ELSEVIER

Journal of Nuclear Materials 283–287 (2000) 917–921

journal of nuclear materials

www.elsevier.nl/locate/jnucmat

Temperature effect of electron-irradiation-induced structural modification in graphite

Shunsuke Muto *, Tetsuo Tanabe

Center for Integrated Research in Science and Engineering, Nagoya University, Chikusa-ku, Nagoya 464-8603, Japan

Abstract

The structural change of graphite under high-energy electron irradiation at a wide range of temperatures was investigated by means of conventional transmission electron microscopy (CTEM), transmission electron diffraction (TED), high-resolution transmission electron microscopy (HRTEM) and electron energy-loss spectroscopy (EELS). The experimentally observed result at lower temperatures (<600 K) could be basically interpreted by the local formation of non-hexagonal atomic rings (loss of the local hexagonal symmetry) in the graphite planes associated with the change in chemical bonding states. At higher temperatures (>650 K), a graphite single crystal was polycrystallized into nano-size crystallites with the original hexagonal network locally retained within each crystallite. The apparent activation energy derived from the present data over the whole temperature range was estimated to be 0.014 eV, which is in agreement with a reported migration energy of a self-interstitial atom between the basal planes. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The present authors' group has recently re-examined the damaging process of graphite with electron-irradiation by means of transmission electron microscopy (TEM) and associated analytical techniques [1–6]. Conventional studies on this subject have treated the observed phenomena as fragmentation and amorphization, in which the underlying structure of disordered regions has not been fully clarified. Several attempts to imagine the damaged structure have been reported, taking the issues specific to materials having covalent bonding and high crystallographic anisotropy into consideration [7–9].

Our new observation [2–5] has strongly suggested that the damaging process was not mere amorphization but the structural changes, such as fragmentation and curling of the basal planes which accompanies a transition of chemical bonding from sp^2 to $sp^{2+\alpha}$ ($0 < \alpha \leqslant 1$) hybridization, an intermediate state between sp^2 and sp^3 resonance bonding. This can be closely connected to a recent finding that the surface of graphite thin foils or carbon nano-tubes transform to closed carbon cages by high-energy electron illumination [10]. The transformation is brought mainly through the displacement damages by high-energy particle irradiation and their reconstruction by a self-organization process [5,6].

In the present report, the structural changes in electron-irradiated graphite at elevated temperatures are described in comparison with the previous results at room temperature. The origin of the observed structural change is discussed by a simple kinetic theory. Preliminary experimental results of conventional TEM (CTEM), energy-loss near edge fine structure (ELNES) and in situ high resolution TEM (HRTEM) at elevated temperatures [11,12] and at lower temperatures [5] are described elsewhere.

2. Experimental

Samples used here were cleaved kish graphite thin foils with fine crystallinity. The sample preparation was described in detail elsewhere [2].

---

* Corresponding author. Tel.: +81-52 789 5200; fax: +81-52 789 5158.

E-mail address: muto@cirse.nagoya-u.ac.jp (S. Muto).

0022-3115/00/$ - see front matter © 2000 Elsevier Science B.V. All rights reserved.
PII: S0022-3115(00)00117-3

The electron irradiation and conventional TEM (CTEM) observations were carried out over the temperature range of 90–680 K in a Jeol-JEM200CX microscope, operated at 200 kV with the electron flux of $\sim 1.8 \times 10^{20}$ cm^{-2} s^{-1}. After the electron irradiation ELNES of carbon K-edge was examined at room temperature in an analytical electron microscope (Philips CM200) equipped with a parallel EELS spectrometer in the National Center for Electron Microscopy (NCEM) at Lawrence Berkeley Laboratory (LBL). This instrument was used also for high-resolution observation at the spots pre-irradiated at 680 K.

