Mater. Res. Soc. Symp. Proc. Vol. 1298 © 2011 Materials Research Society
DOI: 10.1557/opl.2011.497

Responses of Carbon Onions to High Energy Heavy Ion Irradiation

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ABSTRACT

We report evidence for graphene layer rearrangements in heavy ion interactions with carbon onions at 140 MeV and 70 MeV per nucleon kinetic energies. Graphene layer rearrangements have been recently predicted in spherical and cylindrical multi-layer graphene systems. The implications of graphene layer rearrangement on the tribological performance of multi-layer nano-carbons in extreme environments are discussed.

INTRODUCTION

Nano-carbon materials including carbon onions [1], C_{60} [1], carbon nanotubes [2], and graphene [3] are under investigation as nano-property enabled solid lubricants that maintain performance in extreme environments. An extreme environment for lubricants exists whenever the following stressors are present, either singly or in combination: radiation, vacuum and thermal stress. Space satellites and particle colliders are examples of applications in which radiation, vacuum, and thermal stress can seriously degrade current state-of-the-art lubricant performance. Many well publicized failures, including stuck bolts on the Hubble Space Telescope that required space-walk intervention, or accelerated wear and failure of soft gold electrical contacts at the Large Hadron Collider, can be traced back to the failure of current state-of-the-art lubricants due to radiation, vacuum and thermal stress.

The potential for nano-carbon materials is that, first, they demonstrate low friction coefficients in vacuum, where oil, grease [4] and graphite [5] solid lubricants can fail. The best vacuum tribological performances amongst the nano-carbon materials investigated by our group have been achieved with carbon onions (multiple layer concentric fullerene shells) and with multiwalled carbon nanotubes [1,2]. Single walled carbon nanotube and C_{60} films displayed evidence of aggregation, leading to film discontinuities and lubrication failure. Second, theoretical work indicates that nano-carbon materials have high tolerances for thermal stress [6,7]. Therefore, nano-carbons materials have great potential as solid lubricants in space and particle collider applications if they also display radiation resiliency.

In the present work, the responses of multiwalled carbon nanotubes and carbon onions to heavy ion irradiation at the National Superconducting Cyclotron Laboratory (NSCL) at Michigan State University were investigated. Heavy ions are a highly penetrating component of both the space and particle collider environments. The heavy ions used in these experiments were fully stripped Krypton-78, Calcium-48 and Argon-40 primary beams with 140 or 70 MeV per nucleon kinetic energies. We find evidence that multiwalled carbon nanotubes and multi-layer carbon onions respond to heavy ion irradiation with linking of neighboring graphene layers rather than knock-on collision generated amorphitzation. A possible mechanism based on dislocation migration [8] is discussed.

EXPERIMENTAL PROCEDURES

Synthesis Conditions:

Multiwalled carbon nanotube samples were prepared by humidity-enhanced arc synthesis with proprietary post-synthesis cleaning at the NASA Goddard Space Flight Center. Three sets of carbon onion samples were prepared at Tokyo Institute of Technology from crystalline diamond nanoparticles having an average diameter of 5 nm. The diamond nanoparticles were heated in inert ambience in an infrared gold image furnace. A graphite holder filled with 10 mg of diamond nanoparticles was placed inside the furnace, which was evacuated to approximately 1.3 Pa with a rotary pump, and slowly heated in argon gas flow at 1.5×10^5 Pa to 1700°C, 2000°C and 2300°C, respectively. The furnace temperature was held for one minute and then gradually cooled to room temperature in argon flow. These temperatures in the stated conditions produced the known [9] spherical to polygonal transition of carbon onion morphology as a function of synthesis temperature. The carbon onion temperature series enabled investigation of the effects of bond hybridization on heavy ion interactions at relativistic energies.

Irradiation Parameters:

Krypton-78, Calcium-48 and Argon-40 primary beams with initial kinetic energies of 140 MeV/nucleon (MeV/u) were used for irradiation times that resulted in 10,000 Gray (Joule/kg) cumulative total doses for each sample. The Calcium-48 experiments were also performed with an initial kinetic energy of 70 MeV/u to investigate possible energy-time inequivalence for the same total dose. For each experiment, the on-target beam energies subsequent to passage through a 0.075 mm zirconium (Zr) exit window, a 420-500 mm air gap (exactly measured for each run), and a 0.2 mm quartz cover slip were calculated using the Stopping and Ranges of Ions in Matter (SRIM) Monte Carlo program. After passage through stripper foils and the Zr exit window, almost all ions were fully stripped to +78, +48 and +40 respectively, making these particle highly charged compared to particles from ion implantation or focused ion beam sources. Further details and the on-target beam energies for each experiment are given in the Experimental Results.

