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Thermal analysis of the radiation defects annealing in the irradiated graphite crystalline structure

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Abstract. The paper presents methodological approaches to determine the radiation defects annealing parameters and, accordingly, the release of stored energy (Wigner energy). The approaches for graphite sampling from various locations and elements of graphite stack of production uranium-graphite reactors (PUGR) are considered, as well as the design of for thermal-differential analysis of samples, which allowed to obtain Wigner energy release spectra of graphite to test the algorithm for their mathematical processing to determine the activation energy.
Keywords: irradiated graphite, lattice defect, Wigner energy, decommissioning, activation energy.

1. Introduction

Currently, about 250000 tons of irradiated reactor graphite has been worldwide accumulated. The problem of irradiated graphite from shutdown reactors is of substantial significance in justifying the safety of graphite-moderated nuclear reactors decommissioning [1]. It is noted that one of the problems is the stored energy (Wigner energy) accumulated in reactor graphite under the influence of neutron radiation, which under certain conditions, depending on irradiation parameters and annealing conditions, can be released spontaneously and lead to graphite heating above the oxidation temperature [2–5], which consequently affects both fire safety and radiation safety associated with the radionuclides release from graphite when the graphite oxidation onset temperature is reached.

Until now, many different theories have been developed that, in one way or another, describe the processes of defect formation and annealing. In the view point of their practical application for the graphite heating performing model calculations theories based on activation models are of the greatest interest [2, 3]. According to which, the process of radiation defects annealing is determined by such parameters as the total amount of stored energy, the stored energy release rate, the energy release onset temperature and activation energy. The purpose of this study was to develop methodological approaches for representative graphite sampling PUGR, to construct an experimental setup for thermal analysis of the selected samples and determination the radiation defects annealing main parameters according to the activation model. Earlier in Russian Federation, the approach in annealing parameters determination was demonstrated only for stored energy determination in graphite GR-280 (used in RBMK reactor), specially irradiated in the research reactor BOR-60 up to neutron fluence of $3.2 \cdot 10^{26}$ m^{-2}, in the range from irradiation temperatures 450–640 °C up to 1300 °C. The kinetic analysis of the graphite stored energy spectrum was performed and the activation energies and type of radiation defects in graphite were determined. The activation energies for the research “low-temperature” rector BEPO were determined abroad [4].

In general, it should be noted that the approaches have shown their promise, but the application of these results [5–7] is impossible to predict annealing parameters for production reactors in Russian Federation, since the graphite irradiation parameters in them are individual, which leads to the need to perform an individual assessment for each reactor.

2. Peculiarities of the radiation defects formation process and stored energy release in graphite

The Wigner energy accumulation is caused by the fact that different types of radiation defects (Fig. 1) of different size and configuration are formed in the graphite crystal lattice under the

influence of a damaging neutrons flux with neutron energy more than 180 keV. Slowed down in graphite, a fast neutron knocks ~ 10^4 atoms out of the lattice site. Most of them cannot overcome the potential barrier (Fig. 1) to leave the metastable position and are located in the lattice in the form of embeddings, retaining some excess energy compared to the equilibrium atom. The amount of stored energy increases with the accumulation of radiation defects, which leads to an increase in internal energy. By increasing the temperature above the graphite irradiation temperature (~40–80 °C) the potential barrier is overcome and, as a result of recombination, begins to occur the annealing of accumulated defects and the stored energy is released in the form of heat. In this case, in the annealing defects process, they can be transformed into other more complex radiation defects types which are annealed at a higher temperature.

