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9. Pore Structure of Neutron Irradiated PAN Fiber Based Carbon-Carbon 
   Composites: A Small Angle X-ray Scattering Study, 
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Novel isotropic high-density amorphous carbon composites for moderator applications in low-temperature thermal reactors

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Abstract

Making of high-density amorphous carbon composites with substantial thermal and radiation stability is a challenge in itself. Two series of carbon composites were synthesized by making use of novel precursor materials like polyacrylonitrile (PAN) based carbon fibers and carbon black (CB) powder along with phenol formaldehyde resin as binder. The samples were extensively characterized using a large number of characterization techniques. Carbon composites made by this technique are found to retain very high-degree of isotropicity and amorphous nature even when heat-treated at \( \sim 1500 \) °C and above. Besides, they are found to exhibit excellent thermo-mechanical properties like specific heat, compressive strength and coefficient of thermal expansion. Stock composition was varied to find its effect on the thermo-mechanical properties and isotropicity of the samples.

Keywords: A. Amorphous; A. Carbon composite; B. Mechanical properties; B. Microstructure

1. Introduction

Use of graphitic carbon as moderator material is strictly not recommended for nuclear reactors operating below 250 °C, as this might lead to the sudden release of Wigner energy that is locked up in graphite as a result of atoms dislodged from their normal lattice points by impinging radiation, often causing serious accidents [1,2]. Graphite is also likely to undergo post-irradiation densification, thereby inflicting severe changes in the fabricated structures and hence causing failure in them. However despite all these drawbacks, graphitic carbon due to its excellent neutron scattering properties, still continues to be the unanimous choice for the moderator material in high-temperature nuclear reactors [3–5] where the aforesaid drawbacks are essentially overcome due to high-temperature annealing.

Therefore the question arises whether a carbon-based material could be developed that suits the moderator requirements in low-temperature thermal reactors? Obviously the basic requirements are that the material should be amorphous, dense and with very high degree of isotropicity in them. Conventionally amorphous carbon is prepared from petroleum coke. But it tends to graphitize during high temperature processing at and above 900 °C, hence making it useless for the proposed application. So, the key issue remains that the material should retain its isotropic nature even after heat-processing at \( \sim 1500 \) °C and above typically required for structural fabrication. Besides, there should not be much radiation-induced modification of its thermo-mechanical properties. Unfortunately, such a novel carbon with high degree of thermal and radiation stability does not exist. So attempts were made to develop carbon composites that encompass most of the properties and yet remain isotropic over a wide range of temperatures by judiciously choosing the right starting materials that yielded hard and non-graphitizing forms of carbon [6].
this article, we report on synthetic routes for making of novel carbon composites that not only retain isotropicity over a wide range of stock composition but also remain amorphous when heat-treated at high temperatures. Besides these materials offer excellent thermo-mechanical properties such as low coefficient of thermal expansion, high specific heat, high compressive strength etc. and can be processed at very high heating rates typically ~50–100 °C/h as against 5 °C/h recommended for standard petroleum coke samples. An exhaustive study has been carried out on different thermo-mechanical and other material properties of the samples using a wide range of characterization techniques. Herein, we discuss the results of our investigation on carbon composites made from carbonized PAN fiber i.e., carbon fibers and carbon black powder in comparison with a standard carbon sample made from petroleum coke.

2. Experimental

2.1. Sample preparation

2.1.1. Petroleum coke based samples

As reference a sample was prepared from nuclear grade petroleum coke mixed with 25% phenol formaldehyde binder following standard recipe available in the literature [1]. Pellets (10 mm diameter and 10 mm height) were made in a uniaxial press under a pressure of 350 MPa. They were then heat-treated at ~1000 °C in an inert atmosphere to get the desired product.

2.1.2. Carbon fiber based samples

Carbonized PAN (polyacrylonitrile) fibers were chopped into pieces typically ~2 mm in length and dispersed in phenol formaldehyde resin matrix in different weight fractions. The resin along with the fiber was then cast in a dye having 10 mm diameter and 10 mm height and was heat-treated to ~1000 °C in an inert (argon) atmosphere at the rate of 50 °C/h to obtain the desired product. Carbon composites made with 10, 20, 30 and 50 wt% of carbon fibers were characterised ex-situ using a number of techniques.

