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Morphologies and microstructures of carbon nanotubes prepared by self-sustained arc discharging

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We have investigated the morphology and microstructure of carbon nanotubes and nanoparticles in cathode deposits prepared by self-sustained arc discharge. Scanning electron microscopy images indicate that there are two regions exhibiting different morphologies on the top surface of the cathode deposits. In the central region, there is a triangular pattern of spots with a diameter up to 100μm, which consists of carbon nanotubes and nanoparticles. In the fringe region, carbon nanotubes and nanoparticles are distributed randomly. In addition, carbon nanotubes in the central region have a larger inner diameter, compared with those in the fringe region. The outer diameter distribution of tubes in the central region is narrower than that of tubes in the fringe region, while the former has a smaller peak value than the latter. For the nanoparticles, they exhibit a different behaviour from the tubes existing in the same region. The difference between the microstructure of tubes or particles in the two regions is attributed to the different temperatures and temperature gradients during their formation.

Keywords: carbon nanotube, arc discharge, microstructure
PACC: 6146, 5280M, 6480G

1. Introduction

Carbon nanotubes were first discovered in the deposit of electrical arc discharging in 1991.[1] Since then, this remarkable one-dimensional system has attracted more and more attention for its novel properties and promising applications in many fields.[2−12] After ten years of intensive research in this field, there have been great improvements in the synthesis and characterization of their microstructures and properties. Now carbon nanotubes can be prepared in macroscopic quantities by several methods, such as arc discharge, chemical vapour deposition and laser ablation, etc.[15−18] As is well proven by theoretical computation and experimental measurement,[3,4,13,14] the properties of carbon nanotubes depend strongly on their microstructures (diameter, helicity, number of layers and defects), and those we have obtained have a wide spread of size and shape. Therefore, for practical applications, carbon nanotubes with given microstructures should be prepared in macroscopic quantities at first, and then there is still a need to develop and optimize the synthesis techniques for preparing well-defined and well-organized nanotubes in large quantities according to the need of applications. Arc discharge, as one of the main preparation methods of this unique material, has been explored extensively for this purpose because this process can achieve a very high temperature (about 4000 K)[19] and can also yield the most highly graphitized multi-walled carbon nanotubes without being contaminated by metal catalyst. For example, much work has been done on investigating the effects of buffer gas, arc current and electrode temperature on the quality and output of carbon nanotubes obtained in arc discharge, and then the optimal conditions for preparing large area, high density and loosely entangled carbon nanotubes were gained.[20−26] On the basis of experiments, several growth mechanisms have also been postulated.[1,27−33] At the same time, carbon nanotubes synthesized by arc discharge always show the coexistence of carbonaceous nanoparticles, possess undefined morphologies, and have a wide spread of size and shape. These have become one of the main obstacles to the applications of carbon nanotubes and up to now cannot be understood clearly. If we can acquire more details about

the relationship between growth conditions and microstructures of carbon nanotubes (such as outer diameter, inner diameter, number of layers and so on), we are sure to be able to control the microstructure of carbon nanotubes by controlling growth conditions for the purpose of applications in the arc discharge technique.

It is well known that the growth of carbon nanostructures in arc discharges is related to the distribution of the density and velocity of carbon species, temperature and electric field in the growth region, and all these factors are interrelated, thus making the relationship between growth conditions and microstructures more elusory. In the present work, we have investigated the morphologies and microstructures of carbon nanotubes in a different portion of the same cathode deposit prepared by self-sustained arc discharging, and we have found the optimal conditions for carbon nanotubes grown in arc discharges. In different parts of the growth surface during arc discharging, some places have the same growth conditions, but some other places have different growth conditions. We believe that these differences in growth conditions can be reflected by the morphologies and microstructures of the carbon nanostructures. Thus we have gained more information about the relationship between the microstructures of nanotubes and the growth conditions in the growth region in a relatively easy way.

