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Laser-assisted production of multi-walled carbon nanotubes from acetylene

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Abstract

A production method of carbon nanotubes using the catalytic decomposition of acetylene has been developed. Metal clusters are formed by laser vaporisation of solid nickel in situ in a hot reaction tube containing a mixture of acetylene and argon. The laser generated clusters act as catalysts for the growth of nanotubes. With this method multi-walled tubes were obtained with inner diameters of 3–10 nm and outer diameters of 10–100 nm. Transmission electron microscopy shows that the tubes are highly graphitic. The results obtained are explained by a growth model.

1. Introduction

For at least four decades the chemical vapour deposition (CVD) has been known as a technique suitable for the production of filamentous carbon by the catalytic decomposition of carbon monoxide or hydrocarbons on metal catalysts [1–12]. During the past few years new methods for the production of carbon fibrils have been developed which are based on the co-vaporisation of pure carbon and a metal catalyst either in an electric arc discharge [13–16] or by high-power laser irradiation [17,18]. The fibrils usually have an almost perfect graphitic tube structure. However, the samples produced with the arc discharge method always contain a significant amount of amorphous carbon together with the nanotubes [13–15], though significant progress has been achieved recently [16]. Using a laser vaporisation method, tubes can be generated with a very high relative yield [17,18]. This technique allows the independent controlling of most of the experimental parameters, therefore permitting a good optimisation of the process even with the highest laser power available. However, the total amount of material evaporated is much less than with the more common arc discharge method.

We have combined the laser vaporisation technique with the CVD method. In our apparatus the laser is used to vaporise the solid catalyst and generate catalytic metal aggregates in situ in the hot reaction tube while the carbon is being introduced as a gaseous compound. In this way it is possible to achieve higher absolute yields, since the supply of carbon is not limited by the vaporisation of solid graphite. The growth of tubes occurred in the gas phase as well as on the walls of the reaction tube. Most of the process parameters (e.g., laser parame-

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ters, pressure, gas composition, flow, temperature, reaction time) can be controlled independently.

2. Experimental

The experiments have been performed in a reaction chamber originally designed for the laser vaporisation of graphite and modified according to Fig. 1.

A nickel target (2 cm diameter, 99.2 % Ni) was attached to a water-cooled rod in order to suppress unwanted surface reactions. It was placed in the centre of the quartz reaction tube (3.5 cm inner diameter). The reaction chamber was pumped down to 10^{-4} mbar for at least 15 min. After closing the valve to the vacuum pump, the quartz tube was filled with a mixture of argon and acetylene at a pressure of 300 mbar ($P(\mathrm{Ar}) = 260$ mbar, $P(\mathrm{C_2H_2}) = 40$ mbar). The focussed laser beam (~ 1 mm focus diameter) of the high-power laser was scanned over the target in a circle using a rotating mirror. Experimental results were obtained using two different pulsed Nd:YAG lasers with $\lambda = 1064$ nm, $\nu = 20$ Hz, pulse length 5 or 30 ns and pulse energy 700 or 1000 mJ. The laser was operated for 2–4 min generating highly excited nickel aggregates.

The reaction was stopped by switching off the laser and pumping the reaction chamber down to 10^{-4} mbar. While cooling down, the reaction chamber was kept under vacuum. The reaction products were removed from the walls of the chamber and from the target holder, suspended in acetone, toluene or chloroform, and subsequently treated in a supersonic bath. The samples were examined with scanning electron microscopy (SEM, Hitachi S-2700), transmission electron microscopy (TEM, Philips CM 200 FEG) and energy-dispersive X-ray spectroscopy (EDX).

3. Results

Two types of Nd:YAG laser arrangements were used to generate nickel aggregates. The laser parameters were not optimised with respect to the particle size. From TEM pictures of our samples the size of the nickel aggregates were estimated to be between ~ 1 and 100 nm. The reaction product removed from the chamber usually contains $\sim 30\%$ multi-walled nanotubes. The remainder consists of encapsulated large nickel particles and amorphous carbon. Some parts consist almost entirely of multi-walled nanotubes as shown in Fig. 2.

