Carbon 124 (2017) 314–333

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

An understanding of lattice strain, defects and disorder in nuclear graphite

Ram Krishna [a, *], James Wade [a], Abbie N. Jones [a], Michael Lasithiotakis [a, b], Paul M. Mummery [a], Barry J. Marsden [a]

[a] Nuclear Graphite Research Group, School of Mechanical, Aerospace & Civil Engineering, The University of Manchester, Manchester, M13 9PL, UK
[b] Greek Atomic Energy Commission, Agia Paraskevi, 15310, Athens, Greece

ARTICLE INFO

Article history:
Received 12 May 2017
Received in revised form
23 July 2017
Accepted 29 August 2017
Available online 30 August 2017

Keywords:
Graphite
Neutron irradiation damage
X-ray diffraction
Raman spectroscopy
High-resolution transmission electron microscopy
Dislocation density
Micro-strain
Crystallite size

ABSTRACT

In this study, microstructural parameters, such as lattice dimension, micro-strain and dislocation density, of different neutron-irradiated graphite grades have been evaluated using the diffraction profiles of X-ray diffraction (XRD) and the scattering profiles of Raman spectroscopy. Using Generation-IV candidate graphite samples (grade PCEA, GrafTech), subjected to neutron irradiation at 900 °C to 6.6 and 10.2 *dpa*, and graphite samples of similar grain size and microstructure taken from the core of the British Experimental Pile Zero reactor, which have been irradiated at 100–120 °C to 1.60 *dpa*, an investigation is presented on the effect of irradiation dose and temperature on the aforementioned microstructural parameters. Using two complementary techniques in Raman spectroscopy and XRD, which produced agreeable results, the average lateral crystallite size of the two graphites tested was found to decrease with increasing exposure to fast-neutron irradiation or at lower irradiation temperatures. Conversely, dislocation densities and micro-strains were found to increase following the same changes in irradiation conditions. Supporting evidence for the microstructural information obtained is provided by direct observations made using high-resolution transmission electron microscopy. These images demonstrate the presence of irradiation-induced prismatic edge dislocations as well as features that indicate the presence of basal dislocations. They also provide supporting evidence for the progressive deterioration of the graphitic planes via damage mechanisms as proposed in the literature.

1. Introduction

Since the early 1940s, graphite has been the material of choice for many nuclear reactors (operating temperature range from 100 °C to 400 °C) owing to the materials excellent neutron moderation and reflection efficiencies, good machinability, cost effectiveness and high availability. Another principal advantage of graphite is the materials capacity to function as a supporting structure for the fuel/control rods and coolant gas flow channels necessary to sustain nuclear fission reactions [1,2]. More recently, with the development of next generation nuclear reactors, such as high temperature and very high temperature reactors (HTR & VHTRs), gas-cooled fast reactors (GFRs) and molten salt reactors (MSRs), interest in graphite has increased due to the materials excellent thermal and chemical stability. Given the continued international interest in graphite-moderated reactor cores, an essential requirement is to ensure that the lifetime of such reactors is not limited by the performance of the selected graphite grade [3]. A number of irradiation damage studies have shown that the initial degree of crystallinity and the crystallite size both play an important role in asymmetrical dimensional and anisotropic property changes induced by fast neutrons in graphite (altering the magnitude and configuration of internal stresses) [4,5]. Consequently, it is important to develop a comprehensive understanding of the change in microstructural behaviour and associated structural parameters that correlate with bulk material property changes under fast neutron irradiation conditions [3,6].

Irradiation alters lattice parameters, causes graphite crystal lattice expansion in the *c*-axis and shrinkage in the *a*-axis, introduces dislocations and other defects, and generates micro-strains, all of which influence many of material properties of

* Corresponding author.
E-mail address: ram.krishna-2@manchester.ac.uk (R. Krishna).

http://dx.doi.org/10.1016/j.carbon.2017.08.070
0008-6223/

graphite (altering the graphite's capacity to endure the internal stresses present) [4,7–9]. However, despite this, very few in-depth microstructural studies have been conducted on irradiated graphite [10–17]. The majority of those that have been performed have employed high-resolution transmission electron microscopy (HRTEM) to examine irradiation-induced defect formations [15,16] and micro-crack evolution [18] in various nuclear graphite grades. This work looks to expand upon the current knowledge by examining the influence of irradiation dose and temperature on the bulk crystal structure of graphite. The radiation-induced changes to the microstructure are important for an accurate understanding of the stress-state of nuclear graphite during service. Therefore, in addition to assisting the life extension of the advanced gas-cooled reactors currently operating, the results of this work could also be pertinent in the appraisal of developmental graphite grades intended for future Generation-IV high temperature reactors.

