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Stored energy release behaviour of disordered carbon

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ABSTRACT The use of graphite as a moderator in a low temperature thermal nuclear reactor is restricted due to accumulation of energy caused by displacement of atoms by neutrons and high energetic particles. Thermal transients may lead to a release of stored energy that may raise the temperature of the fuel clad above the design limit. Disordered carbon is thought to be an alternative choice for this purpose. Two types of disordered carbon composites, namely, CB (made up of 15 wt. % carbon black dispersed in carbonized phenolic resin) and PAN (made up of 20 vol. % chopped polyacrylonitrile carbon fibre dispersed in carbonized phenolic resin matrix) have been irradiated with 145 MeV Ne^{6+} ions at three fluence levels of 1.0×10^{13}, 5.0×10^{13} and 1.5×10^{14} Ne^{6+}/cm^2, respectively. The XRD patterns revealed that both the samples remained disordered even after irradiation. The maximum release of stored energy for CB was 212 J/g and that of PAN was 906 J/g. For CB, the release of stored energy was a first order reaction with activation energy of 2.79 eV and a frequency factor of 3.72×10^{28} per second. 13% of the defects got annealed by heating up to 700 °C. PAN showed a third-order release rate with activation energy of 1.69 eV and a frequency factor of 1.77×10^{14} per second. 56% of the total defects got annealed by heating it up to 700 °C. CB seems to be the better choice than PAN as it showed less energy release with a slower rate.

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1 Introduction

The lowest energy configuration of an assembly of carbon atoms is the perfect graphite crystal. The introduction of crystal lattice defects by means of irradiation of neutron or charged particles increases the energy of the crystal above that of the parent crystal. If the thermal vibration induced by heating the crystal permits rearrangement of these defects to states of lower energy then the stored energy is released as heat. This energy is known as Wigner energy, after the well known physicist who first suggested that it might occur in neutron irradiated materials. In graphite, irradiated at ambient temperature a large amount of energy as much as 2700 J/g can be stored as lattice defects, which if released as heat under adiabatic conditions would raise its temperature by ~ 1500 °C [1].

Stored energy in graphite has two important practical effects. Firstly, the release of stored energy can lead to an increase in temperature, which is enough to cause thermal oxidation of graphite in the presence of an oxidizing atmosphere. Secondly, it reduces the heat capacity of the graphite inside the rector. These combined effects can cause serious accidents. Such an accident happened in Windscale, UK in 1957 [2] due to energy release during annealing of graphite, which caused burning of fuel.

The use of graphite in high temperature nuclear reactors (HTR), Advanced gas cooled reactors (AGR) and Magnox reactors, as moderator is well known [3]. Here the lattice defects are annealed out by high temperature as soon as they are produced. Therefore, energy does not get accumulated and the chance of accident due to sudden release of stored energy is minimized. However, in low temperature thermal nuclear reactors (where the graphite temperature is below 100 °C) the temperature is low enough to restrict the annealing out of defects immediately, and thus the defects concentration goes on increasing with the internal stored energy until it suddenly gets released with thermal activation. Disordered carbon (a-C), with its low ordering range of atomic arrangement, may be an alternative choice to that of graphite to be used as a moderator in low temperature thermal nuclear reactors [4].

While literature is available on the irradiation behaviour [3, 5–7] and stored energy [8, 9] of graphite, there is no information available on the same for disordered carbon. In the present studies two types of disordered carbon prepared indigenously have been irradiated with 145 MeV Ne^{+6} ions. The stored energy release behaviour of these samples have been studied and analyzed.

2 Experimental

Two types of disordered carbon (a-C) composites were prepared for irradiation. The sample 'CB' was prepared with 15 wt. % carbon black dispersed in carbonized phenolic resin. Another sample 'PAN' was prepared using 20 vol. % chopped polyacrylonitrile carbon fibers dispersed in carbonized phenolic resin matrix. Both the samples were heat treated up to 1500 °C in inert atmosphere. The details of preparation of these composites are given elsewhere [10].

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During irradiation, the samples CB and PAN were kept mounted on an aluminum flange and then irradiated with 145 MeV Ne^{6+} ions. The irradiation was carried out under the fluence level of 1.0×10^{13}, 5.0×10^{13} and 1.5×10^{14} Ne^{6+}/cm^2, respectively. During irradiation the flange was cooled by continuous flow of water. The displacement per atom (dpa) was obtained by Monte Carlo simulation technique using the code SRIM 2000 [11].

