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Solar production of carbon nanotubes; structure evolution with experimental conditions

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In this work we report the production of carbon nanotubes by direct vapourization of graphite targets containing different couples of catalysts using a 2 kW solar furnace. With this small-scale experimental set-up we observed the evolution of the structure of the produced nanotubes with experimental conditions, pressure and flow rate of the inert gas (argon) and target composition. High pressure favours the production of bundles of single-wall nanotubes (SWNTs) and the purity of the produced material depends on the target temperature and the cooling rate of the vapour. We also discuss the influence of the target composition. © *2000 Kluwer Academic Publishers*

1. Introduction

Despite the fullerene and carbon nanotube research has become a major field in condensed matter physics and chemistry, the large scale production of these materials with high yield and selectivity is still a crucial problem. As a consequence, their prohibitive cost reduces the development of practical uses. Various method have been explored to produce single-wall carbon nanotubes (SWNTs) and the most attractive is the vapourization of mixed targets of graphite and catalysts under inert gas atmosphere in which different methods are used to induce target vapourization: laser ablation [1, 2], electric arc [3] and recently solar energy vapourization [4]. Actually, the highest reported yield of SWNTs is obtained by laser ablation by which it can reach 70% [2, 5]. The production can reach 10 g per day with a scaled-up version of the laser method [6] but with a yield of SWNTs significantly lower. Journet *et al*. [3] at GDPC (Montpellier) previously reported that a high yield of SWNTs can also be obtained in the cathodic deposit of an electric arc catalyzed by Ni and Y.

For these two methods, the obtained material contains additionally fullerenes and a significant fraction of undesired nanoparticles, carbon nanospheres and carbon coated metal nanoparticles. It is necessary to separate the SWNTs portion from these undesired nanoparticles. Small scale experiments with a 2 kW solar furnace also give SWNTs but with a lower purity than with the two other methods. Nevertheless, the solar method can lead to a better understanding of the formation mechanisms of these nanotubes as we can easily change the experimental conditions and observe the structure evolution of the produced nanotubes as a function of pressure, flow rate of inert gas and target composition.

2. Experimental

For the production of carbon nanotubes we have used the same small-scale experimental set-up previously described for fullerenes [7], changing the target composition and adjusting the experimental conditions. The 2 kW vertical solar furnace is formed by a flat tracking mirror which reflects vertically the sunlight toward a parabolic mirror. The reactor is shown schematically in Fig. 1. It can be adjusted so that the top of the crucible would be at the focus of the parabolic mirror. The stand part, surrounded by the Pyrex balloon flask, is a water cooled brass cylinder which support the cellulose filter to collect the soot. The target which is a graphite crucible filled with a mixture of powdered graphite and catalysts, is hunged in the graphite pipe linked to the filter with a brass holder. This pipe which canalizes the carbon vapour and is heated at its top by the sunlight,

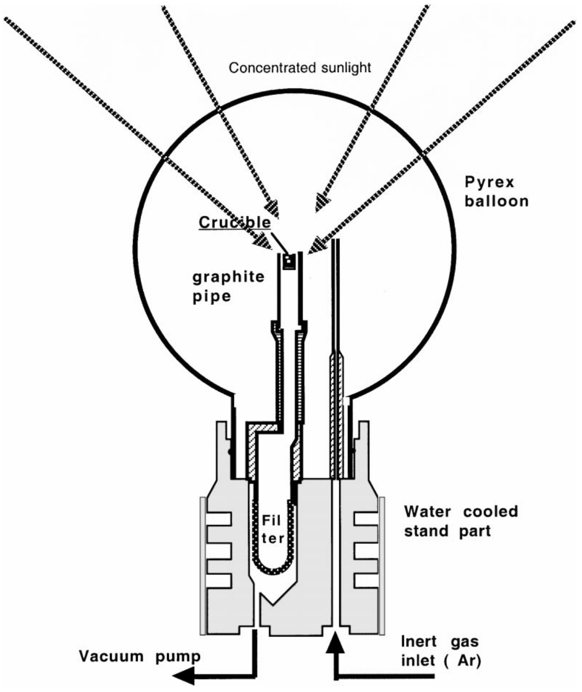


Figure 1 Experimental chamber.

works like a thermal screen and also forms the annealing zone. This chamber was first evacuated and purged and swept by argon gas during vapourization. The pressure could be varied from vacuum to 600 mbar and the gas flow rate adjusted for any values of the pressure. With clear sky conditions, the measured temperature of the crucible usually reaches 3000 K.

