Synthesis and characterization of graphite nanofibers deposited on nickel foams

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Nickel foams were used as catalysts to dissociate acetylene and deposit carbon atoms. Graphite nanofibers with distinct structures were developed at 550°C with nickel foams pretreated with hydrogen. HREM observations showed that the graphite layers of the nanofibers were aligned at a certain angle to the fiber axis. It is suggested that hydrogen treatment and metal catalysts have a tremendous impact on the yields and microstructures of the graphite nanofibers. The growth mechanism of these fish-bone graphite nanofibers is also discussed.

Introduction

Since graphite nanofibers (GNFs) were discovered in the 1970s, much attention has been given to their synthesis and characterization. They consist of concentric graphite layers which are oriented at various angles to the nanofiber axis, while the interlayer spacings are similar to that of bulk graphite. It is well known that GNFs can be prepared by the catalytic decomposition of hydrocarbons or carbon monoxide on the surface of certain metals, such as Fe, Co, Ni and some of their alloys, in a hydrogen atmosphere. The orientation of the graphite layers of catalytically produced GNFs can be controlled by the choice of catalyst (as well as the shape of the catalytic particles) and other parameters such as the time and temperature of their preparation. Through manipulation of various parameters, Rodriguez et al. have produced a variety of fibrous structures ranging from "tube-like" to "ribbon-like" arrangements, which possess a small cross-sectional area, estimated to be on average 50 nm, combined with an abundance of exposed edges. Oberlin et al. observed turbostratic graphite structures when using Fe catalysts to decompose benzene under a hydrogen atmosphere at a temperature of 1100°C.

A structure of graphite-like layers packed at an angle of approximately 45° to the filament axis (so-called "fish-bone" structure) was also found, whereas the GNFs produced on Ni-based catalysts possessed single-filament structures with one metal particle on the "head" of the graphite nanofibers. It was found that this kind of GNF has tremendous potential as a hydrogen storage system. Another structure was also observed when GNFs were produced on Ni-Cu catalysts, here the graphite layers were oriented perpendicularly to the filament axis. In addition, Chen et al. found that the segmented GNFs prepared on nickel foams looked like a line of lens-like segments with nearly equal separation, consisting of well-ordered graphite layers intermediately stacked perpendicular to the filament axis. The catalysts mentioned above were mostly developed in laboratories, the process sometimes being complex and repetition difficult, while nickel foams can be easily obtained commercially rather than being prepared personally. In our

Experimental

Nickel foams (purchased from Shenyang, China) 1.26 mm thick were used as catalysts in this study. A molybdenum boat containing a piece of nickel foam was put into the middle of a quartz tube while the tube furnace was heated to a determined temperature (550°C-700°C). The nickel foams were either treated with flowing hydrogen for a period of time or were untreated. Acetylene was then introduced into the quartz tube as the carbon source. The flow rates of acetylene, hydrogen and nitrogen were 100, 50 and 600 scnm (standard cubic centimetre per minute) respectively. The products deposited on the catalyst at 550°C were found to contain graphite nanofibers of high purity. TEM (JEOL-200CX), HREM (Philips CM200 UT), SEM (AMRAY 1840), co-focus microscopy (ALMEGA, Nicolet) and XRD (XRD-98) were used to study the morphology, microstructure and crystallinity of the as-prepared GNFs.

Results and discussion

In this work, nickel foam was a new type of catalyst to produce GNFs with fish-bone structure. Therefore, different reaction temperatures (550°C-700°C) were first applied to find a suitable temperature at which acetylene could be dissociated to synthesize the GNFs. It was found that 550°C was the preferred temperature. When the reaction time was short (<2 h) or the temperature was high (>650°C), the catalyst was found
to retain its original shape, only loosened and turned black, which meant that under these conditions the acetylene was not fully dissociated and no desired GNFS were found. When the temperature was relatively low (550 °C), there was no trace of the “bulk” nickel foam, it had all turned to powder while the volume was more than 30 times that of the original nickel foam. TEM investigations proved that the final product was closer to GNFS (Fig. 1a). However, the product was not well crystallised and was composed of small pieces of amorphous segments.

It should be emphasized that the results mentioned above were all obtained with nickel foams that had not been exposed to a hydrogen flow. According to ref. 1–6, most GNFS deposited on Fe, Co or Ni were synthesized in the presence of hydrogen. Therefore, to examine the influence of hydrogen treatment on the GNFS growth, the hydrogen was introduced into the tube furnace to pretreat the nickel foams. The treatment temperature and growth temperature were held at 550 °C. The time of treatment with hydrogen was varied (40 min, 90 min and 6 h, respectively for samples A, B and C) and the effect of this on the morphology and microstructure of the GNFS is discussed.