2. Experimental details

In our experiments, dc arc-discharge evaporation of graphite was carried out on the same apparatus as reported previously.[26] A 8mm diameter graphite rod (150mm length) and a 30mm diameter graphite disc (10mm thick) were installed horizontally as anode and cathode, respectively. Both of the electrodes were further water cooled independently. An accurate positioning system was employed to maintain a steady feed rate of the anode, which can be instantly adjusted in the range of 0–3cm min^{-1}. The arc current and voltage were monitored automatically and could be controlled precisely by adjusting the output of the arc power supply and the gap between the two discharging surfaces. The chamber was evacuated by a rotary pump and then the buffer gas (helium, 5.0×10^4Pa) was introduced into this chamber. A self-sustained stabilized arc discharging (18–24V, 85–95A) was established by carefully adjusting the arc-discharge parameters. Self-sustained stabilized arc discharging means that the anode rod was continuously consumed without feeding in, and the cylindrical cathode deposit grew steadily while the gap between the two surfaces remained constant (about 1mm). The plasma of the arc appeared, by eye, to be uniformly extended over the entire electrode surface, and very little fluctuation was seen either as flashes in the brightness of the arc, or as the variations of anode–cathode voltage drop and current. After several minutes of growth, arc discharging was interrupted by cutting off the current. The cathode deposits were investigated by scanning electron microscopy (SEM, S-4200) and transmission electron microscopy (TEM, JEM-200cx at 200 keV).

3. Results and discussion

SEM images indicate that there are two regions with different morphologies. In the central region of the top growth surface, there is a triangular pattern of spots with diameters up to 100μm (Fig.1(a)), while there is no pattern in the fringe region (the region around the central pattern), and this region looks smooth (Fig.1(c)). High-resolution SEM observation indicates that there are highly dense and loosely entangled carbon nanotubes and some carbon nanoparticles, which show a little amorphous in each spot in the central region (Fig.1(b)) and in the fringe region (Fig.1(d)). It seems that there are many more particles among tubes in the central region. Experiments show that the pattern of spots in the central region is related to the stability of the arc. The more stable the arc, the more regular the pattern, and the larger the region of the pattern in the centre of the cathode deposit. At the same time, the best production of nanotubes is consistent with a remarkably stable operating condition of the arc, that is, there are few amorphous carbon or graphitic sheets in the cathode deposit obtained by self-sustained arc discharging. In the case of the 6mm diameter anode, there is no pattern of spots in the central region of the cathode deposit.

