Formation of Carbon Nanotubes in a Microgravity Environment

J. M. Alford[1], G.R. Mason[2], and D.A. Feikema[3]
[1,2]TDA Research, Inc., 12345 W.52 Ave., Wheat Ridge, CO 80033
[3]NASA Glenn Research Center

Introduction

Because of their potential as new materials, there is currently a large interest in the synthesis and characterization of carbon nanotubes. Carbon nanotubes were first discovered in 1991 by Iijima[1] who observed the presence of nanometer sized multi-walled carbon nanotubes (MWNTs) on the graphite electrodes used for fullerene production. Addition of a transition metal catalyst was subsequently shown to produce single-walled nanotubes[2] (SWNTs) such as the C_{60} sized nanotube illustrated in Figure 1. Unlike conventional carbon fibers, the SWNT structure is atomically perfect, thus producing defect free fibers that have many unique electronic and physical properties[3]. For example, with a predicted Young's modulus of ~1 Tera-Pascal, SWNTs represent the strongest known type of carbon fiber and form the ideal basis for new composite materials. Calculations show that a carbon nanotube-based cable could have one hundred times the strength of steel while having just one-sixth of the weight. Carbon fiber composites made from nanotubes would save significant weight in spacecraft and aircraft structures. In addition to their mechanical properties, nanotubes also have interesting electronic properties, which are dependent upon the tubes morphology. Some tubes have conducting electronic structures and can be envisioned as molecular "quantum" wires, while others are semiconducting and can be used to fabricate the world's smallest "single molecule" transistors. The development of field effect transistors and memory elements made from SWNTs has been demonstrated. Other promising uses for SWNTs include tips for atomic force microscopy (AFM) and hydrogen storage.

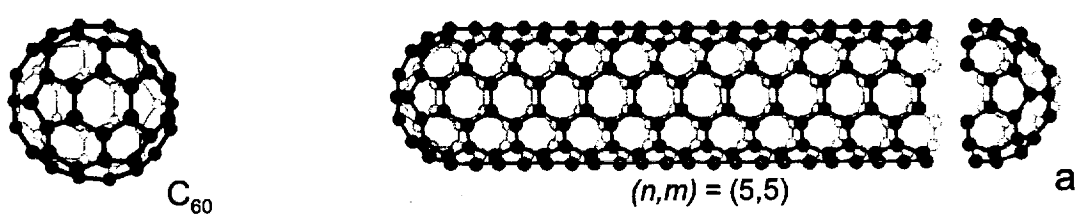

Figure 1. Comparison of C_{60} fullerene and its single-walled nanotube analogue.

To date, most investigations have concentrated on determining the physical properties of the tubes, and very little is known about the fundamental processes involved in nanotube formation. The current nanotube synthesis processes are poorly understood and can only produce small quantities of nanotubes that are less than ~100 microns in length. These sizes and quantities have enabled the successful investigation of electronic devices, but meaningful composite materials research has been severely hindered. If industrial amounts of tubes 10-100 times longer, 1-10mm, could be efficiently produced, then commercial applications in new composite materials would become much more favorable. The key to developing better production processes is to gain a better understanding of the nanotube formation process. Thus, the goal of this investigation is to use microgravity processing to improve our understanding of the nanotube formation process and allow us to produce superior single-walled carbon nanotubes (SWNTs).

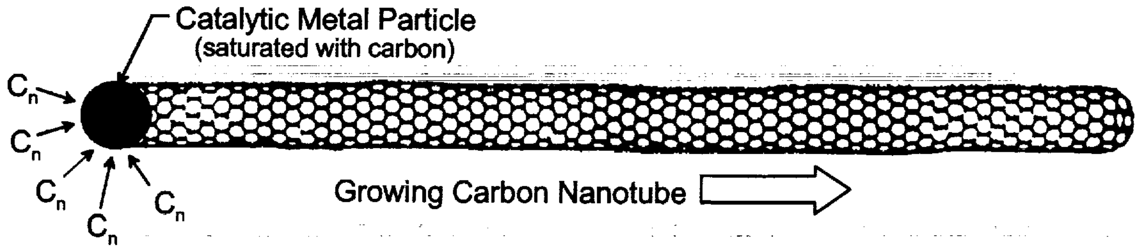

Figure 2. Catalytic growth of a SWNT.

