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Effect of nickel, iron and cobalt on growth of aligned carbon nanotubes

Z.P. Huang[1], **D.Z. Wang**[1], **J.G. Wen**[1], **M. Sennett**[2], **H. Gibson**[2], **Z.F. Ren**[1,*]

[1] Department of Physics, Boston College, Chestnut Hill, MA 02467, USA
[2] Material Science Team, US Army Soldier & Biological Chemical Command, Natick Soldier Center, Natick, MA 01760, USA

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Abstract. The effect of pure nickel, iron and cobalt on growth of aligned carbon nanotubes was systematically studied by plasma-enhanced hot-filament chemical vapor deposition. It is found that the catalyst has a strong effect on the nanotube diameter, growth rate, wall thickness, morphology and microstructure. Ni yields the highest growth rate, largest diameter and thickest wall, whereas Co results in the lowest growth rate, smallest diameter and thinnest wall. The carbon nanotubes catalyzed by Ni have the best alignment and the smoothest and cleanest wall surface, whereas those from Co are covered with amorphous carbon and nanoparticles on the outer surface. The carbon nanotubes produced from Ni catalyst also exhibit a reasonably good graphitization. Therefore, Ni is considered as the most suitable catalyst for growth of aligned carbon nanotubes.

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Since the discovery of carbon nanotubes [1], many studies have been carried out on their synthesis [2–8]. The synthesis of carbon nanotubes can be divided into non-catalytic and catalytic methods [9]. In the catalytic method, nickel, iron and cobalt are the only three transition metals that can be used as pure-metal catalysts for carbon-nanotube growth. In the considerable reports regarding carbon-nanotube synthesis [6–8, 10–15], nickel, iron and cobalt are used either separately in different methods or together as a composite catalyst. For any specific method, no systematic study has been reported comparing the effects of the different metal catalysts on carbon-nanotube growth, morphology and microstructure. Here we report a systematic study of the effect of nickel, iron and cobalt on the synthesis of aligned carbon nanotubes by plasma-enhanced hot-filament chemical vapor deposition (CVD). The study clearly shows that the catalyst strongly influences not only diameter, growth rate, etc., but also morphology and microstructure. Combined with the growth mechanism of carbon nanotubes, the catalytic behavior of nickel, iron and cobalt is also speculated on. As a result, nickel is highly recommended as the first choice for aligned nanotube growth.

*Corresponding author. (Fax: +1-617/552-8478, E-mail: renzh@bc.edu)

1 Experimental

Catalyst films were deposited by magnetron sputtering. Ni, Fe or Co films of 10, 17, 24, 30 and 35 nm were first deposited on a titanium substrate and then they were transferred into a plasma-enhanced hot-filament CVD system. A base pressure of 10^{-6} Torr was reached before high-purity acetylene and ammonia (40:160 SCCM) were introduced. The growth time was fixed at 10 min and the pressure during nanotube growth was maintained at 10–20 Torr. After growth, a JEOL 6340F scanning electron microscope (SEM) and a 2010 transmission electron microscope (TEM) were used to characterize the carbon-nanotube samples.

2 Results and discussion

The SEM images in Fig. 1a, b and c show that as-grown carbon nanotubes from 25 nm thick Ni, Fe and Co films, respectively, are very different. The nanotubes grown from a Ni film (see Fig. 1a) exhibit a straight alignment perpendicular to the substrate, whereas those from Fe (Fig. 1b) and from Co (Fig. 1c) are crooked or twisted. In addition, Fig. 1b shows that holes (openings on the wall) exist on some of the nanotubes, as indicated by the arrows. According to the proposed catalytic growth mechanism [6], the crooked, twisted or helical carbon nanotubes may be the result of a variation of carbon segregation or catalytic activity on the active sites around the catalyst periphery during nanotube growth. Therefore, it can be deduced that Co and Fe exhibit non-uniform catalytic activity and carbon segregation. At a site of reduced catalytic activity, catalysis and carbon segregation may be extremely slow or even stop and consequently induce an opening on the wall. In contrast, the catalytic activity of Ni and carbon segregation from Ni is uniform and stable across the

