

INVESTIGATION OF CARBON CATHODE SURFACE BEFORE AND AFTER THE PASSAGE OF COMBINED DC VACUUM ARC WITH SUPERIMPOSED HIGH-CURRENT ARC PULSES

V. Zavaleyev^a, J. Walkowicz^a, D. Moszyński^b

^a*Faculty of Technology and Education, Koszalin University of Technology, Koszalin, Poland;*

^b*Institute of Chemical and Environment Engineering, West Pomeranian University of Technology, Szczecin, Poland*

E-mail: viktor.zavaleyev@tu.koszalin.pl, zavaleyev@list.ru

The paper presents the results of studies of carbon cathode surface before and after the passage of the combined DC vacuum-arc with superimposed high-current arc pulses. Investigations of surface morphology of carbon cathode showed, that secondary nuclei of high-density are formed after passing of the combined DC-pulse vacuum-arc, which results in the formation of a globular structures. The phase structure analysis by Raman spectroscopy showed that even at a minimum operation time (5 s) of the combined DC-pulse vacuum-arc broadening of the peaks 1355 and 1583 cm^{-1} occurs, which means that the carbon cathode surface undergo phase transformation. Results obtained by XPS spectroscopy demonstrate that the globular structures formed on the cathode surface are composed of sp^3 -bonded carbon atoms and carbon-oxygen bonds.

INTRODUCTION

The first studies of the graphite materials were conducted by Tuinstra and Koenig. In the work [1] they studied Raman spectra of single crystals of graphite, pyrolytic graphite, commercial graphite and soot. Raman spectrum of single crystal of graphite contains a single peak at 1575 cm^{-1} corresponding to the E_{2g} mode of oscillation of the crystal lattice. In the Raman spectra of other carbon materials, along with the peak at 1575 cm^{-1} , an additional peak is observed at 1355 cm^{-1} . The appearance of this second peak was attributed to the presence of graphite crystallites of small size and excitation inside them of standing waves corresponding to the longitudinal acoustic mode of oscillations of the A_{1g} type. Another explanation, related to the presence of disordered carbon material, in particular with the diamond-like bonds, was rejected by the authors. Tuinstra's and Koenig's data were confirmed by calculations of Raman spectra of carbon materials with graphite crystallites of different size (with varying degrees of disorder), done by Lespade et al. [2]. Sensitivity of Raman spectra to the crystallite size was also confirmed by the studies conducted for highly ordered pyrolytic graphite (HOPG), glassy carbon and diamond after argon- or nitrogen ion implantations at different temperatures [3–5]. Measurements have shown that after ion implantation on the surface of the samples both amorphous-like and hydrogenated-like carbon structures were observed. The amount of the amorphous-like structure increased with increasing ion fluence and decreasing sample temperature. Khomenko et al. [6] investigated the interatomic bonds in the transitional forms of carbon by measuring the radial distributions of the electron density. The authors observed peak at 1.58 Å, which in their opinion, is formed by superposition of graphite and diamond-like peaks. They suggested that the diamond-like structures are far from perfect diamond and their size is very small, not exceeding 6...8 Å. The presence

of nuclei of this size does not contribute to the interatomic distance, and therefore only graphite peaks are observed. The presented review of the literature data shows that the study of various graphite structures was the subject of many scientific papers, but the investigations of graphite surface after passage of the vacuum arc are almost unmentioned. In [7] the authors examined the structure of the graphite cathode surface after passage of a stationary vacuum arc. They also observed the formation of surface globular structures, but they did not carried out in-depth studies of the structures.

This paper presents the results of investigations of graphite cathodes surface before and after the passage of combined DC vacuum-arc with superimposed high-current arc pulses. The subject of the study was the influence of combined DC-pulsed vacuum-arc on the graphite cathode surface and the nature of the formed globular structures.

EXPERIMENTAL DETAILS

Experiments were performed in an industrial vacuum-arc device C55CT made by the German company INOVAP GmbH for the deposition of DLC coatings from graphite cathodes [8]. The cathodes of the arc source used in the experiments, 70 mm in diameter, were made from pure graphite. The DC-arc current of 50 A with superimposed high-current arc pulses of 1400 A, normally used for ta-C coatings deposition, was used in the experiments. The pulse duration was set to 300 μs and the pulsing frequency was fixed at 100 Hz. Argon gas (99.999% purity) was used to improve operation stability of vacuum arc. The vacuum chamber was pumped out to a pressure of $1 \cdot 10^{-3}$ Pa. Fig. 1,a,b,c shows photographs of the surface of the graphite cathodes that were studied in this work. In our experiments we used industrial graphite with a grain size of 9 μm .