The irradiated and the original samples were characterized by X-ray diffraction. A Philips PW1710 X-ray diffractometer was used to record X-ray intensities scattered from the examined samples. Cu K_α (wavelength $\lambda = 1.5418$ Å) radiation (40 kV, 40 mA) was used as an X-ray source. Samples were scanned in a step-scan mode (0.02°/step) over the angular range (2θ) of 15° to 70°. X-ray diffraction data were collected for 2.5 s at each step.

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 per minute from 30 °C to 700 °C for all the three levels of irradiation to measure the amount of stored energy at different doses. In order to get the activation energy, the samples were heated at different heating rates (viz. 5, 10, 15 and 20 °C per minute) up to 450 °C.

3   Data analysis

The annealing of point defects caused by irradiation can be expressed in the following form [12]

$$\frac{dN(t)}{dt} = -\upsilon N(t)^\gamma \exp\left(\frac{-E_0}{k_B T}\right) \qquad (1)$$

and $T = at$ [for linear heating rate] ,

where $N(t)$ represents the defect concentration, t the time, T the temperature, k_B the Boltzmann constant, γ the order of reaction, υ the frequency factor, E_0 the activation energy and a the heating rate.
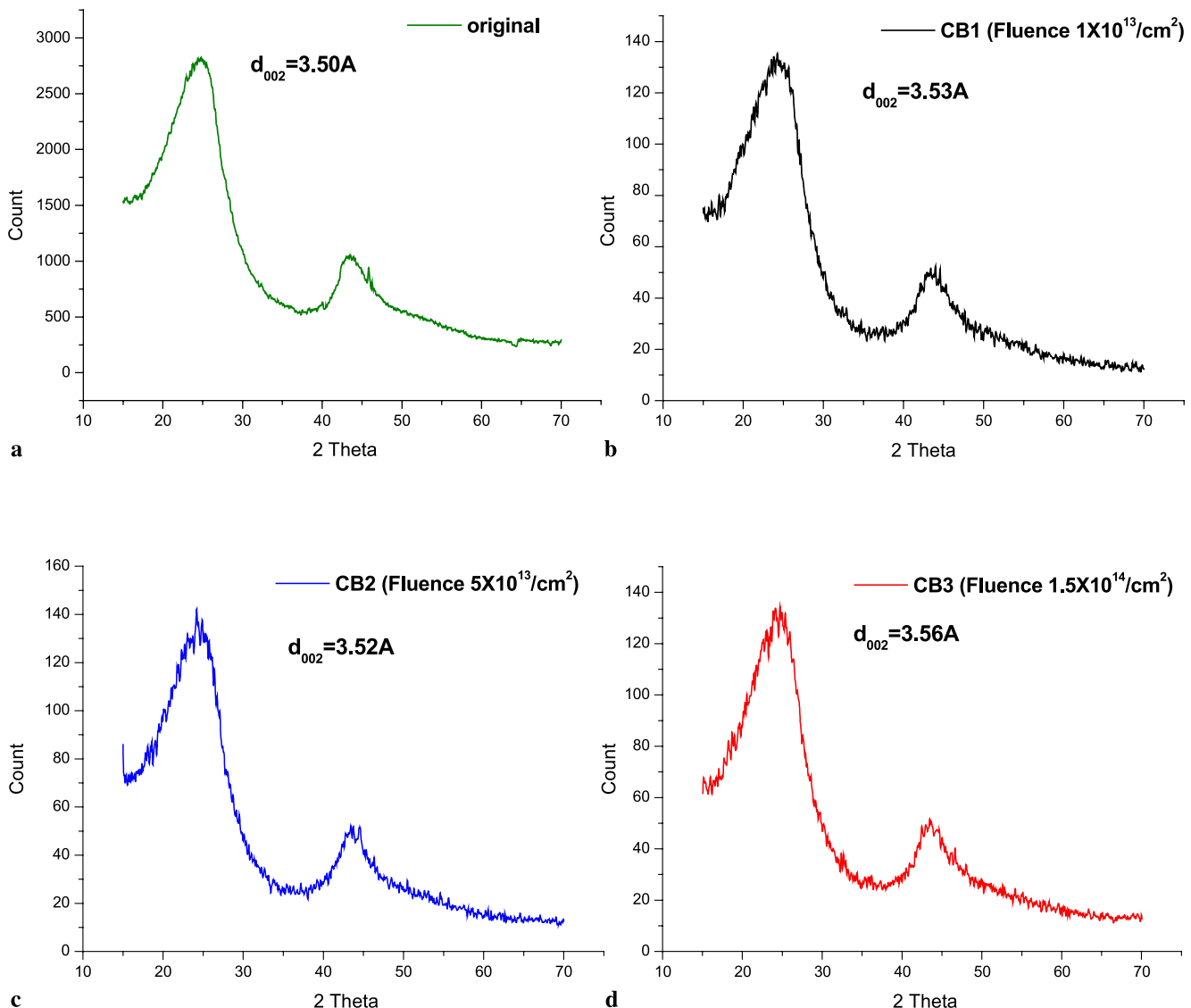

