ADVANCED FUNCTIONAL AND STRUCTURAL THIN FILMS AND COATINGS

Nanostructuring of Metallic Surfaces by Electrospark Alloying Method

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A new method of nanostructuring of the surface by electrospark alloying method (ESA) using special processing media (SPM) with carbon nanotubes is proposed. The influence on the ESA regimes and the composition of the SPM on the microstructure and hardness of the coatings has been considered. While processing the Armco iron, with an increase in the discharge energy, the thickness and continuity of the coating increase. In the microstructures, the nanoscale phases of 40 nm to 1300 nm are detected, and they are evenly distributed in the coatings. Adding nanotubes helps to increase the continuity, thickness and hardness. Because of the ESA process, coatings with a uniform distribution of molybdenum are formed. Carbon, apparently in the form of the carbon nanotubes, is concentrated on the surfaces of the samples being processed, regardless of the discharge energy during the ESA process. The use of the proposed ESA method has a positive effect on the quality parameters of the coating.

INTRODUCTION

The problem of energy saving has become one of the most important human problems. Rational and cost-effective use of natural resources, reduction of harmful emissions into the atmosphere and efficient use of electric and thermal energy are extremely important in modern society. In recent years, Europe has continued to face a growing shortage of energy resources and increasing cost of energy sources. Specialists in many industries, including machine building, have a priority task, which is to increase the energy efficiency of both newly created and already used technological machines and equipment by reducing their energy consumption.

Existing methods of surface modification are energy intensive. In the last years, the quality of surface layers of machine parts has been improved by using surface treatment methods with concentrated flows of energy and matter, one of which is the method of electrospark alloying (ESA), the process of transferring material to the surface of the product by a spark electric discharge.[1] Its specific features, which attract technologists, are[2,3] the locality of the action, low energy consumption, no volumetric heating of the material, strong connection of the applied material to the base, ease of automation and possibility of combining operations.

However, challenges for technologists are the development of technologies to obtain unique coatings with such high-quality properties as increased wear resistance, durability, corrosion resistance, etc. An alternative to the above is a process for nanostructuring a surface by various methods. The technologies of surface micro- and nanostructuring of materials are important for various fields of science and technology. The obtained nanostructures have unique properties. The creation of special nanometer-scale structures on the surfaces of solid bodies results in the improvement of both the physical and mechanical properties of the material. Therefore, there is a need to develop new processes

for surface strengthening which are environmentally friendly and energy efficient, namely, processes based on the electrospark alloying (ESA) methods.

ANALYSIS OF THE LATEST RESEARCH

An effective and economical way to increase the durability of parts operating under conditions of cyclic loads, contact fatigue and abrasion is to create strong, durable and corrosion-resistant layers on their surfaces. The new processes for strengthening the parts, which are based on nanotechnology methods, have been being developed intensively using the impact of concentrated flows of high-energy particles (ions, atoms, molecules and clusters, etc.) on the surface of the part.

Successfully obtaining a nanocoating is the basis for its application. Traditional technologies for obtaining nanostructured coatings are chemical vapor deposition (CVD) and physical vapor deposition (PVD). They regulate the thicknesses and grain sizes of the coatings with the help of the technological parameters. On the other hand, such methods as the sol-gel method, laser deposition, thermal spraying and others have been developed.[4–7]

Nowadays, the methods of surface nanostructuring based on the use of concentrated flows of energy and matter have been developed. One of those is the method of electrospark alloying (ESA). ESA technology is used in various industries because of the high adhesion of the formed coatings, the possibility of local surface treatment of the responsible parts of assemblies and mechanisms, including large-sized parts, the relative simplicity of the alloying process, absence of strict requirements for surface preparation before the use and high reliability of the equipment. The technological process of coating is environmentally friendly and characterized by low energy consumption, high profitability and quick payback of investments.[8,9]

The analysis of the literature[10,11] on the issue of improving the physical and mechanical properties of working surfaces under the effect of the creation of nanostructured electrospark coatings has shown that the ESA method is promising. Thus, in,[12] it was shown that after the ESA process with bronze, the "white layer" of the coating on 41Cr4 steel consisted of the grains of 10 nm to 60 nm size. In,[13] based on the obtained qualitative characteristics, the author established that the ESA method allowed controlling the dispersion of the crystalline structure of coatings. Moreover, the main principles of the application of the ESA process, which contributed to the formation of coatings with nanostructures and ultra-fine grain structures, were there formulated.

The studies showed that, in addition to grinding the fine structure blocks and increasing the density of dislocations due to the application of the ESA method, the process of nanostructuring the coatings can occur because of the use of the anode materials made of nanocomponents. Therefore, the results of the studies indicate that the ESA method really makes it possible to obtain nanostructured layers; however, the technological features for obtaining such coatings have not been presented in the literature; the choice of the mode parameters of the ESA process, as well as of the anode and cathode materials, and others has not been justified. Therefore, the creation of the technological foundations for the development of the processes for surface nanostructuring by the ESA method is an urgent task.

In addition, most of the new technologies based on the ESA method are application oriented to using either powder materials with finely dispersed particles or alloys in the form of composite materials containing the main matrix and various inclusions of nanometer-sized particles therein.[14–18] The authors of[19] had been studying the process of nanostructuring C35 steel using the electrodes based on tungsten carbide with the addition of the Al_2O_3 nanopowders. It was established that on the cathode surface (substrate), ordered accumulations of nanoclusters had been being formed. Those consisted of nanoparticles of up to 30 nm in size. At the same time, it should be emphasized that the addition of only 1% Al_2O_3 to the electrode-anode made from hard alloy (WC $\sim$ 92%, Co $\sim$ 8%) increased the efficiency of the alloyed layer formation three times, and the microhardness of the coating became three to four times higher than the microhardness of 35 steel.

Considering the works[17–19] devoted to the study of the structure and properties of the ESA coatings, it should be noted that the improvement of the physical and mechanical properties, in particular the wear resistance, is facilitated by using the anode electrodes with inclusions of components having nanostructural structures. At the same time, the amount of the nanoadditives may not exceed 1 to 5% of the volume of the electrode.

To create an alloying electrode which contains nanoparticles, the SHS method (self-propagating high-temperature synthesis) is widely used. However, obtaining such electrodes is technologically complex and economically expensive. Based on this, it should be noted that it is necessary to study the possibility of obtaining nanostructured coatings by the ESA method in a simpler way, namely, using special technological media created between the anode and cathode (part) and including nanocrystalline particles of a dosed amount.

The authors have shown that the introduction of the special processing media (SPM) into the inter-electrode space during the ESA process makes it possible to obtain the coatings from non-conductive materials such as sulfur,[20] boron,[21] and nitrogen[22] and create complex coatings.[3] Moreover, the use of the SPM provides an opportunity for significantly improving the quality indicators of the surfaces

being treated, for combining such properties as running-in ability, corrosion resistance, and heat resistance, wear resistance, etc., and also for increasing the reliability and durability of responsible machine parts.

To create the SPM-containing nanoparticles, polymers are widely used as binding agents. In a polymer material containing nanofillers, the most important issue is the dispersion of the nanofillers in the polymer bulk. In practice, various methods for dispersing nanofillers in polymer bulk are used.[23] The most common technologies are ultrasonic dispersion (UD), high-speed mixing, and calendering with the use of a three-roll mixer. Carbon nanotubes are the most widely used non-metallic matrix nanofillers. Sufficient works have been devoted to the development of technology for the production and study of the structures of carbon nanomaterials.

