with the increase in the concentration of carbides. The values of  $I$  presented in Table 2 were received (a) on the substrates of steel with a different content of carbon (20, 35, 40), (b) at the treatment with different working electrodes (T15K6, VK8, NiCr, W, Cr) both without treatment with a graphite electrode and using it, and (c) at different energies of the discharge. It is apparent that regardless of a substantial scatter in the received values of  $I$  (in some cases the standard deviation in  $I$  reached 50% of the average value (Table 2)) the wear resistance of the composites is higher when the content of carbides in the substrate is greater. At the same time, the results presented in Table 2 show that the wear resistance of the strengthened surface layer was, on average, an order of magnitude higher than the wear resistance of the substrate. The results presented in Table 2 are obtained according to the "ball on plate" friction pattern with the corundum counter. These results will be described in detail in another report.



**Fig. 1.** X-ray fluorescence spectrum of surface layer of (1) steel 45 substrate, (2) working electrode VK8, and (3) painted composite obtained after ESA at 0.3 J.

#### *Influence of Working Electrode Material, Discharge Energy, Surface Element Composition, Roughness, and Microhardness on Wear Resistance*

Due to the macroscopic nonuniformity of the surface layer after ESA, its microhardness is usually determined on the surface section. However, during the mechanical tests, the surface layer “works.” Apparently, as shown in [18], the degree of the increase in microhardness after ESA does not always corresponded to the growth in wear resistance for this reason. The wear resistance grew in much lesser a degree than the microhardness. Usually, as a rule, the surface layer responsible for the wear resistance has smaller microhardness than the coating measured on the section, which is confirmed by the obtained data (Fig. 2). The microhardness on the coating section can attain the values of HV 3500, increasing with the growth in the discharge energy, while it has a considerably higher scatter of values when measured over the surface and is decreased by almost an order of magnitude. It is also seen that, after strengthening with the help of electrodes containing tungsten carbides T16K6 and VK8, the additional treatment with the graphite electrode results, as a rule, in the growth of the mea-

sured values of microhardness (Fig. 2). Another picture was observed in the experiments with W as the working electrode.

The application of the tungsten electrode along with the graphite electrode is intended for determining the possibility to form a strengthening carbide phase during treatment. When it is used, the HV increases with the growth in the discharge energy much higher at the measurement on the section; however, it generally decreased after the treatment with the graphite electrode (Fig. 2).

At the transfer of the electrode material to the specimen under the action of discharge, the transfer of carbides in the drops of the electrode material or the formation of them at high temperatures in the discharge channel can take place. Steel 45 contains a noticeable amount of carbon and can be subjected to heat treatment with the formation of various structures depending on the ESA conditions. High surface temperatures at a discharge with the following quick cooling can provide quenching and be a cause for additional strengthening. The initial microhardness HV ~ 220 of the specimen surface increases by several times after ESA. Due to the little thickness of the modified layer

**Table 2.** Influence of substrate material on wear resistance of composites produced by ESA with different electrodes

No.	Substrate material	Wear resistance of substrate, ng/Nm	Wear resistance of ESA composite, ng/Nm
1	Steel 20	$3.6 \pm 0.08$	$0.27 \pm 0.11$
2	Steel 35	$2.88 \pm 0.83$	$0.21 \pm 0.09$
3	Steel 45	$1.45 \pm 0.38$	$0.16 \pm 0.08$

