MODELING OF GRAPHITE OXIDATION IN OXYGEN

A.M. Odeychuk, A.I. Komir
Science and Production Establishment
"Renewable Energy Sources and Sustainable Technologies",
National Science Center "Kharkov Institute of Physics and Technology", Kharkov, Ukraine
E-mail: anodeychuk@kipt.kharkov.ua; tel. +38(057)335-60-43

The problem of nuclear grade graphite oxidation at high temperatures is considered in the paper. A simulation model of the nuclear grade graphite oxidation is developed, taking into account the porosity, granulometric composition and sample density. Analysis of the results approbation showed satisfactory agreement with experimental data.

MODELS ANALYSIS OF CARBON MATERIALS OXIDATION

At present developing nuclear power systems Generation IV caused need of carrying out researches of active zone components. In particular study of the properties and behavior of nuclear grade graphite in oxidizing environments at high temperatures. A large amount of experimental work is executed on the studying dependencies of the carbon materials oxidation processes [1, 3, 4, 8, 9], which allowed for a overview of the main phases of the process of oxidation, as well as perform the appropriate physical and mathematical description. However not enough attention is paid to researches on modeling of such processes: influence of grain-size distribution and graphite porosity.

For example, in [1] the IG-110 graphite oxidation was considered under different conditions. Experiments were carried out in two temperature ranges (540…600, 700…1500 °C), puffing rate ((3…18), 40 l/min), oxygen concentration (2.5…32, 2.5…20%), with the area available for reaction 19.792 mm². In this work Arrhenius equation was used, for which the coefficients specified: n = 0.75 ± 0.146 and the activation energy E_a = (218±4) kJ/mol. It is claimed that the proposed model includes the parameters corresponding to the range of high-temperature gas-cooled reactors.

Modeling of the oxidation process was carried out in a cylindrical coordinate system. During the simulation the following graphite specimen parameters were calculated: temperature, density and specific heat, while blowing it upwards parallel to the side surface of the specimen. Concentration distribution also is given in article for O_2, CO, CO_2 in the surrounding space. However, the paper does not take into account of the porosity and grain-size distribution of the sample, and changing of the sample cell volume with radius increase, which may lead to the error in the modeling of oxidation.

In work [2] the following graphite oxidation stages are analyzed:

a) oxidizer transfer on a graphite surface;

b) oxidizer adsorption on a graphite surface (physical adsorption);

c) formation of carbon-oxide bonds (chemisorption);

d) formation of carbon-hydroxide bonds (for reaction with water);

e) breakage of carbon-carbon bonds;

f) desorption of carbon monoxide or other product of reaction;

g) transfer of products of reaction from a surface.

From above-mentioned stages follows that the factors influencing the rate of oxidation reactions are:

a) intensity of oxidant inflow to the surface;

b) partial pressure of oxidizer;

c) reactionary zone is available to an oxidizer on surface;

d) amount and distribution of catalytic impurities in graphite;

e) temperature;

f) removal rate of the reaction products;

g) graphite damage by fast neutrons;

h) amount of previously oxidized (radiolytic or annealed) material;

i) effective diffusion coefficient.

It is noted that at temperatures less than 350 °C oxidation of graphite is practically absent. With increasing temperature, starting from 400 °C, oxidation becomes measurable. Water as an oxidizer, raises a threshold of oxidation reaction to 800 °C.

Mohamed S. El-Genk [3] investigated the properties of graphite grades IG-110, IG-430, and NBG-25. Dependence between diffusion rates of oxidizer deep into graphite on temperature is considered also. It is suggested to divide oxidation process into 3 modes:

– mode is limited by diffusion in the boundary layer (in this mode, oxidant concentration decreases linearly in a thin boundary layer);

– diffusion mode, diffusion is limited by diffusion inside of pores (at this mode an oxidizer is in the sample volume and its concentration falls linearly to zero at a specific depth of the sample);

– mode, which is limited by the chemical kinetics (in this mode an oxidizer fills the entire sample volume some nonlinear slightly decreasing deep concentration).

