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Development of mesopores in superfine grain graphite neutron-irradiated at high fluence☆

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ABSTRACT

Microstructural changes induced by neutron irradiation of superfine grain graphite G347A (Tokai Carbon, Japan) were examined by nitrogen adsorption at 77 K and by three microscopy techniques (SEM, TEM and FIB-SEM tomography). The specimens were irradiated at doses of up to 30 dpa, covering stages before and after the turnaround fluence at three temperatures (300, 450, 750 °C) of their irradiation envelope. The initial graphite densification at low fluences did not produce any detectable effect in the pore size range (<350 nm) measured by gas adsorption. However, graphite irradiated at high fluences, after turnaround, showed severe structural changes. At all three temperatures and high irradiation fluences, gas adsorption revealed significant increase of the volume of narrow mesopores (<5–20 nm) and up to five times increase of BET surface area, both in linear relationship with the relative volume expansion. Analysis of microscopy images showed multiplication of fine macropores (>50 nm) at high irradiation fluences and more structural changes on multiple scales, from nanometers to microns. This work demonstrates the unique ability of gas adsorption techniques to analyze open pores with sizes between sub-nanometer and sub-micron in bulk nuclear graphite, with supporting microscopy results.

1. Introduction

It has been known from the time of the Manhattan Project that graphite could be used as moderator of fast neutrons in nuclear fission reactors. About the same time, it was also discovered that extended irradiation with high energy neutrons would cause dimensional and structural changes in core graphite components, with significant consequences on the properties critical to reactor operation [1]. The visible effects of neutron irradiation are dimensional changes, but inisidious degradation of thermal and mechanical properties is also very important. Despite the significant progress with characterization and first-principles modeling of irradiation-induced microstructural changes, the exact mechanism is still not clearly understood. The growing interest in development of high-temperature gas-cooled reactors (HTGR) and molten-salt reactors (MSR) stimulates more research into the microstructure of neutron-irradiated graphite used as moderator and structural material in advanced nuclear reactors (generation IV). In fact, graphite is the limiting component of some nuclear reactors' life time, while at the same time graphite maintains the fuel integrity.

Along with filler grains of synthetic graphite and pitch binder, porosity is the third important component of high density nuclear graphite. Open and closed pores represent about 18–20 vol % in graphite and as such it has an important role in ensuring the physical integrity of graphite components in the reactor. Porosity is critical for accommodating thermal expansion [2], absorbing dimensional changes caused by irradiation [3] and for withstanding large internal crystallite strains without severely deteriorating the properties (irradiation-induced creep) [4]. Porosity also affects

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mechanical and thermal properties, gas transport, oxidation behavior and fission products retention. Large pores deflect crack propagation, while fine pores (in smaller grain graphites) make graphite more brittle and may downgrade its thermal properties [5]. Elastic moduli decrease with an increase of pore fraction [6]. Whereas, development of porosity due to oxidation may cause a decrease of thermal conductivity [7] and significant degradation of mechanical properties [8] that may threaten the integrity of graphite components. Porosity is present in the graphite filler, in the binder, and at the filler/binder interface. The volume fraction of pores, their shape, orientation, and size distribution depend intrinsically on the raw materials, number and types of intermediate steps in the manufacturing process, and thermal history of each graphite billet [9]. Control of porosity is possible to some extent during manufacturing (through precursor selection, forming techniques, and impregnation treatments for densification). However, the porosity control techniques have limitations so that, in some sense, and with the best efforts of manufacturers, at the end "you get what you get".

Even less understood are the microstructural changes that accompany bulk volume variations caused by high energy neutron irradiation. The currently accepted views [10] [11], are that crystallites expansion along c-axis is accommodated by closing of large pores, while contraction along a-axis, which is not accommodated, causes the overall bulk shrinkage of graphite artifacts, which increases in magnitude with increasing irradiation dose. At the point of turnaround, when the accommodation pores are filled due to irradiation-induced swelling on c-direction and thermal expansion, the continuous dilation along c-axis overtakes the a-axis contraction resulting in recovery of previous shrinkage and even swelling beyond the initial volume, with severe structural damage [12]. Most information on defect evolution relies on observations made in-situ on either electron- or ion-irradiated graphites. Direct observations on *neutron*-irradiated graphite are more difficult to make, and the information available is limited. Tanabe et al. [13] obtained evidence from Raman spectroscopy on defects in, and/or between basal planes produced at early stages of neutron irradiation; their evolution caused turbulence and bending of basal planes under heavy irradiation. Using small angle X-ray scattering (SAXS), Eeles [14] identified disc-like interstitial aggregates in pile-irradiated polycrystalline graphite. Evidence from X-ray diffraction (XRD) and small angle neutron scattering (SANS) showed that lattice parameters of HOPG graphite crystallites vary by lesser amounts than the overall bulk dimensional changes [15]. Mercury porosimetry was used for pore size distribution measurements from sub-millimeters to nanometers, but there were concerns that the high pressure required to survey nanometer size pores may damage the graphite structure [16]. Electron microscopy shows interstitial defects and microcracks in specimens irradiated by neutrons [17,18], electrons [19,20,21], or ions [22], but it is difficult to assess the global contribution of these localized nanoscale defects to the large dimensional changes measured on bulk specimens. X-ray computed tomography can provide information on the connectivity and geometry of pores, but currently this technique is limited in its ability to resolve small pores in a large volume. There is a need for an analysis technique with resolution at the nano- and mesoscale, and yet capable of providing statistically significant information from bulk measurements on large (millimeter size) specimens. Gas adsorption may fill this need.

