Nuclear Instruments and Methods in Physics Research B 412 (2017) 221–226

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

Raman spectra and modulus measurement on the cross section of proton-irradiated graphite

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ARTICLE INFO

Article history:
Received 1 July 2017
Received in revised form 6 September 2017
Accepted 6 September 2017

Keywords:
Nuclear graphite
Ion irradiation
Raman spectrum
Nano-indentation

ABSTRACT

A method combining proton irradiation and nano-indentation was explored in this study to measure the modulus of irradiated graphite. A IG-110 graphite sample was irradiated with 2.5-MeV protons to a fluence of 1.2×10^{18} ions/cm^2 at room temperature. Proton irradiation produced a damaged layer with a thickness of ~75 μm. A scan of Raman spectrum was performed on cross section of irradiated sample. Analysis of the Raman spectra indicates that the graphite breaks into nano-crystalline graphite at very low dose (0.02–0.04 dpa) during room-temperature irradiation. Nano-indentation tests were performed on the cross section of irradiated sample so that the damage along the loading direction is uniform. Thus, it was able to identify a dpa value for the nano-indentation tests. Using this method, the modulus at 0.015 dpa was deduced to be 2.39 times that of the un-irradiated graphite. The hardness is also more than doubled after irradiation to 0.015 dpa.

1. Introduction

As neutron moderator and reflector in fission reactors, graphite materials are subjected to fast neutron irradiation. Irradiation effects in graphite have been studied for decades by in-pile irradiation and post-irradiation examination. In-pile irradiations usually are expensive and time-consuming, resulting in radioactive samples. In contrast, ion irradiations have the merits of low cost, time saving, and avoidance of high residual radioactivity. There is a growing interest in using energetic ions to understand the effects of neutron irradiation in reactor components.

Graphite materials have been irradiated by 25 keV He ions and various heavy ions with energies lower than 400 keV, resulting in very thin damaged layers (much less than 1 μm) [1–5]. It was impossible to obtain irradiation-induced change of thermal and mechanical properties which are essential for safety evaluation of graphite components in reactors. Raman spectra instead were extensively studied in these ion-irradiated layers. Recently, graphite materials were irradiated by ions with energies of several mega-electron volts [6–8]. Campbell, et al. irradiated stressed graphite samples with several MeV protons, in order to simulate the neutron-irradiation-induced creep of graphite [6]. Irradiation-induced increase of hardness and modulus has been reported for graphite irradiated with 3 MeV protons and 3 MeV C ions by performing nano-indentation tests on the irradiated surface [7,8]. Because the displacement per atom (dpa) value produced by ion irradiation is depth dependent with a peak located near the end of the ion range, specific dpa value cannot be identified for these nano-indentation tests.

In this study, a surface-polished IG-110 graphite sample was irradiated with 2.5 MeV protons. A scan of Raman spectrum was performed on the sample's cross section to characterize the profile of proton-irradiation-induced damage. Parameters extracted from the Raman spectra were obtained as a function of dpa. Modulus and hardness were obtained by performing the nano-indentation tests on the sample's cross section. The corresponding dpa value was also identified because of the merit of uniformly-distributed damage along the loading direction.

2. Experimental procedures

2.1. Pre-irradiation polishing

The as-machined IG-110 graphite sample (8 mm × 8 mm) has a very rough surface which may lead to inconsistent depth profile of ion-irradiation-induced damage. Therefore, a polishing process was used to the IG-110 graphite sample. The sample was first ground by hand with 2000 grit silicon carbide abrasive paper until

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https://doi.org/10.1016/j.nimb.2017.09.004
0168-583X/

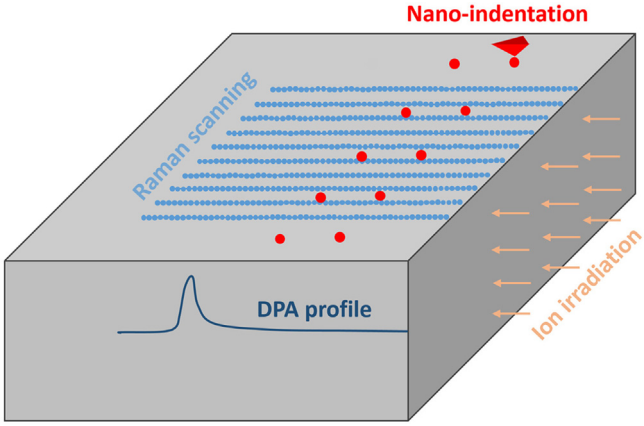

Fig. 1. Sketch of the experimental procedure.

the original surface was entirely removed, and then polished on a cloth with 0.05 μm diamond suspensions for less than 5 min. The polished sample was then immersed in deionized water in an ultrasonic cleaning device in order to remove the residual diamond suspensions from the surface. The surface roughness of another IG-110 sample has been measured by using atomic force microscope (AFM), and the root-mean-squared roughness (Rq) is 25.1 nm [9]. The pores were intentionally avoided during AFM scanning.

Fig. 1 shows the experiment layout including irradiation, Raman spectrum scanning and nano-indentation tests.