The experimental and theoretical mass loss dependence on the time of graphite grade IG-110 oxidation is analyzed, presented as graphs, numerical evaluation of which shows that the average absolute error is 21%. The work has also considered the distribution of energy of adsorption and desorption of the oxidizer and gasification sample rate.

However, as in [1], Mohamed S. El-Genk [3] doesn't take into account of granulometric composition of the sample, which can significantly affect on the modeling of the oxidation process.

In [4] specified refined coefficients of the Arrhenius equation for isothermal conditions at temperatures 600, 612 and 625 °C and in the conditions of constantly increasing temperature − 1, 2, 10 °C/min. Dependence of activation energy on sample burn-up and its mean square error (Fig. 1) is analyzed. It is shown that the average activation energy is 155 kJ/mol.
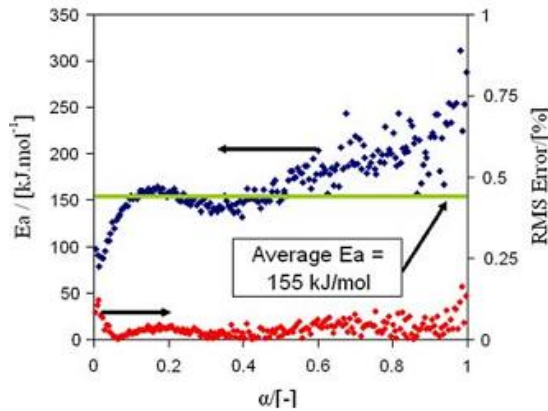

Fig. 1. The activation energy dependence on the sample mass reducing [4]

The proposed analytical description of the oxidation process poorly describes of the experimental data.

Also it should be noted that the description of analytical models is provided in literature, for example in [5-7], in which polynomial approximation of experimental data is used. However this approach doesn't consider the physical nature of oxidation that leads to errors in calculations at the slightest exit from the range of experimental data or insufficient sampling. It is also heavy to approximate data from various sources for creation of the general approximating curve.

In papers [8, 9] provide data on the effective diffusion of oxygen and water into the graphite. The analysis density of graphite after burn-up depending on the depth after the oxidation process during 5 hours in an atmosphere of air at 700 ^{o}C. Developed in [8, 9] models assume carrying out modeling with the diffusion average on a sample that doesn't allow to consider of graphite heterogeneity.

In most existing models used for the separation of oxidation process previously mentioned modes, wherein one of the model parameter is the diffusion of oxidant into the sample, so during the numerical simulation is necessary to take into account the porosity. Construction of the model without this characteristic significantly reduces the reaction surface for the graphite oxidation in the temperature range 400…1200 ^{o}C.

Also in [10] is investigating the effect of grinding on the oxidation rate, and says that the speed increases by mechanical action on the natural graphite. Therefore, in developing an oxidation model should be considered granulometric composition of the graphite structure.

In [11] was used model which contain three main elements – filler binder and porosity for crack initiation and propagation in pile grade A (PGA) reactor core graphite modeling and also have microstructure with good connection filler and binder.

Also various studies try to investigate microstructure of nuclear grade graphite in oxidation conditions [12].

In this paper investigates oxidation behavior with simultaneous study of different properties of microstructure: shape, size. Also significant result is shape of nuclear grade graphite oxidation with catalysts and inhibitors.

Relative sizes of structure elements of filler and binder in other work is filler in the size range 0.1…1.0 mm and these are dispersed in a matrix of fine calcined filler particles, below 10 μm [12].

Therefore, the development of a simulation model for nuclear grade graphite oxidation at high temperatures, which takes into account its porosity, grain-size distribution, diffusion penetration of the oxidizer, temperature and linear dimensions is pressing issue. Consideration of these factors will allow simulating of carbon components oxidation in the operating conditions of nuclear power systems Generation IV, graph of operating temperatures is shown in Fig. 2 [13].
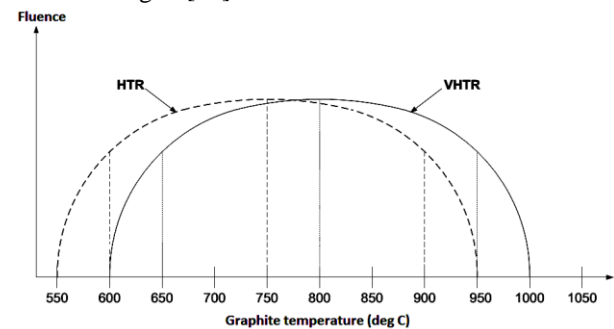

Fig. 2. Temperature range HTR (dotted) and VHTR (solid) [13]

SIMULATION MODEL

Sample splitting into a set of cubic unit cells is the basis of simulation model (Fig. 3).

