

## **Microstructural analysis of irradiated nuclear graphite waste**

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### **ABSTRACT**

The majority of irradiated graphite waste in the UK reactors will originate from moderators and reflector materials, which are exposed to a high irradiation dose during reactor operational lifetime. Irradiation damage induces dimensional change and other physical property changes to graphite, including mechanical properties. During decommissioning it is necessary to fully understand the microstructural and radioisotopic character of the graphite and the effects of proposed decommissioning or immobilisation treatments. Techniques such as encapsulation should limit the diffusion of radionuclides and may fully immobilise the waste, rendering it suitable for future geological disposal. In nuclear graphite, the bulk properties are governed by the porosities, in particular, those at the nanometre scale. Under fast neutron irradiation the crystallites shrink and swell, causing contraction of porosities. The knowledge of the crystallite structure and is therefore important in understanding the mechanism of irradiated damage.

Three nuclear grade graphites, namely PGA from UK Magnox reactors and NBG-10 and NBG-18 from future HTRs (High Temperature Reactors) were chosen for investigation. The manufacturing processes of these graphite grades are distinct, which results different microstructures, including differences in crystal orientations, in the final product. The microstructure of PGA, NBG-10 and NBG-18 graphites were characterised in terms of crystallinity and porosity using Polarised Light Microscopy (PLM), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM).

SEM analysis shows PGA shows a very heterogeneous morphology with areas of ordered particles and a high degree of porosity as compared to the other two graphites. The PLM analysis of the samples confirms that coke particles in PGA are more aligned compared to the other two graphites. This causes the higher degree of anisotropy of PGA graphite. Arrangements of crystallites in graphite are important in determining the mechanical properties, such as strength, thermal conductivity, and thermal expansion. These properties have a significant role in understanding the structure and irradiation resistance of nuclear graphites.

### **OBJECTIVES**

This project aims to help make effective decisions on how to dispose of large volumes of irradiated graphite waste and the consequent effectiveness of the various proposed preparative treatment options. The ultimate aim of this research is to develop and demonstrate advanced immobilisation of graphite waste, and techniques to reduce Intermediate Level Waste (ILW) to of Low Level Waste (LLW).

The research project objectives are to understand the microstructure of virgin graphite, in particular the arrangement of crystallites within the microstructure and the types and distribution of microporosity contained within the graphite structure. This should lead to a fuller understanding of the effect of irradiation damage on the graphite lattice, the arrangement of crystallites within the microstructure and the types and distribution of

microporosity contained within the graphite structure. These have an effect on structural integrity of the bulk material and transport of species within the microstructure.

To date non-destructive high resolution characterisation techniques such as Polarised Light Microscopy, Scanning Electron Microscopy, and Transmission Electron Microscopy have been used to understand the microstructure. An investigation of the effects of radiation on the microstructure and properties of nuclear graphite will commence shortly. Characterisation of the microstructure of graphite before and after irradiation is required in order to gain understanding of the transportation mechanism of C-14 and other radioisotopes in terms of leaching and particulate gaseous release and stability of the final encapsulation matrix.

## INTRODUCTION

Pure graphite is a chemically inert material and resistant to most acids, alkaline and corrosive gases. The chemical reactivity of graphite is considerably influenced by its crystallographic structure [1, 2]. Nuclear graphite is used within reactors as structural components such as the moderator and reflector. In the nuclear reaction, the moderation of neutron flux depends on the density of the graphite. The greater the density, the greater its moderation [1, 2].

The packing of crystallites is not perfect in the binder and filler phases of nuclear graphite due to porosity [2]. These pore structures are related to the arrangement of crystallites, and the interfaces between the filler and binder phases. An understanding of the size distribution of pores is useful in characterising the structure of graphite. The physical properties of polycrystalline graphite depend on the method of production. Different methods of production result in different degrees of crystallite orientation of the graphite. The graphite crystal is anisotropic; i.e. its properties are different in perpendicular and parallel directions relative to the principal alignment of the basic planes [2, 3]. Hence the properties of the microstructure can also be anisotropic, depending on the arrangement of crystallites. The irradiation behaviour of nuclear graphite is therefore strongly influenced by the source of the pitch, the coke and the manufacturing process [1, 2].