FIGURE 1   (a–d): XRD patterns of CB carbon-carbon composites (unirradiated and irradiated at different fluence levels) with diffused peaks. These patterns confirm that the sample remain disordered even after irradiation

The solution for (1) is

$$N(T) = N_0 \exp\left[-\frac{\upsilon E_0}{ak}F\left(\frac{kT}{E_0}\right)\right] \quad \text{for } \gamma = 1 , \tag{2a}$$

$$N(T) = N_0\left[1 + (\gamma - 1)N_0^{\gamma-1}\frac{\upsilon E_0}{ak}F\left(\frac{kT}{E_0}\right)^{\frac{1}{1-\gamma}}\right] \quad \text{for } \gamma \neq 1 , \tag{2b}$$

where $F(x) = \int\limits_0^x \exp\left(-\frac{1}{y}\right)\mathrm{d}y$ and N_0 is initial defect concentration.

The stored energy release rate $\frac{\mathrm{d}S}{\mathrm{d}T}$ corresponds to annealing rate of point defects $\frac{\mathrm{d}N}{\mathrm{d}T}$.

When the release rate become maximum, then

$$\frac{\mathrm{d}^2 S}{\mathrm{d}T^2} = \frac{\mathrm{d}^2 N}{\mathrm{d}T^2} = 0 .$$