The experiments were performed in the Single Event Effects Testing Facility (SEETF) at the NSCL, a facility specifically designed for heavy ion investigation of materials and electronics for space applications. A remotely controlled moveable stage, camera, and laser positioning system enabled irradiation of multiple samples without the need for vault access beyond the initial experimental set-up. In each experiment, a beam spot of approximately 2 x 2 cm^2 was centered using the laser positioning system on a sample that was less than 1 cm in diameter and separated from other samples by at least 5 cm. The mass of each sample was determined prior to irradiation using a Denver Instruments M-220D scale with 0.01 mg sensitivity. The approximate area and thickness of each sample was measured with Mitutoyo CD-6"CS electronic calipers with 10^{-3} mm accuracy. The experimentally measured dimensions and densities were used in the SRIM calculations to determine the required exposure times to achieve a 10,000 Gray (Gy) total dose.

Analytical Techniques

HRTEM experiments were performed in a JEOL 2200FS operated at 200 kV. Samples were suspended in ethyl alcohol and dispersed onto carbon lacey film 200 mesh copper grids (SPI). Care was taken to acquire images from samples that were well suspended over holes and not the carbon lacey film.

EXPERIMENTAL RESULTS

Effects of 140 MeV/u Krypton-78 on Multiwalled Carbon Nanotubes:

Relativistic heavy ion interactions with multiwalled carbon nanotubes were investigated using a primary beam of Krypton-78 with an on-target beam energy of 124.8 MeV/u. A typical pre-irradiation multiwalled carbon nanotube structure had 5-10 well-defined graphene layers with minimal layer breaks around a hollow core, as shown in Figure 1(a). A representative post-irradiation specimen is shown in Figure 1 (b). A new configuration that links the two innermost layers has occurred. The overall number of graphene layers also appeared to increase to 12-20 in most post-irradiation specimens.

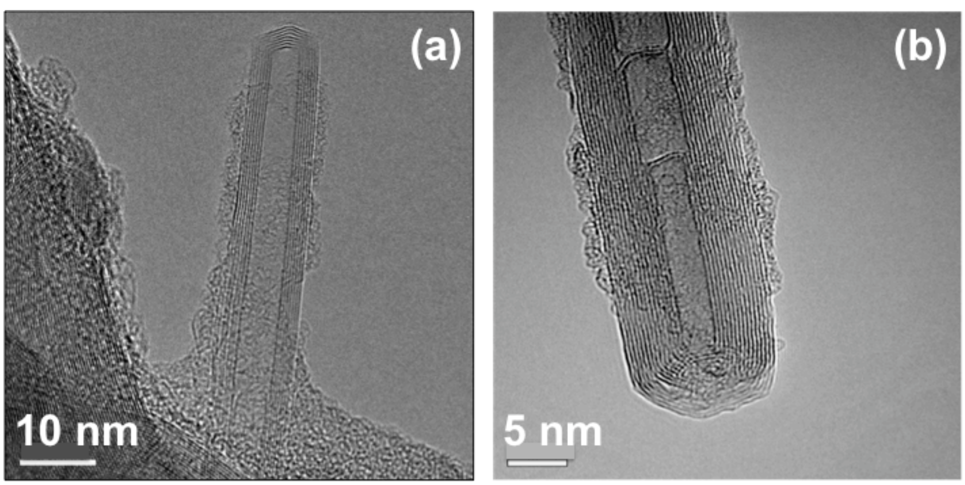

Figure 1. Multiwalled carbon nanotubes (a) pre-irradiation and (b) post-irradiation by 140 MeV/u Krypton-78.

Effects of 140 MeV/u Argon-40 on Temperature Series Carbon Onions:

Relativistic heavy ion interactions with carbon onions synthesized at 1700°C, 2000°C and 2300°C, were investigated using a primary beam of Argon-40 at 140 MeV/u with an on-target beam energy of 134.0 MeV/u. HRTEM images of the pre-irradiation synthesis temperature series are shown on the left in Figure 2 (a-c). Carbon onions synthesized at 1700°C were spherical with defective graphene shells, while carbon onions grown at 2300°C were polygonal with well-defined graphene sp^2 layers connected by sp^3 vertices. HRTEM images of the corresponding post-irradiation samples are shown on the right in Figure 2 (d-f). The 1700°C carbon onions showed an increase in the overall defective appearance and fusion of contiguous onion pairs (arrow). The 2000°C carbon onions showed fewer layer breaks in individual graphene shells and an overall increase in number of graphene layers. The 2300°C carbon onions showed the greatest variety of rearrangements, with development of large crystallites of planar graphite, long, 5-7 layer planar graphene ribbons and occasional amorphous regions. The HRTEM image of Figure 2 (f) is an electron transparent corner of a large graphite crystallite.