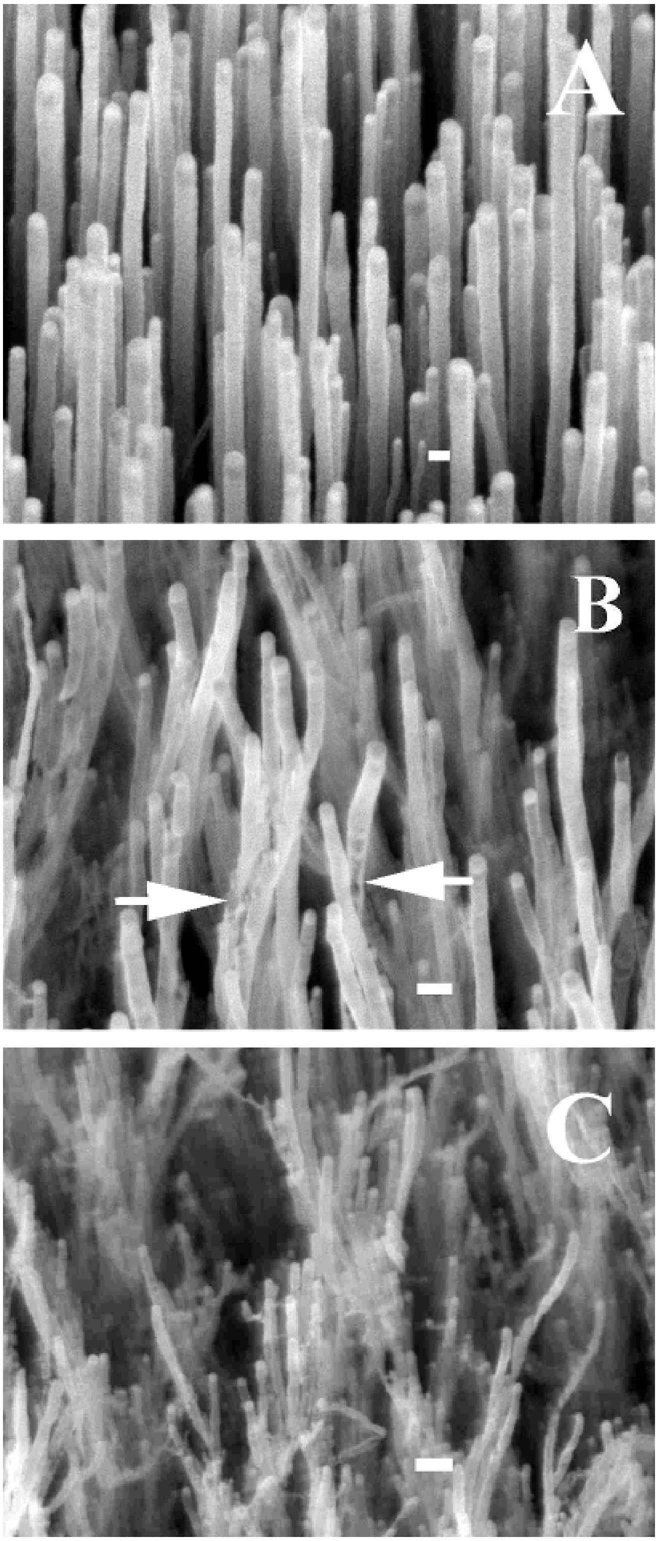

Fig. 1a–c. SEM images of as-grown carbon nanotubes from catalyst **a** Ni, **b** Fe and **c** Co. Two openings on the walls are indicated by arrows in the center of **b**. Scale bar: 100 nm

catalyst surface. As a result, carbon nanotubes grown from Ni have fairly good alignment and regular tubular structure. Clearly, not only do the catalysts affect the nanotube alignment, but also the diameter. For the same thickness of catalyst film (25 nm), the nanotubes grown from Co have the smallest diameter (see Fig. 1c), whereas those grown from Fe have a diameter in between those from Ni and Co. Even though the growth behavior is very much different in terms of nanotube alignment and diameter, they share the same tip-growth mechanism because there is a catalyst particle on the tip of every nanotube, regardless of which catalyst is used.

The curves in Fig. 2 present the typical diameter dependence of carbon nanotubes on catalyst-film thickness. Similar to our previous report on nanotubes from a Ni film [16], carbon nanotubes from Fe and Co films also demonstrate a reduced diameter with decreasing film thickness. This result is also consistent with the conclusion of [17] that a thinner catalyst film usually induces the formation of smaller catalyst particles and thus produces smaller carbon nanotubes. Within

