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HIGH-TEMPERATURE OXIDATION OF NUCLEAR GRAPHITE WITH ACCOUNT OF MOVEMENT OF THE SURFACE LAYER OF OXIDATOR

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At high-temperature oxidation of nuclear graphite, the oxidant flow in the near-surface region is taken into account. Macro- and microscopic modeling of the oxidation of the near-surface layer was carried out. The calculation of the diffusion coefficient of gaseous components as a function of temperature and concentration is given. The influence of the motion of the surface layer of the oxidizer on the concentration of gaseous components is studied.

INTRODUCTION

Macro- and microscopic modeling of the processes of high-temperature oxidation of nuclear graphite of the MPG grade was carried out taking into account the motion of the gas flow near the surface layer of the oxidizer.

Currently, experiments and calculations are being carried out to justify passive safety in the event of an emergency situation for nuclear power systems of the IV generation. In view of the possibility of distinguishing the properties of graphite within 10% in one structural element, a fairly general way of justifying the safety without violating the structural integrity of the structural element and for a wide class of carbon materials is required.

As part of the solution of this problem is given modeling technique which takes into account the microstructure of the oxidation of the sample, and based on the data obtained allows the simulation of the oxidation process.

To investigate the rate of oxidation of nuclear graphite, a series of experiments were carried out, during which activation energies and degrees of oxidation reaction for different types of nuclear graphite were obtained.

In the experimental work [1], the researchers used the stream from the He-O_2 mixture with the stream through the reaction chamber 7…18 of the STLP (Standard liters per minute), which is a rather large flux through reaction chamber with allowance for a small macroscopic reaction surface of 39.58 cm^2, and a high oxidation temperature of 813…903 K, a number of other investigators used oxidation conditions with fluxes given in Table 1.

Table 1

Comparison of flows through the reaction chamber and temperatures of graphite oxidation experiments [1, 2]

Temperature, °C	Concentration O_2	Gas flow, SLPM	Activation energy
450…750	0.2	0.496	201
550…650	0.2	–	210
650…900	0.013	0	324
700…1500	0.05…0.19	0.2…4.5	199.72
540…630	0.03…3.2	7…18	218

The method for separating the modes of oxidation of nuclear graphite in the 3 stages indicated in Fig. 1.

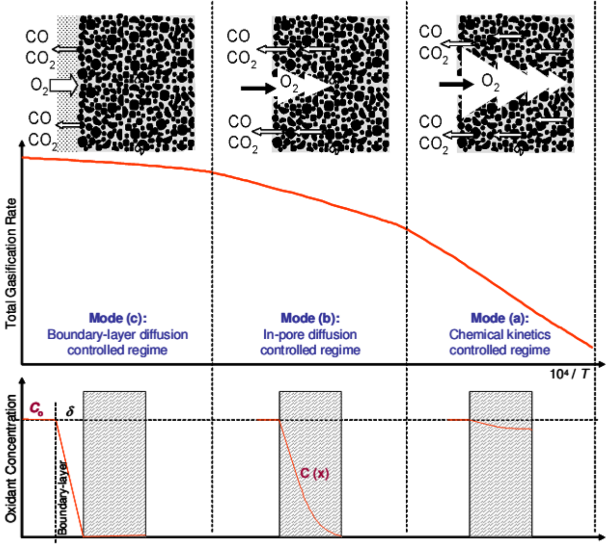

Fig. 1. Modes of oxidation of nuclear graphite [3]

The oxidation regime limited by chemical kinetics (a) is characterized by a slight change in the concentration of the oxidant in the interior of the sample and by the restriction of the rate of oxidation by the processes of chemical kinetics at a given temperature. This mode, according to Mohamed El-Genk, is in the temperature range 400…800 K.

The oxidation regime limited by diffusion in the internal space (b) is characterized by an increased temperature in comparison with regime a of 800…1000 K. Under this oxidation regime, the concentration of the oxidant decreases substantially with increasing distance from the surface and is the main limiting factor in the oxidation of nuclear graphite.

The oxidation regime of the near-surface layer (c) is characterized by high oxidation temperatures > 1200 K and the presence of an oxidizer only in a small near-boundary layer.

Within the framework of this separation by temperature, the dimensionality factor of the samples was not taken into account, which is quite significant. This question was partially considered in the framework of the study [4] which presents analytical solutions of differential diffusion equations that indicate the depth in which 5% of the oxidant concentration is concentrated relative to the concentration of the near-surface level, Fig. 2.

