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ELECTRON MICROSCOPE STUDY OF RADIATION DAMAGE IN GRAPHITE PRODUCED BY D^+ AND He^+ BOMBARDMENT

K. NIWASE [1]*, M. SUGIMOTO [1], T. TANABE [2] and F.E. FUJITA [1]

[1] *Department of Material Physics, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan*
[2] *Department of Nuclear Engineering, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan*

Cleaved highly oriented pyrolytic graphite was irradiated at temperatures between 100 and 700 °C, with D^+ and He^+ ions with the acceleration voltage of 25 keV and the doses up to 3.0×10^{18} ions/cm^2, and examined by transmission electron microscopy. The graphite irradiated by either D^+ or He^+ ions is amorphized at a critical dose, which is monitored by the structureless electron image and the appearance of a halo in the diffraction pattern. The critical dose increases with the irradiation temperature and even the irradiation at high temperature as 500 °C gives the amorphization. Though the critical dose for D^+ irradiation is higher than for He^+ irradiation, the critical dpa calculated from the energy deposition agrees well between the two cases. Therefore it seems that the amorphization of graphite by energetic ion bombardment is mainly controlled by the energy deposition and the difference in chemical nature of the incident particles plays a minor role. The macroscopic defect structures which appeared after the amorphization are, however, somewhat different between the two cases.

1. Introduction

Recently, graphite or other carbon materials became one of the most important candidates for the first wall of next coming DT burning reactors because of their outstanding nature against plasma contamination, heat load, neutron activation etc. [1,2]. For utilization of graphite as the first wall, a large number of studies with various aspects have been carried out. For instance, physical erosion of surfaces caused by irradiation with hydrogen and helium was examined metallographically, and chemical erosion of graphite by methane production under hydrogen irradiation was also extensively studied applying mass spectrometry. Trapping of hydrogen and helium in graphite has been discussed based on re-emission or thermal desorption techniques [3,4]. Changes of bonding structure in graphite given by the ion irradiation have been investigated by Raman spectroscopy [5], which indicates gradual amorphization of the graphite with increasing dose. In recent years, advance in transmission electron microscope (TEM) technique made a detailed analysis of damage structure possible and the amorphization produced by heavy ion irradiation has often been observed [6]. Few investigations have, however, been performed on the defect structure in graphite irradiated by energetic particles except fast neutrons by using TEM. Because of the importance of graphite for high temperature nuclear reactors, several TEM studies have been done on the damage produced by fast neutron irradiation about two decades ago, and black and white contrast was observed in dark field microscope image, which were attributed to interstitial clusters [7]. Unfortunately, no detailed analysis of the defect structure and/or the structural changes were reported at that time.

In the present work we have investigated the microstructural change of graphite irradiated by D^+ and He^+ ions, especially focusing on the amorphization, and we discuss the effect of the implanted gas atoms and irradiation temperature on damage formation utilizing a transmission electron microscope.

2. Experimental

Highly oriented pyrolytic graphite (HOPG) was used in the present study. Thin foil specimens for electron microscopy were prepared by repeated cleavage using adhesive tape. The foils were irradiated along the c-axis with 25 keV He^+ ions or 25 keV D^+ ions at temperatures between 100 and 700 °C with a dose rate of 1.0×10^{14} ions/cm^2 s. Defect structures formed by the irradiations were observed in a JEM-200CX transmission electron microscope operated at 120 kV. Since the diffraction contrast of bright field images of defect structures was low, most of the observations were done by using dark field image technique.

3. Results

Fig. 1 compares dark field images given by $(11\bar{2}0)$ reflection for the foils irradiated with D^+ ions at different temperatures with a dose of 1.0×10^{17} ions/cm^2. It must be noted that white dot contrasts, originating from defect clusters, decrease in their number density with increasing the irradiation temperature, whereas their size markedly increases with the temperature. Fairly large clusters are found at 700 °C irradiation. Irradiation by He^+ ions also produces similar dot contrasts. Such dot contrasts have been already reported in the TEM dark field image of neutron irradiated graphite and were attributed to the interstitial clusters by Bollman and Hennig [7].

* Present address: Department of Physics, Hyogo University of Education, Yashiro, Hyogo 673-14, Japan.

