Structural characterisation of carbon nanotubes in the presence of a Ni catalyst

H K Edwards,[1] M W Fay,[1] M Bououdina,[1] D H Gregory,[2] G S Walker[1] and P D Brown[1]

[1]School of Mechanical, Materials, Manufacturing Engineering and Management, and [2]School of Chemistry, University of Nottingham, Nottingham, NG7 2RD, United Kingdom.

Abstract. Multi-wall carbon nanotubes (MWNTs) grown by chemical vapour deposition (CVD) of an ethene / hydrogen gas mixture on alumina supported and unsupported nickel catalysts for 10, 20 and 120 minutes at 600°C and 700°C are compared. Nano-scale nickel particles were identified at the tube ends and also within the main body of the tubes. The particles exhibited comet like structures suggesting the metal to be highly mobile if not molten during processing. HREM observations demonstrate the carbon planes to be parallel to the nickel particle surfaces, while eventually becoming drawn out to define the carbon tube walls. The tubes are generally found to emanate from larger encapsulated nickel particles. A growth mechanism involving the propulsion of mobile nickel through the precipitation of the carbon is discussed.

1. Introduction

The open structures of carbon nanofibres allow for the storage of hydrogen by adsorption and hence there is much interest in developing their application in fuel cells [1]. There is equal interest in developing the properties of multi-wall carbon nanotubes (MWNTs), although hydrogen storage is found to be more difficult using these more closed structures that are presently finding potential applications in nano-scale electrical conduction and nano-composites instead [2]. Here we report on an investigation into the chemical vapour deposition (CVD) synthesis of MWNTs in the presence of a nickel catalyst, assessed using TEM to gain insight into the reaction pathways and growth mechanisms of the nanotubes.

2. Experimental

MWNTs were grown by CVD on alumina supported or unsupported nickel oxide powder in an alumina boat within a tube furnace under flowing argon at temperatures of 600°C and 700°C, established at a ramp rate of 10°C per minute. At the reaction temperature, the gas flow rates were adjusted to achieve a synthesis gas mixture of 80% ethene / 20% hydrogen. Reaction was allowed to proceed in the chamber for 10, 20 or 120 minutes to allow different stages of the growth to be assessed. After growth the furnace temperature was maintained for 15 minutes and then stepped down to room temperature,
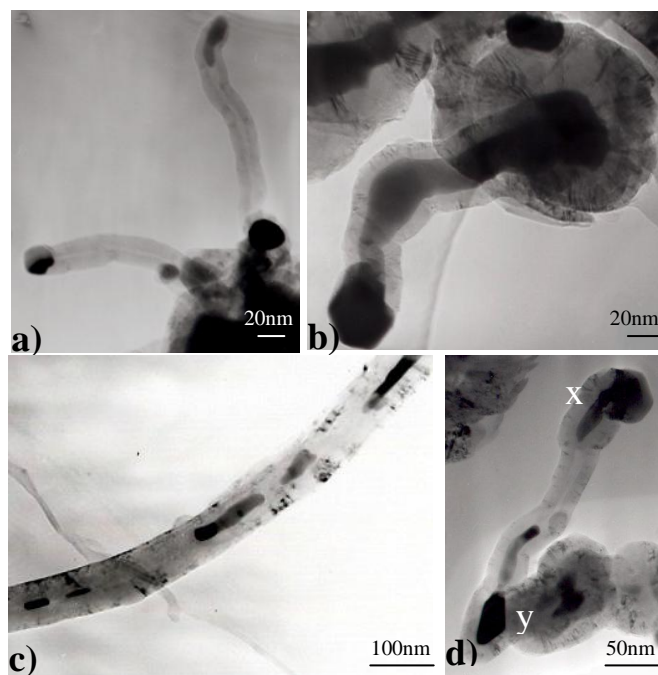
Figure 1 (a,b) Examples of nanotubes grown at 700°C for 10 and 20 minutes, respectively. (c) Nickel catalyst trapped in the hollow core of a nanotube, indicating a highly mobile state has been attained (700°C, 2 hrs). (d) Nanotube with faceted (x) and encapsulated (y) Ni particles at opposite ends (700°C, 20 min).

under flowing argon, to limit further reaction or oxidation of the samples. Powder x-ray diffraction (XRD) confirmed that the initial heating stage was sufficient to fully convert the NiO such that CVD growth proceeded in the presence of a Ni catalyst. Samples of the resultant black powder were removed from the alumina boat and ground or ultrasonically fragmented before being dispersed using acetone onto holey carbon film / copper grids. Specimens were examined using Jeol 2000fx and 4000fx electron microscopes for conventional and high-resolution studies, respectively.

3. Results and Discussion

An initial investigation of tubes grown for a reaction time of 2 hours (using an alumina support) found that those produced at 600°C were more abundant, longer and had larger external diameters than those produced at 700°C for which more carbon encapsulation of the nickel occurred. Tube dimensions were of the order of 1-5 μm in length and 20-100 nm in external diameter at 600°C, and 1-2 μm in length and 15-70nm in external diameter at 700°C, respectively.

