Review

Solid state growth mechanisms for carbon nanotubes

Peter J.F. Harris

Centre for Advanced Microscopy, J.J. Thomson Physical Laboratory, University of Reading, Whiteknights, Reading RG6 6AF, UK

Received 9 May 2006; accepted 18 September 2006
Available online 7 November 2006

Abstract

The mechanisms by which carbon nanotubes nucleate and grow remain poorly understood. This paper reviews the models which have been proposed to explain nanotube growth in the arc-evaporation and laser-vaporisation processes. Many of the early models assumed that growth is a gas phase phenomenon but there is growing experimental evidence that the formation of both multi-walled and single-walled tubes involves a solid state transformation. Heating rate also seems to be important in promoting nanotube growth.

© 2006 Elsevier Ltd. All rights reserved.

Contents

1. Introduction ................................................................. 230
2. Arc-evaporation synthesis of multiwalled nanotubes ................................................................. 230
  2.1. Experimental details .................................................... 230
  2.2. Theories of multiwalled nanotube growth by arc-evaporation .............................................. 231
      2.2.1. Vapour phase growth .............................................. 231
      2.2.2. Liquid phase growth .............................................. 231
      2.2.3. Solid phase growth .............................................. 231
      2.2.4. The crystallization model ...................................... 232
3. Non-CCVD synthesis of single-walled nanotubes ................................................................. 234
  3.1. Arc-evaporation ........................................................ 234
  3.2. Laser-vaporisation ...................................................... 234
  3.3. Theories of single-walled nanotube growth ................................................................. 234
4. Discussion ................................................................. 236
  4.1. Multiwalled nanotubes .................................................. 236
  4.2. Single-walled nanotubes .............................................. 237
5. Conclusion ................................................................. 237
Acknowledgements ...................................................... 237
References ................................................................. 237
1. Introduction

The current explosion of interest in carbon nanotubes began with the discovery by Iijima in 1991 that multiwalled nanotubes (MWCNTs) with an extremely high degree of perfection could be produced by arc-evaporation [1]. Despite a huge amount of research into the catalytic synthesis of MWCNTs, arc-evaporation remains the method which produces the best quality tubes. Thus, most of the experiments demonstrating the outstanding mechanical properties of multiwalled nanotubes (e.g. [2,3]) have been carried out on arc-produced tubes. When produced catalytically, MWCNTs tend to be relatively defective and generally have much inferior mechanical properties (e.g. [4]). There is also the disadvantage that the tube samples are contaminated with catalytic particles. The processes used for removing these particles can introduce further defects into the nanotubes.

In 1993, Iijima and Ichihashi and Bethune et al. independently reported the synthesis of single-walled carbon nanotubes by the arc-evaporation method [5,6]. This was achieved by adding a small amount of an iron-group metal to one or both of the electrodes, and carrying out the discharge under similar conditions to those used for multiwalled nanotube synthesis. Subsequent work showed that single-walled carbon nanotubes of comparable quality could be produced by the laser-vaporisation of a metal–graphite target [7], and this has become an important technique for SWCNT synthesis.

Despite the importance of the arc-evaporation and laser-vaporisation methods of nanotube synthesis, the mechanisms involved remain rather poorly understood. The lack of a detailed understanding of these mechanisms has been a serious impediment to progress in nanotube research. Without such an understanding, there is little hope of developing techniques for preparing nanotubes with defined structures, which are needed for a host of applications [8]. In this paper, a review is given of the various mechanisms which have been put forward for the growth of multiwalled and single-walled carbon nanotubes by the arc and laser methods. Synthesis of nanotubes by catalytic chemical vapour deposition (CCVD) is not considered here, as the growth mechanisms involved are likely to be rather different [9]. For the synthesis of multiwalled nanotubes in the arc, three types of mechanism have been put forward, which could be labelled “gas”, “solid” and “liquid”. The gas phase models assume that nanotube nucleation and growth occur as a result of direct condensation from the vapour, or plasma, phase. In solid phase models, the nanotubes and nanoparticles do not grow in the arc plasma, but rather form on the cathode as a result of a solid state transformation. A variant of the solid state model envisages a “crystallization” of nanotubes from extended assemblies of disordered carbon, while the liquid phase model assumes that nanotubes nucleate within globules of liquid carbon deposited onto the cathode. There is currently no agreement about which of these mechanisms is correct. For single-walled nanotubes, whether produced by arc or laser, the growth mechanism is equally uncertain. The most popular model at present is the vapour–liquid–solid model, in which carbon from the vapour phase is deposited onto liquid phase metal carbide particles, from which the nanotubes then grow. This paper argues that for both multiwalled and single-walled nanotubes there are good reasons to believe that the mechanism involves a solid state transformation. Support for this idea comes from experiments involving the heating to high temperatures of soot produced by arc- or laser-evaporation. Multiwalled and single-walled nanotubes are discussed separately. In each case the discussion begins with a brief description of practical aspects of the production processes.

