

Direct Observation of the Growth of Helical and Spiral Graphite Nanofibers

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ABSTRACT

Controlled atmosphere electron microscopy (CAEM) has been used to directly observe the growth characteristics of graphite nanofibers from the metal catalyzed decomposition of hydrocarbons. From such studies it has been possible to gain a unique insight into some of the factors that influence the manner by which the catalyst particles influence the structural aspects of the nanofibers. Using this approach it is possible to obtain not only qualitative information, but also derive detailed kinetic data from analysis of the recorded sequences. Based on these investigations we have developed a mechanism that highlights the key steps involved in the growth of graphite nanofibers. When the reaction is performed over certain bimetallic particles the nanofibers are observed to grow in either helical or spiral conformations. A video recording of such sequences will be shown and a discussion of the role of the catalyst in such processes.

Key Words: In-situ TEM, Catalytic growth of Graphite Nanofibers, Spiral and Helical Structures.

1. INTRODUCTION

The existence of graphite nanofibers has been known for several decades [1,2], however, it is only in recent years that the materials have attracted tremendous research interest. Some of the early studies were stimulated by the need to understand the growth mechanism of this type of carbon since its accumulation on metal surfaces presented serious problems with respect to the efficient operation of a number of commercial processes [3-6]. Baker and his co-workers used controlled atmosphere electron microscopy (CAEM) to directly observe the formation of carbon nanofibers from the decomposition of hydrocarbons over supported metal particles. From the recorded sequences it was possible to derive the detailed growth kinetics and identify the rate-controlling step in the process [7,8]. Based on this information a growth mechanism was postulated to describe the manner by which the metal particles catalyzed the growth of carbon nanofibers. In the ensuing years the key features of this mechanism, the solubility and diffusion of carbon through the catalyst particle were used in the development of a treatment to inhibit the accumulation of coke on steam cracker tubes [9].

While many of the earlier investigations in this field focused on the specific chemical nature of the catalytic entities and the specific features surrounding the driving force for nanofiber growth [10-15], little research effort was devoted to exploiting the potential of these unusual materials on a commercial scale. The notion of harnessing the mechanical properties afforded by the incorporation of graphite nanofibers in composite structures was reported by Downs and Baker in 1991 [16] and later detailed in subsequent publications [17,18]. Since that time there have been numerous papers and reviews presented in the literature expounding on the

benefits to be derived from utilizing carbon nanotubes and nanofibers for a variety of applications [19-23].

The realization that the data derived from surface science studies performed at low temperatures and low pressures could be used to explain the behavior of hydrocarbon-metal interactions taking place under more extreme conditions has provided the key to being able to manipulate the conformation of graphite nanofibers [24,25]. It has been demonstrated that differences in both the structural and chemical characteristics of the catalytically generated carbon are totally dependent upon the nature of the metal catalyst and can be readily understood from a consideration of the wetting properties of the particles on a graphite surface. Metals that exhibit a strong interaction with graphite will generate highly ordered structures whereas those having a weak interaction will produce structures that will have an amorphous form. It has also been shown that in order for dissolved carbon to be precipitated in a highly crystalline form, there must be a registry between the interstitial spacing of the metal atoms at this interface and the atomic spacing of carbon atoms in graphite [26]. A further feature to emerge was the finding of an intimate link between the role of the metal catalyst in carbon deposition and in hydro-gasification of carbon [27].

In this paper we have focused attention on the growth characteristics of helical and spiral forms of graphite nanofibers. These unusual conformations are believed to originate from perturbations in the diffusion characteristics in the metal catalyst particle that are induced by the presence of sulfur, phosphorus, copper or tin additives that introduce an element of asymmetry into the system [28-34].

2. EXPERIMENTAL

The experiments reported in this paper were performed in a modified JEOL 2000EXII transmission electron microscope. This instrument is equipped with a custom-designed environmental cell, which accommodates a heating stage. Using this arrangement it is possible to heat specimens at a controlled rate up to a temperature of 1000°C while, at the same time being exposed to a gas environment at pressures up to 5.0 Torr. The resolution of this instrument when used in conjunction with a high-sensitivity closed-circuit television camera is better than 0.4 nm [35]. The dynamics of the gas-solid reaction occurring at the specimen surface are displayed on a TV monitor and continuously recorded on videotape. Information from the tapes was measured by frame-to-frame analysis and the rates of motion of various events evaluated as a function of temperature. As a consequence, one can observe changes in quantitative features and also carry out detailed quantitative kinetic studies of events of interest.

