A RADIATION TECHNIQUE FOR STUDYING THE PROPERTIES OF NUCLEAR GRAPHITES IN OXIDIZING ENVIRONMENTS USING CHARGED-PARTICLE ACCELERATORS

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A radiation technique is proposed for investigating nuclear-grade graphites intended for Generation IV nuclear power systems in oxidizing environments using charged-particle accelerators. Graphite samples are irradiated with electron and helium-ion beams in air, oxygen, and air-steam mixtures at 400…1100 °C, as well as at extreme temperatures of 1250…1670 °C. A significant acceleration of corrosion under irradiation, by as much as 6-8 times, has been established. A computational model has been developed to simulate graphite oxidation and radiation-induced dimensional change; a parameterization of radiation enhancement is proposed as a component of predictive degradation models.

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INTRODUCTION

Among Generation IV reactor systems, an important place is occupied by high-temperature gas-cooled reactors (HTGR/VHTR, GT-MHR, and others), which are characterized by high operating temperatures and increased requirements for the stability of core materials. In these systems, carbon materials, primarily nuclear-grade graphites of various grades, are elements that determine not only neutron-physical characteristics (moderation and reflection of neutrons), but also the structural integrity of graphite blocks/matrices, geometric stability, and service life. In specialized studies conducted at NSC KIPT, graphite is considered specifically as a structural and functional material for nuclear power engineering, while oxidation is regarded as one of the determining processes limiting service life [1–3].

Radiation materials science of structural and functional materials for HTGRs remains a key component in substantiating their efficiency and safety, since degradation under actual operating conditions is formed by the combined influence of two groups of factors. The first group is associated with radiation damage: changes in the defect structure, evolution of the pore space, accumulation of damage energy, and, over long periods, dimensional change (shrinkage/swelling) and changes in physical and mechanical properties. The second group is caused by high-temperature oxidation/corrosion in the presence of oxidants, which may appear either as impurities or as manifestations of design-basis abnormal scenarios, in particular emergency depressurization of the circuit with access of air and/or steam. Importantly, these factors are not additive in a linear manner: the radiation state of the surface and porosity changes the kinetics of oxidation, while oxidation, in turn, restructures the pore space and the stress-strain state, thereby modifying the trajectory of radiation-induced dimensional change. Review-based generalizations concerning oxidation mechanisms and the role of pore structure/mass transfer also point to the need for precisely such a mechanistically consistent description of nuclear graphite oxidation.

The practical problem is that neutron irradiation tests, although the most representative, are often resource-limited in both time and cost and do not provide the required flexibility for varying environmental parameters. For this reason, accelerator-based simulation techniques using charged-particle beams, provided they are designed methodically correctly, become a tool for controlled and reproducible investigation of the combined effects of temperature, oxidants, and irradiation.

1. OBJECTIVE OF THE STUDY

The objective of this work is to develop, methodologically substantiate, and experimentally and computationally validate a radiation technique for investigating the oxidation and corrosion of nuclear-grade graphites of different grades in in situ oxidizing environments (air, oxygen, and air-steam mixtures) under accelerated electron and helium-ion beams in the temperature range 400…1100 ºC and at extreme temperatures of 1250…1670 ºC. The technique is intended to provide quantitative separation of the radiation contribution to corrosion intensity and a multiscale description of structural transformation and radiation-induced dimensional change in graphites at the mesoscopic and macroscopic levels.

2. EXPERIMENTAL PART

2.1. IRRADIATION AND OXIDIZING ENVIRONMENTS

At NSC KIPT, a set of techniques for high-temperature irradiation of nuclear graphite samples with accelerated electron and helium-ion beams under in situ oxidizing environments – air, oxygen, and air-steam mixtures – in the range 400…1100 °C, as well as at extreme temperatures simulating emergency depressurization of the primary circuit, has been developed and standardized by enterprise standards [4–7]. A defining feature of the technique is the combination of two controlled "levers": beam parameters (particle type, intensity, and irradiation duration) and environmental parameters (oxidant composition, pressure/flow rate, and temperature regime), which makes it possible to study specifically the interaction between radiation and corrosion mechanisms.