The unit cell is characterized by the weight and the linear sizes. Graphite sample described using a three-dimensional matrix $v_{\Delta x \times \Delta y \times \Delta z}$, which is hereinafter denoted as v, where each element has a mass of i, j, k-th unit cell.

The graphite sample (as a model material is considered graphite GMZ) consists of a filler and binder in the ratio three to one [14]. Filler is a coke granules which have a specific size. In Table shows the dimensions of the GMZ graphite granules [14].

Granulometric composition of GMZ graphite filler [14]

Size, mm	1.5±0.5	0.5±0.3	0.3±0.09	< 0.09
Content, %	26	13	14	47

Based on the provided data, it was offered to carry out stage-by-stage model formation of a graphite sample taking into account granulometric composition.

Grain model formation was carried out using a statistical approach, which was based on the assignment of the distribution law of the unit cells along the axes x, y, z, that allows to set the required form of grains, depending on the grade features of the graphite microstructure: size, shape, percentage of filler granules in the sample.
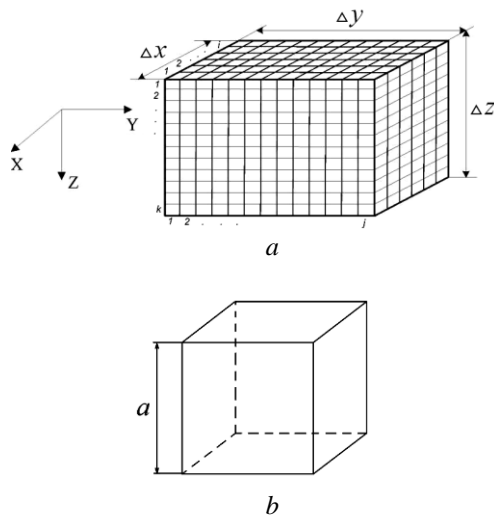
Fig. 3. Scheme of the sample transformation in
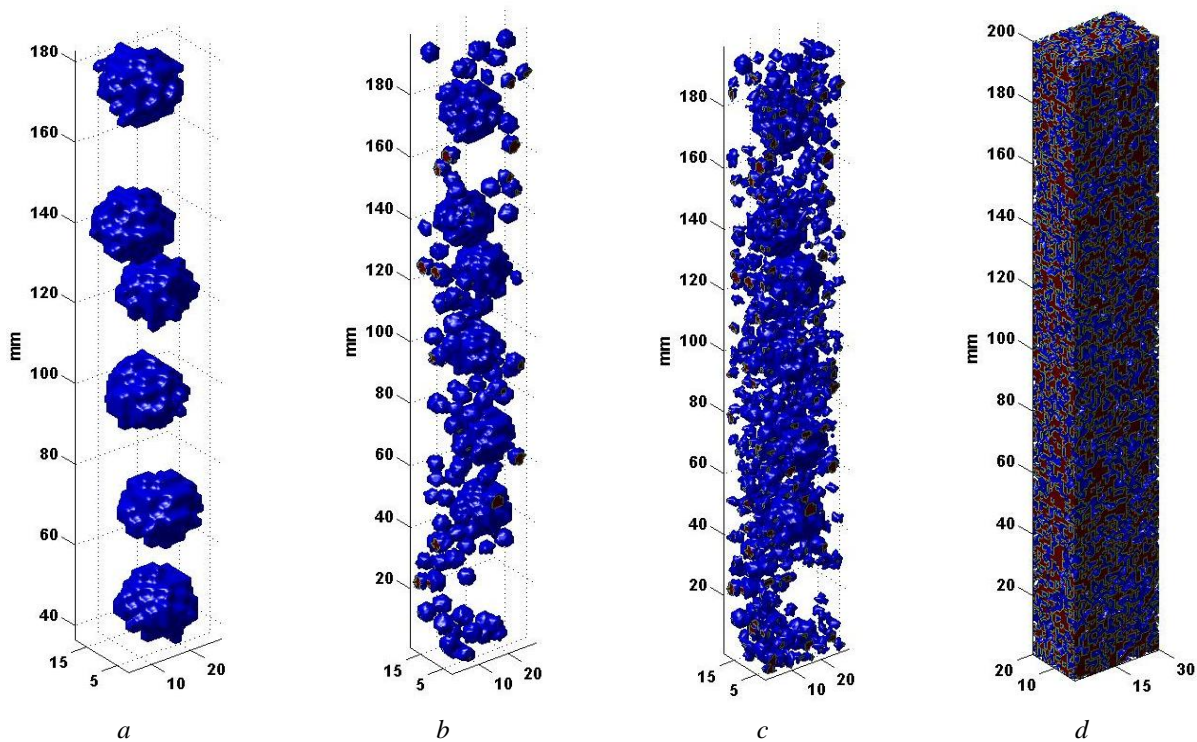three-dimensional matrix v: a − a sample;
b − unit cell i, j, k

