

MODIFICATION OF THE SURFACE INCLUDING BEAMS OF CHARGED PARTICLES, PHOTON FLUXES, AND PLASMA

Elemental Composition, Topography, and Wettability of the Surface of Graphite Modified by Ion-Assisted Deposition of Chromium Coatings

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Abstract—Elemental composition, roughness, and wettability of a graphite surface modified by ion-assisted deposition of a Cr coating ~300–1000 nm thick are investigated using the methods of Rutherford backscattering, atomic force microscopy, and contact angle measurements. It is established that, in addition to chromium, coatings involve hydrogen, carbon, and oxygen from residual gases of a vacuum chamber because of their incomplete pumping by vacuum pumps and 1–2 at % silicon diffusing from the graphite. It is determined that, as the coating thickness increases, the surface roughness of the modified graphite increases and becomes the predominant factor in increasing its hydrophobicity.

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1. INTRODUCTION

Deposition of thin films on various materials is of scientific and practical interest since allows one to form insulating or conducting layers and hard or elastic coatings of the surfaces of articles [1–3]. For this purpose, methods of deposition of coatings with the use of assisted irradiation with accelerated ions are widely used [4, 5]. Such irradiation can provide adhesion of the coating to the substrate at the atomic level owing to mixing of elements of the coating and the substrate located near the phase interface of the structure “deposited coating–substrate” in the cascades of atomic collisions. It is known [6–11] that such factors as the elemental and phase compositions of the coating, their structure, adhesion to the substrate, topography, and some others affect the characteristics of the modified surface of the articles. Therefore, for the deposition of coatings, diagnostics of the properties of the surface is necessary.

In this work, we discuss the results of investigation of the elemental composition, topography, and wettability of the surface of graphite modified by ion-assisted deposition of Cr coatings under conditions of irradiation with chromium ions (self-irradiation and self-ion-assisted deposition of coatings, SIAD method).

2. EXPERIMENTAL

The Cr coatings were deposited on graphite wafers with ion assistance under self-ion-assisted conditions. To do this, we applied the method with the use of a resonant ion source of the vacuum arc plasma according to the procedure reported in [12]. The experimental layout is shown in Fig. 1. Resonant ion source (1) generates

the vacuum arc discharge plasma. Its electrodes are made from the material of the deposited coating, which allows one to obtain the fluxes of neutral atoms (2) and metal ions (3). Under burning of the arc, the neutral fraction of the deposited material evaporates in various directions, including deposition on article (4). Under the effect of electric field (5), which is generated between electrodes (1) (ground potential) and high-voltage electrode with article holder (6) supplied with a negative potential, generated ions (3) are drawn out from the discharge gap and move to the article, being incorporated into its surface simultaneously with the deposition of coating (7). Under the effect of ion irradiation, atoms of the article and deposited coating are mixed in the cascades of atomic collisions. As a result, the modified surface of article (4) with thin film (7) is

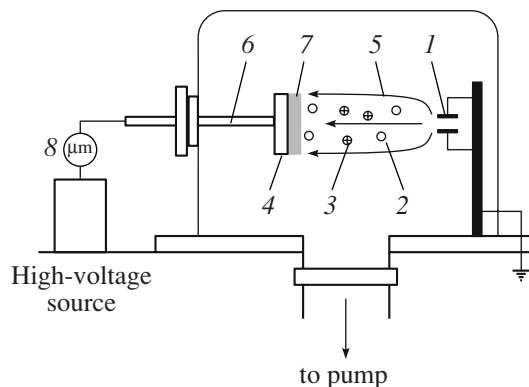


Fig. 1. Schematic diagram of self-ion-assisted deposition of coatings. Explanations see in the text.

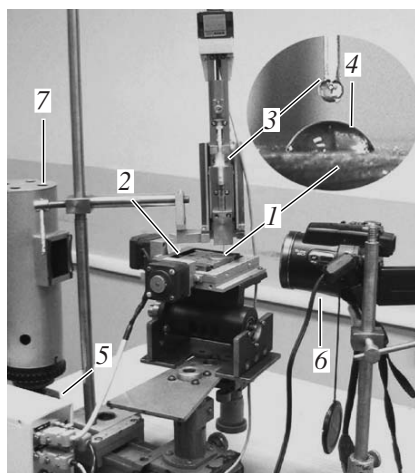


Fig. 2. Setup for the contact angle measurements. Explanations see in the text.

formed. The process of deposition of the coating is controlled by varying the operational mode of the ion source. The ion flux is varied using microammeter (8) via integration of the ion current.

