Cross-sectional Micro-Raman Characterization and Defect Evolution of Nuclear Graphite after 30MeV 107Ag5+ Ion Irradiation at 420℃

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Abstract

In fourth-generation reactors, nuclear graphite serves as a moderator and reflector material in high-temperature and high-flux fast neutron irradiation environments. Fast neutron irradiation generates a large number of Frenkel defect pairs in nuclear graphite. These defects undergo annihilation, diffusion, and eventually form larger defect clusters, thereby altering the microstructure of nuclear graphite, which in turn changes its macroscopic properties. Therefore, studying the defect evolution behavior and mechanisms of nuclear graphite under high-temperature irradiation conditions is of great significance for improving reactor safety. This study employs 30 MeV 107Ag5+ ions to irradiate IG-110 nuclear graphite at 420 °C to simulate the defect evolution behavior of nuclear graphite during fast neutron irradiation. The cross-sectional structure of IG-110 nuclear graphite was characterized by micro-Raman spectroscopy, and the relationship between Raman spectral characteristic parameters at different depths of IG-110 nuclear graphite and irradiation damage dose was compared to investigate the evolution behavior of IG-110 microstructure with irradiation damage dose (DPA, Displacements Per Atom). The results show that with increasing fluence, the characteristic parameters of nuclear graphite Raman spectra—the ratio of D peak height to G peak height (ID/IG), the full width at half maximum of the G peak (FWHM(G), Full Width at Half Maximum of the G peak), and the shift of the G peak—all increase significantly. Compared with 58Ni5+ irradiated samples, under the same irradiation damage dose, the ID/IG and FWHM(G) of the Raman spectra of graphite irradiated with 107Ag5+ are larger. Under the same FWHM(G), the ID/IG of the Raman spectra of graphite irradiated with 107Ag5+ is larger than that of the 58Ni5+ irradiated samples. These results indicate that heavier heavy ion irradiation induces a higher rate of defect accumulation in nuclear graphite, thereby more rapidly reducing graphite grain size and promoting the nanocrystallization process.

Full Text

Preamble

Exploring Defect Evolution in Nuclear Graphite Using Micro-Raman Characterization on the Cross-Section of 30 MeV 107Ag5+ Ion-Irradiated Nuclear Graphite at 420°C

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Abstract

In Generation IV reactors, nuclear graphite serves as both moderator and reflector material in high-temperature, high-flux fast neutron irradiation environments. Fast neutron irradiation generates numerous Frenkel defect pairs in nuclear graphite. These defects undergo annihilation, diffusion, and ultimately form larger defect clusters, thereby altering the microstructure and consequently the macroscopic properties of nuclear graphite. Therefore, investigating defect evolution behavior and mechanisms in nuclear graphite under high-temperature irradiation conditions is crucial for enhancing reactor safety. This study employs 30 MeV 107Ag5+ ions to irradiate IG-110 nuclear graphite at 420°C, simulating defect evolution during fast neutron irradiation. Micro-Raman spectroscopy characterizes the cross-sectional structure of IG-110 nuclear graphite, and the relationship between Raman spectral characteristics at different depths and irradiation damage dose is examined to investigate microstructural evolution with increasing displacement per atom (DPA). Results demonstrate that with increasing fluence, the characteristic Raman parameters—including the D peak to G peak intensity ratio (ID/IG), the full width at half maximum of the G peak (FWHM(G)), and the G peak shift—increase significantly. Compared to 58Ni5+-irradiated samples, graphite irradiated with 107Ag5+ exhibits larger ID/IG and FWHM(G) at the same irradiation damage dose. At equivalent FWHM(G) values, the ID/IG ratio for 107Ag5+-irradiated graphite exceeds that of 58Ni5+-irradiated samples. These findings indicate that heavier ion irradiation induces more rapid defect accumulation in nuclear graphite, leading to faster grain size reduction and accelerated nanocrystallization.