These tubes mainly had outer diameters of 10–40 nm, and in some cases 50–100 nm. Inner diameters were between 3 and 10 nm. High-resolution TEM clearly showed an almost perfect crystalline graphitic structure of the inner walls, while the outer shells were partially amorphous (Fig. 3). Some of the tubes had a nickel aggregate at the end of the tube. Others had open ends, most likely due to the loss of the catalyst particle. The size of the metal aggregates

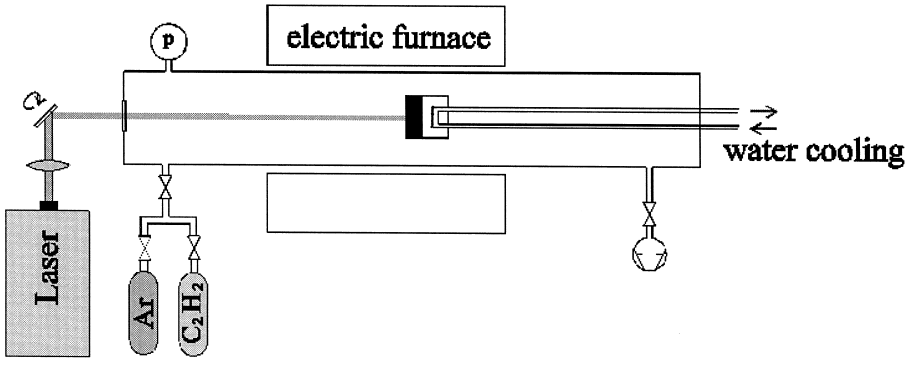

Fig. 1. Experimental arrangement: water-cooled nickel target, pulsed Nd:YAG laser with $\lambda = 1064$ nm, $\nu = 20$ Hz, pulse energy 0.7 or 1 J in 5 or 30 ns, respectively, focal length = 750 mm, oven temperature 750°C, acetylene–argon mixture (1:6.5), pressure 300 mbar.

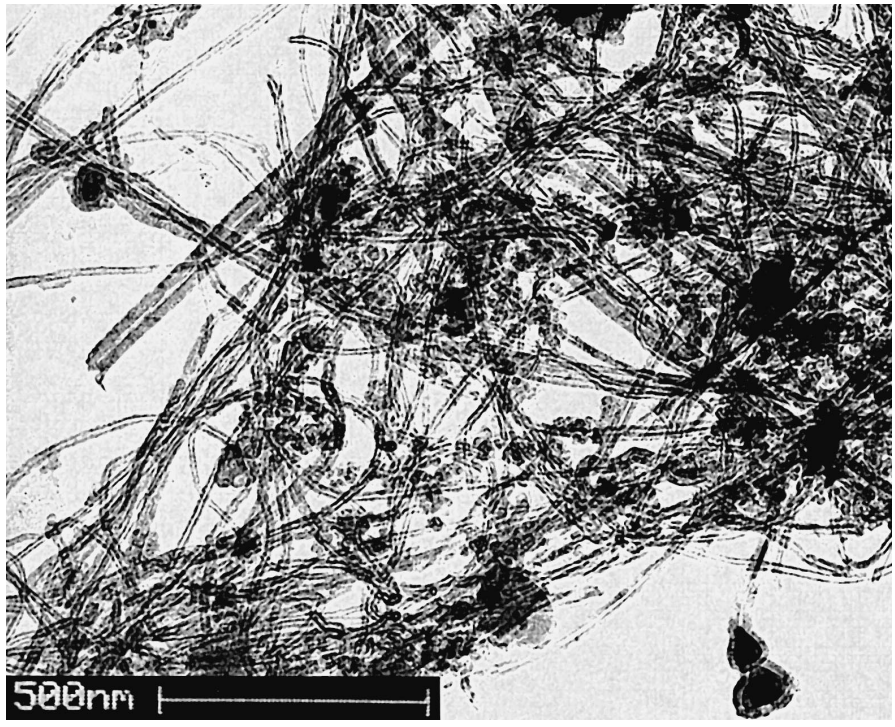

Fig. 2. TEM image of the reaction product containing multi-walled carbon nanotubes, encapsulated nickel particles and some amorphous carbon.

found at the end of the tubes were 15–25 nm for the smallest dimension. They were elongated rather than spherical. Sometimes the tubes were partially filled with nickel. The particles incorporated in the tubes varied between 5 and 10 nm in diameter. Small nickel clusters (< 5 nm) were found to be embedded