In decommissioning terms most irradiated graphite will arise from reactor moderators and reflectors. This will result in very high potential activation of any impurity isotopes [4]. There are also other sources of graphite waste from structural components, such as thermal columns, channel sleeves, spacers, graphite plugs, fuel sleeves and side locating struts. The current estimate is that after Generation II reactors (i.e. Magnox and Advanced Gas Reactors) cease there will be an estimated 88,000 tonnes of graphite waste destined for decommissioning within the UK [5].

On the basis of gross activity, nuclear graphite waste from many of the reactors is classified as Low Level Waste (LLW). British Nuclear Fuels Limited (BNFL) at Drigg in Cumbria placed a limit on the disposal of LLW. For nuclear waste to be classified as LLW it should have an activity below 4GBq/te alpha and 12GBq/te beta/gamma however, there are further radiological restrictions. The  $^{14}\text{C}$  content of the waste is the main restriction associated with the disposal of graphite as LLW. [6]

Graphite has many special features that make it a unique waste form and there a number of technical issues associated with the packaging for disposal of graphite. The main areas of concern are the levels of Wigner energy and the activity associated with the graphite. Wigner energy is produced as a

consequence of the presence of defects [7]. The annealing of this stored energy was a factor in the fire in the Windscale Piles in 1957 [8].

The activity associated with the graphite or the possible release of radioisotopes during decommissioning is also a major concern. The radioactive isotopes, which are considered the most of potential concern to the environmental, are  $^3\text{H}$ ,  $^{60}\text{Co}$ ,  $^{137}\text{Cs}$  and  $^{152}\text{Eu}$  which are short lived isotopes, typically 30 years or less and  $^{14}\text{C}$  and  $^{36}\text{Cl}$  are long lived isotopes (>5000yrs). Some of the radionuclides arise from the activation of impurities which are integral with the material. Other isotopes may arise from the neutron flux from reactor material, i.e., nuclear fuel element, which has then been activated in the core and are associated with the surfaces and inside the graphite crystal lattice transported via the open networked porosity.

## MATERIALS AND EXPERIMENTAL METHODS

### Sample Preparation

Three nuclear grade graphites namely PGA<sup>†</sup> from UK Magnox reactors and NBG-10<sup>‡</sup> and NBG-18<sup>‡</sup> from future HTR reactors were chosen for investigation. These were available to the University of Manchester through the FP6 Euroatom Project Raphael, and had been irradiated in a materials test reactor (MTR) programme at the NRG facilities Petten, Netherlands. All the samples were unirradiated graphite since the investigation is characterising virgin graphite at present.

The specimens were about 10mm x10mm x 10mm in size. For Polarised Light Microscopy and Scanning Electron Microscopy (SEM) observations the sample graphites were mechanically polished. To produce a highly polished scratch-free surface the samples were ground with a selection of Silicon Carbide papers (from 800 grit to 4000 grit) manually and then, polished with diamond pastes on polishing cloth. Finally, the samples were washed with water and ethanol to remove loose materials and were dried with an air blower.

### Analytical Instrumentation

#### *Polarised Light Optical Microscopy*

To understand the distribution of the different constituents, i.e., binder, filler and the coke particles and the types and distribution of porosity within the microstructure of virgin graphite, polarised optical microscopy was employed. During the observation of the graphite samples, the polarising filters were crossed at 90° angles to each other.

<sup>†</sup> - Produced by BAEL

<sup>‡</sup> - Produced by SGL Carbon

When the specimen is illuminated with plane polarised light and the light is reflected from the surface, it becomes elliptically polarised. The wave vector has a component perpendicular to the plane of polarisation of the incident light. With a second polariser placed between the objective lens and the eyepiece with its polarisation plane at  $90^\circ$  to the first polariser, the wave vector component perpendicular to the plane of polarisation of the incident light, can be distinguished by a transmitted intensity [9].

