A New Microscopic Model of Electron Irradiation Damage in Graphite

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Abstract

A new model concerning damage processes in electron-irradiated graphite is proposed based on the experimental results from in situ observation of high resolution transmission electron microscopy (HRTEM), transmission electron diffraction (TED), and extended energy loss fine structure (EXELFS). The model states that electron irradiation damage of graphite proceeds in the following manner: the original crystal lattice is fragmented into pieces of a few nanometers in size with random crystallite orientations, with a relatively coherent layer structure maintained. Within the basal plane of individual crystallites, non 6-fold atomic rings are locally formed, which gives rise to local buckling of the basal planes, though the overall layer structure is unaltered due to π-bonding still being present. The slight change of electronic structure associated with formation of non 6-fold atomic rings may be the origin of homogeneous dilation of the c-axis. In the boundary regions between the randomly oriented fragmented crystallites, non sp^2 bonds are almost certainly formed with the most likely candidates being single and double sp^3 bonds.

1. Introduction

Radiation damage of carbon materials has long been studied, especially from the practical point of view, because those have been the most important candidates for plasma facing materials in fusion reactors [1-3]. Carbon materials for such applications usually consists of a mixture or composite with various structures and constituent elements, often resulting in properties varying from sample to sample depending on the manufacturing process.

Irradiation damage of graphite from the fundamental point of view has been previously studied and interpreted in terms of the conventional concept of crystal defects such as vacancies, interstitials, and their clusters [4-8]. However, it might be argued that changes in physical and chemical properties with irradiation, such as irradiation-induced hardening, reduction of thermal conductivity, and cleavage resistance are still not fully understood. We have previously demonstrated that both local and average structural changes in electron-irradiated graphite cannot be explained through the formation and accumulation of conventional defect clusters [9], but instead suggested the formation of chemical bonds different from the original sp^2 bonds between carbon atoms[10]. The fundamental understanding of damaging processes in carbon crystals (i.e., graphite and diamond) is now open to further investigation, not only due to the recent developments in theoretical and analytical techniques concerning nanoscale regions, but also as the result of the discovery of fullerene related materials which has thrown a new light onto the study of carbon materials.

In this paper we propose an alternative model for the damage process in electron irradiated crystalline graphite, based on initial experimental results obtained concerning structural changes associated with irradiation.

2. Experimental

The primary investigation tool was that of transmission electron microscopy (TEM) together with its associated techniques, including high resolution transmission electron microscopy (HRTEM), transmission electron diffraction (TED), and electron energy 1=1 loss spectroscopy (EELS), with experimental details presented elsewhere[11, 12].

The samples used in the present study were highly graphitized carbon fiber (HGCF) and highly oriented pyrolytic graphite (HOPG). The former was used for HRTEM observations as the stacking of basal planes (c-planes) could be observed without significant sample preparation, whilst observations normal to the graphite basal planes utilized the latter. All the observations were carried out at an accelerating voltage of 200 kV.

3. Experimental Results

In Fig.1 is shown high resolution micrographs of HGCF in the original state(a) and after the electron-irradiation for 30 minutes(b). Insets are the corresponding diffraction patterns. With increasing the irradiation time the original crystal lattice was fragmented into small pieces with each crystallite locally buckled. Certain stacking ordering in the c-direction seems to be still maintained, which is also supported by the corresponding diffraction patterns where the 002 type reflections were quite well defined. In addition, the distance between the origin and the 002 reflection was decreased up to 11% with the irradiation, indicating that the interplanar distance between the basal planes was homogeneously elongated. It should be mentioned here that there is no obvious indication of the formation of interstitial type dislocation loops. The visibility of such dislocation loops is intensively discussed elsewhere[11].