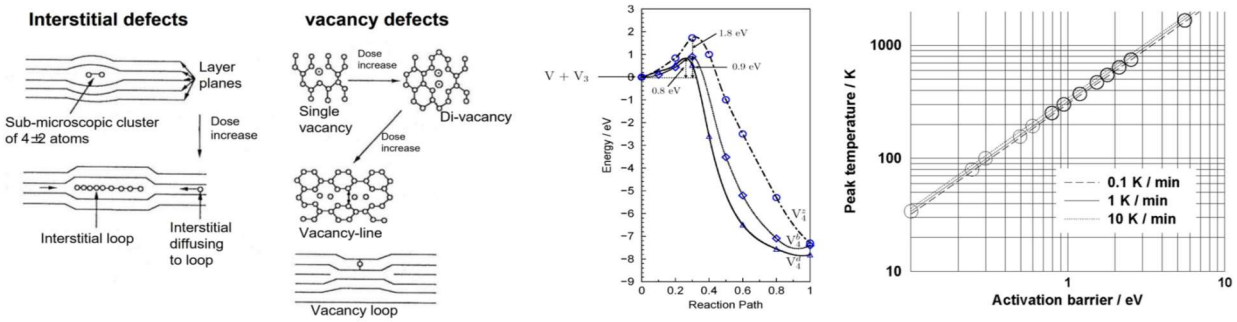


Fig. 1. Defects schemes (left), energy scheme of defects annealing in the isolation process, energy dependence (center) and dependence between activation energy and defect annealing temperature (right).

The energy diagram of the defects annealing process the release of stored energy (Fig. 1) shows the difference between the potential energies of nuclei at the saddle point and in the initial equilibrium state, which is the activation energy. Three activation energies (E_a = 0.8, 0.9 and 1.8 eV), at which potential barrier is overcome by defects of different types are marked in Fig. 1. The amount of stored energy accumulation is determined by the irradiation conditions, including irradiation temperature, time-integrated neutron flux, and, to some extent, the original graphite structure. Each type of defect is annealed by heating in a in a specific sequence characterised by energy and activation temperature. The Wigner energy content can vary significantly depending on the parameters and operating history of reactors, which leads to the need for individual assessment of its accumulation for each reactor. This is especially true for production and research reactors, where parameters variation such as temperature and neutron flux density is significant.

In [3], the processes of stored energy accumulation are described using the Boltzmann equation:

$$\frac{dN(E,t)}{dt} = -\frac{\nu}{a} N(E,t) \exp\left(-\frac{E}{kT}\right), \tag{1}$$

where N – number of displacements per unit volume; E – activation energy ("decay energy"); v – frequency factor; k – Boltzmann constant; T – annealing temperature; t – time; a – heating rate.

3. Methodological approaches to determining the parameters of Wigner energy annealing in graphite

To determine these annealing parameters in graphite from UGR, methodological approaches have been developed that include graphite sampling from various locations and elements of graphite stack from finally shutdown reactors, construction an experimental setup for thermal-differential analysis of samples, which allowed to obtain Wigner energy release spectra of graphite and

application of the algorithm for their decomposition into a superposition of Gaussian distributions to determine the activation energy.

3.1. Graphite sampling methods

During the research, graphite samples (~ 200 pieces) were taken from graphite stacks elements (blocks and sleeves) of two shutdowns PUGR (one is flow type and the other with closed-cycle) with water cooling (Fig. 2).

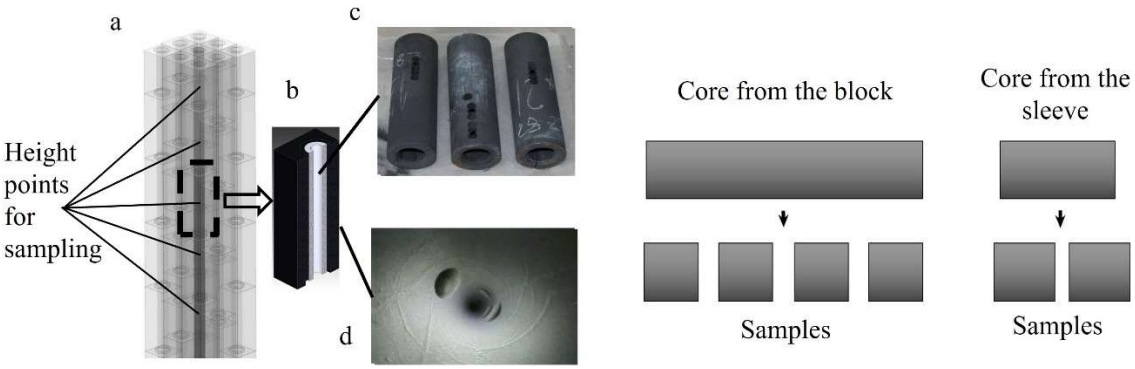


Fig. 2. Scheme of samples selection (left) and production from cores, taken from blocks and sleeves of graphite stacks (right): a – graphite columns; b – graphite block with sleeve; c – extracted graphite sleeves; d – inner surface of the graphite block after coring.

