

SOLID-CORED CARBON NANOFIBER GROWN ON STEELS SUBSTRATES IN ETHANOL FLAMES

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Introduction

This is a continuation of our previous research on synthesis of carbon nanotubes (CNTs) by using an ethanol flame [1,2]. Previously, we reported that carbon nanotubes (CNTs), including well-aligned CNTs, have been successfully produced on austenitic stainless steels within ethanol flame environment. Recently, a novel solid-cored carbon nanofiber (CNF) was found when using carbon steel or low alloy steel as the substrate. In the present paper, the character of the CNFs and the growth mechanism are discussed.

Generally, both CNTs and CNFs are considered to be promising nanomaterials for applications, such as field emission [3], hydrogen storage [4], reinforcement of composite [5], and electrodes for fuel cell [6], because of their unique mechanical and physical properties.

However, up to now, the terminology for CNTs and CNFs are not clearly defined, which means that a “fiber” is actually a “tube” [7-9]. Historically, the term nanofiber is used for both CNTs and CNFs with or without a hollow core. Sometimes, a highly graphitic structure with the basal carbon planes parallel to the tube axis is called a CNT, and the structures, such as the graphitic wall which has an inclined orientation and leaves a small or no central channel, and the multi-walled carbon nanotubes (MWCNTs) which lacks a graphitic structure, refer to CNFs [10-12].

According to the present research, a filament with or without the central hollow core represents the different growth mechanism. Therefore, in this paper, the term CNTs is defined referring to the filament with a center core as described above, while the term CNFs is defined as a filament without a central channel or just a solid-cored fiber.

Experimental

The synthesizing process for the solid-cored CNFs is almost the same as described in our previous work [1,2]. In the present work, only carbon steels or low alloy steels were used as the substrates with size 20×10×10mm or larger. Table 1 lists the chemical compositions of the substrates. The sampling surfaces were firstly mechanically polished to different roughness by using different grade of abrasive papers. And then the surfaces were or were not pretreated by dipping in a solution of 5ml pure nitric acid (HNO₃) +100ml absolute ethanol (C₂H₅OH) for several seconds. The total synthesizing

process generally was not strictly limited. It means that the present CNFs can be synthesized very easily on steels substrates in ethanol flame.

Table 1 Chemical compositions of the substrates

| Substrates | Chemical compositions (wt-%) | | | | | | |
|------------|------------------------------|-------|-----------|-----------|-------|-------|------|
| | C | Si | Mn | Cr | S | P | Fe |
| Q235 | 0.100 | 0.120 | 0.400 | - | 0.020 | 0.073 | Bal. |
| 45# | 0.46 | 0.25 | 0.67 | - | 0.034 | 0.029 | Bal. |
| T8# | 0.82 | 0.33 | 0.71 | - | 0.035 | 0.026 | Bal. |
| 40Cr | 0.37 ~ 0.44 | 0.27 | 0.5 ~ 0.8 | 0.8 ~ 1.1 | - | - | Bal. |
| 16Mn | 0.12 ~ 0.2 | 0.35 | 1.2 ~ 1.6 | - | 0.045 | 0.045 | Bal. |
| 65Mn | 0.62 ~ 0.70 | 0.2 | 0.9 ~ 1.2 | 0.25 | 0.035 | 0.035 | Bal. |

Microstructures and morphologies of CNFs were examined by using Japan Hitachi S-570 scanning electron microscope (SEM), Japan JEOL JEM2010 conventional transmission electron microscope (TEM) and JEOL JEM2010FEF high-resolution transmission electron microscope (HRTEM) installed with an electron energy loss spectrometer (EELS) and Gatan CCD cameras, respectively. The laser Raman spectra were performed in England Renishaw-1000 laser Raman spectroscopy instrument in the back-scattering configuration at room temperature. The excitation source is 514.5nm Ar-ion laser line.

Results and Discussion

Fig.1 illustrates the typical SEM morphologies of the present novel CNFs grown on mild steel (Q235). In a high magnification, it shows the disordered and randomly fibrillous structures (Fig.1a) and has no difference with other observations [12-14]. However, in low magnifications, the combustion products piled up imbricately when it was in a large volume (Fig.1b). TEM observations indicated that the present CNFs had a structure with a completely solid core and some of them also had a helical shape, as shown in Fig.2. When using the other steels, the morphologies of the combustion materials were almost the same.

The diameter of the CNFs varied in a large range, the smallest is 20nm, while the largest around 250nm, and the length could be several tens microns. Generally, a particle was embedded at one end of a fiber, which implied that the CNFs also followed the “deposition – diffusion – nucleation – growth” mechanism [10,15,16]. EELS measurements indicated that the particle containing elements Fe and O, as show in Fig.3. Selected-area electron diffraction (SAD) analysis revealed that the predominant particles belonged to the compound of iron oxide Fe_3O_4 , as shown in Fig.4. Fewer were

iron carbide, such as Fe_7C_3 , Fe_3C , or M_6C , etc. [17,18]. The smaller particles tended to induce smaller diameter fibers, whereas larger ones for larger diameter fibers.