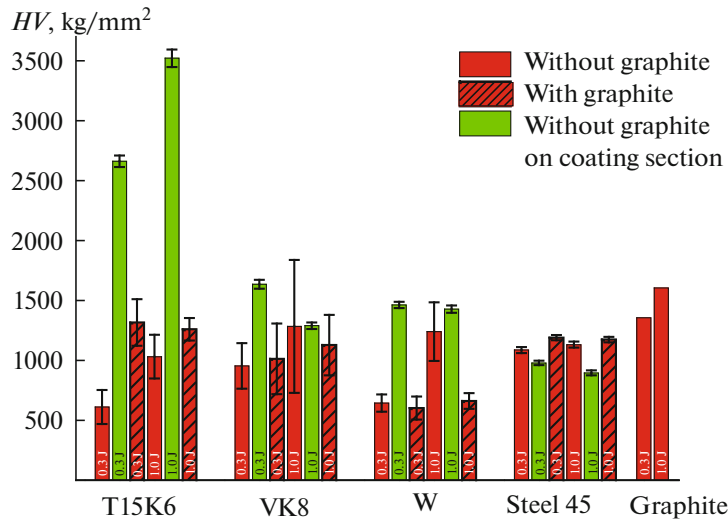


Fig. 2. Microhardness of surface layers of specimens after ESA with different electrodes.

during the measurement on the section, its microhardness is decreased (Fig. 2). The additional treatment with graphite increases the microhardness but only slightly, to approximately 10%.

The roughness of the formed surfaces ( $R_z \sim 20 \mu\text{m}$ ) changed relatively little depending on the nature of the working electrode, the additional graphitization of the surface, and discharge energy; however, it was considerably decreased under the conditions of the treatment of steel 45 and the subsequent treatment with the graphite electrode (Fig. 3).

The results of wear tests using the machine with the reciprocal movement of the specimen with a counterbody of the hardened steel 45 and a sliding path of 800 m are presented in Fig. 4. In all cases, the wear resistance increased after the surface graphitization with spark discharges, and there was no loss in weight during the treatment of the electrode of VK8 and the subsequent treatment with the graphite electrode, but, on the contrary, there was growth in weight due to the transfer of the counterbody material on the surface subjected to ESA (Fig. 4). It is apparent that, with the application of the electrodes, whose composition includes the carbides, the rise in wear resistance (decrease in  $I$ ) happens to a greater extent at the relatively low discharge energies. At higher energies, the surface wear increases, which could be particularly due to the higher roughness. An unusual dependence on the microhardness is also apparent, in particular, if the measurement data on the coating section are used. The microhardness of the composite prepared at the treatment with the hard alloy T15K6 attains  $HV \sim 3500$ , and the wear of these coatings is higher than of the surfaces treated with the alloy VK8 with lower microhardness.

It is possible to explain the obtained results accepting that, under the conditions of mechanical tests with

the used counterbody, not only the modified surface after ESA was subjected to wear but a peculiar composite consisting of the counterbody material transferred to the specimen of the material of the surface layer itself.

Figure 5 presents the mass wear versus the sliding path and the tungsten concentration in the surface as a “marker” of the change in the surface composition during the tests. In particular, this fact is indicated by the measurement results for tungsten concentration in the surface layer at the different slip distances (Fig. 5b). In the case of sufficiently long tests, the tungsten concentration (that is, the presence of carbides) in the surface layer begins to drop with the simultaneous accumulation of the concentration of

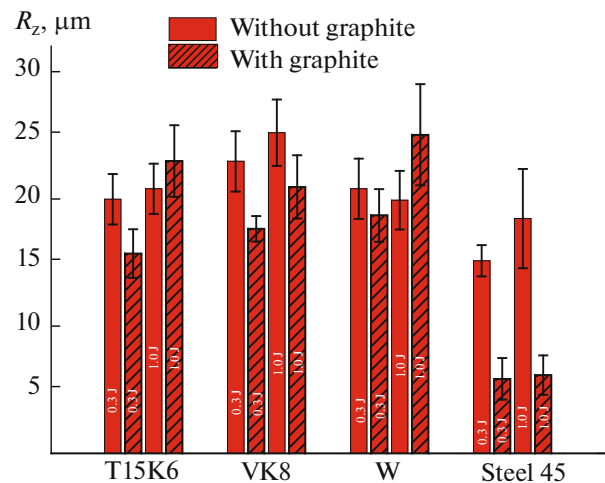


Fig. 3. Surface roughness after ESA with different electrodes.