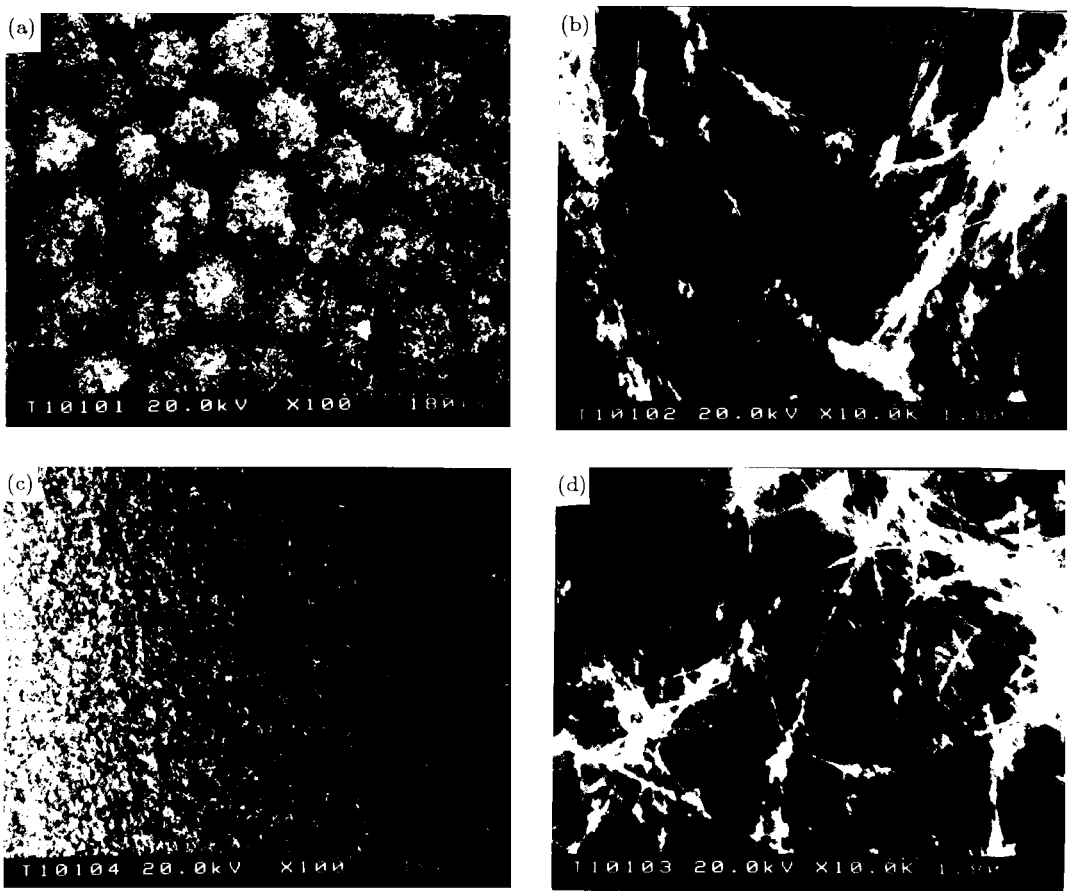


Fig.1. SEM images of carbon nanotubes and nanoparticles in the central (a),(b) and fringe (c),(d) regions of the top growth surface of the cathode deposit.

In order to characterize the microstructure of carbon nanostructures in the central/fringe regions of the cathode deposit, distributions of outer/inner diameters of nanotubes and nanoparticles in these two regions have been found by TEM observations. For each sample, over 100 tubes or particles have been measured. Corresponding histograms are given in Figs.2 and 3. Compared with those in the fringe region, carbon nanotubes and nanoparticles in the central region of the cathode deposit (region of pattern) have narrow outer-diameter distributions (Figs.2(a),(c) and Figs.3(a),(c)) and larger inner diameters (Figs.2(b),(d) and Figs.3(b),(d)). At the same time, these histograms (Figs.2 and 3) also indicate that there are some differences in outer/inner-diameter distributions for tubes and particles. On the one hand, the peak value of the outer-diameter distribution of tubes in the central region (12nm) is smaller than that in the fringe region (14nm) (Figs.2(a),(c)), while the peak value of the outer-diameter distribution of particles in the central region (32nm) is larger than that in the fringe region (26nm) (Figs.3(a),(c)). On the other hand, in the same region the inner-diameter distribution of tubes is sharper than those of particles (Figs.2(b),(d) and Figs.3(b),(d)).

During the arc discharging, we observed that there is a scintillant incandescent edge along the growing surface of the cathode deposit. On the other hand, the growing surface is relatively dim and the arc anchoring on the whole surface is more stable than that on the edge. We conjecture that the arcs on the incandescent edge are a type of arc with a cold cathode and the arcs anchoring on the whole growing surface are a type of arc with a hot thermionic cathode. In the former, the current flows through one or more spots that appear and disappear, and move rapidly along with the edge of the growing surface, and the current density within a spot is very high (estimated to be $j_c \sim 10^4 - 10^7 \mathrm{A/cm^2}$). As for the arcs with the hot thermionic cathode, the current flows through a comparatively large area on the cathode (estimated $j_c \sim 10^2 - 10^4 \mathrm{A/cm^2}$), and the current spot is stationary. Therefore, the cathode is heated as a whole and the highest temperature occurs in the fringe region