Packing of granules in volume of a graphite sample by full search of all possible provisions is extremely difficult from the point of view of time of calculation. Moreover, the complexity of this task increases with the size of the sample. For solving this problem was proposed and realized granules placement algorithm, which comprising in realization of granules arbitrary location that they may be crossed each other, then was used the procedure of step movement of granules inside of specimen volume till the moment of absence of intersection.

Simulation results of the GMZ graphite sample are shown in Figs. 4, 5. By red color specified material located on the boundary of the sample, blue – inside.

Real graphite sample has an open and closed porosity. The model assumed that all sample porosity is open and it is proposed to set it unit cells in which the mass of graphite equals to zero. Porosity distribution on a sample has stochastic character [15].

Fig. 4. Simulation of granulometric composition of nuclear grade GMZ graphite sample: a − grains with size
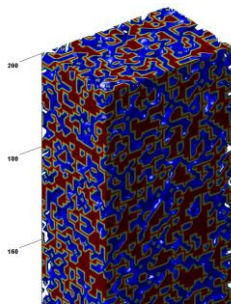(1.5±0.5) mm; b − adding grains (0.5±0.3) mm; c − adding grains (0.3±0.1) mm; d − filler and binder

Fig. 5. Computer model of graphite: filler and binder
(increasing)

Therefore, the selection of a cell which is pore performed by using a random number generator taking into account the distribution of porosity in filler and binder of the sample, which is based on Mersenne twister [16-19].

In the simulation model are not considered the pores, which are smaller than the size of the unit cell.

Sample unit cell weight is determined by the formula:

$$m_{i,j,k} = a^3 \cdot \rho_{i,j,k},\qquad(1)$$

where a – size of the unit cell edge, m; $\rho_{i,j,k}$ – density of i, j, k-th unit cell, kg/m^3.

Mass of the sample is calculated by the formula without taking into account of changing in linear dimensions of the sample:

$$M = \sum_{i=1,\,j=1,\,k=1}^{\frac{\Delta x}{a},\frac{\Delta y}{a},\frac{\Delta z}{a}} m_{i,j,k}, \qquad (2)$$

$$i = 1, 2, ..., \Delta x, \;\; j = 1, 2, ..., \Delta y, \;\; k = 1, 2, ..., \Delta z,$$

where $m_{i,j,k}$ – weight i, j, k-th unit cell, kg, wherein the step of partitioning is multiple of all linear dimensions of the sample.

As mentioned above, the nuclear power systems Generation IV are operating at temperatures ranging from 600 to 1000 °C [13], this simulation model is considering the temperature range from 400 to 800 °C, that is corresponding of diffuse mode, which is described in the papers [3, 20]. A feature of this mode is the uniform distribution of oxidizer over the volume, since the reaction rate is less than the diffusion rate of oxidizer into the sample [8].

