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Pyrocarbon Whisker Growth on the Catalytic Mullite Substrate by the Pyrolysis of Methane

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Abstract

Like bamboo-sprouts after rains, numerous subμm-sized pyrocarbon whiskers growth on the Mullite ($3Al_2O_3 \cdot 2H_2O$) substrate could be observed through a looking glass during methane pyrolysis at the temperature of 1050 °C in this study. If the surface of substrate would be scrubbed strongly with iron metals, then finely sticked iron particles were more effective catalytic for nm-sized whisker growth. Numerous fine flakes of pyrolytic carbon were hanging by invisible nm-whiskers as like as small spiders hanging by a spiderweb. This is the identification of nm-sized whisker growth. Therefore if the pyrolysis would be stopped at the initial stage of the whisker growth, the primary lengthening growth was nm-sized whisker. So could we vary arbitrarily sizes of whisker from nm- to μm-sizes. But μm- and nm-whiskers grown with the different growth mechanism; the former was straight and the latter has twigs, The lengthening growth of whisker was depended on the flow pattern pyrolysis species on the active sites of substrate and on the growth duration. We could obtained straight whisker length of 10~20 μm/min during the primary growth and laboratory spiral whisker of 30~40 μm-diameter/hr during the secondary growth.

Keywords : *Pyrocarbon, Whisker, Methane, Pyrolysis, Catalyst*

1. Introduction

Another form of highly purified artificial graphite which may find more than expecting useful applications are pyrocarbon and graphite whiskers. Unlike metal whiskers, these are not dislocation-free single crystals, exhibiting the highest mechanical strength (20 GPa) and Young's Modulus, (1000 GPa) in the carbon materials (see Table 1) [1]. The axial Young's modulus of the graphite whiskers approach the single crystal $1/S_{II}$ value of 10^{13} dynes/cm^2 (94% of ideal value), and the strain at fracture is about 2% indicating a strength of 2×10^{11} dynes/cm^2 (ca. 3×10^6 psi). It was also shown by X-ray diffraction that the scrolls had a large crystallite size, with the c-axes arranged radially to the whisker [2]. They grow by further deposition of carbon from the vapor at the top and the free basal plane edges, eventually acquiring a hollow tubular form. The volumetric resistivity was 7×10^{-5} Ω-cm, with a positive temperature coefficient [3].

Actually more than 60 years ago Å-sized feeble growth of graphite whisker with length of 1000 Å and diameter of 10 Å was reported by Turnbull and Rappeneau [4], while more thick μm-sized growth of graphite whisker with length of 1.3 mm and diameter of 10 μm on the graphite fiber heated to 2500 °C was reported by Meyer [5]. The more longer graphite whisker with length 30 mm and diameter 0.5~5 μm from graphite vapor through a strong electric current under inert atmosphere was discovered by Bacon and Bowmann in 1957 [6]. The later 1966 Fitzer and Schlesinger [7] and the more later 1972 Fitzer and Rhee [8, 9] have found the polycrystalline carbon whisker growth on the Alsint-substrate during the methane pyrolysis at 1500~1700 °C under the vacuum of 200 Torr. The growth mechanism and rate of the pyrocarbon whisker were discussed by means of the screw and step dislocation theories, while the primary lengthening growth with rate of 43 μm/s by the screw dislocation and the secondary thickening growth with 0.4

Table 1. Tensile Properties of Strong Whiskers

Material Whisker	Modulus of Elasticity (10^6 psi)	Ultimate Tensile Strength (10^3 psi)
Carbon	150	3,000
Iron	29	1,900
Zirconia	62	600
Silicon	23	550
Quartz	11	600

Estimated tensile strength $\sigma_{theor} \fallingdotseq E/10$ for graphite
The elastic constant Cof the graphite single crystal = 1060 GN/m^2 (GPa); graphite whisker = 1000 GPa

μm/s by the step dislocation. The thermal conductivity was measured to 2000 w/m·K and the stiffness of 500 GPa.

In the recent study we could find a massive growth of pyrocarbon whisker on a catalytic Mullite substrate at the low moderate temperature [10]. In the present study a possibility of the μm-, subμm- and nm-sized pyrocarbon-whisker production in arbitrary and of the continuous production could be recognized too. Also we could size down from μm- to nm-sized pyrocarbon whisker by means of finely smeared iron metal on the surface of Mullite substrate.