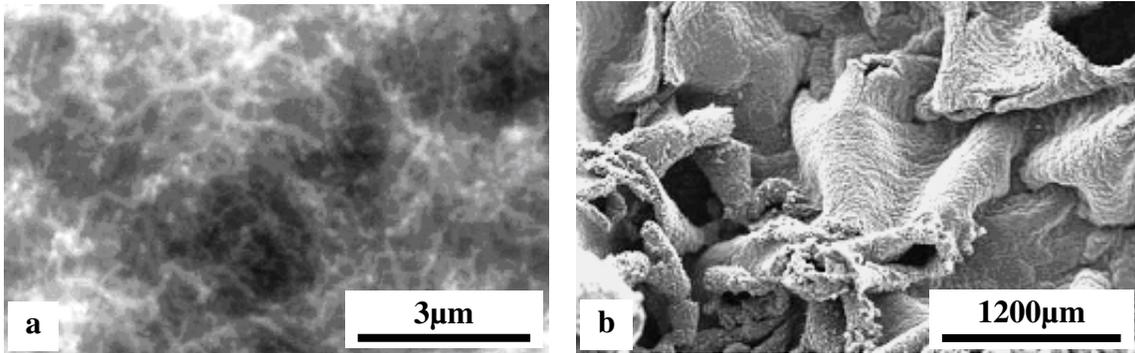


Figure 1 SEM morphologies of CNFs grown on Type Q236 mild substrate: (a) high magnification; (b) low magnification

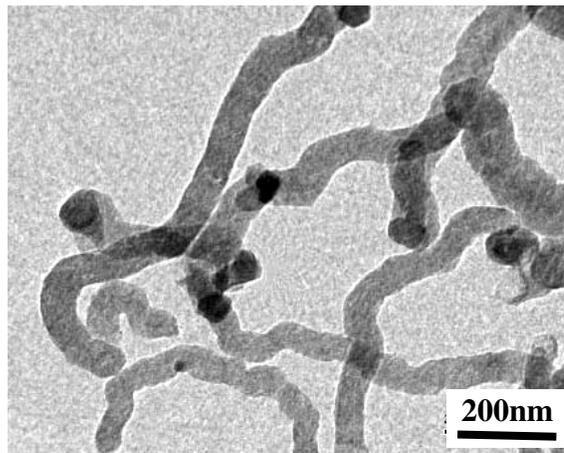


Figure 2 TEM micrographs of CNFs grown on Type Q236 mild substrate

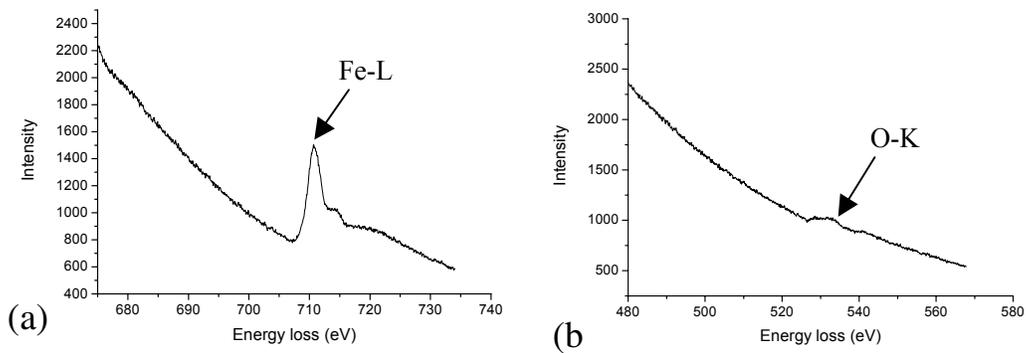


Figure 3 EELS spectra for chemical compositions of the embedded particle: (a) Fe element; (b) O element

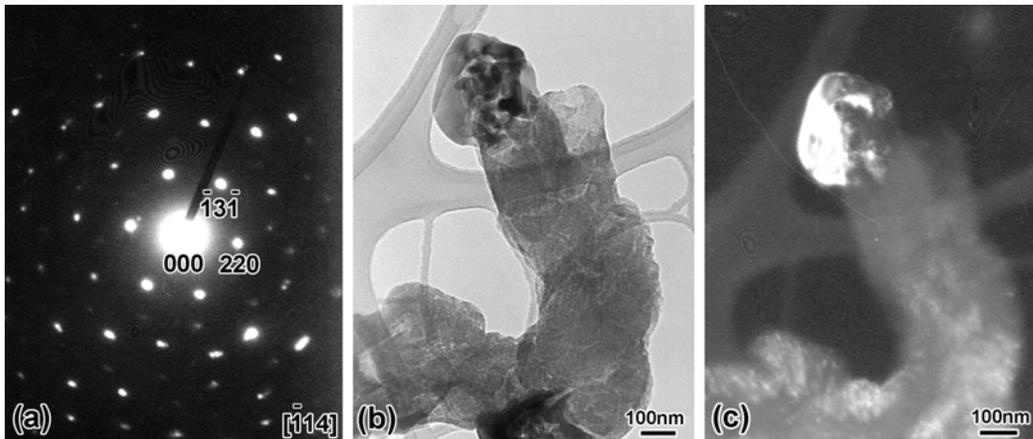


Figure 4 TEM micrographs of iron oxide Fe_3O_4 particle embedded at the end of CNFs grown on 65Mn steel substrate. (a) $[\bar{1}14]$ axis SED pattern; (b) bright field image; (c) (220) dark field image.