2.1.3. Carbon black based samples

Phenol formaldehyde resin (liquid Resol type) was cured at 200 °C and crushed into small pieces. They were subsequently carbonized at a temperature of 1000 °C in inert atmosphere. The heating rate was maintained at 100 °C/h in the temperature range of 200 °C–750 °C. The carbonized product was milled and sieved into different size fractions. The powder was leached by hydrochloric acid to remove metallic impurities like iron that came in from milling. Powder having size below 75 μm was used in the present study. This carbon powder was mixed with 0–15 wt% of carbon black (N330 grade of surface area 83 m²/g) and phenol formaldehyde binder varying from 10% to 20% by weight. Pellets (~10 mm diameter and 10 mm height) were made in a uniaxial press under a pressure of 350 MPa. The green pellets were heat treated upto 1000 °C at a heating rate of 100 °C/h in inert atmosphere to remove volatile organic impurities from the binder.

2.1.4. Densification of the samples

Densification of carbon samples was carried out by impregnation technique. Residual open pores in the samples were impregnated with liquid phenol formaldehyde resin under pressure of 24 kg/cm² and then it was carbonized at ~1000 °C under inert atmosphere. Heating rate was maintained at ~100 °C/h. Impregnation for different span of time and subsequent carbonization was carried out in cycles until there was no appreciable change in the density of the samples.

All samples were subsequently heat-treated at 1500 °C to explore the effect of high-temperature processing on the micro-structural modification of the materials.

2.2. Sample characterization

Chemical analysis of the samples was done by atomic emission spectroscopy (AES). Bulk density of the samples was measured by conventional Archimedes principle using distilled water. Specific heat (Cₚ) data were obtained using a differential scanning calorimeter (DSC) (Mettler make). Coefficient of thermal expansion (CTE) and compressive strength (CST) measurements were carried out, respectively, using a dilatometer and a universal testing machine. Reflection microscopy was done on polished samples using a polarized light source. A retarder plate (λ plate) that introduces a phase shift of 551 nm was used in combination with a set of cross-polarisers to study the samples and a Newton chart for phase shift was used to decode the extent of anisotropy in the samples from different colourations in the micrographs. X-ray diffraction patterns were recorded in a Philips X-ray diffractometer PW 1710 using Cu Kα line (1.54060 Å) from an X-ray generator operated at ~30 kV and 20 mA. Micro-Raman measurements were done using a LABRAM-I spectrometer (ISA make) in a backscattering geometry and with spectral resolution of 2 cm⁻¹. The 488 nm line of a 10 mW Ar⁺ laser was focused onto the sample using a 10 × microscope (Olympus make) objective that corresponds to a spot of less than 1 mm for excitation and a Peltier cooled charge coupled device (CCD) was used for multi-channel detection.

3. Results and discussion

Nuclear grade (N-grade) material was obtained by both the proposed synthetic routes and also from N-grade petroleum coke. Elemental analysis of the samples (Table 1) shows impurities like boron, cadmium and cobalt, with very high neutron cross-section below ppm level. Other impurities also comply with nuclear standards. These metallic impurities especially iron are believed to have been incorporated during milling of the samples. It was observed
that density of the petroleum coke-based samples at a given temperature increased initially and then decreased steadily with weight fraction of the binder. Initially the binder bridges the inter-particular gap thus increasing the sample density, while excess of it contributes to porosity in the sample as it volatilizes during carbonization. Maximum density (\(\sim 1710 \text{ kg/m}^3\) @ 1000°C) was obtained with 25 wt% of binder composition. A standard carbon sample synthesized by cracking this stock composition i.e., 75% petroleum coke and 25% binder at \(\sim 1000\) °C has been used during the present study as a reference material for comparing its thermo-mechanical and other material properties with those obtained from carbon fiber and carbon-black. Fig. 1 shows the variation in density of the two sets of samples as a function of their constituents. The dotted line represents the standard sample made from petroleum coke. Density of carbon fiber based samples increases monotonically with fiber content i.e., with decreasing matrix element. Incomplete binding of the matrix resin with fiber leads to open porosity and hence decrease in the sample density with decreasing percentage of fiber. Carbon-black based samples have higher density than carbon fiber based samples because of lower % porosity but no systematic variation of the sample density with wt% of carbon-black is observed for these samples. For a given wt% of CB, highest sample density is attained with 15% binder that falls off on both sides of it due to binder-effect as has already been explained in case of petroleum coke based samples. The hypothesis is supported by open pore analysis of CB samples (Fig. 2) that shows samples made with 15% binder having lowest percentage of open porosity for a given wt% of CB. Density of the standard coke sample is however very much higher as compared to both carbon fiber and CB based samples. In order to increase their density further, the samples were subjected to impregnation and subsequent carbonization as described in detail in the experimental part. After several cycles of impregnation (Fig. 3) it was found that density increased only by 15% (density 1512 kg/m\(^3\)) in case of 15 wt% CB sample while it increased by more than 40% (density 1510 kg/m\(^3\)) in case of 20 wt% PAN based carbon fiber sample, indicating greater percentage of open pores in as-grown carbon fiber samples. However one major disadvantage of this