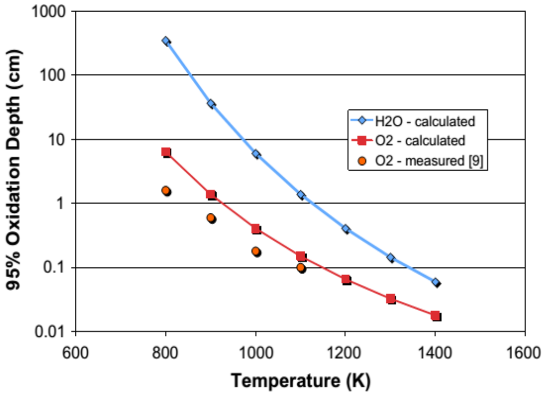

Fig. 2. Depth of 5% oxidant concentration relative to the near-surface concentration level [4]

In Fig. 2 shows the difference between the calculated and changed values of the oxygen concentration, which, based on the extrapolation of the data, can differ by an order of magnitude in the oxidation regime a.

The modeling based on the representation of graphite in the form of a continuous medium was made by the researchers in the work [3], shown in Fig. 3. The diameter of the sample was 21 mm, height 30 mm. Based on the analytical solution for nuclear graphite H451 with an activation energy of 186…960 J/mole oxidation during air oxidation [4]. It can be argued that for simulated temperatures, it is necessary to take into account the volume of the participating in the oxidation, since for a temperature of about 900 K the sample will transfer from the oxidation regime limited by diffusion to the oxidation regime of the boundary layer, since a 5% concentration will be at a depth of less than half the width of the sample, if it is assumed that the difference in the distribution of the oxidant concentration in the interior of the sample for these types of graphite is not significant.

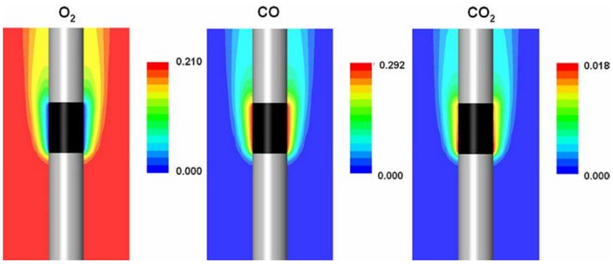

Fig. 3. Simulation of oxidation of nuclear graphite [2]

Based on the modeling presented in the study [2], Fig. 3, semi-empirical formulas on the reaction rate were obtained. The ratio of the resulting concentration of the gas mixture, it was suggested that the main determining factor for the oxidation rate is the near-surface concentration of the oxidant, which is quite true for temperatures over 1200 °C. However, the diffusion to the volume of the sample needs to be clarified for the modeling temperatures used in this work – 700…1500 °C.

In work [2], to obtain a sufficiently accurate correspondence between the accuracy of the simulation and the experimental data, a number of correction coefficients were introduced, including for the Sherwood number.

PURPOSE OF THE WORK

The aim of the work was to consider the distribution of the oxidant concentration in the volume of nuclear graphite taking into account the motion of the surface layer of the oxidizer.

In considering the task posed, the following were decided:

- Macroscopic modeling of oxidizer fluxes in the reaction chamber to find the oxidizer flow rate in the near-surface layer.
- Calculation of the diffusion coefficients for the modeling temperature of 873 K.
- Microscopic modeling of the oxidation of nuclear graphite, taking into account the results of macroscopic modeling with the distribution of the concentration of reaction products.

THE PROCEDURE FOR MODELING OXIDATION PROCESSES

As part of this work was proposed use direct modeling to justify approaching the numerical solution of the problem of oxidation of nuclear graphite temperature range takes into account the diffusion of oxidation mode.

To determine the flows of the near-surface layer of the oxidizer, modeling was carried out using the software package Solid Works Flow Simulation [5] in the model volume of the oxidation chamber.

To simulate microscreen oxidation of nuclear graphite, a package was used to solve the problem of applied hydrodynamics Open FOAM, taking into account the bulk and surface reactions.

The surface reaction was taken into account:

$$2C+O_2 \xrightarrow{surf} 2CO,\ (190...116)\ \text{kJ/mole}.$$

The bulk reaction considered in the simulation:

$$2CO+O_2 \xrightarrow{volume} 2CO_2,\ \ 213\ \text{kJ/mole}.$$

Changes in the coefficients of self-diffusion and mutual diffusion of the oxidant and reaction products as a function of temperature were taken into account.