2.2. Irradiation

Ion irradiation was carried out at a 4 MV electrostatic accelerator at Shanghai Institute of Applied Physics, Chinese Academy of Science. The polished surface of the IG-110 graphite sample was irradiated with 2.5 MeV protons to a fluence of 1.2×10^{18} ions/cm^2 at room temperature. During irradiation, the sample was covered by a fused silica plate with an aperture (diameter = 2.5 mm). The fused silica fluoresces when illuminated with energetic ions, and was used to identify the position of the ion beam. The diameter of the ion beam was larger than that of the aperture. Thus the graphite sample was only exposed to the ions passing through the aperture. The ions irradiated on the sample were collected with an electric charge integrator to obtain the ion fluence, while the ions hitting on the fused silica were intentionally conducted away.

Different from neutrons, energetic protons used in this study interact with electrons in graphite material and cause electron excitations. It has been reported that electron excitations may result in damaged ion track if the electronic energy loss reaches a threshold value. For graphite, this threshold was reported to be 7.3 keV/nm, which is only reached by swift heavy ions [10]. The electronic energy loss of 2.5 MeV proton was calculated by SRIM, and is <0.1 keV/nm, far below the threshold value, indicating that electron excitation did not produce ion tracks in this study. Therefore, the irradiation with 2.5 MeV protons produced only lattice defects by elastic collisions, similar as neutron irradiation.

Although the electronic energy loss is so low that amorphous ion track cannot be formed, each proton will lose most of its energy (2.498 MeV) to electron excitations along its whole journey to a depth of around 71 μm. The electron excitations cause lattice vibration, which may result in a slight temperature rise if the ion beam current is high. In order to minimize the heating effect due to electronic excitations, the ion beam current was kept very low (~ 0.1 μA) during irradiation. Because the charge of the ions need to be conducted to a charge integrator, the thermal couple cannot contact the sample to directly monitor the sample's temperature. Instead, the thermal couple contacts a thin insulator plate which is mounted against the sample. The temperature of the insulator increased from 20 °C to ~30 °C during irradiation. We estimate that temperature rise in the sample is also small.

The ion irradiation process was simulated by SRIM 2008 program using the "Kinchin-Pease quick calculation" mode. It was reported that the "Kinchin-Pease quick calculation" mode could produce equivalent displaced atoms to the well-known mode that developed by Norgett, Robinson and Torrens (NRT model), while the "Full Cascade calculation" mode produced twice the displaced atoms [11]. It has been shown that the calculated number of displaced atoms strongly depends on the displacement threshold energy (E_d) [12]. The value of E_d of carbon has not been agreed upon within the literatures. A value of 31 eV has been used for carbon atoms for neutron irradiation damage calculation [13]. In the analysis of ion- and electron-irradiated graphite, values of 25 eV and 20 eV have been used [7,14]. In this study, the vacancy number derived from SRIM simulation using E_d of 20 eV is used for dpa calculation, and is 1.6 times the vacancy number derived using E_d of 31 eV. The dpa profile was calculated and is shown in Fig. 2(a) for 2.5 MeV protons at a fluence of 1.2×10^{18} ions/cm^2. The dpa value is not uniform through the irradiation layer. The peak dpa value is around 0.5 at a depth of 71 μm.

The proton distribution was calculated using the SRIM program. Most of the protons (99.9%) are distributed in a depth between 68 and 75 μm. The highest concentration of proton is located at depth of 72 μm, and is 3.84×10^{21} cm^{-3} which is 4% of that of carbon atoms.

2.3. Post-irradiation tests

Raman spectrum measurements and nano-indentation tests were conducted on the cross section of proton-irradiated graphite, as they are illustrated in Fig. 1. Because nano-indentation tests need a relatively flat surface, the sample was cut with its cross section being polished after irradiation. As it was reported in previous work [15], polishing did enhance the intensity of the D mode in the Raman spectrum, indicating that polishing produced considerable defects at the surface.

The Raman spectra were collected from 550 points which formed an array of 55×10 and were distributed in an area of 100×60 μm on the sample's polished cross section. A photo of the area that was used for collecting the Raman spectra is shown in Fig. 2(b). The Raman spectra were recorded at room temperature using a Bruker SENTERRA confocal Raman microscope with a 532-nm laser as excitation beam.

C–H bindings exist at the end of the ion range and may influence the Raman spectra. It was reported that the C–H stretching modes around 2920 cm^{-1} can only be detected for UV excitation [16]. In Raman spectra collected by using visible laser excitation, the C–H bindings in carbon materials raises the photoluminescence background with increasing H content [17]. In this study, we investigated the G peak width, G peak position and I_D/I_G which should not obviously be altered by the photoluminescence background.

Nano-indentation tests were performed by using an Agilent Technologies G200 Nano Indenter. A Berkovich diamond indenter tip was used to do the continuous stiffness measurement (CSM). The CSM option allows the continuous measurement of the contact stiffness during loading. This is accomplished by superimposing a small oscillation (with an amplitude of 2 nm in our measurements) on the primary loading signal. With a continuous measure of contact stiffness, one obtains the hardness and elastic modulus as a continuous function of depth from a single indentation test. Nano-indentation tests were performed on the cross section of