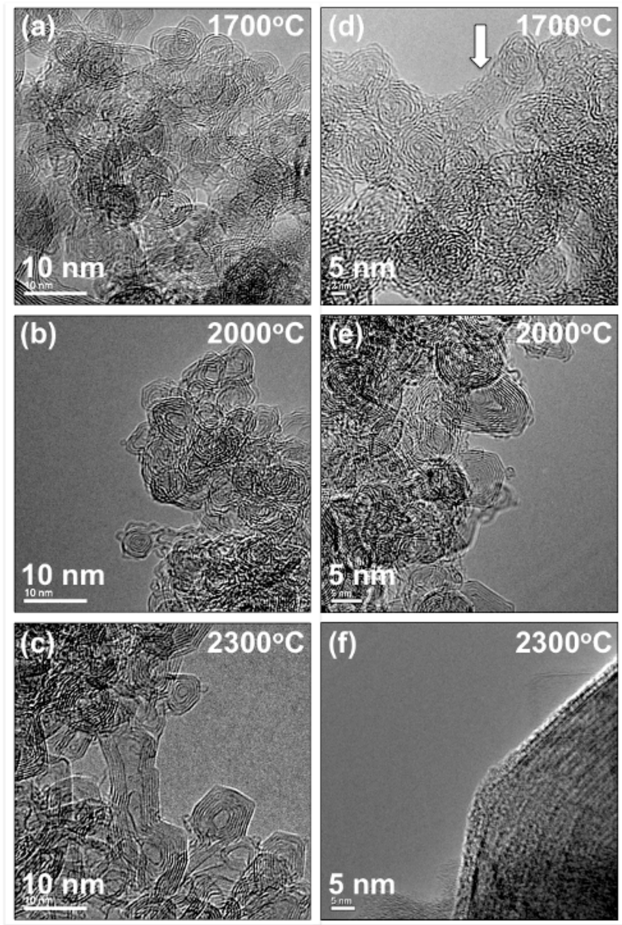

Figure 2. HRTEM of carbon onions synthesized at temperatures 1700°C, 2000°C and 2300°C for (a-c) pre and post (d-f) irradiated by 140 MeV/u Argon-40.

<u>Effects of 70 MeV/u versus 140 MeV/u Calcium-48 on 1700°C Carbon Onions:</u>

Relativistic heavy ion interactions with carbon onions synthesized at 1700°C were investigated using a primary beam of Calcium-48 at energies 140 MeV/u with an on-target beam energy of 134.5 MeV/u, and also 70 MeV/u with an on-target beam energy of 60.52 MeV/u. HRTEM images of the pre-irradiation 1700°C and also 2300°C carbon onions are reproduced in the top row of Figure 3 (a-b). HRTEM images of the post-irradiation 1700°C carbon onions are shown in the bottom row of Figure 3 (c-d). At both energies, the post-irradiation 1700°C carbon onions displayed a polygonal structure similar to that observed for pre-irradiation carbon onions synthesized at the higher 2300°C temperature. They also showed a decrease in the number of layer breaks in individual graphene shells compared to the pre-irradiation 1700°C carbon onions, especially those irradiated at the lower energy.

DISCUSSION

Heavy ion interactions with carbon materials are generally assumed to proceed through carbon displacement or "knock-on" collisions. In planar graphite, displacement collisions result in inter-layer aggregation of displaced carbon atoms into wedges, which eventually force the layers apart causing a local amorphous region. However, the anticipated effects of knock-on collisions were not observed in these experiments. The major effect observed was linking of neighboring graphene shells into new arrangements. Individual carbon nanotubes and onions appeared to have increased numbers of graphene layers without corresponding decrease in radius (agglomeration). Total rearrangements such as fused carbon onions, and long 5-7 layer graphite ribbons were also observed. For 2300°C carbon onions irradiated by on-target 134.0 MeV/u Argon-40, a few large graphite crystallites developed in addition to long ribbons and what appeared to be the fusion of multiple neighboring onions. The number of layer breaks in individual graphene shells appeared to decrease compared to the pre-irradiation structures, for both onions and nanotubes and the fused rearrangements. By this measure, the post-irradiation structures were less defective than the pre-irradiation structures.