Keywords: Heavy ion irradiation; IG-110 nuclear graphite; Micro-Raman spectroscopy; Defect evolution; High-temperature irradiation; Cross-sectional Raman imaging

1. Introduction

Nuclear graphite possesses excellent properties including high-temperature resistance, radiation tolerance, corrosion resistance, and machinability. Since its successful application in the Chicago Pile I, it has been widely used as an outstanding neutron moderator and reflector material in nuclear reactors [1]. With the rapid development of Generation IV reactors, high-temperature gas-cooled reactors and molten salt reactors also employ nuclear graphite as moderator and reflector materials [2,3]. Although research on nuclear graphite has spanned half a century, renewed emphasis has emerged in recent years due to advances in graphite production technology and higher performance requirements for new reactor designs [4-7], particularly regarding its behavior in high-temperature, high-flux fast neutron irradiation environments [8,9].

Nuclear graphite is typically manufactured from petroleum coke as aggregate particles with coal tar pitch as binder, undergoing kneading, molding, baking, impregnation, and graphitization [10]. During reactor service, fast neutron irradiation generates numerous Frenkel defect pairs in nuclear graphite. These point defects undergo annihilation, migration, and recombination to form larger defect clusters, causing microstructural changes that alter the macroscopic dimensions and properties of graphite components and ultimately affect core lifetime [11]. Therefore, investigating defect and microstructural evolution processes in nuclear graphite under irradiation is necessary to understand irradiation damage mechanisms and improve graphite reactor safety and performance.

Conducting fast neutron irradiation tests in material testing reactors is costly, time-consuming, and produces highly radioactive samples [12]. Ion beam irradiation offers advantages over fast neutron irradiation in test reactors, including faster defect production rates, more precise temperature control (\$±\$10°C) [12], lower residual radioactivity, and greater availability of facilities. Consequently, ion irradiation is commonly used to simulate fast neutron irradiation for studying nuclear graphite damage behavior [13]. Ion irradiation is generally categorized as light ion irradiation (including protons and helium ions) and heavy ion irradiation [12]. Light ions exhibit greater penetration depth and lower sample activation but tend to cause sample heating due to larger electronic energy loss fractions [12]; additionally, light ion irradiation produces smaller cascade collision volumes with sparser defect densities [12]. Heavy ion irradiation provides higher defect production rates and cascade collision dimensions more similar to fast neutron irradiation [14]; moreover, high-energy heavy ion irradiation (typically 4-30 MeV to avoid swift heavy ion effects [15]) can create irradiation damage regions with defect concentration gradients in nuclear graphite. Combined with post-irradiation microstructural analysis of graphite cross-sections, this approach enables investigation of structural evolution across different damage concentrations using a single fluence sample, which is particularly valuable for studying irradiation effects in nuclear graphite with significant property variability [16].

Raman spectroscopy is highly sensitive to defect structures in nuclear graphite, offering high sensitivity and non-destructive analysis capabilities [17], and is frequently used to analyze point defects and defect clusters in graphite materials [18], enabling quantitative assessment of defect density [19]. The D peak in graphite Raman spectra (1360 cm^{-1} with 532 nm excitation) corresponds to the aromatic ring breathing vibration mode [20], which only appears when defects break the crystal symmetry and enable otherwise forbidden phonon transitions. The G peak (1580 cm^{-1}) corresponds to the stretching mode of sp^2-hybridized carbon bonds [21]. Ferrari et al. [18,22] proposed a three-stage model for the evolution from graphite to amorphous carbon based on changes in Raman spectral parameters (ID/IG, FWHM(G), G peak position, etc.). The first stage corresponds to graphite nanocrystallization, where increasing defects and decreasing grain size cause ID/IG, FWHM(G), and G peak position to increase proportionally. The second stage represents graphitic amorphization, characterized by decreasing ID/IG and G peak position while FWHM(G) increases, breaking the linear ID/IG-FWHM(G) relationship as defects increase and graphite gradually amorphizes. The third stage involves transition from amorphous to disordered carbon, with decreasing ID/IG and increasing FWHM(G) and G peak position as further defect accumulation leads to disordering. These Raman parameters are commonly used to describe irradiation defect density and microstructural evolution in nuclear graphite.