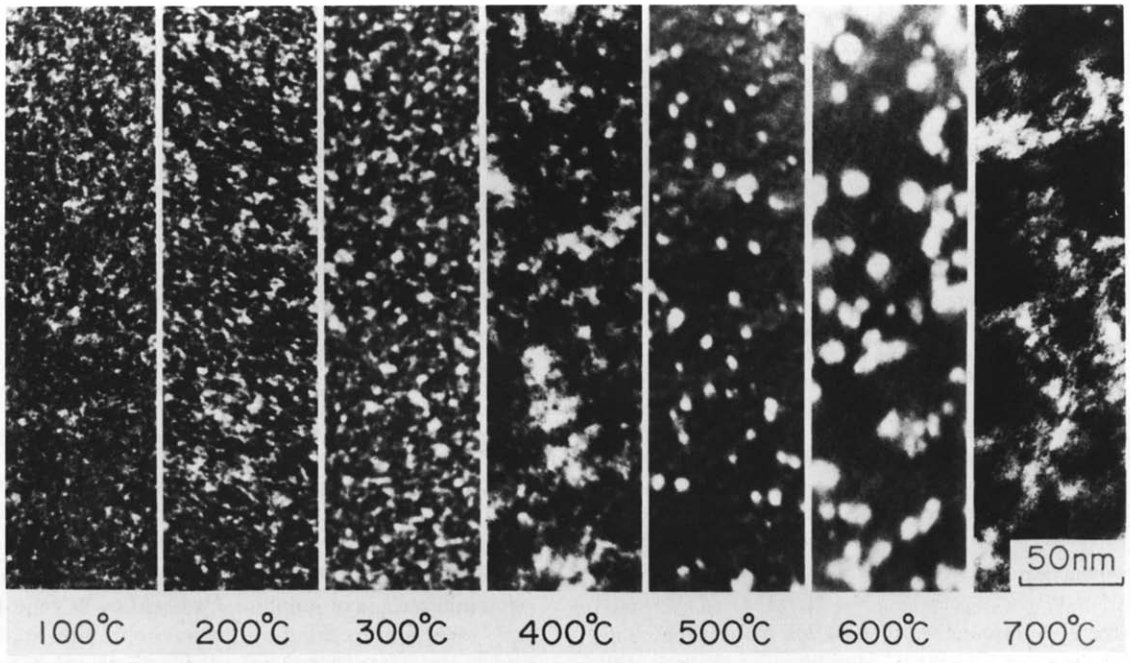

Fig. 1. Dark field images of graphite foils irradiated by D^+ ions at different temperatures with a dose of 1.0×10^{17} ions/cm^2.

The white dot contrasts, however, gradually become faint when increasing the dose, and finally the TEM images completely lose the contrast in any reflection condition. Fig. 2 shows the change of the dot contrasts given by D^+ irradiation with the increasing dose. The left hand side area, a, which has been covered by a mesh wire, is free from the irradiation and keeps the original crystal structure as confirmed by the single crystal diffraction pattern shown underneath. On the other hand, the right hand side area, c, irradiated with a dose