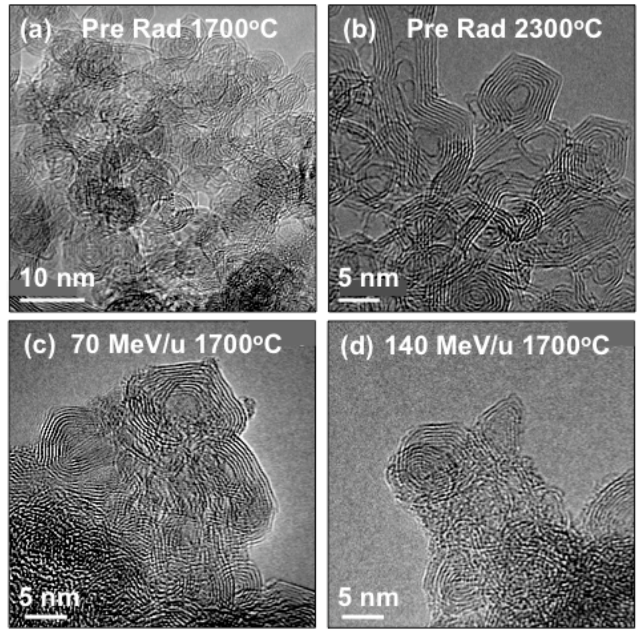

Figure 3. Pre-irradiation carbon onions synthesized at (a) 1700°C and (b) 2300°C. Post irradiation 1700°C carbon onions at irradiation energies of (c) 70 MeV/u and (d) 140 MeV/u Calcium-48 resemble 2300°C pre-irradiation carbon onions.

New theoretical work suggests that inequivalent outer/inner dislocation loops are possible in multilayer spherical and cylindrical structures that are not present in planar graphite [8]. Furthermore, these can enable dislocation migrations that can result in the unzipping and re-zipping of neighboring graphene layers, which is the result that we observe.

Energy loss calculations by our group (to be published separately) indicated that heavy ion interactions including knock-on collisions and bond ionization should have been comparatively rare at the140 MeV/u and 70 MeV/u energies for all of the primary beams and nano-carbon materials investigated. The radiation effects described in the present work were typical. In general, the amount of energy required for dislocation migration is much less than the amount of energy required for knock-on collisions or for bond ionization. We have also analyzed over a hundred pre-irradiation specimens by HRTEM during the synthesis and tribological characterization experiments, in addition to the radiation effects experiments. We have not observed any structural changes induced by TEM electron irradiation on the time scale (minutes) of our investigations.

The present observations of graphene layer rearrangements in an energy regime where little interaction would be expected may be a physical manifestation of the new predicted dislocation migration pathways in multi-layer carbon nanotubes and carbon onions. Graphene layer rearrangement could have both positive and negative implications for the tribological performance of multi-layer nano-carbons in a heavy ion radiative environment. Ongoing rearrangement into nano-carbons that retained the good tribological features of the originals would be a self-healing way of dealing with radiation–induced defects. However, rearrangements that resulted in the formation of planar graphite could have negative consequences for tribological performance.

The new nano-carbon options extend the range of possible solid lubricants for the vacuum and radiation environments of space and particle colliders. Further investigation of the fundamental nature of the observed responses to heavy ion irradiation is ongoing.

ACKNOWLEDGEMENTS

The authors thank the NSCL operations staff for providing the beams and their technical support. This research was supported by the National Aeronautic and Space Administration under Grant No. NAG 5-12735, the NASA Graduate Student Researchers Program Fellowship, by the Advanced Degree Program at Saudi Aramco, and by the National Science Foundation under Grant No. PHY-0110253.

REFERENCES

1 A. Hirata, M. Igarashi, and T. Kaito, "Study on Solid Lubricant Properties of Carbon Onions Produced by Heat Treatment of Diamond Clusters or Particles", Tribology International 37: 899–905 (2004).

2 A. Hirata and N. Yoshioka, "Sliding Friction Properties of Carbon Nanotube Coatings Deposited by Microwave Plasma Chemical Vapor Deposition", Tribology International 37: 893–898 (2004).

3 C.L. Lee, X. Wei, Q. Li, R. Carpick. J.W.Kysar, J. Hone, "Elastic and Frictional Properties of Graphene", Phys. Status Solidi B 246: 2562-2567 (2009)

4 N. Ohno, S. Mia, S. Morita, and S Obara, "Friction and Wear Characteristics of Advanced Space Lubricants ", Tribology Transactions, 53: 249-255 (2010)

5 P.J. Bryanta, P.L. Gutshalla and L.H. Taylora, "A study of mechanisms of graphite friction and wear", Wear 7: 118-126 (1964)

6 S. Berber, Y-K. Kwon, and D. Tománek, "Unusually High Thermal Conductivity of Carbon Nanotubes", Phys. Rev. Lett: 84, 4613 (2000)

7 D. Baowan, N. Thamwattana and J. M. Hill, "Continuum modelling of spherical and spheroidal carbon onions", Eur. Phys. J. D: 44, 117 (2007)

8 E. Akatyeva, J.Y. Huang, and T. Dumitrica, "Edge-Mediated Dislocation Processes in Multishell Carbon Nano-Onions?", Phys. Rev. Lett. 105: 106102 (2010)

9 O.O. Oleksandr, Y.M. Solonin, D.N. Batchelder and R. Brydson, "Transformation of Nanodiamond into Carbon Onions", J. Appl. Phys: 97, 074302 1-16 (2005)