Micro-Raman spectrometers coupled with microscope objectives achieve submicrometer spatial resolution, making them ideal for cross-sectional analysis of graphite samples irradiated with high-energy heavy ions, enabling investigation of structural evolution across different irradiation damage doses from a single sample [16]. Our previous work employed 30 MeV 58Ni5+ ions to irradiate nuclear graphite at 420°C, analyzing the irradiated graphite cross-section with micro-Raman spectroscopy to successfully characterize defect evolution patterns at this temperature. However, numerous heavy ion species exist, and at the same energy, increasing atomic number leads to higher average energy transferred to primary knock-on atoms (PKA) and larger cascade collision dimensions, potentially influencing defect evolution processes [14]. Experimental studies on nuclear graphite irradiated with heavy ions of different atomic numbers remain limited, necessitating further investigation.

Building upon our previous work with 30 MeV 58Ni5+ ion irradiation of IG-110 nuclear graphite at 420°C [23], this study employs 30 MeV 107Ag5+ ions to irradiate IG-110 at the same temperature with varying fluences. Micro-Raman spectroscopy characterizes the irradiated cross-sections, yielding two-dimensional Raman mapping. The influence of 30 MeV 107Ag5+ ion irradiation on IG-110 microstructure is investigated using Raman parameters ID/IG, FWHM(G), and G peak shift. Comparative analysis with previous 58Ni5+ results examines how different atomic number ions affect graphite structure across various irradiation damage doses.

1.1 Experimental Materials

This study utilized fine-grained nuclear graphite IG-110 manufactured by Toyo Tanso Co., Ltd., with nominal properties listed in Table 1 . Prior to irradiation, IG-110 samples were cut into 20 × 3 mm (length × width) plates approximately 40 m thick, ultrasonically cleaned in deionized water and acetone to remove surface contaminants, then dried at 120°C in vacuum. Copper fixtures held the graphite samples for convenient handling during irradiation.

1.2 107Ag5+ Ion Irradiation Experiments

Ion irradiation was performed using the 5 MV accelerator at the Dalton Cumbrian Facility (DCF), University of Manchester [24]. A negatively biased suppressor ring between the aperture and sample suppressed secondary electron emission. Ceramic heaters maintained the temperature at 400°C, monitored in real-time by thermocouples and thermal imaging. Thermal imaging revealed that ion beam irradiation increased sample temperature by 20°C, yielding an actual irradiation temperature of 420°C. Defocused 30 MeV 107Ag5+ ion beams provided relatively uniform fluence across samples, with ion fluence determined by measuring sample current. The 107Ag5+ ion was selected based on accelerator capabilities and atomic number, offering greater atomic mass, sufficient penetration depth, and higher damage rates compared to 58Ni5+ ions, facilitating both irradiation experiments and subsequent characterization. IG-110 samples were irradiated with various 107Ag5+ fluences, with detailed irradiation conditions and comparison to previous 58Ni5+ experiments [23] provided in Table 2 .

1.3 Raman Spectroscopy Measurements

Figure 1 [Figure 1: see original paper] schematically illustrates micro-Raman characterization on the cross-section of 107Ag5+-irradiated nuclear graphite. To acquire Raman spectra from the cross-section, irradiated samples were sandwiched between copper blocks, embedded in conductive resin, ground with 3 m sandpaper, and polished sequentially with 1 m sandpaper and 50 nm diamond suspension to ensure a smooth, flat cross-section. After cleaning and drying, samples were characterized using a Renishaw inVia Raman spectrometer with 532 nm green laser excitation in confocal mode (Via Reflex, Renishaw). Raman spectra were collected using 5 mW laser power and 10 s acquisition time to avoid sample damage, with spectral range set to 1000-2000 cm^{-1} to include the D, G, and D' peaks. A 50× objective enabled high spatial resolution line and area scans, achieving approximately 1 m spatial resolution using the micro-XY stage. For two-dimensional mapping, the x-axis (depth direction) step size was 1 m and y-axis (lateral direction) step size was 2 m, producing 20 (depth) × 15 (lateral) pixel images covering a 20 m × 30 m scan area. WiRE 5.1 software fitted the D, G, and D' peaks using Lorentzian-Gaussian mixed functions [25] to extract peak position, height, full width at half maximum, and other parameters for analyzing microstructural changes at various depths.