### Scanning Electron Microscopy (SEM)

To investigate the microstructure and the types and distribution of microporosities observed at high resolution of the graphite samples scanning electron microscopy was used.

Scanning Electron Microscope (SEM) produces high-resolution images of a sample surface. The secondary electron image is dominated by surface topography. [9]. To produce a highly polished scratch-free surface the samples were ground with a selection of Silicon Carbide papers (from 800 grit to 4000 grit) manually and then, polished with diamond pastes on polishing cloth.

### Transmission Electron Microscopy (TEM)

The objective of the TEM examination was to understand the arrangement of crystallites within the microstructure and the types and distribution of microporosity contained within the graphite structure. The graphite samples were cut to a size of about 10mm x 10mm with a thickness of about 10 mm. Then, it was ground to a thickness of about  $30\mu\text{m}$  by polishing both sides of the graphite. A circular disc with a diameter of 3mm was cut from this polished thin film graphite using a hollow diamond-impregnated drill and was glued on to 3.05 mm diameter molybdenum TEM disc with Araldite. Finally, the graphite disc samples were thinned to optical transparency using a Gatan PIPs (6 KeV) with an Ar ion beam.

## RESULTS AND DISCUSSION

### Polarised Light Optical Microscopy (PLM)

Polarised light micrographs that illustrate the microstructure of the nuclear grade graphites PGA, NBG-10 and NBG-18 are shown in Figure 1. XRD analysis has previously shown that PGA has more aligned coke particles than the other two graphites [10]. The porosity sizes are larger than NBG-10 and NBG-18 graphites (Figure 1) and are somewhat elongated. Aligned regions (red or blue) are observed, together with regions of poor alignment graphite whose appearance is insensitive to the alignment of the polariser.

PGA is anisotropic, and shows larger regions of good crystallite alignment. The NBG-10 and NBG-

18 graphites have a more isotropic structure, with smaller regions of good alignment.