Vapourizing the usual mixture of graphite, cobalt and nickel, we have observed the evolution of the nanotubes in terms of the variations of the pressure and flow rate of the argon gas. We have also tested mixtures with nickel and yttrium or nickel and lanthanium ($LaCl_3$) which also catalyze the growth of single-wall nanotubes [8]. As for fullerenes, this process can be scaled up and experiments are also planed with the 1000 kW solar furnace of the Odeillo Institute.

For all experiments, we found that the highest amount of nanotubes is condensed into the graphite pipe where the temperature is maximal in the overall condensing zone. When nanotubes are produced, the deposit has a rubbery aspect and large sheets can be easily peeled off from the pipe. SEM observations show the fibrillar structure of the material which contains, in addition, carbon coated metal nanoparticles, amorphous carbon and carbon nanospheres. The soot collected in the filter is essentially constituted of these undesired nanoparticles with a very small number of nanotubes. In addition, fullerenes are detected by soaking the as prepared soot in toluen and studying the UV-Visible absorption spectra of these solutions.

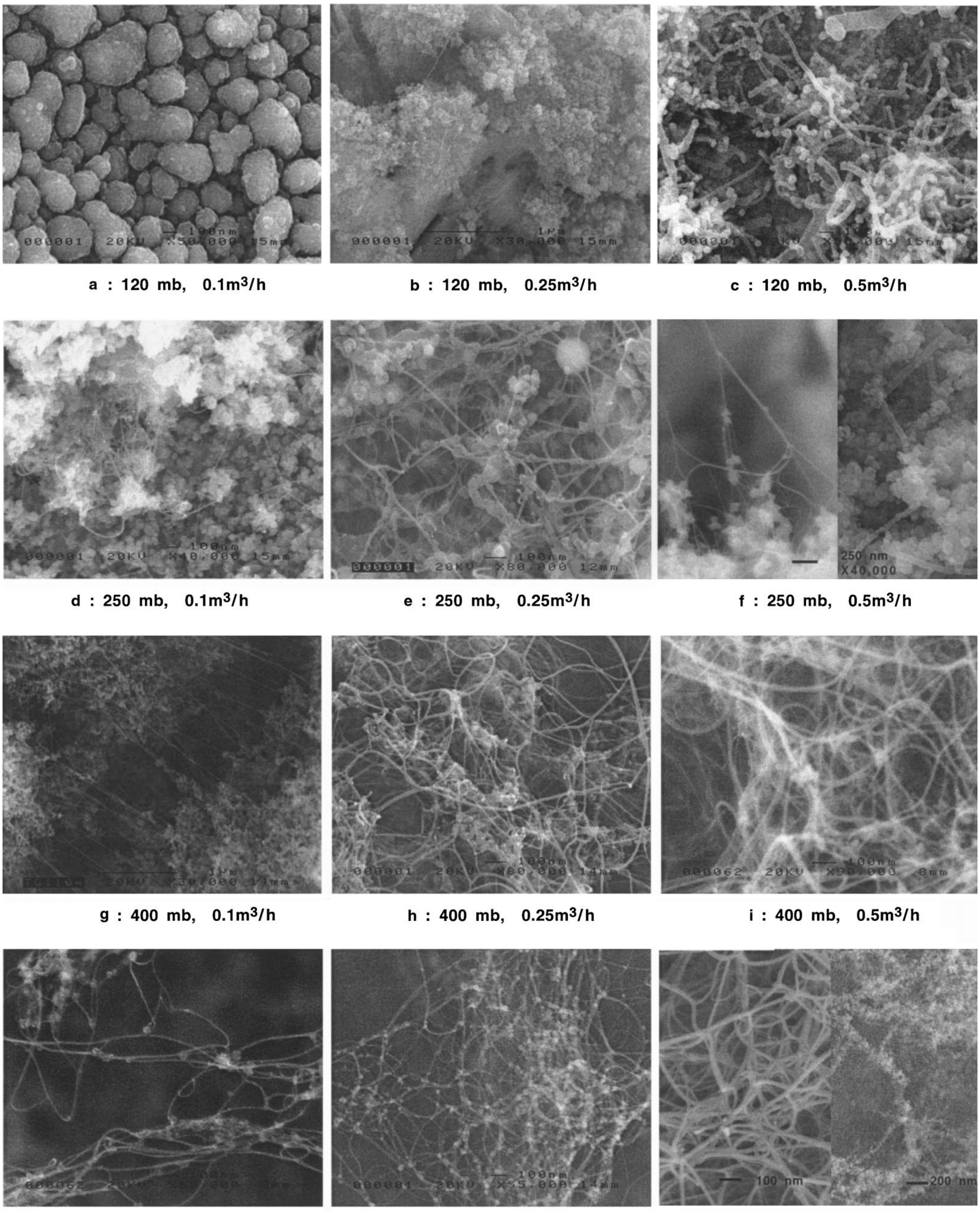
3. Pressure and flow rate effects

We have synthesized carbon nanotubes with the same mixture of powdered graphite, cobalt and nickel (2 at % of Co and 2 at % of Ni) under argon atmosphere, at various pressures (120, 250, 400 and 600 mbar) and for each pressure with three different flow rates (0.1, 0.25 and 0.5 m^3/h). From the whole set of experiments, we have selected only those done with the same incident solar flux, about 950 W/m^2 corresponding to a peak power of 1330 W/cm^2 at the focus of the solar furnace. The measured temperature of the crucible, which remains the same for all the experiments, is around 3000 K. As the vapourization rate is mainly depending on the target temperature, we can assume that it remains constant for all the experiments.

The samples were first studied by SEM and the results are shown in Fig. 2. At low pressure, the production of nanotubes is not observed. We have found a certain amount of large carbon fibrils whose number increases with the flow rate. Carbon nanotubes are detected when the pressure reaches 250 mbar. In this case, the material contains carbon fibrils with very different diameters and a lot of catalyst particles embedded in amorphous carbon. For higher pressures (400–600 mbar), it appears high density areas of entangled fibrils (bundles of SWNTs) that could be as long as few micrometers. A better purity and homogeneity of the material is noted, but the fraction of undesired particles remains large and increases with the flow rate.