The most widely used method for dispersing carbon nanotubes is the ultrasonic dispersion method, which allows uniformly distributing carbon nanofillers in both various solvents and low-viscosity epoxy oligomers as well as some polymers. The authors of work[24] showed that the process of mixing components by ultrasonic waves made it possible to distribute nanofillers sufficiently evenly in epoxy resin. The use of this method of the distribution of the nanotubes avoids the occurrence of the defects associated with the violation of the integrity of their structure.

The analysis of the literary sources has shown that one of the most promising methods for improving the properties of the product surface layers is the ESA method. It has been also noted that when using the SPM, the metal surfaces of the parts can be alloyed by both the conductive materials and the dielectrics, which include, for example, materials consisting of a combined matrix [epoxy resin with nanofiller (two-dimensional boron nitride and zero-dimensional silica)].[25]

Thus, the purpose of the work is to improve the quality of the surface layers of the responsible parts, which limits the life of the products. In this regard, the work is aimed at studying the peculiarities of the structure formation of the coatings obtained by the method of electrospark alloying steel surfaces using a special technological environment containing nanotubes.

RESEARCH METHODOLOGY

For conducting the study, $15 \times 15 \times 8$-mm samples were made of Armko iron. This material was chosen because when studying the coatings formed on technically pure iron, the factors of the alloying element influencing the structure formation during the ESA process could be excluded. Surface preparation of the samples was performed according to standard methods.[8]

When forming the coatings by the ESA method, molybdenum electrodes were used in the form of a wire. Table I presents the SPM compositions being investigated.

To disperse the carbon nanotubes in the matrix, the ultrasonic dispersion method was used in compliance with the technology presented in.[24] The composition of the SPM was chosen empirically. This situation was conditioned by the need to obtain a homogeneous distribution of nanoparticles in the non-metallic matrix.

The Armco iron samples had been being treated for three stages: in the first stage, the surface was alloyed with a molybdenum electrode at the discharge energy of 0.13 J or 0.52 J. At the second stage, the SPM-containing nanoparticles were applied to the surface and, without waiting for them to dry, the treatment was repeated using the ESA method with a molybdenum electrode at the same discharge energy as at the first stage.

To carry out the electrospark alloying process, the ESA unit of the Elitron-22A model was applied. For the research, the discharge energies of Wp = 0.13 J and 0.52 J were used. For comparison, samples made of Armco iron without the SPM were studied after alloying by a molybdenum electrode at the discharge energy of 0.13 J or 0.52 J.

After completing the ESA process, the surface roughness was determined using a profilograph-profilometer device, model 201, produced by the Kalibr plant. The measurement results were displayed through a special device on the computer monitor in the form of graphs.

To identify the structural components by metallographic methods, the sections in different cross-sections (transverse, longitudinal, oblique), mainly relative to the processing surface, were made from the samples after the ESA process. To increase the optical contrast between different structural components and provide selective coloring, the process of chemical etching of the sections was carried out using special reagents. Manufacturing the thin sections, preparing the surfaces, and carrying out the metallographic studies were performed according to the known methods.[26] A 3% to 5% solution of nitric acid in ethyl alcohol was used as a reagent for the procedure of chemical etching of Armco iron.

The study of the microstructural parameters of the coatings was carried out on microsections using a scanning electron microscope (SEO-SEM Inspect S50-B model) equipped with an AZtecOne type energy-dispersive spectrometer with an X-MaxN20 model detector (manufactured by Oxford Instruments plc).

To analyze the Vickers hardness distribution in the surface layer and by the depth of the thin section from the surface, a NOVA 330/360 hardness tester (manufacturer: INNOVATEST Europe BV, The Netherlands) was used in accordance with ISO 6507. The load was 20 g.

Table I. SPM composition and alloying modes for obtaining functional coatings by the ESA method

Stages of applying the coatings	SPM composition	ESA modes, W_p, J
Stage I: ESA by Mo, Stage II: applying the SPM, Stage III: ESA by Mo	Multi-walled ARKEMA carbon nanotubes (0.2% by weight) in the epoxy resin of Epoxy 510 type without curing agent	0.13
		0.52

Table II. Summary data of the parameters for the obtained coatings

Electrode materials, ESA technology	SPM composition	Wp, J	Thickness of the "white" layer, μm	Micro hardness of "white" layer, HV	Continuity of "white" layer, %	Surface roughness, Ra, μm
Cathode: Armko iron, anode: Mo	Without SPM	0.13	20–30	446	50	0.98
Cathode: Armko iron, anode: Mo (stage I: ESA by Mo, stage II: applying SPM, stage III: ESA by Mo)	Multi-walled ARKEMA carbon nanotubes (0.2% by weight) in the epoxy resin of Epoxy 510 type without curing agent	0.13	30–40	608	50	1.26
		0.52	30–40	1300	70	2.67
Cathode: Armko iron, anode: Mo (stage I : ESA by Mo, stage II: applying SPM, stage III: ESA by Mo)	Multi-walled CABOT carbon nanotubes (0.25% by weight) + water with surfactant (sulfanole)	0.13	30–40	551	80	1.60
		0.52	30–40	534	70	3.33
Cathode : Armko iron, anode: Mo (stage I: ESA by Mo, stage II: applying SPM, stage III: ESA by Mo)	Single-walled Tuball Ocsial carbon nanotubes (0.01% by weight) in the epoxy resin of Epoxy 510 type without curing agent	0.13	30–40	1438	80	1.72
	Single-walled Tuball Ocsial carbon nanotubes (0.6% by weight) in polycarbonate	0.13	40-50	949	40	1.85

RESEARCH RESULTS

Analysis of the topography of the surface of the samples after ESA using the proposed method showed that the surface roughness depends on the energy parameters of alloying (Table II). The composition of SPM practically does not affect Ra.

For example, Fig. 1 represents the topographies of the surfaces of the Armco iron samples after the ESA processes at different alloying modes according to the Mo-SPM-Mo scheme. The SPM comprises 0.2% of the multi-walled ARKEMA carbon nanotubes. While analyzing the topography of the surfaces of the samples being studied, it can be concluded that with an increase in the discharge energy, the formation of a uniform and continuous coating is noted, but with increased roughness (Table 2). Figure 2 represents the surface roughness profilograms of the samples after the ESA process. While the ESA process with Wp = 0.52 J, nano-sized inclusions were formed in the coatings. They are evenly distributed in the coating surface layers (Fig. 1d).