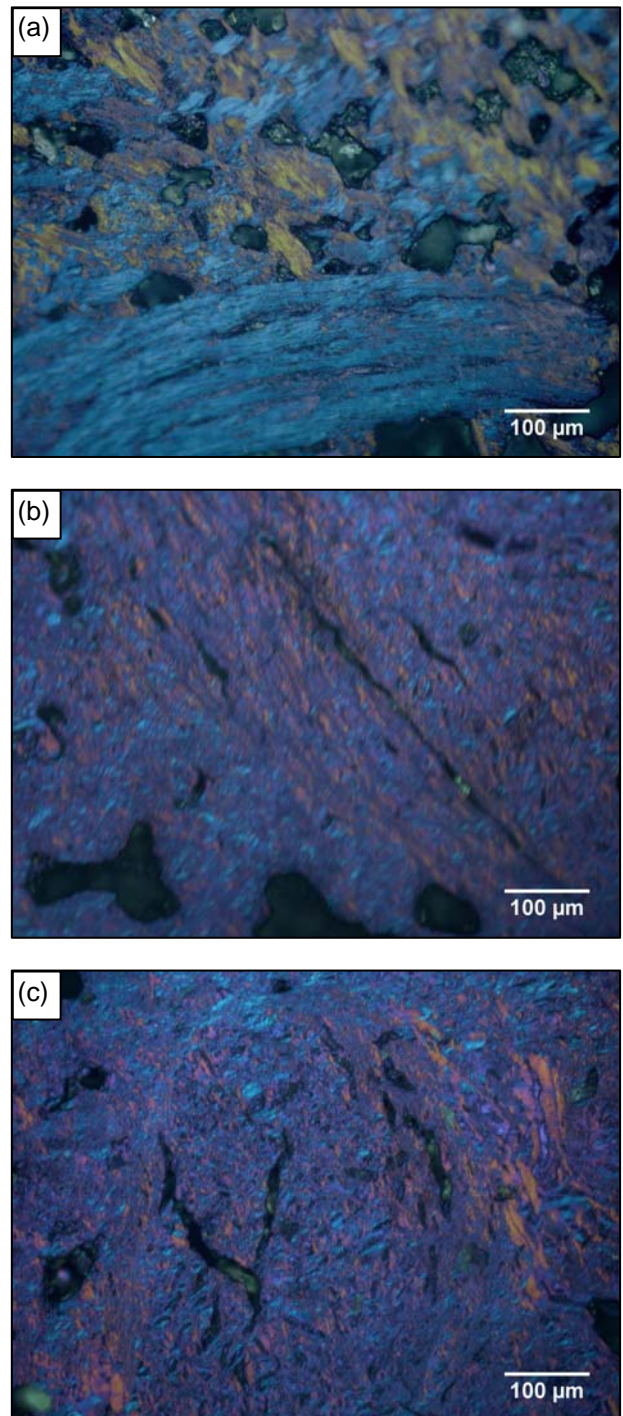


Figure 1 Polarised light optical micrographs of nuclear grade graphites: (a) PGA (b) NBG-10 and (c) NBG-18. The scale bar is  $100\mu\text{m}$

### Scanning Electron Microscopy (SEM)

Figure 2 shows Scanning Electron micrographs of (a) PGA, (b) NBG-10 and (c) NBG-18 graphites all scaled to  $100\mu\text{m}$ . These microscopic examinations of samples cut from graphitised blocks appear to show the original filler grains incorporated in a graphitised binder structure. The apparent size of the filler particles observed is taken as the grain size of the materials, and is typically calculated as approximately  $840 \pm 20\mu\text{m}$ ,  $560 \pm 20\mu\text{m}$  and  $410 \pm$

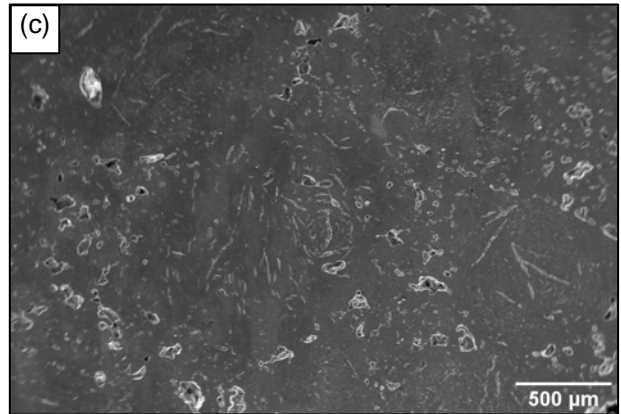
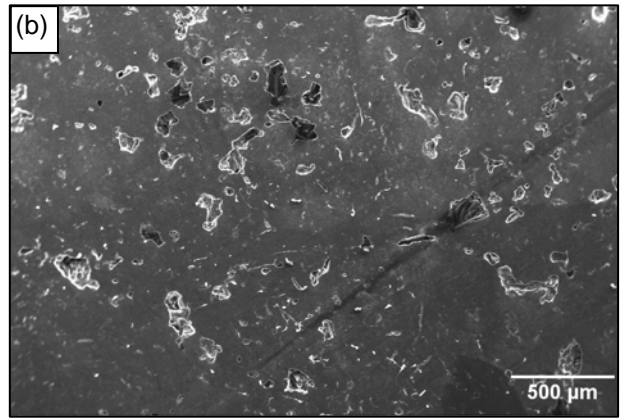
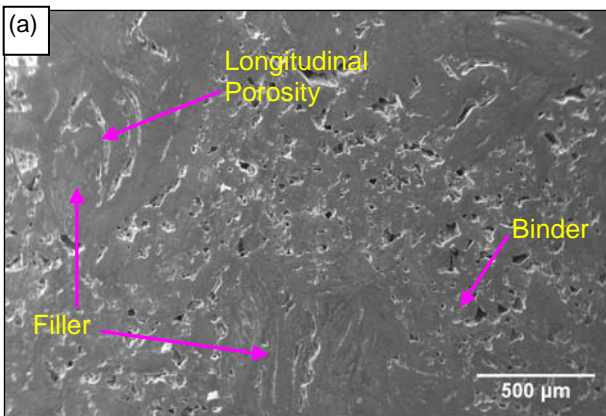
20 μm in diameter for PGA, NBG-10 and NBG-18 respectively. Generally, graphite materials of finer grain size are stronger and more consistent in their properties than coarser materials [11]. All show considerable porosity, with some long thin cracks, and some nearly spherical.