The flux density of assisting ions varied in the range $I = 10^{14} - 10^{15} \text{ cm}^{-2} \text{ s}^{-1}$. Its ratio to the flux density of neutral atoms (A) was established experimentally, and in various experiments, it was $I/A = 0.2 - 0.4$. The deposition rate of coatings varied in a range of 1–5 nm/min, and the thickness of deposited layers varied in a range of 200–1100 nm. The potential supplied to the article holder for acceleration of assisting ions was 10 kV. The residual pressure during the deposition of coatings was $\sim 10^{-2} \text{ Pa}$ and the process duration was 1–12 h.

For elemental analysis of formed coatings, the Rutherford backscattering (RBS) method was used. The layer-by-layer concentration of elements was investigated via modeling the composition of the surface using the RUMP program [13], which allows one to reconstruct the experimental RBS spectrum by the elemental composition at preliminarily specified parameters of the installation and experimental conditions.

The data on hydrophilicity of the sample surface were obtained by measuring the equilibrium contact angle using the setup shown in Fig. 2.

Table 1. Characteristics of the surface topography of the starting and modified graphite samples

Coating	Deposition time, h	Average roughness, nm	Ratio total/projective area
Absent	–	24.27	1.06
Chromium	1	17.38	1.05
	3	23.71	1.04
	6	28.43	1.05
	12	34.36	1.07

A drop of bidistilled water (4) having a volume of $\sim 0.05 \text{ ml}$ was placed on the surface of sample (1) mounted on movable table of tilt-and-swivel stand (2) using medical syringe (3). The sample was positioned and the drop was extruded using stepper motors equipped with control unit (5). The sample–drop system was stabilized for 120 s. Then, using digital camera (6) having the possibility of remote shutter release, the image of the drop illuminated by monochromatic optical source (7) was recorded.

The contact angle was measured by the slope of the tangent to the drop's surface from its left and right sides using computer modeling of the location of the tangent to the three-phase line by the drop's image. This procedure was repeated ten times for five different parts of the sample surface. The air temperature during the experiment was 24°C. As the wetting liquid, we used bidistilled water. The error in determining the contact angle was less than 1%.

Since the surface topography can affect wetting, we investigated it by atomic force microscopy in the contact mode using an NT 206 multifunctional scanning atomic force microscope with Surface Explorer software for obtainment of two-dimensional and three-dimensional images of the surface and determination of its roughness.

3. RESULTS AND DISCUSSION

3.1. Surface Topography of the Modified Graphite

Surface topography of the starting graphite samples and the one modified by the deposition of chromium-based coatings is shown in Figs. 3 and 4, and its characteristics are presented in Table 1. It is established that the average roughness of the areas of the starting graphite $25 \mu\text{m}^2$ in size is 24.27 nm. After deposition of the Cr coating for 1 h, it decreases by $\sim 28\%$. Then, with time, the average roughness increases, and after 3 h, it becomes comparable with that of the starting sample, and after 12 h, it reaches a value of 34.36 nm ($\sim 141.5\%$ with respect to the starting one).

The observed surface profiles of the graphite without coating and the modified one differ from each other. The surface of the starting sample comprises the ensemble of hills having close heights (see Fig. 3a) with surface roughness of $\sim 24 \text{ nm}$. After deposition of the Cr coating for 1 h, inhomogeneities with a very high local roughness appear in the section profiles in valleys between the hills (see Fig. 3b). Since the total difference in heights over the area and, consequently, the roughness decreases, this leads to its general increase. This can indicate that the film material at the beginning of the deposition process as if slides into the depressions between the natural surface irregularities of the graphite substrate. As the deposition time and, consequently, coating thickness increase, these new formations grow and gradually occupy existing depressions, and upon attainment of a certain thickness, they exceed