### Table 1

Impurity analysis data of carbon samples prepared from different sources (ppm)

<table>
<thead>
<tr>
<th>Source</th>
<th>Boron</th>
<th>Cadmium</th>
<th>Cobalt</th>
<th>Iron</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-grade petroleum coke</td>
<td>&lt;1</td>
<td>0.5</td>
<td>0.3</td>
<td>380</td>
</tr>
<tr>
<td>Carbon fiber</td>
<td>&lt;1</td>
<td>0.7</td>
<td>0.6</td>
<td>400</td>
</tr>
<tr>
<td>Carbon black</td>
<td>&lt;1</td>
<td>ND(^a)</td>
<td>ND</td>
<td>620</td>
</tr>
</tbody>
</table>

\(^a\) ND implies not detected, i.e., below detection limit of AES.
The impregnation technique is that during high-temperature processing, stress is developed in the samples due to unequal expansion of the matrix and core material, often resulting in the formation of cracks in them. Fig. 4 shows the variation in compressive strength of the same set of samples as a function of their constituents. The dotted line as in the previous graph represents the standard coke sample. By and large the trend is the same as that observed for density. In case of CB samples, 15% binder yields the highest compressive strength irrespective of wt% of CB, while it is highest for 50% carbon fiber sample. The most significant observation is that CST of the 50% PAN based carbon fiber sample and a few other CB samples far exceeds that of the standard coke sample. Coefficient of thermal expansion (CTE) along two mutually perpendicular directions has been recorded for the samples and is presented along with that of the standard coke sample in Fig. 5(a) and (b). It is observed that CTE\textsubscript{II} increases while CTE\textsubscript{I} first increases and then steadily decreases with wt% of fiber in carbon fiber samples. In case of CB samples, CTE\textsubscript{I} varies rather unevenly while CTE\textsubscript{II} exhibits an increasing trend with wt% CB for a given percentage of binder. However, it may be noted that for the entire range of composition studied CTE values for both carbon fiber and CB samples are very much lower than the standard coke sample as required for the proposed application. Moreover, CTE\textsubscript{II} and CTE\textsubscript{I} values differ significantly in the standard coke sample implying development of anisotropic graphite phase in it, whereas there is not much of difference in the values for the CB and carbon fiber samples except for the 50% fiber composition. Fig. 6 shows the mean specific heat of the carbon fiber samples and CB samples with 15% binder composition over the temperature range of 50–550 °C. Samples with 15% binder have been typically chosen as they exhibit higher specific heat and excellent material properties over other binder compositions. Mean specific heat decreases drastically from 1710 to 1120 J/(kg K) as fiber increases from 10% to 20% and then tends to saturate at higher wt% of fiber. In contrast, specific heat first increases significantly from 1210 to 1700 J/(kg K) upon addition of 10% carbon black and then decreases at higher
wt% of CB. It is well known that higher specific heat minimizes the risk of releasing Wigner energy suddenly [1]. The arrows in the graph describe the mean (1250 J/(kg K)), upper (1700 J/(kg K)) and lower (800 J/(kg K)) limiting values of specific heat for the standard coke sample in the specified range. Although the mean values are slightly lower for carbon fiber samples, they are very much on the higher side for CB samples as compared to the standard. Besides all data points for both the samples measured in the specified temperature range lie within the limiting band for the standard sample. Apart from these very important thermo-mechanical parameters discussed above, the material property that matters most for the proposed application is the isotropic and amorphous nature of the samples. The extent of anisotropy in amorphous carbon sample due to formation of graphitic phase can be qualitatively studied using an optical polarized microscope equipped with a set of cross-polarizers and a retarder plate ($\lambda$-plate) [7,8]. According to Newton’s chart for evaluation of phase shifts, a $\lambda$-plate that introduces a shift of 551 nm would show up an isotropic phase as blurred magenta colored background [black in gray scale], while the anisotropic graphite crystals would appear either as greenish blue or deep yellow [bright patches with contrast in gray scale] depending on whether its aromatic plane is perpendicular or parallel to the $\lambda$-plate. Development of such coloration (greenish/yellowish) due to anisotropic graphite phase is referred to as optical activity. The technique has been described in detail in one of our previous articles [7]. Fig. 7(a) shows the micrograph of the standard coke sample that clearly shows development of optical activity due to the formation of graphite micro-crystallites. Fig. 7(b) shows the micrograph of the same sample heat treated at ~1500 °C. It is evident from the figure that the graphite micro-crystallites have grown bigger upon heat treatment resulting in enhanced optical activity of the sample. The observation is also supported from XRD measurements that will be discussed subsequently. Fig. 8(a) and (b) shows the micrographs of two typical samples grown with 20% and 50% carbon fiber. The optical activity of the 50% fiber sample is quite high (Fig. 8(b)), whereas the 20% fiber sample barely shows any activity (Fig. 8(a)). This has been explained on the basis of graphitization due to stress induced by the fiber ends. The stress distribution along the fiber length due to fiber matrix interaction during heat treatment of composite is uneven. The stress is maximum at the fiber end and minimum at the fiber centre [8]. The greater is the fiber content the more is the stress generated at the fiber matrix interface, which lead to anisotropy by means of graphitization. However, even after heating to 1500 °C, no optical activity is developed in the 20% fiber sample [Fig. 8(c)]. The carbon-black samples on the contrary do not show up any activity for the entire range of composition discussed above. Fig. 9 (a) shows the micrograph of a typical CB sample with 15% CB and 15% binder composition. Extensive magenta background [black in gray scale] confirms the isotropic nature of the composite. The sample remains isotropic and amorphous even when heated to 1900 °C [Fig. 9(b)] implying that no stress is developed at the interface of as-grown CB samples. Here, the CB particles because of their near spherical geometry actually act as stress reliever as against the pointed fiber ends in carbon fiber based samples. Turbostratic modeling of XRD data provides a simple and straightforward technique for quantitative estimation of the degree of graphitization in amorphous carbon [9]. According to this model, the limiting value for the distance between two adjacent layers in turbostratic graphite is taken to be 0.344 nm, while that for pure 100% graphitic structure is taken to be 0.3354 nm. The percentage degree of graphitization in turbostratic graphite is therefore defined in terms of deviation of the interlayer spacing from that of the pure structure according to the equation