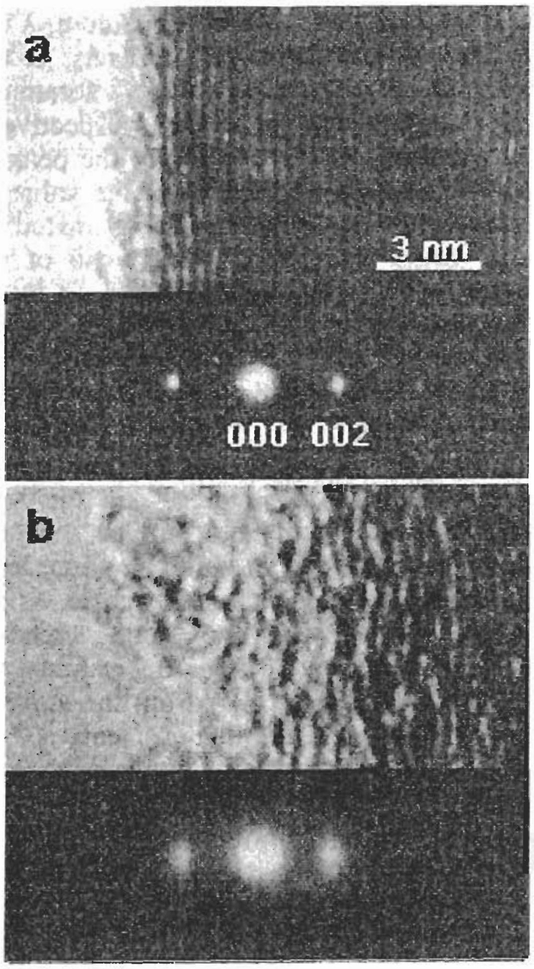

Fig. 1 HRTEM images of HGCF and their corresponding diffraction patterns: (a) as received and (b) following electron-irradiation for 30 minutes.

In order to trace a structural change accompanied by the irradiation within a basal plane, we investigated the change in the radial distribution function (RDF) of electron irradiated HOPG by the analysis of an extended energy 1=1 loss fine structure (EXELFS). EXELFS is a weak intensity oscillation appearing on the smoothly decaying tail of a core loss spectrum about 50 eV larger loss regions from the absorption edge [13]. The origin of EXELFS is the same as extended X-ray absorption fine structure (EXAFS) and the RDF around absorbate atoms can be deduced from the Fourier transform of the spectrum oscillation [14].

The extracted intensity oscillations on the K-edge spectra electron-irradiated by 0, 0.5 and 1 dpa are shown in Fig.2. This was done first by subtracting the background from the original

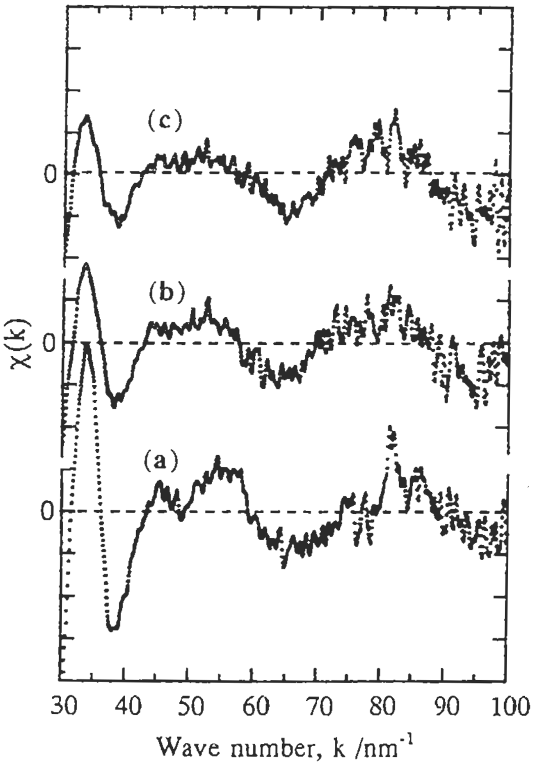

Fig. 2 Interference functions, $\chi(k)$, extracted from the K-edge of original EELS spectra for HOPG samples. (a) as received, (b) following 0.5 dpa irradiation, and (c) following 1 dpa irradiation.

spectra, followed by normalizing the isolated K-edge spectra by a smoothly decaying fitting function[12]. These functions are called as an interference function, χ(k). The RDF is obtained by the Fourier transform of the χ(k).

The change in the RDF with the irradiation, calculated from Fig.2, is shown in Fig.3. The incident electron was nearly parallel to the c-axis and the corresponding electron diffraction at each stage is inset. In this figure no correction for the phase shift was conducted and hence the relative change of interatomic distances should be noted.

