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On the nature of cracks and voids in nuclear graphite

H.M. Freeman [a, *], A.N. Jones [b], M.B. Ward [a], F.S. Hage [c], N. Tzelepi [d], Q.M. Ramasse [c], A.J. Scott [a], R.M.D. Brydson [a, c]

[a] Institute for Materials Research, School of Chemical and Process Engineering, Univ. Leeds, LS2 9JT, UK
[b] Nuclear Graphite Research Group, Materials Performance Centre, Univ. Manchester, M13 9PL, UK
[c] SuperSTEM Laboratory, SciTech Daresbury Laboratories, Daresbury, WA4 4AD, UK
[d] National Nuclear Laboratory, Central Laboratory, Sellafield, CA20 1PG, UK

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ABSTRACT

Microcracks in neutron-irradiated nuclear grade graphite have been examined in detail for the first time using a combination of transmission electron microscopy (TEM), electron energy loss spectroscopy (EELS), energy dispersive X-ray (EDX), and energy filtered TEM (EFTEM). Filler particles from both unirradiated Pile Grade A (PGA) and three irradiated British Experimental Pile 'O' (BEPO) graphite specimens were investigated with received doses ranging from 0.4 to 1.44 displacements per atom (dpa) and an irradiation temperature of between 20 and 120 °C. We suggest that the concentration and potentially the size of microcracks increase with increasing neutron irradiation and show that disordered carbon material is present in a range of microcracks (of varying size and shape) in all specimens including unirradiated material. EFTEM and EELS data showed that these cracks contained carbon material of lower density and graphitic character than that of the surrounding bulk graphite. The presence of partially filled microcracks has potentially significant implications for the development of microstructural models for the prediction of radiation-induced dimensional and property changes in nuclear graphite.

1. Introduction

The majority of the UK's operating nuclear reactors contain significant levels of graphite which not only moderates the energies of fast neutrons due to the high scattering cross section, but provides structural support, accommodates fuel and control rods, and allows for coolant flow. High levels of neutron irradiation and temperature result in chemical and physical property changes which consequently affect the structural integrity and functionality of the channel which would affect the safe running of the reactor. The reactor lifetime is therefore limited by the condition of the irreplaceable graphite, so an understanding of its behaviour is essential for plant safety and maximised power output.

Nuclear graphite consists of a coke-based filler, filler-binder matrix, and voids. The voids are in the form of gas-escape pores and cracks of varying dimension accounting for ca. 20% of the total volume. This graphite composite is often imparted with a preferred orientation via extrusion which assumes the filler crystallites (particularly if they are needle shaped) are aligned with their *c*-axes perpendicular to the extrusion direction. The removal of volatiles during the manufacturing process produces gas-escape pores which are open and do not accommodate thermal expansion due to their larger dimension [1]; however they do affect properties such as strength, thermal conductivity and Young's modulus, particularly under radiolytic oxidation during reactor operation [2]. Gas-escape pores have therefore not been considered in this study.

During almost every step in the high temperature graphitisation process associated with the manufacture of nuclear graphite and also during reactor operation, cracks arise due to a number of factors. Firstly, as a result of gradients in both temperature (during manufacture and operation) and neutron flux (during operation) and, secondly, as a result of the anisotropy of the coefficient of thermal expansion (CTE) in crystallites and the consequent generation of internal stresses beyond the elastic limit of graphite crystals [3–5]. The internal stresses act on both the carbon bonds between crystallites and on the Van der Waals forces between basal planes; to relieve this stress cracks form, more usually between the weaker bound basal planes. Since the CTE is higher in the crystallographic *c*-direction (ca. 20–40 $\times$ 10^{-6} K^{-1} compared to $<1.5 \times 10^{-6}$ K^{-1} in the *a*-direction), lenticular cleavage cracks

* Corresponding author.
E-mail address: pmhmf@leeds.ac.uk (H.M. Freeman).

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between basal planes, known as Mrozowski (micro)cracks, are observed to form lying approximately perpendicular to the crystallographic *c*-direction as a result of anisotropic contraction following post graphitization cooling during manufacture [2–4].

The basic understanding of irradiation-induced dimensional change in a perfect graphite crystal involves growth in the *c*-axis and contraction in the *a*-axis. This is presumed to arise from the formation of interstitial and vacancy defects during neutron bombardment which can accumulate as clusters. However the microstructure of nuclear graphite is complex and at low doses, it is suggested that *c*-axis expansion is accommodated by the microcracks [3,6] leaving solely to shrinkage along the *a*-axis which leads to the observed net volume shrinkage. With increasing dose during reactor operation, the rate of contraction or shrinkage reduces and eventually the cracks are presumed to close and *c*-axis expansion is no longer accommodated producing net volume expansion, the critical point at which this reversal occurs is known as “turnaround” which can vary with operating temperature [7].

Microcracks can be classified into two categories: intra and inter-granular, where the former are found within crystallites and lie perpendicular to the crystallographic *c*-direction (e.g. Mrozowski cracks [2,4]). The latter lie between crystallites at grain boundaries with, in principle, no specific orientation with respect to neighbouring basal planes, unless crystallites are aligned as a result of mesophase development. Within thermally anisotropic filler particles, (closed) calcination cracks form due to volumetric shrinkage during the 1300 °C calcination stage in the manufacturing process [3].