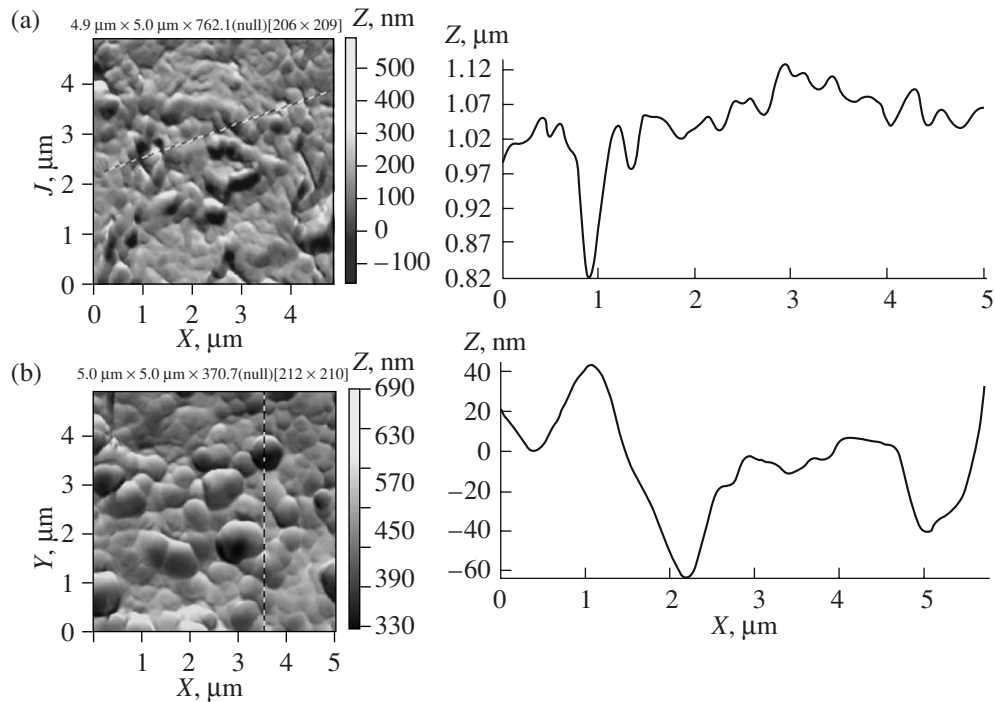


Fig. 3. Surface topography and section profile of (a) starting graphite sample and (b) graphite sample modified by self-assisted deposition of Cr coating for 1 h.

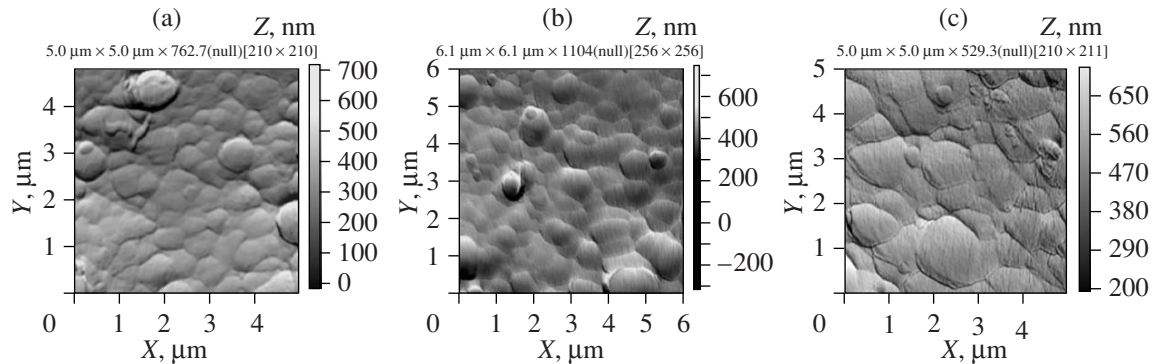


Fig. 4. Surface topography of graphite modified via deposition of Cr coatings for (a) 3, (b) 6, and (c) 12 h.

the height of the natural hills on the starting graphite surface. In this case, the roughness increases (see Fig. 4c) and becomes larger than that in the starting sample by a factor of 1.4.

3.2. Elemental Composition

Figure 5 represents the experimental RBS spectrum of helium ions from the graphite sample with the deposited Cr coating (solid line) and the one reconstructed using the RUMP modeling program (dashed line). It follows from the presented data that, in addition to chromium atoms, silicon, oxygen, and carbon are present in the coating. Moreover, when simulating the experimental RBS spectrum, we revealed that the coating composition also involves hydrogen atoms. The last

fact was confirmed in independent experiments with the use of the resonant nuclear reaction ${}^1\text{H}({}^{15}\text{N}, \alpha\gamma){}^{12}\text{C}$, which occurs during the interaction of hydrogen with N^+ ions (energy of 6.4 MeV, resonant width of 1.86 keV) [14, 15]. We believe that the presence of hydrogen, oxygen, and carbon in these coatings is associated with their ingress into the atomic flux of the material of the coating during its growth from the atmosphere of the vacuum chamber pumped by an oil-diffusion pump. The appearance of silicon in the concentration of several atomic percent in coatings is apparently caused by the effect of removal of impurity Si atoms from the near-surface region of the graphite substrate owing to the interdiffusion in much the same way as the diffusion of Ca and S atoms from rubber into metal

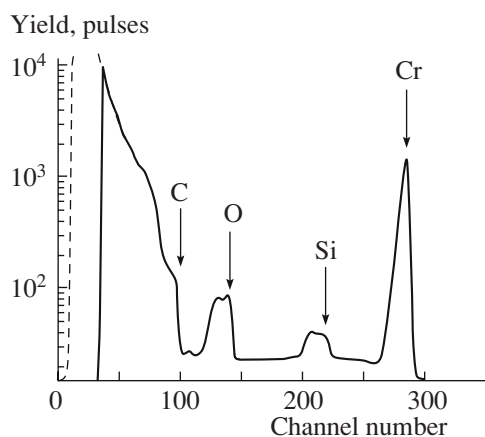


Fig. 5. RBS energy spectra of He^+ ions with energy of 1.4 MeV of graphite sample with chromium deposited on its surface with assisting energy of 10 keV. The solid curve is the experimental spectrum, and the dashed curve is the spectrum simulated with the use of the RUMP program.

coatings deposited on the elastomer by the SIAD method [11].

