Radionuclides in Irradiated Graphite of Industrial Uranium– Graphite Reactors: Effect of Irradiation and Thermochemical Treatment on the Graphite Structure

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Abstract—The structure of irradiated graphite from decommissioned industrial uranium–graphite reactors was studied. The extent of disturbance of the graphite structure is closely correlated with temperature and integral neutral fluence. The perfection of the structure of graphite samples (data of X-ray diffraction and Raman spectroscopy) does not correlate with their radioactivity, which is due to low absolute concentration of the radionuclides. Mapping of the samples using Raman spectroscopy reveals spatial heterogeneity of the distribution of graphite lattice damages, which casts doubt on the representativeness of the spectra of individual points. The spatial distribution of domains differing in the crystal lattice perfection was studied for the first time and was compared with the radionuclide distribution. Satisfactory correlation between the radiographic and spectroscopic mapping data is observed for some samples. Irradiated graphite is strongly textured and contains amorphous microvolumes, which are probably radionuclide carriers. Thermochemical treatment (oxidation in O₂, thermal shock) leads to degradation of the irradiated graphite structure on the submicron level, accompanied by a drastic decrease in the mechanical strength of the samples.

Keywords: uranium-graphite reactors, irradiated graphite, thermochemical treatment

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Despite large volume of the studies performed, no approaches have been found by now to selective removal of the major fraction of radionuclides from graphite without its incineration. Solution of this problem requires, in particular, a detailed study of the radionuclide localization in the irradiated graphite matrix. Although processes of defect formation in graphite are being studied for more than 50 years [1–6], many principal problems remain a matter of discussion. The mechanism of the damage of the graphite lattice under irradiation with neutrons [7, 8], electrons [9], or ions [10–12] has been studied in detail by transmission electron microscopy and molecular dynamics [13]. Although graphite, on the whole, preserves the layered structure, accumulation of point defects in the basal plane and formation of more complex structural elements (e.g., dislocation loops) leads to shortening of continuous graphene layers and to disturbance of ordering in the (002) layer plane. It should be noted that the majority of studies dealt with samples of highquality pyrolytic graphite, whereas real nuclear graphite is a material of complex phase composition.

Already in early steps of studying nuclear graphite, the need for studying specific graphite grades became clear because of the complex structure of the material. Irradiated graphite from Soviet industrial uranium– graphite reactors (IUGRs) remains relatively poorly studied in the structural aspect. This work is a part of comprehensive studies on decontamination of irradiated graphite from decommissioned IUGRs. In our previous studies [14, 15], we evaluated the efficiency of various thermochemical treatment procedures. Here we report on a comprehensive study of the structure of irradiated graphite both in the initial state and after various kinds of physicochemical treatment.

EXPERIMENTAL

We studied samples of block graphite of B-15 and B-16 grades from I-1 and ADE industrial uranium– graphite reactors. The samples were taken by drilling a cylinder and sawing it into pellets 8 mm in diameter and 2 mm thick, to analyze the materials from various parts of blocks and sleeves. The conditions of thermochemical decontamination experiments are described in [14, 15].

The overall perfection of the crystal lattice of graphite samples was evaluated by X-ray diffracttion (Cu K_{α} radiation, Bragg–Brentano geometry) and small-angle X-ray scattering.

The Raman spectra were recorded with laser excitation at 532 and 785 nm; the size of the area being analyzed was 2–5 μ m. For some samples, we obtained not only the spectra of separate areas, but also the spectral maps with the spatial step from 2–5 to 10–20 μ m. The deconvolution of the experimental spectra was performed using Fityk program [16] after subtraction of the linear background; the number of components was chosen proceeding from the number of inflection points. The shape of separate peaks was described using the Voigt profile (Gaussian and Lorentzian convolution), allowing various kinds of broadening of symmetrical peaks to be described correctly.

The structure of the samples on the micrometer and submicrometer levels was studied by scanning (SEM) and transmission (TEM) electron microscopy. SEM examination was performed for end faces of cylindrical graphite pellets and for mechanical chips without special sample preparation and/or sputtering, because the electrical conductivity of the material was sufficient. A JEOL JSM-6480LV microscope equipped with an Oxford X-Maxⁿ 50 spectrometer was used. TEM analysis was performed with a JEM-2100 device (JEOL). The sample preparation consisted in dry mechanical grinding of submillimeter graphite crumb in an agate mortar and in trituration in ethanol, followed by application onto copper grids (Quantifoil). Both sample preparation procedures give similar results except for thermally expanded graphite.



Fig. 1. (a, b) X-ray diffraction patterns and (c) small-angle X-ray scattering curves for three samples of block graphite subjected to the effect of different integral fluences and temperatures in the course of reactor operation: (a) (002) reflection and (b) range of large angles (the distortion of the peak corresponding to the two-dimensional ordering of graphene layers in sample no. 3 is noticeable). The curves in Figs. 3a and 3b are shifted relative to each other for clarity.