2. Arc-evaporation synthesis of multiwalled nanotubes

2.1. Experimental details

An illustration of the kind of set up used to produce multiwalled nanotubes by arc-discharge is shown in Fig. 1. The electrodes are two graphite rods, usually of
high-purity, although there is no evidence that exception-
ally pure graphite is necessary. Indeed, nanotubes have
been successfully produced using very impure forms of car-
bon, such as coal, as electrodes [10]. The anode is typically
a long rod approximately 6 mm in diameter and the cath-
ode a shorter rod 9 mm in diameter. Efficient water-cooling
of the cathode has been shown to be essential in producing
good quality nanotubes. The position of the anode is usu-
ally adjustable from outside the chamber, so that a con-
stant gap can be maintained during arc-evaporation.

Discharge is typically carried out at a voltage of 20 V, with
a current usually in the range 50–100 A. A key factor in
producing high yields of nanotubes is the pressure of
helium. A pressure of below 100 Torr is optimum for C_{60}
production but, as first shown by Ebbesen and Ajayan
[11], a pressure of 500 Torr results in a dramatically
improved yield of nanotubes. Arc-discharge usually lasts
for a few minutes, and results in the deposition of fullerene
soot (plus fullerenes) on the walls of the vessel, and the
formation of a hard cylindrical deposit on the cathodic rod. It
is the central part of this deposit that contains carbon
nanotubes, invariably accompanied by nanoparticles and
some disordered carbon.

There have been a number of variations on the “classic”
arc-evaporation method since the original work in the early
1990s. Several groups have experimented with using alter-
atives to helium in the chamber. These alternative gases
include H_{2} [12] and N_{2} [13]. Other groups have shown that
arc-discharge can be carried out under liquids, such as
liquid N_{2} or water [14]. However there is little evidence that
these approaches produce major benefits in terms of nano-
tube yield or quality.

2.2. Theories of multiwalled nanotube growth by
arc-evaporation

2.2.1. Vapour phase growth

Most early theories of nanotube formation in the arc
assumed that nucleation and growth occurred as a result
of direct condensation from the vapour, or plasma, phase.
It was also thought that the electric field of the arc played
an essential role in inducing the “1-dimensional” growth
which leads to the formation of tubes. The most detailed
analysis of the gas phase nucleation and growth of
MWCNTs in the arc was given by Gamaly and Ebbesen
in 1995 [15]. These authors began by assuming that the
nanotubes and nanoparticles form in the region of the
arc next to the cathode surface. They then analysed the den-
sity and velocity distribution of carbon vapours in this
region, taking into account the temperature and the prop-
erties of the arc, in order to develop their model. They sug-
gested that in this layer of carbon vapour there will be two
groups of carbon particles with different velocity distribu-
tions. This idea is central to their growth model. One group
of carbon particles will have a Maxwellian, i.e. isotropic,
velocity distribution corresponding to the temperature of
the arc (~3700 °C). The other group is composed of ions
accelerated in the gap between the positive space charge
and the cathode. The velocity of these carbon particles will
be much greater than those of the thermal particles, and in
this case the flux will be directed rather than isotropic. The
process of nanotube (and nanoparticle) formation is con-
sidered to occur in three stages. In the first stage the isotro-
pic velocity distribution results in the formation of approxi-
mately equiaxed structures such as nanoparticles.

As the current becomes more directed, open structures
begin to form which Gamaly and Ebbesen consider to be
the seeds for nanotube growth. In the second stage, a
stream of directed carbon ions flows in a direction perpen-
dicular to the cathode surface, resulting in rapid tube
growth. Finally, instabilities in the arc-discharge lead to
abrupt termination of nanotube growth by the formation of
caps.