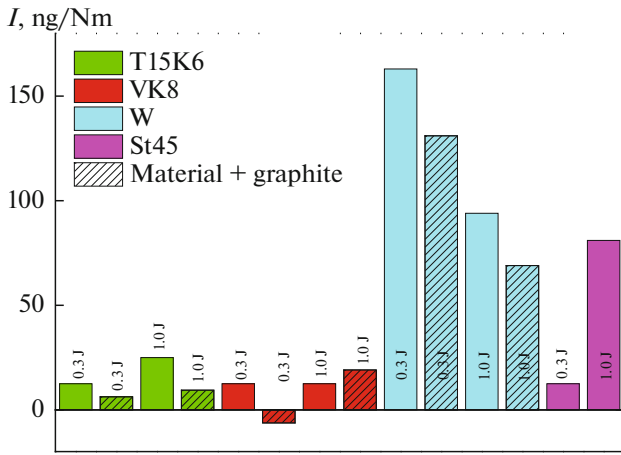


Fig. 4. Wear resistance of surface layers depending on material of working electrodes and discharge energy.

iron transferred from the counterbody at a high wear of the counterbody.

The possibility of formation of carbides in the treatment process and their influence on the wear resistance can be explained on the basis of the results obtained on the specimens treated with the tungsten electrode (Fig. 4). It is apparent that the wear resistance grows (a) during the increase in the discharge energy and (b) during the subsequent treatment with the graphite electrode. These are the conditions under which the concentration of carbides in the surface layer must increase. However, the wear resistance of the prepared layers is substantially smaller in all cases than that during the treatment with the electrodes containing the carbide phases. Nevertheless, the results presented in Fig. 4 definitely indicate the possibility of the carbide formation at the ESA, and the search for its optimal conditions calls for further investigations.

The profile diagrams presented in Fig. 6 show how a high mass wear of the surface is provided after treatment with the tungsten electrode, unlike the surfaces treated with the alloy VK8.

With the use of steel 45 as a working electrode at relatively low discharge energies, it is possible to achieve a high wear resistance that is reduced at the transition to the treatment with a higher energy (Fig. 4). It is evident that, in this case, higher discharge energies increase the counterbody material transfer into the surface with the growth in the wear as a consequence.

The influence of the electrode material at different discharge energies on the ratio of the wears of the counterbody to the specimen  $I_{cb}/I_c$  is shown in Fig. 7. This ratio is the highest after treatment with the alloy VK8, in particular, at a low discharge energy. It is also apparent that, under these conditions,  $I_{cb}/I_c$  increases with the growth in the sliding path and the difference attains almost two orders of magnitude (Fig. 7a).

