Materials Science-Poland, *Vol. 27*, *No. 3*, *2009*

Effect of growth time on the morphologies of vapour grown carbon fibres and a suggested mechanism of growth

H. ZHANG[1,2], J. SHI[1], Y. SONG[1], J. ZHAO[1], K. WANG[1,2], Q. GUO[1], G. ZHAI[1], L. LIU[1*]

[1]Key Laboratory of Carbon Materials, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, Shanxi, 030001, PR China

[2]Graduate University of Chinese Academy of Sciences, Beijing, 100049, PR China

The microstructure of vapour grown carbon fibres is two-double layered. This paper addresses the question of morphology transformation of vapour grown carbon fibres. Special attention is given to developing understanding of the growth mechanism of the outer layer of the fibres. The influence of growth time on the morphologies of as-prepared carbon fibres was investigated using scanning electron microscopy. Results showed that with the prolongation of reaction time, their morphology changed from linear fibres to carbon micro-bead chains and then again to thicker linear fibres, which led to the increase of the carbon fibres diameters from 200 nm to several micrometers. Furthermore, several kinds of carbon fibres with special morphology such as carbon micro-beads, chains, etc., could be obtained by adjusting the growth time. A growth mechanism, henceforth referred to as *fibre–bead–thicker fibre*, for the outer layer of vapour grown carbon fibres is proposed.

Key words: *vapour grown carbon fibres; vapour deposition; electron microscopy; microstructure*

1. Introduction

Vapour grown carbon fibres (VGCF) have attracted much attention in recent years, due to their desirable properties and potential applications [1–4]. Chemical vapour deposition (CVD) is a widely used method to prepare VGCF based on the deposition of hydrocarbons or other gaseous carbon sources over small metal particles such as iron, cobalt, nickel or their alloys [5–8]. It is well known that the deposition process plays an important role in the morphology and structure of VGCF. It is very important to understand clearly the growth mechanisms of VGCF in further technical improvements and innovations for large-scale synthesis and structural controls. Up to now, the

*Corresponding author, e-mail: liulang@public.ty.sx.cn

structure of VGCF is two-double layers [9, 10]: the inner layer is the core structure of VGCF formed of oriented carbon layers, while the outer layer is made of decomposed carbon. The most popular mechanism of catalytic growth of VGCF has two stages, as follows: in the first stage, metal-catalytic growth of the core structure occurs, and then, in the second stage, deposition growth of the outer layer of VGCF occurs. The growth mechanism of the metal-catalytic growth of the core structure of VGCF has been extensively studied. The adsorption–diffusion–precipitation (ADP) model developed by Baker et al. [11] has been widely accepted [12–15]. In this model, C_n species are first adsorbed on the surface of a metal particle, then they diffuse through the metal particle, and finally they precipitate in a crystalline tubular form. However, little information about the growth of the outer layer of VGCF in the second stage has been reported in the published literature.

The aim of this work was to to obtain VGCF synthesized at various growth times, in order to clarify the growth mechanism of the outer layer of VGCF.

2. Experimental

VGCF was synthesized through the catalytic pyrolysis of methane. A graphite substrate was merged in a catalyst-contained solution, dried at room temperature for at least 8.0 h and then heated in an oven at 383 K for 2.0 h. The catalytic decomposition of methane was carried out in a flow reactor under the atmospheric pressure. The graphite substrate was placed in the centre of the reactor tube (inner diameter 36 mm, length 800 mm). A methane/hydrogen gas mixture (volume ratio 1:1) was introduced into the reactor when the temperature was raised to 1373 K. The growth time was varied from 0.5 h to 6.0 h. Subsequently the as-prepared VGCFs were examined by the scanning electron microscopy (SEM).

3. Results and discussion

3.1. Morphology evolution of VGCF at prolonged growth time

The morphologies of VGCF, synthesized at various times from 0.5 h to 6 h are shown in Fig. 1. Figure 1a shows that the linear and smooth carbon fibres coexist with rough fibres when the reaction time is 0.5 h. The diameter of smooth carbon fibres is about 200 nm, while the diameter of rough fibres is about 300 nm. When the reaction time is prolonged to 1.0 h, the morphology of carbon fibre transforms from linear carbon fibres to carbon micro-bead chains (Fig. 1b). In addition, the surface of carbon micro-beads is rough, while the surface of the segment 1 beside carbon micro-beads is relatively smooth and the diameter of this part is about 200 nm. This implied a transitional morphology of carbon micro-beads having diameters of approximately 200 nm.

