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Irradiation studies on carbon nanotube-reinforced boron carbide

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ABSTRACT

Radiation response of carbon nanotube (CNT) reinforced boron carbide composite has been studied for its application as a structural component in nuclear engineering. The composite was bombarded by 140 keV He ions at room temperature to a fluence ranging from 1×10^{14} to 1×10^{17} cm^{-2}. Two-dimensional Raman mapping shows inhomogeneous distribution of CNTs, and was used to select regions of interest for damage characterization. For CNTs, the intensities ratio of D–G bands (I_D/I_G) increased with fluence up to a certain value, and decreased at the fluence of 5×10^{16} cm^{-2}. This fluence also corresponds to a trend break in the plot of FWHM (full width at half maximum) of G band vs. I_D/I_G ratio, which indicates amorphization of CNTs. The study shows that Raman spectroscopy is a powerful tool to quantitatively characterize radiation damage in CNT-reinforced composites.

1. Introduction

Boron carbide (BC) possesses unique properties such as low specific weight, high elastic modulus, high hardness, and excellent physical and chemical stabilities at high temperatures [1–3]. BC has been used as a neutron absorber in certain types of fission reactors and has been tested for its applications as core components in some fast breeder reactors [4]. But its application is limited by poor ductility. Incorporating carbon nanotubes (CNTs) into BC matrix can enhance materials' mechanical properties, and increase its resistance to thermal shock and crack growth. However, in order to use CNT-reinforced BC composites as structural components in fission and fusion reactors, material's radiation tolerance needs to be studied. Neutron interactions with boron atoms lead to creation of energetic particles through the transmutation reaction $^{10}B(n, \alpha)^7Li$. Efforts have been made to understand radiation induced structural changes under a high burnup [4,5]. But little is known about radiation responses of CNTs. Similar to other nanomaterials, characterization of damage buildup in CNT-based materials is challenging. Although high resolution transmission electron microscopy, in conjunction with modeling, is able to identify stable defect configurations in CNTs, it does not provide quantitative information [6,7]. Interpretation of electrical resistivity measurements, on the other hand, is difficult because of the mixed semiconducting and metallic properties of CNTs and possible irradiation induced transitions. In this study, Raman spectroscopy was used to quantitatively characterize radiation damage.

2. Experimental procedure

CNT-reinforced BC composite (Nano-Lab Inc., Waltham, MA) was fabricated by hot pressing a mixture of CNTs and BC powders at 2000 °C under 10 ton load, and pressureless sintering at 2000 °C for 2 h. The composite contained about 3–5% of hollow-structured multi-walled carbon nanotubes (MWNTs) with diameter ranging from 15 to 45 nm and average length of 10 μm. MWNTS were produced by standard chemical vapor deposition process, description of which can be found elsewhere [8].

Composite specimens, with a dimension of $4 \times 3 \times 0.5$ mm, were irradiated at room temperature with 140 keV He^+ ion beam to a fluence ranging from 1×10^{14} to 1×10^{17} cm^{-2}. Irradiated samples were characterized by using techniques such as Raman spectroscopy and transmission electron microscopy (TEM). Raman spectra were excited with He–Ne (633 nm) laser line, and measured in backscattering geometry by using Horiba Jobin–Yvon LabRam IR system with spectral resolution of 1.3 cm^{-1}. The laser power was kept constant to prevent sample heating, and a spatial resolution of 20 μm was achieved using a microscope with a 50× objective lens. All peak parameters were acquired using fits to the Lorentzian line shapes in LabRam Analysis Software. Plain view TEM specimens were examined in a JEOL JEM-2010 electron microscope, equipped with Gatan SC1000 ORIUS CCD camera, operated at an accelerated voltage of 200 kV.

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3. Results and discussion

Fig. 1 shows a high resolution transmission electron micrograph of unirradiated composite. The boron carbide–carbon nanotube interface, marked by an arrow, suggests a good adhesion between CNTs and ceramic matrix. TEM examination over a large area suggested clustering of CNTs in the form of networking in certain regions, and branching of small CNTs from large nanotubes, which might be caused by the sintering process.

Fig. 2 shows Raman mapping of the unirradiated CNT–BC composite. Fig. 2(a) is an optical microscope image of the specimen surface, with the box referring to the mapping domain in which Raman spectra were acquired. The two-dimensional Raman map, obtained by scanning over the box area, is shown in Fig. 2(b). The green, red and blue colors present the integrated signals over different regions of Raman shifts. Fig. 2(c) shows a three-dimensional plot of the mapping region. This 3D map contains two spatial (X and Y coordinates) and one spectral dimensions (intensities of the bands). The pattern observed in an optical image is consistent with the one observed in Raman mapping, which suggests that dispersion of CNTs is not uniform. To determine uniformity of CNTs distribution, Raman spectra were collected from three typical regions marked as 1, 2 and 3, and compared.

