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CONFORMATION AND MICROSTRUCTURE OF CARBON NANOFIBERS DEPOSITED ON FOAM Ni*

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Abstract: Bundles of pure carbon nanofibers were prepared by catalytic decomposition of acetylene on foam Ni. The morphological and structural characteristics of the carbon nanostructures, in the as-prepared state, were analyzed by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HTEM). A special conformation of carbon nanofibers composed of segmented structures was found among the products by both SEM and TEM observations. Further HTEM examination indicated that the segments were stacked with well ordered graphite platelets arranged perpendicular to the axis of the filaments.

Key words: conformation, microstructure, carbon nanofiber, foam Ni
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INTRODUCTION

It had been well known for decades that carbon nanofibers can be prepared by the catalytic decomposition of hydrocarbons and carbon monoxides on the surface of certain metals, such as Fe, Co, Ni and some of their alloys, in hydrogen atmosphere (Baker et al., 1972; Oberin et al., 1976; Oya et al., 1979; Audier et al., 1981; Tibbetts et al., 1984). In the conventional catalytic decomposition method, metal powders or films were used for the catalysts. The nanofibers appeared in a number of different forms. In addition to the cylindrical hollow cored or solid whisker-like structures, some more intricate conformations, such as helical, branched and coiled structures were reported (Baker et al., 1973; Boehm, 1973; Baker et al., 1975; Tavares et al., 1986; Motojima et al., 1991). Saito et al. (1993). presented "bamboo" shaped graphitic carbon tubes consisting of a series of long compartments. Furthermore, it was possible to control assorted conformations of produced carbon nanofibers by choosing suitable catalysts and reactants and by careful manipulation of various reaction parameters (Rodriguez et al., 1993). Today, the synthesis and characterization of the carbon nanofibers are still of great interest from both the fundamental and the applied perspectives (Chen et al., 1995; Rodriguez et al., 1995; Fan et al., 1998; Chambers et al., 1998; Fan et al., 1999; Soneda et al., 2000). Although the conventional catalytic decomposition method using transition metal powders as the catalysts is suitable for the production of large quantities of carbon nanofibers, the preparation of the catalysts is a tedious process. Seeking for alternative forms of catalysts for easier preparation of the carbon nanofibers seems to have great significance for various industrial applications of carbon nanofibers. Soneda et al. (2000) reported that they used a stainless steel plate as a catalyst and produced a carbon film composed of carbon filaments by the decomposition of CO, though their reaction lasted 100 h.

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In this work, bundles of pure carbon nanofibers were obtained using foam Ni as the catalyst in the conventional catalytic decomposition method. Their morphological and structural characteristics were analyzed in the as-prepared state by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HTEM). A special conformation of carbon nanofibers composed of segmented structures was found among the products by both SEM and TEM observations. Further examination by HTEM indicated that the segments were stacked with well ordered graphite platelets arranged perpendicular to the axis of the filaments.

EXPERIMENTAL DETAILS

The reactions were accomplished in a conventional flow reactor system. A ceramic boat containing a piece of foam Ni (grade 110, PPISM 70, from Shenzheng Energy Storage Corporation Limited) was positioned in the middle of a horizontal quartz tube located in the chamber of a cylindrical electric furnace. The quartz tube was 5 cm in diameter and 75cm in length. Acetylene (99%) and hydrogen (99.99%) were mixed in a glass tube and then introduced into the quartz tube reactor. The flow rates of the two gasses were monitored and controlled separately with a mass flow gauge (± 0.1 ml/min.) before they were mixed. The reactions were carried out at temperatures ranging from 550 ℃ to 850 ℃ and allowed to proceed for 15 – 150 minutes. The products deposited on the foam Ni were examined in the as-prepared state by SEM, TEM and HRTEM, respectively.

RESULTS AND DISCUSSION

Fig. 1(a) shows an SEM image of the carbon deposits produced by the catalytic decomposition of acetylene at 600 ℃ on foam Ni with flow rates of 15 ml/min and 150 ml/min for acetylene and hydrogen, respectively. The reaction was allowed to last for 30 minutes. It can be seen from the scope that the deposits had almost pure filamentous structures. This indicates that the foam Ni used was extremely active in promoting the formation of the carbon filaments under the described conditions. Besides, from the figure we can also see that some of the fibers paralleled each other, as indicated by the arrows in the figure, forming quasi-parallel bundles. This feature facilitates our cutting of the filaments into small pieces for various applications, such as for molecular electronic devices, as material for batteries, as adsorbent for gases, as supporter for catalysts, etc..