From the micrographs, it can be seen that PGA has a heterogeneous structure, due to the distribution of matrix phase and filler particles. It exhibits a very mixed morphology, with large numbers of pores, which can be characterised as both gas evolution spherical pores found on the binder phase and longitudinal porosities which are formed on the binder phase.

**Table 1** Density of PGA, NBG-10 and NBG-18 nuclear grade graphites [12, 13]

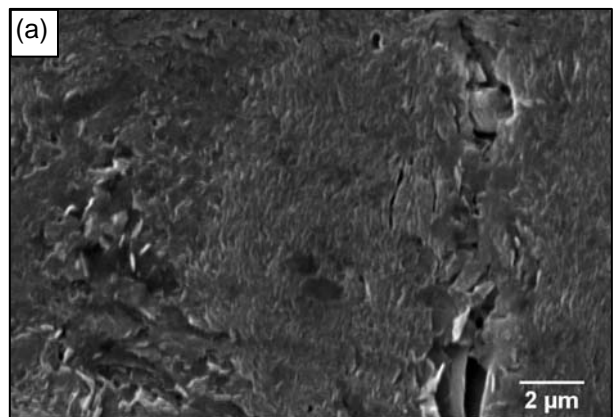
	Typical Density (g/cm <sup>3</sup> )
PGA	1.74
NBG-10	1.81
NBG-18	1.85

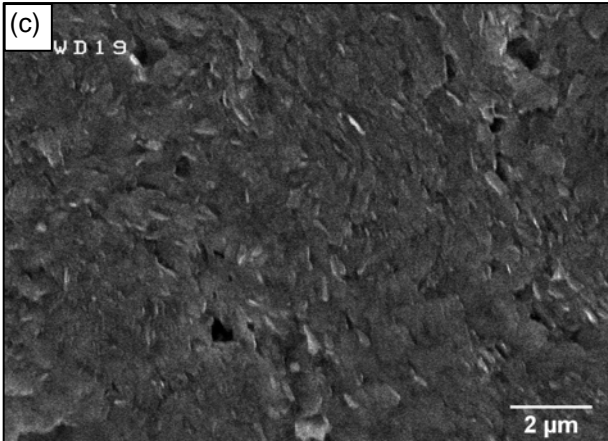
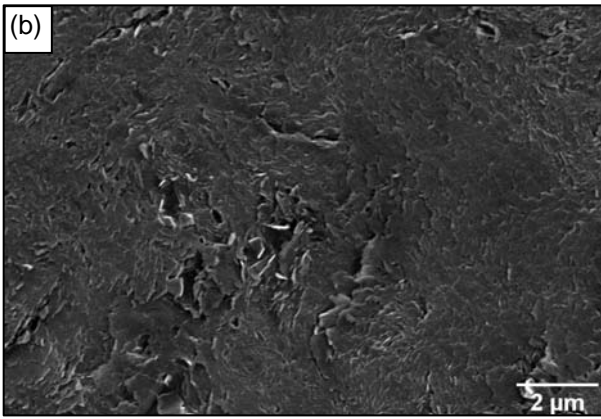
The pores highlighted in the binder phase are characteristic of those caused by entrapped gases during the manufacturing process [14]. In all graphites, longitudinal porosities are observed within the filler particles, but the pores on the binder phase are spherical in shape. NBG-10 and NBG-18 have a relatively homogeneous structure. Moreover, from SEM analysis, PGA appears more porous than the other two graphites, which is consistent with its lowest density (Table 1).