Characteristic features depicted from the figure can be summarized in the following: (i)even though the diffraction pattern turns to complete halo, the RDF still shows distinct peaks up to the fourth neighbor shell, which is unusual for disordered (amorphous) structures. (ii)The peak positions of the first and second neighbor shells remain almost unchanged, whereas that of the third shell is shortened. These three atomic shells are considered to correspond to atomic pairs within a basal plane. (iii)The fourth peak which is considered as an interatomic distance of neighboring basal planes shifts to the longer distance side with the irradiation. (iv)The full width at the half maximum (FWHM) of the first peak is slightly increased by the irradiation.

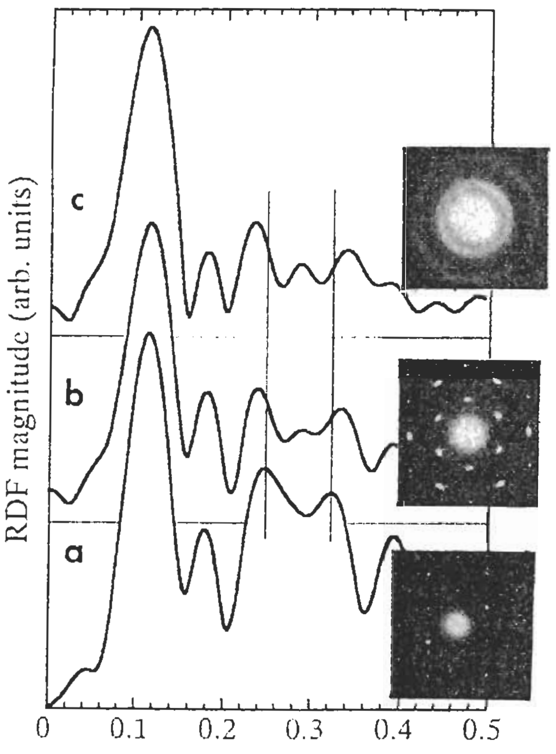

Fig. 3 Change in radial distribution functions (RDFs) for electron-irradiated HOPG together with their corresponding electron diffraction patterns: (a) as received, (b) following 0.5 dpa, and (c) 1 dpa irradiation. Note that no correction was made for the phase shift.

In order to estimate the standard structural parameters such as the coordination number and the mean square displacement from the RDFs, we first extracted the first peak in each RDF by a smooth window function, followed by the inverse Fourier transform. The resulting curve, the interference function, χ(k), includes only the information of the first peak in the RDF. This is expressed by the following equation [13, 14]:

$$\chi(k) = \frac{N}{r^2}\frac{f(k)}{k}\exp(-2r/\lambda)\exp(-2\sigma^2k^2) \sin[2kr+\phi(k)] \qquad (1)$$

where N is the coordination number, r the interatomic distance, $f(k)$ the form factor for electron scattering by the scattering atom, λ the mean free path of scattered electrons, σ the mean square displacement of the interatomic distance, and ϕ(k) the phase shift, respectively. By the equation (1) the FWHM of the peak in the RDF is directly derived from the value σ. The relative change of σ can be estimated by plotting natural logarithm of the ratio of the amplitude terms of the right hand side in eq.(1) as a function of k^2 [14]:

$$\ln\frac{A_u}{A_s} = \ln\left(\frac{N_u}{N_s}\frac{r_s^2}{r_u^2}\right) + 2(\sigma_s^2 - \sigma_u^2)k^2 \qquad (2)$$

The subscripts u and s are referred to an unknown structure of interest and the well known standard structure similar to the unknown, respectively. In studying disordered structures the standard is usually taken as the crystalline phase with the same elements. According to the eq.(2) one can evaluate the change of σ, $\Delta\sigma^2$ ($=\sigma_u^2-\sigma_s^2$) from the slope of the linear curve and the relative change of the coordination number from the intersect with the ordinate.