Fig. 1(b), an enlarged SEM image of the sample after a short time milling in a mortar, clearly shows that the surfaces of the carbon nanofibers are rather smooth, which implies that there are almost no amorphous carbon deposits on the outside of the filaments. This kind of carbon fiber is favorable for purification.

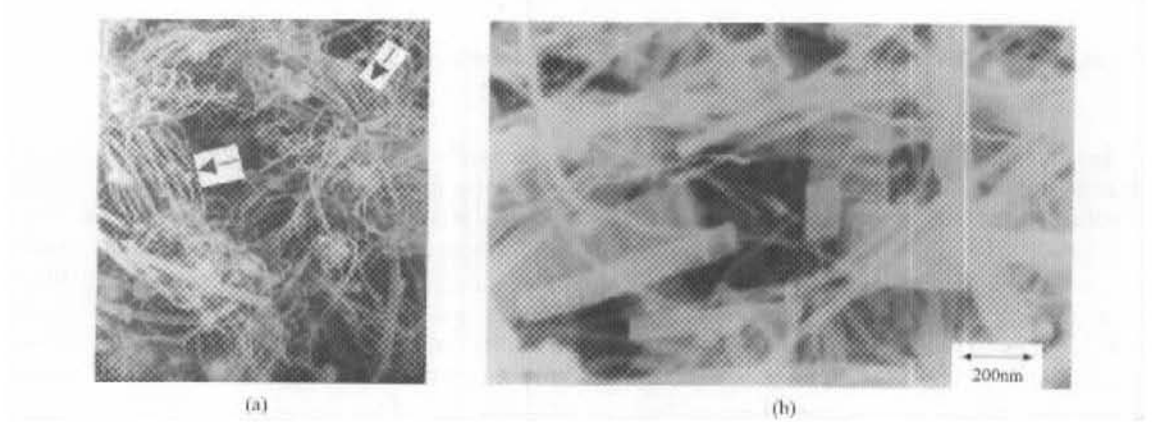

Fig. 1 (a)SEM image of filamentous carbon deposits produced by the catalytic decomposition of acetylene at 600 ℃ on foam Ni with flow rates of 15 and 150 ml/min for acetylene and hydrogen, respectively; (b) Enlarged SEM image of the carbon deposits after short time milling in a mortar

Fig. 2(a), a TEM image of the deposits, clearly shows that the flat catalyst particles inserted in the middle of the filaments (as shown by the arrows in the Fig.). Furthermore, the fibers forming a bundle originated from a single point and the catalyst particles are the same distance apart from the origin. So we believe that, at the reacting temperatures and in the existing atmosphere, the surface of the foam Ni underwent fragmentation that produced tremendous amount of flat and round shaped particles with diameters ranging from tens to hundreds of nanometers that was responsible for the catalytic decomposition of acetylene forming the carbon nanofibers. The mechanism for the fragmentation is very likely caused by the germination of dissolved carbon atoms in the bulk of foam Ni. Several earlier workers had observed carbon germination at grain boundaries on metal sheets (Renschaw et.al., 1971; Lobo et al., 1973; Derbyshire et al., 1975). The variation in fibers' diameter indicates the grain size variation of the particles produced from the fragmentation.

Fig. 2(b), a TEM image of the deposits after short time milling in a mortar, clearly shows the special morphology quit different from the other forms of the coexisting carbon filaments. They are composed of a series of short segments and so we name them "segmented carbon nanofibers". In fact, this feature can also be seen from the SEM image in Fig. 1(b), although it is not very clear. The diameter of the segmented carbon nanofibers ranging approximately from tens to over two hundred nanometers, is distinctively larger than that of the other coexisting ones. This means that the bigger sized catalytic particles were responsible for the formation of the segmented carbon nanofibers.

