POSTER

NANOTUBES AND NANOENCAPSULATES MADE THE OLD-FASHIONED WAY

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Introduction

In recent years there has been significant interest in carbon molecules (fullerenes) and carbon clusters (nanotubes and nanoencapsulates) produced by evaporation-condensation processes such as carbon arc discharge. On the other hand, carbon clusters have been formed for many years from carbon-containing gaseous compounds by deposition on catalyst metals. We have produced various carbon deposits by catalytic carbon monoxide disproportionation at temperatures around 500°C, and subjected them to high-resolution electron microscope analysis. Nanotubes and certain nanoencapsulates thus made "the old-fashioned way" are directly comparable to those produced by arc discharge. This presentation will discuss some interesting aspects of catalytic carbon formation, with an emphasis on the role of hydrogen.

Catalytic Formation of Filaments

The most common form of carbon deposition studied in the literature of the last four decades has been the filament. A filament consists of a tubular carbon cluster formed when various hydrocarbons or carbon monoxide are decomposed in the presence of a catalyst [1]. Small faceted particles are broken away from the bulk catalyst metal, and are carried by the growing cylindrical 'tails' of graphitic carbon. A diagram of a typical filament as it appears in a transmission electron microscope (TEM) is given in Fig. 1. Note that the graphite basal planes are not parallel to the axis of the filament. Filaments shown in the literature have a variety of orientation angles between basal planes and the filament axis.

The mechanism of filament growth is believed to consist of several steps [2]:

- Catalytic decomposition of the gas precursor at the leading edge of the metal particle,
- diffusion of carbon through the particle, and,
- ordered precipitation of carbon to add another conical graphite layer to the filament.

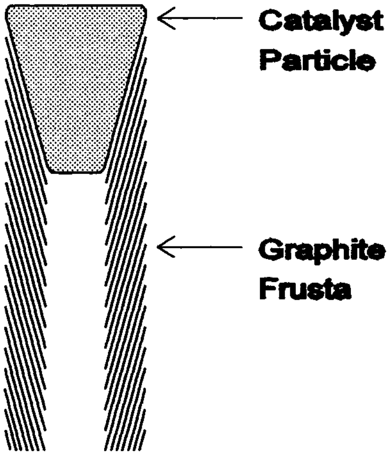

Figure 1. Illustration of the cross-sectional appearance of a carbon filament.

Carbon Nanotubes

Nanotubes differ from filaments by their graphite orientation: the basal planes are parallel to the tube axis. An example of a nanotube as it may appear during growth is illustrated in Fig. 2. The growth mechanism of nanotubes is not understood.

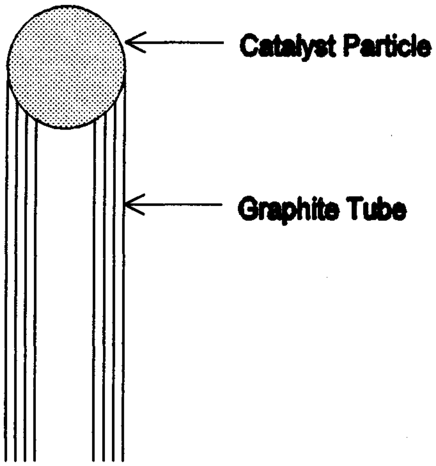

Figure 2. Cross-section of a carbon nanotube, with a catalyst particle shown at its end. Typical tube radius is 10 nm.

Encapsulating Carbon

Another graphitic formation consists of 'shells' of carbon encapsulating the catalyst particle. Called nanoencapsulates, these carbon formations are generally spherical in shape. They appear as metal particles with several layers of graphite surrounding them [3]. A feature that nanoencapsulates have in common with nanotubes is that there are no open graphite plane edges, such as those on the outside (and inside) of filaments.

Discussion

The primary factor that determines whether filaments with open graphite edges, or nanotubes and shells with no open edges are formed appears to be the availability of hydrogen during deposition [4]. The partial pressure of hydrogen and reaction temperature determine whether open edges can form. Hydrogen can serve to satisfy valences at graphite edges. Increasing the amount of H_2 in a CO/CO_2 gas mixture can thus govern the graphite orientation, from nanotubes to filaments--with increasing angle between the orientation of graphite basal planes and the axis of the tube. TEM micrographs of this phenomenon will be shown. Raising the temperature de-stabilizes the carbon-hydrogen bonds, causing nanotubes and nanoencapsulates to form at temperatures above about 600 °C, even in the presence of small amounts of hydrogen. Hydrogen may derive from many sources, e.g., water.

The carbon formations that can be produced under specific catalytic deposition conditions show promise for industrial applications. Nanoencapsulates can serve as ultra-fine magnetic particles. Nanotubes can be used to produce composites with tailored properties of thermal and electrical conductivity, or material strength. The ability to set the graphite orientation in tubular formations by regulating the hydrogen presence during carbon deposition should allow direct control over their stress/strain properties.

Additional information on the mechanisms of catalytic nanotube and nanoencapsulate growth, and kinetics of formation of the different carbon clusters, will be presented based on our latest data.

Acknowledgement

Primary funding for this work was provided by the UA/NASA Space Engineering Research Center.

References

1. R. T. K. Baker and P. S. Harris. In *Chemistry and Physics of Carbon* (Edited by P.L. Walker and P.A. Thrower) Vol. 14, pg. 83-165, Marcel Dekker, New York (1978).
2. R. T. Yang and L. P. Chen, *J. Catal.* **115**, 52 (1989).
3. J. Guinot, M. Audier, M. Coulon, and L. Bonnetain, *Carbon* **19(2)**, 95 (1981).
4. P. E. Nolan, M. J. Schabel, D. C. Lynch, and A. H. Cutler, *Carbon* **33**, 79 (1995).