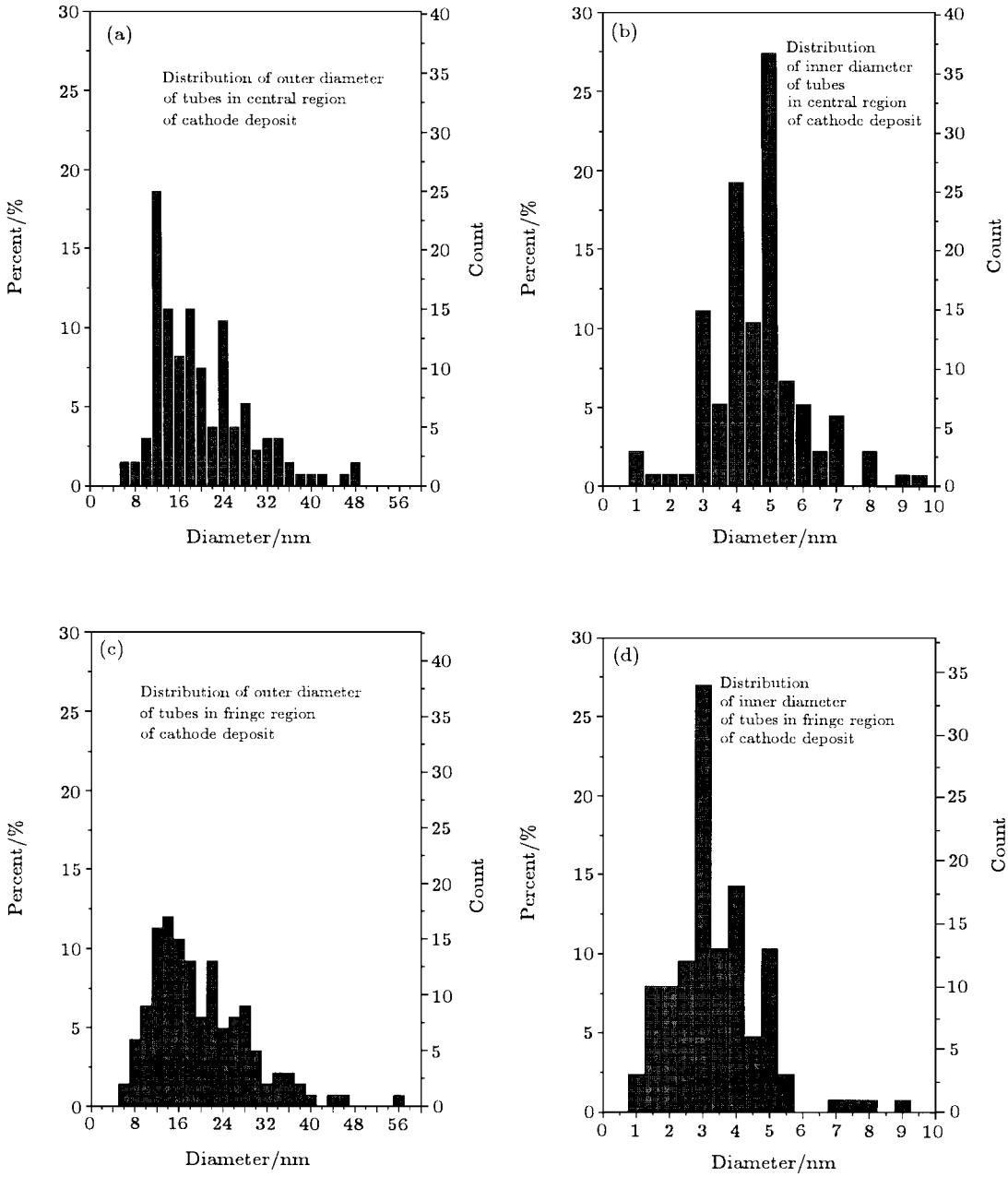


Fig.2. Distributions of outer (a) and inner (b) diameters of nanotubes in the central region of the cathode deposit, and distributions of outer (c) and inner (d) diameters of nanotubes in the fringe region of the cathode deposit.

near the edge of the growing surface. Wang *et al.*[34] reported similar results in the case of a 12.7mm diameter rod. Just as in the previous report,[27] we suppose that, in the central region with a stable arc, there is some kind of convection, such as Bénard convection, which leads to the formation of the triangular pattern of spots, while at the fringe of the arc there is a larger temperature gradient, so that some carbon atoms will get away from the arc region and then no convection exists as in the centre of the arc. At the same time, it is the higher temperature and larger temperature gradient in the fringe region that give a good explanation for the smaller inner diameter and the wide spread of the outer diameter of nanotubes and nanoparticles in this region. A high temperature favours the growth of tubes and particles with small inner diameter, and a steep temperature gradient induces an important range of conditions for the formation of tubes and particles with a wide spread size and shape. In order to validate this conjecture, we raise the temperature of the fringe region by adopting an outer graphite heat preservation shelter. Because many carbon atoms es-

cape away from the region of the arc, and then there are more anisotropic carbon ions (accelerated by the electric field) and less isotropic carbon atoms in this region than in the central, more tubes can have larger outer diameter and more particles have smaller outer diameter in the fringe region of the cathode deposit, just as shown in Figs.2(a),(c) and Figs.3(a),(c).