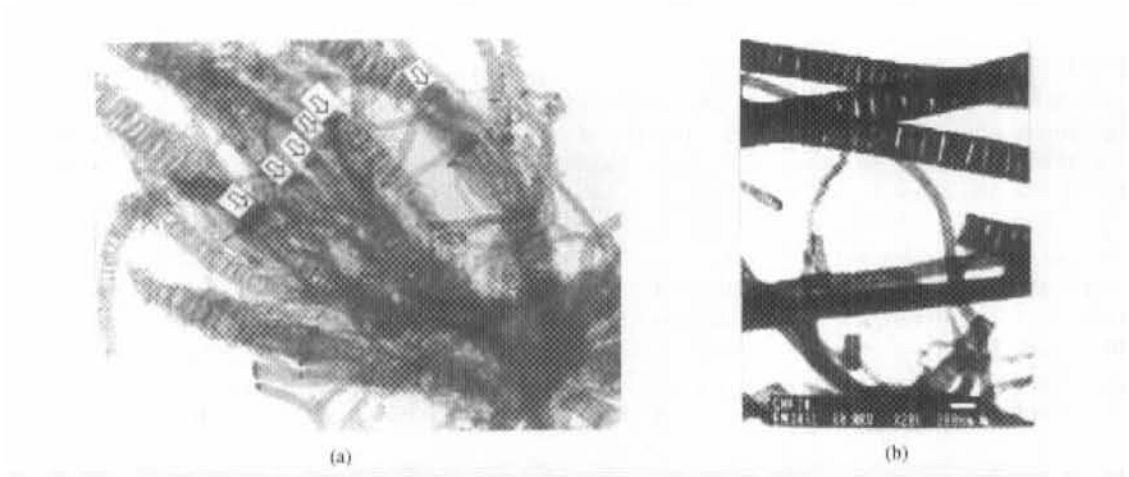

Fig. 2 (a) TEM image of a bundle of segmented carbon nanofibers; (b) TEM image of the segmented carbon nanofibers after short time milling in a mortar

Fig. 3, an HRTEM image of the segmented carbon nanofibers, shows that the segments of the carbon nanofibers were stacked by well-ordered graphitic platelets aligned perpendicular to the axis of the fibers. This kind of structure is similar to that presented by Chambers et al. (1998). They reported that, by catalyzed decomposition of carbon-containing gases and their mixtures over selected metal and alloy surfaces, they developed a new type of carbon material, graphite nanofibers (GNF), composed of graphite platelets aligned parallel, perpendicular, or at an angle to the fiber axis. But in our situation, the graphitic structure contains two kinds of sub regions as can be seen in the picture. The thick regions in the picture present highly ordered graphitic platelets that are spaced by light regions of less ordered graphitic platelets. This was probably caused by a small fluctuation of some growing condition and can be avoided by careful manipulation of the reaction parameters. We emphasize that, as Chambers et al. (1998) reported, this kind of carbon material may become prospective material for hydrogen storage at ca-

pacity of over an order of magnitude higher than that of conventional hydrogen storage systems. We also emphasize that it is much easier to use foam Ni as the catalyst for the preparation of this kind of carbon nanofibers compared to other methods because the foam Ni is commercially available and the manipulation of the preparation of the products is simpler, and therefore mass production of the carbon material can be expected.

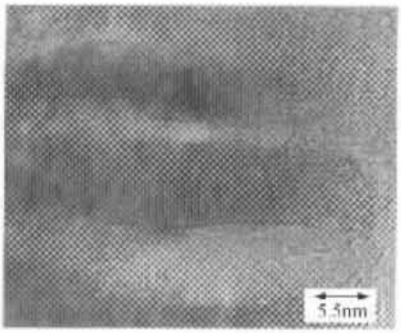

Fig.3 HRTEM image of the segmented carbon nanofibers

CONCLUSIONS

It has been proved that commercially available foam Ni is one kind of effective catalyst precursor for producing pure carbon nanofibes by catalytic decomposition of carbon containing gasses. The products show a special morphology and contain segments quite different from the conventional carbon nanofibes. The segments were stacked with well ordered graphite platelets aligned perpendicular to the axis of the fibers.

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