A variation of the vapour phase growth model has been
given by Louchev and colleagues [16–19]. Here, the key
process is not the direct condensation of carbon atoms
onto a growing edge, but the adsorption of atoms onto a
nanotube surface followed by surface diffusion to the
growth edge. The kinetics of nanotube growth in this
model have been analysed in detail [17]. Recent work by
Liu et al. has extended the Louchev model by considering
heptagon formation at the growing edge [20].

2.2.2. Liquid phase growth

The liquid phase model of multiwalled nanotube growth
was put forward by De Heer and colleagues in 2005 [21].
These workers studied MWCNTs formed on the surfaces
of columns within the cathodic deposit. They found that
these tubes were often decorated with beads of amorphous
carbon. The appearance of these beads was suggestive of
solidified liquid droplets, and this led them to conclude that
liquid carbon played a central role in nanotube nucleation
and growth. Based on their observations, and on the
known properties of liquid carbon, they proposed the fol-
lowing nanotube formation scenario. When arc-discharge
is initiated, the carbon anode is locally heated by electron
bombardment from the cathode, causing the surface to
locally liquefy and liquid carbon globules to be ejected
from the anode. Initially, because of the high vapour pres-
sure of liquid carbon, the surface of a globule will evapo-
rationally cool very rapidly. However, the cooling of the
interior of the globule occurs much more slowly, and this
causes the liquid carbon to supercool. It is within this
supercooled liquid carbon that carbon nanotubes and
nanoparticles are envisaged to homogeneously nucleate
and grow.

2.2.3. Solid phase growth

The solid phase theory of MWCNT growth by arc-evap-
oration was first put forward by the present author and his
colleagues in a paper published in 1994 [22]. In this paper,
fullerene soot was heated to approximately 3000 °C in a
positive-hearth electron gun. This resulted in the formation
of single-walled cones and tubes, such as those shown in
Fig. 2 (incidentally, these structures closely resemble the so-called “carbon nanohorns” which have been studied by Iijima and colleagues [23]). The observation that nano-tube-like structures can be produced by high temperature heat-treatment of fullerene soot prompted us to put forward a solid state model of nanotube growth, in which fullerene soot is an intermediate product. The model can be summarised as follows. In the initial stages of arc-evaporation, carbon in the vapour phase (consisting largely of C₂ species) condenses onto the cathode as a fullerene soot-like material. This condensed carbon then experiences extremely high temperatures as the arcing process continues, resulting in the formation firstly of nanotube “seeds” and then of multiwalled nanotubes. Growth terminates when the supply of carbon is exhausted or when arcing finishes. The model is illustrated in Fig. 3. An important element of the model is that it requires rapid heating to high temperature. Slow heating of fullerene soot results in the formation of carbon nanoparticles rather than nanotubes [24].

Following this early work, it has been demonstrated that multiwalled nanotubes can be produced from “conventional” carbons, as well as from fullerene soot, by high temperature heat-treatments. Work by Chang and colleagues in 2000 showed that heating a non-graphitizing microporous carbon (doped with boron) to 2200–2400 °C produced multiwalled nanotube structures very similar to those formed by arc-evaporation [25]. This is perhaps not surprising, since non-graphitizing carbons are believed to have structures similar to that of fullerene soot [26,27]. Subsequent work by the same group showed that MWCNTs could be produced from carbon black by similar heat-treatments [28–30]. Some images from this work are shown in Fig. 4. Chang et al. point out that the transformation of these carbons into nanotubes must be a solid state process since the temperatures used are below the melting point of carbon (3527 °C). They propose a mechanism which involves the migration of pentagonal and heptagonal rings in carbon black to the stems of nanotubes under tensile strain. The tensile strain results from thermal shrinkage of the carbon black. At the stems these pentagons and heptagons are converted into hexagons, resulting in tube growth.

There are other examples of the solid state synthesis of MWCNTs. Chadderton and Chen reported the production of nanotubes by thermal annealing of mechanically milled graphite powder at temperatures around 1400 °C [31]. Again, the formation of nanotubes at such low temperatures must have been a solid state process, and the authors emphasise the importance of surface diffusion in the transformation. They also suggest that the nanotube growth may have been partly catalysed by impurity particles from the milling process. Hsu et al. described an electrochemical method for the synthesis of multiwalled nanotubes, the mechanism of which also seems to have involved a solid state transition [32].