Figures 1a,b illustrate MWNTs formed following 10 and 20 minutes of growth at 700°C, respectively. The tubes for these shorter reaction times were typically 100 to 500nm in length, and often found emanating from larger nickel particles encapsulated in carbon. Regardless of reaction time and temperature, highly elongated Ni particles were often situated at both ends of each tube and on occasion distributed along their hollow cores (Figure 1c), the morphology of which might indicate that the catalyst had attained a highly mobile or molten state during synthesis, despite the melting point of Ni being 1453°C.

Figures 2a-c. Three varieties of elongated Ni particles characteristic of the nanotube samples (grown at 700°C for 20 min; 600°C for 2hrs; and 700°C for 2 hrs, respectively).

Nanotubes such as those shown in Figure 1d with a faceted particle at one end (x) and a particle encased in carbon at the other end (y) were also frequently observed.

In particular, three distinct varieties of elongated Ni particles were identified, as illustrated by Figures 2a-c. The first type took the form of faceted particles (Fig. 2a, arrowed) with a trailing tail exhibiting clean faces free from carbon at the presumed growth front. It is considered that these clean facets correspond to the catalytically active part of the particle, responsible for adsorbing and absorbing carbon into the metal as part of the mechanism to promote tube growth. The second type of particle observed was 'comet-like' in shape and bounded by carbon walls of graded thickness (Fig. 2b). Thirdly, loosely faceted particles were identified encased in a thick continuous layer of carbon (Fig. 2c). The first variety of particle was more prevalent at shorter reaction times, whereas the latter two types were more abundant in samples grown for 2 hours. Intriguingly, in Fig. 2b the implication is of a graded build up of carbon walls from the trailing edge of the particle, suggesting the release of carbon from the particle is part of the tube growth mechanism.

Observation of the graphitic planes using HREM around the catalysts and along the tube walls confirmed that the nanotubes displayed varying levels of crystallinity. As a general observation the carbon walls followed the shape of the catalyst but then transformed with increasing distance from the catalyst into the parallel-sided walls of the NTs, whilst also become more disrupted and broken up.

Starting from the initial transformation of NiO to Ni, these combined observations implicate the following mechanism in the formation of MWNTs trailing behind clean faceted Ni particles (Figure 3):

- On the surface of a catalyst particle, ethene decomposes to carbon that is adsorbed, whilst hydrogen is released. A resultant carbon monolayer presumably covers the exposed faces of the particle (Figures 3i,ii).
- It is suggested that the Ni faces that have a high carbon diffusion rate preferentially absorb the carbon atoms, creating a low C-content Ni-alloy. (The combined TEM and XRD evidence confirmed that a distinct nickel carbide had not formed.)
- A concentration gradient of carbon will presumably develop within the particle between the catalyst-vapour surface (Fig. 3ii(x)) and the Ni-support interface (Fig. 3ii(y)). The absorbed carbon will thus undergo bulk diffusion through the Ni to the precipitating planes where individual atomic planes of carbon are produced and sequentially build up parallel to the trailing surface of the Ni particle.
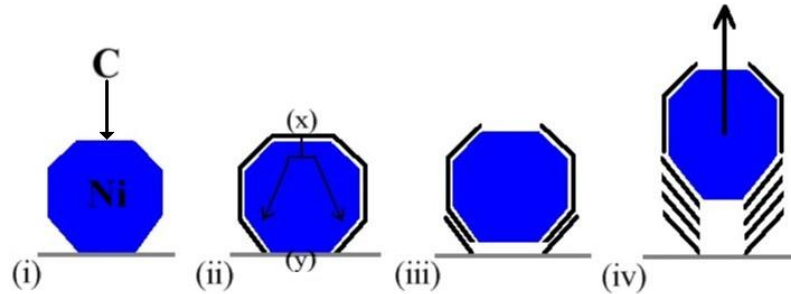
Figure 3. Proposed nanotube growth mechanism including the adsorption, absorption, diffusion and precipitation of carbon.

- This precipitation of carbon causes the propulsion of the Ni particle away from its original location (Fig .3iii).
- As the catalytic reaction proceeds more carbon is adsorbed, absorbed and diffused through the Ni particle to be precipitated and perpetuate the growth of the nanotube (Fig. 3iv). During this process the nickel apparently approaches an almost liquid state.

While it is possible that there is some surface diffusion of carbon around each particle, the evidence suggests that the absorption planes remain clean or only lightly carbon covered throughout the nanotube growth (Figs. 2a,b), whilst thick encapsulated particles are possibly indicative of continued carbon growth at the end of the reaction process (Fig. 2c). The diffusion and precipitation of carbon causes elongation and separation of the particles resulting in Ni being left at the nucleating end of the nanotube or distributed along the core body, before growth eventually terminates and the propagating particle becomes encapsulated. It is suggested that the small particle size with its large surface area to volume ratio, combined with the formation of a Ni-C alloy, promote the molten-like behaviour of the Ni particles observed. To support this suggestion it is noted that a Co-C system theoretically displays molten-like behaviour at elevated temperatures (but well below its melting point) [3]. The details of carbon plane reorientation from the Ni particle to the walls of the tube are not fully understood, however, the formation of tube walls of constant thickness suggests a uniform rate of carbon precipitation.

4. Summary
The initial stages of multi-wall nanotube growth by CVD at 600°C and 700°C have been characterised. Elongated Ni catalyst particles initiating or terminating tube growth, or distributed within the body of the tubes, implicate a highly mobile or liquid state of the Ni that actively promotes the mechanism of tube growth.

5. References
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