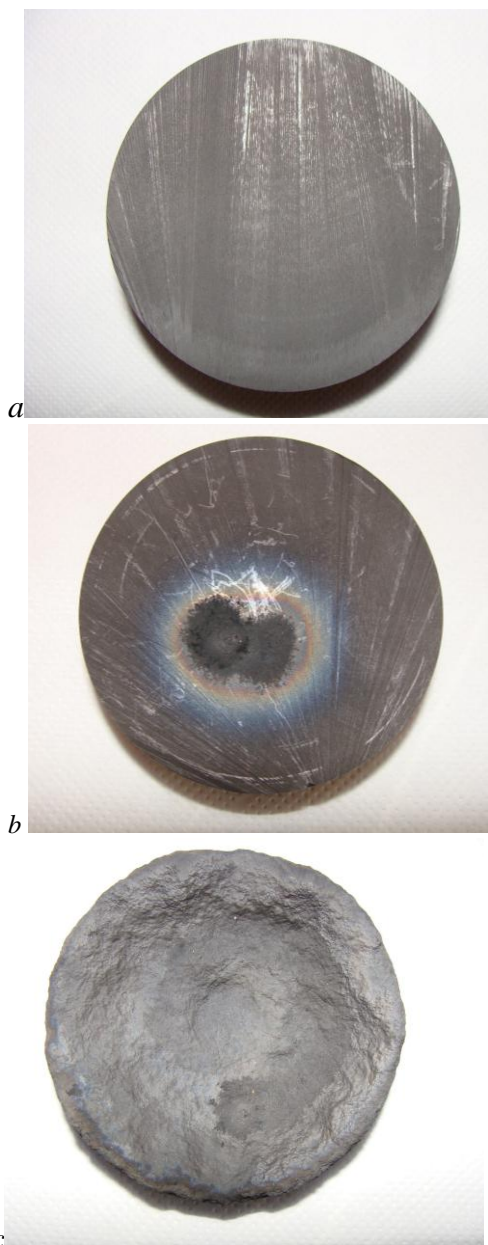


Fig. 1. Photographs of the surface of carbon cathodes: the new graphite cathode (a); the surface of the graphite cathode after minimum duration (5 s) of passage of the combined DC-pulsed vacuum-arc (b); the surface of the graphite cathode after 3 hours of ta-C coating deposition (c)

A detailed study of the surface of the graphite cathodes were performed with a scanning electron microscope JSM-5500 LV of the company JEOL. The XRD patterns, used to investigate the changes in the phase composition of graphitic cathodes, were recorded using a Philips X'Pert PRO and Dron-3M Bragg-Brentano diffractometers with Cu-K α radiation. X-ray diffraction (XRD) was carried out with step interval of 0.1° in the range of scattering angles $2\theta = 25 \dots 110^\circ$ and the acquisition time of 20 s. In order to ensure high sensitivity and resolution of the X-ray analysis the monochromatization of the X-ray beam was performed using pyrolytic graphite [9].

Measurements of Raman spectra were carried out using the device Renishaw inVia, the Raman scattering

spectrometer working at the wavelengths of 514 and 785 nm in the geometry of the reverse scattering. Raman spectra were stimulated by radiation of an argon-ion laser with the power of 50 mW and energy equal to 2.41 eV (514 nm) focused on a sample in a spot with the diameter of $\sim 1 \mu\text{m}$. The use of the maximal power resulted in essential local overheating of the sample and changed the spectra, that's why reproducible results were obtained at decreased power of the incident radiation to 1.5 mW. In order to analyze the position, intensity, and line width of the peaks, of visible spectrums were fitted two Gaussian peaks. For consistency with the published literature, we define these two peaks as G and D respectively [10].

The X-ray photoelectron spectra were obtained using Al-K α ($h\nu = 1486.6 \text{ eV}$) radiation with a Prevac system equipped with Scienta SES 2002 electron energy analyzer operating at constant transmission energy ($E_P = 50 \text{ eV}$). The spectrometer was calibrated using the following photoemission lines (with reference to the Fermi level): $E_B \text{ Cu } (2p_{3/2}) = 932.8 \text{ eV}$, $E_B \text{ Ag } (3d_{5/2}) = 368.3 \text{ eV}$ and $E_B \text{ Au } (4f_{7/2}) = 84.0 \text{ eV}$. The instrumental resolution, as evaluated by the full-width at half maximum (FWHM) of the Ag ($3d_{5/2}$) peak, was 1.0 eV. Data processing involved background subtraction by means of "S-type" integral profile and a curve-fitting procedure (a mixed Gaussian-Lorentzian function was employed) based on a least-squares method (software Casa XPS). The experimental errors were estimated to be $\pm 0.2 \text{ eV}$ for the photoelectron peaks of carbon and nitrogen. The samples were attached to the molybdenum sample holder by means of a double-side adhesive tape. The analysis chamber during experiments was evacuated to better than $1 \cdot 10^{-7} \text{ Pa}$.