Mass reducing of the unit cell as a result of oxidation is calculated by the formula:

$$\frac{dm_{i,j,k}}{dt} = \left(1 - \xi\left(m_{i,j,k}\right)\right) \cdot K_g \times$$
$$\times \sum_{h=-1,\,l=-1,\,\chi=-1}^{1,1,1} \xi\left(m_{i+h,\,j+l,\,k+\chi}\right), \qquad (3)$$

where $\xi(m) = \begin{cases} 0, |m| > 0 \\ 1, m = 0 \end{cases}$ – unit impulse function;

$K_g = K \cdot (C_0)^n \cdot S$ – oxidation rate, kg/s; K – reaction constant, whose temperature dependence obeys the Arrhenius equation, kg/(m$^2 \cdot$s) [14]: $K = K_0 \cdot e^{-\frac{E}{RT}}$, K_0 – function of graphite properties, which is characterized by a degree of crystallinity of the material and its porosity, kg/(m$^2 \cdot$s); E_a – surface activation energy, J; R – gas constant, (m$^2 \cdot$kg)/(s$^2 \cdot$K$\cdot$mol); T – temperature, K; C_0 – oxidizer concentration near the surface; n – reaction order (n depends on many factors including the oxidation mode and anisotropy and takes a value from 0.5 to 3) [14]; S – reaction surface (the area of one unit cell S = a^2), m^2, what is more, when leaving the range of the mass cells matrix v, when the index is 0 or size is larger than matrix in the corresponding dimension – $m_{i,j,k}$ equals zero. The rate of sample mass change is calculated by adding of mass changes over all sample cells:

$$\frac{dM}{dt} = \sum_{i=1,\,j=1,\,k=1}^{\frac{\Delta x}{a},\frac{\Delta y}{a},\frac{\Delta z}{a}} \frac{dm_{i,j,k}}{dt}.$$

Simulation model is constructed on the assumption, that an internal pores of a sample contains an oxidizer and it oxidizes of internal cells with the same speed, as the outside oxidizer. Setting cell mass $m_{i,j,k}$ performed by formula (1).

For determining of model accuracy (4) relative to the dimensions of the unit cell was carried out numerical simulation of the oxidation of graphite sample at the temperature 560 °C (Figs. 6, 7). Calculation of error modeling was carried out using the mean absolute percentage error MAPE [24], which describes how large modeling errors in comparison with the experimental series values data:

$$MAPE = \frac{1}{n} \sum_{t=1}^{n} \frac{|Y_t - H_t|}{Y_t} \cdot 100, \qquad (4)$$

where n – number of measurements; Y_t – experimental data [26]; H_t – modeling data.
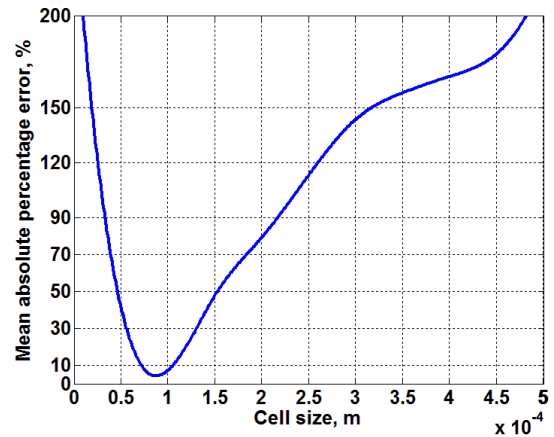

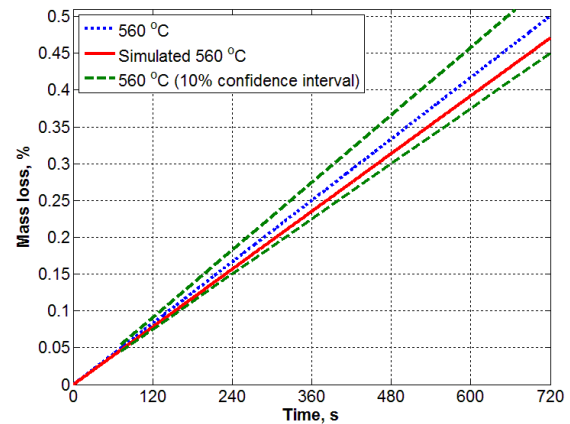Fig. 6. Mean absolute percentage error of the graphite oxidation simulation model