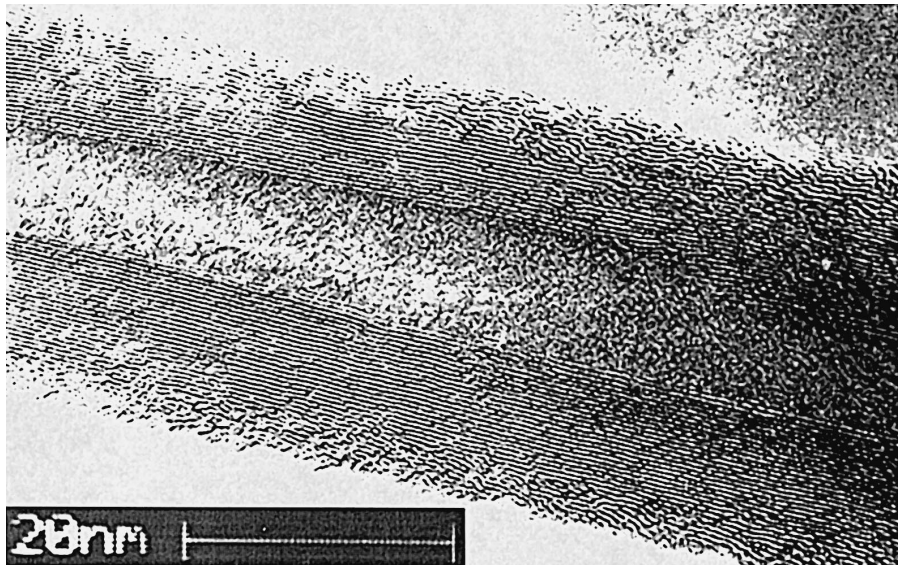

Fig. 3. High-resolution TEM image showing the highly graphitic nature of the multi-walled carbon nanotube.

in the amorphous carbon between the tubes. Large particles (>25 nm) were encapsulated by a multilayer graphitic skin.

The large number experimental parameters (oven temperature, laser parameters, pressure, metal, reaction time) would require many experiments to optimise the system. In the following we give some preliminary quantitative results of this procedure: lowering the temperature below 700°C resulted in a very low product yield with a much higher relative content of amorphous carbon. Higher temperatures have not yet been studied. The laser focusing is less critical. Changing the focus diameter of the laser beam on the target surface in the range of 0.7–1.5 mm did not significantly influence the quantity and quality of our product. However, if the nickel target was placed precisely in the distance of the focal length of the lens, the product yield decreased due to the reduced amount of nickel evaporated under these conditions. Lasers (Nd:YAG, Eximer) with the same pulse energy but much longer pulse time (e.g., 1 μs) generated relatively large nickel droplets. Hardly any carbon was deposited on their surfaces. Only two alternative experiments to study the effect of the acetylene pressure were done. An overall pressure of 300 mbar with a content of 200 mbar acetylene led to polymerisation of the acetylene. When only a small amount of acetylene (20 mbar) was used, the product yield was low.

4. Discussion

The growth model for CVD grown carbon nanotubes was adapted from Baker et al. [5] who found a remarkable correlation between the activation energies directly measured for the growth of the carbon fibrils and those for the diffusion of carbon through the corresponding metals. His proposed temperature-driven diffusion mechanism is strongly supported by the experimental results of Yang and Yang [19]. They let different hydrocarbon gases stream past one side of a thin nickel film and found that the side of the carbon deposit formations was dependent on the heat of decomposition of the hydrocarbon gases tested. Contrarily to our results, the nanofibres produced by Baker [5] were filled with amorphous carbon. We made only small changes to his model in order to describe most of our experimental results. The growth model describes the formation of carbon nanotubes in four stages:

(1) Hydrocarbon molecules are adsorbed on different parts of the surface of small metal aggregates. The different surfaces have different catalytic activity due to their crystal orientation [7,20] (Fig. 4a).

(2) The active metal surfaces crack the carbon–hydrogen bonds. The carbon diffuses into the bulk material. For unsaturated hydrocarbons this process is highly exothermic, increasing the surface temperature of the catalytic active sites [5] (Fig. 4b).