$$\% \text{Degree of graphitization} = \frac{(3.44 - d_{002})/(3.44 - 3.354)} \times 100 \quad (1)$$

where $d_{002}$ denotes the interlayer spacing as obtained from the analysis of the XRD peak at ~27°. According to this model any sample having an interlayer spacing higher than that of the limiting value i.e., 0.344 nm is considered to be 100% amorphous or isotropic in nature. The turbostratic model has also been used to analyze amorphous carbon [10] and is found to work well for all the
carbon samples under discussion irrespective of their source and composition. Results on structural analysis and % degree of graphitization along with detailed sample composition are given in Table 2. As evident from the table, the standard coke sample is 25% graphitic. Except for the 50% fiber sample which exhibits graphitization of 73%, all carbon fiber and CB samples are found to be isotropic or 100% amorphous in nature for the entire range of composition discussed above. Although it is ascertained that as-grown CB samples are by and large isotropic in nature on a macroscopic scale and remains so even after heat treatment of 1500 °C, it remains to be verified at microscopic level especially in the context of the novel densification process discussed above that involves impregnation of the open pores by liquid resin under high-pressure followed by carbonization. Micro-Raman spectroscopy in combination with polarized microscopy provides a direct probe to the issue. Fig. 10 shows the μ-Raman spectra of three representative CB samples made from a fixed (15%) binder composition but with different wt% of CB. For comparison, Raman spectrum of a standard graphitic sample is also attached to the figure. The graphitic sample exhibits a strong and sharp peak at ~1580 cm\(^{-1}\) corresponding to zone centre vibrational mode of \(E_{2g}\) symmetry labeled ‘G’ peak and a hump at ~1355 cm\(^{-1}\) called ‘D’ peak, assigned to have originated from disorder, induced in the sample along its graphitic planes [11]. It is known from the literature that with decreasing long-range order the peaks become broader [12] and ‘D’ peak intensity relative to that of ‘G’ peak (i.e., D/G ratio) increases, often exceeding that of the later. The spectra are fitted with multi-