3. Results

3.1. Temperature dependence of the changes in electron diffraction pattern

The original single crystal structure of graphite was fragmented into nano-pieces by the irradiation, each portion of which was gradually rotated about the basal plane normal. The [0 0 0 1] electron diffraction pattern turned to diffuse halo rings by the irradiation below 600 K, whereas to sharp Debye–Scherrer rings above 650 K. The ELNES of the C K-absorption edge did not appreciably change with the irradiation above 650 K, in contrast with the case below 600 K, where the specific broad spectral feature commonly seen in higher order fullerenes appeared [4,11,12]. These suggest that below 600 K, the structural change of graphite under high-energy electron irradiation proceeds by competition between the damage production and self-restoring through the rotation of crystallites about the basal plane normal and formation of non-hexagonal atomic rings [2–4,6]. On the other hand, above 650 K the structural change is characterized by mere fragmentation and rotation of the crystallites with the hexagonal atomic rings strictly maintained within the crystallites. After very long irradiation, another Debye-ring intensity, corresponding to the (0 0 0 2) planes, appeared. This indicates that the graphitic sheets are highly curled, as also shown in the HRTEM image (Fig. 2(b)). The interplanar spacing between the basal planes estimated from this diffraction pattern was 0.346 ± 0.05 nm and remained nearly unchanged, compared to the value before irradiation.

The critical doses, D_c, necessary for the transformation from the [0 0 0 1] diffraction pattern to the closed halo or Debye–Scherrer rings are plotted as a function of irradiation temperature in Fig. 1. This curve seems to consist of two straight lines, suggesting two types of competing phenomena, as so far reported [13]. Apparent activation energy for each line was estimated to be 0.31 and 0.016 eV. A very sophisticated consideration based on kinetic equations has attributed this feature to di-interstitials, which start mobile around 500 K [13]. The theoretical model, however, does not take the damaged structure specific for covalent bonding materials with large anisotropy into account but apply the concepts same as those valid for metals. It is still doubtful whether the concepts of interstitial, vacancy and its clusters hold for graphite in the same manner as metals because, for example, unsaturated chemical bonds will be reconstructed, as we have shown in [2–4]. This point is discussed in a later section.

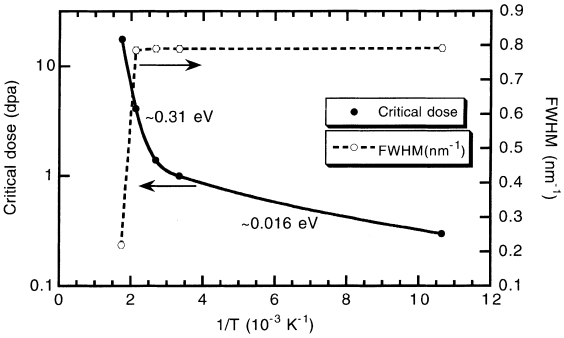

Fig. 1. The critical dose, D_c, necessary for the transformation of the (0 0 0 1) diffraction pattern to the closed halo or Debye–Scherrer rings as a function of inverse of irradiation temperature. The full width at half maximum (FWHM) of the intensity profile of the first ring is also presented for each stage.

The change in the full width at half maximum (FWHM) of the intensity profile of the first halo or Debye–Scherrer ring is also presented in Fig. 1. The FWHM of the halo ring ($T < 600$ K) exhibits no temperature dependence, which indicates that the size of fragmented crystallites is nearly constant irrespective of irradiation temperature. The approximate unit sizes of the crystallites were also estimated from the inverse of the FWHMs to be ~1 nm for the halo rings and ~5 nm for the Debye-rings.

3.2. HRTEM observation along the [0 0 0 1] axis

HRTEM images of the sample after the irradiation at 680 K for 4 and 8 h are, respectively, shown in Figs. 2(a) and (b) together with fast Fourier transform (FFT) power spectra of the respective HREM images in (c) and (d). As seen in the images (a) and (c), the resultant structure is constructed by polycrystals, each rotated about the basal plane normal with locally well-arranged lattice fringes. The patchy contrasts and disturbed lattice fringes are dispersed among the well-defined hexagonal patterns and the approximate size of a unit crystallite is estimated to be ~1 nm. Assuming that the disturbed contrasts are superposition of fragmented graphite crystallites having several different orientations, a computer image simulation was carried out, which quite well

