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The synthesis of carbon coils using catalyst arc discharge in an acetylene atmosphere

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Abstract

Novel carbon coils were synthesized by an arc discharge process on a metal plate under different gas pressures from 160 to 460 Torr. The morphology and yield of carbon coils were examined by scanning (SEM) and transmission (TEM) electron microscopy. The influence of the gas pressure and impurities such as sulfur and phosphorus on the growth of product is also discussed. It was demonstrated that the morphology and yield of the coils were greatly controlled by the gas pressure. On the other hand, a new model was proposed to describe the coil growth. Our method offers a preferable alternative for the efficient, abundant and economical growth of carbon coils.

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Keywords: A. Carbon coils; A. Metal catalyst; B. Arc discharge; C. Scanning and transmission electron microscopy

1. Introduction

Since coiled carbon fibers were discovered in 1953 [1], the structure has continuously attracted much attention. These carbon coils, as new carbon material with special DNA-like structures and unique properties, may have many applications such as micro sensors, hydrogen material and electromagnetic material [2,3]. Therefore, it is valuable to explore a controlled, reliable, efficient process to produce carbon coils on large scales. Among various preparation processes, the chemical vapor deposition (CVD) process has the most potential for large scale preparation. Many researchers dedicate themselves to synthesizing them in various CVD reaction systems, using all kinds of catalyst, carbon sources and types of impurity as promoter, in the presence of electromagnetic field or not [4–6]. However, the yield of carbon coils in this method is a little low and it requires a high continual gas flow rate which results in most of the gas being released directly into atmosphere without participation in the CVD process. In addition, it is usual to require fine metal powders or films prepared by design as the catalyst for the reaction [7–9].

In the work presented, carbon coils are produced by decomposition of acetylene using an arc discharge process on a metal plate at various pressures, without the complex preparation of catalyst and introduction of impurities by design. The aim of this paper is to investigate the synthesis and growth model of carbon coils with arc discharge. In particular, we attach importance to the function of the metal plate and the morphology of products affected by reaction pressure changes. In addition, it was found that different types of gas source influence the forms of products.

2. Experiments

The reaction apparatus in the experiment is composed of an electrode, reaction chamber, vacuum pump, circulatory system, DC power supply, and so on. A spectral pure graphite rod with size of ϕ 12 × 200 mm and a metal plate (80 mm × 80 mm × 15 mm) treated by ultrasonics were used as anode and cathode, respectively. After evacuation of

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the system to a pressure of 0.2 Torr, the acetylene (industry-grade acetylene) was introduced into the chamber. In succession the arc was generated with an output current of 96 A and voltage of 35–40 V in an acetylene atmosphere at a pressure of 160–460 Torr. The circulatory pump operated constantly in order to utilize the acetylene to the extreme. Three minutes later, a large number of club-shaped products, whose size is approximately 1 mm, developed vertically on the surfaces of plate. They arrange with each other with orderliness like a comb. The club-shaped samples were characterized by X-ray diffraction (D/MAX–3B, XRD), scanning electron microscopy (S–520, SEM), transmission electron microscopy (JEM–100CXII, TEM), and energy dispersive X-ray spectroscopy (JEM2010, EDS) attached to the transmission electron microscope.

3. Results and discussion

3.1. The function of the metal plate and coil growth model

As already mentioned, the products developed vertically on the surfaces of the plate, which serves not only as the electrode but also as the substrate. On the other hand, experimental findings demonstrated that the plate also provided catalyst particles for the growth of the carbon micro coils. Fig. 1(a) shows the representative morphology of the coils. There could be found a dark dot locating at the node of two coiled fibers. The result of electron diffraction confirms that the dot is Ni single crystalline, as shown in Fig. 1(b). It is easy to deduce that the Ni comes from the metal plate. In fact, it has been observed that there were some small cavities in the arc area of the cathode, indicating that the catalyst grains derive from a splash in the arc discharge process on the metal plate.

It is very interesting that two coiled fibers in Fig. 1(a) have opposite helical state (one is left-handed, the other is right-handed), identical cycle number, coil diameter, coil length, coil pitch, and fiber diameter, grown from the dot. We think that the symmetry of the crystal faces' structure [10,11] and some other external factors result in the enantiomorphous morphology of the carbon coils. Moreover, the morphology of the carbon coils shows their growing model of bottom growth. Ni comes from the metal plate and serves as a catalyst in the growth process. The acetylene is decomposed into carbon atoms on the surface of the catalyst and diffuses into the Ni grains. With the concentration of carbon in the Ni catalyst increasing, the nucleus grows up to forms into straight fibers in the beginning, and then the straight fibers are transformed into the filaments of coils by outer factors.