The peak temperature T_m and the heating rate a follow the following relation

$$\frac{a}{T_m^2} = Z \exp\left(-\frac{E_0}{kT_m}\right) , \tag{3}$$

where

$$Z = [\gamma - (\gamma - 1)Q]\frac{k\upsilon}{E_0}N_0^{\gamma-1}$$

$$Q = \frac{1}{x_m^2}\exp\left(\frac{1}{x_m}\right)F(x_m)$$

$$x_m = \frac{kT_m}{E_0} .$$

Equation (3) can be rewritten as
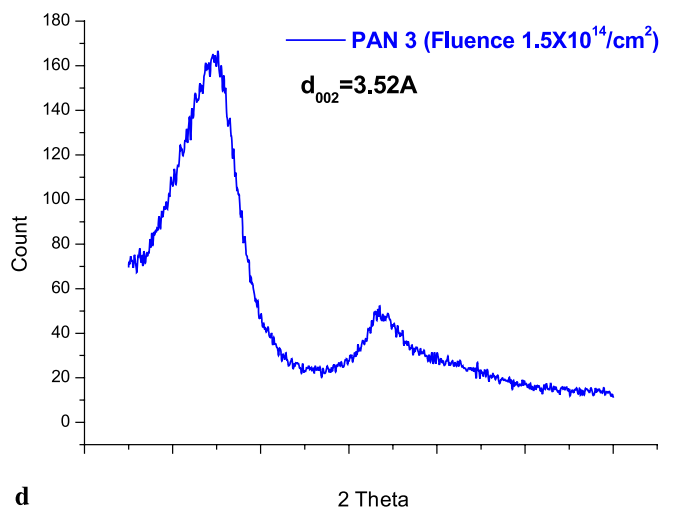
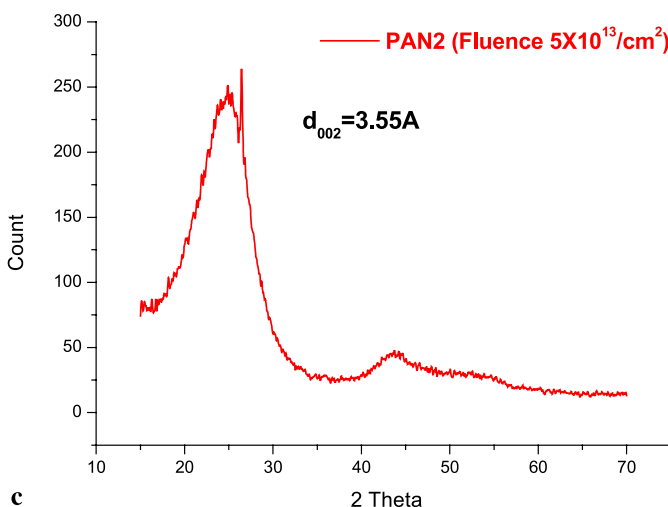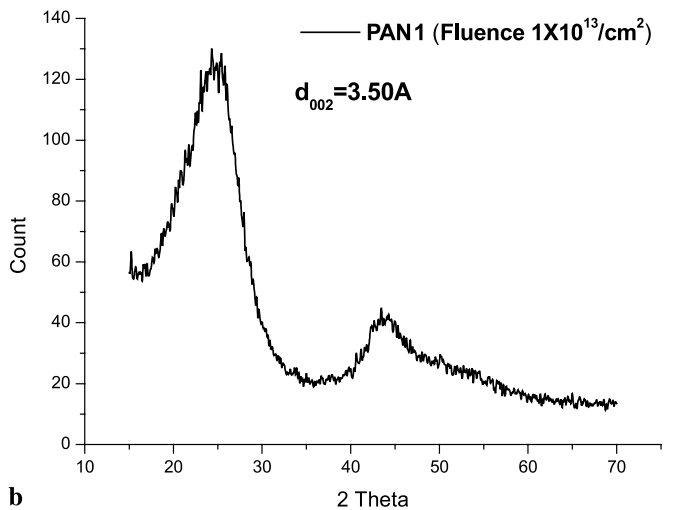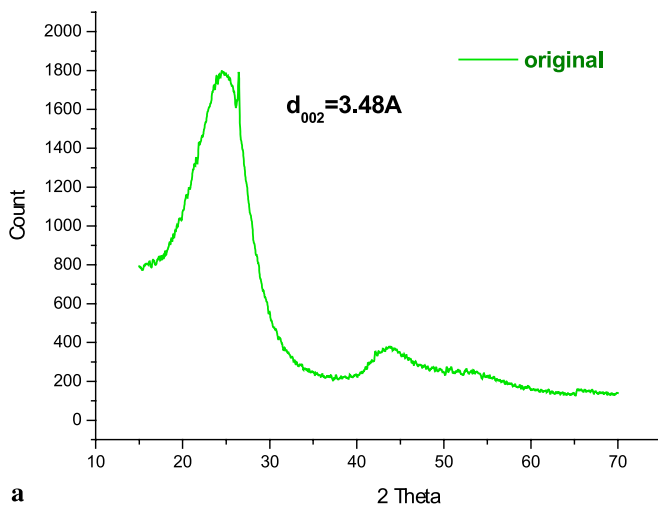$$\ln\frac{a}{T_m^2} = \ln Z - \frac{E_0}{kT_m} . \tag{4}$$