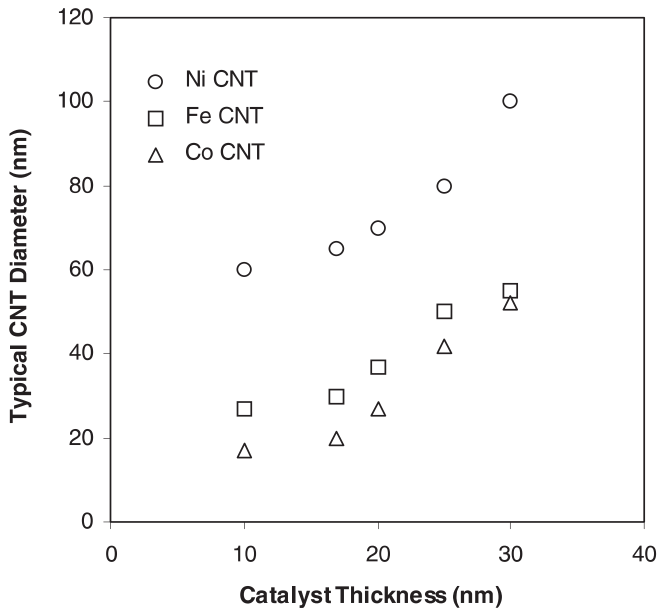

Fig. 2. Typical diameters of carbon nanotubes grown from Ni, Fe and Co as a function of catalyst-film thickness

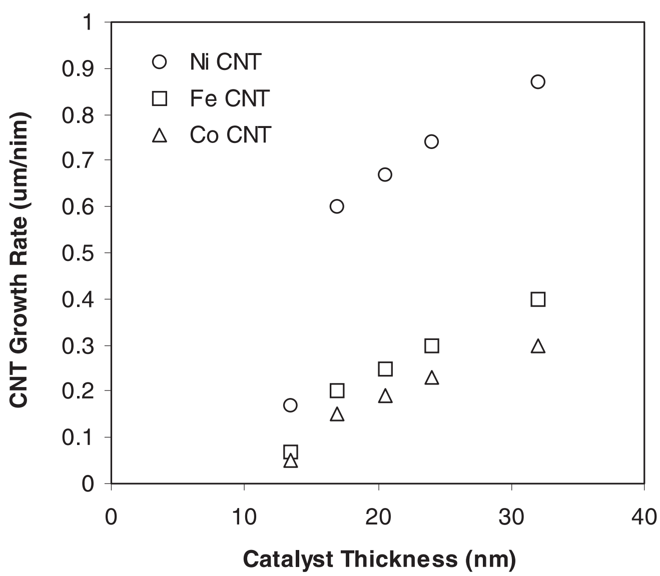

Fig. 3. Growth rates of carbon nanotubes grown from Ni, Fe and Co as a function of catalyst-film thickness