The surface composition of the samples was obtained on the basis of the peak area intensities of the C(1s) and O(1s) transitions using the sensitivity factor approach and assuming homogeneous composition of the surface layer.

RESULTS AND DISCUSSION

THE STUDY OF SURFACE MORPHOLOGY OF GRAFITE CATHODES

Investigations of the morphology of the graphite cathode surfaces were performed using scanning electron microscopy. Fig. 2,a,b,c,d shows photographs of the graphite cathode surface before and after the passage of the combined DC vacuum-arc with superimposed high-current arc pulses.

Fig. 2,a presents structure of the graphite cathode surface, which has been treated in the cutting process (the cutting surface is shown in picture 1,a). More interesting are the surface images of the graphite cathode after the passage of the combined DC-pulsed vacuum-arc (see Fig. 2,b–d). The cathode surface presented in Fig. 2,b looks like remelted and the craters are visible, which could be formed in the process of detachment from the cathode surface of the microparticles transported next with the plasma stream, which is emitted from a cathode spot. At higher resolution the "cauliflower-like" morphology of the surface can be seen, which consists of many small globules (see Fig. 2,c,d).

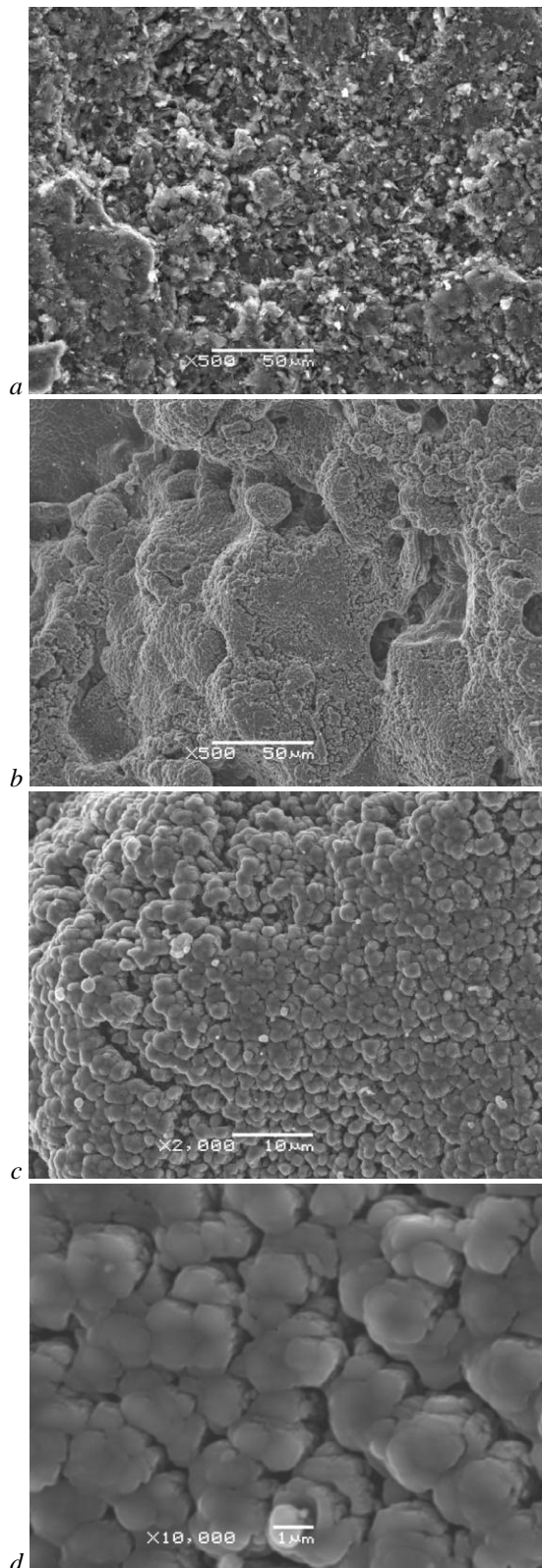


Fig. 2. Photographs of the graphite cathode surfaces made by a scanning electron microscope: the surface of the new graphite cathode (a); the surface of the graphite cathode after passage of the combined DC vacuum-arc with superimposed high-current arc pulses at different magnifications (b, c, d)