The experiments described in this paper were carried out by observing the interaction of graphite supported metal particles with 2 Torr acetylene as the temperature was progressively raised to 900°C. For this purpose, various metals and alloys, in the form of spectrographically pure wires, were deposited onto transmission sections of single crystal graphite (~50nm thickness) by evaporation from a heated tungsten filament at a residual pressure of 10^{-6} Torr. By careful control of the weight of the wire and distance between the filament and the specimen it was possible to produce a metal coating of approximately one monolayer in average thickness. The gases utilized in this work, acetylene, hydrogen and helium were obtained from Scientific Gas Products with stated purities of 99.99% and were used without purification.

3. RESULTS AND DISCUSSION

When samples of graphite supported metal and bimetallic films were initially treated in 1 Torr hydrogen nucleation into discrete particles was observed at temperatures ranging from 200 to 275°C. It was significant to find that as the temperature was gradually raised so the particles underwent a structural reconstruction from a globular to a faceted morphology. Figure 1 is an example of this behavior showing the hexagonal-shaped appearance of copper-nickel particles during reaction with hydrogen at 425°C. When acetylene was introduced into the reactant mixture the ensuing sequence of events was dependent upon a number of factors, including the chemical nature of the catalyst, the strength of the metal catalyst particle-support interaction and the composition of the reactant gas. Under conditions where the interaction between the two components was relatively weak then the nanofiber growth resulted in the relocation of the catalyst particle from the support to the carbon structure, as depicted in the schematic diagram Figure 2. In this model the catalyst particle and carbon diffusion characteristics adopt a symmetrical geometric pattern that results in the growth of relatively straight nanofibers.

Single metal catalyst systems tended to produce nanofibers where the particle remained at the growing tip of the structure, which formed via a whisker-like mode.

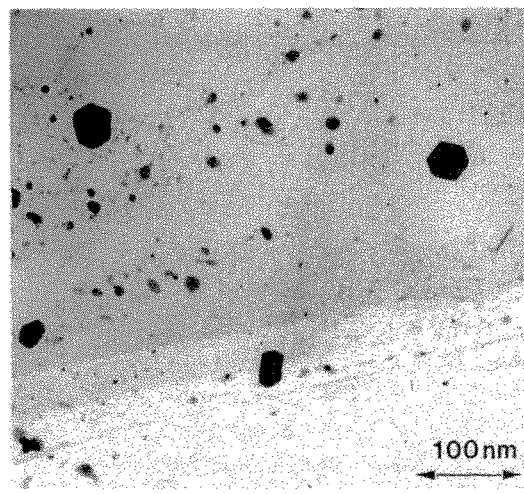


Figure 1. Reconstruction of Cu-Ni particles into highly faceted crystallites following treatment in H_2 at 425°C

Under conditions where a strong metal-support interaction existed then the catalyst remained attached to the support throughout the nanofiber growth sequence. In this case, the nanofiber was formed by an extrusion mode and during growth metal fragments from the catalyst were dispersed within the nanofiber structure.

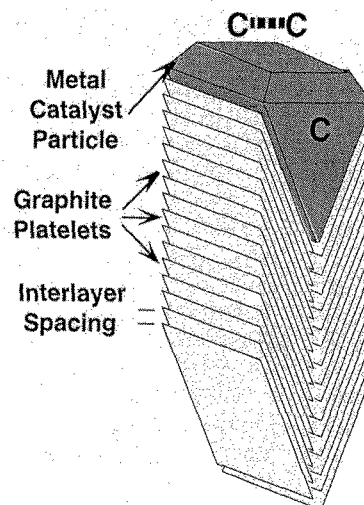


Figure 2. Schematic diagram showing the major steps involved in the symmetrical growth of "whisker-like" nanofibers

In systems where the active catalytic entity was a bimetallic or contained a non-metal additive and a weak interaction existed between the catalyst particle and the support, the nanofibers grew in a bi-directional mode. In this type of nanofiber conformation the particle was located within the carbon structure. Under these circumstances, it was frequently found that the presence of such additives in the catalyst particle introduced an element of asymmetry into either the dissociative chemisorption or carbon diffusion steps and as a consequence, there was a strong tendency for the nanofiber to develop a helical or spiral morphology as seen in Figure 3.