Consider the peculiarities of the coating structure formation while processing Armco iron by the ESA method with a molybdenum electrode and using the SPM composed of the multi-walled ARKEMA carbon nanotubes (0.2%) in the epoxy resin of Epoxy 510 type without a curing agent. The ESA process was carried out at discharge energies of 0.13 and 0.52 J. Figure 3 shows the microstructures of the coatings and Vickers hardness distribution.
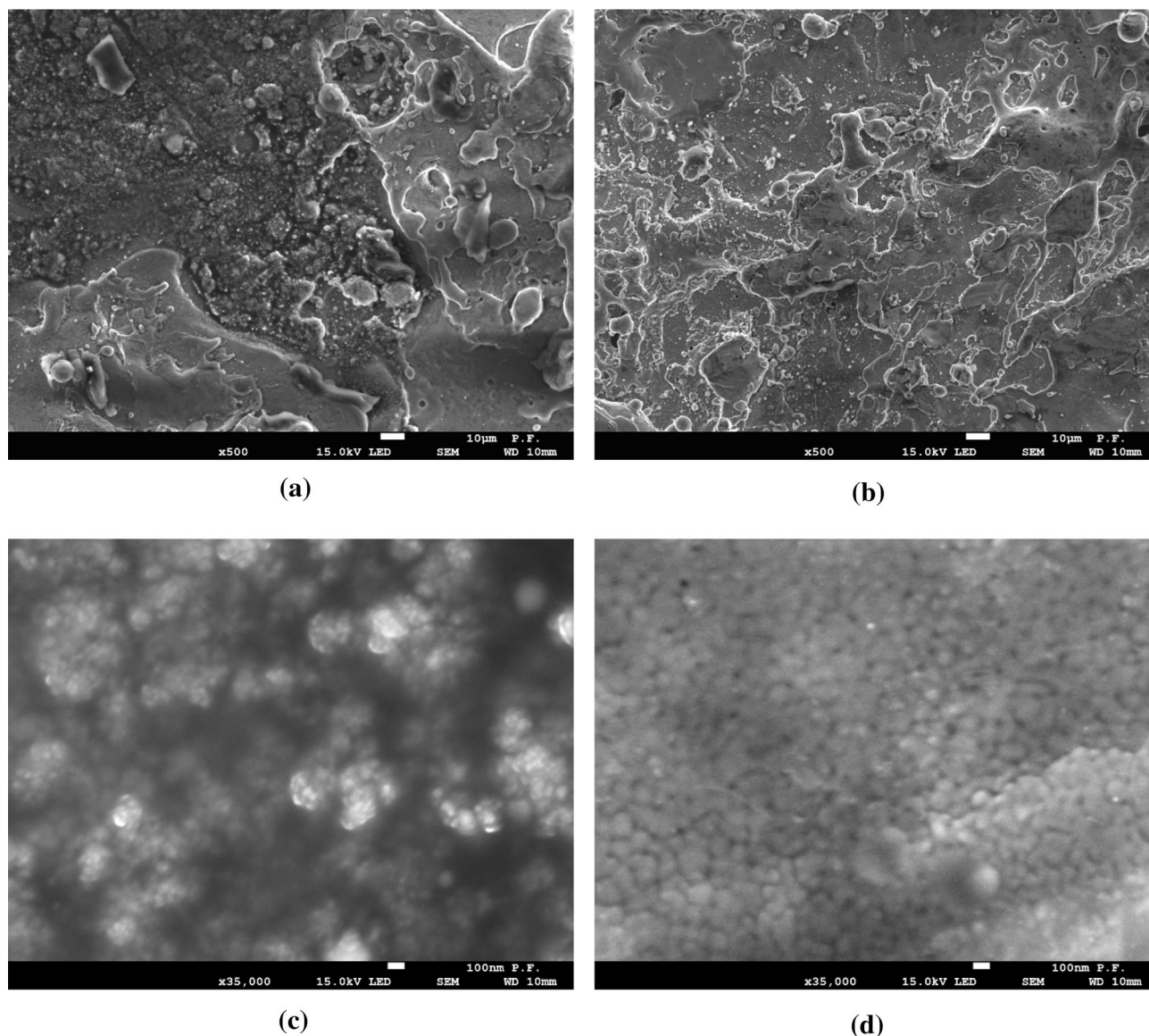
Fig. 1. Topographies of the surface areas of the Armco iron samples after the ESA process by molybdenum and SPM components [multi-walled ARKEMA carbon nanotubes (0.2% by weight) in the epoxy resin of Epoxy 510 type without curing agent] at different magnifications: (a, c) after the ESA process by the Mo-SPM-Mo at Wp = 0.13 J; (b, d) after the ESA process by the Mo-SPM-Mo at Wp = 0.52 J.

The microstructure after ESA process consists of three zones, namely, the upper "white" layer, which is not etched in the reagent, the diffusion zone and the base with a ferrite structure corresponding to Armco iron. While processing Armco iron, with an increase in the discharge energy, the thickness and continuity of the coating increase. In addition, there is an increase in hardness from 446 to 1300 HV. It is necessary to note the effect of ARKEMA nanotubes on the hardness characteristics. At the ESA process with Wp = 0.13 J, the coatings without the SPM have hardness of 446 HV, those with ARKEMA nanotubes (0.2%) 608 HV. There is also a slight increase in the thickness of the "white" layer and the continuity of the coating due to the use of the SPM (Table 2). Obviously, the positive effect of the

nanotubes on the quality parameters and the properties of the coatings is related to the formation of the nanostructures (Figs. 4 and 5). In the microstructures, the nanoscale phases of 40 to 60 nm size are found, and they are evenly distributed in the coatings.

Figures S1 and S2 in the supplementary material present the maps of the distributions of the elements in the electrospark coatings obtained at Wp = 0.13 J and Wp = 0.52 J using the SPM composed of multi-walled ARKEMA carbon nanotubes (0.2%) in epoxy resin of Epoxy 510 type without a curing agent. Because of the ESA process, coatings with a uniform distribution of molybdenum are formed. Generally, during the ESA process, carbon, apparently in the form of carbon nanotubes, has
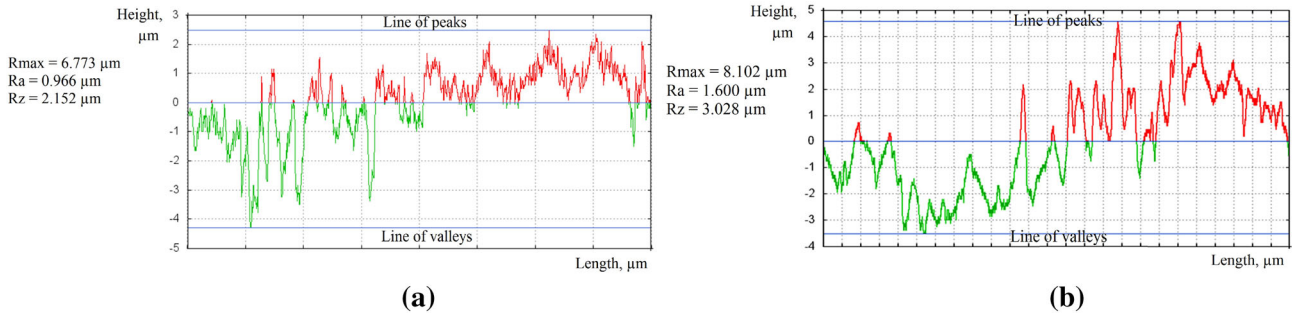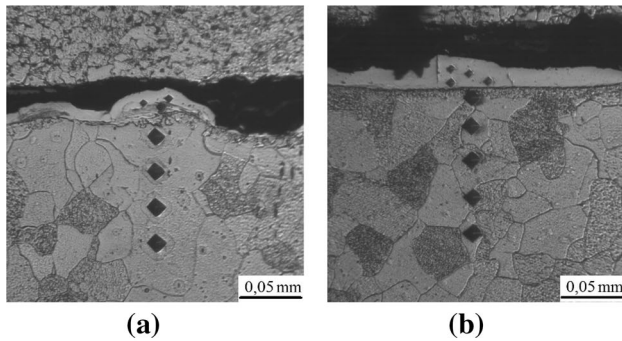
(a)