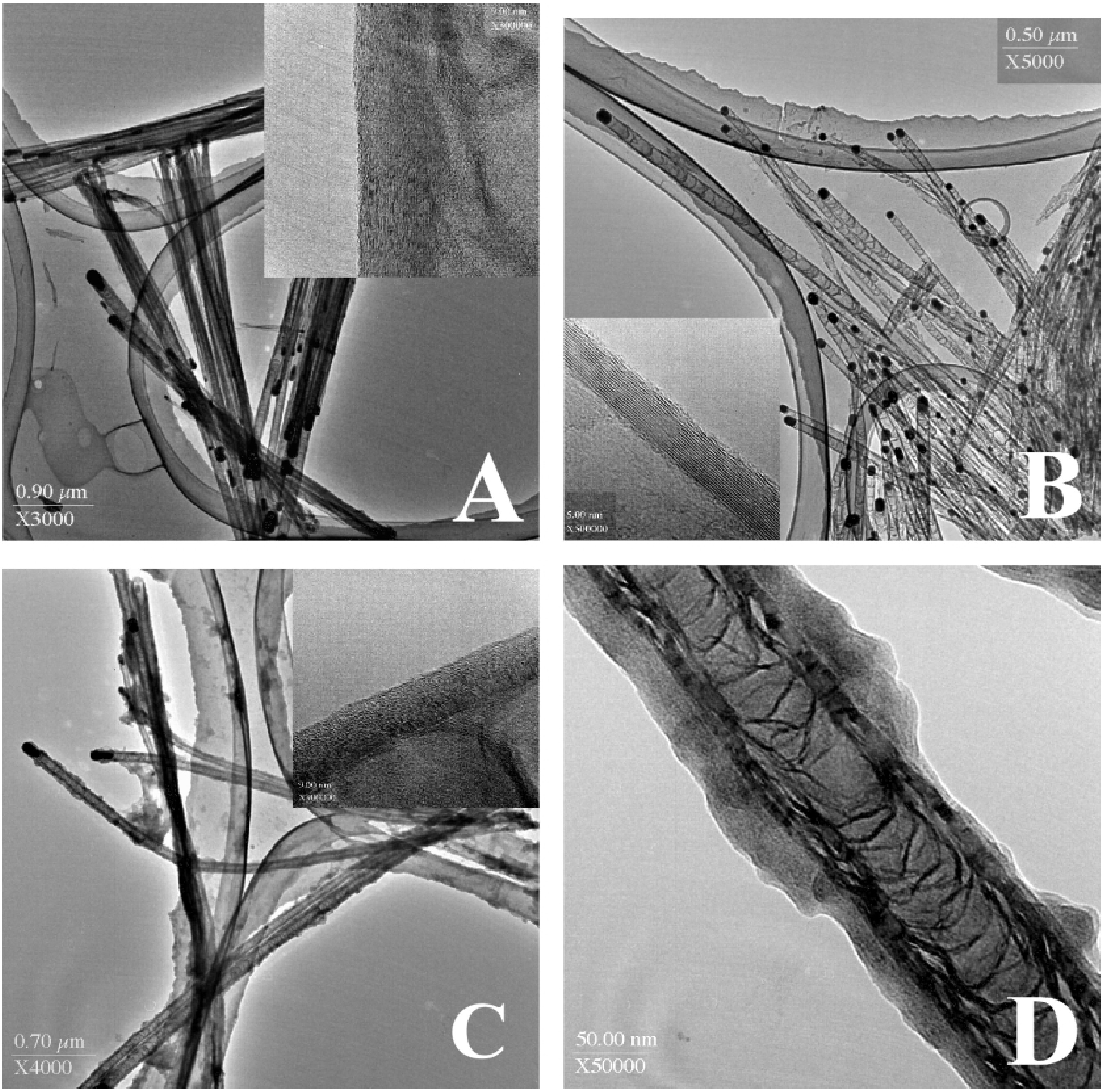

Fig. 4a–d. TEM images of carbon nanotubes from catalyst **a** Ni, **b** Fe and **c** Co and their microstructures (*insets*); **d** a nanotube grown from Co to show the existence of amorphous carbon and carbon nanoparticles on the outer wall

the range 10–35 nm, carbon nanotubes grown from a Ni film always have the largest diameter and those from a Co film possess the smallest diameter, whereas the diameter of nanotubes from a Fe film is consistently in between. Accordingly, it can be deduced that, for a given catalyst-film thickness, the sizes of catalyst particles or grain sizes that are produced from Ni, Fe and Co films are different and they follow the relation $Ni_{size} > Fe_{size} > Co_{size}$.

Figure 3 shows the growth rate of carbon nanotubes as a function of catalyst-film thickness. For a given film thickness, Ni always exhibits the highest nanotube growth rate and Co produces nanotubes with the lowest growth rate. The carbon nanotubes from a Fe film exhibit an intermediate growth rate. In the nanotube-growth mechanism, the growth rate is related to carbon diffusion and segregation at the catalyst particle. Accordingly, we can deduce that carbon should segregate and diffuse on nickel faster than on cobalt and iron so that the carbon nanotubes from Ni exhibit the highest growth rate. Similarly, carbon diffusion and segregation are faster on iron than they are on cobalt. For Ni, Fe and Co films, the nanotube-growth rates are all diminished with the reduction of catalyst thickness. It should be noted that the growth rate increases sharply from 10 to 20 nm thickness and the rise is as high as 400%. This rapid rise explains our previous observation that the non-uniformity in carbon-nanotube height was increased when the growth happened on a catalyst film in the above-mentioned thickness range [18]. It indicates that in the thickness range 10–20 nm, a sharp variation of growth rate can be caused by a small deviation in catalyst distribution and thus result in a visible fluctuation in nanotube height. In order to suppress the fluctuation, a two-step growth process has been developed as reported in [18].

The TEM observations of carbon nanotubes grown from Ni, Fe and Co are shown in Fig. 4a, b and c. All nanotubes demonstrate a hollow tubular structure. The inserted images in Fig. 4a, b and c also clearly show the graphitized wall of nanotubes from Ni, Fe and Co catalysts respectively. From the inserted images, it can be found that nanotubes from Ni and Fe have smooth and clean surfaces, but nanotubes from Co have a rough surface of amorphous carbon. The graphitized nanotube wall is underneath the amorphous carbon and carbon nanoparticles as shown in Fig. 4d. The open-walled carbon nanotubes from Fe and Co are also confirmed by TEM. The images in Fig. 5a and b show the openings on the wall of nanotubes produced from Fe and Co respectively. Figure 5a shows a microstructure of graphite layers disturbed by an open wall. A full view of open-walled carbon nanotubes is also given in the inserted image. The TEM images firmly prove that all graphite layers are discontinuous in the open-wall area, thereby forming a channel through the nanotube wall.