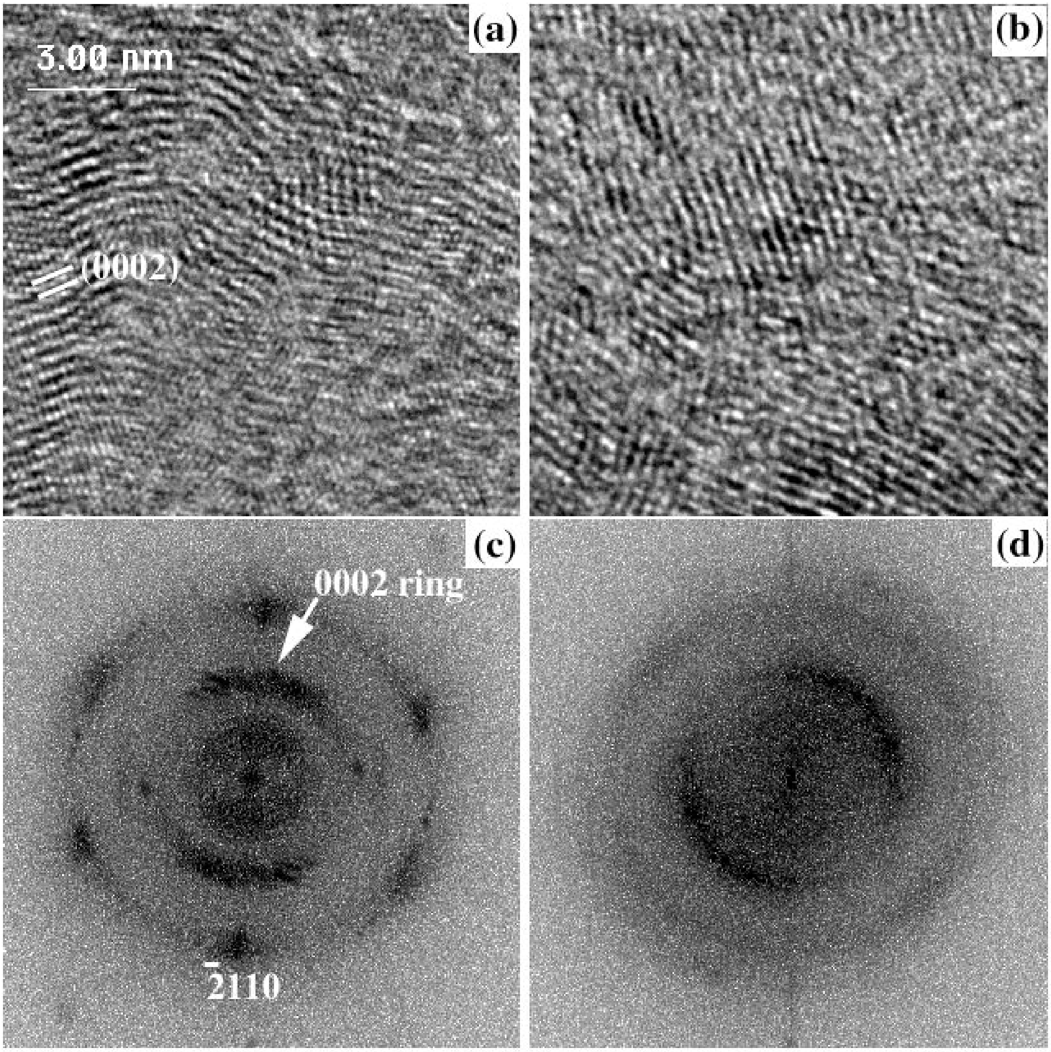

Fig. 2. HRTEM images of electron-irradiated graphite viewed along the original *c*-axis direction at 680 K for 4 h (a) and 8 h (b). Fourier transformed power spectra of (a) and (b) are shown in (c) and (d), respectively.

reproduces the image [12]. At the upper left corner of the image (a), curled lattice fringes with larger spacing are observed. These are corresponding to the (0 0 0 2) lattice planes. The other lattice fringes across the (0 0 0 2) lattice fringes in these areas are continuously connected or making an angle of ~30° to the one of three sets of ($\bar{2}$ 1 1 0) lattice fringes. These orientation relationships between the curled (0 0 0 2) and ($\bar{2}$ 1 1 0) fringes indicate that the graphitic sheets are bent or curled along 'zigzag lines' and 'arm-chair lines', which is similar to the ion-irradiation-induced surface ridge structure, as reported previously by the present authors' group [14]. These highly distorted regions also maintain the original intra- and inter-plane structural correlations and coherency with the matrix.