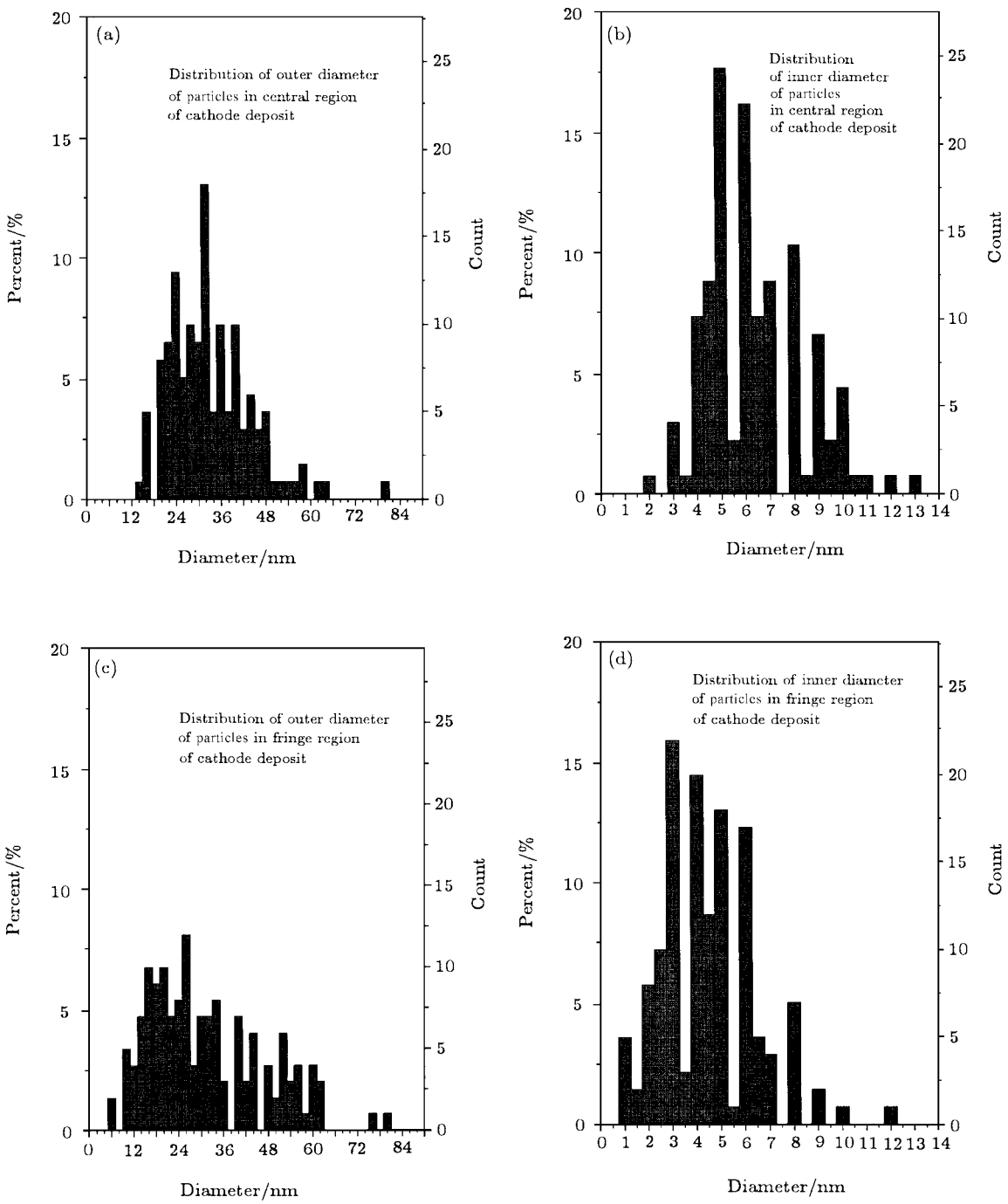


Fig.3. Distributions of outer (a) and inner (b) diameters of nanoparticles in the central region of the cathode deposit, and distributions of outer (c) and inner (d) diameters of nanoparticles in the fringe region of the cathode deposit.

4. Conclusion

We have investigated the morphology and microstructure of carbon nanotubes in different portions of the same cathode deposit prepared by self-sustained arc discharging. SEM images indicate that, in the central region of the top surface of the cathode deposit, there is a triangular pattern of spots, while the surface around the central pattern is smoother. TEM observation indicates that carbon nanostructures in these two regions have different microstructures. In the region of the pattern, carbon nanostructures have a narrow distribution of the outer diameter and a larger inner diameter, and the tubes obtained have smaller peak value while the particles have a larger peak value of the outer-diameter distribution. As a whole, the distribution of tubes is narrower than that of particles in these two regions.

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