Gas adsorption techniques provide information on open pores from the sub-nanometer to sub-micron scales, but these techniques have not been used so often for characterization of polycrystalline nuclear graphite. Very recently, Jones et al. [23] used low pressure gas adsorption and He pycnometry in combination with mercury porosimetry and a modeling technique to obtain information covering four orders of magnitude between the smallest and the largest pores in graphite. Hoinkis et al. used N_2 adsorption and SAXS to analyze the change in porosity of pristine, oxidized [24], and irradiated A3-3 matrix graphite [25]. They found that irradiation at about 7 dpa (displacements per atom[1]) caused pronounced development of micropores and small mesopores, of which most were accessible to nitrogen. Banares-Munoz et al. measured adsorption isotherms of N_2 and Ar on AGOT nuclear graphite [26] and pyrolytic graphite [27] and derived textural information by comparing the isotherm shapes and the BET surface areas (calculated by the Brunauer-Emmett-Teller method) [28]. They interpreted the changes in slope of adsorption isotherms at sub-monolayer coverage as an indication for occurrence of sites with different adsorption potential on graphite (lattice defects, layer boundaries) combined with the effect of lateral interactions in the adsorbed monolayer. In continuation of this argument, Olivier and Winter [29] postulated that adsorption sites on the graphite basal plane surface are characterized by an adsorptive potential centered at 57 ± 2 K (based on N_2 adsorption at 77 K); edge sites on the prismatic graphite surface were identified with lower adsorptive potential (20–40 K) while defective sites (dislocations, surface steps) were assigned higher values (up to 80–90 K).

Further advancing the use of nitrogen adsorption at 77 K, this communication reports on a lesser known aspect of microstructural changes in neutron-irradiated superfine graphite at fluences before and after turnaround, up to (high) doses of 30 dpa. The changes in nanoporosity uncovered by nitrogen adsorption, and the associated changes in BET surface area, are supported by three microscopy techniques which provide complementary information on pores ranging from tens of nanometers to hundreds of microns. This information sheds unique light on microstructure evolution in superfine grain graphite irradiated before and after turnaround. A complementary Data-in-Brief manuscript shows video files for FIB-SEM tomography, TEM images, and gas adsorption data.

2. Materials and techniques

The material examined was superfine grain graphite G347A manufactured by Tokai Carbon Co., Ltd. by cold isostatic pressing. According to the manufacturer's website [30], G347A is obtained from coal coke filler and a pitch binder, and has a specific density of 1.85 g/cm^3. According to indirect information from literature [31], graphite G347A is isotropic, with 11 μm grain size (superfine grade) and porosity of only 12% volume. Optical microscopy imaging using polarized light supports this information (Fig. 1). The effects of neutron irradiation on this graphite's properties were reported recently by Campbell et al. [32] Irradiation was performed at the High Flux Isotope Reactor (HFIR) on Oak Ridge National Laboratory (ORNL) campus. The properties characterized at ORNL before and after irradiation include volume and dimensional changes, elastic and shear moduli, electrical resistivity, equiaxial strength, thermal conductivity and coefficient of thermal expansion.

In this study, a small subset of the irradiated specimens was characterized by nitrogen adsorption at 77 K. A pristine specimen was also measured for comparison. All selected specimens were thin slabs with $48 \times 6 \times 1$ mm^3 size. They have been previously irradiated at three different nominal temperatures (300, 450 and 750 °C) and doses of up to 30 dpa, covering stages before and after the turnaround point of their irradiation envelope. The capsules

[1] The multiplier for conversion of dose units in n/m^2 [E > 0.1 MeV] to displacements per atom (dpa) used in this work was 7.3E-26 [see T D Burchell, Fission reactor applications of carbon, in "Carbon Materials for Advance Technologies", Ed. T D Burchell, Pergamon, 1999, p.459].