Prolonged irradiation revealed remarkable image features. As shown in Figs. 2(b) and (d), the structure can be characterized by the randomly oriented lattice fringes. Since the radii of the rings in the FFT power spectra of (c) and (d) are almost unchanged, the graphite crystal structure is considered to be still maintained locally within a certain volume at this stage.

4. Discussion

It should be mentioned that the interplanar spacing between the basal planes was gradually widened by increasing the irradiation time in the RT irradiation, whereas it was unaltered in the 680 K irradiation [1,11].

This could be caused by the slight change in the electronic structure and the interplanar spacing increased accordingly. The lattice dilation is saturated at ~11% corresponding to ~1 dpa irradiation. This suggests that there is an upper limit in the possible amount of non-hexagonal atomic rings formed within a fragmented crystallite. After reaching this limit, the apparent structure does not change by further irradiation, though the bond breaking and reconstruction would dynamically occur. In this regime, the density of the material is decreased [2] because a part of displaced atoms will escape away.

A simple kinetic theory leads to a relation for the fraction of the disordered region, f_a, as a function of irradiation temperature, T [15]:

$$f_a = 1 - \exp\left[-\phi\sigma t + \left(\frac{t}{\tau}\right)\exp\left(-\frac{E_a}{kT}\right)\right]. \tag{1}$$

The first term in the square bracket represents the production rate of displacement damage, where ϕ denotes the electron flux and σ the cross-section of elastic collision. The second term is temperature-dependent damage recovery rate with a characteristic time τ and activation energy E_a. If one assumes that the continuous ring formation of halo or Debye–Scherrer rings is achieved by the same damage level, f_a^0, as defined by the time t_0, Eq. (1) can be expressed as

$$\frac{C}{t_0} = -\phi\sigma + \left(\frac{1}{\tau}\right)\exp\left(-\frac{E_a}{kT}\right), \tag{2}$$

where C is a negative constant, corresponding to $\ln(1 - f_a^0)$. Since the electron flux is a constant, the critical dose, D_c, is proportional to t_0 and finally the relation between D_c and the temperature can be given as

$$\frac{1}{D_c} \propto \phi\sigma - \frac{1}{\tau}\exp\left(-\frac{E_a}{kT}\right). \tag{3}$$

The experimental results fit well with the relation, Eq. (3), for the whole temperature range irrespective of halo or Debye ring formation, as shown in Fig. 3. It gives $E_a = 0.014$ eV, which is consistent with the migration energy of self-interstitial carbon atoms in the basal planes, $E_a = 0.016$ eV, theoretically estimated by Iwata et al. [16]. Therefore, the orientational and structural disordering of graphite by electron irradiation would be controlled by the mobility of interstitial atoms produced by displacement damage.

On the other hand, the characteristic time for damage recovery, τ, was estimated to be ~210 s with $\phi = 1.8 \times 10^{20}$ cm^{-2} s^{-1} and $\sigma = 20 \times 10^{-24}$ cm^{-2} [17] at the present experimental conditions. The recovery in this case should correspond to the orientational ordering of small crystallites fragmented by the displacement damage. The very large value of τ indicates that the recovery process is very slow because it involves dynamical processes of the large structural units, presumably trying to find a more stable reconstruction of broken bonds between the fragmented crystallites.

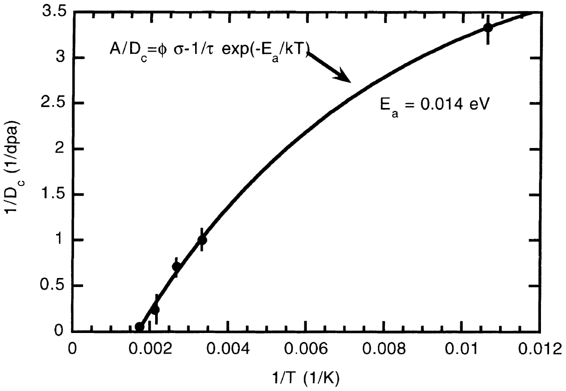

Fig. 3. Replot of Fig. 1 as $1/D_c$ vs $1/T$. The solid curve is the best fit result according to the equation inset.