**Figure 2** Scanning electron micrographs of nuclear grade graphites: (a) PGA (b) NBG-10 and (c) NBG-18. The scale bar is 100 μm

The scanning electron micrographs in Figure 3 show the microstructure of the nuclear grade graphites under investigation graphites all scaled to 2 μm. As it can be seen from the micrographs PGA has plate-like structures are randomly oriented in preferred orientation. On the contrary NBG 10 graphite has a nearly homogenous microstructure, but the platelets tend to be arranged with a preferred orientation like PGA. NBG 18 has similar microstructure and orientation to NBG 10 but has less porosity.



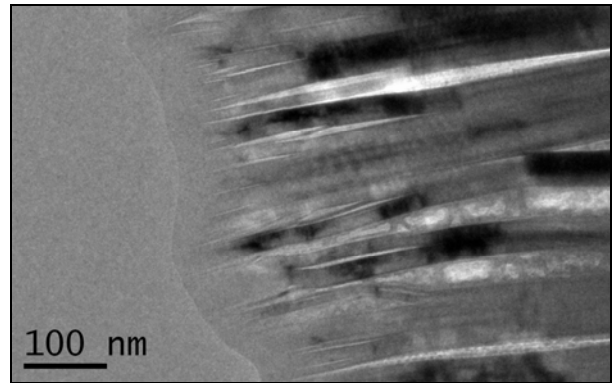


**Figure 3** Scanning electron micrographs of nuclear grade graphites: (a) PGA (b) NBG-10 and (c) NBG-18. The scale bar is 2  $\mu\text{m}$

#### Transmission Electron Microscopy (TEM)

Figure 4 shows the microstructural features of PGA nuclear graphite observed by TEM. This sample foil shows extensive Mrozowski microcracks. The lenticular “Mrozowski” microcracks run parallel to the graphite basal plane, and were formed due to the thermal expansion coefficient difference along the grain and normal to the grain of graphite during slow cooling process of graphitisation [13, 15]. The graphite shows local areas of well ordered crystallites which are parallel to the basal plane such as those found on highly orientated pyrolytic graphites [16].

In nuclear graphite, the bulk properties are governed by the pores, in particular those at the nanometre scale. The closure of Mrozowski cracks was observed after electron beam irradiation, giving similar structures which have been observed before graphitisation. [14]



**Figure 4** Transmission electron micrographs of PGA nuclear grade graphite. The scale bar is 100 nm

#### CONCLUSION AND FUTURE WORK

The microstructure of PGA, NBG-10 and NBG-18 graphites were characterised in terms of crystallinity and porosity using Polarised Light Microscopy (PLM), SEM and for PGA TEM analysis. From SEM analysis PGA shows a very heterogeneous morphology with areas of order particles and a high degree of porosity as compared to the other two graphites. The PLM analysis of the samples shows that PGA has more aligned coke particles than the other two graphites.

TEM investigation shows the lenticular “Mrozowski” microcracks running parallel to the graphite basal plane. These cracks were formed due to the thermal expansion coefficient difference along the grain and normal to the grain of graphite during slow cooling process of graphitisation.

Work to prepare TEM samples by the Focused Ion Beam – FEGSEM technique will commence shortly to investigate the effects of irradiation damage to the graphite lattice, the arrangement of crystallites within the microstructure and the types and distribution of microporosity contained within the graphite structure. Here the distribution of microporosities will be studied using Confocal Scanning Microscopy and surface sorption BET measurements. In addition RAMAN spectroscopy will be used to determine the lattice parameters and crystallite size of an irradiated material.

The next stages of this research will focus on the cement encapsulation of irradiated graphites. This study will be performed to ensure the encapsulant chemical stability, compatibility with the waste and to establish its physical properties. . Samples of the encapsulants will be prepared with a reasonable size and the amount of water in the encapsulation material after curing will be determined. Then, wetting and leaching tests with simulated water will be carried out. The microstructure of the matrix and crack formation and propagation on the surface of the encapsulant will be studied optical, scanning and transmission microscopy in order to quantify the affect on encapsulation on the microstructure Finally repository leaching tests will be performed

on the encapsulated waste form in order to quantify any isotopic release from the encased material.

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