Microstructural characterization of nuclear graphite: from the microscale to the nanoscale

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Abstract

Multiple reactor designs use graphite as a moderator of the nuclear reactions and as structural support. During the lifetime of the reactor, multiple aging factors such as neutron irradiation, oxidation, and temperature along with others induce changes in the microstructure and crystal lattice of graphite components. The pore morphology and crystal structure of some phases in graphite can be used to trace the evolution of irradiation defects and mechanical properties of graphite. We present a combination of results from several microscopy techniques to investigate the differences between nuclear graphite grades and the effects of neutron irradiation and oxidation at multiple length scales. This multiscale approach is needed to understand the microstructural variations caused by the raw materials and manufacturing processes as well as how the different phases of graphite are affected by the reactor environment. The results provide insight into the oxidation- and radiation-induced changes of graphite and create a robust baseline of microstructure information that can be used for the selection of materials for the next generation of nuclear power stations. Moreover, the experiments conducted in this work provide an overview of the advantages and limitations of the most common techniques used to characterize nuclear graphite and how

This work was supported by the U. S. Department of Energy, Office of Nuclear Energy, under the Advanced Reactor Technologies (ART) program. This manuscript has been authored by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the US Department of Energy (DOE). The US government retains and the publisher, by accepting the article for publication, acknowledges that the US government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this manuscript, or allow others to do so, for US Government purposes. DOE will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (http://energy.gov/downloads/doe-public-access-plan).

these techniques might be applied to study other carbon-based materials used in the nuclear industry.

Introduction

Nuclear graphite moderates fast neutrons and acts as structural support in various reactor designs. Graphite can be considered as a composite material formed by filler and binder. Filler particles can have different shapes and sizes and are normally sourced from naturally occurring cokes, petroleum cokes, or coal-tar pitch [1]. Filler particles serve several important functions in nuclear graphite, which contribute to the composite's strength, thermal conductivity and stiffness. The binder contributes to the adhesion of the mixture of materials holding the graphite particles together to form a cohesive structure. Another critical aspect of nuclear graphite is the porosity content. The void space in nuclear graphite can represent 17 to 20% of the volume space [2]. Nuclear graphite porosity significantly influences mechanical behavior, fracture response and irradiation response.

During the normal operation of the reactor, several aging mechanisms degrade the mechanical properties and microstructure of graphite. These degradation mechanisms include neutron irradiation, oxidation, temperature, and irradiation creep [3]. The porosity, defect identification, and crystal lattice parameters are three characteristics in graphite that can be used as forensic fingerprints that can be used to track the evolution of irradiation effects or other damage generated in graphite. This work shows some of the microscopy techniques that are commonly used to characterize the degradation in nuclear graphite at multiple length scales. A multiscale approach allows for a better understanding of the degradation mechanisms that occur at the atomistic level as well as in the bulk material. In this research, we summarize the results of several techniques used at Oak Ridge National Laboratory to characterize nuclear graphite. These results demonstrate the importance of microstructural characterization for understanding nuclear graphite properties and behavior in nuclear reactors.

Methods

The characterization process involved examining the filler and binder phases of the graphite material at multiple length scales, as well as analyzing pore size distribution, pore shape, estimated density, and open versus closed porosity fraction of the different grades.

Techniques such as optical microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray computed tomography (XCT), electron energy loss spectroscopy (EELS), mercury porosimetry, and helium pycnometry were employed to characterize the material microstructure of different grades of nuclear graphite. The sample preparation and microscopy examinations were carried out in the low activation materials development and analysis (LAMDA) facilities at Oak Ridge National Laboratory (ORNL). A summary of the relationship between properties, constituents and characterization techniques is shown in Figure 1. As can be seen from Figure 1 five of the six aspects included in the diagram can be characterized using various microscopy techniques. The raw materials or initial materials influence the porosity content, grain size and porosity structure of graphite. These aspects of graphite can be studied with several bulk type of characterization techniques such as XCT, mercury porosimetry and helium pycnometry that provide information of the porosity. Higher magnification techniques complement the other techniques by providing data of the defects generated by the reactor environment or neutron irradiation.