RESULTS AND DISCUSSION

X-ray Diffraction and Small-Angle X-ray Scattering

According to the diffraction data, the samples consist of graphite with different extents of ordering. The diffraction patterns of different end faces of cylindrical samples (depth of the layer being analyzed about 100 μ m) are identical, demonstrating uniformity of the phase composition of the material on the scale of millimeters. The dependence of the graphite lattice perfection on the sample position in the reactor stack is clearly observed, reflecting the heterogeneity of the distribution of temperature and neutron flux (see, e.g., [17]).

Figure 1 shows an example of a comparative study



Fig. 2. SEM images of (a-d) block and (e, f) sleeve graphite (secondary electrons).

of block graphite samples from different heights in the stack. As can be seen, sample no. 3 strongly differs from the other two samples subjected to the action of higher temperatures in the course of reactor operation. Sample no. 3 is characterized by higher extent of structure degradation, manifested in broadening of (001) reflections and their shift toward smaller angles. Such behavior reflects an increase in the interlayer spacing and a decrease in the crystallite size from ~10 to ~7.1 nm (calculation by the Selyakov-Scherrer formula). Also, the intensity of the (101) reflection decreases at virtually unchanged intensity of the "twodimensional" (10) peak. The anisotropy of the radiation swelling of the samples is manifested in contrast behavior of (00l) and (110) reflection: The (110) reflection in the most damaged sample is shifted toward larger angles, which indicates that the corresponding interplanar spacing decreases. The other two samples from the same stack are similar to each other, except small variations in the relative intensity of the (101)reflection. These differences are not artifacts caused by difference in the orientation of the texture of specific samples relative to the diffractometer geometry; they reflect variations in the extent of the lattice damage, which is confirmed by the Raman spectra. In all the samples studied, the intensity of the background from strongly disordered carbon is low and is independent of the extent of the lattice damage.

Small-angle X-ray scattering (SAXS) confirms the diffraction data. According to SAXS, sample no. 3 contains a large amount of nanosized defects characterized by high electron density contrast with the matrix. Clusters of vacancies and dislocation loops can be such defects, but unambiguous identification of scattering defects seems impossible yet. For some cylindrical samples, small-angle scattering curves were obtained using a microbeam (diameter 0.1 mm). No significant differences between the points over the cross section of individual samples were observed. However, it should be taken into account that, when recording in the transmission mode, the signal is averaged over the sample thickness (1–2 mm).

Scanning and Transmission Electron Microscopy

Representative SEM images of samples of irradiated block and sleeve graphite are shown in Fig. 2. The heterogeneity and porosity of the material, inherited from the graphite production process, are clearly seen on scales from fractions of micrometer to fractions of millimeter. Separate relatively perfect thin planar blocks of graphite (filler) with the transverse size of 5-10 µm are seen. It can be concluded from the limited statistics that the graphite from the sleeves studied is more uniform than the block graphite on the scale of hundreds of micrometers.

Pronounced texture of block graphite should be noted. It has been preserved despite high integral fluence and the concomitant anisotropic expansion of graphite. The texture is also preserved on the submicrometer level, as revealed by electron diffraction (see below).

An attempt was made to determine the localization of domains containing ³⁶Cl. Although chlorine was detected in some points (~0.1% concentration, according to semiquantitative estimation), it is impossible to make reliable conclusions on the chlorine distribution because of high probability of contamination in the course of sample fabrication.

The microstructure of the initial (unirradiated) and thermochemically treated samples [15] was studied by TEM. The initial graphite samples (Fig. 3) are characterized by the presence of perfect domains with the stack thickness of 5-10 nm, which reasonably agrees with the X-ray diffraction data. Separate single crystal grains with a size of units of micrometers were also



Fig. 3. TEM images. First row: to the left, representative image of an unirradiated graphite sample, with both uniform volumes and spherulite-like domains seen; to the right, crystallographically perfect microvolumes. Second row: to the left, spherulite in the unirradiated material; to the right, spherulite in irradiated graphite. Third row: to the left, diffraction from a polycrystalline sample; to the right, an example of strongly textured microvolume.

detected. No amorphous domains were detected in unirradiated graphite; this, however, can be caused by the limited sample size. In unirradiated graphite, there are carbon spherulites up to $0.5-0.7 \mu m$ in diameter (Fig. 3), typical of petroleum pyrolysis cokes [3]. In the irradiated samples, the spherulites are amorphized, but preserve the shape and size. Probably, the radiation resistance of spherulites is appreciably lower than that of pyrolytic graphite particles, because even in the samples with the highest integral fluences there are



Fig. 4. TEM images of an irradiated graphite sample, demonstrating different cases of coexistence of amorphous and crystalline microvolumes.