More accurate observations have been performed by TEM and the more significant micrographs are shown in Fig. 3. At low pressure, we observed large objects which are not nanotubes and look like the precursors of carbon fibers. When the pressure reaches 250 mbar, the collected chips contain both multi-walled nanotubes, ropes of single wall nanotubes and carbon vesicles (Fig. 3c). We can note the presence of mixted catalysts nanoparticles (Co and Ni) at the end of multi-walled nanotubes, bamboo like shaped (Fig. 3d) and HRTEM observations show that the distance between the graphene sheets is around 0.34 nm. Large fibers are found, especially for higher flow rates. When the pressure becomes higher than 400 mbar, TEM micrographs show that the fibrils are bundles of SWNTs with diameters in the range 10–40 nm. In these bundles, the diameter of each nanotube can be estimated to be about 1.3 nm. According to these TEM overviews, it seems that the size of the bundles is greater for the lower flow rates. The presence of bundles of SWNTs is confirmed by Raman spectroscopy. These Raman spectra display the same features as those obtained with SWNTs produced by laser ablation [9]. But, for our samples, in the low frequency range, the radial breathing band which is strongly correlated to the tube diameters [10], shows a large number of peaks. The number of peaks is greater than those observed with samples produced by electric arc or laser ablation. Some of them appear at frequencies smaller than 180 cm^{-1}, corresponding to large diameter tubes.

These experiments show clearly that the dilution of carbon vapour which increases with the pressure of the inert gas, favours the production of SWNTs and reduces the proportion of nanoparticles and amorphous carbon in the samples. When all the other parameters remain constant, the pressure increase prevents the fast and disordered clustering of carbon atoms which can be important in our experiments, as the temperature of the target is lower than in laser ablation or electric arc methods.