In TEM observations, it has also been found that for the same outer diameter, nanotubes grown from Fe or Co have a thinner wall than those from Ni. A possible explanation is that wall thickness (the number of graphitized layers) is related to not only the nanotube diameter but also the geometry of the catalyst particle. As shown in Fig. 6, a catalyst particle can be approximated as an upside-down cone. For the aligned nanotubes shown here, all graphite layers grow from the tapered surface of the cone. The graphite layers are aligned perpendicular to the substrate, and have a fixed spacing (approximately 0.334 nm). Suppose the cone angle, β, is different for Ni, Fe and Co particles. With decreasing β, more graphite layers aligned perpendicular to the substrate surface can be initiated from the particle surface, which consequently produces a thicker-walled nanotube (Fig. 6a). On the contrary, the number of graphite layers on the particle surface decreases with increasing β as shown in Fig. 6b. Therefore,

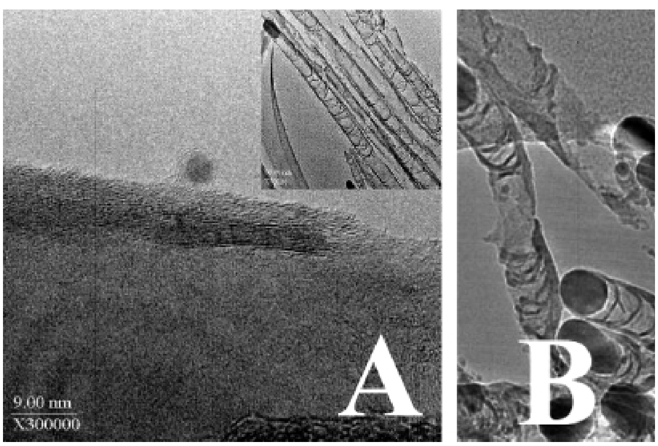

Fig. 5a,b. TEM images: **a** a nanotube with openings on the wall, (*inset*) lower magnification to show the appearance of openings on more nanotubes; **b** carbon nanotubes with openings on the wall from catalyst Co

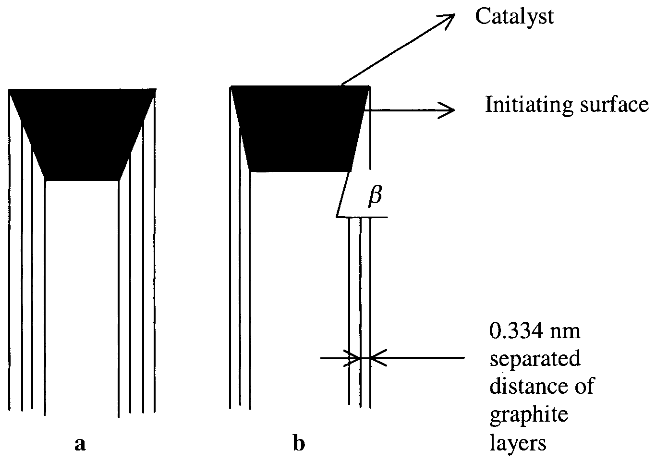

Fig. 6a,b. A schematic of wall-thickness dependence on the angle β. **a** four graphite layers resulting from a smaller β and **b** three graphite layers due to a larger β

we can assume that a Ni particle may have an angle β smaller than Fe and Co particles. So the nanotubes from Ni always show a wall thicker than those from Fe and Co for the same outer diameter.

3 Conclusion

The effect of a catalyst on aligned carbon nanotube growth has been studied. The study reveals that the catalyst strongly affects not only nanotube diameter and growth rate but also morphology and microstructure. Nanotubes grown from Ni have the largest diameter, the highest growth rate and the best alignment. They also exhibit a reasonably good graphitized tubular microstructure. Nanotubes catalyzed by Co show the smallest diameter and lowest growth rate. Fe and Co both produce crooked and twisted carbon nanotubes and these nanotubes possess a thinner wall compared to Ni-catalyzed nanotubes. Some openings on the walls have also been observed among carbon nanotubes produced from Fe and Co. Carbon nanotubes grown from Ni and Fe are relatively free of amorphous carbon, but those from Co are covered with amorphous carbon and carbon nanoparticles. In conclusion, Ni is the most suitable pure-metal catalyst for the growth of aligned multiwall nanotubes.

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