The formed structure of the cathode surface is of great interest, as such globular structures, of different types [11], are formed on the inner structural elements of fusion devices as a result of redeposition of the

installation erosion products that come into contact with the plasma. The mechanisms of erosion of the tokamak structural elements are affected by many factors (the discharge mode, the surface temperature, etc.), which leads to a synergistic effects, complicating study of the erosion processes. The synergistic effects are manifested by radiation-enhanced sublimation of graphite (i. e. erosion at high temperatures ($> 100\text{ }^{\circ}\text{C}$) when irradiated with accelerated ions and neutral atoms). The authors of [11] also report that the formation of globular forms can occur in different temperature range (from 50 to $2000\text{ }^{\circ}\text{C}$), and the surface relief has a number of hierarchical levels (i.e. large granules consist of smaller elements, which in turn consist of even smaller ones (see Fig. 2,d)). Note the similarity of the surface “cauliflower-like” morphology, to the usually seen in the CVD deposited diamond films with the use of hydrocarbon [12]. The authors of the mentioned work investigated the morphology of nanostructured diamond coatings obtained in a wide range of conditions of synthesis from the gaseous phase. The conducted studies have shown that the structure of the coating changes from globular-type to the plate-type and then back to the globular-type in a narrow temperature range. The above description of the formation of globular structures, and the paramount influence of the temperature, is in agreement with our experiments. We use in our experiments graphite cathodes. It is known that the arc spot on the graphite surface is moved not so chaotic as on the metal cathode [13, 14]. In our case, on the cathode surface there is a movement of spots of the combined DC vacuum-arc with superimposed high-current arc pulses in argon atmosphere, which locally heat the cathode and form a stream of plasma of vaporized material. The temperature of the cathode surface in the places where the cathode spot resides is high, it can be seen in the photo (see Fig. 1,b) – a colour halo is visible around the crater of the arc, which possibly leads to the formation of globular structures on the graphite cathode surface. Our hypothesis is consistent with the data of [7], where the authors investigated the surface craters on different carbon cathodes, after the passage of a constant vacuum arc of 80 A . They also observed in the investigated craters the growth of the globular structures that were formed after the passage of vacuum arc and came to the conclusion that the formation of globular structure is affected by the temperature in the cathode spot. The study of the globular structures created at the cathode surface is of great interest in understanding of the processes occurring at the graphite cathode surface during passage of the combined DC vacuum-arc with superimposed high-current arc pulses.

X-RAY DIFFRACTION

X-ray diffraction method is a useful analytical method for determining changes in the phase structure that may occur in the graphite. We conducted the research of the graphite cathodes shown in Fig. 1,a and 1,c using X-ray analysis. X-ray diffraction pattern of the original cathode from Fig. 1,a is shown in Fig. 3.

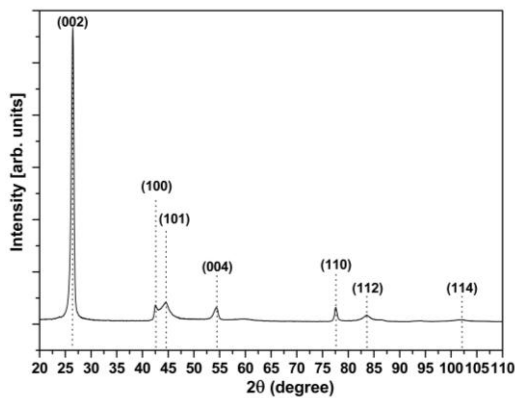


Fig. 3. XRD pattern of the original graphite cathode

As it is seen from the XRD pattern of the original cathode, 7 major peaks of graphite are present at: 26.5° , 42.3° , 44.4° , 54.5° , 74.4° , 83.6° , and 101.6° corresponding to the planes (002), (100), (101), (004), (100), (112), and (114) respectively. All visible peaks are the characteristic peaks of pure graphite [15]. The study of the cathode presented in Fig. 1,c, especially of its surface after 3 hours of the ta-C coating deposition was problematic. Due to the fact that the surface topography was not flat, it was impossible to install the cathode in the plane to get a reliable result. In order to obtain reliable results, graphite cathode was broken up into smaller pieces, the part of the pieces surface was scraped off and the resulting powder was kneaded at vacuum grease, which has no proper diffraction reflections. The mixture was placed in a quartz cuvette, included in the goniometer set, and installed in attachment for the X-ray analysis. Fig. 4 shows the XRD pattern of the powder, which was scraped from the cathode surface after 3 hours of ta-C coating deposition.

