Journal of Nuclear Materials 404 (2010) 19–24

Contents lists available at ScienceDirect

Journal of Nuclear Materials

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

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

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ARTICLE INFO

Article history:
Received 26 February 2009
Accepted 14 June 2010

ABSTRACT

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 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 2.52×10^{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

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0022-3115/$ - see front matter
doi:10.1016/j.jnucmat.2010.06.021

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 μm. 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 1″ × 1″ × 0.4″ size and carbonized at a slow heating rate of 0.1 °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 °C under inert atmosphere with a heating rate of 6 °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

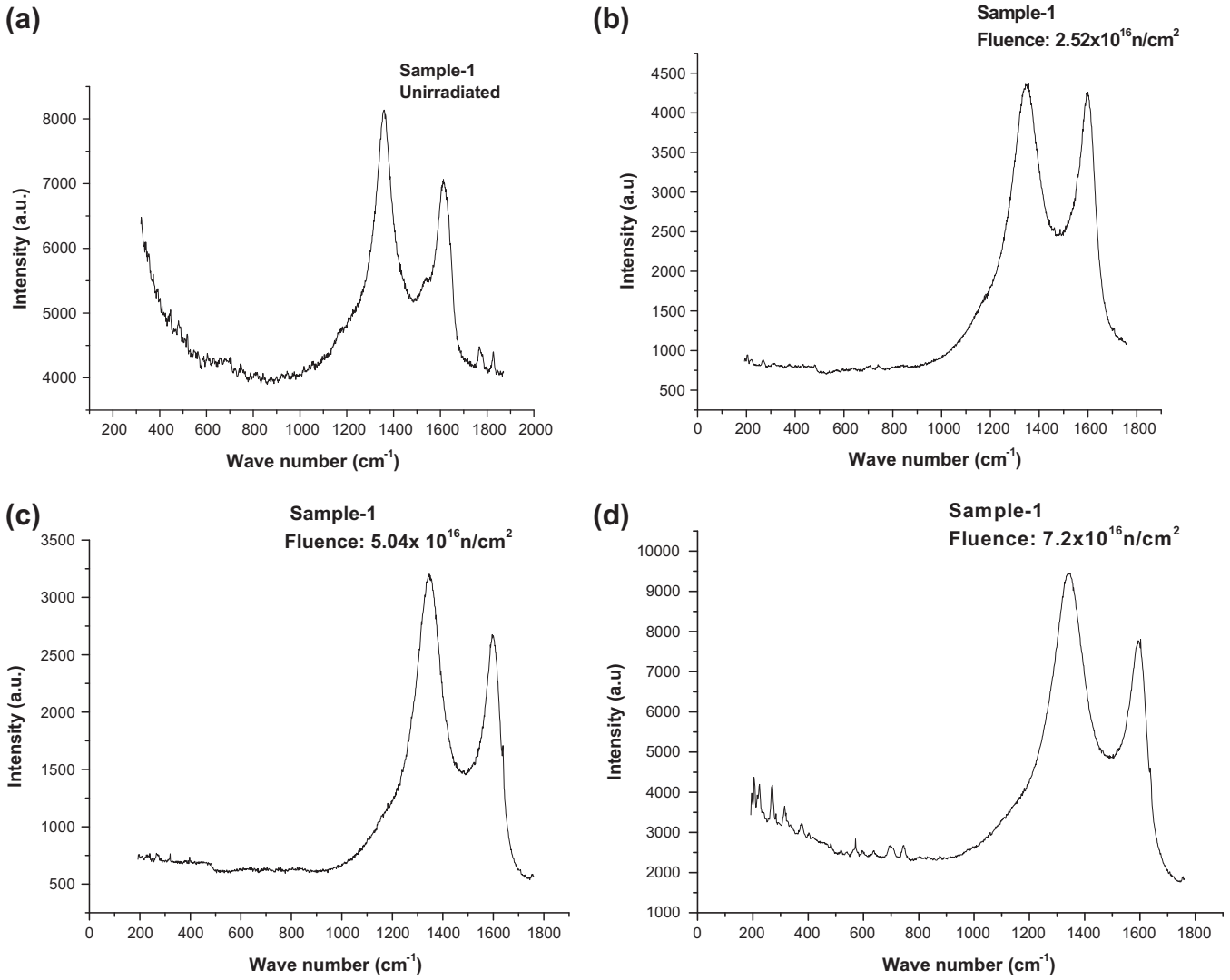

Fig. 1. Change in I_G/I_D for unirradiated and irradiated carbon/carbon composites Sample-1 at fluence levels: (a) unirradiated, (b) 2.52 × 10^1 n/cm^2, (c) 5.04 × 10^{16} n/cm^2 and (d) 7.2 × 10^{16} n/cm^2.

30 bars for 20 h. The irradiation flux was 1×10^{12} n/cm^2/s for seven hours, fourteen hours and twenty hours for both Sample-1 and Sample-2. The respective fluence was 2.52×10^{16} n/cm^2, 5.04×10^{16} n/cm^2 and 7.2×10^{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 Kα line (1.5418 Å) from an X-ray generator operated at ~30 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

Table 1
Variation of I_G/I_D with irradiation fluence levels.

S. No	Sample code	I_G/I_D			
		Unirradiated	2.52×10^{16} n/cm^2	5.04×10^{16} n/cm^2	7.2×10^{16} n/cm^2
1	Sample-1	0.73	0.87	0.85	0.80
2	Sample-2	0.82	0.92	0.93	0.91