Fig. 5. Size of the areas damaged by a ¹⁴C recoil nucleus of 41.4 keV energy in carbon materials of different densities. Calculation using SRIM program, displacement energy 28 eV; the whole displacement cascade is taken into account. (*I*) Graphite ($\rho = 2.23 \text{ g cm}^{-3}$) and (*2*) α -C ($\rho = 1.65 \text{ g cm}^{-3}$).

long domains that have preserved high degree of ordering.

Not only polycrystalline grains but also grains with the developed texture were observed in both initial (graphite from adjacent stores that has not been in operation) and irradiatred samples. The texture of such samples suggests close coexistence of microvolumes with strongly different orientation. The behavior of ordered (graphite) grains in the samples that we studied is qualitatively similar to that of pyrolytic graphite [18]. On the whole, in samples of irradiated graphite relatively perfect microvolumes (according to electron diffraction and direct lattice imaging methods) coexist with adjacent amorphous domains (Fig. 4).

Figure 5 shows the results of calculating, using the SRIM program [20], the damages of the crystal lattice of ideal graphite with a density of 2.23 g cm⁻³ and of the carbon material with the density average for nuclear graphites, 1.6-1.85 g cm⁻³. In both cases, the dis-



Fig. 6. TEM images of thermally expanded graphite.



Fig. 7. (a) Representative first-order Raman spectra of irradiated graphite with an example of deconvolution into three components; (b) straggling of position and FWHM of the *G* peak in samples 1 and 2 with different extents of radiation damage (see also Fig. 8).

placement energy for C atoms was assumed to be equal to 28 eV. In such cases, each recoil nucleus causes 190–200 displacements at the mean range of ~95 and 130 nm (at normal incidence), respectively; however, large straggling of the range is observed. These distances appreciably exceed the transverse size of graphite crystallites (5–15 nm) in the samples. Such heterogeneous structure was observed previously in a sample of irradiated graphite from France; the amorphized domains were assumed to be the localization sites of such radionuclides as ³⁶Cl [19]. However, the absolute concentration of radionuclides is too low to statistically reliably detect them in such microvolumes. According to the EDX data, the only element in the material is carbon. The amorphous domains that we detected are most frequently sufficiently large, which is due to very high neutron fluxes to which they have been exposed; most probably, the relative contribution made by recoil nuclei to amorphization is low. There are no essential differences between samples with strongly different radionuclide concentrations.

Significant changes in the graphite microstructure are observed after the thermochemical treatment (Fig. 6). After thermal expansion and oxidation of graphite in an O₂ stream, the material integrity is disturbed on the macroscopic level, with strong crumbling. On the other hand, the X-ray diffraction patterns of the samples before and after treatment are identical; no significant changes are observed in the Raman spectra either. However, TEM examination revealed significant changes in irradiated graphite samples, caused by the subsequent thermochemical treatment. The images of a heat-treated graphite sample prepared without using liquids cannot be interpreted unambiguously because of the moiré pattern observed in the overwhelming majority of cases. In the sample prepared using ethanol, there are numerous very fine (10-50 nm) elongated graphite pieces weakly bound with coarse aggregates. As shown in [14], the thermochemical treatment used does not ensure complete decontamination of the irradiated graphite, despite significant changes in the microstructure. Most probably, the graphite oxidation in the course of the thermochemical treatment occurs mainly along (micro)cracks and other defects and affects considerably more strongly the binder (processed pitches etc.) than graphite crystallites (filler). Thus, relatively weakly bound ¹⁴C is removed (e.g., from the vicinity of pores), but ¹⁴C in the crystal lattice of graphite remains intact. Probably, the major source of strongly bound radiocarbon is the activation reaction ${}^{13}C(n,\gamma){}^{14}C$, whereas in the ${}^{14}N(n,p){}^{14}C$ reaction the energy of the recoil nucleus (41.4 keV) is sufficient for breaking the lattice (see above).

Raman Spectroscopy

Among the methods that we used, Raman spectroscopy is the most sensitive to defects on the atomic level. A typical first-order Raman spectrum of irradiated graphite is shown in Fig. 7a; such spectra are