FIGURE 2   (a–d): XRD patterns of PAN carbon-carbon composites (unirradiated and irradiated at different fluence levels). The diffused patterns confirm that the sample remain disordered after irradiation
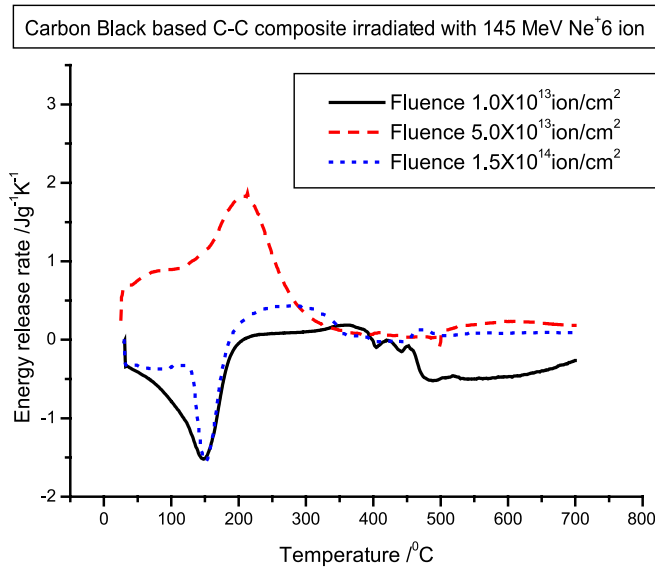
FIGURE 3 Stored energy release spectra of CB composite at different fluence levels. The two peaks around 200 °C and around 400 °C represent the annealing of single and coupled defects respectively
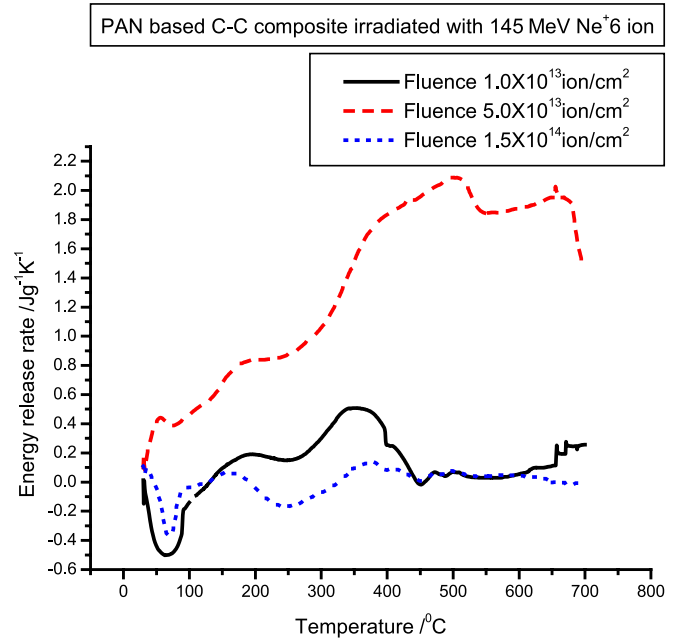

FIGURE 4 Stored energy release spectra of PAN composite at different fluence levels. They show several peaks starting from 100 °C up to 500 °C representing the annealing of defects having different nature

The plot of $\ln \frac{a}{T_m^2}$ against $\frac{1}{T_m}$ gives E_0 and Z from the slope and the intercept respectively. The reasonable determination of γ and υ are made from the value of Z through the following relation

$$\frac{ZE_0}{k} = \upsilon \quad \text{for } \gamma = 1 \,,$$
$$= 1.06\upsilon N_0 \quad \text{for } \gamma = 2 \,,$$
$$= 1.12\upsilon N_0^2 \quad \text{for } \gamma = 3 \,,$$
$$\cdots \quad\quad\quad\quad\quad\quad (5)$$

4   Results and discussions

The X-ray diffraction (XRD) patterns of the original and the irradiated CB samples are shown in Fig. 1a–d and that of the PAN samples are shown in Fig. 2a–d. It is clear from the XRD patterns that both the samples remain in the disordered state even after irradiation. The values for interlayer spacing d_{002} are tabulated in Table 1 for both samples at different fluence levels. A carbon with d_{002} value more than 3.44 Å is called a disordered carbon. The details of the changes in lattice parameters, interlayer spacing and degree of disorderliness with irradiation dose are discussed in [13].

The damage is found to be 0.3×10^{-3} dpa, as calculated from SRIM 2000 [11] for the highest dose (1.5×10^{14} Ne^{6+}/cm^2) of irradiation. Figure 3 shows the stored energy release rate of CB samples with respect to the temperature at different fluence levels. The samples were heated at a constant rate of heating of 5 °C per minute. The area under the curve gives the total energy stored in the sample. From the figures it is understood that at the lowest level of irradiation (i.e., 1×10^{13} Ne^{+6}/cm^2) the amount of energy stored is very less (about 20.5 J/g). With an increase in the irradiation dose to 5×10^{13}/cm^2 the stored energy increased to 212 J/g. The stored energy release rate for the PAN samples is shown in Fig. 4. Table 1 lists the stored energy value of CB and PAN samples at three levels of fluence. Interestingly, the value of stored energy has come down at the highest fluence level (i.e., 1.5×10^{14} Ne^{+6}/cm^2) for both CB and PAN samples.