1 The effects of hydrogen treatment time on the growth of GNFS

1.1 TEM and HREM studies. TEM and HREM were both used to study the morphology and microstructure of the GNFS. From the TEM observations (Fig. 1b,c and d), it was found that once the catalysts had been treated with hydrogen, they became more suitable to grow GNFS and the GNFS turned out to be more uniform as the treatment time was increased. Considering the results in more detail, in Fig. 1b for sample A, there was still a large quantity of congeries which were probably amorphous carbon fibers, while others were thick GNFS of about 300 nm in diameter which were assessed to occupy 20 vol% of the sample. The result was almost the same in Fig. 1c except that the quantity of GNFS in sample B increased to about 40 vol% and the diameter of the GNFS could vary from 100 to 300 nm, not quite as thick as sample A. As the hydrogen treatment time increased to 6 h, much longer GNFS were synthesized, as shown in Fig. 1d, where the quality of the GNFS was found to be better with smoother walls, more uniform diameters and no evidence of the other less ordered forms of carbon. They were also found to have a unique structure by HREM and selected area electron diffraction (SAED), shown in Fig. 2. One part of the HREM image (Fig. 2b) is magnified in the right-hand corner of Fig. 2.

HREM studies (Fig. 2a and b) revealed that the nanofibers have the so-called “fish-bone” structure that consists of worm-like graphite layers at a certain angle to the fiber axis in the beam projected direction, which was consistent with the SAED pattern (Fig. 2f). If the graphite layers of the sidewalls of the GNFS were parallel or perpendicular to the fiber axis, the (002) type reflections of the pattern would only have two segments (one pair) symmetrically at the two sides of the central spot. The SAED pattern in Fig. 2f shows four segments (two pairs) and therefore it can be concluded that the graphite platelets were neither parallel nor perpendicular but at an angle to the fiber axis. Detailed measurement on the SAED pattern established that the projected angle between two of the graphite platelets is about 46°, thus the angle between the graphite platelets and the fiber axis is about 23°. Fourier transformation of a different part of the HREM image (Fig. 2a) of the GNF further confirmed the above results (Fig. 2c, d and e). It should be mentioned here that there is little in the literature describing such a particular pattern when mentioning fish-bone structures, and this SAED pattern was not only found in one GNF, but in all randomly oriented GNFS observed by TEM, which implies that their graphite layers formed a conical (or with a polygonal cross-section) structure along the fiber axis. In addition, it suggests that the unique conformation of GNFS with graphite platelets at an angle to the fiber axis and exposed edges on the sidewall provides this material with unique properties that are highly desirable for gas sorption applications, such as hydrogen sorption.

Although similar structures have also been found in other graphite fibers and even some minerals such as serpentinides and their microstructure and diffraction aspects have been fully analyzed in detail, it is still not yet known whether the GNFS with fish-bone structure are composed of scroll or concentric graphite layers.
1.2 Mechanism. The above studies indicate that hydrogen and its treatment time play an important role in the synthesis of GNFs using nickel foam as a catalyst. For example, when there was no hydrogen treatment of the nickel foam, no GNFs were formed (Fig. 1a), but when the catalysts were exposed to hydrogen for 6 h, GNFs with a fish-bone structure (Fig. 2) and in good yields could be obtained. These results led us to consider the mechanism of the synthesis in the presence of hydrogen.

Nickel foams are like sponges that have many micropores and a large surface for catalytic reactions. During the reaction process, the micropores offer the main passages for the molecules of reactant and product to move and diffuse. Therefore, in order to react favorably, the micropores should not be blocked. It is also known that most catalysts which are stored or used for long periods show a decrease in activity and after some time become useless. This phenomenon is called deactivation. There are many causes of catalyst deactivation which include fouling and poisoning. Fouling means deposition of reactor debris, such as scale and rust, on the particles. At the best, these materials may clog the outside of particles, plugging pores and blocking active surfaces. At the worst, the particles are cemented together, resulting in a loss of void space within the reactor and complicating catalyst removal. Poisoning is a chemical effect in which a poison is any agent that reacts permanently with an active site. Poisoning may be reversible or irreversible, regenerable or not, depending on the type of poison, catalyst, and service. If it is regenerable, one of the methods is to treat it with pure hydrogen or a hydrogen-containing stream. In our case, hydrogen is used mainly to activate the catalysts in the process. Furthermore, nickel tends to oxidize when exposed to air, and hydrogen can reduce the oxidation, resulting in an increase in the number of nickel particles.

The above arguments are confirmed by SEM investigation of an untreated nickel foam (Fig. 3a) and of nickel foam treated with hydrogen for 6 h (Fig. 3b). The arrow in Fig. 3a shows the active particles of the nickel foams. Comparing the two images, it is clear that the density of active particles in the hydrogen-treated nickel foam is higher than in the untreated nickel foam. This reveals that hydrogen, as a reductive gas, has activated the catalyst, resulting in a different product of the catalytic process. Moreover, the morphology and microstructure of the treated catalysts should also be different from the untreated catalysts.