common for graphite-like carbon with sp^2 hybridization. The major peaks are the well-known G, D, and D'peaks (the latter peak is manifested as a shoulder of the G peak), corresponding to the stretching vibrations of pairs of sp^2 -hybridized carbon atoms and to breathing modes of carbon rings in the vicinity of defects [21]. As a rule, analysis of the Raman spectra of graphites as a whole and of irradiated graphite in particular is based on description of specifically the G and D peaks. However, in many cases the use of only two peaks does not allow satisfactory description of the experimental spectrum. For correct description of the spectrum, it is appropriate to consider a third peak with a maximum at approximately 1500 cm^{-1} (let us denote it as A band); in the overwhelming majority of cases, this band has approximately Gaussian shape, which reflects large scatter of bond angles. Similar approach was used previously (see, e.g., [22-25]), and the band at approximately 1500 cm⁻¹ was interpreted as a G band of strongly disordered sp^2 -C. In the recent calculation study, this band is attributed to the interaction of breathing modes and asymmetric vibrations in the vicinities of defects [26]. Apparently, consideration of additional components in the spectrum deconvolution influences also the relative intensities and positions of the major G and D bands. Such approach to describing the Raman spectra of graphite is not the only possible, because satisfactory description of the spectra can be reached when describing the shape of the G peak by the Breit-Wigner-Fano profile with the parameters depending on the phonon density of states of graphitelike carbon [27]. However, for such a structurally complex material as irradiated nuclear graphite these parameters are model-dependent. Thus, the phenomenological approach to describing the first-order Raman spectrum by a set of components seems to be substantiated.

The structural features of carbon materials are often described using the I(D)/I(G) intensity ratio. As expected, the intensity of the *D* peak and, correspondingly, the I(D)/I(G) ratio increase when using an IR laser (785 nm). However, as shown in a number of studies (see, e.g., [28]), this radio depends on the sample preparation procedure, e.g., on the graphite polishing. Because the graphite sample preparation involves sawing, unambiguous interpretation of the I(D)/I(G)ratio is impossible.

It is known that the G and D bands in Raman spectra can exhibit strong dispersion depending on structural features of carbon materials (see, e.g., [21]).

Combination of small dispersion of the *G* peak position (excitation lasers with the wavelengths of 532 and 785 nm), which does not exceed $\sim 5-15$ cm⁻¹, with large dispersion of the *D* peak, reaching 40 cm⁻¹, shows that the carbon material under consideration can be considered as micro- or nanocrystalline graphite with insignificant contribution of amorphous carbon.

Comparison of the Raman spectra and X-ray diffraction characteristics of a set of samples taken from different parts of the reactor stack shows that the sample with the strongest structural disturbances according to the X-ray diffraction data (the lowest curve in Fig. 1a) is also characterized by larger full width at half-maximum (FWHM) of the D and A bands. However, some areas of the sample that is the most perfect from the X-ray diffraction viewpoint are characterized by comparable FWHM of the D band. The cause of this contradiction becomes clear when analyzing the spectral mapping data.

The spectral maps were constructed for graphite samples taken from different parts of the reactor stack. The network density and the area studied differed for different samples, which was caused by variations in the surface quality: To obtain reproducible results, the laser should be focused on the sample surface. Analysis of a large number of spectra shows that the samples studied are characterized by large scatter of the spectral parameters. The positions and FWHM of the Gpeak for the samples with different extents of the lattice damage are plotted in Fig. 7b. As can be seen, the sample with the more disturbed structure is characterized by somewhat larger FWHM of the G peak and by a shift of its position closer to 1600 cm⁻¹, the position characteristic of nanocrystalline graphite. On the other hand, for the less disturbed sample there are no less than two subsets of points, which most probably reflects the heterogeneity of the initial graphite. These results, in particular, show that it is impossible to characterize nuclear graphite using the spectra of separate points.

Figure 8 shows the distribution maps for various characteristics of the Raman spectra in comparison with the autoradiographic images (i.e., with the radionuclide distribution). Some samples show correlation between "hot" spots and increased FWHM of the D peak, but this is not a general trend. The lack of strict correlation can be attributed to the fact that an autoradiographic image integrates the signal from a depth of several micrometers, whereas the Raman



Fig. 8. Optical photograph of a sample of block graphite (top, to the left), its autoradiographic image (top, to the right; "white" areas correspond to lower radionuclide concentrations), and distribution maps for Raman peak parameters (the maps in the left column correspond to the optical and radiographic images, and those in the right column, to a part of another pellet with high induced activity).

spectroscopy of graphite furnishes information only on a thin surface layer. Also, it cannot be ruled out that strongly damaged microvolumes of the graphite lattice, characterized by broadening of the D peak in the Raman spectra, are not necessarily radionuclide concentrators because of relatively low absolute concentrations of radionuclides.

Thus, a study of graphite from decommissioned Russian industrial uranium–graphite reactors by a set of mutually supplementing analytical methods revealed spatial heterogeneity of the distribution of graphite lattice damages on the scales of the first tens of micrometers. The discovery of this fact indicates that the data obtained for single small samples may be insufficiently representative. For some samples, satisfactory correlation is observed between the radionuclide distribution and perfection of the graphite lattice, but these correlations are not universal. The graphite texture is largely preserved even at high integral fluences, and amorphous microvolumes appear. The structure of irradiated graphite degrades on the submicrometer level upon oxidation in O_2 or thermal shock, which restricts the use of these decontamination methods.

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