Based on the work [6], the calculation was used for the diffusion coefficients for each component of the three component gas mixture:

$$D_{A,mixture}=\frac{1-x_A}{\dfrac{x_B}{D_{A,B}}+\dfrac{x_C}{D_{A,C}}}, \tag{1}$$

where $D_{A,mixture}$ – the diffusion coefficient, respectively, of component A of the gas mixture relative to the whole mixture, m^2/s; $D_{A,B}$ and $D_{A,C}$ – coefficient of mutual diffusion, respectively, of components A and B, and A and C of the gas mixture component; x_A, x_B, and x_C – molar fraction, respectively; of components A, B, and C of the gas mixture.

To calculate the diffusion coefficients of a binary mixture, we used the expression [6]:

$$D_{12} = 2.6280 \cdot 10^{-7} \times \times \frac{\sqrt{T^3 (M_1 + M_2) / 2M_1 M_2}}{p\sigma_{12}^2 \Omega_{12}^{(1,1)} * (T_{12} *)}, \qquad (2)$$

where D_{12} is the diffusion coefficient of the binary mixture, m^2/s; T – the temperature, K; M_1, M_2 – the molecular weight of the first and second components; p is the pressure, atm; $T_{12}*$ – the reduced temperature is equal, is a dimensionless quantity $\frac{kT}{\varepsilon_{12}}$; σ_{12}, Å; $\frac{k}{\varepsilon_{12}}$, K – parameters of the potential energy of molecules, characterizing the interaction of molecules of types 1 and 2; $\Omega_{12}^{(1,1)} * (T_{12} *)$ is the collision integral for molecular diffusion, which is a function of the reduced temperature.

To calculate the diffusion coefficient in the first approximation, it is sufficient to use an integral with values l,s equal to 1, both for pure gas and for a gas mixture [7], indices 1, 2 denote the types of two molecules participating in the collision.

For the components of a binary gas mixture, the Lennard-Jones potential constants were calculated from the following expressions [6]:

$$\varepsilon_{AB} = \sqrt{\varepsilon_A \varepsilon_B}, \qquad (3)$$

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2}. \qquad (4)$$

To calculate the diffusion tensor, the values of the Lennard-Jones potential constants for the simulated gases are required [7], and the results of calculations for the binary diffusion of O_2-CO, O_2-CO_2, CO-CO_2 (Tabl. 2).

Based on the Lennard-Johnson constants (Tabl. 3) we find the values of the reduced temperature.

The intermediate values of the collision integral $\Omega^{(1,1)} *$ were calculated by linear interpolation based on the nearest values.

The tabulated values of the collision integral were taken from the work [8].

Table 2

The Lennard-Jones potential constants

Gas	$\frac{\varepsilon}{k}, K$	σ, Å
O_2	113	3.433
CO	110	3.590
CO_2	190	3.996
O_2-CO	111.49*	3.5115**
O_2-CO_2	146.53*	3.7145**
CO-CO_2	144.57*	3.793**

*Calculated on the basis of (1), **calculated on the basis of (2).

Table 3

The reduced temperature and the values of the collision integral for gases and mixtures of gas components

Gas and mixtures	$T*$	$\Omega^{(1,1)} *$
	873.2 K	1073.2 K
O_2	9.4973	0.7490
CO	9.7564	0.7456
CO_2	5.6484	0.8229
O_2-CO	9.6260	0.7473
O_2-CO_2	7.3241	0.7836
CO-CO_2	7.4234	0.7818

Based on the data obtained in Tables 2 and 3 values, the diffusion tensors of the three-component mixture were found for three simulated temperatures (Tabl. 4).

Table 4

The diffusion tensor

T, K	The diffusion tensor D_{ij}, x10^{-4} m^2/s
873.2	$\begin{bmatrix} 1{,}85 & 1.83 & 1.4 \\ 1.83 & 1.82 & 1.4 \\ 1.4 & 1.4 & 1.06 \end{bmatrix}$

Index 1 corresponds to O_2, 2 – CO, 3 – CO_2.

In calculating the diffusion coefficients, 3 significant figures were taken, since the proposed approach has an accuracy in percent of the change to experimental data [6], which is the third significant figure.