a : 120 mb, 0.1m^3/h b : 120 mb, 0.25m^3/h c : 120 mb, 0.5m^3/h

d : 250 mb, 0.1m^3/h e : 250 mb, 0.25m^3/h f : 250 mb, 0.5m^3/h

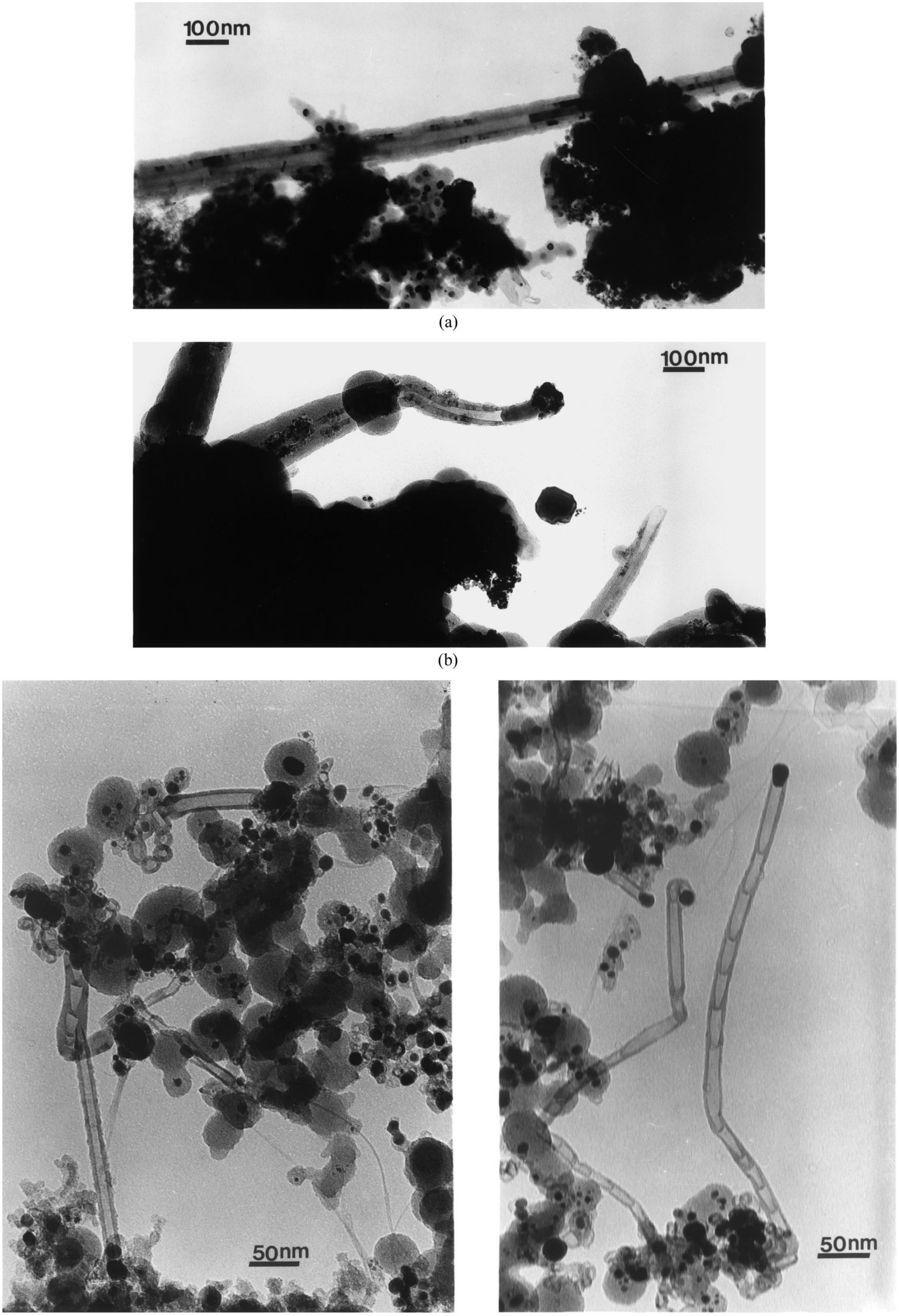
g : 400 mb, 0.1m^3/h h : 400 mb, 0.25m^3/h i : 400 mb, 0.5m^3/h

j : 600 mb, 0.1m^3/h k : 600 mb, 0.25m^3/h l : 600 mb, 0.5m^3/h

Figure 2 SEM micrographs showing the structure evolution of the produced materials as a function of pressure and flow rate of the inert gas (argon). Target composition: powdered graphite, Ni (2 at %) and Co (2 at %), vapourization temperature 3000 K.