In order to obtain the most complete information on the amount of stored energy and its release parameters, samples were taken from different locations and elements (blocks and sleeves) of graphite stacks which allowed obtaining samples of graphite irradiated in a wide temperature range from 20 °C to 650 °C. Samples of graphite sleeves and reactor graphite stack cells were selected with a service life ranging from 4 to 22 years. As a result, the sampling covered the entire range of time integral damaging neutron flux and irradiation temperature. The information obtained, depending on the sampling locations is presented in Table 1.

Table 1. Information on Wigner energy release parameters depending on sampling sites.

	Sampling locations	**Information**
1	Sampling from sleeves and blocks along the height of stack	Altitude distribution of the stored energy value
2	Sampling from the “coldest” parts of the stacks – top sleeves	The energy release onset temperature and its maximum value
3	Sampling uniformly through the wall thickness of graphite blocks	Distributions of the stored energy amount and parameters of its release along the horizontal section of graphite blocks

Cores were taken from the graphite sleeves using a hollow cutter after they were removed from the stack. Then the obtained core, 8 mm in diameter and 20 mm in length was sawed in half. Each half was ground on a grinding plate using a jig to a height of 8 mm. An axial hole 1.3 mm in diameter and 4 mm depth was drilled in the center of the sample for the tip of the thermocouple. The cores of sleeves with a sleeve wall thickness of 10 mm were not swan and were ground on a grinding plate to a height of 8 mm. Cores from graphite blocks were taken directly from the stack using a horizontal drilling device. Then the core was sawed into 4 parts, from which samples were made in the same way as samples from sleeves.

3.2. Thermal analysis method for graphite samples

To determine the Wigner energy in graphite, the method of differential thermal analysis (DTA) was used, which consists of heating samples at a certain rate and recording the time dependence of the temperature difference between the sample under study and the reference sample (standard) in a specific temperature range.

To implement the method, a special experimental setup DTAG was constructed (Fig. 3) with the help of which the integral values and dependences of the intensity of the stored energy release on the annealing temperature were determined for selected graphite samples.

The experimental setup characteristics:

- mass of samples and standards m = 0.5–3 g;
- sample shape – cylindrical d = 7–15 mm; h = 8–20 mm;
- increasing the annealing temperature according to a linear law up to 800ºC at a rate of 10–15 °C/min;
- double-walled scheme of the calorimeter providing equalization of the temperature field along the cross-section of the operating volume;
- working medium – technical vacuum (~10^{-2} mm Hg) allowing to minimize the non-uniformity of the temperature field under the convective flows influences, increasing the thermal effect in Wigner energy release.