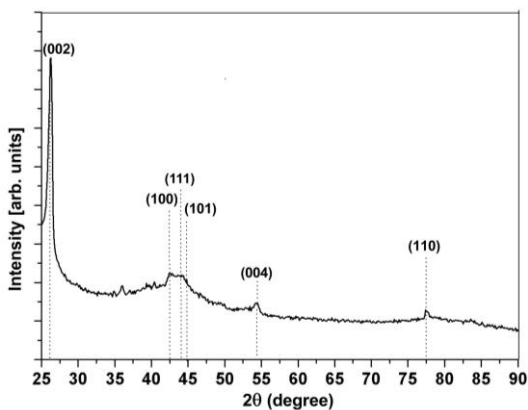


Fig. 4. The XRD pattern of the powder scraped from the cathode surface after 3 hours of ta-C coating deposition

In general, the resulting XRD pattern does not differ from the pattern, which was obtained for the original graphite cathode. But when looking at the location of the peaks corresponding to the planes (100) and (101) one can observe their broadening and also the appearance of an additional peak at 43.3° , corresponding to the diamond plane (111) [15]. In our opinion this peak appears due to the creation of the globular structure of diamond nanoparticles whose size is less than 2 nm. Within the hierarchical structure of the globules [11], the formed diamond cores are surrounded by graphite-like structures with sp^2 -bonds,

and therefore the observed diamond peak is less pronounced in the background of graphite peaks, since its intensity depends on the of diamond nanoparticles size. Our results correlate well with the results of S. Tomita et al., who investigated, using the XRD analysis, the temperature-activated transition of diamond nanoparticles of 5 nm in diameter into graphite structure [16]. As shown by S. Tomita et al., at higher temperatures the diamond core is reduced in size and the outer layers are converted into a graphite structure (they observed conversion of diamond-like sp^3 -bonds into graphite-like sp^2 -bonds). In our case, we observe the reverse transformation of graphite sp^2 -bonds into diamond sp^3 -bond. During the passage of combined DC-pulsed vacuum-arc over the graphite cathode surface, in the local overheated areas globular structures, containing diamond nanoparticles, are formed. The carried out additional studies confirm our hypothesis.

RAMAN SPECTROSCOPY

Fig. 5 presents the Raman spectra in the visible range of excitation wavelengths (514 nm) for the Raman shift within the range of $800 \dots 3000 \text{ cm}^{-1}$ for graphite cathodes, which were presented in Fig. 1,a,b,c.

Fig. 5,a shows a Raman spectrum of the graphite cathode surface shown in Fig. 1,a. The spectrum demonstrates five spectral features characterized in the work of Y. Wang et al. [3]. The first peak at 1355 cm^{-1} is due to a breathing mode of vibrations of A_{1g} symmetry (called D band), while the vibrations of E_{2g} symmetry (C-C in-plane stretching mode) corresponds to the second peak at 1583 cm^{-1} (called G band). The three following peaks are second-order Raman spectral features of graphite. The second-order Raman spectrum of graphite corresponds to the overtones and combinations of the disorder-induced bands. It results from double-resonant Raman scattering by two phonons instead of a phonon and a defect [24]. The peaks at 2455 and 2706 cm^{-1} can be attributed to overtones of fundamental modes and are assigned by Y. Wang et al. [3] as 2×1225 and $2 \times 1355 \text{ cm}^{-1}$ respectively, while the peak at 2940 cm^{-1} comes from combination of bands and is assigned as $E_{2g} + D$. All peaks identified in the spectrum presented in Fig. 5,a are consistent with the data given by Y. Wang et al., which means that the structure of graphite used as the cathode material corresponds to the structure of highly ordered pyrolytic graphite (HOPG). Fig. 5,b presents Raman spectrum obtained in the middle of the crater on the graphite cathode (see Fig. 1,b) after minimum time (5 s) of passage of the combined DC-pulsed vacuum-arc. The graph shows that after a minimum time of passage of the combined DC-pulsed vacuum-arc the graphite surface was modified into an amorphous structure. The broadening and shifting of two major spectral peaks occur, namely the peak at 1355 cm^{-1} is shifted to 1350 and the peak at 1583 cm^{-1} is shifted to 1596 cm^{-1} (due to vibrations of sp^2 -bonded carbon atoms). Moreover, the peaks at 2455 , 2706 and 2940 cm^{-1} are substantially broadened in one line and only two weak peaks at 2700 and 2900 cm^{-1} can be identified, which refer to the G band [17].