(b)

Fig. 2. Profilograms of the surface roughness of the samples after the ESA process: (a) without the SPM, (b) after the ESA process by Mo-SPM-Mo [SPM: multi-walled CABOT carbon nanotubes (0.25% by weight) + water with a surface active agent, namely surfactant (sulfanole)], Wp = 0.13 J.
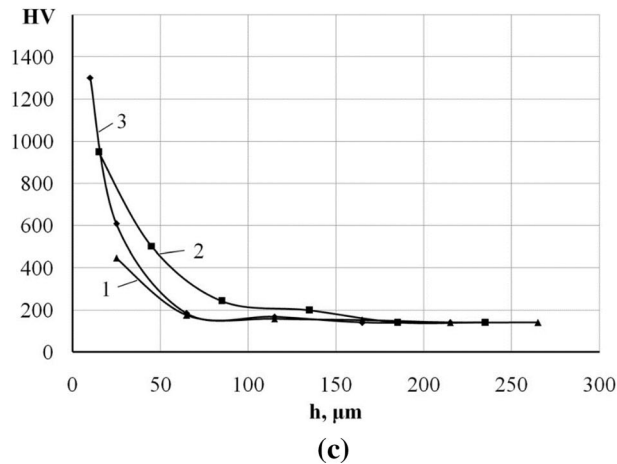

(a)   **(b)**

(c)

Fig. 3. Microstructures (a-b) and distribution of microhardness (c) in coatings on samples made of Armco iron after the ESA process by Mo-SPM-Mo; the SPM is composed of multi-walled ARKEMA carbon nanotubes (0.2%) in the epoxy resin of Epoxy 510 type without a curing agent : (a) coating obtained at Wp = 0.13 J; (b) coating obtained at Wp = 0.52 J; on the graph (c): 1: without the SPM, Wp = 0.13 J; 2: Wp = 0.13 J; 3: Wp = 0.52 J.

been being concentrated on the surfaces of the samples being processed regardless of the discharge energy values.

There is a need to consider the peculiarities of coating structure formation during processing of Armco iron by the ESA method with a molybdenum electrode and using the SPM composed of multi-walled CABOT carbon nanotubes (0.25% by weight) in water with a surfactant (sulfanole). The ESA
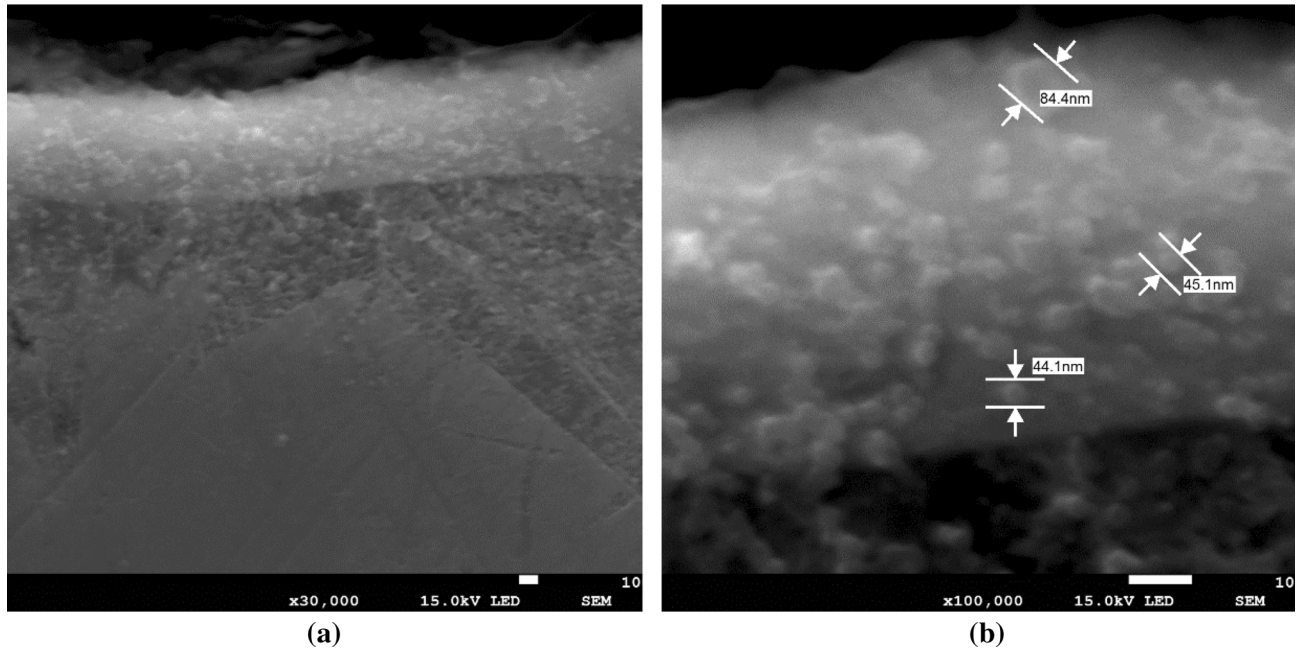
process was carried out at discharge energies of 0.13 J and 0.52 J. Figure 6 shows the microstructures of the coatings and dependences of Vickers hardness distribution.

As in the previous study, the microstructure after the ESA process consists of three zones, namely, the upper "white" layer, which is not etched in the reagent, the diffusion zone and the base with a ferrite structure corresponding to Armco iron. A thin discontinuous layer is formed on the surface of the sample subjected to alloying process without the SPM. While processing the Armco iron sample with the use of the SPM at the same mode, a change in the coating parameters is observed. The thickness and continuity of the coating increase. In addition, there is an increase in the hardness values from 446 to 551 HV. Further increasing of the discharge energy values has no effect on increasing the hardness and continuity of the coating (Table II).

There is a need to consider the peculiarities of the coating structure formation during processing Armco iron by the ESA method with a molybdenum electrode and using the SPM composed of the following:

1. A single-walled Tuball Ocsial carbon nanotube (0.01% by weight) in the epoxy resin of Epoxy 510 type without a curing agent.

2. The single-walled Tuball Ocsial carbon nanotubes (0.6% by weight) in polycarbonate.

The ESA process was carried out at discharge energies of 0.13 J. Like the classic electrospark coatings, the above ones each also consists of a "white" layer, a diffusion zone and a ferrite structure of Armco iron (Fig. 7). The thickness and hardness values of the obtained coatings are affected only by the compositions of the SPMs. The discharge energy values and the initial electrode materials did not change for this study. Notably, the availability of the nanotubes in the course of the ESA process has a positive effect on the quality parameters of coatings obtained. Thus, the content of the Tuball Ocsial nanotubes for 0.01% in the SPM contributes to increasing the continuity, thickness, and hardness from 446 to 1438 HV, i.e., three times. A further increase in the content of the