Fig. 7. Dependence of the graphite sample mass loss from time

Analysis of the results shows that the error under reducing of the unit cell dimensions to 0.0001 m is about 7%, however, with further decrease of the size seen an increase of error associated with the fact that the developed simulation model does not consider meso- and nano-scale phenomena, which begin to play an important role [22-24] under dimensions comparable with the mean free path of the molecule [23]. Thus, the results indicate that the area of application of the developed simulation model with an error 7% is sample discretization which commensurate with 0.0001 m.

APPROBATION OF SIMULATION MODEL

Approbation of the simulation model was carried out using mathematical statistical apparatus [21] in the medium of mathematical package Octave 3.6.4. Was modeled of the nuclear grade GMZ graphite sample oxidation process (as a model material), which has the following characteristics: density 1850 kg/m^3, porosity 20%, granulometric composition (see Table) [14], linear sample dimensions − width 0.002 m, length 0.003 m, height 0.02 m, partitioning step of the sample on cubic unit cell with given edge length − 0.0001 m.
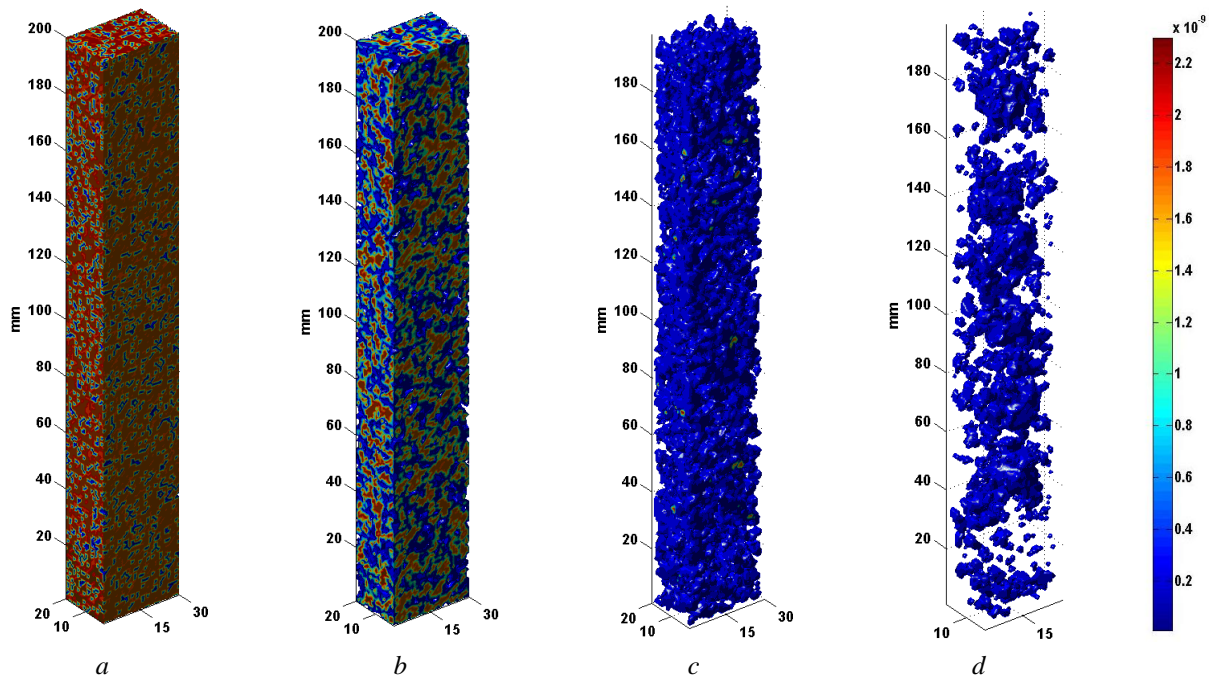
CONCLUSIONS

Theoretical researches are conducted and the simulation model of nuclear grade graphite oxidation is developed. Model takes into account porosity, factionalism, density of the sample and diffusion of oxidizer for oxidation in the chemical kinetics regime, which is in the temperature range 400…800 $^{\circ}$C.

