GAMMA RADIATION EFFECTS ON NUCLEAR RECTOR GRADES GRAPHITE

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ABSTRACT

This manuscript describes the experimental methodology used to conduct radiolytic oxidation at varying temperatures and gaseous environments, and the characterization used to examine the resulting microstructures. Microstructural changes in radiolytically oxidised graphite have been investigated using Raman spectroscopy, Brunauer-Emmett-Teller (BET) and scanning electron microscopy (SEM). Gamma irradiation at varying doses has been employed for radiolytic oxidation. Nuclear Block Graphite-18 (NBG-18), Gilsocarbon and Pile Grade-A (PGA) graphite grades were used in this study. Energetic gamma rays from a mono-energetic gamma-ray source-Cobalt-60 generate several MeV photons through Compton scattering and absorption interactions that create excitation within atoms, which results in broken chemical bonds and atomic displacement, causing a loss of crystallinity. Gamma rays at a dose rate of 20.6kGy/h or above are employed for catalytic oxidation to induce damage resulting in microstructural evolution near to and inner regions of the pores and cracks from meso- to macro- ranges. The damage produced by the exposure of 1.1MeV gamma rays was approximately up to a total dose of 5MGy (equivalent to 5000J/g). After radiolytic oxidation, high-resolution SEM images from the evolved microstructure are acquired to compare with virgin graphite. There were no changes in the shape of the Raman spectra, however, the induced localized damage in the lattice structure, resulted change in the D-peak vibration relative to the G-peak vibration. Electron microscopy analyses revealed confined localized damage in the graphite crystallites from micron to nano-scale. The change in BET surface area and pore size distribution were observed in all grades of graphite.

INTRODUCTION

Advanced Gas Cooled Reactors (AGRs) are second-generation reactors using graphite as neutron moderator and carbon dioxide under high temperature and pressure as a coolant (Marsden and Hall, 2012). The reactor core consists of stacked graphite bricks, which not only moderating the energy of neutrons for the fission reaction, but also provides structural support and the channel required for fuel, control rods and necessary coolant flow. The graphite bricks in the reactor core are subjected to high levels of irradiation both by neutron and ionising radiations, during the anticipated lifespan of a reactor. Neutron irradiation of the graphite resulting in mechanical and physical property changes, whereas ionising irradiation contributes graphite oxidation under the atmosphere of the carbon dioxide coolant and gamma rays (Neighbour, 2001). Oxidation under gamma irradiation leads to weight loss of the graphite bricks and evolution of internal porosity due to catalytic reaction of carbon atoms with the oxidising species from the catalytic reduction of the reactor coolants, leading to a reduction in mechanical and thermal strength (Best et al., 1985; Burchell et al., 1986; Neighbour, 2001).

Nuclear graphite is a polycrystalline artificially produced material, and commercially available as reactor grade graphite. The microstructure of these graphite grades are characterised by the forming processes, source coke utilised in their manufacturing, particle grain size, filler and binder phases and randomly distributed multi-scaled pores and cracks. The complex microstructure of the graphite is identified by
various carbonaceous phases such as coke filler particles, pitch binder phase, quinoline insoluble particles and turbostratic phase. The complex nature of the constituents complicates the nature of the graphite microstructure damage under radiolytic oxidation. Several studies of the effect of radiolytic oxidation on the graphite microstructure were conducted in the 1960s, 1970s and 1980s, based on various experimental parameters such as pores morphology and distribution, coolant type and concentration, oxidising temperature etc., (Best et al., 1973; Best et al., 1972; Best et al., 1982; Best et al., 1976; Best and Wood, 1975; Brocklehurst et al., 1982; Dominey and Morley, 1971; Feates and Poole, 1971; Feates and Walker, 1971; Johnson et al., 1982a; Johnson et al., 1982b; Kelly et al., 1975; Kelly et al., 1983; Labaton et al., 1969; Martin and Caisley, 1978; Murdie et al., 1984; Murdie et al., 1986; Mustafaev et al., 1988; Standring and Ashton, 1965). These investigations illustrate that loss in load bearing capacity of graphite due to radiolytic oxidation is a primary limiting factor in carbon dioxide cooled nuclear reactor design.

In the presence of ionization radiation, enhanced chemical activity of the coolant gas, carbon dioxide for AGR type design, reacts with graphite selectively. In principal, the fundamental radiolytic oxidation reaction mechanisms may be presented as (Kelly et al., 1983): $CO_2 + \gamma \rightarrow CO_2^* + e$ and $CO_2^* + C \rightarrow 2CO$; where $CO_2^*$ is the radiolytic activated species (Burchell et al., 1986). The above reactions have been observed to occur predominantly in the open porosity of the graphite, in which the active species diffuse to the inner surface of the pore walls and reacts with carbon atoms (Burchell et al., 1986). Kelly et al. (1983) showed changes in permeability of graphite and the diffusivity ratio with oxidation in carbon dioxide with methane and carbon monoxide additives, and compared the results from other studies conducted on the direct measurements of the oxidation of pores. Murdie et al. (1986) also investigated changes induced in porosities during the radiolytic gasification of graphite in carbon dioxide atmosphere.