Fig. 4. Microstructures of coatings on the Armco iron samples after the ESA process, the Mo-SPM-Mo coating is obtained at Wp = 0.13 J, the SPM is the multi-walled ARKEMA carbon nanotubes (0.2%) in the epoxy resin of Epoxy 510 type without a curing agent: at magnifications: (a) 30,000 times and (b) 100,000 times.
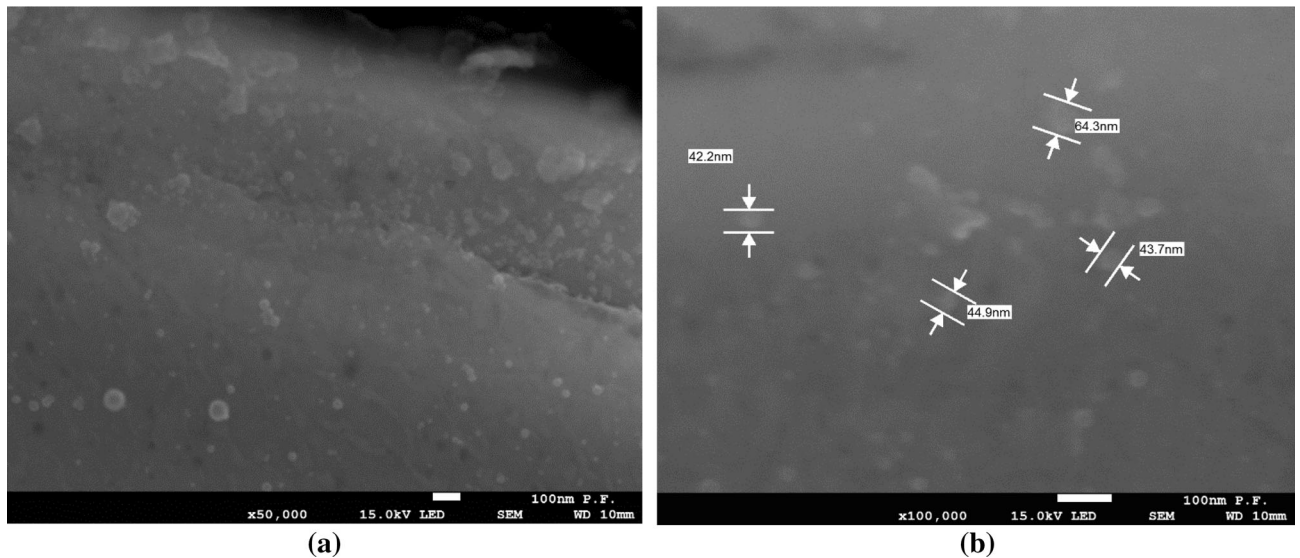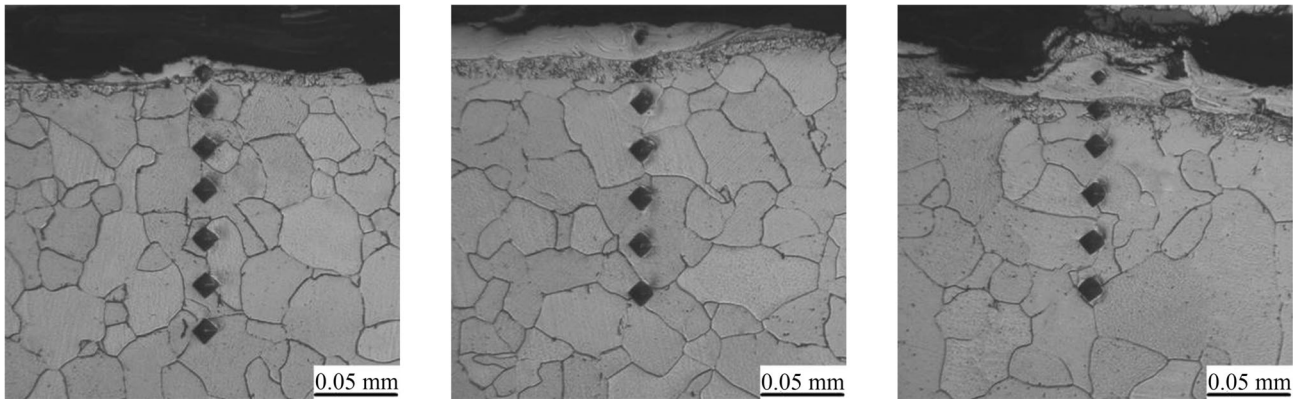

Fig. 5. Microstructures of the coatings on the Armco iron samples after the ESA process, the Mo-SPM-Mo coating obtained at Wp = 0.52 J, the SPM is the multi-walled ARKEMA carbon nanotube (0.2%) in the epoxy resin of Epoxy 510 type without a curing agent: at magnifications: (a) 50,000 times, (b) 100,000 times.

nanoparticles up to 0.6% has no effect on ensuring the quality indicators of the coatings. In this case, sufficient continuity is not provided (Table II).

Analysis of the microstructure of the coating, which had been obtained applying the ESA method by the molybdenum electrode without using the SPM, has shown that the dendritic structure has been being formed during the course because of carrying out the process of accelerated cooling after processing (Fig. 8, a). The introduction of the SPM

containing Tuball Ocsial nanotubes (for 0.01% by weight) significantly affects the microstructure of the coating. In the surface layer, there is a sharply defined zone of the crystals directed normally to the surface (Fig. 8b–d). This testifies to the directed and accelerated heat removal during the crystallization process. Because of adding the nanotubes to the SPM, the process of grinding the crystallites is also noted in the coating.
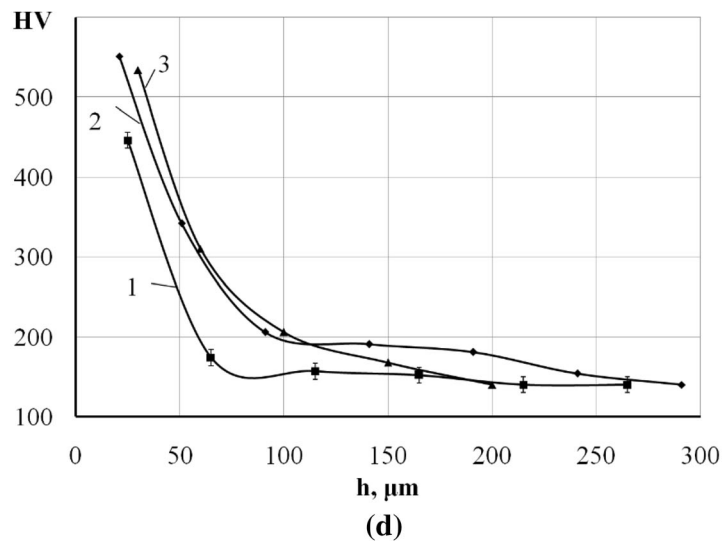
Fig. 6. Microstructures (a-c) and distributions of microhardness (d) in the coatings on the Armco iron samples after the ESA process by the Mo-SPM-Mo; the SPM is composed of multi-walled CABOT carbon nanotubes (0.25% by weight) in water with a surfactant (sulfanole): (a) without SPM, Wp = 0.13 J; (b) the Mo-SPM-Mo coating obtained at Wp = 0.13 J; (c) the Mo-SPM-Mo coating obtained at Wp = 0.52 J; on the graph (d): 1: without SPM; 2: the Mo-SPM-Mo coating obtained at Wp = 0.13 J; 3: the Mo-SPM-Mo coating obtained at Wp = 0.52 J.