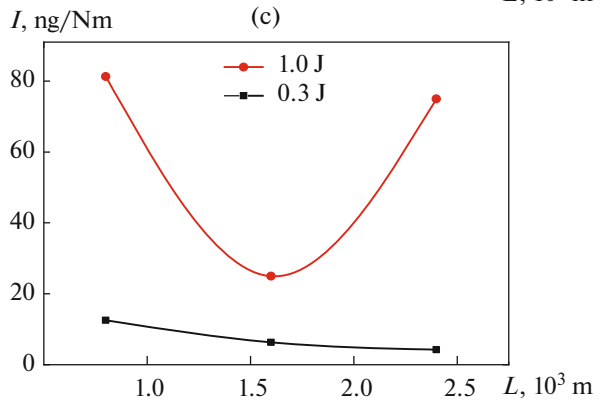
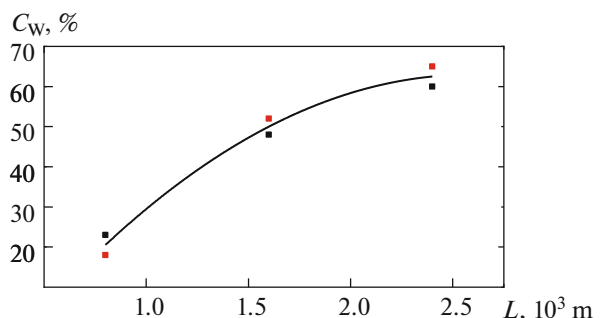
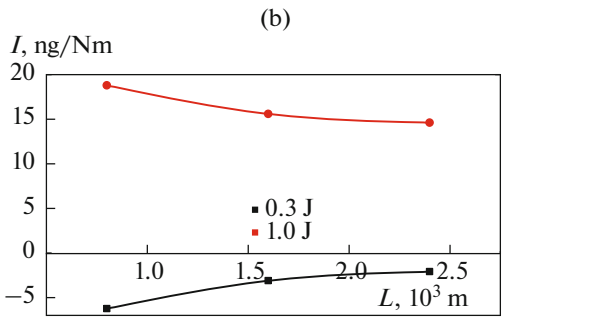
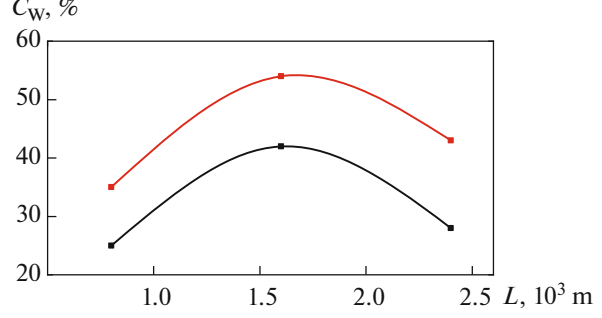
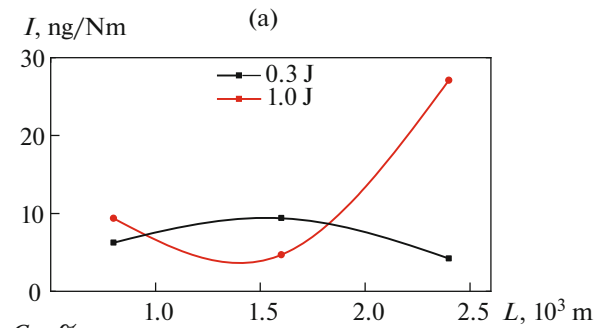
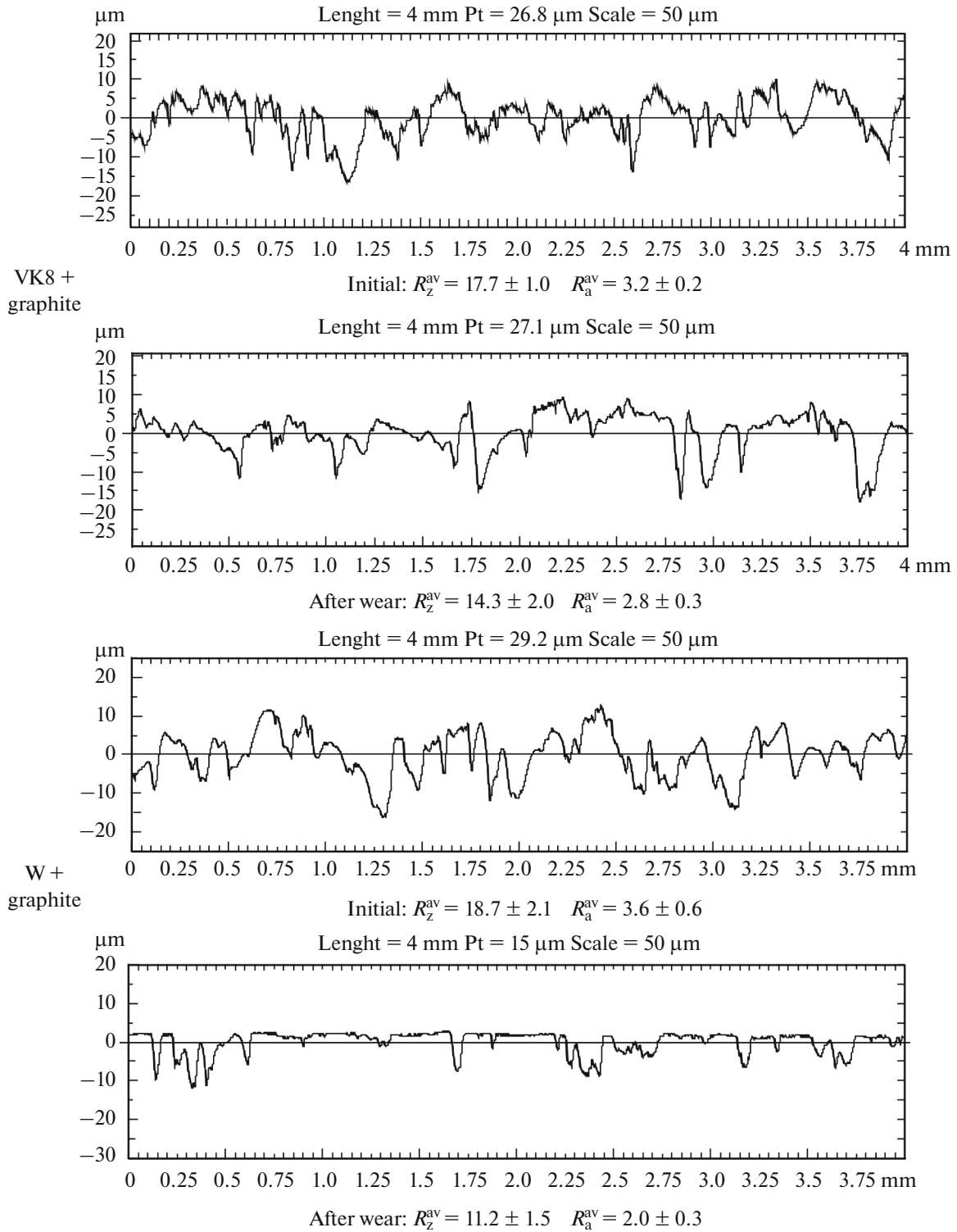