For a separate, already published segment of the research – oxidation in oxygen under electron

irradiation – tests of MPG, ARV, and GSP graphite samples were carried out on the ELIAS accelerator in an oxygen flow at temperatures of about 600 and 800 °C [8, 9]. The work of the NSC KIPT team also provides a detailed description of the "baseline" (non-irradiated) technique for determining oxidation kinetics in oxygen at 400, 600, and 800 °C, which provides the necessary reference for the subsequent separation of the radiation contribution [10].

The component associated with helium ions is methodologically important because helium is the coolant in HTGRs, while ion beams make it possible to realize a different mode of energy deposition and damage profile compared with electrons. At the infrastructure level, a linear helium-ion accelerator (He^+) with energies up to 4 MeV has been commissioned at NSC KIPT, and techniques are also being developed for irradiating structural materials with helium ions followed by investigation of their physical properties. This provides the basis for implementing and comparatively analyzing the "electron" and "ion" channels of accelerator-based simulation.

2.2. RADIATION-INDUCED ACCELERATION OF CORROSION

The set of experiments performed made it possible to observe qualitatively and, in part, quantify a substantial acceleration of graphite corrosion/oxidation under irradiation with charged particles. For the "oxygen + electron irradiation" system, it was established that, as temperature increases, oxidation proceeds much more intensively, and the oxidation rate increases by a factor of 6–8. This acceleration is accompanied by evolution of the surface morphology and a transition from initial loosening to reduction of geometric dimensions and destruction, which emphasizes not only the chemical but also the structural nature of degradation at high temperatures.

An important materials-science outcome is the differentiation of the behavior of different graphite grades. It has been shown that GSP graphite produced by NSC KIPT, with a density of 1.77…1.9 g/cm^3, exhibits the best corrosion resistance under irradiation within the studied temperature interval, which is consistent with the conclusions obtained both for electron irradiation and for oxygen testing without irradiation under comparable temperature conditions [9, 10]. This difference among graphite grades is of fundamental practical importance because it means that the technique is capable of revealing material-dependent effects associated with porosity, binder structure, and the nature of the reactive surface.

3. MATHEMATICAL MODELING

Mathematical modeling was used as the linking element between in situ accelerator experiments and prediction of degradation of HTGR graphite components. Its purpose is to transform measured mass loss and other experimental observations into quantitative parameters that separate the contributions of the chemical reaction, oxidant supply into pores, and radiation effects. As a result, the experiment "shows the effect," while the model explains what causes this effect and how it can be transferred to other temperatures, environments, and operating conditions.

The basis of the computational part is a model of porous graphite oxidation, in which the degradation rate is determined not only by the reaction on the external surface, but also by processes in the pore space. The model takes into account that the oxidant must penetrate into the pores, and only there is the reactant consumed on the internal reactive surface. Therefore, the oxidation rate is governed by two interrelated factors: reaction kinetics and oxidant mass transfer in the porous body; at the same time, porosity, specific reactive surface area, and, consequently, the effective process parameters change over time. This description makes it possible to correctly reproduce cases in which burn-off is volumetric rather than purely near-surface and explains why the same graphite grade may exhibit different corrosion intensities depending on temperature and oxidant supply conditions.

The model parameters are determined by fitting to experiment. In practice, this means solving an inverse problem: from mass-loss curves and known conditions (temperature, environment composition, time), the parameters characterizing the "chemical" part (effective reactivity) and the "transport" part (oxidant supply in the pore space) are reconstructed, taking into account structural evolution during burn-off. It is precisely this step that makes the experimental data suitable for calculations: one obtains not only mass-loss plots but also a parameterized description of degradation.

For high-temperature regimes and experimental configurations with intense oxidant supply, it is important to take into account that the process rate may be limited not by transport in the pores, but by oxidant delivery to the sample surface through the near-surface gas layer. Therefore, a separate line of modeling of near-surface mass transfer has been developed, which sets the correct boundary conditions for the main oxidation model. The meaning of this block is straightforward: it answers the question of whether the oxidant has time to reach the sample surface under the given hydrodynamic conditions and how this changes the reactant concentration at the surface and, accordingly, the integral burn-off rate. In high-temperature configurations, this effect becomes comparable in influence to internal diffusion in the pore space, and therefore ignoring it leads to a systematic error in estimating the corrosion rate.