The introduction of the Tuball Ocsial nanotubes for 0.6% in the SPM significantly changes the structure. No dendritic structures are detected (Fig. 9a). In the surface layer of the coating, the nanoscale inclusions of 90 nm to 130 nm (Fig. 9b) are recorded in the matrix, which is similar to the amorphous state, and these inclusions have different chemical compositions compared to those of the coatings, as evidenced by the image of the microstructure in a backscattered electron detector (BED) (Fig. 9c). Notably, the samples being studied were subjected to ESA treatment by a molybdenum electrode at Wp = 0.13 J. Thus, the changes in microstructure are associated with the influence of the nanotubes on the structure formation.

Figure 10 shows the results of the electron microscopic studies. Those are clear from the areas of the surface layers on the Armoco iron samples after the ESA process at Wp = 0.13 J: without the SPM (Fig. 10a) and with the SPM, which contains Tuball Ocsial carbon nanotubes in the amount of 0.01% by weight (Fig. 10b). The distribution of the carbon, iron and molybdenum along the depth of the layer is also shown. The results of the analysis
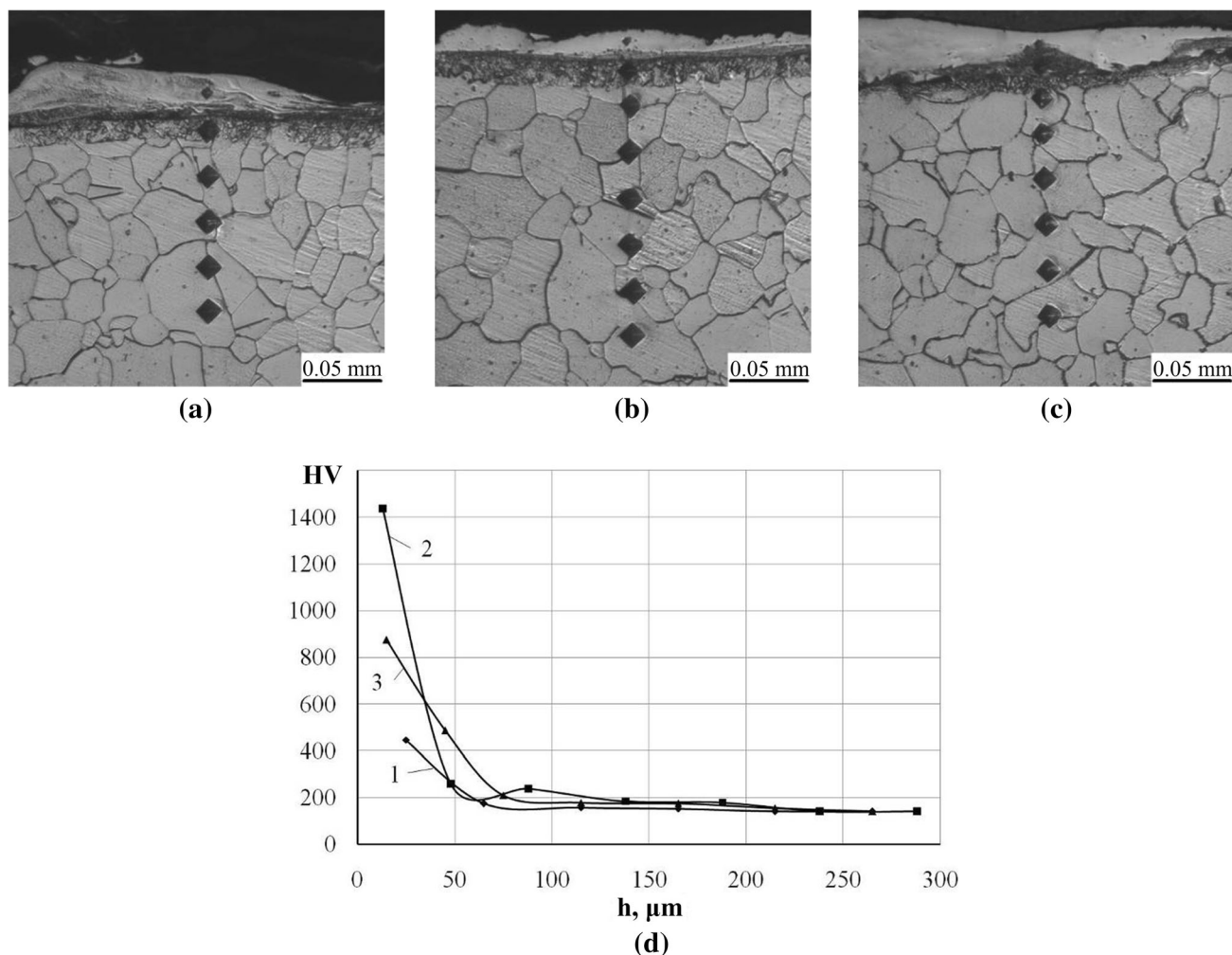
Fig. 7. Microstructures (a-c) and distributions of microhardness (d) of the Armco iron samples after the ESA process by Mo-SPM-Mo: a: without the SPM; b: the Mo-SPM-Mo coating obtained at Wp = 0.13 J, the SPM: the single-walled Tuball Ocsial carbon nanotubes (0.01% by weight) in the epoxy resin of Epoxy 510 type without a curing agent; c: the Mo-SPM-Mo coating obtained at Wp = 0.13 J, the SPM: the single-walled Tuball Ocsial carbon nanotubes (0.6% by weight) in polycarbonate; on graph (d): 1: without the SPM; 2: Mo-SPM-Mo coating; the SPM contains Tuball Ocsial nanotubes (0.01% by weight); 3: Mo-SPM-Mo coating; the SPM contains Tuball Ocsial nanotubes (0.6% by weight).

indicate that the carbon content remains unchanged in both cases; the diffusion zone of molybdenum is 12 to 14 microns. The addition of nanotubes to the SPM contributes to obtaining the uniform chemical composition and continuous coating.

CONCLUSION

1. The analysis of the topography of the sample surfaces after the ESA process by molybdenum and with the use of SPM has shown that with an increase in the discharge energy, the formation of a uniform and continuous coating is noted, however, with increased roughness. In addition, the coating contains the nano-sized inclusions, which are evenly distributed in the surface layer.