In addition, different temperatures (500°C-650°C) were adopted to grow GNFs, where the catalysts had been treated with hydrogen for 6 h. It was also found both by TEM and macroscopic observations that a temperature between 550 and 600°C was the preferred temperature. Products prepared outside this range were either conglomerates of amorphous carbon.
or of low purity and poor yield. Below 550°C the temperature was too low to effectively activate the nickel foams, while above 600°C, the catalysts were easily sintered resulting in the undesirable products.

According to the research of Dowden,\textsuperscript{12} for mono-phase metal catalysts, when the temperature reaches the Tammann temperature, the catalytic particles can easily conglomerate and the sinter velocity increases rapidly decreasing the activity of the catalysts. The relationship between the Tammann temperature ($T_t$) and the melting point ($T_m$) is

$$T_t \approx 0.5 \ T_m (K)$$

As a result, the Tammann temperature of nickel is about 590°C. In fact, considering other factors, the Tammann temperature of the nickel foams was a little more than 590°C, above 600°C, was an acceptable value. So the products prepared at temperatures above 600°C were of very low purity and poor yield.

2 Raman spectrum and XRD pattern

Fig. 4 shows the Raman spectrum of GNFs generated by a catalyst treated with hydrogen for 6 h (sample C) (Fig. 4a), as well as the spectrum of graphite (Fig. 4b). There are two peaks in the Raman spectrum of GNFs, a strong peak at 1308 cm$^{-1}$ and a medium strong peak at 1593 cm$^{-1}$, while there is only one peak (at 1574 cm$^{-1}$) in the graphite spectrum. It is well known that the Raman spectrum of low-ordered carbon also has two peaks, one at about 1346 cm$^{-1}$ and the other at about 1578 cm$^{-1}$. Therefore, the spectrum of GNFs is closer to that of low-ordered carbon than to that of graphite. The degree of long-range order of GNFs is relatively low in comparison with that of graphite. In addition, according to ref. 13-15, the peaks at 1308 cm$^{-1}$ and 1593 cm$^{-1}$ can be ascribed respectively to the fundamental frequencies D and G of GNFs.

The XRD pattern of GNFs with catalysts treated with hydrogen for 6 h and the pattern of graphite are shown in Fig. 5 (a) and (b). From the two patterns, one can draw similar conclusions: the degree of long-range order of our GNFs is lower than that of graphite, the representative peak (at 26.5°) of graphite (b) is much sharper than that of GNFs (a), and the curve is much smoother.

3 Growth mechanism

The microstructure and degree of crystallization of the GNFs are apparently governed by the nature and the shape of the catalyst particles and the orientation of the precipitating faces.\textsuperscript{7} Fig. 6 shows that the nickel particles, used as catalysts, are usually observed in the middle of the fish-bone GNFs (arrow in Fig. 6). The width of the nanofiber is determined by the size of the associated catalyst particle. This bi-directional growth of filaments was also found by other groups.\textsuperscript{1,7} Comparing with the work of Chen, it is believed that the different microstructures of the GNFs, although using the same catalysts, were due to different conditions during their production. Fig. 6 indicates that the nickel particles adopt the shape of a quadrangle. Because the exposed surface of the catalytic particles always exhibits round morphology, we believe that a reshaping of the nickel particles occurs during the growth process, most probably due to the hydrogen treatment and the temperature gradient.

It is well known that the interaction of a given gas molecule with a metal surface is frequently limited to certain crystal faces of the solid.\textsuperscript{17} It becomes particularly evident for small metal particles undergoing reaction in a hydrocarbon environment, where the particles adopt unique geometric shapes. Due to the quadrangular shape of the catalytic particles (Fig. 6), four graphite faces were generated. The procedure (as shown in Fig. 7) was: 1. Carbon is derived from the decomposition of acetylene and is dissolved in the four faces of the nickel particle. 2. Two cones (each quadrangular particle) composed of graphitic carbons occur. If either of the two cones is closed,
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References


Conclusions

Graphite nanofibers with fish-bone structure are synthesized on nickel foams by the method of chemical vapor deposition. Hydrogen can have a large effect on the morphology and microstructure of graphite nanofibers. If the catalyst is not treated with hydrogen, no GNFs are formed. However, after hydrogen treatment for a period of time, GNFs with the structure of graphite platelets at an angle to the fiber axis develop. It is also suggested that the growth characteristics of the fishbone GNFS are controlled by the nature and shape of the catalytic particles. Because the nickel particles have a polygon shape, this peculiar structure of GNFS is formed. It is suggested that GNFS with this unique structure could be favorable for hydrogen storage.