Fig. 5. Influence of sliding path on wear of specimens treated with electrodes (a) T15K6 + C, (b) VK8 + C, and (c) steel 45 and change in W content in surface layer during tests.



**Fig. 6.** Profile diagrams of specimens before and after wear tests.

Using corundum as a counterbody, the ratio  $I_{cb}/I_c$  is approximately an order of magnitude (Table 2), and the microhardness of the hardened steel is substantially higher than the microhardness of the substrate.

Such high values of the ratio  $I_{cb}/I_c$  have to be explained. It is assumed that the cause of the observed effect is associated with the mutual influence of the wear of the treated surface and the counterbody when



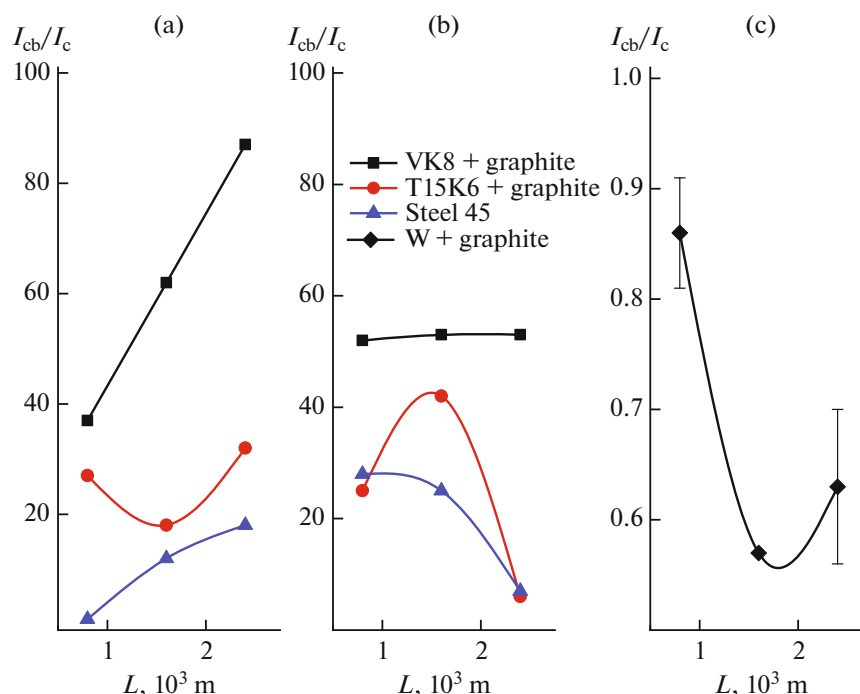


Fig. 7. Counterbody to modified surface wear rate ratio versus sliding path. ESA at discharge energy (a, c) 0.3 and (b) 1 J.