1.4 SRIM Simulations

SRIM (Stopping and Range of Ions in Matter) software [26] with the full cascade damage model simulated defect distributions, energy loss processes, and implanted ion profiles for 30 MeV 58Ni5+ and 107Ag5+ ions in standard nuclear graphite ICRU-906 (density 2.26 g/cm^3, displacement energy 28 eV).

2. Results and Discussion

Calculated energy loss, defect distribution, and ion implantation profiles for 30 MeV 58Ni5+ and 107Ag5+ ion irradiation of nuclear graphite are presented in Figure 2 [Figure 2: see original paper]. Figure 2(a) shows electronic energy loss versus depth, revealing gradual decrease with increasing depth. The electronic energy loss of 107Ag5+ ions approaches zero at approximately 6.9 m, while 58Ni5+ ions decrease gradually beyond ~8 m. Figure 2(b) displays nuclear energy loss versus depth, with 107Ag5+ peaking at ~116 keV/nm at 6.4 m depth and 58Ni5+ peaking at ~57 keV/nm at 8.2 m depth, attributable to the greater nuclear stopping power of the heavier 107Ag5+ ion. Figure 2(c) shows total energy loss, demonstrating the transition from electronic to nuclear energy loss dominance until complete energy deposition. Figures 2(d) and 2(e) present vacancy and ion distributions: 58Ni5+ induces vacancy and ion peaks at ~8.3 m and ~8.5 m depth, respectively, while 107Ag5+ produces peaks at ~6.7 m and ~7.0 m. The larger nuclear energy loss peak of 107Ag5+ yields higher defect production efficiency (18,265 displacements/ion) compared to 58Ni5+ (9,873 displacements/ion). SRIM calculations also show that 107Ag5+ transfers an average energy of ~3.408 MeV to PKAs, versus ~1.554 MeV for 58Ni5+.

To investigate defect evolution at various depths, micro-Raman line scans were performed along the ion implantation direction on graphite cross-sections. Figure 3 [Figure 3: see original paper] presents normalized Raman spectra, with Figures 3(a) and 3(b) showing line scan results for fluences of 0.3$×10^{16}$ and 0.9$×10^{16}$ ions/cm^2, respectively. Typical Raman spectra at different depths for both fluences are displayed in Figures 3(c) and 3(d). The line scans reveal two distinct regions: a 0-7 m irradiated region within the ion range, and an unirradiated region beyond 7 m. Within the irradiated zone, Raman spectra change significantly with depth, while remaining essentially constant in the unirradiated region.

Typical spectra at the surface, 1 m, 3 m, 5 m, 7 m depths, and unirradiated regions are shown in Figures 3(c) and 3(d). All spectra exhibit prominent D (~1360 cm^{-1}), G (~1580 cm^{-1}), and D' (~1620 cm^{-1}) peaks with relatively independent D and G peaks and low saddle height between them. This indicates that the high-temperature irradiation condition partially anneals radiation-induced defects [28], though complete recovery to the unirradiated state is impossible [29]. Lasithiotakis et al. [30] observed reduced ID/IG after post-irradiation annealing, while Johns et al. [31] reported stable defect generation and recovery during high-temperature neutron irradiation, as vacancies and other defects can

diffuse at elevated temperatures, potentially recombining or forming larger clusters [32]. Consequently, graphite at 420°C maintains relatively good crystalline structure despite irradiation [13].

In Figure 3(c), within the irradiated region (<7 m depth), the D peak intensifies and both D and G peaks broaden with increasing depth, reaching maximum D peak height and FWHM values at ~7 m. Beyond 7 m in the unirradiated region, the D peak remains small and constant. Since increased D peak height and broadening correspond to higher defect concentrations [33], defects increase with depth up to 7 m, matching the simulated defect distribution in Figure 3(e). Figure 3(d) shows identical trends, with maximum D peak height and FWHM occurring at ~7 m depth.

Two-dimensional Raman mapping of the 107Ag5+-irradiated IG-110 cross-section was performed to further investigate microstructural effects. Spectra were fitted by first subtracting a polynomial baseline, then deconvoluting with Lorentzian-Gaussian mixed functions. Typical fitting results for pristine and heavily irradiated regions are shown in Figure 4 [Figure 4: see original paper], where cyan shading represents the removed background, red indicates the D peak, blue the G peak, and green the D' peak. Both unirradiated and heavily damaged regions are well-fitted by these three peaks.