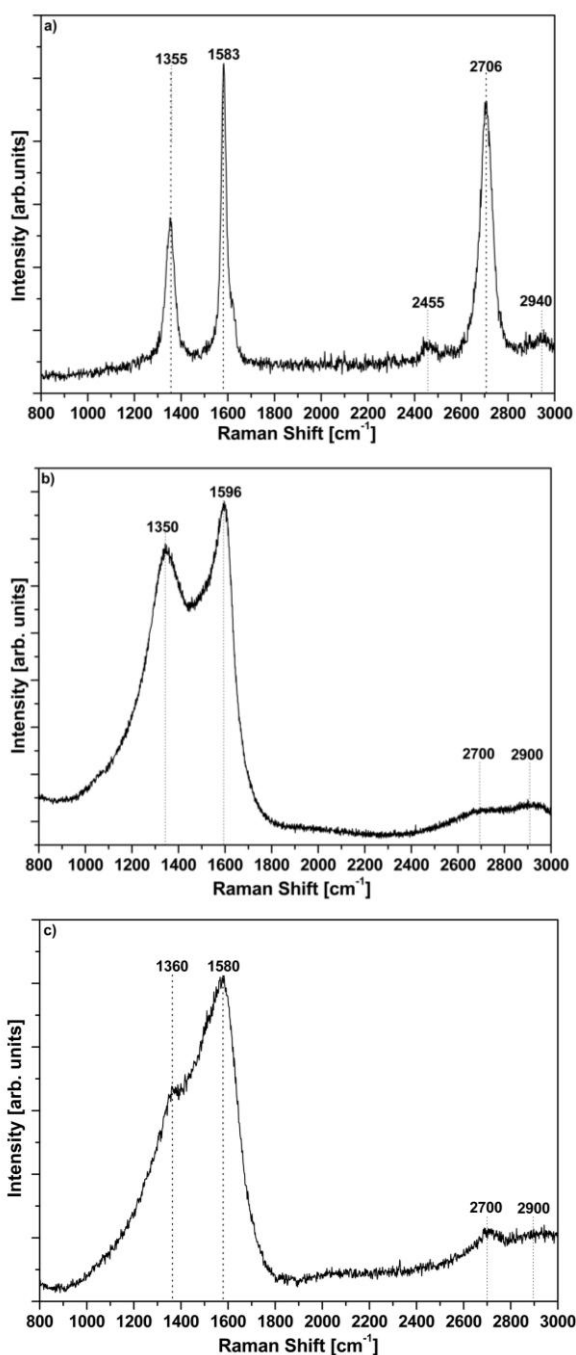


Fig. 5. Raman spectra of the surface of the graphite cathodes: spectrum of the surface of the new graphite cathode (a); spectrum made in the middle of the crater in the graphite cathode after the passage of a combined DC-pulsed vacuum-arc during 5 s (b); spectrum made at the graphite cathode surface after 3 hours of ta-C coating deposition (c)

A similar Raman spectrum was obtained by the authors of the work [18], who investigated carbon microparticles collected in a vacuum chamber, which passed through the T-FAD filter, and their Raman spectrum is very similar to the spectrum shown in Fig. 5,b. Based on these data, we can assume that in the middle of the surface crater an amorphous structure was formed, most likely consisting of nanoparticles. The Raman spectrum presented in Fig. 5,c was obtained for the graphite cathode surface after 3 hours of ta-C coating deposition (see Fig. 1,c). The spectrum contains

one broad peak centered at 1580 cm^{-1} (associated with the vibrations of sp^2 -bonded carbon atoms in the two-dimensional hexagonal lattice in a graphite layer) with weakly pronounced peak at 1360 cm^{-1} . Such a structure of the spectrum is usually observed in the spectra of the synthesized amorphous carbon coatings [19, 20], which means that the surface structure of the globules, which are present on the cathode surface is amorphous and contains a different ratio of sp^3/sp^2 -bonds. The results of Raman spectroscopy confirmed the data obtained by XRD, that the diamond nanoparticles consisting of sp^3 hybridized carbon atoms are present at the cathode surface, but because of the intensity of graphite sp^2 bonds vibrations a broad peak of amorphous structure consisting of sp^3/sp^2 -bonds is visible. For a detailed study of the possible presence of diamond nanoparticles in the globular structures at the cathode surface, we carried out additional research using XPS spectroscopy.

X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

Due to the fact that the sample size for the research using X-ray photoelectron spectroscopy must have a certain size not exceeding $10 \times 10\text{ mm}$ we investigated two samples. The first sample was made of pure graphite (see Fig. 1,a) and the second was made from one of the pieces of the graphite cathode after 3 hours of ta-C coating deposition (see Fig. 1,c), by its fracture. It was impossible to prepare such a sample from the cathode after the passage of a combined DC-pulsed vacuum-arc during 5 s (see Fig. 1,b). Detailed analysis of high-resolution XPS spectra let one learn a difference between the chemical composition of the examined surfaces. In Fig. 6 the superimposed XPS C 1s spectra acquired for both samples are shown. The maxima of these peaks are distinctly shifted what suggests that the chemical environment on the surface of both samples differs. The maximum of C 1s peak coming from the “new cathode” sample (see Fig. 1,a) is located at the binding energy of 284.6 eV . The respective maximum for the “used cathode” sample (see Fig. 1,c) is placed at the binding energy of 285.0 eV . Additionally a noticeable feature at the binding energy of 289 eV is visible in the spectrum of the “used cathode” sample.