The results of plot (2) are shown in Fig.4 for the both cases of 0.5 and 1 dpa irradiation. As seen in the figure the slope of the curve is increased with the irradiation. This means σ is decreased with the irradiation. The estimated $\Delta\sigma^2$ is -5.4 x 10^{-5} nm^2 and -6.5 x 10^{-5} nm^2 for the cases of 0.5 and 1 dpa irradiation, respectively. These magnitudes are comparable

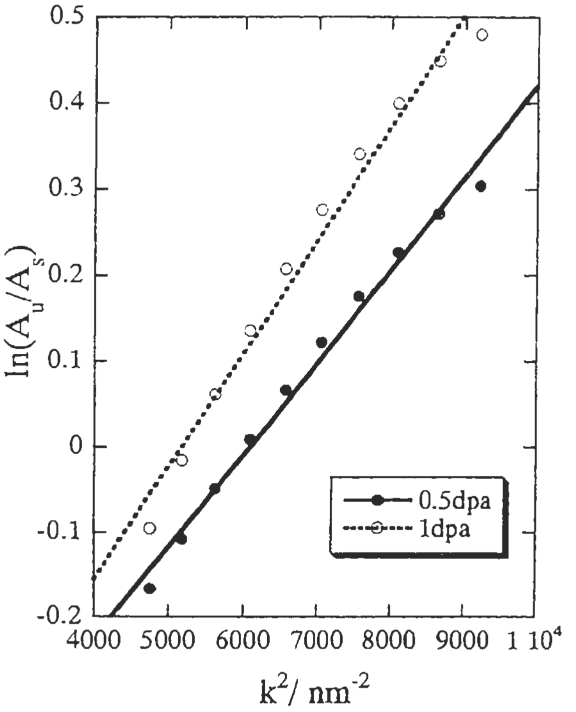

Fig. 4 Plot of $ln(A_u/A_s)$ vs. k^2 for (a) 0.5 dpa and (b) 1 dpa irradiation. Note the A_s was taken to be the amplitude for unirradiated graphite.

with those caused by thermal vibrations (Debye-Waller factor). This indicates that the fluctuation of the first neighbor distance is reduced by the structural disordering, though the FWHM of the first peak in the RDF is increased. We cannot but consider that this contradiction is originated from the extracted interference functions including more than one component. Thus the broadening of the first peak in the RDF is most likely caused by the superposition of multiple peaks with slightly different interatomic distances and σ. The new component produced by the irradiation must have a smaller σ than that of the original sp^2 bonding.

4. Discussion

From the experimental results obtained above we depict a picture on what is going on in the electron-irradiated graphite by the results (i)-(iv), summarized in the previous section, obtained from the change in the RDF with the irradiation: the result (i) suggests that a short range order within a basal plane still remains over the dimension of a few nanometers, estimated from the lateral coherent length of electron microscopy. This size well corresponds to the dimension of the fragmented crystallites observed HRTEM as in Fig.1(b). If those small crystallites are randomly distributed in orientation perpendicular to the average basal plane normal, the diffraction pattern in the c-direction can give rise to a halo pattern.

The result (ii) can be explained by a local buckling of the basal planes of each crystallites without altering the overall honeycomb network. Such local bending does not alter the first neighbor distance but affect the higher order neighbor distances within the basal plane. This can be realized by the formation of non-sixfold atom rings, as shown in Fig.5, which does not significantly alter the original chemical bonding but can cause a local buckle of a basal plane, as actually manifested in fullerenes. This idea has been already presented by Koike and Pedraza [15] and consistent with the fact that the layer structure is rather maintained within each fragmented crystallites because the sp^2 bonding basically remains unchanged. Furthermore, the slight change of the electronic structure due to the formation of non 6-fold atom rings could alter the magnitude of the van der Waals force between the basal planes and give rise to the uniform dilation of interplanar spacing between the basal planes, as observed in Fig.1. Finally, (iii) just indicates the homogeneous dilation of interplanar distance between basal planes, which is consistent with the result obtained by HRTEM above.