Figure 6 represents the distributions of elements in the coating and substrate obtained by the reconstruction of the experimental RBS spectrum (see Fig. 5). The Cr content decreases from 10 at % on the coating surface to ~ 0.6 at % in the region of the coating–substrate phase interface denoted as the location of the starting surface of the substrate. In this case, chromium atoms with a concentration of ~ 0.5 at % are revealed in the graphite substrate at a depth >350 nm, which indicates its radiation-stimulated diffusion into the substrate during the deposition of the coating since the projective path length and struggling of the path length of the Cr^+ ions with $E = 10$ keV in graphite are ~ 11 and ~ 2.6 nm, respectively [16].

The distribution profiles of the O and Cr atoms over the depth are similar, but the oxygen content in the coating is higher by a factor of 6–9. In graphite, starting from a depth of ~ 100 nm or larger, the O concentration is lower compared with that of Cr by a factor of ~ 3 . As for hydrogen and carbon, their amounts in the coating are comparable and reach 40–50 at % at different

Table 2. Equilibrium contact angle of the surface of starting graphite and graphite with chromium coating

h , nm	Equilibrium contact angle, deg	Relative variation of the equilibrium contact angle, %
0	59.3	–
320	58.9	–0.7
540	59.8	0.8
700	67.8	14.3
1050	62.9	6.1

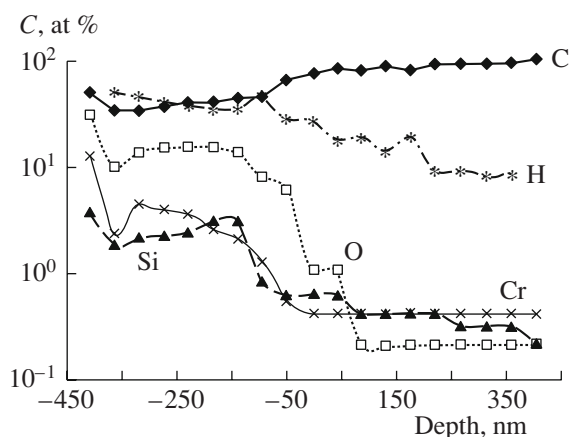


Fig. 6. Variation in concentrations of elements over depth in the chromium–graphite system obtained by simulation based on the experimental RBS data.

depths. However, in contrast to the systems coating–steel, coating–aluminum, and coating–silicon, in which hydrogen is localized only in the metal coatings [14], with the use of a graphite substrate, penetration of hydrogen with a concentration up to 8–9 at % to a graphite depth up to ~ 350 nm is observed.

3.3. Contact Angle

It follows from the data of Table 2 that modification of graphite by deposition of chromium-based coatings leads to hydrophobization of its surface. We can assume that, as the coating thickness (h) increases, irregularities on the graphite surface are filled with the deposited material, and at $h \geq 400$ nm, the additive contribution of the material diffusing from the substrate on the surface becomes small, i.e., the elemental composition of the coating surface stabilizes. Consequently, the variation in the contact angle with increasing h is due to the variation in the surface roughness (see Table 1), which is quite satisfactorily described by the Deryagin–Ventsel’ formula [17].

4. CONCLUSIONS

Using the Rutherford backscattering method, the elemental composition of chromium-based coatings deposited on graphite is determined. It is revealed that, in addition to chromium atoms, they contain hydrogen, carbon, and oxygen from residual gases of the deposition chamber as well as a silicon impurity. The layer-by-layer analysis of the surface of the coating–graphite structures showed that the SIAD process is accompanied by interdiffusion of the components of the deposited coating into the graphite bulk and Si atoms from the graphite bulk on the surface of the formed coating–substrate structure.

The investigations of topography and water wettability of the graphite surface modified by the deposition

of Cr coatings of various thicknesses using the SIAD method showed that the hydrophobicity of the chromium coating is affected by its elemental composition and roughness, which increases as its thickness increases. The analysis of the results obtained allows us to conclude that it is possible to form the surface of graphite articles with a specified water contact angle by controlling the composition and roughness of the surface.

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