The increase of the flow rate (at constant pressure and vapourization temperature) also produces a dilution of carbon vapour but it also changes the residence time of the carbon vapour in the hot part of the reactor. As the temperature gradient in the reactor is large, the cooling rate of the carbon vapour increases with the flow rate, leading to more disordered materials. This effect is more important at low pressure at which different species of carbon fibrils are observed in some cases. For the highest pressures (upto 400 mbar), the amount of undesired nanoparticles becomes larger when the flow rate increases and these nanoparticles appear sometimes on the ropes of SWNTs. The presence of multi-walled nanotubes at low pressure (250 mbar) mixed with other species, can also be interpreted in this way, because the size of catalyst nanoparticles is also affected by the cooling rate.

This interpretation is in agreement with the proposed growth mechanisms of SWNTs produced by electric arc or laser ablation for which different authors [1, 11, 12] assume that the tubes are formed in the plasma close to the target and are drawn by the flow of inert gas or convection processes into the cold part of the reactor. On the solar oven experiments we can explain why the



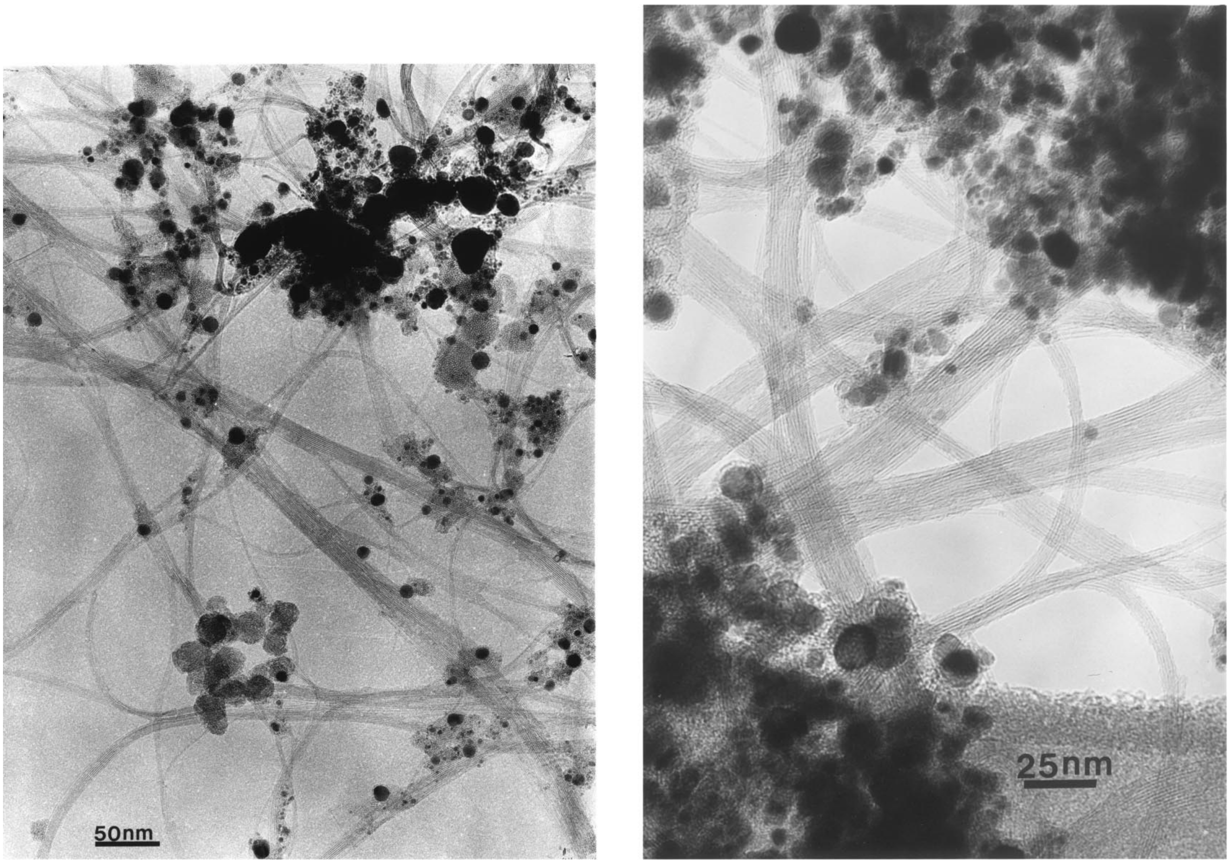
(a)