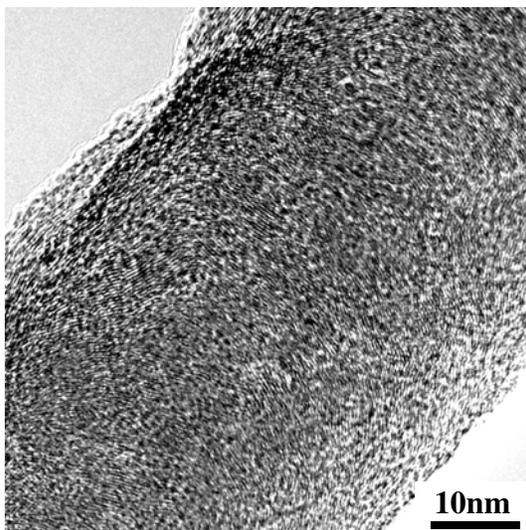


Figure 5 HRTEM micrographs of CNFs grown on Type Q236 mild substrate.

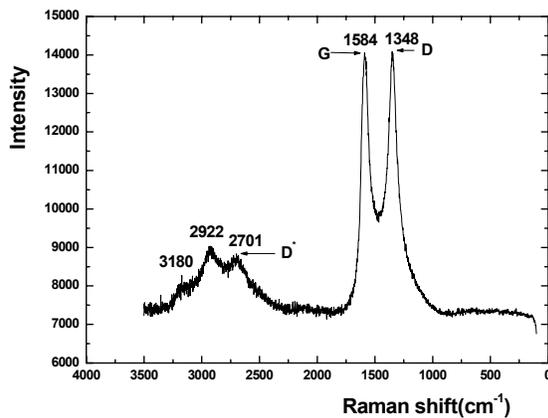


Figure 6 Raman spectra of the CNFs grown on Type Q236 mild substrate

The further HRTEM observation, as shown in Fig.5, revealed that the whole fiber consists of disordered graphitic layers. Fig.6 illustrates the Raman spectra of the CNFs with a large D-band at 1346cm^{-1} , which were related to the disorder-induced phonon mode.

According to the above results, the present CNFs has two unique characters: One is that the CNFs always grow upon the carbon steels or low alloy carbon steels substrates, which implies that the iron-contained compounds or particles play a key role during synthesis. The other is that its microstructure is completely different from the so-called vapor-grown carbon nanofibers (VGCNFs) or hydrocarbon pyrolyzed CNFs, which

generally have a hollow core and high-crystallinity graphite filament surrounded by a pyrocarbon layer with low graphite crystallinity [19] or a “herringbone” [6,12] or “fishbone” [16] wall or a highly crystalline wall [6,8].

Different CNFs structures may relate to different growth mechanisms. Here, we classify it as the “solid-cored mechanism” and “hollow-cored mechanism”, in addition to the “base-type” and “tip-type” mechanisms [15]. According to catalytic growth mechanisms [10,15,16], the growth process of a fiber with or without a center hollow core is quite different, regardless of the thickness and structure of the walls which generally depends upon the synthesizing conditions, such as longer sampling time or higher sampling temperature [10,11,13,20].

The “hollow-cored mechanism”, actually, refers to the well-described CNTs growth mechanism as described elsewhere [16,21]. It is well known that VGCNFs were obtained via the following processes: first, a hollow and high-crystallinitic graphite carbon nanotubes is formed as the inner region, and then, a low graphitic crystallinitic pyrocarbon layer is deposited on the nanotubes as an outer layer [19].

Morphologically, the present solid-cored nanofibers are the real CNFs. Previously, this kind of CNFs was also observed by other researchers [22-24]. Preliminarily, here, we propose a “solid-cored mechanism” based upon the theory that “iron has a strong affinity for carbon” involved in the present CNFs growth. Generally, it has been concluded that iron carbides precipitated in steels are associated with this affinity property, however, element Ni has very small affinity for carbon [25]. Therefore, it is reasonable to understand the present results. That is, the pyrocarbon can easily deposit and diffuse through the interior of the Fe-contained compounds particles due to the affinity phenomenon, and then form solid-cored CNFs. However, when pyrocarbon deposited upon the Ni-contained particles, carbon atoms generally move faster along the external surface than the interior, and a hollow core tube is formed.

Unfortunately, the present “solid-cored mechanism” cannot be used to explain the widely applied Fe catalyzed CNTs growth by using arc-discharge, chemical vapour deposition (CVD) and other methods [10, 26,27]. The reason may be because the ethanol flaming growth conditions. The further research is being proceeded.

Conclusions

In conclusion, ethanol flame may provide a special conditions for growing a kind of solid-cored and low-ordered graphitic CNFs upon carbon steels substrates, and the iron-contained compounds particles are considered to be the key factor to control the process.

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