A separate, but methodologically consistent, block is the model of radiation-induced dimensional change in nuclear graphite at high temperatures and high neutron fluences, which is necessary for predicting geometric stability and the evolution of properties of graphite elements [11–14]. The model proposed by the authors describes shrinkage and swelling of isotropic and anisotropic graphite under irradiation and leads to a kinetic equation that takes into account the contribution of diffusion-driven processes and a term reflecting the influence of intense neutron flux. Inclusion of this block in the overall scheme makes it possible to consider graphite degradation not only as "mass loss," but as a combination of two interrelated consequences: structural changes caused by oxidation and changes in

geometry/state caused by radiation-induced dimensional change.

This work proposes a parametric separation of radiation and chemical-transport contributions to the corrosion rate. To this end, a calibrated radiation acceleration factor is introduced into the kinetic part of the model and is determined from an inverse problem by comparing experimental data obtained "with irradiation" and "without irradiation" under identical environmental and temperature conditions. In this formulation, the transport parameters account for oxidant availability and changes in porosity, while the radiation factor accounts for changes in the effective reactivity of the material under charged-particle irradiation. This translates the result of a "6-8-fold acceleration" from the level of empirical observation to the level of a model parameter that can be used in calculations and comparisons.

To harmonize the electron and helium-ion test channels, a unified comparison scale is introduced at the level of equivalent damage, taking into account dose/fluence and the nature of energy deposition for a given particle type. This generalized parameter is then related to the radiation acceleration factor in the corrosion model, which ensures a methodologically correct comparison of results obtained on different accelerators and with different beams. As a result, a unified computational description is formed that improves the transferability of accelerator experiments to HTGR design conditions and makes it possible to compare graphite grades within a single system of parameters.

4. COMPREHENSIVE ANALYSIS OF GRAPHITE STRUCTURE TRANSFORMATION UNDER IONIZING IRRADIATION

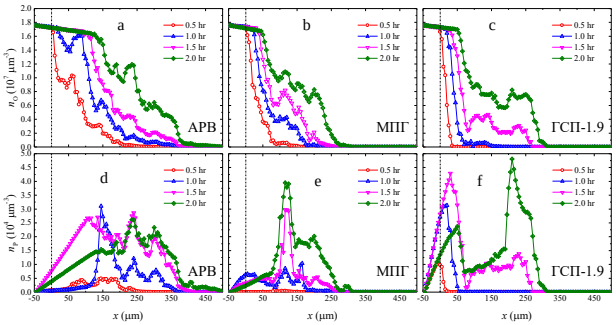
To analyze the transformation of graphite structure (based on current data from metallographic and electron-microscopic studies), methods of computer modeling and theoretical investigations were applied.

In the course of comprehensive studies, the following theoretical and software products were developed, making it possible to explain the transformation of graphite structure under irradiation: - a 3D simulation model for the statistical description of heterogeneous oxidation of nuclear graphite with a specified particle-size distribution; – 3D gas-dynamic modeling in the ELIAS oxidation/irradiation chamber; - computational dosimetry of simulation experiments on the ELIAS electron accelerator; - modeling of diffusive propagation of the oxidant in graphite samples; - fractal analysis of the porosity of irradiated nuclear graphites; - a fractal model for synthesis of the structure of porous nuclear graphites; - a mesoscopic kinetic model of oxidation of fractal-porous nuclear graphites; - a radiation-vacancy phenomenological model of dimensional change in nuclear graphites under reactor neutron irradiation.

Based on the comprehensive analysis of metallographic and electron-microscopic data and the application of the developed methods of computer modeling and theoretical investigations, the following results were obtained.

Mesoscopic modeling of the diffusion dynamics of O_2 oxygen and oxidation products (CO, CO_2) in porous graphite revealed that they are significantly influenced by motion of the near-surface oxygen layer: in comparison with the results of a gas-static calculation, the product concentration and oxidation rate decrease by approximately a factor of 2.

Theoretical analysis of previously obtained analytical data from optical metallography and scanning electron microscopy proved scale invariance (fractal character) of the microstructure and porosity over a wide scale range of about 1…100 μm. Trial modeling demonstrated that the kinetics of corrosive oxidation differs substantially among graphites of different grades, which is associated with differences in the micro- and nanostructural parameters of their porosity (Figure).