2. Features of the coating structure formation during ESA processing of the Aarmco iron by the molybdenum electrode using the SPM composition of the multi-walled ARKEMA carbon nanotubes (0.2%) in Epoxy 510 type resin without a curing agent were considered. The microstructures after the ESA process consist of three zones: the upper "white" layer, which is not etched in the reagent, the diffusion zone and the base of a ferrite structure corresponding to the Armco iron. While processing the Armco iron, with an increase in the discharge energy, the thickness and the continuity of the coating increases. In addition, there is an increase in hardness from 608 HV to 1300 HV. The positive effect of the nanotubes on the quality parameters and hardness of the coatings is associated with the formation of the nanostructures. In the microstructures, the nanoscale phases of 40 nm to 60 nm are detected, and they are evenly distributed in the coatings. Because of the ESA process, coatings with a uniform distribution of molybdenum are formed. Carbon, apparently in the form of the carbon
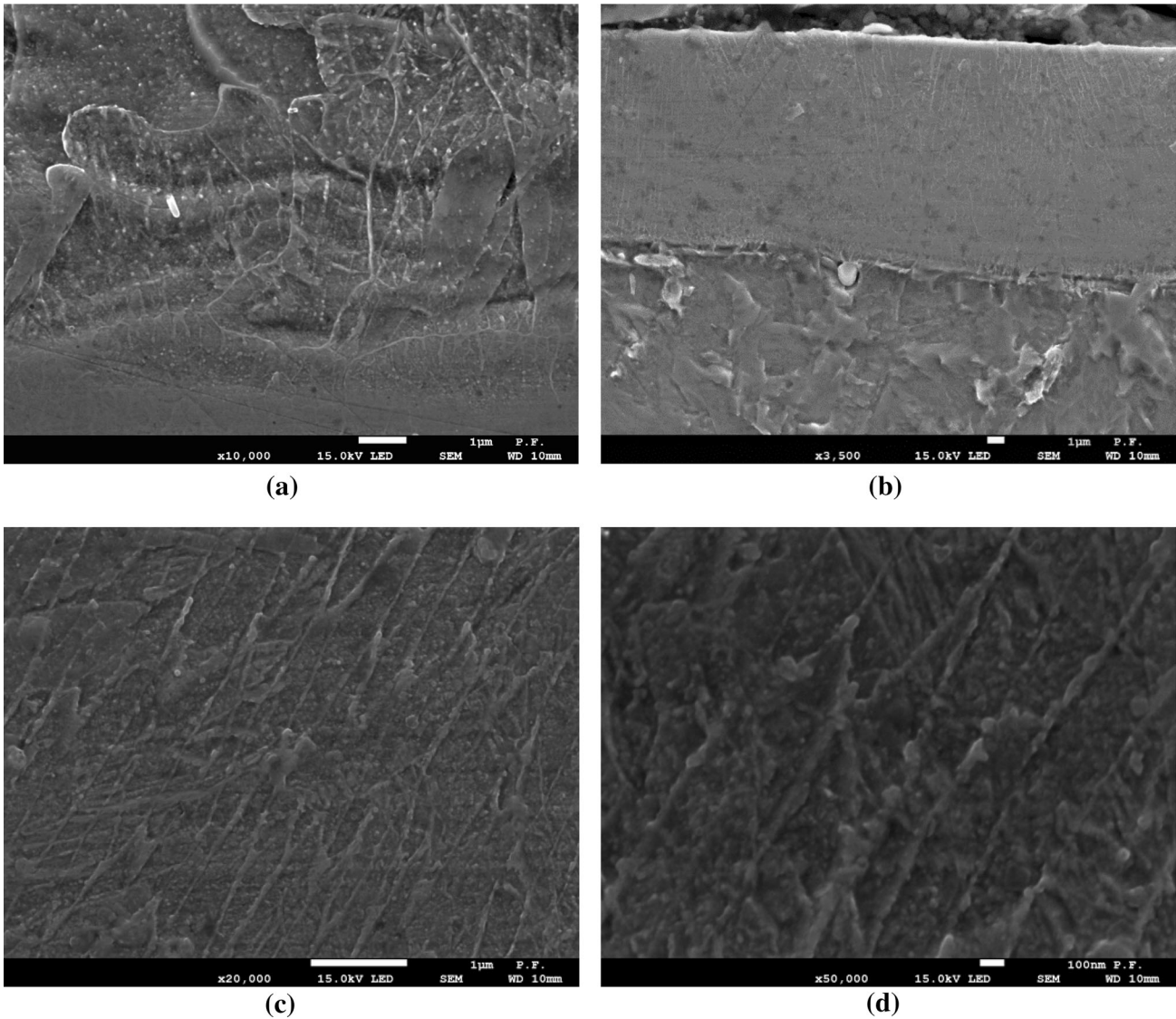
Fig. 8. Microstructures of the coatings on the Armco iron samples obtained after the ESA: (a) without the SPM at Wp = 0.13 J, (b-d) Mo-SPM-Mo coating obtained at Wp = 0.13 J, the SPM: single-walled Tuball Ocsial carbon nanotubes (0.01% by weight) in the epoxy resin of Epoxy 510 type without a curing agent: at magnifications of (b) 3500 times, (c) 20,000 times, (d) 50,000 times.

nanotubes, is concentrated on the surfaces of the samples being processed, regardless of the discharge energy during the ESA process.

3. Features of the coating structure formation in the course of the ESA processing the Aarmco iron by the molybdenum electrode using the SPM composition of the multi-walled CABOT carbon nanotubes (0.25% by weight) in the water with a surfactant (sulfanole) have been considered. A thin discontinuous layer is formed on the surface of the sample subjected to alloying without the SPM. While processing the Armco iron with the SPM on the same mode, changes in the coating parameters are observed. The thickness and continuity of the coating increase. An increase in hardness from 446

HV to 551 HV is noted. Further growth of the discharge energy does not have any effect on increasing hardness and continuity of the coating.

4. We considered the features of the coating structure formation during the ESA processing the Aarmco iron by the molybdenum electrode using the following SPM compositions:

(1) Single-walled Tuball Ocsial carbon nanotubes (0.01% by weight) in the Epoxy 510 type resin without a curing agent.

(2) Single-walled Tuball Ocsial carbon nanotubes (0.6% by weight) in polycarbonate.

The presence of the nanotubes during the ESA process has a positive effect on the quality parameters of the coatings. Thus, the content of Tuball Ocsial nanotubes for 0.01% in the SPM helps to
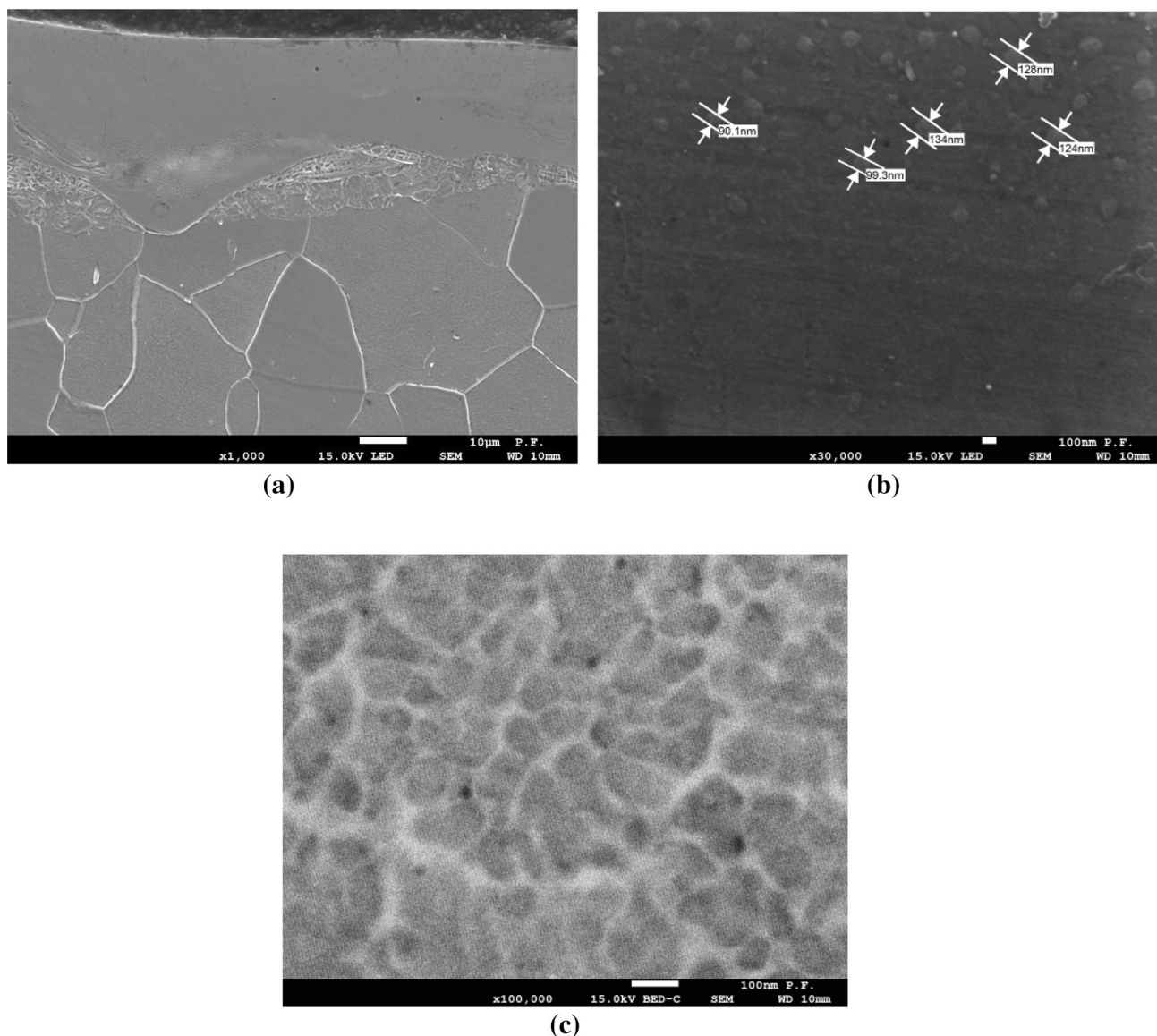
Fig. 9. Microstructures of the coatings on the Armco iron samples after the ESA process; Mo-SPM-Mo coating is obtained at Wp = 0.13 J, SPM: single-walled Tuball Ocsial carbon nanotubes (0.6% by weight) in polycarbonate: at magnifications: (a) 1000 times, (b) 30,000 times, (c) 100,000 times.