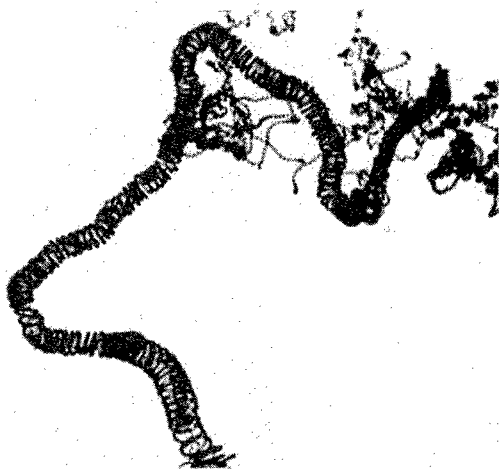


Figure 3. TEM micrograph showing the appearance of a helical nanofiber

From the dynamic observations of the bi-directional growth sequences several fascinating features were revealed. Quantitative kinetic measurements showed that the rate of growth of each nanofiber leg was identical. Furthermore, any imperfection introduced into one section was replicated in the corresponding location in the opposite leg. Figure 4 is an electron micrograph showing the duplication of structural features in a helical carbon nanofiber either side of the catalyst particles whose locations are marked by arrows. Based on these observations one may conclude that there are two equal and opposite diffusion paths through the bulk of the catalyst and any perturbations that exist during the growth period are distributed throughout the particle in a uniform fashion.

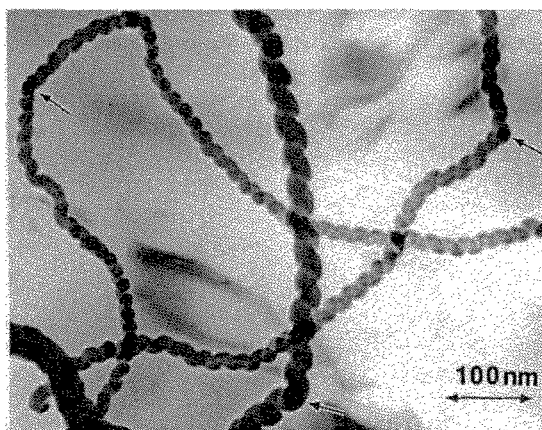


Figure 4. TEM micrograph showing the existence of matching defects on either side of catalyst particles in spiral GNF structures

Growth rate curves of individual nanofibers produced from decomposition of acetylene over various catalyst systems at 700°C are presented in Figure 5. Examination of the sigmoidal shaped curves reveals the existence of three distinct regions; an initiation step followed a period of constant growth and finally, a gradual deactivation step.

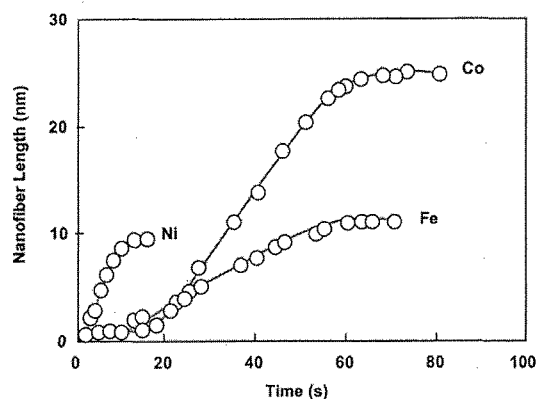


Figure 5. Growth rate curves for nanofibers generated from the interaction of selected metal particles with acetylene at 700°C

At any given temperature the rate of nanofiber growth is faster from small catalyst particles than larger ones. A plot of the rate of nanofiber elongation as a function of catalyst particle size reveals the existence of an inverse square root dependence, which is indicative of a diffusion-controlled reaction, Figure 6.

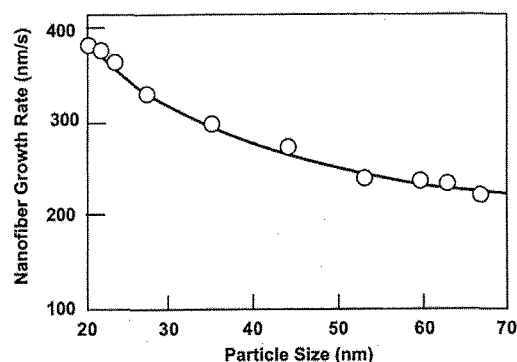


Figure 6. Variation of the rate of nanofiber growth as a function of metal catalyst particle size

