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Site specific, high-resolution characterisation of porosity in graphite using FIB-SEM tomography☆

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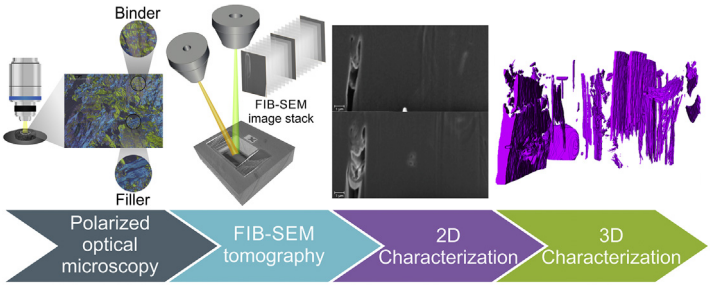
GRAPHICAL ABSTRACT



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ABSTRACT

Graphite is used as a moderator of fast neutrons in some types of nuclear reactors and for other industrial applications. The influence of smaller pores on the mechanical and physical properties of graphite remains to be fully understood. In this work, focused ion beam-scanning electron microscopy (FIB-SEM) tomography was applied to characterise the porosity of AGX graphite – an electrode material. FIB-SEM tomography consists in alternating the ion milling and SEM imaging at an area of interest with the objective of creating a 3D reconstruction. Regions containing a filler and a mixture of filler and binder were selected as the areas of interest. Resolutions of a few nanometers were achieved in volumes up to 1400 μm^3 for both regions. Typical porous structures were detected in the filler and binder regions such as thermal cracks, gas evolution porosity and lenticular pores. The resolution achieved with these experiments made possible detection of pores smaller than 150 nm in diameter, that is of the length scale of voids generated by neutron irradiation, and an improvement in spatial resolution of traditional x-ray tomography studies. The resolution achieved by FIB-SEM tomography may be essential for the study of the microstructure of graphite, providing complimentary data to x-ray tomography experiments.

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1. Introduction

Graphite is used as the moderator of fast neutrons in nuclear fission reactors. Nuclear graphite grades are polycrystalline materials composed of binder and filler phases and porosity of various sizes. These phases of graphite have different microstructures and porosity content due to their raw constituents and changes produced during the manufacturing processes. The filler material is obtained from petroleum or pitch coke and is expected to be fully graphitised during the fabrication process of graphite [1]; the binder materials come from coal tar pitch or petroleum pitch and the compositions of these materials can vary depending on the manufacturer. The degree of graphitisation of the binder material is controlled by the characteristics of the former materials (content of volatile components and quinoline insoluble particles), temperature and time however, full graphitisation of coal tar pitch can be achieved in some cases [2]. The wide diversity of existing graphite grades comes from the mixtures and proportions of filler and binder, raw materials, porosity and manufacturing process [3]. In order to understand how these variations affect the physical properties of the material, it is crucial to understand the microstructure of graphite.

Graphite porosity content and morphology can be controlled to a certain extent by several factors. For example, coal-tar pitch is normally used to increase the density of a billet and to reduce the pore content. Another factor to consider is forming of the graphite billet and nature of the filler particles. Extruded grades tend to have filler particles with basal planes preferentially aligned to the extrusion direction resulting in a preferential alignment of the porosity structures and anisotropic mechanical properties. Newer forming techniques (vibramolding and isostatic pressing) have been developed to obtain isotropic bulk properties. Some older grades use round-shaped filler particles that are molded to create a more random orientation of the porosity and to some extent isotropic mechanical properties. The newer forming techniques can use fine needle-shaped filler particles and still obtain isotropic bulk properties.

Porosity in nuclear graphite grades may represent as much as 20% of the bulk volume [4] and can range in size between 10 Å up to a few millimeters [5,6]. Each phase of graphite contains different amounts and types of porosity; these can be classified into three types: gas entrapment pores, thermal cracks and unfilled pores. Gas entrapment pores are generated by off gassing of the binder phase during the baking stage [6]. Thermal cracks, also referred to as Mrozowski cracks, are a result of the anisotropic coefficient of thermal expansion of the crystal structure, and are formed by internal stress relaxation when crystalline graphite is cooled from temperatures above 2000 °C.

