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High temperature irradiation damage of carbon materials studies by laser Raman spectroscopy

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ABSTRACT

In order to characterize carbon materials exposed to hydrogen, deuterium and helium plasmas at elevated temperature, we have applied laser Raman spectroscopy. We have found that the exposure to high dense plasma at an elevated temperature, 700–1200 K, does not amorphize the carbon materials. The specimen exposed to the plasma keeps two-dimensional structure orders, though their grain sizes or crystallites are fragmented into very fine ones. Heavier ions irradiation (He) results in more fragmentation than lighter ions (H). Hence the displacement played more important role and the chemical effect of hydrogen which is not appreciable because of spontaneous release of hydrogen at high temperatures. This indicates that hydrogen retention in carbon materials can be significantly reduced at elevated temperature operation. Furthermore the Raman spectroscopy could be used for in situ analysis of carbon based plasma facing materials.

1. Introduction

Carbon materials are used as plasma facing materials in fusion devices and have been extensively studied by means of various methods, because the erosion owing to hydrocarbon formation and hydrogen retention in redeposited carbon are concerned for tritium safety and maintenances of fusion devices [1–3]. Hydrogen retention in carbon materials is quite dependent on their structure and temperature [1]. Until now, however, little studies have been devoted to high temperature and high flux irradiations relevant to ITER divertor condition, where heat loads and fluxes are very high.

The structure of carbon materials is quite dependent on hydrogen content and temperature. Laser Raman spectroscopy is one of powerful tools for characterizing various carbon materials and has capability to make remote measurements with using a fiber transmission technique.

In this work, we have applied the laser Raman spectroscopy to evaluate carbon materials irradiated and/or redeposited at elevated temperatures under very high hydrogen, deuterium and helium ion flux, and compared the obtained date with previous work by Niwase et al. [4], in which carbon materials are irradiated by ion beam bombardments. And the difference of the plasma species was compared.

2. Experiment

Samples of nuclear grade graphite (IG-430U) were exposed to hydrogen plasma with ion energy of ~50 eV in a linear plasma device, NAGDIS-II in Nagoya University at a temperature of 700–1200 K. The samples exposed to deuterium and helium plasma were also prepared. Exposed fluence was up to $\sim 7.7 \times 10^{26}$ ions/cm^2 and the exposure temperature was 700–1200 K. The details of the plasma exposure were described elsewhere [5]. Before and after the exposure, the samples were analyzed by means of laser Raman spectroscopy to characterize their structures.

3. Raman spectroscopy

Generally, Raman spectra of the carbon materials are constructed with two characteristic peaks at 1580 cm^{-1} and 1355 cm^{-1}, referred as G-peak and D-peak, respectively. Fully crystallized carbon or single crystalline graphite shows only G-peak, while D-peak (D comes from disorder) appears by the introduction of defects in graphite i.e. disordering of the basal plane. For highly oriented pyrolytic graphite (HOPG), changes of the intensities and peak widths for the both peaks given by high energy H^+ ion irradiation with a fluence between 1.3×10^{15} and 5.0×10^{17} ions/cm^2 and at a temperature form RT to 1000 K were examined in detail as given in Fig. 1, where the G-peak widths (W_{1580}) were plotted against the peak intensity ratio (I_{1355}/I_{1580}). The electron diffraction patterns of the same samples were also observed and the diffraction patterns categorized into three types, i.e. spot (s), halo and spot (hs), and halo (h)

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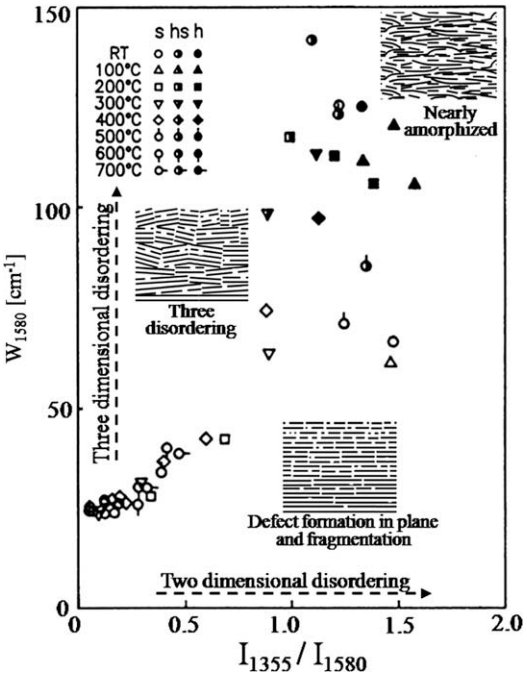

Fig. 1. The G-peak width (W_{1580}) versus peak intensity ratio (I_{1355}/I_{1580}) of Raman spectra for HOPG foils irradiated with various doses of 25 keV H^+ ions at a temperature ranging from RT to 973 K. The diffraction patterns of spot (s), halo and spot (hs), and halo (h) observed by TEM were indicated as open, half closed and closed symbols, respectively [4].

corresponding to a well crystalline structure, disordered structure and mostly amorphous structure, respectively. They are indicated in the figure together with the irradiation temperatures [4]. The insets of the Fig. 1 are schematics for the microstructure of the irradiated HOPG for very early stage of the irradiation, three-dimensional disordering and nearly amorphized state. The peak intensity ratio could be correlated to grain size of the irradiated graphite as indicated in the top horizontal axis, while the vertical axis corresponds to three-dimensional disordering.