2. Experimental

2.1. Pyrolysis Furnaces

A tubular horizontal furnace (max. Temp., 1100 °C) with length of 40 cm, diameter of 8 cm and heating zone of 10 cm was used (see. Fig. 1). An Alsint-tube of 50 cm long and of 6 cm diameter as the heating tube was inserted into the furnace and 4 smaller Mullite-hemitubes (consisted of two hemitubes with 4 cm dia. and two 1/4 hemitubes with similar sizes with 7.5 cm long) as substrates were inserted into the heating zone. By means of several reproducible experiments the optimum arrangement was recognized that a space between the upper and middle substrates was ca. 1.5 cm, the space of the middle parts ca. 0.8 cm and the space of the bottom ca. 1.0 cm. The front of the heating tube was tightly covered with a looking-glass cylinder with 3 inlets of gases CH_4, Ar and H_2. Through the looking glass could be observed the inside of heating zone, photographed and estimated the length of whisker growth. After every experiments the substrate could be withdrawn from the furnace, collected whiskers, measured length and diameter of whiskers by means of a computer aided microscope. With SEM-photos could be discussed the growth mechanism.

2.2. Temperature-dependent

The CVDs of pyrolytic carbon are possible at the temperature range from 900 to 2000 °C and catalytic CVDs at even lower temperature of 600 °C [9]. Their density depends on the temperature strongly as shown in Fig. 2. The more higher density indicate the higher order of crystallization [6].

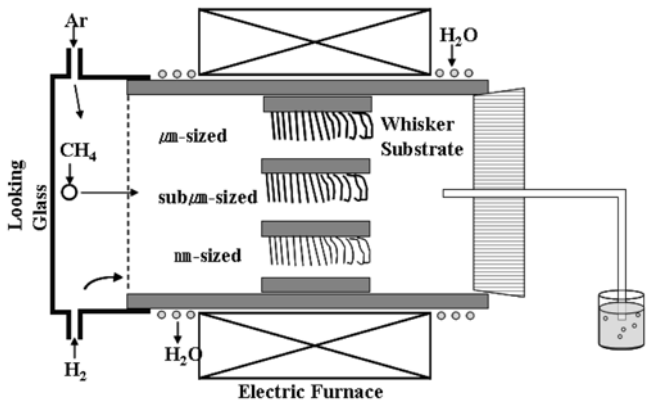

Fig. 1. Batch process of pyrocarbon whisker growth.

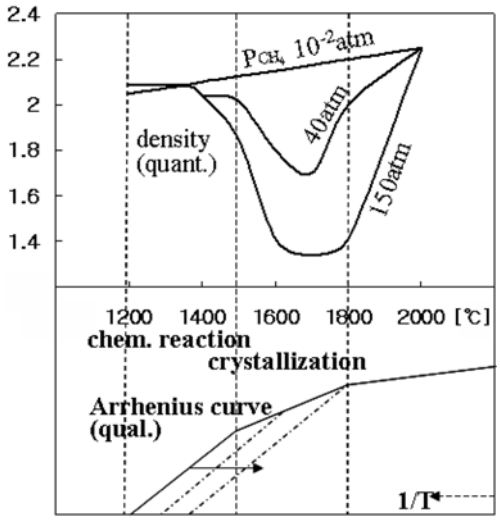

Fig. 2. Illustration of influences of deposition temperatures on the density of pyrocarbon through the velocity of individual steps in Arrhennius diagram.

The pyrocarbon whiskers grow slowly on the surface of Mullite substrate by the methane pyrolysis without or with addition of H_2 at the temperature of 900 °C and very rapidly at 1100 °C. But because of limit of the existing furnace 1050 °C was moderated for the continuous growth. If the temperature is higher than 1100 °C, the pyrolysis could accelerate and offers lower density of the whisker. Under 900 °C the pyrolysis could be decelerated and whisker growth was impossible.

2.3. Method

Any ceramic substrates, even quartz glass could be applied for the whisker growth, if the surface was scrubbed strongly with metal iron. Mullite was particularly preferred catalytic substrates without Fe-smeared. While heating up to the working temperature of 1050 °C, Ar and H_2 were supplied and then only Ar was exchanged with CH_4. However H_2 was needed for the initiation of the pyrolysis process, but excess of H_2 inhibited the process. So the optimum ratio of H/CH_4 was 1/5 [10]. The concentration of the precursor was a important factor for the whisker growth. The optimum flow rate of methane at 1050 °C was ca. 8.0 cm/s, that was about one second residence time through the deposition zone (7.5 cm length).