the counterbody material is transferred to the surface. This sinergetic effect of the counterbody wear is not only a consequence of the high tribological characteristics of the treated surface (the wear of the counterbody of hardened steel is greater by an order of magnitude and more than the wear of the treated surface) but also the high roughness of it. However, the wear of the counterbody is substantially lower than the wear of the surface when using a tungsten electrode (including the case with the subsequent treatment with graphite) with a roughness close to that observed for the carbide-containing electrodes (see Figs. 3, 6, 7c). It is obvious that the surface strengthening under the conditions of ESA is mainly attained due to the carbide formation in the surface layer, and a high wear of the counterbody happens due to its lower hardness in comparison with the hardness of carbides: 500 and 1000–3000 HV, respectively.

#### *Modification of the Surface without Applying an Additional Layer*

In the experiments described above, a layer with a finite thickness was produced due to the treatment as the electrodes containing carbide were used, and the time of the graphite electrode application was not more than one third of the total treatment time. In the experiments described below, the surface was modified with a graphite electrode or, alternatively, with an electrode of W or T15K6 and the graphite electrode. The total number of the treatment stages is 5–7 at the discharge energy (0.05–2 J). The results of the

mechanical tests are also presented in Table 3. It is apparent that the lowest wear is typical for the systems T15K6 + C and VK8 + C.

The test results for the system W + C are noteworthy (Table 3, tests 1, 4, and 7). Low wear was attained one of them (high wear resistance) (Table 3, test 1), while the surface wear grew by several times in two others. There were some reasons for so significant differences. The first (and, seemingly, the main) reason consisted in the fact that, in the case of test 1 (Table 3), a sequential treatment with different electrodes (W-graphite-W-graphite, etc.) was performed. The weld penetration of the previously applied layer consisting of a mixture of iron and wolfram must lead to the formation of carbides when carbon is transferred from the working electrode. In two other tests, this condition was not satisfied. In addition, the experiment was carried out with the highest time of treatment with graphite at the last stage (approximately one third of the total treatment time being 6.6 min/cm<sup>2</sup>). Thus, the treatment time at the last stage was 2 min/cm<sup>2</sup>, which was twice as high as in the corresponding experiments described in the previous section. The third possible reason consisted in the fact that, in this case, a substrate of steel St45 was used that, due to a sufficiently high content of carbon, can be subjected to heat processing, and it can incandesce at the electrospark discharge due to the weld penetration and subsequent rapid cooling.

Apparently, particularly the consequent treatment with different electrodes—previously used to increase



**Table 3.** Physico-mechanical and tribological properties of the graphitized nanocomposites

No.	Substrate material	Working electrode(s)	Microhardness HV, kG/mm <sup>2</sup>	Roughness of composites $R_z$ , $\mu\text{m}$		Wear resistance of composites $I$ , ng/Nm
				after application of them	after wear test	
1	Steel 45	W + C	490 ± 60	20.1 ± 2.4	20.7 ± 0.64	20.4 ± 2.2
2	Steel 35	Graphite	1040 ± 100	19.6 ± 3.55	23.7 ± 3.9	40.7 ± 4.5
3	Steel 35	T15K6 + C	1500 ± 400	14.6 ± 3.63	18.8 ± 5.3	11.0 ± 6.6
4	Steel 20	W + C	950 ± 190	23.4 ± 3.84	21.2 ± 3.5	129.7 ± 2.3
5	Steel 45	VK8 + C	1140 ± 100	19.9 ± 3.13	18.2 ± 2.51	18.8 ± 8.8
6	Steel 20	NiCr + C	377 ± 17	22.5 ± 2.03	22.1 ± 2.44	42.2 ± 11.0
7	Steel 35	W + C	552 ± 140	11.2 ± 1.26	9.67 ± 1.73	107.8 ± 11.0

the layer thickness [19, 20] and proposed in [3, 4] as an effective method to control the surface properties with the aim of its strengthening—provided the growth in wear resistance in this very case without application of any working electrodes based on hard alloys containing WC.

