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Ion irradiated graphite exposed to fusion-relevant deuterium plasma

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ABSTRACT

Graphite samples were irradiated with 5 MeV carbon ions to simulate the damage caused by collision cascades from neutron irradiation in a fusion environment. The ion irradiated graphite samples were then exposed to a deuterium plasma in the linear plasma device, MAGPIE, for a total ion fluence of $\sim 1 \times 10^{24}$ ions m^{-2}. Raman and near edge X-ray absorption fine structure (NEXAFS) spectroscopy were used to characterize modifications to the graphitic structure. Ion irradiation was observed to decrease the graphitic content and induce disorder in the graphite. Subsequent plasma exposure decreased the graphitic content further. Structural and surface chemistry changes were observed to be greatest for the sample irradiated with the greatest fluence of MeV ions. D retention was measured using elastic recoil detection analysis and showed that ion irradiation increased the amount of retained deuterium in graphite by a factor of four.

1. Introduction

There are a number of fusion devices, including KSTAR [1] and DIII-D [2], that operate with carbon-based plasma facing materials (PFM). Collisions of ions and neutrals originating from the fusion plasma with PFM result in fundamental plasma–surface interactions issues such as erosion of material, contamination of the plasma and retention of fuel [3]. PFM will also sustain damage from neutron irradiation. Thus it is necessary to understand how these damaged states will interact with plasma.

Ion irradiation can be used to simulate the effects of neutron damage [4]. A rational choice to simulate the damage caused by the 14 MeV neutrons from the D–T fusion reaction is that of the most damaging knock-on atoms; 14 MeV neutrons can produce carbon knock-ons of energy up to 4 MeV, which via their cascade effects are the most damaging particles. Previously, graphite has been irradiated with 5 MeV ions to 10 dpa (10^{18} ions cm^{-2}), and then exposed to a plasma with an ion flux $\sim 1 \times 10^{17}$ cm^{-2} s^{-1} [5]. Ion irradiation prior to plasma exposure resulted in erosion yield ratios for irradiated materials/undamaged samples of about 2.6–4.8 atoms per incident plasma ion, however no rise of erosion rate was observed for ion irradiations above the minimum-studied 1 dpa. This was attributed to saturation of irradiation effects [5]. Plasma exposure and erosion therein was performed in two steps. In the first step half the damaged layer was eroded (2–3 μm) and in the second the region of maximal damage (3–6 μm) was eroded and was found to do so at a faster rate [6].

While characterisation of ion irradiated samples [4] and plasma exposed samples have previously been undertaken [7], there have been few other experiments characterising ion damage and subsequent plasma exposure of candidate PFM [5,6,8,9].

Graphite has previously been irradiated with neutrons in test reactors [10–14], though it should be noted that the neutron spectrum in these tests feature few of the 14 MeV neutrons that dominate the D–T fusion spectrum, hence will feature a lower rate of primary knock-ons per neutron. Indeed, by considering the energy dissipated from primary knock-on atoms it is estimated that the number of displaced atoms within a few microns of carbon will be approximately an order of magnitude larger in the case of 14.1 MeV neutrons, compared with 1 MeV neutrons [15]. An advantage to using 5 MeV carbon ions is that they can produce cascade-like damage that might be expected from a D–T neutron-spectrum [4].

Over the past two decades Atsumi reported on the trapping of hydrogen gas in neutron-irradiated graphite [10–14]. Graphite was irradiated in the Japan Materials Testing Reactor up to neutron

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fluences of 5.4×10^{20} cm^{-2} [16]. Two kinds of hydrogen trapping sites were reported that were thought to be produced during irradiation. "Trap 2" sites are preferentially created at low neutron fluences and annealed at high temperatures, whereas "trap 1" sites are created above 0.017 dpa and do not significantly anneal at temperatures below 1873 K [12]. The diffusion coefficients of hydrogen were found to reduce by 1–2 orders of magnitude with irradiation [12].

Formation and deposition of hydrocarbon material has also been shown to be an issue for carbon-based plasma facing materials [17], leading to accelerated chemical erosion. In the case of graphite, dust particles on the micron-scale that have formed due to plasma exposure have been observed [18,19].

2. Experimental

Graphite samples were obtained from ESPI Metals (ESPI Corp. Inc.) and were of ESPI Super Conductive grade. Samples were irradiated with 5 MeV C^{2+} ions using the HVE 2 MV STAR accelerator at the Australian Nuclear Science and Technology Organisation (ANSTO). A broad beam was produced using rectangular slits so that the beam spot irradiated only the 10 mm × 10 mm sample. The fluence was monitored by measuring the beam current on the sample via the sample holder, and was nominally 200 nA. Irradiations were performed at room temperature and at a chamber pressure of 1×10^{-3} Pa.

Three different C^{2+} ion irradiation fluences were used: 5×10^{14} ions cm^{-2}, 5×10^{15} ions cm^{-2} and 4×10^{16} ions cm^{-2}. For the highest fluence, the Monte-Carlo software SRIM [20] predicts dpa of approximately 0.5 dpa, when averaged across the 3.7 μm ion range. Two identical sets of irradiated graphite samples were produced, with one set exposed to deuterium plasma after ion irradiation.