These findings collaborate those of earlier investigations, which found changes induced in existing fine porosities with no evidence observed of the creation of new porosities from within the bulk microstructure. Further no changes in the structure of pores larger than 100μm$^2$ were observed because of inhibition of oxidation by deposition of active carbonaceous species from the methane inhibitor (Clark et al., 1983; Standring and Ashton, 1965). Best and Wood (1975) have identified the oxidation rate for a given graphite depends on gas density, radiation intensity and G(-C) (the efficiency with which radiation energy is used, expressed as the number of carbon atoms gasified per 100eV of energy absorbed by the gas in the accessible pore volume). In addition, a model was provided for predicting $G(-C)$ values from the pore structure data for a given graphite and was used for estimating changes in the pore structure resulting from radiolytic oxidation.

Radiolytic oxidation in carbon dioxide/carbon monoxide atmosphere takes place randomly in graphite microstructure and the chemical bond breakage from the internal surfaces of pores results in mass loss and affects the physical properties of the graphite. The chemical interaction changes the atomic shifts in position causing a loss of crystallinity, which is observed as spreading of spots in an electron diffraction pattern (Eapen et al., 2013). Several studies have been conducted on properties after radiolytic oxidation (Brocklehurst et al., 1970; Burchell et al., 1986; Hawkins, 1966). Hawkins (1966) reported the PGA graphite properties after radiolytic oxidation in carbon dioxide and mixture of carbon monoxide and carbon dioxide and showed that radiolytic oxidation causes less reduction in modulus and strength than thermal oxidation. Hawkins (1966) also observed that mode of reactions of thermal and radiolytic oxidation is completely different. Kelly et al. (1983) showed that the effects on the Young’s modulus, thermal resistivity and strength of radiolytic oxidation of nuclear graphites for a given weight loss ‘x’ could be described by: $E = E_0 \exp(-3.6x)$, $\frac{1}{K} = \frac{1}{k_0} \exp(2.7x)$ and $S = S_0 \exp(-4.0x)$. These results showed that reduction in graphite properties are more severe for thermal oxidation than radiolytic oxidation and are well established. However, there is very little work reported on accompanying changes in the graphite microstructure. In this paper, we present the effect of microstructural changes after
radiolytic oxidation in nuclear graphite grades at ambient conditions using Raman spectroscopy and electron microscopy.

MATERIAL & EXPERIMENTAL DETAILS

The characteristics of graphite grades used in the present study are presented in Table 1. All graphite grades are polycrystalline and diverse in nature, full details of these graphite grades are published elsewhere (Krishna et al., 2015). Samples were cut from these graphite grades in 3mm diameter and 1mm thickness. The effect of gamma radiation on samples is studied at the University of Manchester’s Dalton Cumbrian Facility (DCF) using the self-shielded $^{60}$Co irradiator (a Foss Therapy Serviced Model 812), with an average energy of 1.1MeV and at a dose rate of 20.6kGy/h, as determined by the Fricke dosimeter.

Table 1: Characteristics of reactor grade graphite used in the present study.

<table>
<thead>
<tr>
<th>Graphite Grade</th>
<th>Manufacturer</th>
<th>Forming/moulding process</th>
<th>Bulk density (g/cm$^3$)</th>
<th>Particle Grain size Range (μm)</th>
<th>Source Coke</th>
<th>Porosity (%)</th>
<th>Microstructure</th>
<th>Crystallite Size ($L_a$) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PGA</td>
<td>BAEL and AGL</td>
<td>Extrusion</td>
<td>1.74</td>
<td>1 – 800</td>
<td>Petroleum</td>
<td>18.3</td>
<td>Anisotropic</td>
<td>87.3</td>
</tr>
<tr>
<td>Gilsocarbon</td>
<td>AGL, BAEL, UCAR</td>
<td>Vibration</td>
<td>1.92</td>
<td>1 - 300</td>
<td>Gilsonite</td>
<td>16.2</td>
<td>Near-to-isotropic</td>
<td>62.5</td>
</tr>
<tr>
<td>NBG-18</td>
<td>SGL, Germany</td>
<td>Vibration</td>
<td>1.85</td>
<td>1 - 300</td>
<td>Pitch</td>
<td>17.8</td>
<td>Isotropic</td>
<td>35.4</td>
</tr>
</tbody>
</table>