There are currently several methods for the production of single-walled carbon nanotubes, including: the carbon arc[6], laser vaporization of graphite[7], chemical vapor decomposition[8] (CVD), high pressure disproportionation of CO[9], and flame synthesis[10]. All rely on catalytic growth of the nanotube from either carbon or hydrocarbon vapor in the presence Co/Ni or other transition metal catalysts as shown in Figure 2. As vaporized carbon (or hydrocarbon) and metal catalyst atoms cool, they condense into small nanometer sized clusters that continually collide and grow. When the metal carbide clusters produced from the transition metal catalyst become super-saturated with carbon, the carbon re-crystallizes as a nanotubes. The metal particle remains on the head of the tube and channels the remaining carbon it encounters into the tube. Studies performed on the vapor plume produced during laser ablation of graphite suggest that nanotube growth can continue as long as the catalyst particle remains saturated with carbon and the temperature remains high enough for carbon to efficiently diffuse through the particle[11].

The two most common and well-characterized processes for nanotube production are the carbon arc and laser ablation method. Both are gas phase processes that resemble the formation of soot during combustion processes. Buoyancy is known to have a large effect on soot formation, and we hypothesize that the same is also true for nanotube formation. Both processes vaporize carbon in a high temperature (5000-10000 °C) plasma that induces strong convective flows. In arc reactors, large convection currents are readily observed and explain the wide variation in reported operating conditions[12] and why the quality of nanotube deposits varies greatly depending on their position in the apparatus. The formation of a nanotube is undoubtedly a strong function of the time/temperature/concentration history of the growing tube and its precursors, and buoyancy produces an uncontrolled environment that makes estimation and optimization of these critical factors difficult. Microgravity conditions provide a much more controlled environment for measurement, modeling, and optimization of these parameters.

Experimental

The carbon arc method was selected as the basis of our microgravity apparatus because it is simpler and provides a greater amount of carbon vapor than the laser method. However, several challenges were presented in moving the carbon arc from the production lab to the drop tower. The typical carbon arc apparatus[6,12] employs large 6-12 mm diameter electrodes and consumes several kilowatts (or more) of power that is supplied continuously from a large welding power supply. The metal catalyst required to produce SWNTs is introduced by simply drilling holes in the electrodes and packing them with metal powder. During operation, the arc gap is usually adjusted manually while observing the arc through a viewport. Substantial innovation was required to adapt this configuration to a drop tower rig while maintaining a production rate high enough to produce meaningful quantities of nanotubes.

A schematic of the mini arc we developed is shown in Figure 3. The carbon electrodes are now downsized to ~0.5 mm while the absolute power was decreased to about 1 KW for the 2.2 second drop time. Note however, that the power density for the cross-sectional area of the electrode is now much higher than the larger arc machines, and this "mini-arc" actually produces more nanotubes per second than its bigger brethren. A new impregnation method was developed to dope the rod with Ni/Y metal catalyst, and the arc gap is now continuously adjusted with a spring-loaded electrode. Power for the arc is supplied by a large (0.5 F) capacitor bank that is charged to 60 volts prior to each drop. Before producing nanotubes, the reaction chamber is purged of air by pumping to vacuum and then filled with Ar at 600 torr. The arc vaporizes ~10 mg of carbon during each 2.2 second run, and the resulting SWNTs agglomerate into web like fibers that are easily observed and collected for analysis.