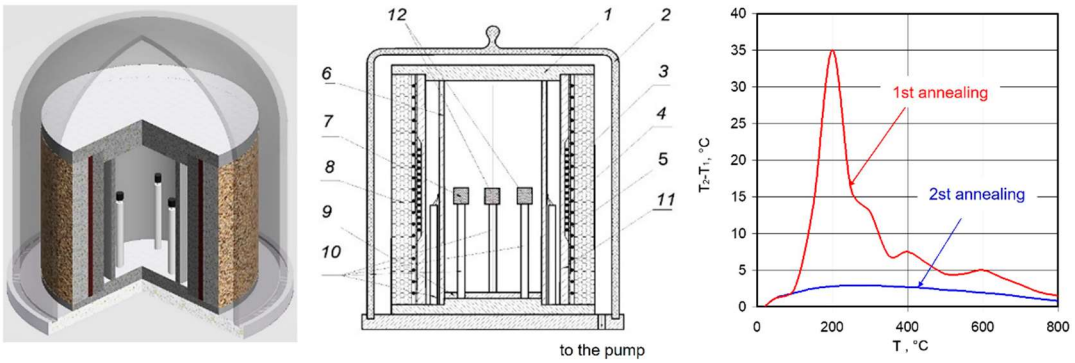


Fig. 3. Schemes of the experimental setup for differential thermal analysis of graphite samples (DTAG) (left and center) and the resulting characteristic spectrum of energy release (right): *1* – calorimeter cover; *2* – glass cap; *3* – internal winding of the heater; *4* – external winding of the heater; *5* – electrical insulation (mica); *6* – inner wall of the calorimeter; *7* – sample; *8* – thermal insulation (asbestos cloth); *9* – bottom of the calorimeter (stainless steel); *10* – thermocouples; 11 – calorimeter outer wall; *12* – standards.

The necessity to develop the experimental setup DTAG was due to the fact that, despite the higher sensitivity of integral thermal effects measurement, standard DSC calorimeter systems (type DSC-404C or similar) are in certain cases have disadvantages in determining the dynamic characteristics, such as release spectrum. The differences are mainly related to the way samples and recording thermocouples are placed. Thus, in the experimental setup, sample is in contact with the tip of a thermocouple tightly mounted in a hole drilled in the sample. The junction of the thermocouple is located at its geometric center. In the DSC-404C or similar systems, the sample is located at the bottom of the crucible, and the thermocouple junction is in contact with the end of the bottom, which makes the thermal effect on the DSC-404C more inertial increase and attenuation, its amplitude is also reduced (by dissipating the heat generated in the sample into the crucible mass). Distortions may occur due to gaps in the contact area of the sample with the crucible. It is also possible to anneal lager samples in the experimental setup.

3.3. Methods for determining activation energy

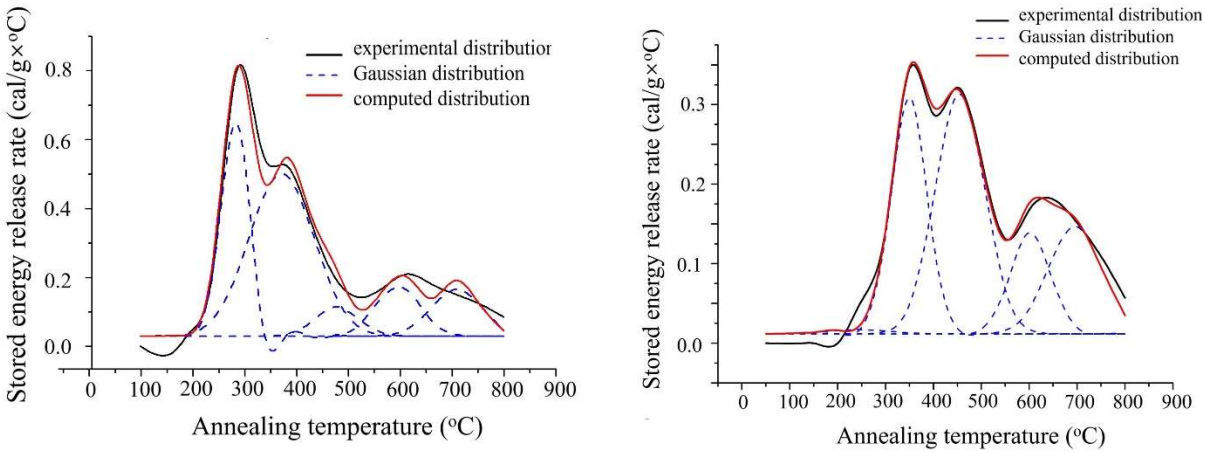
As can be seen from Fig. 3 and equation (1), the Wigner energy release spectrum is a superposition of peaks, each of which refers to the defects annealing of a certain type. In order to determine the activation energies of different defects types formed in samples the decomposition of the experimental spectra into separate peaks was performed within the framework of the present work.

The decomposition of the spectrum into its individual components was performed by the least squares method using Gaussian distributions of the following form (2):

$$N_{\max} = y_0 + \frac{A}{\sigma\sqrt{\pi/2}} \exp\left(-2\left(\frac{h-h_0}{\sigma}\right)^2\right), \quad (2)$$

where N_{max} – number of counts at maximum; y_0 – background level; A – amplitude; h_0 – centroid, σ^2 – dispersion. The dispersion values σ^2 are determined by the software during the calculation process.