Samples of all the grades of graphite were subjected to varying irradiation doses of 2, 5, 10, 25 and 50MGy at ambient to high temperature in air, CO$_2$ and CO$_2$/H$_2$O at atmospheric pressure and the evolution in the graphite microstructure was studied using Raman spectroscopy, X-ray photoemission spectroscopy, Brunauer-Emmett-Teller (BET)/Barret-Joyner-Halenda (BJH) analyses, X-ray tomography, and electron and optical microscopy. In this manuscript, the authors present the principal microstructural change in the gamma-irradiated graphite samples at ambient temperature (323K) in air up to 5MGy dose. Scanning electron microscopy was conducted using a FEI Quanta FEG 250 SEM at low accelerating voltage of 5kV and small working distance (5mm). Raman Spectroscopy was conducted using a SENTERRA Raman microscope (Bruker Optics, Inc.) and the Raman vibrational spectra were measured using a 532nm wavelength excitation laser with 20mW power and 10s integration in the confocal mode of operation at a resolution of 3cm$^{-1}$. Sample heating, heat transfer and dissipation to the graphite surface were negligible. TriStar II 3020 automated gas adsorption analyser was used to analyse surface area and pore size distribution.

RESULTS & DISCUSSION

Gamma rays interactions with bulk materials are different from that of charged ions and neutrons. It is well known that the probability of photoelectric interaction and pair production is insignificant for the case of energetic gamma rays and low atomic number absorber material such as graphite. Therefore, the Compton effect is believed to be a major interaction mechanism of high-energy photons with

Figure 1: Interaction mechanisms between gamma rays and absorbing material
carbon atoms in graphite lattice (L’Annunziata, 2012). Fig. 1 shows the interaction mechanisms between gamma rays and materials over a wide range of gamma photons energy and atomic numbers of the interacting materials, in which Compton scattering interactions are important consideration for the carbon related materials for given energy spectrum range of gamma rays. Fig. 2, Fig. 3 and Fig. 4 show localised Raman spectra from PGA, Gilscarbon and NBG18 graphite grades, peak intensity \( \frac{I_D}{I_G} \) ratio as a function of irradiation dose before and after irradiation. The Raman spectra showing two prominent features G-band (~1580cm\(^{-1}\)) and D-band (~1333cm\(^{-1}\)) in the first order Raman spectrum and \( G' \)-band (~2720cm\(^{-1}\)) at the second order Raman spectrum. It is well known that the D-band arises from the defects in the graphite; the D-band in the virgin graphite is due to accumulated defects during the graphitization process. On irradiation the D-band strengthened considerably with accumulated dose, indicating the augmentation of defects in the lattice that are purely irradiation induced. Defects are quantified as integrated area intensity peak ratio and shown with the Raman spectra of respective graphite samples. Ionising radiation produces loss of crystallinity or weight loss in graphite by breaking the chemical bonds, which results in creation of defects and causes loss of the regular structure. On continued irradiation, fraction(s) of defects will condense and may form extended defects by arranging carbon atoms in the basal layers.

The Raman spectra also show minor \( D' \)-band adjacent to the G-band, it is also observed that \( \frac{I_D}{I_{D'}} \) is linearly correlated with \( \frac{I_D}{I_G} \). Both D and \( D' \)-bands are allowed vibrations in graphite and visible in virgin and irradiated graphite. Comparing all the graphite grades, the Raman shift for defect peak (D-band) in virgin NBG18 is highest from that in other grades, indicating more defects/disorders residue in the constituents of NBG18 graphite after graphitization process (Fig. 4). On increasing gamma dose, the calculated \( \frac{I_D}{I_G} \) ratio increases sharply in all graphite grades and the Raman shift for defect peak ratio in irradiated Gilscarbon is highest among all the irradiated grades for the given highest dose (Fig. 3). Scanning electron microscopy (SEM) results in Fig. 5 reveal that gamma irradiation damaged graphite microstructure in air. They are observed preferentially and damage localised regions are randomly
distributed in the internal surface of pores. The damage regions are observed with nanocrystallites clusters. The pores and cracks in fillers regions are more susceptible to damage than binder phase.

Figure 3: Raman spectra of Gilsocarbon graphite at different accumulated dose. (b) Peak intensity ratios for different levels of total gamma dose and the data fit curve showing the effect is linear. (c) Localised crystallite size near to the low phonon confinement spacing.