The results of our initial tests now allow a comparison of the arc plasma at normal gravity and microgravity, Figure 3. The observed behavior is remarkably similar to a sooting flame. At 1g, the development of a convective jet that carries the resulting nanotube soot to the top of the chamber is readily apparent. Under microgravity, the behavior of the plasma resembles a weightless sooting flame and the nanotubes form at the spherical boundary of the reaction zone. Several of the microgravity tests produced good yields of nanotubes that are currently being analyzed and compared to the 1g runs using high resolution scanning and transmission electron

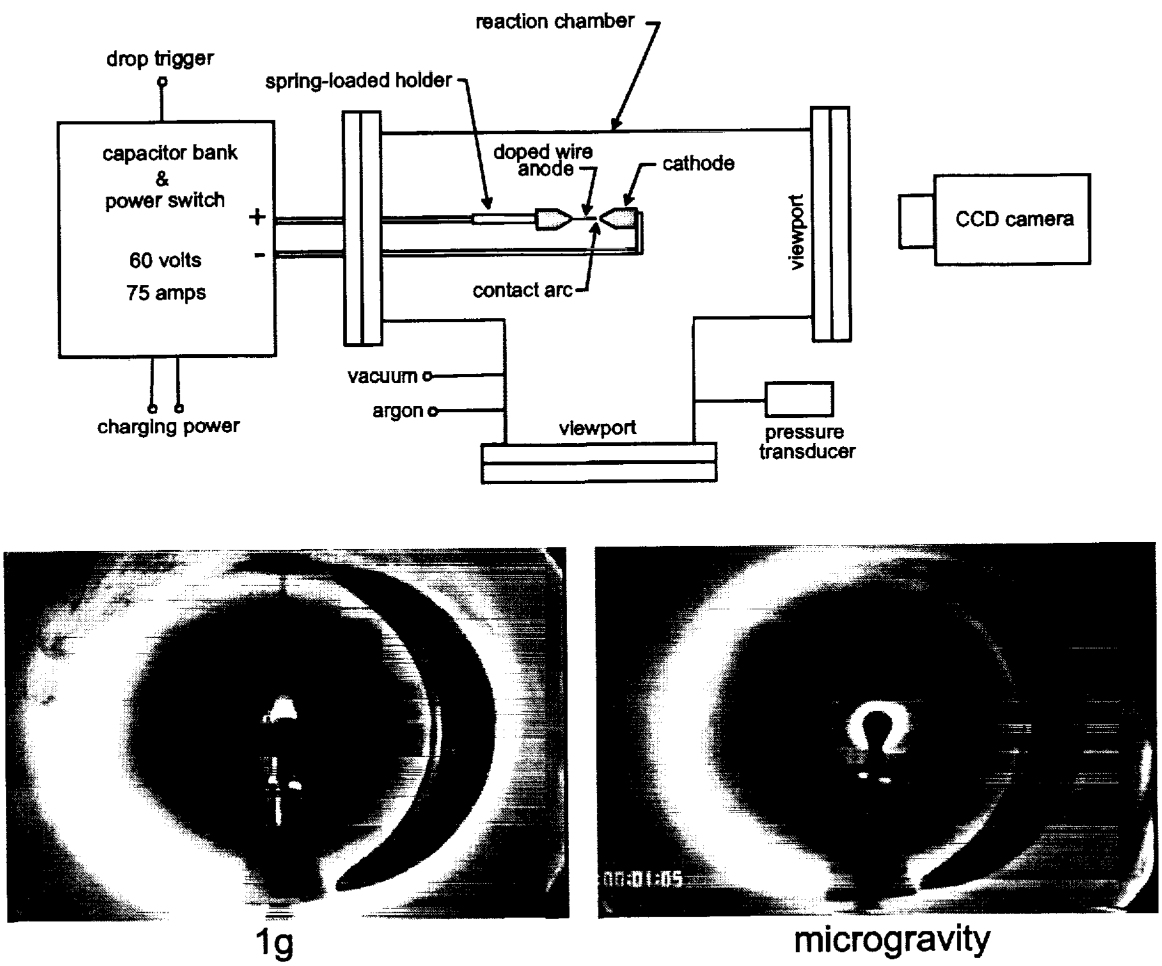

Figure 3. Apparatus schematic and video stills illustrating the difference between the 1g arc and the microgravity arc.

microscopy. When this testing is completed, the production process will be optimized. The ultimate goal is to obtain a controlled, spherically uniform reaction zone in which rapid nanotube growth can be sustained undisturbed for the entire drop time of 2.2 and eventually 5 seconds.