The law of an ideal gas was used to obtain the gas density as a function of temperature.

In microscopic modeling, a reconstructed graphite microstructure was used in the size of 50 samples with a size of 5000x1000 μm.

The porous structure of the nuclear graphite was reconstructed using the S gems multicriteria statistics package, the source codes of which are available in free access. Subsequently, the result of the reconstruction was ported as the initial geometry for modeling in a freely distributed package for solving the problems of numerical hydrodynamics Open FOAM [9].

THE DISCUSSION OF THE RESULTS

Figs. 4–7 shows the results of simulating gas flows in the oxidation chamber.

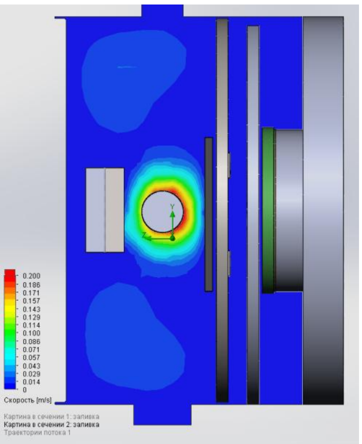

Fig. 4. Distribution of velocities in the volume of the oxidation chamber in the section of the YZ plane

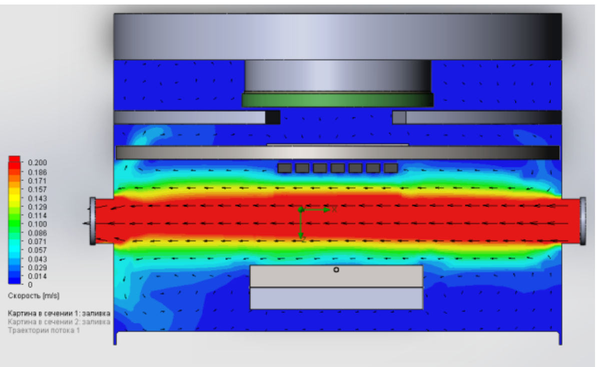

Fig. 5. Distribution of velocities in the volume of the oxidation chamber in the section of the XZ plane

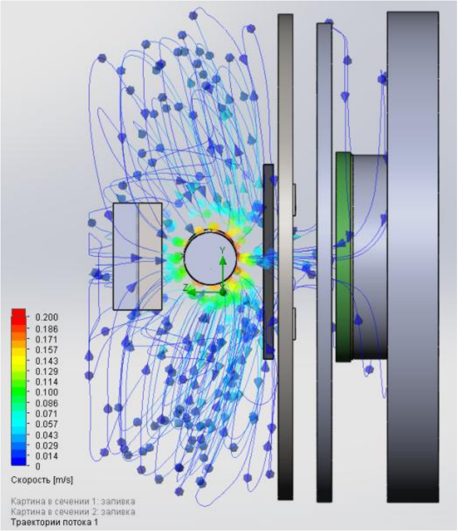

Fig. 6. Flow trajectories in the volume of the oxidation chamber in the section of the YZ plane

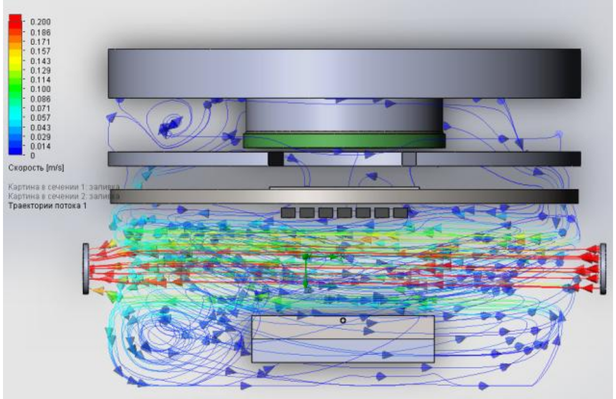

Fig. 7. Flow trajectories in the volume of the oxidation chamber in the section of the XZ plane

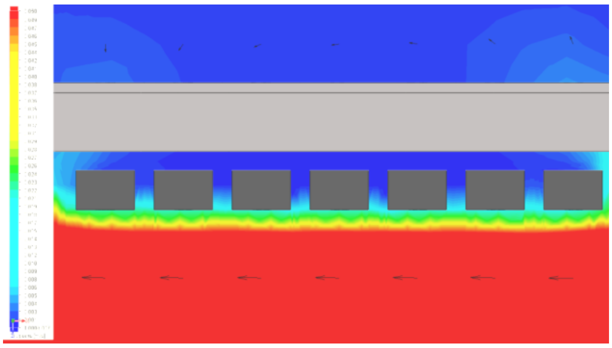

Fig. 8. Increased cross section of gas flow velocities near the samples

Based on the simulation results presented in Figs. 4–8, we can conclude that at 873 K the near-surface currents have velocities in the range 0.001…-0.027 m/s. These data were used as the basis for specifying a near-surface flow for modeling the oxidation of the microstructure of nuclear graphite.