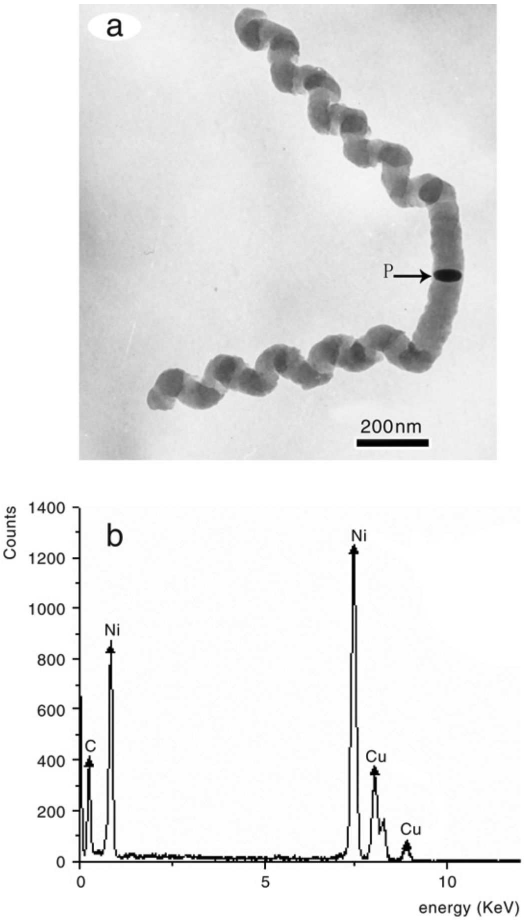

Fig. 1. (a) TEM image of carbon coils on the metal plate, and (b) the EDS of the dot P.

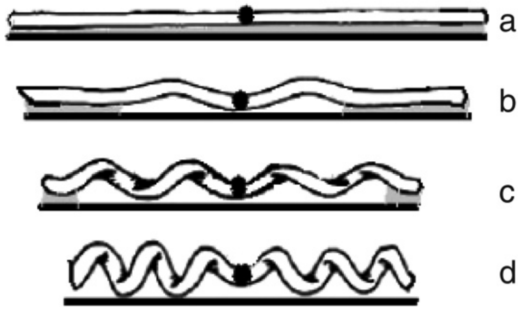

Fig. 2. (a)–(d) illustrate the growth mechanism of the carbon coils. The gray area and dark area represent the van der Waals forces area and metal plate, respectively.

We propose four steps to describe the formation of a carbon coil. First (the initial stage), straight carbon fibers form from the catalyst particles, which are attached on the plate because of their rough surface by van der Waals forces; second, with the van der Waals force decreasing due to temperature changing, the stress along the fiber axis causes the distortion of fibers; third, the elastic module of the straight fibers mainly controls the coil diameter, coil length, coil pitch, and so on; fourth, angular momentum conservation dictates that the two coils, which derive from the same catalyst grains, have opposite helix. Fig. 2(a)–(d) illustrates the four-step model. Therefore, in our view, carbon coil formation is influenced by not only the anisotropy of catalyst grains but also the appropriate module and stress of straight fibers, gas pressure, temperature field, etc.

In fact, coils with opposite handedness appear in a wide range of biological and physical systems, such as climbing plants [12], super-coiling of DNA structures [13,14], and morph genesis in bacterial filaments [15,16]. The former model is in view of these natural phenomenons [17–19].