In this works, Raman spectra for the plasma exposed samples were obtained using a 514.5 nm line of Ar^+ laser with a back scattering geometry. The diameter of the analysis point was 1μm. The laser power was controlled to be below 10 mW in order to avoid any laser heating effects. Thus obtained Raman spectra were deconvoluted into two Lorenzian peaks (1580 cm^{-1} and 1355 cm^{-1}) and peak intensities (I_{1580} and I_{1355}) and the peak widths (W_{1580} and W_{1355}) were determined by a curve fitting method and compared to those of the ion irradiated HOPG.

4. Results

Fig. 2(a) and (b) shows sample surfaces exposed to H plasma at 700 K and 1200 K, respectively. At the 700 K exposure, the surface

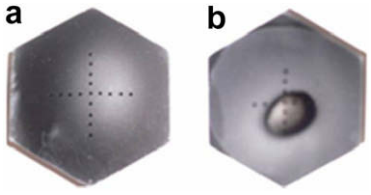

Fig. 2. Graphite surfaces after exposure to hydrogen plasma at (a) 1200 K and (b) 700 K.

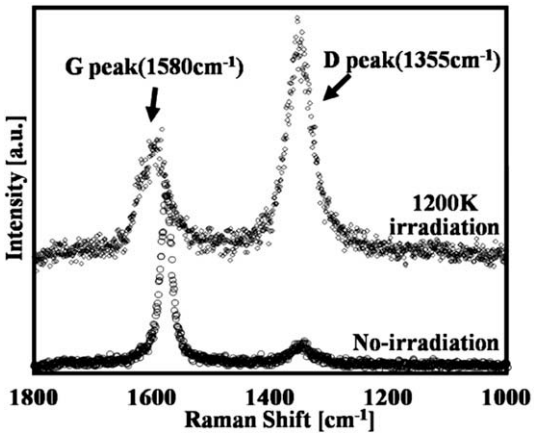

Fig. 3. Comparison of Raman spectra of the non-irradiated rear surface and the front surface exposed to H plasma.

was uniformly eroded, while redeposition appeared as grayish colored area in the center at the 1200 K exposure. This is due to the lower ion temperature of the central of the plasma column as often observed in a linear plasma machine like NAGDIS and deposition always starts in the center and extended to the edge in the deposition dominated regime. Fig. 3 compares the Raman spectra of the sample surface exposed to the H plasma at 1200 K and that of non-exposed sample surface. The latter showed typical Raman spectra for sintered graphite, with two sharp peaks at 1580 cm^{-1} and 1355 cm^{-1}. To examine the variation of the spectra in detail, peak intensity ratios (I_{1355}/I_{1580}) and peak widths (W_{1580} and W_{1355}) for the samples exposed to the H plasma were determined and superposed on Fig. 1 resulting in Fig. 4. The H plasma exposure varied the Raman spectra but the variation was not so significant compared to those given by the high energy ion irradiation. One can note the all data points for the sample exposed to the H plasma

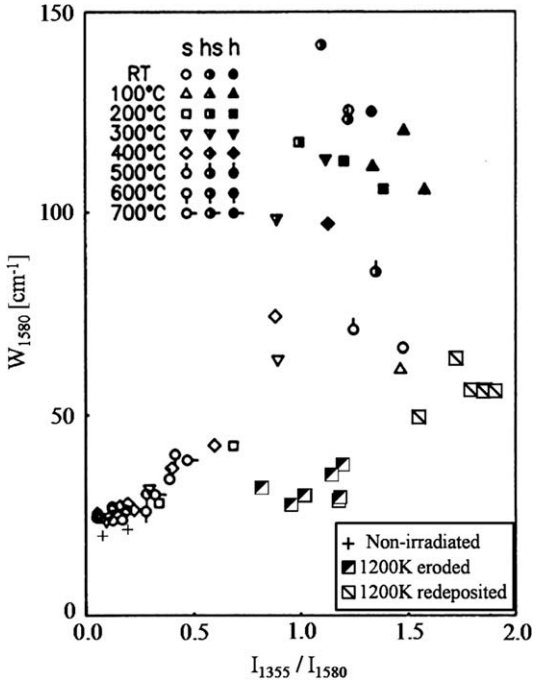

Fig. 4. Comparison Raman data for the re-deposited area and the eroded area for the samples exposed to the H plasma at 1200 K with those higher energy ion irradiated ones given in Fig. 1.