Summary

Even though nanotube science has become one of the worlds most rapidly advancing areas of research, very little is known about the processes involved in nanotube synthesis. To study the formation of carbon nanotubes in an environment unhindered by the buoyancy induced flows generated by the high temperatures necessary to vaporize carbon and grow nanotubes, we have designed a miniature carbon arc apparatus that can produce carbon nanotubes under microgravity conditions. During the first phase of this project, we designed, built, and successfully tested the mini carbon arc in both 1g and 2.2 sec drop tower microgravity conditions. We have demonstrated that microgravity can eliminate the strong convective flows from the carbon arc and we have successfully produced single-walled carbon nanotubes in microgravity. We believe that microgravity processing will allow us to better understand the nanotube formation process and eventually allow us to grow nanotubes that are superior to ground-based production.

References

(1) S. Iijima, *Nature* **354** (1991) 56.

(2) (a) S. Iijima and T. Ichihashi, *Nature* **363** (2000) 603. (b) D.S. Bethune, C.H. Kiang, M.S. de Vries, G. Gorman, R. Savoy, J. Vazquez, and R. Beyers, *Nature*, **363** (2000) 605.

(3) The following reviews and references therein provide a good introduction into the current issues in carbon nanotube production, their physical properties, and applications. (a) P. Ajayan, *Chem. Rev.* **99** (1999) 1787. (b) T.W. Ebbeson (Ed.) *Carbon Nanotubes, their Preparation and Properties*, CRC Press, Boca Raton, FL, 1997. (c) R. Satio, M. Dresselhaus, G. Dresselhaus *Physical Properties of Carbon Nanotubes*, Imperial College Press, London, 1998. (d) B.I. Yakobson and R.E. Smalley, *American Scientist* **85**, (1997) 324.

(6) Journet, C., W.K. Maser, P. Bernier, A. Loiseau, M. Lamy de la Chapelle, S. Lefrants, P. Deniard, R. Lee, and J.E. Fischer, *Nature* **388** (1997) 756.

(7) T. Guo, P. Nikoleav, A. Thess, D.T. Colbert, and R.E. Smalley, *Chem. Phys. Lett.* **236** (1995) 419.

(8) J.F. Colomer, C. Stephan, S. Lefrant, G. Van Tendeloo, I. Willems, Z. Konya, A.Fonseca, Ch. Laurent, and J.B. Nagy, *Chem. Phys. Lett.* **317** (2000) 83.

(9) R. Dagani, *Chem. Eng. News* **78** (2000) 78.

(10) (a) R.L. Vander Wal, T.M. Ticich, and V.E. Curtis, *Chem. Phys. Lett.* **323** (2000) 217. (b) M.D. Diener, N. Nichelson, and J.M. Alford, *J. Phys. Chem. B* **104** (2000) 9615.

(11) (a) A.A. Puretzkey, D.B. Geohegan, X. Fan, and S.J. Pennycook, Appl. Phys A. **70** (2000) 153. (b) F. Kokai, K. Takahashi, M. Yudasaka, and S. Iijima, *J. Phys Chem B* **104** (2000) 6777.

(12) (a) Z. Shi, Y. Lian, F.H. Liao, X. Zhou, Z.Gu, Y. Zhang, S. Iijima, H. Li, K.T. Yue, and S. Zhang, *J. Phys. Chem. Solids.* **61** (2000) 1031. (b) Y. Ando, X. Zhao, K. Hirahara, K. Suenaga, S. Bandow, and S. Iijima, *Chem. Phys. Lett.* **323** (2000) 580. (c) A. Huczko, H. Lange, and T. Sogabe, *J. Phys. Chem. A* **104** (2000) 10708.