<table>
<thead>
<tr>
<th>Graphite Grade</th>
<th>MGy</th>
<th>ID/IG</th>
<th>Crystallite Size, La (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin</td>
<td>0.313</td>
<td>61.490</td>
<td></td>
</tr>
<tr>
<td>0.809</td>
<td>0.544</td>
<td>35.361</td>
<td></td>
</tr>
<tr>
<td>1.111</td>
<td>0.729</td>
<td>26.376</td>
<td></td>
</tr>
<tr>
<td>1.549</td>
<td>0.999</td>
<td>19.237</td>
<td></td>
</tr>
<tr>
<td>1.764</td>
<td>0.893</td>
<td>21.524</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4: Raman spectra of NBG18 graphite at different accumulated dose. (b) Peak intensity ratios for different levels of total gamma dose and the data fit curve showing the effect is linear. (c) Localised crystallite size near to the low phonon confinement spacing.

<table>
<thead>
<tr>
<th>Graphite Grade</th>
<th>MGy</th>
<th>I_L/IG</th>
<th>Crystallite Size, Lc (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin</td>
<td>0.559309</td>
<td>34.372</td>
<td></td>
</tr>
<tr>
<td>0.809</td>
<td>0.609717</td>
<td>31.663</td>
<td></td>
</tr>
<tr>
<td>1.111</td>
<td>0.644401</td>
<td>29.833</td>
<td></td>
</tr>
<tr>
<td>1.549</td>
<td>0.807037</td>
<td>23.821</td>
<td></td>
</tr>
<tr>
<td>1.764</td>
<td>0.873003</td>
<td>22.021</td>
<td></td>
</tr>
</tbody>
</table>
Figure 5: Scanning electron micrographs of different grades of graphite after and before irradiation. A. Gilsocarbon (virgin, 0.809 and 1.764MGy), B. PGA (virgin, 0.809 and 1.764MGy), and C. NBG18 (virgin, 0.809 and 1.764MGy).

SEM micrographs from before and after gamma irradiation of NBG18 graphite are shown in Fig. 6. The damage regions are localised and presented in lower panel of Fig. 6. High magnification images in Fig. 6(d-f) show very fine crystallites structures. As discussed above, gamma photon interacted with carbon nucleus mainly through Compton scattering and absorption. The recoiled electrons with sufficiently high energy are originating from the Compton scattering causing collision with the neighbour carbon nuclei. Carbon atom shifts from their lattice position would be caused by such knock-on collisions and energy could transfer from knock-on carbon atoms to its neighbouring carbon. If energy exceeded the threshold for further interactions and displacements, then damage cascade would form (Florian, 1999).

The multiscale pores are formed by the binding of crystallites with various binding materials used in the manufacture of graphite. The nature of binding materials may have an influence on the distribution of pores. Although experimental evidence is sparse, other factors those are different in given graphite are method of manufacture, graphitization temperature, particle size before binding or presence of impurities(Nightingale et al., 2013).
Figure 6: (a) SEM image of NBG18 graphite before the gamma irradiation, (b) SEM image of NBG18 after irradiation, total accumulated dose of 4.5MGy. (c) and (e) showing the images from the local area of damage that are magnified (marked) and arrows show those images.
These factors may account in part for the variation in surface characteristics. The surface area found by the summation of the area in the pores in the range of 20 to 3000Å diameter. Fig. 7 shows variation of BET surface area and average pore size in different graphite grades with increasing gamma dose, with a variability of about ±5% in data. The difference in surface area magnitude exists in different grades due to the presence of difference in pore size variations. In this experiment, it is found that the BET surface area and average pores size decreased for PGA and NBG-18, whereas the BET surface area and average pores size increased for Gilsocarbon. It is probable that the shrinkage of micropores in PGA and NBG-18 and opening of nanopores in Gilsocarbon at ambient conditions under gamma irradiation (Nightingale et al., 2013).

Residual elastic and plastic strains are developed into graphite during graphitization and manufacturing. This consequently contributes into a significant drop in carbon atom displacement threshold energy ($T_d$) to a smaller value, due to a lower coordination number (Crespi et al., 1996). As strain weakens carbon-carbon chemical bond, less energy is required for bond rupture. Possibly bond breaking by gamma irradiation would release large strain energy and thus stabilize the defects or strain energy would not be sufficient to stabilize the defects. Moreover, higher local kinetic energy from the interaction of photons with carbon nucleus can bring more damages locally (Krasheninnikov and Nordlund, 2010).

**SUMMARY**

In this paper the results presented show the microstructural features of graphite grades after radiolytic oxidation under gamma irradiation and ambient condition. Raman spectroscopy and electron microscopy were used to examine the radiolytic oxidised graphite grades. Electron microscopy analysis showed that damaged regions are very localised and random. Fine precipitates in the nanosized range were observed near to the internal surfaces of the pores. Cracks and pores in the filler particles are more prone to damage than in the binder phase. Further work is in process to study the graphite grades behaviour in different gas atmosphere with varying temperatures and resulting microstructure will be investigated using the latest advances in the analytical techniques.
REFERENCES