Laterally averaged, over the plane (y, z) parallel to the initial sample surface (t = 0), profiles of the volume concentrations of oxidant n_O (a–c) and oxidation products n_P (d–f) along the x-axis of corrosion-front propagation for ARV (a, d), MPG (b, e), and GSP-1.9 (c, f) graphites

Modeling tools established that the dose load depends only very weakly on sample density and is the same for all graphite grades (ARV, MPG, GSP-1.77, and GSP-1.9) irradiated in the electron-beam experiments. No effect of the fractal parameters of the microstructure of thin samples on dosimetric characteristics was found.

The radiation-vacancy phenomenological model of dimensional change in nuclear graphites under reactor neutron irradiation makes it possible to describe both the initial stage of shrinkage of nuclear graphite with accumulation of neutron fluence and the transition to the stage of rapid swelling at high fluences. The results explain known empirical trends and contribute to the IAEA international knowledge base on the properties of irradiated nuclear graphites.

5. PRACTICAL SIGNIFICANCE AND RECOMMENDED CONCLUSIONS

Application of the in-situ radiation technique in oxidizing environments makes it possible to obtain degradation parameters for nuclear graphites in configurations where temperature, oxidant, and irradiation act simultaneously. This is fundamentally important for Generation IV nuclear power systems, where graphite is considered as a structural material for HTGR reactors and where the mechanisms of oxidation/porosity/mass transfer are directly related to service life and safety. The experimentally established

acceleration of oxidation under charged-particle irradiation provides grounds for considering the radiation factor not as a secondary correction, but as a dominant multiplier in certain regimes, which requires special consideration in engineering calculations and in the selection of graphite grades.

The multiscale modeling approach developed by the authors provides a transition from qualitative observations to quantitative description, including the effects of porosity and mass transfer and, for high-temperature configurations, the processes in the near-surface oxidant region. Taken together, this creates the basis for a comprehensive formulation of the materials-science principles governing graphite structure transformation and for recommendations regarding practical implementation, in particular in the selection of grades with enhanced corrosion resistance (at the level of the established advantage of GSP graphites with densities of 1.77…1.9 g/cm^3 under the studied conditions).

CONCLUSIONS

The radiation technique developed at NSC KIPT for high-temperature irradiation of nuclear graphites with accelerated electron and helium-ion beams in in situ oxidizing environments provides experimental reproduction of the combined effects of temperature, oxidant, and irradiation in regimes relevant to Generation IV HTGRs. A substantial acceleration of graphite oxidation/corrosion under charged-particle irradiation has been experimentally recorded; for electron irradiation in an oxygen flow at about 600 and 800 °C, the oxidation rate was found to increase by a factor of 6-8, and GSP graphites with densities of 1.77…1.9 g/cm^3 showed the best corrosion resistance.

The specialized multiscale modeling algorithms developed make it possible to perform quantitative analysis of empirical data, describe oxidation while taking porosity and mass transfer into account, and extend the computational framework to high-temperature regimes with allowance for near-surface processes. An additional theoretical foundation for describing radiation-induced dimensional change is provided by a model of shape change in isotropic and anisotropic graphite at high temperatures and neutron fluences.

The element of novelty proposed within the report consists in introducing a calibrated radiation acceleration parameter for corrosion, identified from experiment and integrated into the multiscale model, as well as in the methodological unification of electron- and helium-ion-irradiation data on the basis of a comparable damage scale.

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РАДІАЦІЙНА МЕТОДИКА ДОСЛІДЖЕННЯ ВЛАСТИВОСТЕЙ ЯДЕРНИХ ГРАФІТІВ В УМОВАХ ОКИСНЮЮЧОГО СЕРЕДОВИЩА З ВИКОРИСТАННЯМ ПРИСКОРЮВАЧІВ ЗАРЯДЖЕНИХ ЧАСТИНОК

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Запропоновано радіаційну методику дослідження ядерних графітів для ядерних енергетичних систем IV покоління в окиснювальних середовищах із використанням прискорювачів заряджених частинок. Зразки графітів опромінюють пучками електронів та іонів гелію у повітрі, кисні та повітряно-парових сумішах при 400…1100 °С, а також за екстремальних температур 1250…1670 °С. Встановлено істотне (до 6–8 разів) прискорення корозії під опроміненням. Розроблено обчислювальну модель для моделювання окиснення та радіаційного формозмінення графіту; запропоновано параметризацію радіаційного підсилення як складову прогнозних моделей деградації.