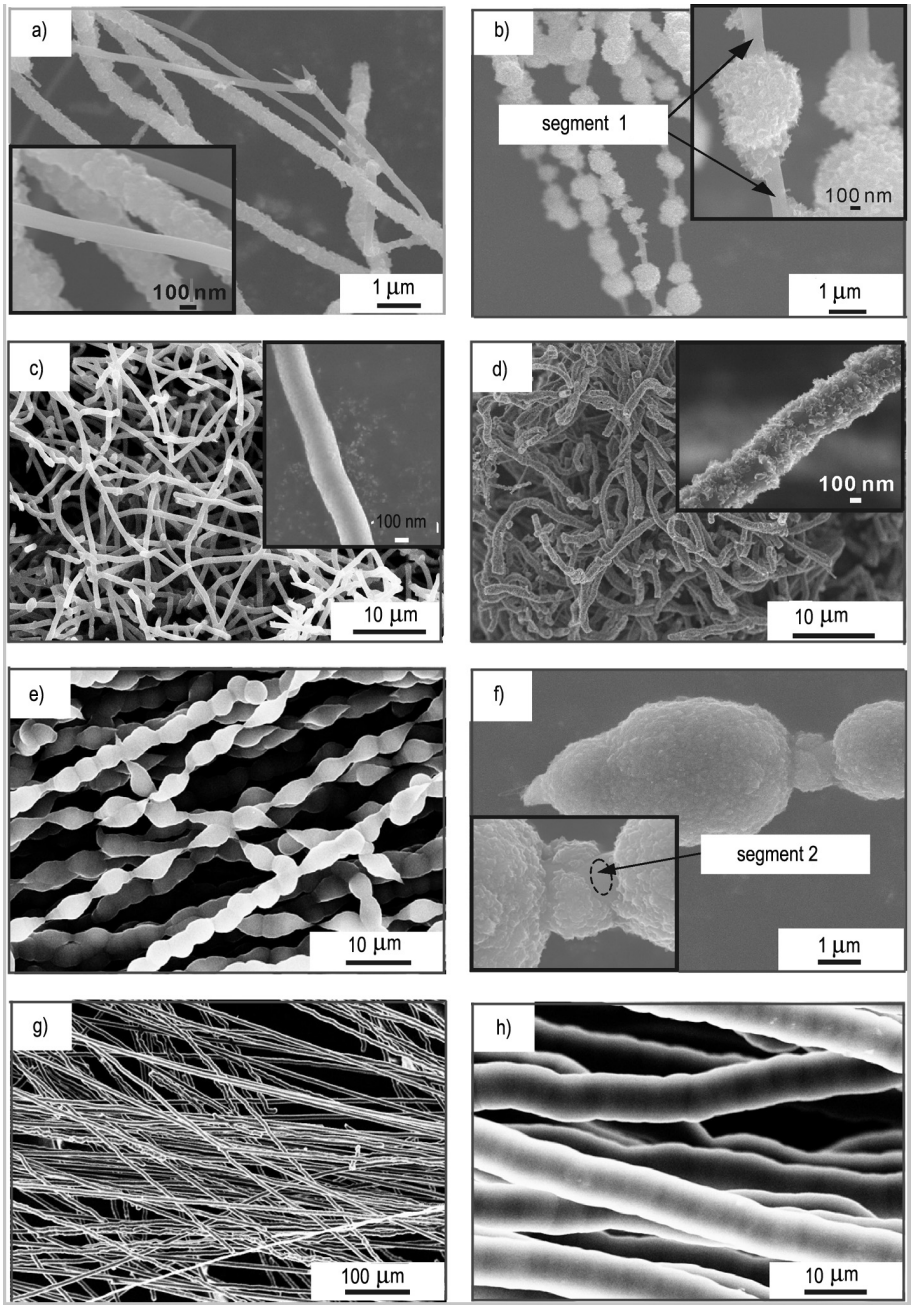

Fig. 1. Effect of growth time on morphologies of VGCF:
a) 0.5 h, b) 1.0 h, c) 2.0 h, d) 2.5 h, e, f) 4.0 h and g, h) 6.0 h