The analysis of the roughness effect shows that the increase in roughness causes the growth in wear; however, this factor is not so important since the maximum wear appears at the lowest roughness (Table 3, Fig. 8). Apparently, the major cause of the growth in wear resistance is the change in the carbide content after treatment.

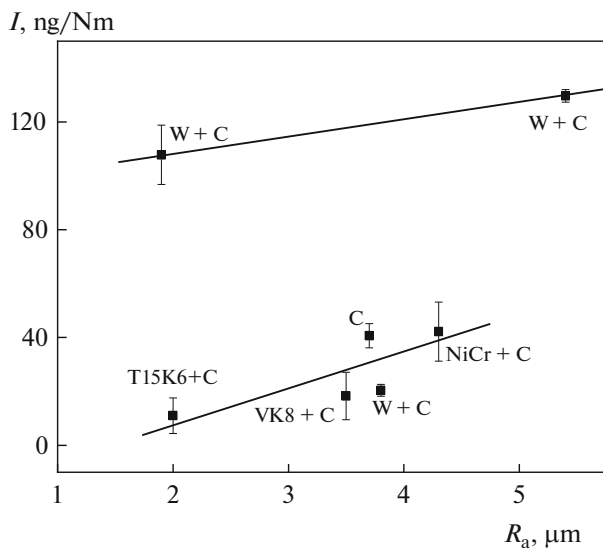
A similar conclusion can be made taking into account the dependence of the surface wear on the microhardness of the surface layer. It decreases but to a much lesser extent than should be expected at the increase in microhardness (Fig. 9); this fact was earlier noted in [18].

CONCLUSIONS

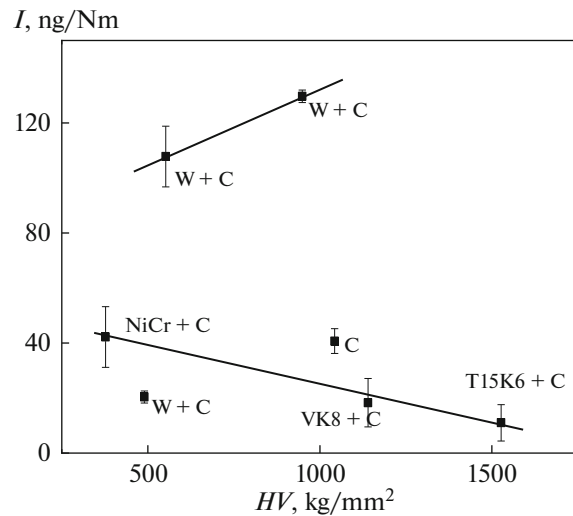
We showed that, in the case of strengthening using the ESA method, the forming surface layer is a composite consisting of the material of the working electrode and the substrate. The fraction of the working electrode material grows with the increase in the discharge energy.

The effect of the treated surface microhardness and roughness on the value of wear resistance of the surface layer is shown. And a major role is played by the presence of carbides in the surface composite layer, including the case of steel 45 used as a working electrode. The carbide concentration in the substrate increasing the wear resistance of the produced surfaces grows.

High values of the microhardness of the produced layers up to HV 3500 (on the section of the changed layer) lead to the fact that, when heat processed steel with HV 500 is used as a counterbody, its material is transferred to the specimen during friction, and there



**Fig. 8.** Influence of surface roughness after ESA with different electrodes on wear rate.



**Fig. 9.** Influence of microhardness on wear resistance of surface layers after ESA.

appears an effect of the mutual influence of the friction surfaces. In this case, the ratio of the counterbody weight wear to the modified layer weight wear can reach almost two orders of magnitude.

With the use of tungsten and graphite as working electrodes during the consequent application of layers in the process of strengthening by the ESA method, it is possible to produce carbide-containing surface layers, which allows controlling their wear resistance.

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#### CONFLICT OF INTERESTS

The authors declare that they have no conflicts of interest.

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