Grayscale maps of various D and G peak parameters (position, area, FWHM, height) are presented in Figure 5 [Figure 5: see original paper] for fluences of 0.3$×10^{16}$ and 0.9$×10^{16}$ ions/cm^2. The maps show left-to-right progression along the ion injection direction, with grayscale values representing parameter magnitudes. Figures 5(a, c, e, g) and (a1, c1, e1, g1) display D peak position, FWHM(D), G peak position, and FWHM(G), all showing maximum brightness at ~7 m depth, consistent with the defect distribution in Figure 2(e). These parameter variations reflect microstructural defect evolution, though boundary curvature may result from the porous structure of artificial nuclear graphite [34]. Nuclear graphite comprises complex arrangements of graphitized coke filler particles and pitch-based binder particles, creating micrometer-scale pores during fabrication [35] that do not affect ion energy loss.

Figures 5(b, f) and (b1, f1) show D and G peak area maps, which exhibit unclear depth dependence and difficulty separating G and D'peaks at high damage levels, making area parameters unreliable for defect analysis [36]. Figures 5(d, h) and (d1, h1) present D and G peak height maps. While D peak height shows weak depth dependence, G peak height maps (Figures 5(h, h1)) clearly distinguish irradiated (darker) and unirradiated (brighter) regions at the 7 m boundary, indicating sensitivity to microstructural changes.

According to the three-stage graphite evolution model [18,22], FWHM(G) correlates with grain size [37,38], with increasing FWHM(G) corresponding to decreasing grain size. The FWHM(G) maps (Figures 5(g, g1)) show significantly broader G peaks in the irradiated region at 7 m depth compared to the unirradi-

ated region, confirming radiation-induced defect accumulation. Higher fluence (Figure 5(g1)) produces larger FWHM(G) in the irradiated zone, indicating more defects and smaller grain size.

The ID/IG ratio quantifies defect density, as the D peak arises from symmetry-breaking defects enabling phonon transitions [22], with larger ID/IG indicating higher defect concentration [37,39]. ID/IG grayscale maps (Figure 6 [Figure 6: see original paper] a, b) were generated by dividing D and G peak heights from Figure 5. Clear boundaries at ~7 m separate higher-ID/IG irradiated regions from lower-ID/IG unirradiated areas. Scatter plots of ID/IG versus depth (Figures 6(c, d)) show peaks at ~7 m for both fluences, decreasing rapidly in unirradiated regions. The 0.9$×10^{16}$ ions/cm^2 fluence yields higher peak ID/IG than 0.3$×10^{16}$ ions/cm^2, indicating more defects, smaller grain size, and nanocrystallization according to the Tuinstra-Koenig model [40], confirming the first stage of graphite structural evolution.

G peak position shifts also reflect defect accumulation, with blue shift indicating increased defects [41,42]. Figure 7 [Figure 7: see original paper] compares heavily irradiated and unirradiated spectra, showing 7 cm^{-1} blue shift for 0.3$×10^{16}$ ions/cm^2 and 17 cm^{-1} for 0.9$×10^{16}$ ions/cm^2, confirming greater defect production at higher fluence [22,43]. Mean G peak position versus depth (Figures 7(c, d)) shows blue shift from 1573 cm^{-1} to 1583 cm^{-1} (0.3$×10^{16}$ ions/cm^2) and from 1580 cm^{-1} to ~1584 cm^{-1} (0.9$×10^{16}$ ions/cm^2), both peaking at the maximum damage depth (~6-7 m). The larger G peak shift at higher fluence corresponds to the first stage of nanocrystallization, corroborating ID/IG and FWHM(G) analyses. Larger deviations at shallow depths (~1-2 m) may result from phenolic resin effects and higher background noise affecting peak fitting.

To compare defect accumulation between different heavy ions, depth-dependent defect concentrations were converted to DPA using Equation (1):

$$DPA = \frac{Vacancies \times Fluence}{10 \times Density}$$

where Vacancies represents average vacancies per ion per unit depth, Fluence is ion fluence (ions/cm^2), and Density is atomic density (atoms/cm^3).