As shown in Fig. 1c, the diameter of as-prepared fibres at 2.0 h is about 2 µm and most of them are straight and smooth. Figure 1d shows that when the reaction time is

prolonged to 2.5 h, the carbon fibres of the diameters of ca. 2 μm are rough. The morphology of carbon fibres changes from linear fibres to carbon micro-bead chains again, when the reaction time is prolonged to 4.0 h (Figs. 1e, f). The carbon micro-beads on the fibres are homogeneous and the distance between the centres of two adjacent micro-beads is about 5–7 μm. Figure 1f shows that the surface of carbon micro-beads is rough, while the surface of the segment 2 between two adjacent carbon micro-beads is relatively smooth and the diameter of this part is about 2 μm, indicating that carbon micro-bead chains transformed from linear fibres approximately 2 μm in diameter

When the growth time is prolonged to 6.0 h, as-prepared carbon fibres having diameters of ca. 6 μm are straight and smooth (Figs. 1g, h). It is noticed that there are some indistinct protuberances, just like the shadow of carbon beads among carbon fibres, as shown in Fig. 1h. This suggested that these carbon fibres were obtained from carbon micro-bead chains.

Gradual enlargement of fibre diameters is not the only feature characterizing the morphological evolution of VGCF as a function of prolonged reaction time: linear carbon fibres change to carbon micro-bead chains and then to thicker linear fibres.

3.2. Growth mechanism of the outer layer of VGCF

Based on the SEM observations, a simple growth mechanism of the outer layer of VGCF is proposed, and henceforth referred to as fibre–bead–thicker fibre (Fig. 2).

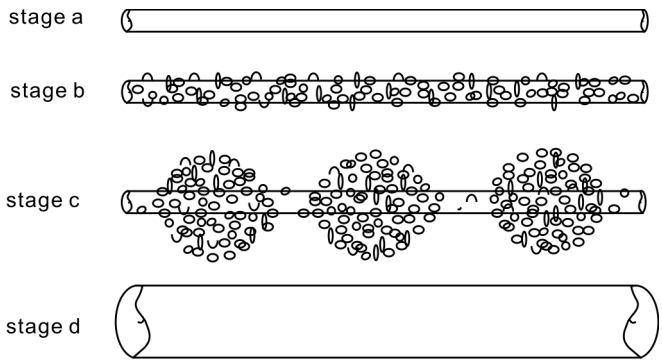

Fig. 2. Two-dimensional scheme of the proposed growth mechanism of the outer layer of VGCF

First, the linear and smooth carbon nanofibres appear (stage a). Secondly, the carbon nanoparticles pyrolyzed from methane precipitate on the surface of VGCF symmetrically, and then carbon fibres with rough surfaces form the stage b. Thirdly, with the prolongation of the reaction time, more and more carbon nanoparticles precipitate on the surface of the fibres formed earlier, and, at the same time, they self-assemble to shape micro-beads. The carbon fibres look like the carbon micro-bead chains (stage c).

Finally, carbon nanoparticles precipitate continuously and fill in the interstice between the adjacent carbon beads, and therefore thicker, linear and smooth fibres appear (stage d).

In stage c, it is reasonable to ask the following question: why should carbon-bead chains appear? It is presumed that at high temperature carbon nanoparticles from carbon source have high surface energy. If these nanoparticles precipitate on the former fibres symmetrically, they will have higher surface areas and higher energies. It is known that conglobulations possess the lowest surface area and the surface energy. A new microstructure-like sphericity may form, which has simultaneously lower surface area and lower surface energy, thus nanoparticles self-assemble to form carbon micro-beads. In stage d, the indentations on carbon micro-bead chains might have higher energy and higher surface areas. With the prolongation of the growth time, the carbon nanoparticles pyrolyzed from methane are adsorbed in the interstice between the adjacent carbon beads, and then carbon fibres with many protuberances appear. Because the least energy principle governs the growth process at all times, thicker, linear and smooth carbon fibres can be finally obtained with the continuous deposition of carbon nanoparticles.