Samples were exposed to an ion flux of $\sim 1 \times 10^{17}$ ions cm^{-2} s^{-1} in a deuterium plasma in the MAgnetized Plasma Interaction Experiment (MAGPIE) [21]. The sample was inserted and the vessel evacuated to a base pressure of 3×10^{-3} Pa prior to each experiment. Deuterium was then introduced into the chamber via a mass flow controller and an operating pressure of 1.33 Pa was obtained. The plasma was operated with a 50% duty cycle (pulse length of 45 ms) and the total plasma exposure time of the materials was 2000 s, resulting in a total deuterium ion fluence of $\sim 1 \times 10^{24}$ ions m^{-2}. From the measured electron temperature of 5 eV and since the samples were maintained at the floating potential, the ion energy was estimated to be ~18 eV ($E_i \sim 3.6T_e$). The gas temperature in front of the sample holder in MAGPIE has been measured by optical emission spectroscopy to be ~600 K for H plasmas; therefore the sample temperature during plasma exposure was in the 300– 600 K range. Here we note that throughout this manuscript we label the samples irradiated with 5 MeV C^{2+} ions using the STAR accelerator as "ion irradiated", and those exposed to deuterium plasma as "plasma exposed".

Raman spectra were collected using a Renishaw inVia Raman spectrometer equipped with the Argon ion laser (514 nm) and a Peltier cooled CCD detector. Stokes shifted Raman spectra were collected in the range of ~100–2000 cm^{-1} with a spectral resolution of ~1.7 cm^{-1} for the 1800 lines mm^{-1} grating. The spot size was around 1.5 μm for 50× magnification. It should be noted that Raman has a limited depth range in graphite due to scattering. For example, the thickness through which a 488 nm laser may pass before intensity reaches $1/e$ is 50 nm [22]. Spectra were fit by subtracting a parabolic baseline and fitting a single Lorentzian curve for each peak at 1360 cm^{-1} and 1580 cm^{-1}.

NEXAFS spectroscopy [23] measurements were recorded using the soft X-ray spectroscopy beamline at the Australian Synchrotron [24]. The carbon K-edge was recorded over an incident photon energy range of 280–320 eV. There was 45° angle between the incident X-ray beam and sample surface. The NEXAFS signal was recorded in Auger electron yield (AEY) mode using a SPECS Phoibos 150 Hemispherical Analyser, with the analyser adjusted to measure an electron kinetic energy of 240 eV. The mean free path of electrons in carbon is of the order of a few nm [23], and NEXAFS is therefore highly surface sensitive. The photon energy scale was calibrated against the sharp, 291.65 eV HOPG exciton peak [25] of the C K spectra obtained using a HOPG reference foil, partially inserted into the beam before the main analysis chamber. All NEXAFS spectra were normalized to the incident photon intensity using the drain current signal recorded from a gold mesh inserted into the X-ray beam before the sample. This signal was corrected using a reference photodiode measurement to remove any intrinsic self-absorbance due to carbon impurities on the gold mesh. Further details on carbon NEXAFS calibration and normalisation can be found elsewhere [26]. The sp^2/sp^3 fraction was calculated from the NEXAFS data using the well-established method that is regularly applied to electron energy loss spectroscopy (EELS) [27], whereby the 285 eV sp^2 peak is normalised by the area of the entire spectrum and compared to a reference graphite spectrum, a material assumed to have an sp^2 fraction of 100%. NEXAFS is surface sensitive, hence this value is a measure of the near surface region.

ERDA was conducted on ANSTO's STAR accelerator, with 1.7 MeV He^+ impinging ions. An incident angle of 75° normal to the surface, and a low scattering angle of 21° was used in order to achieve enhanced depth resolution. For these conditions recoil energies of 952 keV and 1320 keV, for H and D, respectively, were predicted using calculations of ion-scattering kinematics [28]. After passing through the 6 μm Mylar range foil, which is used to stop scattered He before the detector, these energies would be reduced to 720 keV and 1029 keV, respectively. Although the cross sections for deuterium forward scattering from the He are non-Rutherford, they are fairly flat in the energy range relevant to this investigation hence the analysis is straightforward. During ERDA the spectra were collected with the same fluence of incident ions, which was monitored by collecting the sample current to give a total collected charge, which was 3 μC (or 2×10^{13} ions) for each spectrum. By modelling a number of layers in SIMNRA [28], the maximum depth to which D could be separated from the H signal was estimated to be 1200×10^{15} at. cm^{-2}, which is equivalent to a depth of 133 nm assuming a material density of 1.8 g cm^{-3}.

3. Results

Fig. 1 shows Raman spectra of the graphite samples, wherein black dots are before exposure in MAGPIE and red solid lines are following deuterium plasma exposure. A graphitic peak (G) at 1580 cm^{-1}, and a disordered carbon peak (D) at 1360 cm^{-1} are observed. The intensity of the graphitic peak, relative to the disorder peak, is greatest for the virgin sample.

The full-width at half maximum (FWHM) of the G peak for unexposed samples (G_i) is smallest for the unirradiated sample, which is indicative of a narrow distribution of defects and defect-free crystalline. The FWHM of the G peak, listed in Table 1, increases with ion irradiation fluence as a result of the ion irradiation creating isolated defects within graphitic regions. The FWHM of the D peak is relatively unchanged for the unirradiated and two lowest fluence ion irradiations, but approximately triples for the most heavily irradiated sample. This indicates that for fluences greater than 5×10^{15} ions cm^{-2} the type of induced disorder transitions to a larger distribution of defect types.

The $G/(G+D)$ values charted in Fig. 1(b) are indicative of the amount of graphitic material of each sample. This ratio decreases