(3) When the saturation limit for carbon on the cooler parts of the surface of the particle is reached, the carbon is precipitated off the metal surface: this is an endothermic process [5]. The resulting temperature gradient between the active, carbon dissolving surface and the opposite carbon emitting side leads to further carbon diffusion through the particle. The relatively slow diffusion determines the overall reaction rate. The only way to avoid the energetically unfavourable dangling bonds of the carbon deposit is to form a carbon tube with a closed cap (Fig. 4c).

(4) If excess carbon on the surface does not diffuse fast enough to build up the filament, the

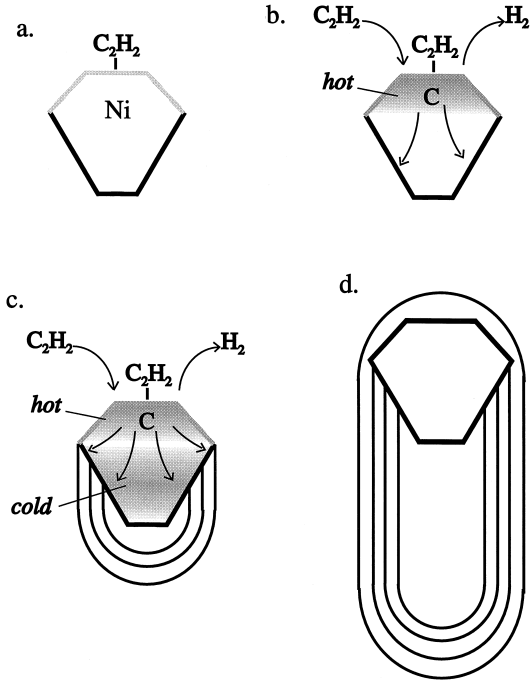

Fig. 4. Proposed mechanism of carbon nanotube formation.

particle becomes completely encapsulated, stopping further growth (Fig. 4d).

Several studies have suggested that the inner diameter of the nanofibres produced by the CVD method is determined by the size of the catalyst particles [9,12]. However, from our study, it seems that this is only very roughly the case. Although cluster sizes vary between 1 and 100 nm, the tubes are generated in most cases with inner diameters of 3–10 nm. Our findings suggest rather that only particles of a certain narrow size range (from 15 to 25 nm) are active for the formation of nanotubes. The longish form of the inclusions we find indicates that the nickel particles are at least partially molten during the growth of the tube took place. From our experiment we cannot decide whether the fibre formation starts from a molten metal droplet, or if the exothermic nature of the reaction combined with the freezing-point depression due to the solvating of carbon in the metal causes the melting. Bearing in mind that similar multi-walled carbon nanotube formation can take place at temperatures as low as 390°C [3], we did not address the melting by the growth model we used.

The model restricts the range of catalyst particle diameter where effective growth is possible. For large particles the reaction is too slow due to the long diffusion lengths. This explains why there is almost no contribution of aggregates larger than 25 nm. These large particles become easily encapsulated with excess carbon and completely inactive before any fibre growth can start. The smaller the particles are, the faster the growth rate should be. However, very small metal particles (< 3 nm) are also not useful for the growth of carbon nanotubes. To avoid dangling bonds during the growth process the whole tube cross-section must be in contact with the metal surface. However, tubes of very small diameters are energetically unfavourable because of their inner strain. This implies that there is a minimum particle diameter for the formation of nanotubes [6]. In our reaction conditions only tubes with diameters larger than 3 nm are formed. If the catalytic particle's diameter is less than this minimum tube size of 3 nm, no tubes can be formed.

In the hot reaction chamber the acetylene also reacts with itself, leading to the formation of a tar-like side product. This material condenses on the tubes after their formation and carbonises further. This explains the amorphous coating of our graphitic multiple tubes. By changing the reaction gas from acetylene to carbon monoxide it may be possible to suppress the polymerisation [12], but even in this case we expect some amorphous product (which is inevitable if one has a plasma flame inside the reactor). Further optimisation of laser and reaction parameters should also lead to a higher quality of the samples.

5. Conclusions

We have reported a new laser method for the production of carbon nanotubes by the catalytic decomposition of acetylene. With this method, multi-walled tubes were obtained with inner diameters of 3–10 nm and outer diameters of 10–100 nm. TEM analysis shows a high degree of graphitisation of these tubes. The results obtained are in good agreement with a growth model developed by Baker et al. [5] for the formation of carbon nonofibres.

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