(b)

(c)

(d)

Figure 3 Some significant TEM micrographs of the as grown materials (same experimental conditions as for Fig. 2). At low pressure (120 mbar) we observe large objects which look like the precursors of carbon fibers (a, b). When the pressure reaches 250 mbar, the soot contains multi wall nanotubes, some ropes of SWNTs and carbon vesicles (c, d). Under pressure up to 400 mbar (e, f) we found only self-organized bundles of SWNTs, the estimated diameter of the tubes being around 1.3 nm. (*Continued*)

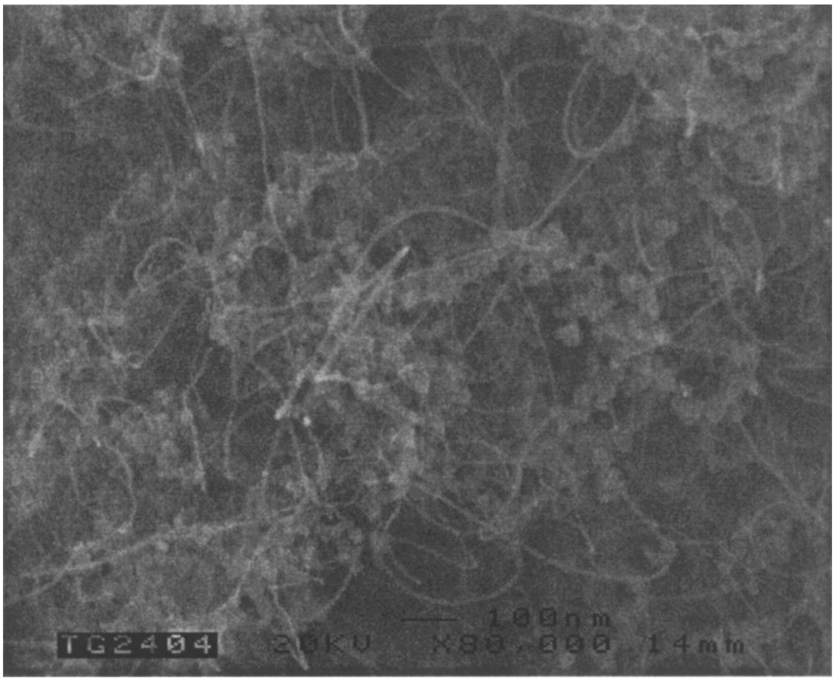


(e) (f)

Figure 3 (*Continued*).

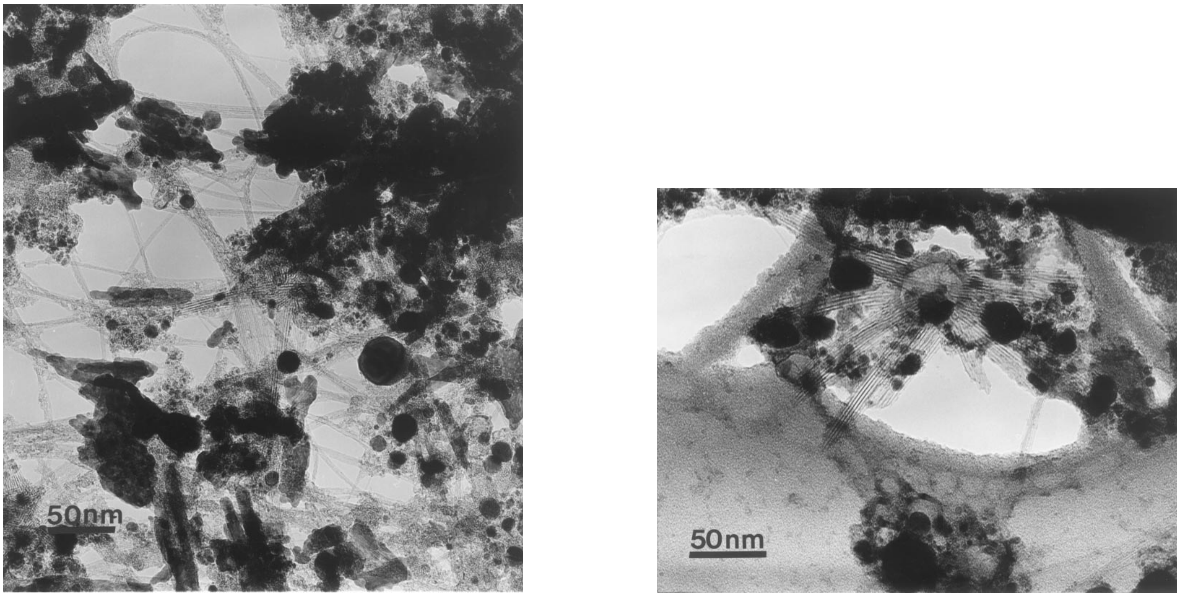
tubes are deposited into the graphite pipe: as they grow near the crucible, they are drawn by the gas through a very weak annular aperture where turbulent effects favour their deposition.