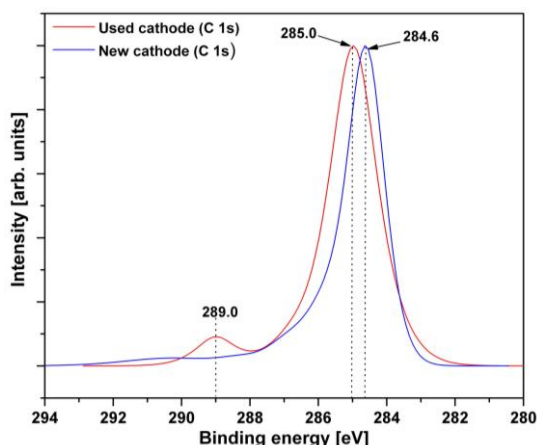


Fig. 6. C 1s deconvolution for both samples: blue line – for the new graphite cathode; red line – for the graphite cathode after 3 hours of ta-C coating deposition

The general shape of the spectrum from the “new cathode” sample is very similar to the spectra observed for graphite-like structures [20]. A relatively narrow main peak is accompanied with a diffused “tail” at the high-binding energy side of the maximum. Moreover a weak local maximum at the binding energy of 289 eV is also apparent. On the other hand the main peak of the spectrum from the “used cathode” sample is rather symmetrical, with very prominent secondary maximum at the binding energy of 289 eV. No features are observed for binding energy around 290 eV. The latter envelope resembles organic compounds with dominating sp^3 -carbons rather than containing sp^2 -carbons [22].

To differentiate the chemical species present on the surface of both samples a deconvolution was performed and its results are shown in Fig. 7,a,b.

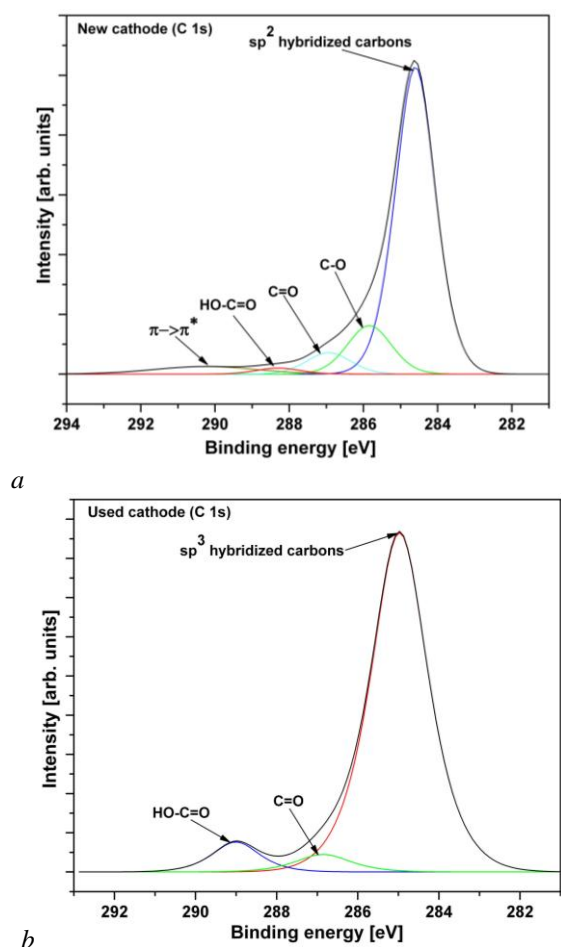


Fig. 7. C (1s) deconvolution for both samples: a – for the new graphite cathode; b – for the graphite cathode after 3 hours of ta-C coating deposition

The spectra were fitted with the use of Gaussian-Lorentzian peaks. A model containing several simulated components was required for both samples. Starting from the component located at the lowest binding energy they are attributed as follows: BE = 284.4 eV – sp^2 -hybridized carbons, from graphite-like structures, BE = 285.0 eV – sp^3 -hybridized carbons, BE = 286 eV – C–O bindings, BE = 287.0 eV – carbonyl groups, BE = 289 eV – carboxyls HO–C=O. The wide peak located at the highest binding energy of about

290 eV is ascribed to a shake-up structure caused by the $\pi \rightarrow \pi^*$ -transition in the graphite rings [23].