The activation energy values for certain temperatures of the obtained spectra peak maxima were determined (example in Fig. 4).



No. 1 **No. 2**

Fig. 4. Examples of Wigner energy release spectra decomposition into individual single Gaussian distributions: experimental distribution, Gaussian distribution and computed distribution.

For spectrum No. 1 (Fig. 4, left panel): 1st – peak maximum – T_{max} ~ 241 °C, E_a = 1.6 eV; 2nd – T_{max} ~ 352 °C, E_a = 1.9 eV; 3rd – T_{max} ~ 454 °C, E_a = 2.25 eV; 4th – T_{max} ~ 509–628 °C, E_a = 2.6 eV; 5th – T_{max} ~ 695–731 °C, E_a = 2.95 eV. For spectrum No. 2 (Fig. 4, right panel), the same values were obtained except for the first peak T_{max} ~ 241 °C, which is due to the difference in the irradiation temperature of samples No. 1 and No. 2 by approximately about 50–100 °C (seen by the temperature at which the stored energy begins to be released).

4. Conclusions

As the results have shown, methodological approaches for determining the parameters of radiation defects annealing and, consequently, the release of stored energy, applied to analyse the final state of PUGR graphite, have shown their reliability and can be adapted for other types of UGRs (RBMK, EGP-6, etc.).

The experimental installation of DTAG allows to reduce the negative influence of thermal effects scattering in the annealing chamber structures on the spectra of stored energy release. As a result, a sufficient resolution of individual maxima of the energy release intensity on the annealing curves

allows the application of decomposition algorithms and, accordingly, determination of defect activation energy values.

The other methods application of Wigner energy release spectra mathematical processing to determine the variation of the obtained activation energy values is relevant as a direction for further research. The values of defects activation energies largely determine the accuracy in mathematical modeling of stored energy annealing thermal effects under various conditions [6, 7] when resolving the safety issues of irradiated graphite.

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5. References

[1] A. Wickham, H.-J. Steinmetz, P. O'Sullivan, M.I. Ojovan, Updating irradiated graphite disposal: Project «GRAPA» and the international decommissioning network Ojovan, *Journal of Environmental Radioactivity*, vol. **171**, 34, 2017, doi: 10.1016/j.jenvrad.2017.01.022

[2] R.H. Telling, M.I. Heggie, Radiation defects in graphite, *Philosophical Magazine*, vol. **87**, 4797, 2007, doi: 10.1080/14786430701210023

[3] T. Iwata, Fine structure of Wigner energy release spectrum in neutron irradiated graphite, J. *Nucl. Mater*, vol. **133&134**, 361, 1985, doi: 10.1016/0022-3115(85)90168-0

[4] M. Lasithiotakis, B.J. Marsden, T.J. Marrow, Application of an independent parallel reactions model on the annealing kinetics of BEPO irradiated graphite, *J. Nucl. Mater*, vol. **427**, 95, 2012, doi: 10.1016/j.jnucmat.2008.07.039

[5] E.V. Bespala, et al., Analysis of Wigner energy release process in graphite stack of shut-down uranium-graphite reactor, *IOP Conf. Ser., Mater. Sci. Eng*., vol. **93**, 012065, 2008, doi: 10.1088/1757-899X/93/1/012065

[6] A.O. Pavliuk, S.G. Kotlyarevskiy, E.V. Bespala, I.Y. Novoselov, Dynamics of temperature fields during wigner energy release in bulk graphite irradiated at low temperature, *Journal of Nuclear Materials*, vol. **515**, 303, 2019, doi: 10.1016/j.jnucmat.2018.12.044

[7] A.O. Pavliuk, S.G. Kotlyarevskiy, E.V. Bespala, V.N. Kotov, I.Y. Novoselov Analysis of heat release processes inside storage facilities containing irradiated nuclear graphite, *Science and Technology of Nuclear Installations,* vol. **2022**, 2957310, 2022, doi: 10.1155/2022/2957310