RESULTS OF MICROSCOPIC MODELING

The results of microscopic modeling are shown in Figs. 9–13.

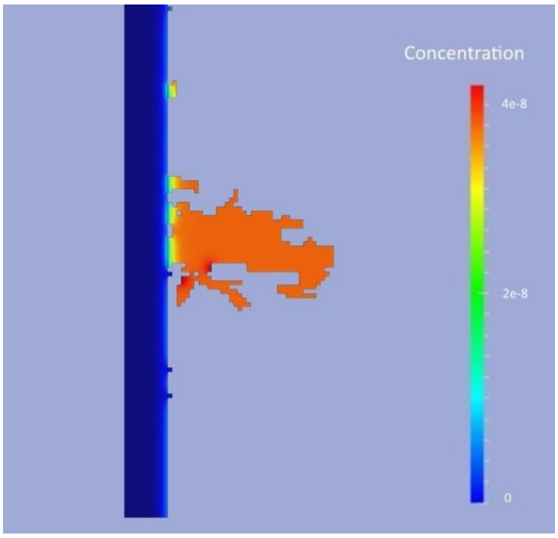

Fig. 9. Distribution of CO concentration in the near-surface region with a speed of oxidizer 0.027 m/s

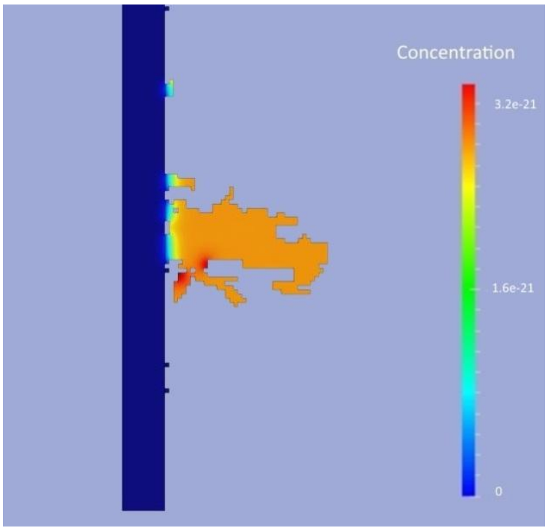

Fig. 10. Distribution of CO_2 concentration in the near-surface region with a speed of oxidizer 0.027 m/s

The presented results indicate a decrease in the reaction products in the porous volume of graphite by more than 2 times, which can significantly influence the modeling of the diffusion oxidation regime in samples with a significant decrease in the oxidant concentration in depth and with geometric dimensions comparable to a depth of 95% of the oxidant concentration for the simulated temperature.

It can be seen from the simulation of a slight change in the oxidant concentration in the meso porosity.

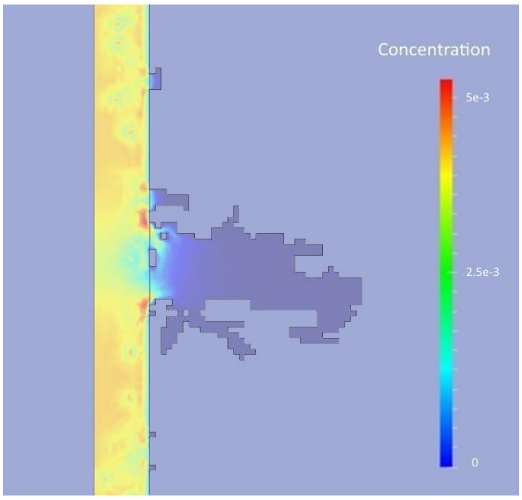

Fig. 11. The distribution of the velocities of gas flows in the near-surface region of nuclear-graphite modeling