2.2.4. The crystallization model

In 2003, Zhou and Chow described detailed high resolution TEM observations of defective nanotube-like structures produced by arc-evaporation [33]. These observations suggested to the authors that the formation and growth of multiwalled nanotubes does not proceed from one end to the other, as assumed in most previous theories, but that the formation of the tubes was a crystallization process which began at the surface and progressed toward the centre. Their theory of MWCNT growth could therefore be described as the “crystallization” model. Like the mechanism first put forward by the present author and colleagues [22], the model proposed by Zhou and Chow is a two-stage, solid state, process. In the first stage, amorphous carbon “assemblies” are formed on the surface of the cathode. These assemblies can have a variety of shapes, depending on their surface energy and the local discharge conditions. In the second stage, which occurs during the cooling process, graphitization of the assemblies occurs from the surface toward the interior region. The formation
of extended tubes would seem to require that the original assemblies also had extended shapes. This may seem unlikely, but Zhou and Chow state that under certain arc-discharge conditions, cylindrical amorphous assemblies may be preferred.

Support for the crystallization model has come from a recent study by Huang and colleagues [34]. These workers grew amorphous carbon nanowires in situ by electron-beam deposition inside a HRTEM. The wires were then resistively heated to temperatures higher than 2000 °C,
and were observed to evolve into graphitized structures which in some cases resembled multiwalled nanotubes.

3. Non-CCVD synthesis of single-walled nanotubes

3.1. Arc-evaporation

As noted in Section 1, single-walled nanotubes are formed by arc-evaporation when a metal “catalyst” is added to one of the graphite electrodes. Importantly, the single-walled tubes are not formed in the core of the cathodic deposit, but instead are deposited on the walls of the arc-evaporation vessel. Single-walled tubes typically have diameters of around 1 nm, and are generally much more uniform in size than multiwalled nanotubes. When produced by arc-evaporation they are invariably accompanied by amorphous carbon and metal particles. Since the early work of Iijima and Bethune and their colleagues [5,6], a number of improvements have been made to the arc-evaporation synthesis of single-walled nanotubes (e.g. [35–38]). Journet et al. showed that higher yields of single-walled nanotubes could be achieved by using a nickel/yttrium mixture as catalyst, rather than a pure metal [35]. Subsequent work [36,37] has showed that the ratio of metals in the bimetallic catalyst can have a strong effect on both the yield and diameter distribution of nanotubes. The gas pressure in the arc-evaporation vessel can also have a strong influence on SWCNT yield [38].

3.2. Laser-vaporisation

The apparatus used for the laser-vaporisation synthesis of single-walled nanotubes is illustrated schematically in Fig. 5. The furnace is heated to a temperature of approximately 1200 °C and an inert gas (typically argon) flows through the 5 cm diameter tube at a constant pressure of 500 Torr. A cylindrical graphite target doped with small amounts of catalyst metal (typically 0.5–1.0% each of Co and Ni) is mounted at the centre of the furnace. Vaporization of the target is typically performed by a Nd:YAG laser. In a refinement of the process [40], a double laser pulse is used to provide a more even vaporisation of the target. Several groups have studied the effect of oven temperature on nanotube yield [41,42], and all have shown that the yield is very low at temperatures below about 600 °C, with 1100–1200 °C being the optimum temperature.

3.3. Theories of single-walled nanotube growth

There are good reasons for assuming that the mechanisms of single-walled nanotube formation in the arc-evaporation and laser-vaporisation processes are broadly similar. Both use similar starting materials, namely a graphite–metal mixture, and both involve the vaporisation of this mixture followed by condensation in an inert atmosphere. Moreover, the nanotube-containing soot produced by both methods is identical in appearance, containing bundles of SWCNTs together with disordered carbon and metal particles. Therefore, in the discussion which follows, we assume that mechanisms proposed for one process are applicable to both.