The pore size, morphology, and pore connectivity control the generation and evolution of cracks in graphite under a mechanical force or load as well as their mechanical, thermal and electrical conductivity properties. In general, larger amounts of pores in graphite lower the Young's modulus, the coefficient of thermal expansion (CTE) and the electric conductivity [7]. Porosity plays three main roles in the fracturing of graphite components, it may initiate cracks, promote crack propagation, or conduct the crack growth to a region where it gets arrested.

In nuclear reactor applications, displacement damage caused by exposure to energetic neutrons alters the microstructure in such a way that the bulk physical, mechanical, and thermal properties of the material are modified. Irradiation causes the anisotropic swelling of crystals. During the early stages of irradiation, so-called accommodation pores absorb this swelling and that results in bulk shrinkage. The anisotropic crystal swelling continues throughout irradiation, but after all the accommodation porosity is filled, the shrinkage ceases and bulk swelling is observed. The anisotropic crystal swelling results in the generation of new porosity and expansion of the original pores. The evolution of damage and dimensional change is closely related to porosity changes and microstructure in graphite. Highly porous nuclear graphite is undesirable due to its low mechanical properties, whereas very dense (i.e. high strength) graphite would not be able to accommodate the irradiation-induced dimensional changes in the bulk material leading to an early failure of the component. A better understanding and prediction of the damage and mechanical performance of an irradiated graphite component requires detailed information of the micro- and macroscopic pore structure.

In this work serial-sectioning on site specific regions using focused ion beam (FIB) and scanning electron microscopy (SEM) (a technique commonly known as FIB-SEM (or FIB) tomography) is used to study the pore characteristics in an electrode graphite. This technique alternates the SEM imaging of the area of interest and the material removal via sputtering induced by the FIB Ga^{+} beam. The origins of FIB-SEM tomography started with a combination of secondary ion mass spectrometry (SIMS) and FIB milling for subsurface chemical analysis of integrated circuit-production [8]. Following this, FIB milling and imaging was implemented to study a section of a nanoindented Cu-Al multilayers [9]. The development and improvement of dual beam FIB-SEM systems led to automated serial-sectioning and SEM imaging. One of the first examples of this type of FIB tomography was proposed by Holzer [10]. Current FIB-SEM systems have the capacity of using FIB, SEM or SEM tiled images; this allow multiple ways to optimise the visualisation of multiple materials. Other techniques such as electron backscatter diffraction (EBSD), energy-dispersive x-ray spectroscopy (EDX) can also be combined with FIB-SEM tomography and combined with additional data to generate 3-dimensional information on the local microstructure and chemistry. FIB tomography has also been part of study that identifies the porosity structure on a nuclear graphite grade pile grade A (PGA) [11,12]. Comprehensive reviews and history of FIB-tomography can be found in the literature [13–15].

Here the feasibility of FIB-SEM tomography as a newer additional technique to study the graphite microstructure – in particular porosity – is explored and presented. Furthermore, the methodology for the image acquisition and general steps required to segment the images to create a 3D reconstruction are provided. The advantages and disadvantages of this technique as applied to the examination of porosity in graphite are also discussed.

2. Materials and methods

A general-purpose extruded graphite designated AGX was chosen for this study. The decision to use this graphite grade is because filler particles are as large as 1 cm so specific features are easily discerned. A polarised light micrograph of the polished surface of the sample showing the different phases and microstructure is shown in Fig. 1. Filler particles can be identified as sections that contain crystallites with the same orientation, this in this case they can be identified as yellow or blue domanins. The difference of colours is produced by different orientations of the crystal planes in the filler particles (Fig. 1a) with regard to the polarised light. The binder phase is composed of several smaller crystalline structures that reflect the light in multiple directions that resemble a mosaic pattern (Fig. 1b). This graphite sample contains pores that vary greatly in their size, from a few microns to some millimeters (Fig. 1c).

Optical micrographs at higher magnifications were obtained to identify two regions of interest: Region 1 and Region 2. The size and shape of the original sample, the locations of the regions and how the areas of study were prepared to perform FIB-SEM tomography are shown in Fig. 2.