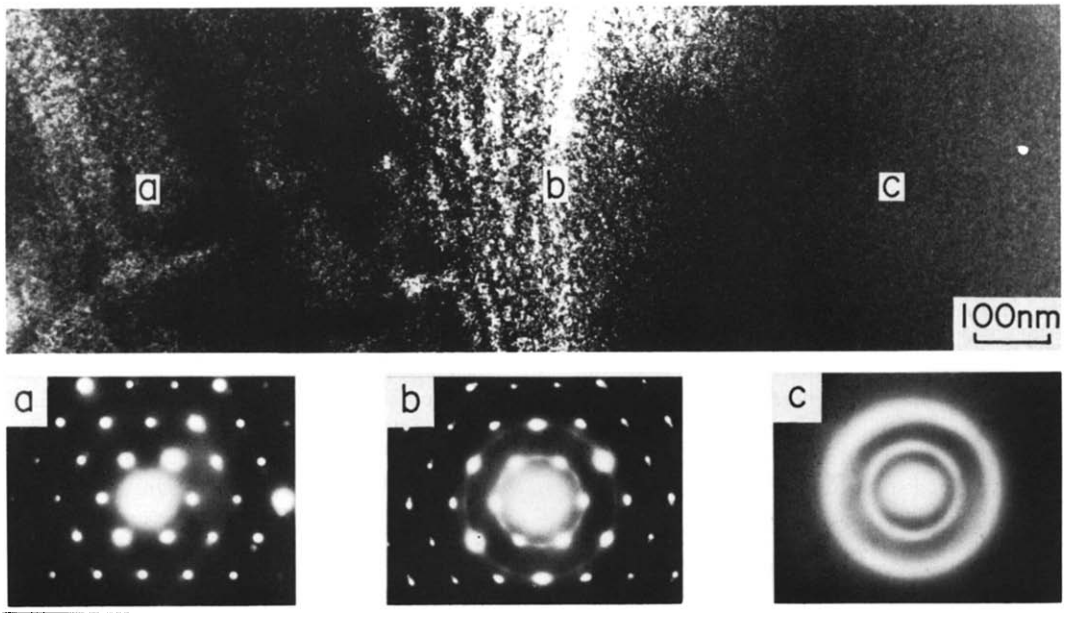

Fig. 2. A change of dot contrasts in graphite given by D^+ irradiation at 200 °C. The left hand side area, a, of the picture is a part of the specimen covered by a mesh wire and the right hand side area, c, is a part irradiated to a dose of 2.5×10^{17} ions/cm^2. Selected area diffraction patterns corresponding to the areas, a, b and c, are given below the photograph.

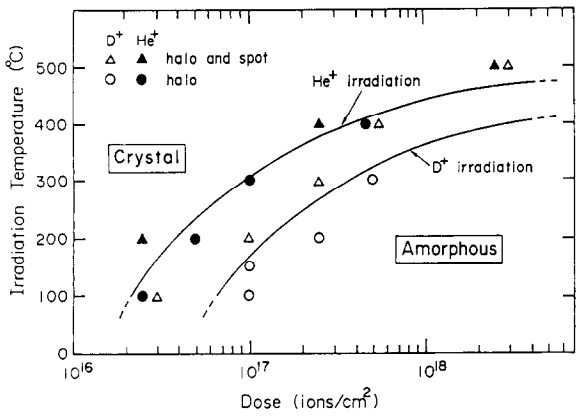

Fig. 3. Changes of diffraction patterns by D^+ and He^+ irradiation. The dose needed for appearance of the halo and that for disappearance of the spots in the diffraction pattern are plotted against the irradiation temperature in the both cases. The solid curves indicate the critical conditions of amorphization.

of 2.5×10^{17} ions/cm^2, completely loses the extinction contours and coarse dotty contrast, only halo pattern being seen in the associated diffraction pattern. The midst part, b, irradiated with an intermediate dose shows a mixed diffraction pattern, spots and halo. Thus, initially perfect crystalline graphite gradually loses the atomic ordering in crystal structure with the increasing dose and becomes amorphous when the implanted dose is above a critical value.

The amorphization, characterized by the disappearance of the white dotty contrast in the dark field image and the transition from the spots to the halo in the diffraction pattern, is also given by He^+ irradiation.

The critical dose for the amorphization becomes larger when the irradiation temperature is higher and D^+ irradiation needs a much higher dose than He^+ irradiation as seen in fig. 3, where the dose needed for appearance of the halo and that for disappearance of the spots in the diffraction pattern are plotted against the irradiation temperature in both cases. It is notable that the amorphization does occur even at such a very high temperature as 500 °C, where most of the implanted particles are expected to be immediately released [4,8].

4. Discussion

It is often claimed that hydrogen plays an important role in the formation of amorphous carbon films by plasma process, because hydrogen occupies dangling bonds in graphite, changing the bonding nature from sp^2 hybridization to sp^3 [9]. In the present work, both D^+ and He^+ ion irradiation, in spite of the quite different chemical nature of deuteron and helium, results in amorphization of the graphite as shown in fig. 3. This suggests the importance of the energy deposition rather than a chemical effect on the amorphization in particle irradiations. In order to compare the effect of energy deposition between D^+ and He^+ irradiation, the critical doses given in fig. 3 are replotted by using the number of displacements per atom (dpa) based on the Kinchin–Pease model, employing the energy deposition calculated by the TRIM-3D code and the threshold energy of 28 eV along c-axis given by Iwata et al. [10]. Fig. 4 shows the result. It is rather surprising that the critical dpa values for amorphization in He^+ and D^+ irradiation agree quite well with each other.

Thus the amorphization of the graphite irradiated by these two types of light energetic particles is basically controlled by the displacements of the lattice atoms (energy deposition) and the difference in the nature of the incident particles or the chemical effect seems to play a minor role. This is also confirmed by the appearance of amorphization at elevated temperatures as high as 500 °C where most of the implanted particles would be released [4,8]. It is noteworthy that the above mentioned sp^3 hybridization could be formed without hydrogen, when the graphite structure becomes very defective due to irradiation, leading to the amorphous structure.