<table>
<thead>
<tr>
<th>Source</th>
<th>CB (wt%)</th>
<th>Binder (wt%)</th>
<th>PAN fiber (wt%)</th>
<th>Matrix (wt%)</th>
<th>(d_{002}) Graphitization %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petroleum coke</td>
<td>25</td>
<td>75</td>
<td>3.42</td>
<td>NIL</td>
<td>25</td>
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<tr>
<td>Carbon black</td>
<td>0</td>
<td>15</td>
<td>85</td>
<td>3.48</td>
<td>NIL</td>
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<tr>
<td></td>
<td>5</td>
<td>10</td>
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<tr>
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<td>75</td>
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<tr>
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<tr>
<td></td>
<td>50</td>
<td>50</td>
<td>3.38</td>
<td>73</td>
<td></td>
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</table>
Lorentzian line shape in order to extract quantitative information regarding peak position, FWHM and D/G ratio from the fitted parameters. It may be seen from the graph that both the ‘D’ and ‘G’ bands get broadened and D/G ratio increases in case of samples made from 0% and 5% of CB as compared to that of graphite, implying significant disorder in the samples. Apart from the ‘D’ and ‘G’ bands, another band at ~1610 cm\(^{-1}\) that corresponds to first order zone boundary phonon mode also appears in these samples. The bands are further broadened in case of samples made from 15% CB indicating an increase in their amorphous nature with increasing weight percentage of CB. Fig. 11 shows the Raman spectra of 15% CB sample before and after impregnation cycle. No appreciable change in the Raman profile could be observed following impregnation of the samples. This is further supported from the respective polarized optical micrographs (inset of Fig. 11) that do not show up any sign of optical activity in the samples even after third cycle of impregnation. In order to get a quantitative estimation of the trapped Wigner energy composites made from both carbon fiber and CB, they are subjected to irradiation by different projectiles. Results of irradiation tests on composites made from varying stock composition will be communicated separately in future. Finally a channel tube having diameter of 75 mm and length of ~1.4 m (Fig. 12 shows photograph of the channel tube actually used) has been fabricated with amorphous carbon composite made by the proposed technique from a stock composition of 15% CB and 15% binder and is ready to be tested under actual reactor conditions.

4. Conclusions

Two novel processing routes that involve use of carbonized polyacrylonitrile fibers and carbon black powder for making nuclear grade amorphous carbon composites have been proposed. It has been demonstrated that composites made from both these routes show very high density and
exceptional thermo-mechanical properties like coefficient of thermal expansion, compressive strength, specific heat etc. and are isotropic and amorphous over a wide range of stock composition that reduces the risk of releasing Wigner-energy when used as moderator material in thermal reactors. This has been verified from experiments carried out under actual reactor conditions.

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Neutron irradiation studies on low density pan fiber based carbon/carbon composites

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A B S T R A C T

Carbon has been extensively used in nuclear reactors and there has been growing interest to develop carbon-based materials for high-temperature nuclear and fusion reactors. Carbon–carbon composite materials as against conventional graphite material are now being looked into as the promising materials for the high temperature reactor due to their ability to have high thermal conductivity and high thermal resistance. Research on the development of such materials and their irradiation stability studies are scant. In the present investigations carbon–carbon composite has been developed using polyacrylonitrile (PAN) fiber. Two samples denoted as Sample-1 and Sample-2 have been prepared by impregnation using phenolic resin at pressure of 30 bar for time duration 10 h and 20 h respectively, and they have been irradiated by neutrons. The samples were irradiated in a flux of $10^{12}$ n/cm$^2$/s at temperature of 40°C. The fluence was $2.52 \times 10^{16}$ n/cm$^2$. These samples have been characterized by XRD and Raman spectroscopy before and after neutron irradiation. DSC studies have also been carried out to quantify the stored energy release behavior due to irradiation. The XRD analysis of the irradiated and unirradiated samples indicates that the irradiated samples show the tendency to get ordered structure, which was inferred from the Raman spectroscopy. The stored energy with respect to the fluence level was obtained from the DSC.

The stored energy from these carbon composites is very less compared to irradiated graphite under ambient conditions.

1. Introduction

Carbon is a wonderful material having wide range of structures and possess several excellent properties such as their capability to withstand high temperature (up to 3000°C in protective environment), increased strength up to 2500°C, chemical inertness, low coefficient of thermal expansion, low friction, good thermal and electrical conductivities, low density and good thermal shock resistance. Carbon and carbon-based materials are used in nuclear reactors and in the recent past there has been growing interest to develop graphite and carbon-based materials for high-temperature nuclear and fusion reactors. Efforts are underway to develop carbon materials with high density as well as amorphous isotropic carbon for use in low temperature thermal reactors. An amorphous structure is needed in order to avoid accumulation of Wigner energy [1], which is the stored energy in carbon lattice due to dislocation of atoms induced by irradiation. This amorphous carbon should be isotropic and dense in order to achieve dimensional stability under irradiation.

Graphitic carbon due to its excellent neutron scattering properties, continues to be the unanimous choice for the moderator material in high-temperature nuclear reactors [2–4] where the aforesaid drawbacks are essentially overcome due to high-temperature annealing. The effect of particle irradiation on graphite has gained lot of importance due to its use as nuclear material. Some literature on irradiation behavior of graphite [5–8] and stored energy in graphite [9,10] is available. However the studies on radiation damage in the disordered forms of carbon are scant. Few investigations on heavy ion irradiation of disordered carbon in carbon/carbon (C–C) composite made of particulates and chopped carbon fibers have been reported, but there is not much literature on architecture carbon/carbon composites. Burchell et al. [11] irradiated 1D, 2D, and 3D C–C composites at 600°C up to damage doses 1.5dpa. 3D C–C composites were shown to have more isotropic dimensional changes than that of 1D or 2D composites.