Received results of researches were tested at modeling of oxidation at high temperature of nuclear grade GMZ graphite that agree satisfactorily with experimental results.

Fig. 8. The view of the GMZ graphite sample during oxidation in the oxidizing environment at oxidizer concentration 10% O$_2$ at temperature 560 $^{\circ}$C: a − initial state; b − after 10 days; c − after 20 days; d − after 30 days (on the right is shown scale of the mass change of the unit cell)

Oxidation process parameters: temperature − 560 $^{\circ}$C, oxidizer concentration − 10% O$_2$, oxidation rate $K_g = 10^{-7}$ kg/s, duration of the process − 30 days. The modeling results of the oxidation process of GMZ graphite using the simulation model are shown in Fig. 8.

Analysis of simulation results (see Fig. 8) shows the presence of oxidation dynamics of the sample, but significant structural changes were observed after 10 days. After 20 days sample loses properties of support structure, and after 30 days complete destruction of the sample is observed. Moreover, it should be noted that the simulation with taking into account the porosity of the sample has allowed take into account the non-linearity and stochasticity of the graphite oxidation process. As seen from Fig. 8,d, accounting at modeling oxidizer penetration into the sample has a significant impact on the destruction process, since oxidation takes place not only on the outer surfaces, but also by the entire sample volume.

The obtained results of simulation with using the developed simulation model are well correlated with the experimental results obtained in the work [26].

REFERENCES

1. E.S. Kim, H.C. No. Experimental study on the oxidation of nuclear graphite and development of an oxidation model // *Journal of Nuclear Materials*. 2006, v. 349, Issue 1-2, p. 182-194.

2. Irradiation damage in graphite due to fast neutrons in fission and fusion systems // *IAEA-TECDOC-1154*. 2003, p. 207-213.

3. M.S. El-Genk, J.-M.P. Tournier. Comparison of oxidation model predictions with gasification data of IG-110, IG-430 and NBG-25 nuclear graphite // *Journal of Nuclear Materials*. 2012, v. 420, Issue 1-3, p. 141-158.

4. H. Badenhorst, B. Rand, W.W. Focke. Modelling of natural graphite oxidation using thermal analysis techniques // *Journal of Thermal Analysis and Calorimetry*. 2010, v. 99, Issue 1, p. 211-228.

5. W.S. Cornwall. *Wigner Stresses:* United Kingdom Atomic Energy Authority, TRG Report 40(R), 1962, 133 p.

6. M. Lasithiotakis, B.J. Marsden, T.J. Marrow. Application of an independent parallel reactions model on the annealing kinetics of BEPO irradiated graphite // *Journal of Nuclear Materials*. 2012, v. 427, p. 95-109.

7. H. Li, A.S.L. Fok, B.J. Marsden. An analytical study on the irradiation-induced stresses in nuclear graphite moderator bricks // *Journal of Nuclear Materials.* 2008, v. 372, p. 164-170.

8. J.J. Lee, T.K. Ghosh, S.K. Loyalka. Oxidation rate of nuclear-grade graphite NBG-18 in the kinetic regime for VHTR air ingress accident scenarios // *Journal of Nuclear Materials.* 2013, v. 438, Issue 1-3, p. 77-87.

9. R.P. Wichner, T.D. Burchell, C.I. Contescul. Penetration depth and transient oxidation of graphite by oxygen and water vapor // *Journal of Nuclear Materials.* 2009, v. 393, Issue 3, p. 518-521.

10. H. Badenhorst, W. Focke. Comparative analysis of graphite oxidation behaviour based on microstructure // *Journal of Nuclear Materials.* 2013, v. 442, p. 75-82.

11. P.J. Heard etc. Crack initiation and propagation in pile grade A (PGA) reactor core graphite under a range of loading conditions // *Journal of Nuclear Materials.* 2010, v. 401, p. 71-77.

12. H. Badenhorst, W. Focke. Comparative analysis of graphite oxidation behaviour based on microstructure // *Journal of Nuclear Materials.* 2013, v. 442, p. 75-82.