Let us consider the boundary regions across the

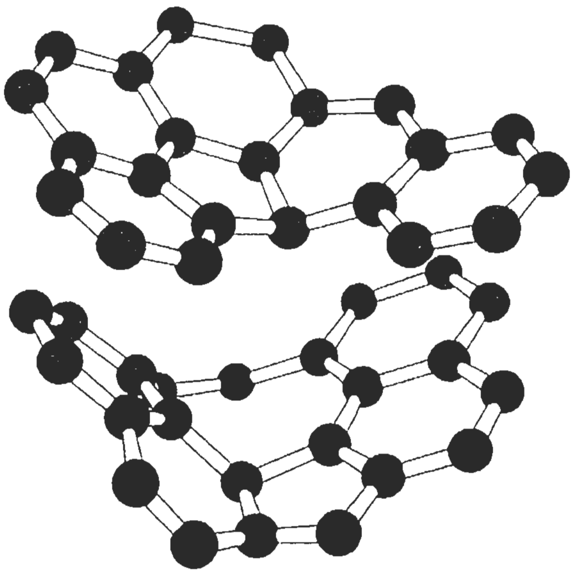

Fig. 5 Schematic representation illustrating the buckling of basal planes due to the formation of non 6-fold atomic rings. The model has been constructed so as to minimize the energy associated with local changes in bond length and angle.

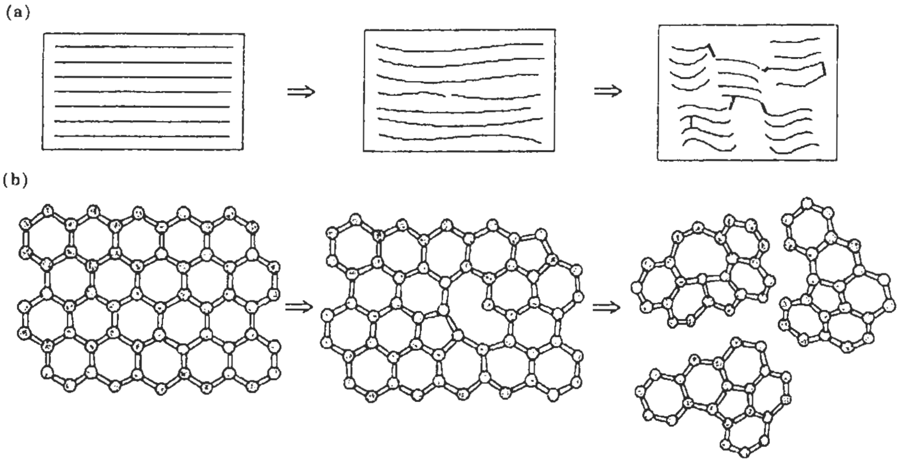

Fig. 6 Schematic drawing of damage processes in graphite due to the electron irradiation: (a)Viewed parallel to and (b) normal to the basal planes. Note that the solid lines represent basal planes whereas thick solid lines indicate bridging between the basal planes of fragmented crystallites, possibly due to sp^3 type bonds.

fragmented crystallites, concerning (iv). In these regions the structure is considered more likely to glassy carbon or amorphous carbon whose building units consist mainly of sp^2 bonding. It has been known that graphite crystals irradiated by electron, neutron and other energetic particles are significantly hardened [6], and some three dimensional structure must be formed by bridging between basal planes, which can act as a resistance for cleavage and raise the material hardness. These facts strongly suggest that the transition of chemical bonding from sp^2 to sp^3 is considered to take place. There have been several reports showing that the spectroscopic signature of sp^2 bonding in graphite is reduced with the irradiation [16, 17], and the extra components presently observed in the RDF are also presumably derived from the formation of sp^3 bonding. The damaging procedure discussed above is schematically drawn in Fig.6. This last part of discussion is rather speculative and further experiments to prove the proposal are in progress.

5. Conclusions

We have conducted HRTEM, TED and EXELFS to investigate structural changes in graphite due to high energy electron irradiation. The present results suggest the damage procedure to be dominated by fragmentation into small crystallites of a few nanometers in size, rather than the previously held view of the formation and accumulation of point defects. The orientation of fragmented crystallites was randomized following irradiation, though the layer structure normal to the basal planes was retained within individual crystallites. The formation and recovery of conventional point defects would contribute to the creation of non 6-fold atomic rings, which gives rise to local buckling of basal planes without altering the overall layer structure within crystallites. The boundary regions connecting fragmented crystallites were considered to act as resistance to mechanical deformation, with a bridge between basal planes formed by transition from sp^2 to sp^3 bonding.

Acknowledgments

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