The present study aims at determining if the particle irradiation causes formation of crystalline phase in the amorphous carbon leading to any storage of Wigner energy. There is a possibility of self-organization phenomena under irradiation leading to localized ordered arrangement in disordered structure of atoms in amorphous samples leading to crystallinity [12–14]. In the present work, we have carried out neutron irradiation on the carbon–carbon
composites. We have characterized the structural parameters like extent of local ordering along c-axis, the average spacing of the \(d_{(002)}\) i.e. the (0 0 2) crystallographic planes using X-ray diffraction (XRD) technique. This is further validated using Raman spectroscopy.

2. Experimental

2.1. Preparation of carbon/carbon composite samples

The fabrication of a suitable preform is the first step for manufacturing the carbon–carbon composite. This may also be referred to as fiber architecture. It not only imparts rigidity to the composite, but also in combination with fiber properties it determines the properties of the composite. In the present studies preform has been made using PAN carbon fibers. PANEX 35 carbon fiber of yield 48 k has been used. The carbon fiber diameter was 7.2 \(\mu\)m. In the present work green preform in the shape of rectangular blocks have been fabricated using 2D matted PAN carbon fiber which was stacked to a 2-D preform using phenol formaldehyde resin. This preform was cut into 1000 \(\times\) 1000 \(\times\) 0.4 mm size and carbonized at a slow heating rate of 0.1 \(^{\circ}\)C/min in inert atmosphere. This carbonized samples had density of 1100 kg/m\(^3\). The carbonized sample is highly porous and has to be densified for any application. Hence these samples were densified by resin impregnation technique up to two cycles. The samples were impregnated with liquid phenol formaldehyde resin under a pressure of 30 bar and with varying time duration of 10 and 20 h. The impregnated samples were cured and then carbonized at 1000 \(^{\circ}\)C under inert atmosphere with a heating rate of 6 \(^{\circ}\)C/h. The samples were then further subjected to a second cycle of impregnation at the same pressure and varying time duration as carried out during the first cycle. These samples were then cured and carbonized as done in the first cycle. Two cycles of impregnation and carbonization were carried out and then used for further studies.

2.2. Irradiation of the samples

The carbon–carbon (C–C) composite samples have been irradiated with thermal neutrons at Apsara Reactor in Bhabha Atomic Research Center, Trombay. The energy spectrum for irradiation was 98% thermal neutron component for which neutron energy was up to 0.55 eV and 2% is epithermal component (above 0.55 eV).

Two samples, Sample-1 and Sample-2 having density of 1314 kg/m\(^3\) and 1310 kg/m\(^3\) respectively were taken for these studies. Sample-1 was prepared by impregnation of resin at 30 bars for 10 h while Sample-2 was prepared by impregnation at 50 bars for 20 h.

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**Fig. 1.** Change in IG/ID for unirradiated and irradiated carbon/carbon composites Sample-1 at fluence levels: (a) unirradiated, (b) 2.52 \(\times\) \(10^{16}\) n/cm\(^2\), (c) 5.04 \(\times\) \(10^{16}\) n/cm\(^2\) and (d) 7.2 \(\times\) \(10^{16}\) n/cm\(^2\).
30 bars for 20 h. The irradiation flux was $1 \times 10^{12}$ n/cm$^2$/s for seven hours, fourteen hours and twenty hours for both Sample-1 and Sample-2. The respective fluence was $2.52 \times 10^{16}$ n/cm$^2$, $5.04 \times 10^{16}$ n/cm$^2$ and $7.2 \times 10^{16}$ n/cm$^2$ at temperature of 313 K during irradiation. The stored energy in the composite due to irradiation was measured using DSC and the changes in the structure were observed by X-ray diffraction and Raman spectroscopy.

2.3. Characterisation of the irradiated sample

XRD technique is employed to characterize the degree of graphitization of carbon–carbon composites with low crystallinity. X-ray diffraction patterns were recorded using a Philips X-ray diffractometer PW 1710 using monochromatised Cu K$_\alpha$ line (1.5418 Å) from an X-ray generator operated at $24$ kV and 20 mA. Samples were scanned in a step of 0.02°/step over the angular range of (2θ) from 10° to 70°. Micro Raman measurements were done using a LABRAM-I spectrometer (ISA) make in a back scattering geometry. The stored energy release spectra were measured by a differential scanning calorimeter at a constant heating rate in argon atmosphere. Both the samples were heated at the rate of $5$ °C/min from RT to 1000 °C.