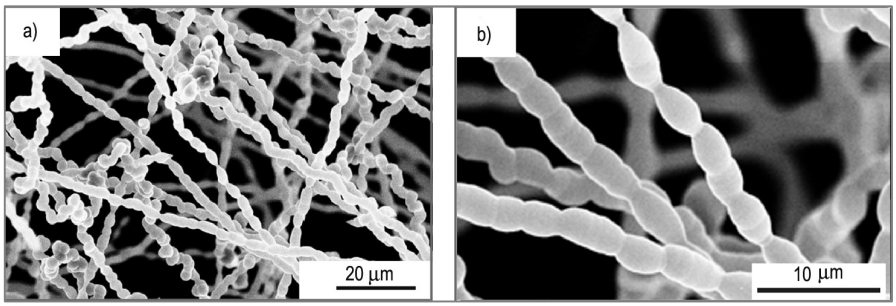

Fig. 3. SEM of as-prepared carbon fibres at 5.0 h

To test this model, an additional experiment with the reaction time 5.0 h was carried out and as-prepared carbon fibres were examined (Fig. 3). Figure 3a shows many protuberances on the carbon fibres. In Figure 3b the distance between the centres of two adjacent protuberances is 5–7 μm, which corresponds to the distance between the centres of two adjacent carbon micro-beads (Figs. 1e, f). This suggests that carbon fibres with many protuberances were representative of the transitional morphology from carbon micro-bead chains to linear carbon fibres. This result is consistent with the growth process fibre–bead–thicker-fibre.

4. Conclusions

The growth time has a significant influence on the morphologies of VGCF synthesized through the catalytic pyrolysis of methane. As the syntheses of VGCF proceed,

the morphology of VGCF changes from linear carbon fibres to carbon micro-bead chains, and then to thicker linear fibres, the diameters of VGCF increase from 200 nm to several micrometers. Furthermore, some kinds of VGCF with unusual morphology, such as carbon micro-bead chains etc. can be obtained by adjusting the reaction time. The growth mechanism of outer layers of VGCF fibre–bead–thicker fibre is proposed: first, growth of linear and smooth carbon nanofibres occurs, then decomposed carbon deposites on a smooth surface and assembly into carbon micro-bead chains occurs: lastly, pyrolytic carbon continuously precipitates in the interstice between adjacent carbon beads and thicker, linear and smooth fibres form.

Acknowledgements

This work was performed in the Key Laboratory of Carbon Materials, Institute of Coal Chemistry, Chinese Academy of Sciences and supported by the National 863 Programs of China.

References

[1] SHIBUYA M., SAKURAI M., TAKAHASHI T., Comp. Sci. Techn., 67 (2007), 3338.
[2] LEE B.J., SIVAKKUMA S.R.R, KO J.M., KIM J.H., JO S.M., KIM D.Y., J. Power Sources, 168 (2007), 546.
[3] ZHU H., LI X., XU C., WU D., Mater. Res. B., 37 (2002), 177.
[4] CHOI Y.K., SUGIMOTO K., SONG S.M., GOTOH Y., OHKOSHI Y., ENDO M., Carbon, 43 (2005), 2199.
[5] REN X., ZHANG H., CUI Z.L., Mater. Res. B., 42 (2007), 2202.
[6] MÉNDEZ A., FREITAS M.M.A., FIGUEIREDO J.L., Carbon, 44 (2006), 2350.
[7] BENISSAD-AISSANI F., AÏT-AMAR H., SCHOULER M.C., GADELLE P., Carbon, 42 (2004), 2163.
[8] SCHLÜTER O.F.K., WEHNER B.I., HU D., XIA W., QUANDT T., MARGINEAN G., BRANDL W., MUHLER M., Appl. Catal. A, 274 (2004), 71.
[9] TIBBETTS G.G., Carbon, 27(1989), 745.
[10] TING J.M., HUANG N.Z., Carbon, 39 (2001), 835.
[11] BAKER R.T.K., BARBER M.A., HARRIS P.S., FEATES F.S., WAITE R.J., J. Catal., 26 (1972), 51.
[12] SNOECK J.W., FROMENT G.F., FOWLES M., J. Catal., 169 (1997), 250.
[13] DUPUIS A.C., Prog. Mater. Sci., 50 (2005), 929.
[14] LEE C.J., PARK J., J. Phys. Chem. B, 105 (2001), 2365.
[15] LIU L., FAN S.S., J. Am. Chem. Soc., 123 (2001), 11502.

Received 3 September 2008