Figure 8 [Figure 8: see original paper] compares ID/IG and FWHM(G) versus DPA for 107Ag5+ and 58Ni5+ irradiations (58Ni5+ data from previous work [23]), limited to DPA $\leq$ 6 for comparison. Both ID/IG and FWHM(G) increase with DPA, but 107Ag5+ shows faster growth rates. At ~6 dpa, 107Ag5+ yields ID/IG 1.34 and FWHM(G) 55.18 cm^{-1}, while 58Ni5+ produces ID/IG 1.08 and FWHM(G) 48 cm^{-1}. At equivalent DPA, 107Ag5+ irradiation generates larger ID/IG and FWHM(G) in IG-110, indicating higher defect accumulation efficiency. From a cascade collision perspective, 107Ag5+ transfers higher average energy to PKAs (~3.408 MeV) than 58Ni5+ (~1.554 MeV), producing larger cascade volumes and more defects [14,45]. From electronic energy loss

perspective, higher electronic energy loss promotes defect annealing and stability [27]. SRIM calculations show 58Ni5+ has higher average electronic energy loss (~29.481 MeV) than 107Ag5+ (~29.052 MeV), resulting in more defect annealing during 58Ni5+ irradiation. These combined factors cause 107Ag5+ to produce more defects than 58Ni5+ at the same DPA. Gawęda et al. [46] similarly observed higher ID/IG for heavier Ar+ versus He+ irradiation, confirming that heavier ions generate more defects.

The continuous increase of ID/IG and FWHM(G) with DPA without saturation indicates that the irradiated graphite remains in the first stage of the three-stage evolution model [18,22], characterized by nanocrystallization [39,47]. Increasing irradiation dose generates numerous PKAs and cascade collisions, creating defects within and between graphene layers [14], such as interlayer atoms, spiral dislocations, prismatic edge dislocations [48], and layer buckling, breaking, and wrinkling [49-51]. Defect accumulation and grain size reduction drive graphite nanocrystallization.

Figure 9 [Figure 9: see original paper] plots ID/IG versus FWHM(G) for both irradiations, with linear fits summarized in Table 3 . For 107Ag5+, FWHM(G) ranges from ~30-60 cm^{-1} with a fitted slope of 0.02058. Unirradiated regions show FWHM(G) of ~20-26 cm^{-1}. Both irradiation datasets follow the graphitization trend line [13], confirming that graphite maintains relatively intact crystalline structure during the first-stage nanocrystallization process. At equivalent FWHM(G), 107Ag5+ irradiation yields higher ID/IG than 58Ni5+, indicating more microstructural defects, higher accumulation efficiency, smaller grain size, and accelerated nanocrystallization.

3. Conclusions

This study investigated the effects of 30 MeV 107Ag5+ ion irradiation on nuclear-grade graphite IG-110 at 420°C using Raman spectroscopy. Combined with SRIM simulations validating damage depth profiles, analysis of ID/IG, FWHM(G), and G peak position yielded the following conclusions:

1. 30 MeV 107Ag5+ ion irradiation creates a ~7 m thick defect layer in nuclear graphite. Cross-sectional Raman analysis enables investigation of defect evolution across a damage gradient (0-6 dpa) within a single sample.
2. At 420°C irradiation temperature and damage doses up to 6 dpa, ID/IG, FWHM(G), and G peak position increase with fluence. According to the three-stage graphite evolution model, the graphite structure remains in the first stage, with decreasing grain size and progressive nanocrystallization. Linear fitting of ID/IG versus FWHM(G) for both 107Ag5+ and 58Ni5+ irradiations confirms that the graphite maintains good crystalline structure during this nanocrystallization stage.
3. At equivalent DPA, 107Ag5+ irradiation produces larger ID/IG and FWHM(G) than 58Ni5+ irradiation, indicating that heavier ions with

more nucleons exhibit higher defect accumulation efficiency in nuclear graphite, leading to more rapid nanocrystallization.

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Author Contributions

Li Yiyan: Data processing and analysis, manuscript drafting and final revision; He Zhoutong: Experimental design and feasibility analysis, overall planning and revision; Zhao Xiuliang: Framework guidance and revision; Peng Shancheng, Ma Huilei: Sample testing.

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Note: Figure translations are in progress. See original paper for figures.