3. Results and discussion

3.1. Raman spectroscopy studies

Raman spectroscopy was used for the structural analysis and to find if graphitization was occurring during the processing of the samples. Usually Raman spectra of most of the carbon–graphite...
materials contain two peaks at ~1580 cm\(^{-1}\) and at ~1360 cm\(^{-1}\) except for natural graphite, which has a single sharp Raman band at 1580 cm\(^{-1}\) [15]. The 1580 cm\(^{-1}\) peak is known to correspond to graphite structure and the 1360 cm\(^{-1}\) peak is correlated to graphitized carbon structure called ‘D’ peak, assigned to have originated due to the disorder. The ratio of the integrated intensities of the two peaks, \(I_D/I_G\), has been considered to be a good parameter to estimate the degree of graphitization. The higher the ratio of \(I_D/I_G\), lower is the degree of graphitization of the carbon materials. The 1580 cm\(^{-1}\) peak comes from the flex vibration of chemical bonds in atomic hexagonal net plane while the 1360 cm\(^{-1}\) peak is associated with local unsymmetrical structure, which exists, in graphitized carbon or non-integrity graphite crystals containing defects.

The change in structural parameters and the energy stored due to displacement of atoms from lattice position during irradiation have been studied using Raman Spectroscopy. From Fig. 1a–d shows the variation of \(I_D/I_G\) ratio of irradiated Sample-1. From Table 1 it is seen that the \(I_D/I_G\) ratio increased from 0.73 to 0.87 with increase in fluence and then further decreased with further increase in fluence. Fig. 2a–d shows the variation of \(I_D/I_G\) ratio of irradiated Sample-2. While in Sample-2 there was an increase in the ratio of \(I_D/I_G\) with increase in fluence from 0.82 to 0.93 and remains almost same on further increase in fluence. Study was carried out to see if the different processing parameters caused marked change in the \(I_D/I_G\) ratio of irradiated Sample-1 and Sample-2. There was no appreciable change observed which may be due to the fact that both had nearly the same density. It can be inferred that density is the factor which governs the irradiation defects rather than the processing parameter.

3.2. XRD studies

Carbon–carbon composites are composed of carbon fibers and carbon matrix, which are fabricated by different processing techniques. The carbon matrix is usually obtained by either impregnation with an organic precursor or chemical vapor infiltration (CVI) or by combination of these two ways that lead to hybrid matrix. The degree of graphitization in carbon–carbon composites is inhomogeneous and this is the reason why the material is difficult to graphitize. According to Bragg equation, the interlayer spacing \(d_{002}\) can be obtained and on the basis of the model given by Maire and Mering [16], the degree of graphitization can be calculated from the equation given below:

\[
g(\%) = \frac{(0.3440 - d_{002})/0.3440 - 0.3354) \times 100}{(1)}
\]

where \(g\) is the degree of graphitization, 0.3440 is the interlayer spacing of fully non graphitized carbon (in nm), 0.3354 is the interlayer spacing of the ideal graphite crystallite and the \(d_{002}\) is the interlayer spacing obtained from XRD. 0.3440 nm represents a specific structure proposed by Franklin [17] who considered it as interlayer spacing of non graphitic carbon, i.e. the turbostratic structure put forward by Warren and co-workers [18,19]. Sometimes the apparent interlayer spacing of turbostratic structure is greater than 0.344 nm, as \(d_{002} > 0.3440 \text{ nm}, g < 0 \text{ in Eq. (1) represents a structure which is far from ideal graphite structure}.

From the XRD patterns Fig. 3a and b of the irradiated and unirradiated samples it is found that the \(d_{002}\) peaks for the irradiated samples are becoming broader and appearance of a new peak indicate the tendency to get ordered structure. Table 2 gives the change in \(d_{002}\) values of unirradiated and irradiated Sample-1 and Sample-2.

XRD is the most common analytical tool for determining structure of the ordered and disordered carbons [20–23]. In graphite the carbon layers have the ABAB-stacking along the c-axis. The disorder can occur due to random shifts between the adjacent layers, unorganized carbon atoms which are not part of the layer, presence of local 3R stacking and strain in the layers. These defects affect the extent of local ordering \(L_c\) along c-axis designated as crystalline height.