Details in macroscopic damage at high doses show some difference between D^+ and He^+ irradiation. Fig. 5 shows the bright field images of graphite specimens irradiated by D^+ and He^+ ions at 400 °C to a dose of 5.0×10^{17} ions/cm^2. The images are mainly formed by the absorption contrast because the specimens are almost in the amorphous state. The difference between the structures of the two cases could be explained by the effect of implanted gas atoms. Hydrogen atoms are considered to be chemically trapped by carbon atoms and, therefore, they will not move and locally accumulate. Helium atoms, in contrast, are not chemically trapped and may result in the interlayer accumulation, making a special microstructure a little more complex than deuteron irradiation case. The damage structure in (b) looks similar to the bubble formation. Since the thermal desorption study [4,8] demonstrates that helium

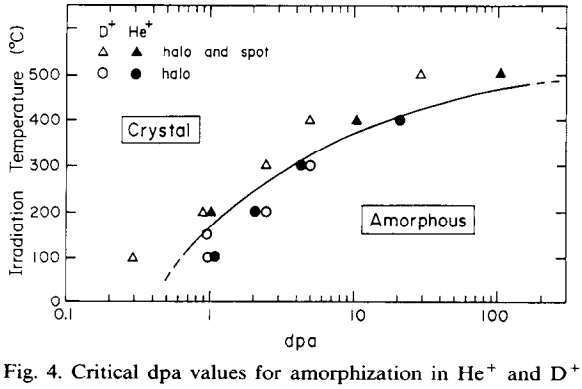

Fig. 4. Critical dpa values for amorphization in He^+ and D^+ irradiation. The doses given in fig. 3 are replotted by using dpa. Note that the critical dpa of amorphization by D^+ irradiation almost coincides with that by He^+ irradiation.

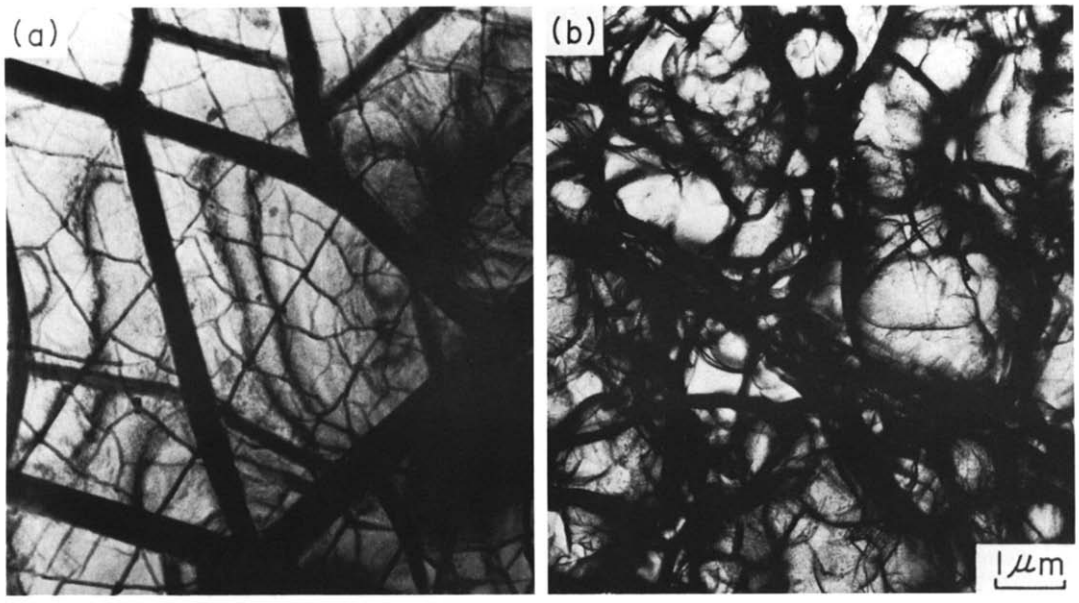

Fig. 5. Bright field images of graphite foils irradiated by (a) D^+ and (b) He^+ ions at 400 °C to a dose of 5.0×10^{17} ions/cm^2.

implanted in graphite is released at a slightly lower temperature than that of deuterium, further electron microscopic studies and detailed analysis of the defect structure are awaited.

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