increase the continuity, thickness and hardness from 446 to 1438 HV, i.e., three times. A further increase in the content of the nanoparticles up to 0.6% has no effect on ensuring the quality indicators of the coatings. The introduction of the SPM containing Tuball Ocsial nanotubes (0.01% by weight) significantly affects the microstructure of the coating; the addition of the nanotubes to the SPM contributes to grinding of crystallites in the coating and to forming nanoscale inclusions of 90 nm to 130 nm in the matrix, which is similar to the amorphous state, and these inclusions have a different chemical composition compared with that of a coating.

5. The introduction of the nanotubes into the SPM has a positive effect on the quality parameters of ESA coatings. The single-walled Tuball Ocsial carbon nanotubes for 0.01% and multi-walled ARKEMA carbon nanotubes for 0.2% are the most effective. The positive effect of nanotubes is
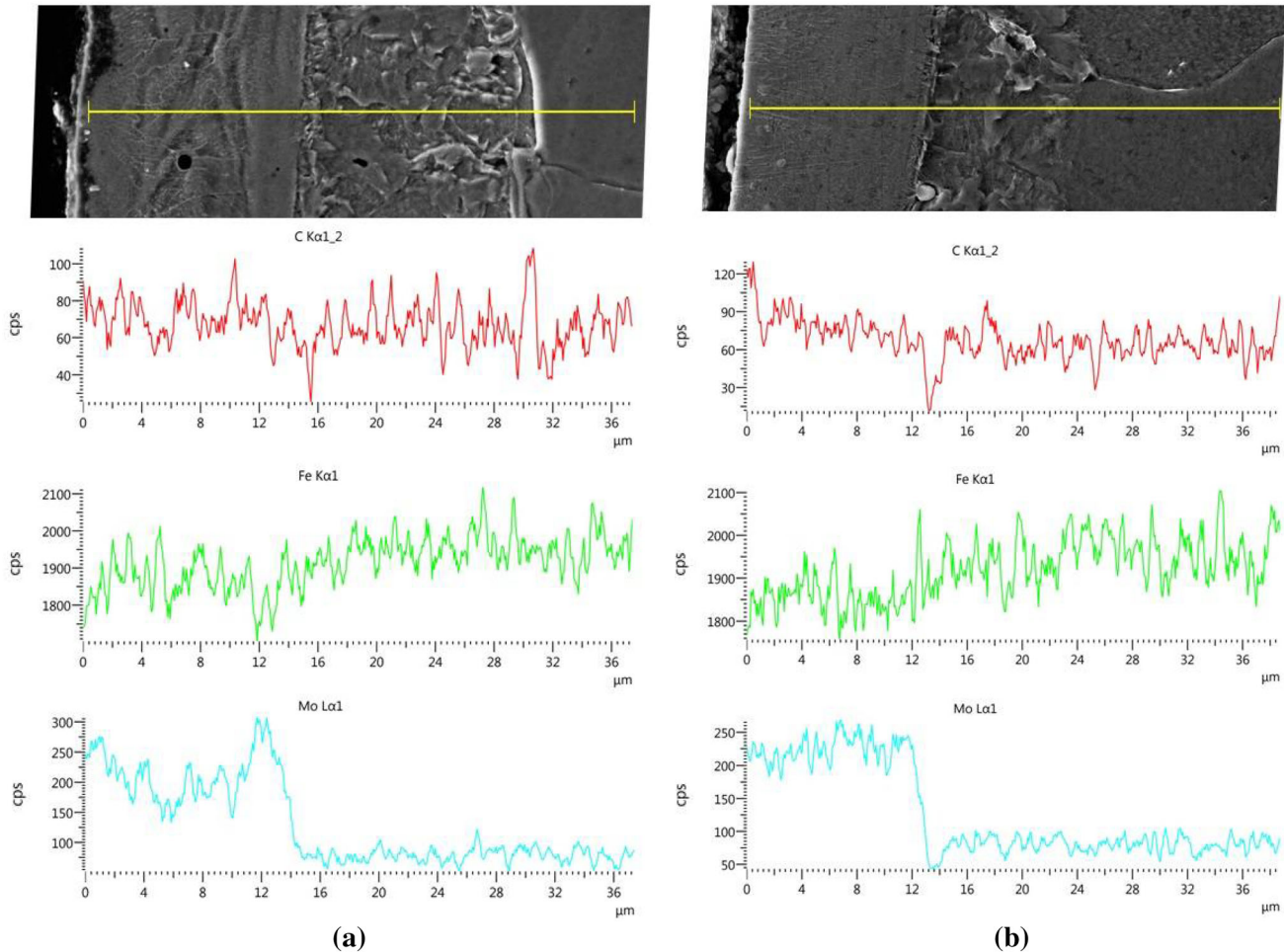
Fig. 10. Distribution of the elements in the electrospark coatings obtained at Wp = 0.13 J: (a) without the SPM, (b) with the SPM containing the Tuball Ocsial carbon nanotubes in the amount of 0.01% by weight.

associated with the formation of a nanostructure in the coating. Their introduction to the SPM helps to increase hardness and continuity.

CONFLICT OF INTEREST

On behalf of all authors, the corresponding author states that there is no conflict of interest

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