The reconstruction *within* the crystallites which involves the formation of non-hexagonal atomic rings at lower temperature could have apparent activation energy much larger than 0.014 eV, instead of the longer characteristic time for recovery involved, which makes the term from this process negligible in Eq. (3). This could be a reason why the data points in Fig. 3 fit well with the single equation. The data points are not available here between room temperature and 94 K in Figs. 1 and 3. These lacking data points may give an alternative expression or additional term to Eq. (3) because the term with larger activation energy will be manifested at a lower temperature range. It is hence necessary to bridge the wide gap for further discussion.

The structural changes observed in the present study are not recovered by post-annealing at temperatures lower than 800 K. Hence the structural changes presented here give no explanation for the origin of the unusual energy release around 600 K, which is known as the Wigner energy [18]. The analysis presented here might be too simplified, though we would like to show an alternative interpretation for the phenomenon other than the sophisticated one in [14] and further investigation is still needed to fully understand the damaging process of this material.

5. Summary and conclusions

Amorphization of electron-irradiated graphite has been well characterized so far by X-ray diffraction and TEM as fragmentation and rotation of the crystal, though the underlying structure of disordered regions or each fragmented crystallite has not been clarified. A series of our studies give an answer for the question:

what is the two-dimensional disordered structure under the constraint condition that the bond length between atoms remains almost unaltered. As a conclusion slight variation of bond lengths associated with the local formation of non-hexagonal atomic rings at lower temperatures is necessary to give a diffuse halo pattern in electron diffraction and this inevitably induces the fragmentation and curling of the basal planes. The long-range disordering should proceed only by polycrystallization through orientational disordering about the plane normal without the transition of bond lengths and three-dimensional distortions. These two modes at different scales of disordering process correspond, respectively, to the irradiation-induced structural changes at RT and 680 K. The two modes depend only on the recovery rate characterized by one parameter, E_a, which may be connected to the migration energy of self-interstitial atoms within the basal plane.

Acknowledgements

This work is partly supported by Grant-in-Aid from the Ministry of Education, Science, Sports and Culture (Tokutei-Kenkyu(A)(2), 1998, Grant No. 10136220). The authors thank Messrs C. Echer and C. Nelson of NCEM for their cooperation in the EELS measurements and HREM observation.

References

[1] S. Muto, T. Tanabe, Philos. Mag. A 76 (1997) 679.
[2] M. Takeuchi, S. Muto, T. Tanabe, S. Arai, T. Kuroyanagi, Philos. Mag. A 76 (1997) 691.
[3] S. Muto, M. Takeuchi, T. Tanabe, J. Surf. Anal. 3 (1997) 420.
[4] S. Muto, M. Takeuchi, T. Tanabe, H. Kurata, K. Hojou, Jpn. J. Appl. Phys. 38 (1999) 1514.
[5] M. Takeuchi, S. Muto, T. Tanabe, H. Kurata, K. Hojou, J. Nucl. Mater. 271&272 (1999) 280.
[6] S. Muto, S. Horiuchi, T. Tanabe, J. Electron Microsc. 48 (1999) 767.
[7] B.T. Kelly, Physics in Graphite, Applied Science Publishers, Barking, 1981, p. 405.
[8] T. Iwata, J. Nucl. Mater. 133&134 (1985) 361.
[9] J. Koike, D.F. Pedraza, J. Mater. Res. 9 (1994) 1899.
[10] D. Ugarte, Nature 359 (1992) 707.
[11] S. Muto, T. Tanabe, J. Electron Microscopy 48 (1999) 519.
[12] S. Muto, T. Tanabe, in: Proceedings of the International Conference on Solid–Solid Phase Transformations, PTM'99, Kyoto, 1999, p. 785.
[13] K. Niwase, Phys. Rev. B 52 (1995) 15785.
[14] S. Muto, T. Tanabe, M. Takeuchi, Y. Kobayashi, S. Furuno, K. Hojou, J. Nucl. Mater. 271&272 (1999) 285.
[15] W.J. Weber, L.M. Wang, Nucl. Instrum. and Meth. B 91 (1994) 63.
[16] T. Iwata, F.E. Fujita, H. Suzuki, J. Phys. Soc. Jpn. 16 (1961) 197.
[17] W.A. McKinley, H. Feshbach, Phys. Rev. 74 (1948) 1759.
[18] L. Binkele, J. Non-Equilibr. Thermodyn. 3 (1978) 257.