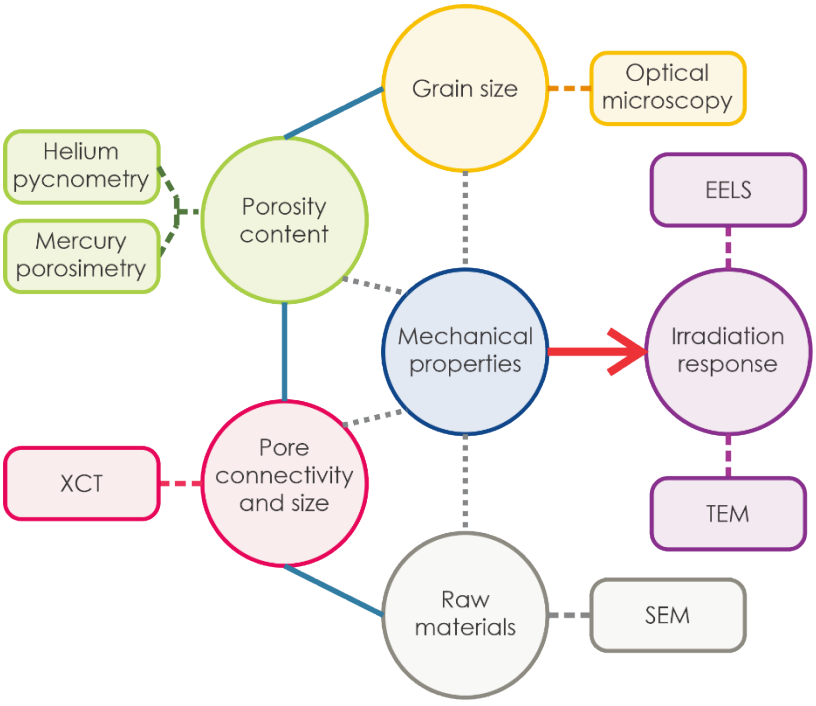

Figure 1. Links among different aspects of nuclear graphite and techniques used to characterize these aspects.

Results and Conclusions

Examples and illustrations of the results compiled in this research are included in Figure 2. A description of how the techniques were used for this research are described below:

a) **Optical microscopy** – this technique was conducted to study the surface of polished samples. This characterization technique can use polarized light that enhances the contrast between phases with differing crystallographic orientations, allowing for the identification of various regions, such as filler and binder domains.
b) **SEM** – this characterization technique was performed on fractured surfaces of nuclear graphite to understand the 3D structure of the main phases of graphite filler, binder, and porosity. The SEM data showed some features that cannot be observed in polished surfaces, such as thermal cracks and the morphology of filler particles.
c) **TEM** – liftouts were prepared from neutron-irradiated and as-received material were imaged. These images were used to compare the neutron induced defects in nuclear graphite.
d) **XCT** – scans generated from multiple grades were segmented and processed to understand the pore connectivity and pore size distribution of nuclear graphite.
e) **Mercury porosimetry** – specimens of nuclear graphite were infiltrated with mercury to estimate the pore content and the pore size distribution in graphite.
f) **Helium pycnometry** – mercury porosimetry measurements were complemented with helium pycnometry to estimate graphite density and open porosity.

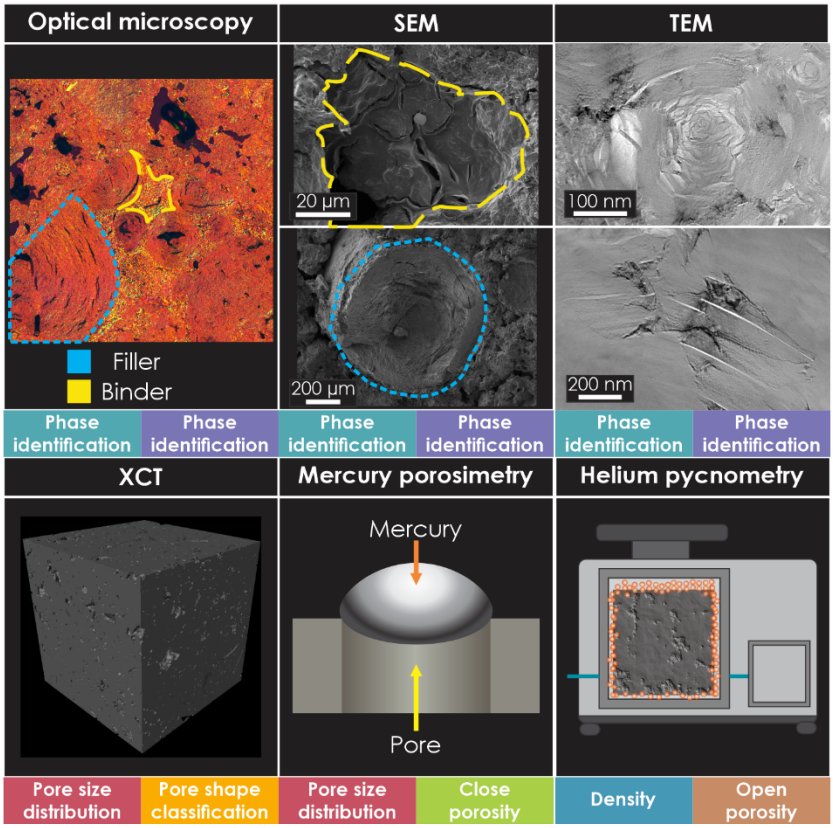

Figure 2. Summary of results for each characterization technique used in this research.