In nuclear graphite, microcracks have been reported to range in size from less than ca. 5 nm–200 nm in width and up to 10 μm in length [2–4,6]. The nature of the material within a crack depends on the crack type; it has been proposed that microcracks in Pile Grade A, Gilsocarbon, baked carbon [6], and highly ordered pyrolytic graphite (HOPG) [6,8] contain low density disordered carbon perhaps arising from interstitial atoms migrating from the bulk following irradiation and sintering-induced diffusion. However, limited research has been carried out to characterise this material in both non-irradiated and irradiated graphite, which could better the understanding of the mechanisms involved in crack expansion and contraction [2,8], and hence their influence on macroscopic properties such as CTE and elastic modulus during reactor operation.

Delannay et al. [5] used crystal plasticity finite element modelling to predict irradiation-induced dimensional change and variations in CTE at a variety of reactor temperatures. Predictions were in agreement with experimental data showing bulk material shrinkage with irradiation and turnaround after crack closure. All cracks in this model were empty; extending the model to 3D and including a proportion of filled cracks could be of interest in relation to the results subsequently described in this paper.

The investigation of a variety of microcracks in non-irradiated nuclear graphite and HOPG has been undertaken by Wen et al. [6] who showed the presence of lenticular cracks of up to 10 μm long and up to 100 nm wide in Pile Grade A (PGA) nuclear graphite; a fine structure of smaller cracks was also observed with crack lengths down to 10 nm. Both empty and filled microcracks were identified in non-irradiated and electron irradiated material; cracks in the latter were suggested to contain low density, amorphous material. Via a comparison of transmission electron microscope (TEM) samples produced by both ion beam thinning and microtome sectioning techniques, it was confirmed that this amorphous material observed within the cracks was not a result of TEM sample preparation. In-situ heating of samples to 800 °C under a 200 kV electron beam showed a gradual closure of cracks along the *c*-axis. Electron beam exposure without in-situ heating also caused cracks to close; after 15 min a 60 nm crack was observed to reduce in width to 6 nm, and in some areas to close completely.

Neutron irradiated nuclear graphite was also investigated by Karthik et al. [9], who used TEM to observe changes in both the microcracks and the nanostructure. In both filler and binder phases of NBG-18 and IG-110 graphites irradiated to 1.42 dpa and 1.91 dpa respectively, there were no significant changes in the size distribution of microcracks as compared to non-irradiated specimens. The absence of microcracks in specimens irradiated to ca. 6.7 dpa at ca. 670 °C was attributed to the closure of pre-existing microcracks from significant *c*-axis swelling. Open microcracks within filler particles in all specimens appeared to contain amorphous carbon but no further analysis on this material was performed. TEM lattice images of specimens irradiated to 6.78 dpa at 678 °C provided evidence for intense nanostructural damage through the fragmentation and bending of basal planes, however the retention of (002) spots in selected area electron diffraction (SAED) patterns showed that the layered structure was preserved. Noise filtering of lattice images was used to highlight extended interlayer defects and prismatic dislocations, similar to those found following electron irradiation [10,11].

This paper extends this work and presents a study of microcracks in irradiated graphite samples removed from the British Experimental Pile ‘O’ (BEPO) reactor as well as in non-irradiated Pile Grade A (PGA) graphite for comparative purposes. Using TEM, energy dispersive X-ray spectroscopy (EDX), electron energy loss spectroscopy (EELS) and energy filtered TEM (EFTEM), the material within a variety of cracks is characterised in detail and suggestions are made regarding its origin and importance for understanding radiation-induced property changes in these materials. The material investigated in this work has also been studied using Raman spectroscopy by Krishna et al. [12], and the present results are correlated with their findings.

2. Experimental procedure and sample preparation

The nuclear graphite grades examined were BEPO and PGA; three BEPO samples of varying received dose were used from the same trepanned column. BEPO1 was farthest from the reactor core and received a dose of 0.4 dpa ($\approx 3.1 \times 10^{20}$ n cm^{-2}), BEPO16 was in the middle of the channel and received a dose of 1.27 dpa ($\approx 9.8 \times 10^{20}$ n cm^{-2}), whilst BEPO20 was closest to the core and received a dose of 1.44 dpa ($\approx 1.1 \times 10^{21}$ n cm^{-2}). The irradiation temperature during operation (in air) was between 20 °C and 120 °C, which is lower than the usual advanced gas cooled reactor operating temperature of ca. 350 °C. During the last 5 years the air was recirculated and temperatures were increased up to ca. 180 °C to achieve a higher thermal output. The reactor was also annealed twice to ca. 230 °C, once during operation and once after to release the 200 °C Wigner peak [13]. BEPO graphite is an extruded coke-based grade containing elongated needle filler particles (similar to those found in PGA) within a porous binder phase where the binder and crystallites do not have preferential alignment. The filler particles are fairly consistent in size, of the order 1 mm × 0.5 mm [14]. The BEPO reactor was in operation from 1948 to 1968 at Harwell in the UK and used natural or low-enriched uranium fuel and a graphite moderator to demonstrate the design for the Windscale Piles and to provide a facility for materials testing and radioisotope production [15]. For comparison, a non-irradiated PGA graphite specimen was also studied. It is believed that there is no remaining non-irradiated BEPO graphite. Specimens for transmission electron microscopy (TEM) were prepared using an FEI Nova200 dual beam SEM/FIB fitted with a Kleindiek micromanipulator for in situ lift out. Using this sample preparation technique allowed for areas of filler to be specifically selected. The analysed