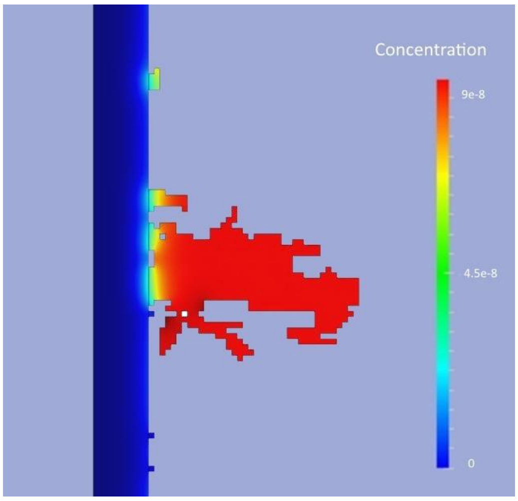

Fig. 12. Distribution of CO concentration in the near-surface region without taking into account the motion of the near-surface layer

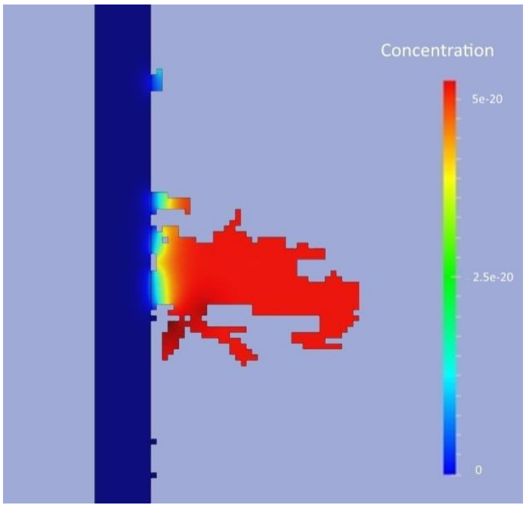

Fig. 13. Distribution of CO_2 concentration in the near-surface region without taking into account the motion of the near-surface layer

CONCLUSIONS

1. For the first time, macroscopic and microscopic modeling of the oxidation of the near-surface layer of nuclear graphite was carried out, taking into account the motion of the near-surface layer.

2. The tensor of binary diffusion of gaseous oxidant components and reaction products is calculated for the temperature of 873 K.

3. In simulation, the concentration of reaction products is shown to be smaller by a factor of 2, taking into account and without taking into account the motion of the near-surface layer, which implies a comparable influence of the motion of the near-surface layer and the diffusion of gaseous reaction products when considering mesoprostability.

4. The necessity of modeling the microstructure of nuclear graphite is shown, in view of the presence of an essentially unchanged oxidant concentration in the mesopores, which can significantly affect the oxidation dynamics upon transition to higher temperature oxidation modes of the samples, with linear dimensions comparable to the penetration depth of the oxidizer.

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ВЫСОКОТЕМПЕРАТУРНОЕ ОКИСЛЕНИЕ ЯДЕРНОГО ГРАФИТА С УЧЕТОМ ДВИЖЕНИЯ ПРИПОВЕРХНОСТНОГО СЛОЯ ОКИСЛИТЕЛЯ

А.И. Комир, Н.П. Одейчук, В.И. Ткаченко, А.Л. Улыбкин, А.А. Николаенко

При высокотемпературном окислении ядерного графита учтен поток окислителя в приповерхностной области. Проведено макро- и микроскопическое моделирование окисления приповерхностного слоя. Приведен расчет коэффициента диффузии газообразных компонент в зависимости от температуры и концентрации. Исследовано влияние учета движения приповерхностного слоя окислителя на концентрацию газообразных компонентов.

ВИСОКОТЕМПЕРАТУРНЕ ОКИСЛЕННЯ ЯДЕРНОГО ГРАФІТУ З УРАХУВАННЯМ РУХУ ПРИПОВЕРХНЕВОГО ШАРУ ОКИСЛЮВАЧА

А.І. Комір, М.П. Одейчук, В.І. Ткаченко, А.Л. Улибкін, А.О. Ніколаенко

При високотемпературному окисленні ядерного графіту врахований потік окислювача в приповерхневій області. Проведено макро- і мікроскопічне моделювання окислення приповерхневого шару. Наведено розрахунок коефіцієнта дифузії газоподібних компонент у залежності від температури і концентрації. Досліджено вплив обліку руху приповерхневого шару окислювача на концентрацію газоподібних компонентів.