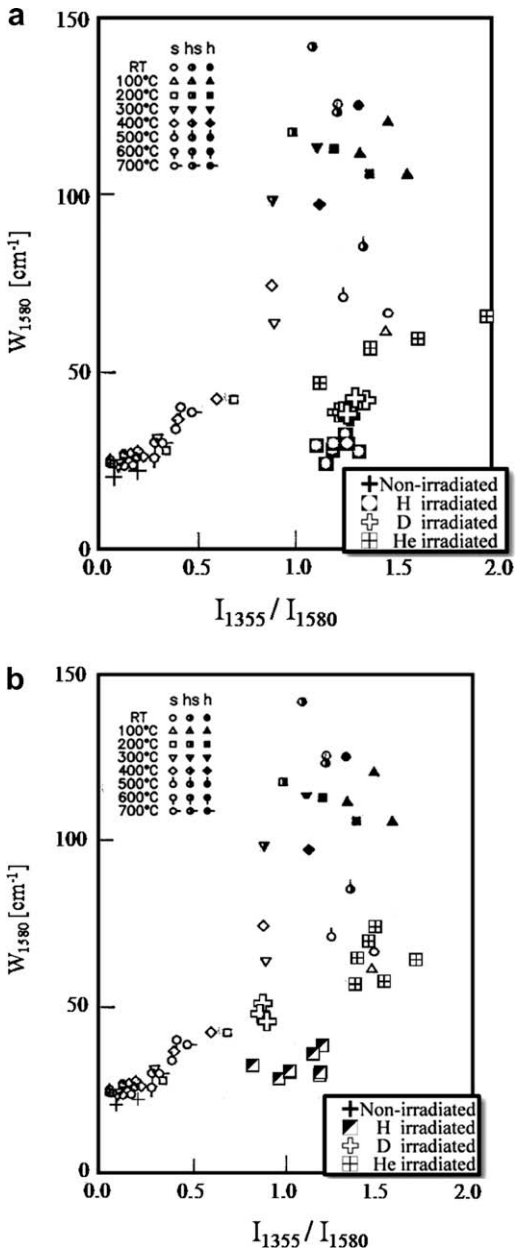

Fig. 5. Comparison of the peak intensity ratio and the peak widths of G-peak of the Raman spectra of the carbon materials irradiated with different ions under 700–800 K irradiation (a) and 1100–1200 K irradiation (b).

are located on lower bottom in Fig. 4. Still the data for the eroded area and for the deposited area were clearly separated. The irradiated samples kept some crystalline order, but their grains were fragmented into very finer ones compared with the ion irradiation case. The redeposited area appeared at 1200 K exposure were more fragmented than the eroded area. Nevertheless, they still kept layered structure. Fig. 5 compares the Raman spectra of the samples exposed to H, D and He plasmas at 700–800 K (a) and at 1100–1200 K (b). The heavier plasma ion gave more fragmentation. The chemical effect of hydrogen is not appreciable most probably due to spontaneous hydrogen recombination and desorption.

700 K irradiations gave slightly heavier fragmentation than 1200 K one. However even helium irradiation at high temperature did not amorphized the samples.

5. Discussion

The main differences between the previous work and the present one are the incident energy of the ions and the irradiation flux. In the previous work, the irradiation with 25 keV H^+ ions gave significant damage i.e. the fragmentation into fine grains, loss of three-dimensional ordering and amorphitization. The ion energy (~50 eV) of the H plasma is too low to give large displacement of carbon atoms, defects would be mainly produced by the chemical effect of hydrogen to make C–H bonding. However, the decrease of the free energy of C–H bonding with increasing temperature and very high flux irradiation resulting in the easy recombination of hydrogen once bonded to carbon would not allow accumulation of high density defects which could cause three-dimensional disorder Although the chemical effect of D must be similar to H, D irradiation gave the heavier damage, indicating that the mass effect or displacement damage still plays important role as appeared as the heaviest damage by He irradiation. Nevertheless the defect structure remained only fragmented, i.e. layered structure was kept without bending of the basal plane or making fullerene type three-dimensional structures [6]. This is most likely owing to spontaneous annealing, which does not allow the accumulation of three-dimensional damages. With increasing temperatures, the effect of the spontaneous annealing becomes more significant and need higher flux to produce the defects or to give fragmentation.

6. Conclusion

Laser Raman spectroscopy was applied to reveal the structure change of carbon materials exposed to high density plasmas of hydrogen, deuterium and helium at elevated temperature. Compared with the higher energy irradiation [4], the defects introduced in the samples were quite different. Although the grain size was significantly reduced, the grains kept layered structure without bending or making fullerene type three-dimensional structures [6]. Heavier ions irradiation (He) results in more fragmentation than lighter ions (H). Hence the displacement played more important role and the chemical effect of hydrogen which is not appreciable because of spontaneous release of hydrogen at high temperatures. Helium ions also could be released through boundaries of crystallite and hardly existed in carbon materials. The significant fragmentation compared to the ion irradiation could be attributed to high flux irradiation of plasma.

All these results indicate that hydrogen retention in carbon materials can be significantly reduced at elevated temperature operation. In addition, the Raman spectroscopy could be used for in situ analysis of the carbon based plasma facing materials.

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