Although many different models have been put forward for the growth of SWCNTs by the arc or laser methods, it is generally accepted that the mechanism probably involves “root growth” rather than “tip growth”. In other words, the tubes grow away from the metal particles, with carbon
being continuously supplied to the base. This is supported by the fact that metal particles are not found at the tips of SWCNTs produced by arc-evaporation or laser-vaporisation, as would be the case if tip growth had occurred [43]. Also, most of the particles observed in the SWCNT-containing soot have diameters much larger than those of the individual tubes. As far as detailed mechanism is concerned, a theory which has gained wide popularity is the vapour–liquid–solid (VLS) model, as noted above. This was put forward by Saito in 1995 to explain SWCNT growth in the arc [44] and assumes that the first stage of nanotube formation involves the co-condensation of carbon and metal atoms from the vapour phase to form a liquid metal carbide particle. When the particles are supersaturated, solid phase nanotubes begin to grow. A number of detailed modelling studies, for example by Gavillet and colleagues [45,46] have been carried out based on this mechanism. Other workers have focussed on the effects of arc parameters [47,48] on the formation of SWCNTs, but always with the assumption that the initial step involves either the co-condensation of carbon and metal atoms or the condensation of vapour phase carbon onto a metal particle. However, a number of experimental studies have suggested that SWCNT growth, like MWCNT growth, may involve a solid state transformation, thus casting doubt on the validity of the VLS model. The solid state growth of carbon nanotubes by thermal annealing of mechanically milled graphite powder [31] has already been mentioned. In this work it was claimed that some single-walled nanotubes, as well as multiwalled tubes, were formed, but no clear images of SWCNTs were shown. The first unambiguous evidence for solid state growth of single-walled nanotubes was given by Geohegan and colleagues in 2001 [49], whose work will now be summarised.

This group had been studying the preparation of SWCNTs by Nd:YAG laser vapourisation of a graphite/Ni–Co target [50,51]. Their studies suggested that nanotube growth did not occur during the early stages of the process when carbon was in the vapour phase, but at a later stage when the “feedstock” would be aggregated clusters and nanoparticles. In order to test the idea that SWCNT growth is a solid state transformation, they carried out further experiments involving the heat-treatment of nanoparticle containing soot having short (~50 nm long) nanotube “seeds.” This “seeded” soot was produced by carrying out laser-vapourisation for shorter periods at a lower temperature than that used to produce full-length nanotubes. The soot collected from the laser-vapourisation apparatus was placed inside a graphite crucible under argon, and heated by a CO$_2$ laser to temperatures up to 1600 °C. It was found that these heat-treatments could produce micron length SWCNTs, with optimum growth occurring at temperatures in the range 1000–1300 °C. Interestingly, when soot was heated slowly to temperatures in this range in a conventional oven, no nanotube growth was observed. This suggests that heating rate may be important in SWCNT growth from solid precursors, just as it appears to be for MWCNTs.

Geohegan and colleagues put forward the following growth mechanism for SWCNTs by laser-vapourisation. The Nd:YAG laser pulse initially produces an atomic–molecular vapour containing both carbon species and Ni/Co atoms. This evaporated material remains in the vapour phase for approximately 100 µs. The plasma then cools rapidly, and the carbon condenses and forms clusters ~200 µs after ablation (the metal catalyst atoms condense much later, at about 2 ms). The size of the carbon particles within the plume at these times does not exceed 20 nm at temperatures around 1100 °C. Geohegan et al. estimate the onset of SWCNT growth to occur at 2 ms after ablation. By this time, both the carbon and the metal atoms are in a condensed form, so nanotube growth is largely a solid state process.

Studies similar to those of Geohegan and colleagues were carried out at about the same time by two other groups. Gorbunov et al. prepared soot using laser-vapourisation, but at a temperature too low to induce nanotube formation [52]. This soot was then annealed at 1200 °C in an Ar atmosphere. This resulted in the formation of large numbers of single-walled nanotubes. On the basis of this observation they put forward a growth model which involved the conversion of solid disordered carbon into nanotubes via liquid phase metal particles. The mechanism, which they named the solid–liquid–solid (SLS) mechanism, is illustrated in Fig. 6. The first stage involves a molten catalyst nanoparticle penetrating a disordered carbon aggregate, dissolving in it and precipitating carbon atoms at the opposite surface. These atoms then form a graphene sheet, whose orientation parallel to the supersaturated metal–carbon melt is not energetically favourable. Any local defect of this graphene sheet will therefore result in its buckling and the formation of a SWCNT nucleus.