13. M. Davies. *Qualification of selected graphites for a future HTR.* Technical Meeting on High-Temperature Qualification of High Temperature Gas-Cooled Reactor Materials. 10–13 June 2014. IAEA Vienna [Electronic resource]. Access mode: http://www.iaea.org/NuclearPower/Meetings/2014/2014-06-10-06-13-TM-NPTD.html. Header from screen.

14. V.V. Goncharov et al. *Effect of irradiation on graphite of nuclear reactor.* M.: «Atomizdat», 1978, p. 9-38.

15. V.S. Ostrovsky et al. *Changes in the porosity and permeability of the carbon material during heat treatment.* Structural materials on basis of graphite. The collection of works N 3. M.: «Metallurgy», 1967, p. 204-208.

16. V.P. Kichor et al. *Economic and statistical modeling and forecasting.* Lviv: Publishing House of National University "Lviv Polytechnic", 2007, 156 p.

17. M. Matsumoto, T. Nishimura. Mersenne Twister: A 623-Dimensionally Equidistributed Uniform Pseudorandom Number Generator // *ACM Transactions on Modeling and Computer Simulation*. 1998, v. 8, N 1, p. 3-30.

18. SIMD-oriented Fast Mersenne Twister (SFMT): twice faster than Mersenne Twister [Electronic resource]. Access mode: http://www.math.sci.hiroshima-u.ac.jp/~m-mat/MT/SFMT/index.html. Header from screen.

19. R. Tor. Collusion-Secure Fingerprinting. A simulation of the Boneh and Shaw Scheme. Coding theory and cryptography [Electronic resource] // Bergen: Department of Informatics Universitas Bergensis, 2005, 119 p. Access mode: http://www.ii.uib.no/~georg/coding/Students/Tor/collusion_secure_fp.pdf. Header from screen.

20. H. Badenhorst. Graphite Oxidation // *DST Chair in Carbon Materials and Technology*. 2009, 38 p.

21. A.M. Odeychuk, A.Yu. Gud. Simulation model for the study heteroskedastic time series in information systems // *Visnyk of the Academy of Customs Service of Ukraine.* 2010, N 1, p. 102-110.

22. Processes of micro- and nanotechnology. *Educational and methodical complex on St .P. SETU discipline*. St.-Petersburg, 2010, 266 p.

23. N.F. Morozov, R.V. Goldshtein, V.A. Gorodstov. *Modeling of the mechanical behavior of nanostructured formations*. St.-Petersburg State University, Institute for Problems in Mechanics named A. Yu. Ishlinsky RAS. M., 2009, 35 p.

24. A.S. Lobasov, A.V. Minakov. Computer modeling of heat and mass transfer processes in microchannels with using CFD-package Flow // *Computer studies and simulations.* v. 4, N 4, 2012, p. 781-792.

25. A.N. Odeychuk. Generalized criterion for efficiency of time series forecasting models in information systems // *Bionica Intellecta: scientific-technical magazine.* 2009, N 1 (70), p. 113-119.

26. S.J. Gregg, R.F.S. Tyson. The kinetics of oxidation of carbon and graphite by oxygen at 500–600 °C // *Carbon.* 1965, v. 3, Issue 1, p. 39-42.

МОДЕЛИРОВАНИЕ ОКИСЛЕНИЯ ГРАФИТА В СРЕДЕ КИСЛОРОДА

А.Н. Одейчук, А.И. Комир

Рассматривается проблема окисления ядерно-чистого графита при высоких температурах. Разработана имитационная модель окисления ядерно-чистого графита с учетом пористости, гранулометрического состава и плотности образца. Анализ результатов апробации показал удовлетворительное согласие с экспериментальными данными.

МОДЕЛЮВАННЯ ОКИСЛЕННЯ ГРАФІТУ В СЕРЕДОВИЩІ КИСНЮ

А.М. Одейчук, А.І. Комір

Розглядається проблема окислення ядерно-чистого графіту при високих температурах. Розроблена імітаційна модель окислення ядерно-чистого графіту з урахуванням пористості, гранулометричного складу і щільності зразка. Аналіз результатів апробації показав задовільну згоду з експериментальними даними.