Table I. Comparison of measured activation energies for nanofiber growth with those for carbon diffusion through the corresponding metal/alloy catalysts

Catalyst	Ea (kcal/mol)	
	GNF growth	Carbon Diffusion
Ni	34.7	33.0-34.8
α-Fe	16.1	12.5-16.5
β-Fe	33.9	33.3-37.4
Co	33.2	34.4
Cr	27.1	26.5
Mo	38.8	39.7-41.0
Fe-Ni	33.6	34.0
Cu-Ni	34.6	34.8
Fe-Sn	33.9	34.2
Ni (sulfur)	34.7	33.0

By measuring the rates of nanofiber growth from similar sized catalyst particles as a function of temperature it was possible to derive apparent activation energies for the process. It was found that the measured activation energies were in excellent agreement with

those reported for carbon diffusion through the corresponding metals and alloys, Table 1. These findings are consistent with the postulate that carbon diffusion through the bulk of the catalyst particle is the rate-controlling step in the nanofiber growth process.



Figure 7. Bright-field TEM micrograph of a highly crystalline spiral nanofiber

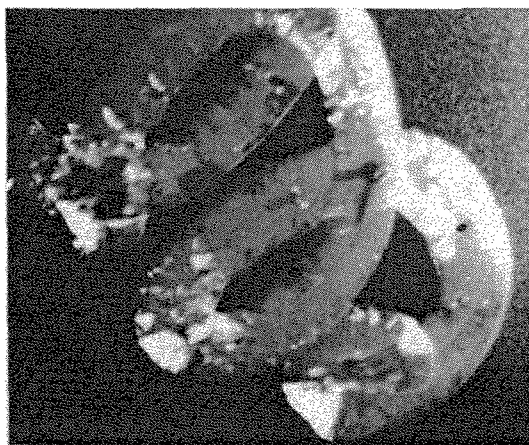


Figure 8. Corresponding dark-field TEM image of the spiral nanofiber shown in Figure 6

One of the intriguing questions that demand an answer is whether one can induce changes in the behavior of the catalyst particles via external methods. Clearly one can increase the rate of nanofiber growth by merely increasing the temperature. Care must be taken during such a step to ensure that this procedure does not result in a modification of the particle crystallography, a phase change or preferential surface segregation of one of the components. Other options that should be addressed are the influence of magnetic fields on the nanofiber growth characteristics. In this regard one must be cognizant of the fact that an in-situ TEM reaction facility the sample is directly exposed to the magnetic fields generated by the electromagnetic lens system of the instrument. As a consequence, under such conditions one might expect to observe some unusual nanofiber growth characteristics.

High-resolution TEM examination has revealed some interesting aspects regarding the structural characteristics of some types of spiral nanofibers. A

schematic rendition of the arrangement of the graphite sheets constituting the structure is presented in Figure 9. A close scrutiny of the interlayer spacing between adjacent graphite sheets indicates that while the value will be about 0.34 nm in the central section of the structure, the spacing at the exposed edge regions will be significantly wider. This arrangement holds some intriguing possibilities for the storage and separation of various gas molecules.

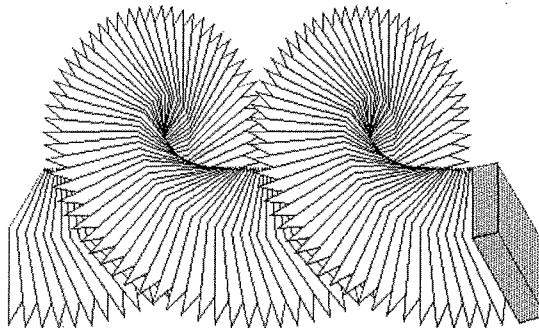


Figure 9. Schematic rendition of spiral nanofiber where the interlayer spacing at edges is wider than that at central regions

4. SUMMARY

It is evident that following careful choice of the correct catalyst and reaction conditions one can engineer the structure of graphite nanofibers to any desired architecture. The ramifications of this capability are that one can design a nanofiber structure for a particular application. It is anticipated that the incorporation of helical or spiral nanofibers into a polymeric matrix will result in not only an enhancement in the mechanical properties, but also the furnish the composite with electrical conductive properties. The commercial potential for these unusual carbon nano-materials is very exciting.

5. REFERENCES

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(Received October 11, 2003, Accepted December 15, 2003)