Examples of the microscopy results for Gilsocarbon nuclear graphite are included in Figure 3. The polarized optical micrograph shows the three main phases of graphite: binder, filler particle, and porosity. As can be seen in these micrographs, the polarized micrographs reveal the onion-like shape of filler particles in Gilsocarbon. Moreover, the binder region shown in Figure 3 shows the typical mosaic pattern of this phase. The SEM micrographs in Figure 3 complemented the optical microscopy results by showing the 3D morphology of the fracture surfaces of Gilsocarbon's filler and binder. Another feature commonly found in graphite, quinoline insoluble particles, is included in this figure's bottom region. TEM results of as-received material show nuclear graphite's most minor cracks and pores. The final portion of Figure 3 shows examples of XCT, a reconstructed slice, the segmentation, and 3D reconstruction of the closed and open porosity.

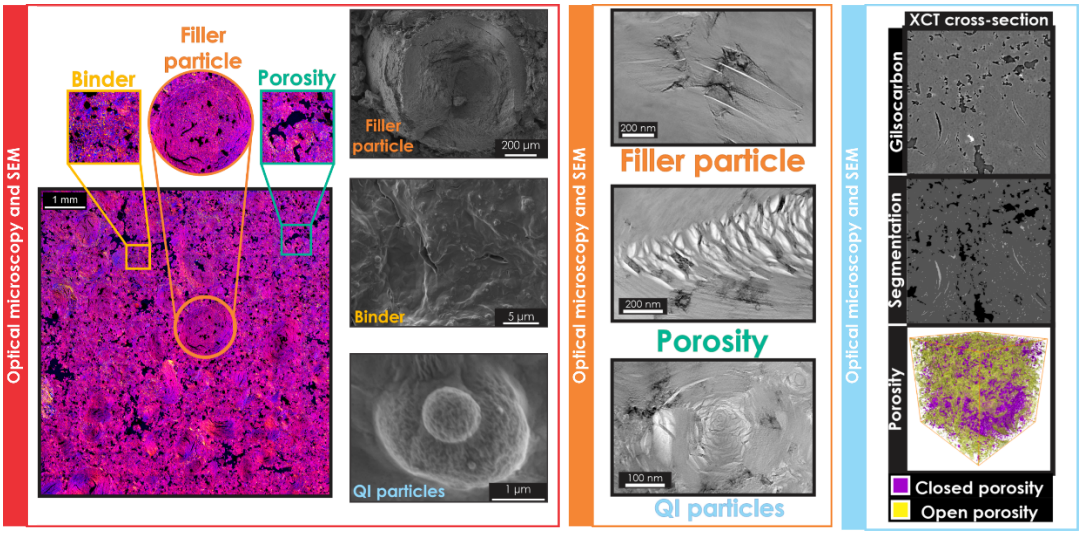

Figure 3. Microscopy results for Gilsocarbon nuclear graphite. These results exemplify the typical results of optical microscopy, SEM, TEM and XCT.

The microstructure of various grades of graphite that are relevant for nuclear power applications, both historically, currently, and in the future, is closely connected to their irradiation behavior and thermo-physical properties. This paper offers a comprehensive examination of the microstructure of multiple grades of graphite used in nuclear applications, with a particular emphasis on their porosity content, as well as the filler and binder phases. These efforts are being conducted to produce a robust library of microstructures that can be used by industry to compare different materials and contribute to their selection of materials.

Acknowledgments

This work was supported by the U. S. Department of Energy, Office of Nuclear Energy, under the Advanced Reactor Technologies (ART) program. A portion of this work was supported by the Office of Nuclear Energy under DOE Idaho Operations Office Contract DE-AC07-051D14517 as part of a Nuclear Science User Facilities experiment. This research used the resources of the Low Activation Materials Development and Analysis Laboratory (LAMDA), a DOE Office of Science research facility operated by the Oak Ridge National Laboratory (ORNL). Oak Ridge National Laboratory is managed by UT-Battelle under contract DE-AC05-00OR22725.

References

[1] J.D. Arregui-Mena, R.N. Worth, W. Bodel, B. März, W. Li, A. Selby, A.A. Campbell, C. Contescu, P.D. Edmondson, N. Gallego, SEM and TEM data of nuclear graphite and glassy carbon microstructures, Data in Brief 46 (2023) 108808.
[2] J.D. Arregui-Mena, R.N. Worth, W. Bodel, B. März, W. Li, A.A. Campbell, E. Cakmak, N. Gallego, C. Contescu, P.D. Edmondson, Multiscale characterization and comparison of historical and modern nuclear graphite grades, Materials Characterization 190 (2022) 112047.
[3] J.D. Arregui-Mena, D.V. Griffiths, R.N. Worth, C.E. Torrence, A. Selby, C. Contescu, N. Gallego, P.D. Edmondson, P.M. Mummery, L. Margetts, Using porous random fields to predict the elastic modulus of unoxidized and oxidized superfine graphite, Materials & Design 220 (2022) 110840.