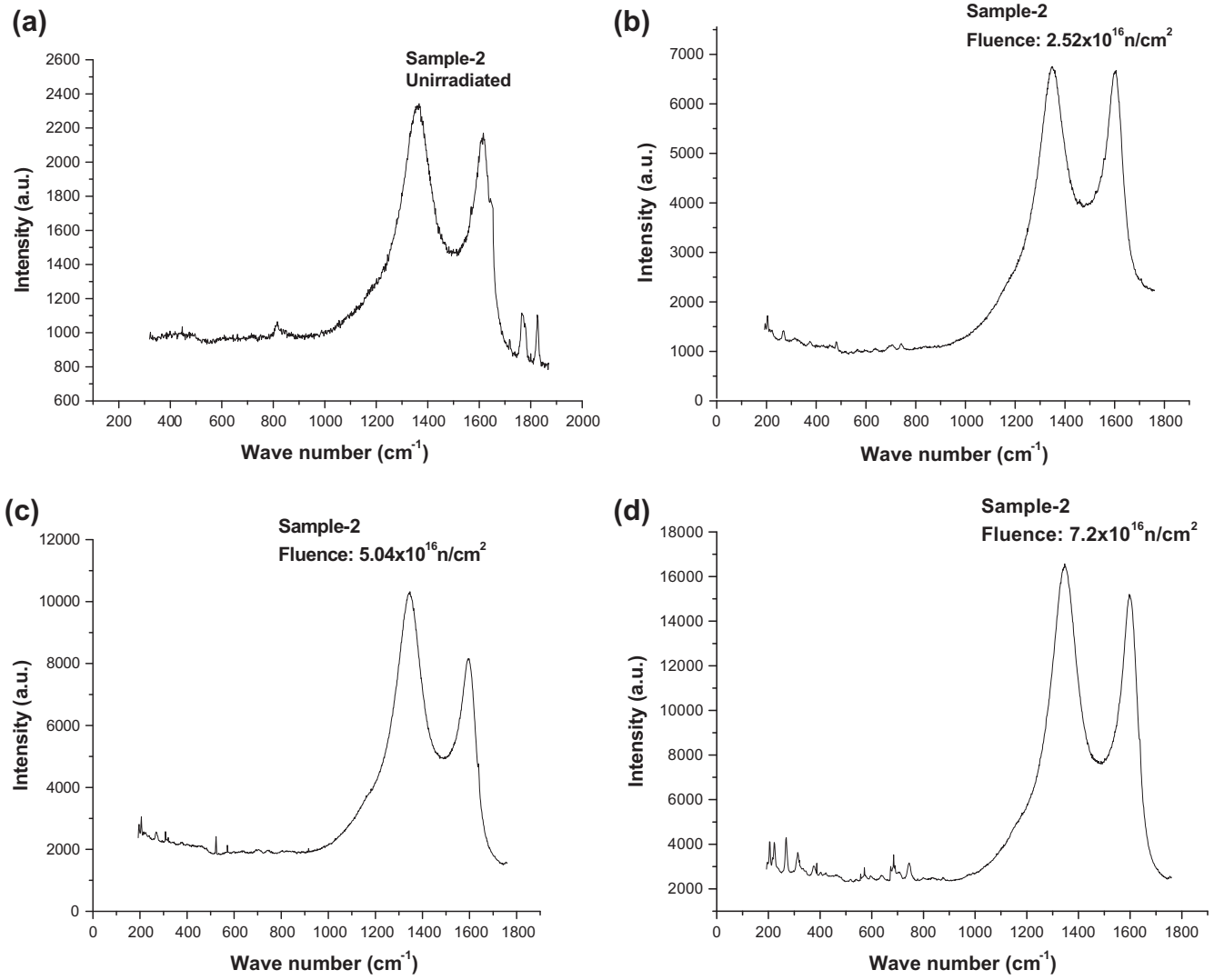

Fig. 2. Change in I_G/I_D for unirradiated and irradiated carbon/carbon composites. Sample-2 at fluence levels: (a) unirradiated, (b) 2.52×10^{16} n/cm^2, (c) 5.04×10^{16} n/cm^2 and (d) 7.2×10^{16} n/cm^2.

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 i.e. 'G' 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_G/I_D ratio of irradiated Sample-1. From Table 1 it is seen that the I_G/I_D 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_G/I_D ratio of irradiated Sample-2. While in Sample-2 there was an increase in the ratio of I_G/I_D 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_G/I_D 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:

$$g(\%) = (0.3440 - d_{(002)}/0.3440 - 0.3354) \times 100 \quad (1)$$

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 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 $d_{(002)} > 0.3440$ nm, $g < 0$ 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.