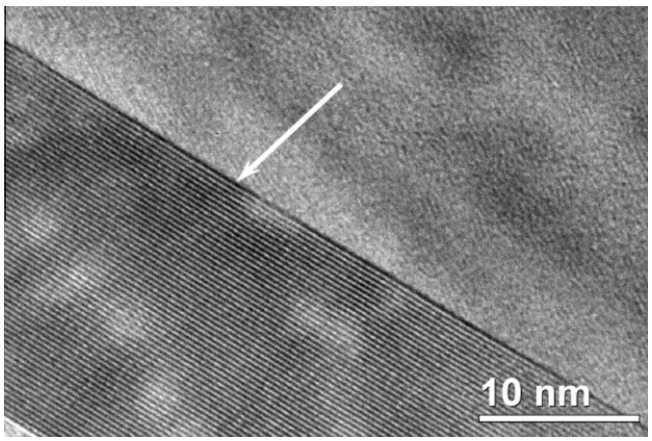

Fig. 1. Transmission electron micrograph of unirradiated CNT-reinforced BC composite. The white arrow marks the BC–CNT interface.

Raman spectra corresponding to three regions marked in Fig. 2(a) are shown in Fig. 3(a)–(c). Raman spectrum of spot located in the dark region (region 1) of the optical image contains bands positioned at 1346, 1593 and 2664 cm^{-1}. These bands are characteristic to CNTs, which implies that the region corresponds to CNTs enriched area. The band at 1346 cm^{-1}, known as D band, is related to the scattering caused by symmetry-breaking defects, and is typically absent in defect free carbon materials [9]. G mode at 1593 cm^{-1} is assigned to zone center phonons of E_{2g} symmetry and is known as an intrinsic vibration feature of sp^2 carbon sheet [9]. Even though G mode is typically referred to as Raman-allowed Γ-point mode, latest studies indicate that its origin is also defect-induced and double-resonant [10]. The band at 2664 cm^{-1} refers to as the D^* band, and is caused by double order resonant Raman scattering process. However, its relevance to defects is still debatable [11,12].

Fig. 3(b) shows the spectrum collected in region 2. CNT's D and G modes are superimposed on a broad spectrum, with a peak at 1090 cm^{-1}. This peak is attributed to BC [13]. The spectrum acquired in region 3 is given in Fig. 3(c). The spectrum has a sharp peak at 1090 cm^{-1} and does not show any distinctive CNTs bands. This supports our observation that region 3 in Fig. 2(a) corresponds to BC, region 1 to CNTs, and region 2 to the boundary of BC and CNT enriched areas.

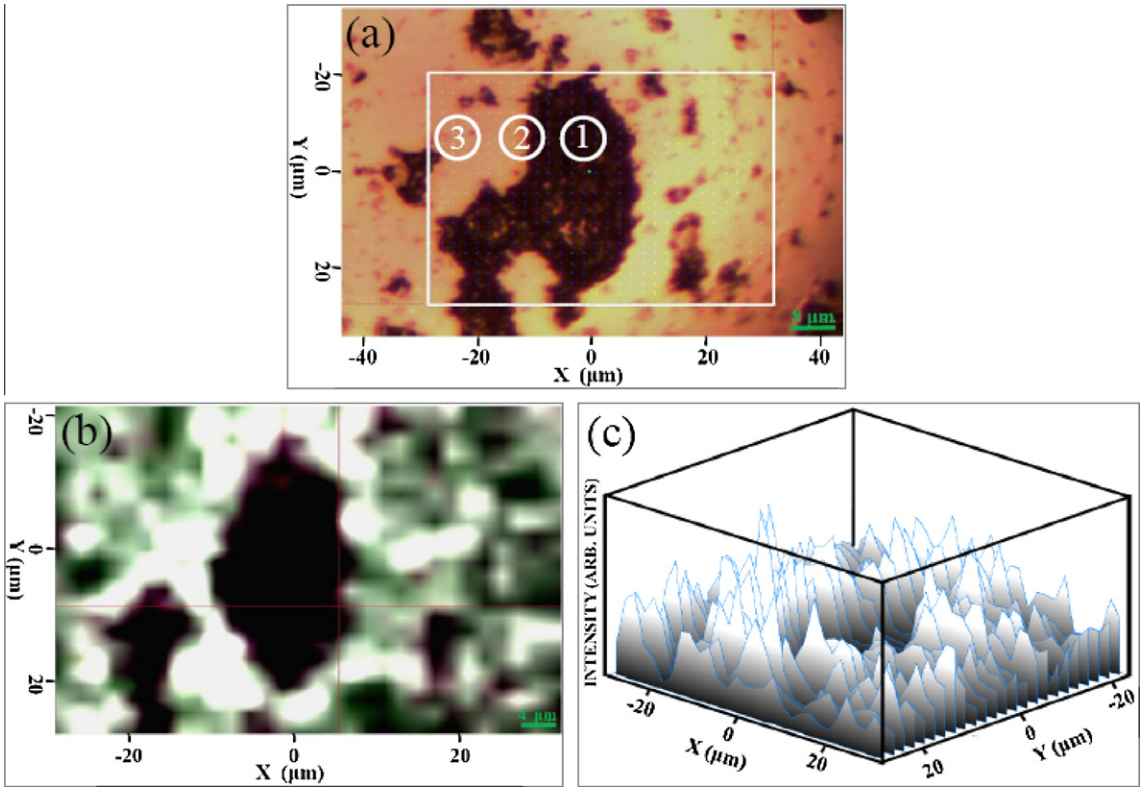

Fig. 2. (a) An optical image of unirradiated CNT-reinforced composite; (b) 2-D Raman map and (c) 3-D Raman map of the region marked by the box.