The third study which independently demonstrated solid phase growth of single-walled nanotubes was described by Kataura and colleagues [53]. Here, soot was obtained by
laser ablation of Ni–Co–graphite composite targets at temperatures in the range 25–700 °C. The soot was then heated to 1200 °C in Ar. It was found that the soot which had been prepared using temperatures above about 550 °C yielded single-walled nanotubes after the 1200 °C treatment, but the soot prepared at lower temperatures did not. This is a very significant finding, for reasons we will return to below.

On the basis of these observations, and of previous studies [42], Kataura and colleagues proposed a model for SWCNT growth which is generally similar to the Geohegan mechanism, but which emphasises the key role played by fullerene-like carbon fragments in nucleating growth. The model is illustrated in Fig. 7. In the first phase, which occurs at a very early stage (µs) and at very high temperatures (2000–3000 °C), small carbon clusters nucleate. These have fullerene-like structures, rich in pentagonal rings. At this stage the metal atoms are still in the gas phase. As the system cools, metal atoms condense, forming particles or droplets, which become supersaturated with carbon, at around the eutectic temperature. The particles then become covered with fullerene-like carbon fragments. The “open edges” of these fragments tend to stick to the particles to eliminate dangling bonds, and TEM observations suggest that in some cases the fragments form close-packed arrays. The fragments then act as precursors for SWCNT growth, with carbon being supplied by precipitation from the particles or from the disordered carbon which surrounds the particles. The close-packed arrays are precursors for the growth of bundled SWCNTs. The merits of this mechanism are discussed in Section 4.2.

4. Discussion

4.1. Multiwalled nanotubes

Here, we compare the various theories of multiwalled nanotube growth by arc-evaporation which were outlined in Section 2.2. Considering first vapour phase growth, the model proposed by Gamaly and Ebbesen [15] assumes that the electric field plays a central role in the formation of nanotubes. The field produces a directed flux of carbon particles in a direction perpendicular to the cathode surface, resulting in the rapid 1-dimensional growth of nanotubes. It is suggested that nanoparticles form in the early stages of arcing, when the velocity distribution of carbon particles is isotropic. However, as discussed above, it is now well established that MWCNTs very similar in structure to those produced by arc-evaporation can be formed from pure carbon by simple heat treatments. This shows that an electric field is not essential for nanotube growth. The Gamaly–Ebbesen model would also seem to imply that the nanotubes formed in the cathodic deposit should be aligned perpendicular to the surface of the cathode. Although the macroscopic fibrils which form on the cathode tend to be aligned, there is little evidence that the nanotubes inside the fibrils are aligned.

Turning now to the liquid phase growth model, this is based on the observation by De Heer and colleagues of spheroidal beads of amorphous carbon on the surfaces of MWCNTs formed by arc-evaporation [21]. The assumption was made that these beads were frozen droplets of liquid carbon, but similar features on the surfaces of nanotubes were observed many years ago in contexts which certainly do not involve liquid carbon (e.g. Fig. 11 of ref. [54]). De Heer et al. also fail to explain in detail why nanotubes and nanoparticles crystallise out of the liquid carbon, rather than graphite which would normally be expected to form [55,56].

This leaves us with the solid state theory. As noted in Section 2.2.3, the key to this theory is high temperature annealing of fullerene soot inside the cathodic deposit. An important question is: why does this annealing process lead to nanotubes rather than nanoparticles? In the “crystallization” model, which is a variation of the solid state theory [33], tubes form when the original fullerene soot assemblies have an extended shape. The work of Huang and colleagues has shown that such a transformation is possible [34]. However, there is no evidence as yet that such an extended shape is favoured by the carbon which deposits onto the cathode. It seems possible that the explanation

Fig. 7. Illustration of a model for SWCNT growth proposed by Kataura and colleagues [42]. In Step 1, carbon clusters with fullerene-like structures form, and some of this carbon is dissolved in metal particles. When the metal particles are saturated with carbon, their surfaces become covered with carbon fragments (Step 2). Finally, in Step 3 SWCNTs grow out from the particles.
for the growth of nanotubes lies instead in the heating rate experienced by the cathodic soot. It was noted above that MWCNTs only appear to be formed when fullerene soot is heated rapidly to high temperatures. Heating the soot more slowly tends to result in the formation of carbon nanoparticles rather than tubes [24]. Rapid heating also seems to be essential in producing nanotubes from other forms of solid carbon. For example, it is well established that heating carbon black to high temperatures normally produces nanoparticle-like structures [57], whereas Chang and colleagues have shown that rapid heating of carbon black in an arc furnace produces nanotubes [28–30].