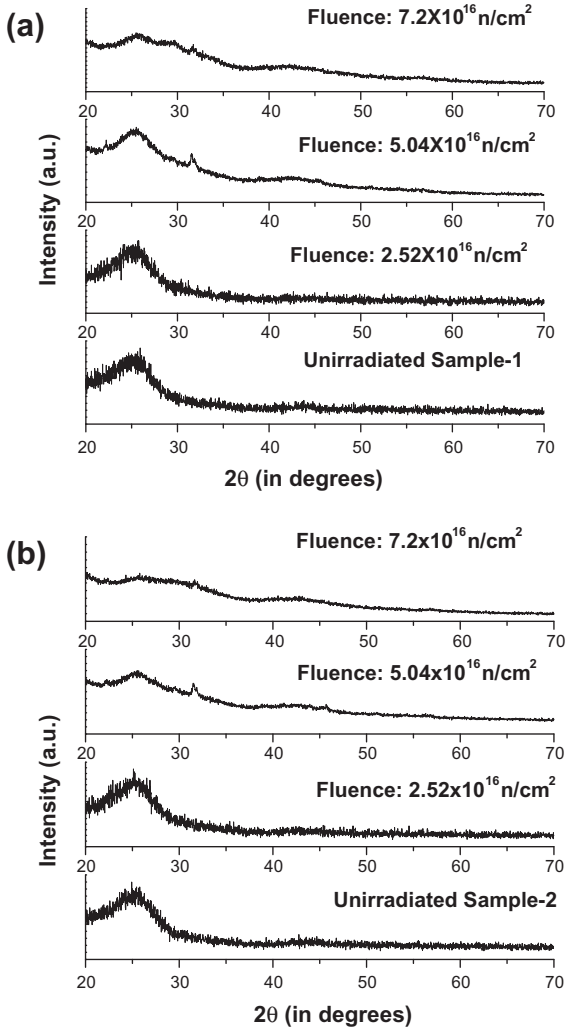

Fig. 3. XRD patterns of irradiated carbon/carbon composite: (a) Sample-1 and (b) Sample-2 at different fluences.

Table 2
Variation of d_{002} with different fluence levels.

Dose (neutron) (n/cm^2)	Sample-1 d_{002} (Å)	Sample-2 d_{002} (Å)
Unirradiated	3.66	3.719
2.52×10^{16}	3.60	3.64
5.04×10^{16}	3.51	3.49
7.2×10^{16}	3.49	3.50

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.

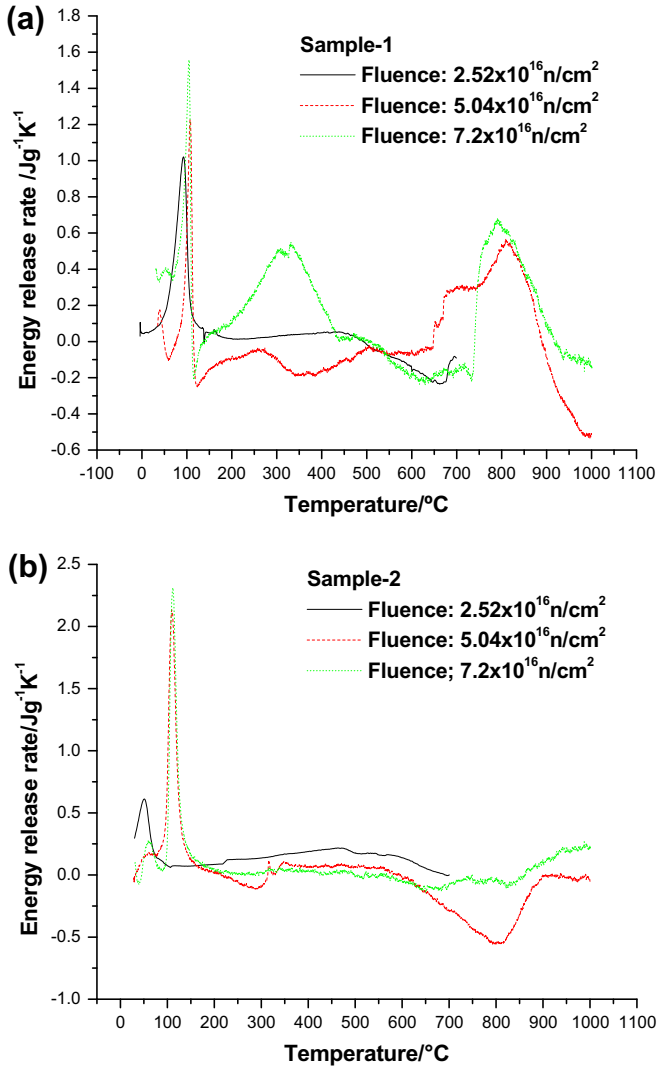

Fig. 4. Stored energy release spectra of carbon/carbon composite at different fluence levels: (a) Sample-1 and (b) Sample-2.

Table 3
Stored energy at different irradiation fluence levels.

Dose (n/cm^2)	Sample-1 stored energy (J/g) (RT-1000 °C)	Sample-2 stored energy (J/g) (RT-1000 °C)
2.52×10^{16}	82.20	100.02
5.04×10^{16}	119	66
7.2×10^{16}	185	51.65

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 crystallite 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 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 graphite 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_G/I_D 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_G/I_D 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

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.

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