As stated above, HRTEM is a common and highly effective technique used to study defects in graphite crystal structure. The results of TEM are important in correlating with the asymmetrical microstructural changes observed in graphite after neutron irradiation [15,16]. However, the complexity of the technique, associated with electron beam damage and the introduction of additional dislocations during sample preparation, limits its suitability for routine application. Scanning tunnelling microscopy (STM) is another useful method to study surface defects on a molecular level in irradiated graphite microstructures and nanostructures [19,20]. The majority of previous work has used this technique to detect crystallite boundaries, topological defects, and the edges of the basal layers in graphite [21,22]. However, this technique has some limitations as it requires a pristine, conducting surface, an atomically-sharp tip (radius of curvature of the scanning tip determines the system resolution) and can only be used to detect atomic-scale details across a small region. Whilst HRTEM and STM can provide us with information about the crystal defect structures that form in graphite during neutron irradiation, it is the quantity of these defects and the internal stresses/strains they impose on graphite that will improve our understanding of how different graphite grades respond to particular irradiation conditions (i.e. different irradiation doses and temperatures). In this respect, other fundamental experimental techniques that are better suited to investigate this are X-ray diffractometry and Raman spectroscopy, both of which provide data that can be analysed to obtain microstructural information of materials. Both the techniques are well established, non-destructive, have a practical significance and provide information on the bulk properties of polycrystalline materials averaged over the whole sample volume (~1 μm below the top layer) [23,24]. As a result, a number of different studies have been performed employing either technique to measure a variety of crystal properties [10–14,25]. Tuinstra and Koenig (1970) Cançado et al. (2006) and Lu et al. (2001), for example, have both performed systematic X-ray diffraction and Raman studies on graphitised samples [10,26,27]. However, literature sources report several X-ray line profile fitting procedures and a variety of XRD and Raman models that are underutilised in graphite. These methods are routinely used to quantitatively characterise the microstructural parameters of metallic and ceramic materials, including alloys with nuclear applications [28,29].

In this study, two different graphite grades irradiated under different reactor operating conditions are characterised for microstructural evolution using XRD and Raman spectroscopy. The graphite grades examined are very similar in microstructure. One grade has been obtained from the core of the British Experimental Pile Zero reactor (BEPO), while the other one is a PCEA grade irradiated in the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory (ORNL), USA. For the latter neutron irradiation experiment, the mechanical, thermal and electrical properties changes displayed have been reported by Burchell and Strizak elsewhere [30]. Microstructural parameters of lattice disordering, crystallite size, micro-strain, and dislocation defect density are obtained from X-ray diffraction line profiles and compared with Raman spectrum analysis. These results are then judged against HRTEM observations of both sets of samples. The quantified values extracted from the measured diffraction data and Raman spectrums are then discussed in relation to the established damage mechanisms associated with neutron irradiation.

2. Materials and experimental details

2.1. The graphite microstructure

The graphite used in the nuclear industry is a synthetic product consisting of coke filler particles impregnated with a pitch binder phase (from a petroleum or coal tar source). Once graphitised at

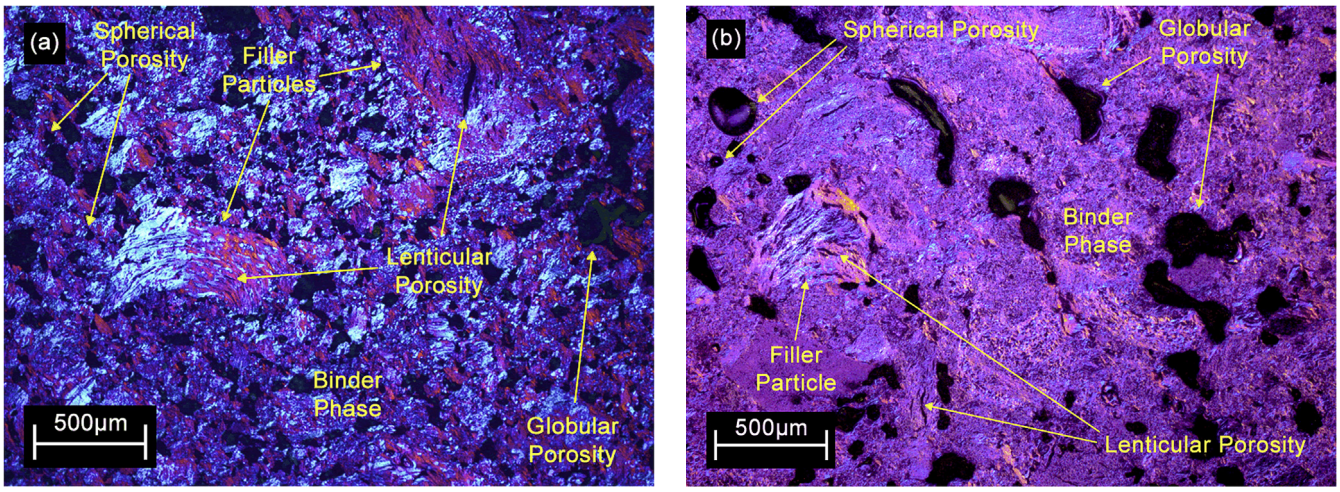

Fig. 1. Optical polarised light micrographs depicting: (a) BEPO and (b) PCEA graphite, both showing medium-grained needle-like filler particles and binder phase containing multidimensional pores. Filler grain size was approximately 650–950 μm and pore area fractions were 13–22% in both BEPO and PCEA grades. (A colour version of this figure can be viewed online.)