3.3. DSC studies

The neutrons transfer their kinetic energy by knock off of atoms from the lattice when the carbon–carbon composites are irradiated. These in turn cause displacement cascades by successive collisions. Stored energy arises due to the fact that after irradiation by neutrons the crystal lattice of graphite possesses increased potential energy due to the presence of defects stable under the
conditions at which the irradiation was carried out. The defects are of two general types, vacancy and interstitial, but with varying complexity depending on the irradiation conditions. Defects may be annealed to more stable configuration by increasing the vibrational energy of the lattice by heating. Most of the energy release may be caused by the annihilation of interstitials and vacancies. The stored energy was measured by release of the energy at constant rate. Fig. 4a and b shows the DSC plot, of the energy release rate with respect to temperature for the irradiated samples. The samples were heated at constant rate of heating of 5 °C per minute in the range from RT to 1000 °C. The stored energy is obtained from the area under the curve. The stored energy release data for Sample-1 and Sample-2 at varying fluence levels is given in Table 3.

The stored energy is found to increase with increasing fluence in Sample-1. At lower fluence the defects are simple and are getting annealed at around 100 °C. While at higher fluence levels complex defects are formed which are getting annealed by heating at higher temperatures. In Sample-2 the stored energy was found to decrease with increasing fluence indicating that the defects created are less and simple in nature and are getting annealed at lower temperatures. It has been earlier reported in literature [24] that the stored energy decreases with increase in fluence level for ion irradiation of both carbon black based composite and PAN based composite. Irradiation at high doses causes formation of complex defects and the stored energy may be released at higher temperatures. The samples in our experiments are carbon/carbon composites made of reinforced PAN fiber and matrix of carbon char obtained from phenol formaldehyde resin. Both the carbon present in the samples is in disordered form. The amount of energy stored in graphite varies with the crystal size, more energy being stored in the more highly crystalline material [25]. In case of irradiated graphitic samples they require high activation energy to overcome the activation energy barrier to reach at a lower energy state (stable form) and so higher temperature is required. So the energy release peak is seen around 150–200 °C for graphite samples irradiated at 30 °C associated with the recombination of single interstitials and vacancies. With increasing neutron dose this peak becomes broader and maximum release rate is reduced. The disordered carbon is already at higher energy level and the activation energy barrier is less, as compared to graphite therefore lower temperature is sufficient to overcome the activation energy barrier. The accumulation of stored energy in graphite is both dose and irradiation temperature dependent. With increasing irradiation temperature the total amount of stored energy and its peak rate of release diminish and above temperature of ~300 °C stored energy ceases to be a problem. The amount of stored energy in graphitically irradiated at ambient temperature is very large, which is 2700 J/g, can be stored as lattice defects. This heat, when released under adiabatic conditions would cause an increase in temperature of ~1300 °C. Annealing is required as observed in highly irradiated graphite [26–29] where the sample has to be heated to 2000 °C to release all the stored energy.

4. Conclusions

The neutron irradiated carbon composite samples have been characterized by XRD and Raman spectroscopy before and after neutron irradiation. DSC studies have also been carried out to see the stored energy release behavior due to irradiation. From the XRD analysis of the irradiated and unirradiated samples it is found that the values of $d_{002}$ peaks for the unirradiated samples are higher than that of the irradiated samples indicating the tendency to get ordered structure. This is also inferred from the Raman spectroscopy. The $I_D/I_G$ ratio of irradiated samples was found to increase with increasing fluence when compared to unirradiated samples initially but decreased further with increasing fluence in Sample-1. While in Sample-2 there was an increase in the ratio of $I_D/I_G$ with increase in fluence and is almost same on further increase in fluence. The stored energy with respect to the fluence level was obtained from the DSC. These results indicate that simple defects created due to low fluence of irradiation are annealed by heating and releasing the stored energy at lower temperature while if complex defects are formed high temperatures are required for annealing these defects. The flux/fluence used is lower than the actual scenario in the upcoming compact higher temperature reactor; however the present study could definitely be an initial step in the direction of investigation of damage caused by neutrons on carbon/carbon composite materials for its use in the

<table>
<thead>
<tr>
<th>Dose (n/cm$^2$)</th>
<th>Sample-1 stored energy (J/g) (RT-1000 °C)</th>
<th>Sample-2 stored energy (J/g) (RT-1000 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2.52 \times 10^{16}$</td>
<td>82.20</td>
<td>100.02</td>
</tr>
<tr>
<td>$5.04 \times 10^{16}$</td>
<td>119</td>
<td>66</td>
</tr>
<tr>
<td>$7.2 \times 10^{16}$</td>
<td>185</td>
<td>51.65</td>
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</table>
upcoming reactor. Currently the available flux was low in the range of $10^{12}$ n/cm$^2$/s. However these samples have to be evaluated by irradiating at a higher dose for any nuclear application. We have severe limitation of not being able to use the fluence of $10^{20}$ n/cm$^2$. However an extension of work on carbon/carbon (C/C) composites irradiation with higher flux in some international neutron irradiation facility would be taken up in near future. Currently some irradiation studies with high energy neutrons are being carried out. The results of which will be discussed in forthcoming publication.

References