Neon being a heavy ion transfers sufficient kinetic energy to the primary knock on atoms, which in turn produce displacement cascades. As the primary knock on proceeds through the sample, losing energy in successive collisions, the displacement cross-section increases [14]. This displacement of atoms increased the stored energy in the samples. The stored energy in the samples was measured by the release of energy during heating at constant rate. When the samples were irradiated at lower dose the nature of the defects was simple. Therefore, almost all the defects got annealed during heating up to 700 °C and almost all stored energy came out.

Dose (Ne^{6+}/cm^2)	CB composite		PAN composite	
	d_{002} (Å)	Stored energy (J/g) [30–700 °C]	d_{002} (Å)	Stored energy (J/g) [30–700 °C]
Unirradiated	3.50	–	3.48	–
1.0×10^{13}	3.53	20.58	3.50	99.91
5.0×10^{13}	3.52	212.24	3.55	906.4
1.5×10^{14}	3.56	87.23	3.52	22.52

TABLE 1 Interlayer spacing and stored energy of CB and PAN carbon-carbon composites at different fluence levels

But irradiation at the highest dose might have caused formation of complex defects and all the stored energy could not be released by heating up to 700 °C. Such phenomena were also observed in highly irradiated graphite [15], where the graphite sample was heated to 2000 °C to release all the stored energy.

If the stored energy release curves of CB samples are examined carefully, it is observed that there are two peaks in each curve. The first peak is around 200 °C, which represents the annealing of single point defects. The second peak is around 400 °C, which represents the annealing of complex coupled defects. With an increase in fluence from the first level to the third level, the peaks shifted to the right. This means that the defects become more complex with an increase in fluence and they need higher temperature to anneal. The stored energy release curves for PAN samples are more complex than those of CB samples. This means the nature of defects is more complicated in PAN samples. In addition to 200 °C and 400 °C peaks there are more peaks at lower and higher temperatures.

The released stored energies in the PAN samples are more than that of the CB samples after the first and second level of irradiation. However, it reverses at the third level of irradiation. The d_{002} values of the unirradiated CB and PAN samples reveal that PAN is more ordered than CB. Therefore, PAN is in a lower energy state than CB before irradiation. After first and second levels of irradiation, the change in disorderliness is more in the case of PAN as discussed in [13]. That is why the stored energy is more for PAN sample. In the highest level of irradiation, due to complex defect formation the release of stored energy is lower in PAN sample.

In order to find out the activation energy of the 200 °C peak both CB and PAN samples irradiated at 5×10^{13} Ne^{+6}/cm^2 were heat treated at different heating rates (viz. 5, 10, 15 and 20 °C per minute) up to 450 °C. Figures 5 and 6 show the stored energy release curves at different heating rates for
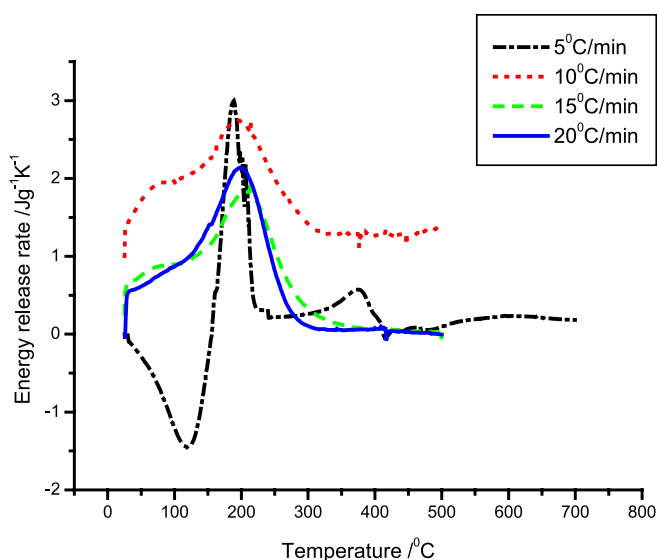