The way to understand these findings may be in terms of the balance between thermodynamics and kinetics. It has been shown that any capped configuration is more stable than any open ended geometry [58]. However, if hexagonal ring formation is more rapid than pentagonal ring formation then under conditions where kinetics dominate tube formation will be favoured. In other words, slow growth conditions will favour pentagon formation and therefore closure, while rapid heating to high temperature will favour open-ended tube growth. If this analysis is correct, there is no need to invoke electric fields [59] or lip–lip interactions [58] to explain why nanotubes remain open during growth. The explanation is simply that nanotube growth is a kinetic rather than a thermodynamic process. The kinetics of pentagon/hexagon formation have been analysed by Louchev and colleagues in the context of their surface diffusion model [17].

The solid phase theory may help us to understand the effect of variables such as electrode cooling and helium pressure on nanotube production. Water cooling seems to be essential in order to bring the cathode temperature down to the level required to avoid tube sintering. Similarly, the role of helium can be explained in terms of its effect on the temperature of the cathodic deposit. Since helium is an excellent thermal conductor, higher pressures would tend to reduce the electrode temperature, bringing it down to the region in which nanotube growth can occur without sintering.

4.2. Single-walled nanotubes

The experimental work of the Geohegan, Gorbunov and Kataura groups provides clear evidence that the formation of single-walled nanotubes, like that of multiwalled nanotubes, is a solid state process. Models for the solid phase growth of single-walled tubes were proposed by all three groups; these were outlined in Section 3.3. The model suggested by Geohegan and colleagues [41] gives a picture of the processes at increasing times from the initial laser-vaporisation which is probably broadly correct, but does not seem to include a detailed mechanism for the transformation of solid carbon into nanotubes. The solid–liquid–solid mechanism of Gorbunov et al. [52] assumes that this transformation involves the dissolution of solid carbon in a liquid metal–carbon particle, followed by the precipitation of nanotubes at the surface of the particle. A problem with this theory is that it does not explain the findings of Kataura and colleagues [53]. The Gorbunov theory assumes that the “seeds” for nanotubes form when carbon precipitates out of the carbon–metal particles. This would suggest that nanotubes could be grown from a mixture of metal and any form of carbon, if it is subjected to a suitable heat-treatment. Kataura and colleagues showed that this is not the case: soot which had been prepared using temperatures below about 550 °C yielded no nanotubes on annealing at 1200 °C. This suggests that the growth of nanotubes requires the presence of fullerene-like seeds, which are presumably not formed when low oven temperatures are used. The model put forward by the Kataura group assumes that some fullerene-like carbon fragments remain undissolved in the metal–carbon particles, and are deposited onto the particle surfaces, where they act as the seeds for nanotube growth. This model would seem to offer the best currently available explanation for SWCNT production by the arc and laser methods.

5. Conclusion

This paper has discussed the arc-evaporation and laser-vaporisation methods for the synthesis of multiwalled and single-walled carbon nanotubes, and has reviewed the various theories which have been put forward to explain these processes. It seems that progress is being made in understanding the growth mechanisms involved, and in particular there seems to be growing evidence that a solid state transformation is involved in the formation of both multiwalled and single-walled tubes. Although the mechanisms for the two types of nanotube differ in several respects, it appears that in both cases the precursor is a fullerene soot type material which contains the “seeds” for nanotube growth. If this is correct, might it suggest a way of making nanotubes with defined structures, the holy grail of nanotube research? This certainly seems conceivable, at least for single-walled tubes. It is well established that the structure of a nanotube is defined by the structure of its cap. Therefore, if it were possible to prepare hemi-fullerenes with known structures (perhaps by chemical scission of fullerenes) and use these as seeds for nanotube growth under the conditions used by the Geohegan, Gorbunov and Kataura groups, then the result might be large quantities of single-walled tubes with identical structures.

Acknowledgements

I thank Oliver Jost and Hiromichi Kataura for comments.

References