Finally, the structure of the SWNTs obtained in this solar furnace, under a pressure higher than 400 mbar is very similar to those observed for nanotubes produced by laser ablation or electric arc, with the difference



(a)

Figure 4 SEM (a) and TEM (b, c) micrographs of the as grown soot produced with mixture of graphite, Ni (2 at %) and $LaCl_3$ (2 at % La). (*Continued*)



(b) (c)

Figure 4 (*Continued*).

that the as grown material contains generally larger amount of nanoparticles and amorphous carbon. This difference arises from the vapourization temperature which is lower than in the two other methods. To obtain SWNTs with higher purity even under the highest pressure which lowers the disordered clustering of carbon atoms, the target temperature must be higher than 3000 K and this can be achieved by using the 1000 kW solar furnace.

4. Target composition

Various tests have been performed in which the target composition were changed under maintainance of the best experimental conditions (pressure around 450–500 mbar and low flow rate). We have produced SWNTs using the same catalyst couple Ni and Co (2 at % of 1/1 mixture of Ni and Co) mixed with different varieties of carbon: cruched graphite tips (Alfa, Johnson Matthey) as used with electric arc at GDPC (Montpellier), powdered graphite (Aldrich) or granulated activated coal (Pica). It appears very weak differences in the production, purity and structure of the SWNTs as confirmed by SEM and TEM observations which are very similar with the reported ones in the preceding part.

Tests have been performed with various catalysts. On one hand, by using pure cobalt as the catalyst, we found a very small amount of nanotubes in the TEM image. The size of the catalyst nanoparticles is small (20–30 nm) and the ropes contains a small number of tubes. On the other hand, vapourization of mixture with nickel gave large catalyst nanoparticles (75–100 nm) from which start very large bundles of SWNTs. This result is in agreement with the one reported by Saito [13] using an electric arc catalyzed by Ni alone. The vapourization of mixtures with nickel and yttrium gave ropes of SWNTs which can be longer than 2 mm, each of them formed by a great number of SWNTs. But we obtained always a large amount of nanoparticles in addition.

Futhermore tests have been done with mixtures of graphite, nickel and lantanium chloride (2 at % of Ni and 2 at % of La). SEM and TEM observations show the presence of bundles of SWNTs, with a large amount of needle shaped nanoparticles. Chemical analyses of these particles are now in progress. The micrograph shown in Fig. 4 shows that the samples contain bundles of nanotubes with different diameters in the range 0.9–1.6 nm. Raman spectra, published elsewere [9], display complex bands in the low frequency range in agreement with the presence of SWNTs of different structures and diameters.

5. Conclusion

Experimental results are presented which demonstrate that the production of carbon nanotubes is possible by direct vapourization of mixture of graphite and catalyst using concentrated solar energy. SEM and TEM observations have shown that the structure of the condensed material is dependent of the pressure and flow rate of the inert gas. In the used small-scale reactor, we could obtain SWNTs at pressures higher than 400 mbar. It clearly appears that the dominant process parameters are the temperature of the target and of the surrounding zone. To obtain high-purity SWNTs with uniform structure it is necessary to increase this temperature to about 3400 K and to control the cooling rate of the vapour. As for solar fullerene production, one possibility to produce large amounts of high-purity SWNTs can be the use of the 1000 kW solar furnace for which the predicted target temperature is 3400 K.

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