FIGURE 6 Stored energy spectra of PAN composite irradiated at 5×10^{13} Ne^{+6}/cm^2 with different heating rates. From the shift of the 200 °C peak the activation energy and the frequency factor were calculated to be 1.69 eV and 1.77×10^{14} /s respectively
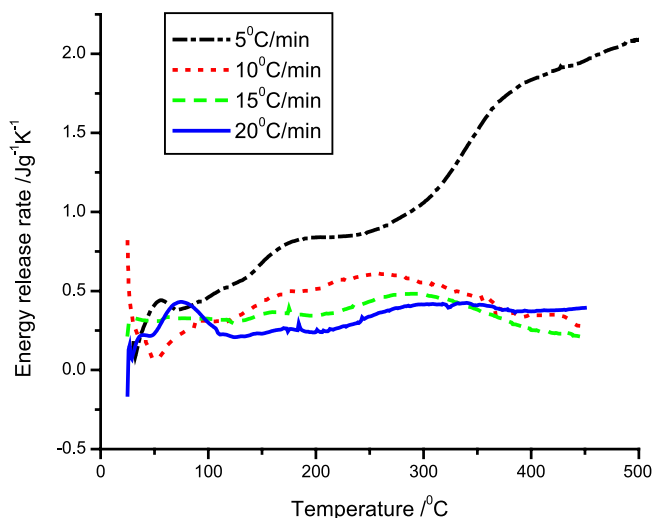
CB and PAN respectively. The activation energy and the frequency factor calculated as per (4) and (5) are listed in Table 2.

The activation energy E_0 for CB was found to be 2.79 eV and the frequency factor υ to be 3.72×10^{28} per second considering first order reaction ($\gamma = 1$). For $\gamma \geq 2$, the frequency factor increases to a value, which is unrealistic. The energy release is caused by the annihilation of interstitials and vacancies. Iwata [16] discussed that for carbon one interstitial C_2 molecule is annihilated by recombination with two vacancies. In this process about 14 eV energy may be released per constituent interstitial atom [17]. In CB sample at fluence level 5×10^{13} Ne^{+6}/cm^2 (calculated dpa = 1×10^{-4}) the amount of released stored energy was 212 J/g. If this stored energy was to release due to annihilation of C_2 interstitial the concentration is found out to be 1.3×10^{-5}, which is 13% of the dpa.

For PAN sample, the activation energy was found to be 1.69 eV. The frequency factor was calculated to be 1.98×10^6 /s for $\gamma = 1$, 1.87×10^{10} /s for $\gamma = 2$ and 1.77×10^{14} /s for $\gamma = 3$. The reaction is not likely to be the first order ($\gamma = 1$) as the value of υ comes out to be very less (1.98×10^6 /s). Most probably it is third order reaction for which the value of υ becomes a realistic one. The concentration of the C_2 interstitial, which was annihilated, was found to be 5.6×10^{-5}, which is 56% of the dpa.

If disordered carbon is to be used as a moderator, the total amount of stored energy is not of great concern. The main concern is how it is released. A slow release rate is favourable. In that respect CB is a better choice than PAN.

FIGURE 5 Stored energy spectra of CB composite irradiated at 5×10^{13} Ne^{+6}/cm^2 with different heating rates. From the shift of the 200 °C peak the activation energy and the frequency factor were calculated to be 2.79 eV and 3.72×10^{28} /s respectively

Sample	Order of reaction (γ)	Frequency factor (υ) s^{-1}	Activation energy (E_0) eV
CB	1	3.72×10^{28}	2.79
PAN	3	1.77×10^{14}	1.69

TABLE 2 Kinetic parameters for stored energy release of CB and PAN composites

5   Conclusion

Two types of disordered carbon composites, namely, CB (made up of 15 wt % carbon black dispersed in carbonized phenolic resin) and PAN (made up of 20 vol. % chopped polyacrylonitrile carbon fibre dispersed in carbonized phenolic resin matrix) have been irradiated with 145 MeV Ne^{6+} ions at three fluence levels of 1.0×10^{13}, 5.0×10^{13} and 1.5×10^{14} Ne^{6+}/cm^2 respectively. The maximum dose corresponds to 0.3×10^{-3} dpa, as calculated from SRIM 2000. The XRD patterns revealed that both the samples remained disordered even after irradiation. The amount of stored energy was more for PAN composite than CB composite. The maximum release of stored energy for CB was 212 J/g and that of PAN was 906 J/g. For CB the release of stored energy was a first order reaction with activation energy of 2.79 eV and a frequency factor of 3.72×10^{28} per second. 13% of the defects got annealed by heating up to 700 °C. PAN showed a third-order release rate with activation energy of 1.69 eV and a frequency factor of 1.77×10^{14} per second. 56% of the total defects got annealed by heating it up to 700 °C. CB seems to be the better choice than PAN as it showed less energy release with a slower rate. However, before these materials are used in the nuclear reactor for practical purpose, they need to be irradiated with neutrons in a material test reactor.

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