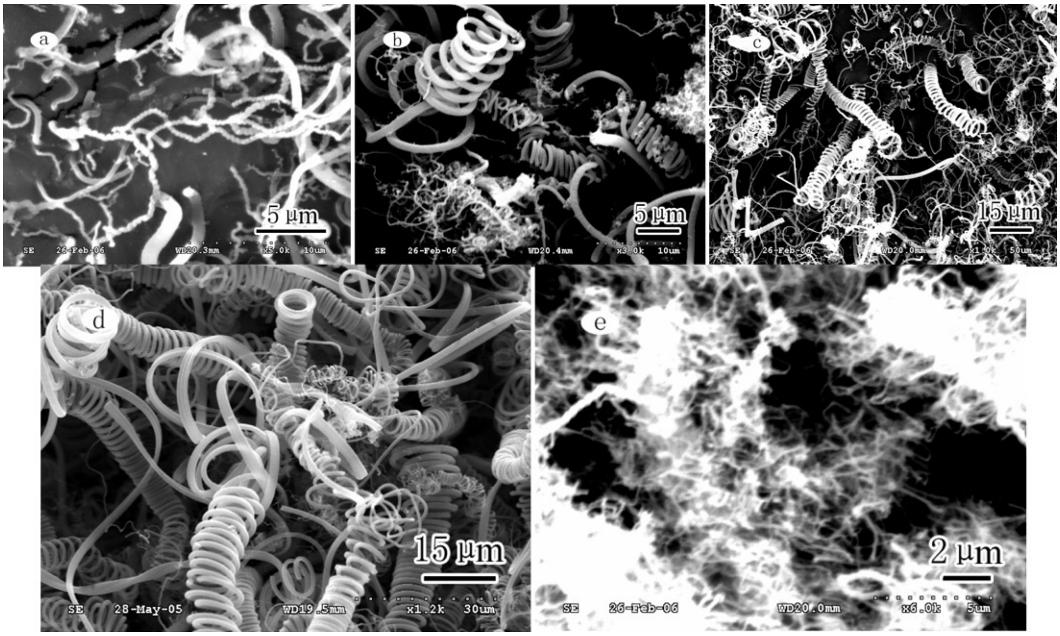

Fig. 3. SEM images of CMCs at different gas pressure: (a) 160 Torr, (b) 235 Torr, (c) 310 Torr, (d) 385 Torr and (e) 460 Torr.

3.2. The influence of gas pressure on the growth of products

Fig. 3 shows the morphology of the samples corresponding to different acetylene gas pressure ranging from 160 to 460 Torr in the reactor. The pressure of 160 Torr is not good for the fabrication of carbon coils. Fig. 3(a) show that under this pressure most of the products are other carbon forms such as straight fibers, with just a small fraction being coils, which have an average coil diameter and pitch of 0.5–0.8 μm and 0.8–1.2 μm, respectively. With the reaction pressure rising to 235 Torr, some double carbon coils with the diameter of 2–4 μm and small pitch are obtained (Fig. 3(b)), but most products are still other carbon forms such as nanofibers and normal fibers. Fig. 3(c) and (d) show that with the pressure of 310–385 Torr, carbon coils are in the majority, though some straight carbon fibers or strips exist. The distribution of the coils becomes more regular. In particular, 385 Torr is the best pressure condition for forming the coils because the proportion accounts for 80%–90%. It is a fact that nearly all the products are double coils, as shown in Fig. 3(d). The coil size become much bigger than previously, and their diameter and length are about 6–10 μm and 50–80 μm, respectively. The experiments also indicate that very high pressure is not helpful. As the gas pressure becomes higher than 460 Torr, carbon coils almost disappear from Fig. 3(e). The diameter of products is approximately 50–100 nm; the sample turns into nanotubes, which are testified by other TEM images (not shown here).

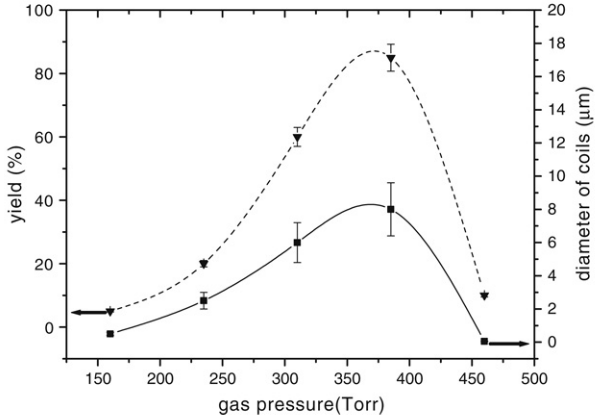

Fig. 4. The influence of pressure on the yield and diameter of coils. The dashed line and the solid line show that the changes of yield and coil diameter with the pressure increase, respectively.

Fig. 4 describes concretely the influence of acetylene gas pressure on the yield and diameter of coils. It is easy to find that the yield and diameter of coiled fibers increase with pressure from 160 to 375 Torr, but decrease when the value of the pressure is beyond 375 Torr. As to the yield of the coils decreasing, an explanation is that the density of acetylene is so high that the catalyst is poisoned. As to the coil diameter changing, we think the gas pressure through controlling the fiber module influences the coil diameter.

3.3. The influence of impurity

In experiments, we found that when pure acetylene was substituted for industry-grade acetylene, only little amorphous carbon was obtained, and no other products existed. Industry-grade acetylene contains a few kinds of impurities such as sulfur and phosphorus. The behavior of S and P may greatly affect the formation of carbon coils. We think S and P join together with the carbon atoms, forming an S (P)–C at the reaction temperature. As a result, S (P)–C can be absorbed effectively by the catalyst grains, which facilitate the formation of the carbon coils, and in our experiments, no carbon coils were obtained in the absence of impurities, suggesting that they serve as a promoter for the preparation of carbon coils. This finding is in agreement with the conclusion drawn by Kawaguchi [20].

4. Conclusions

Carbon coils were prepared by decomposition of acetylene using an arc-discharge process with a metal catalyst. A four-step growth model was proposed to explain the coil growing. It is found that the diameter and the morphology of the coils are greatly influenced by acetylene gas pressure. By comparison, 310–385 Torr is the best pressure condition for the preparation of the carbon coils. It is also found that no coils were obtained without S or P impurity, which should be a promoter for coil growth.

Acknowledgements

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