As mentioned before the diffused structure at about 290 eV is observed only for the “new cathode” sample Fig. 7,a, indicating that $\pi \rightarrow \pi^*$ -transitions occur only for that sample. Together with the position of the main maximum (at 284.4 eV) it can be taken as a strong evidence that the “new cathode” sample is of graphite-like structure, with dominating sp^2 carbons. Small fraction of carbon atoms is bound to oxygen atoms what gives rise to the components located at 286, 287 and 289 eV, coming from C–O, C=O and HO–C=O bonds, respectively.

The spectrum of the “used cathode” Fig. 7,b surface is dominated by peak at 285 eV originating from sp^3 -hybridized carbons. A prominent local maximum at 289 eV originates from carboxyls formed on the surface. A fairly low component from carbonyls is also present.

CONCLUSIONS

On the basis of the research results presented in the paper, the following conclusions can be drawn. It was revealed that on the surface of graphite cathodes, after the passage of the combined DC vacuum-arc with superimposed high-current arc pulses, globular structures are formed. The formation of globular structures occurs in the traces of the cathode spot passage, where local intensive heating of the cathode surface takes place. The resulting X-ray diffraction patterns obtained for the powder scraped from the graphite cathode surface after 3 hours of ta-C coating deposition showed that diamond nanoparticles of a size of less than 2 nm can be present in the globules structure. Raman spectra of the cathode surface structure, taken in the crater created after passage of the cathode spot with minimum duration of 5 s, has shown that the surface of the graphite cathode begins to be modified into amorphous structure. Raman spectra of the graphite cathode surface after 3 hours of ta-C coating deposition are identical with the spectra obtained for amorphous carbon coatings. The data obtained using XPS spectroscopy showed that at the surface of the graphite cathode, after 3 hours of ta-C coating deposition, a diamond-like phase with sp^3 -bonds dominates, and the maximum of C 1s peak is located at the energy of 285 eV. This means that the globular structures created at cathode surface are amorphous and consist essentially of diamond-like sp^3 -bonds.

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ИССЛЕДОВАНИЕ ПОВЕРХНОСТИ УГЛЕРОДНОГО КАТОДА ДО И ПОСЛЕ ПРОХОЖДЕНИЯ КАТОДНОГО ПЯТНА ВАКУУМНОЙ ДУГИ ПРЯМОГО ТОКА В КОМБИНАЦИИ С НАЛОЖЕННЫМИ СИЛЬНОТОЧНЫМИ ИМПУЛЬСАМИ

В. Завалеев, Ж. Валкович, Д. Мозинский

Представлены результаты исследования поверхности углеродного катода до и после прохождения катодного пятна вакуумной дуги прямого тока в комбинации с наложенными сильноточными импульсами. Исследования морфологии поверхности углеродного катода показали, что после прохождения катодного пятна вакуумной дуги прямого тока в комбинации с сильноточными импульсами формируются вторичные зародыши высокой плотности, в результате чего появляется глобулярная структура. Фазово-структурный анализ с использованием раман-спектроскопии показал, что даже при минимальном времени работы (5 с) вакуумной дуги происходит уширение пиков 1355 и 1583 см⁻¹, указывающее на то, что поверхность

углеродного катода подвергается фазовым превращениям. Результаты, полученные ХР-спектроскопией, показали, что глобулярные структуры, сформировавшиеся на поверхности катода, состоят из sp^3 связанных атомов углерода и углерода–кислорода.

ДОСЛІДЖЕННЯ ПОВЕРХНІ ВУГЛЕЦЕВОГО КАТОДА ДО І ПІСЛЯ ПРОХОДЖЕННЯ КАТОДНОЇ ПЛЯМИ ВАКУУМНОЇ ДУГИ ПРЯМОГО СТРУМУ В КОМБІНАЦІЇ З НАКЛАДЕНИМИ СИЛЬНОТОЧНИМИ ІМПУЛЬСАМИ

В. Завалєв, Ж. Валкович, Д. Мозинський

Представлені результати дослідження поверхні вуглецевого катода до і після проходження катодної плями вакуумної дуги прямого струму в комбінації з накладеними сильноточними імпульсами. Дослідження морфології поверхні вуглецевого катода показали, що після проходження катодної плями вакуумної дуги прямого струму в комбінації з сильноточними імпульсами формуються вторинні зародки високої щільності, внаслідок чого з'являється глобулярна структура. Фазово-структурний аналіз з використанням раман-спектроскопії показав, що навіть при мінімальному часі роботи (5 с) вакуумної дуги відбувається розширення піків 1355 і 1583 cm^{-1} , що вказує на те, що поверхня вуглецевого катода піддається фазовим перетворенням. Результати, отримані ХР-спектроскопією, показали, що глобулярні структури, що сформувалися на поверхні катода, складаються з sp^3 пов'язаних атомів вуглецю і вуглецю–кисню.