At the beginning of pyrolysis it needed H_2 supply during 15 min for the deposition of basal plane of pyrolytic carbon which gives the basis and offers the step dislocation besides screw dislocation for the whisker growth. In the early study it was enough 4 minutes at 1500 °C [8]. Whisker began to

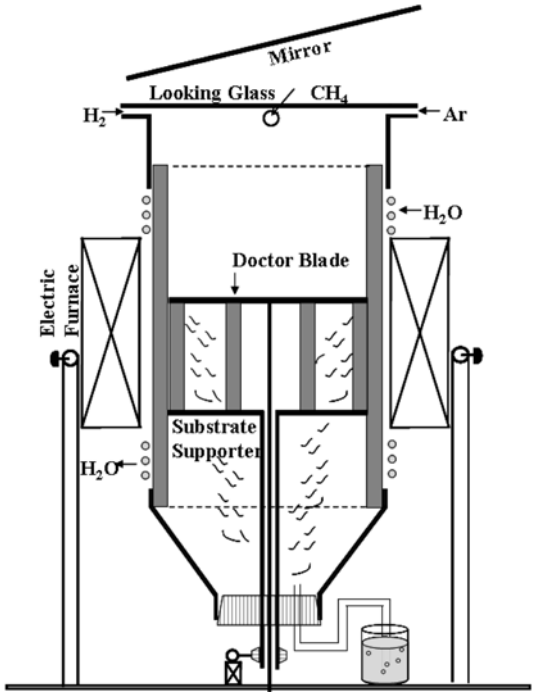

Fig. 3. Continuous process of pyrocarbon whisker growth.

grow after 16 min after that suddenly we could observe fine flakes hanging from the ceiling but could not see their strings. After prolonged thickening growth it has became a visible long filaments and whiskers. Because of nm-size scaled whisker at the initial stage it could be not observed and then after 30 minutes a visible lengthening growth up to 1~1.5 cm and a thickening growth up to subμm- and nm-sized whisker with twigs were progressed simultaneously.

2.4. A possible continuous production

After cool down and remove of the grown whisker by means of a doctor blade made of quartz glass, the pyrolysis was repeated again and again with the old pyrocarbon basal plane in order to grow new whiskers. This test was for the possibility of continuous production of whiskers. If this process is possible during the working, whisker growth could be continued, removed and collected down from the vertical furnace. Like this growth, remove and collection of pyrocarbon whiskers should be carried out inside of the furnace during the course of methane pyrolysis. The period of the repeating process was a half hour. For the remove of whiskers, we needed a device of a doctor blade rotating or fixed, otherwise substrates with a supporter rotate by manual in the furnace as Fig. 3 which is a concept from the experimental knowhow would be installed in vertical and attached the looking glass on the top and inserted the supporter of 4 medium and small hemitubes of Mullite substrates with 3 doctor blades hanging from the upper arm. This device could be rotated by mechanicals.

3. Result and Discussion

The pyrocarbon whisker growth depends on the various factors, namely temperature, pressure, concentration of precursor and diluent gases and the more strictly arrangements of catalytic substrates. The most important factor was catalytic substrate, that was Fe-smeared Mullite substrates and their arrangements for μm-, subμm- and nm-sized whisker growth simultaneously.

The flow pattern of pyrolysis should be laminar flow. As soon as the methane flows through the dark spaces between substrates, it become bright and then we could observed clearly the whisker growth through pyrolysis of methane. At the beginning of growth we could observed several slender long whiskers which arrived in few minutes on the backside of middle substrate, while nm-sized whisker were grown in the middle space and then began to grow bushes of whisker as Fig. 4(a). Some whisker grown as a long rod, followed by vertical growth. Fig. 4(b) shows a progress of whisker growth under the substrate. The forms of whisker were depend on the flow pattern of pyrolysis species. Therefore the spaces and arrangement between the substrate were most important. In the Fig. 4(b) shows small flakes of pyrolytic carbon hanging from a thin invisible fiber which late grown up thick filaments as like as a small spider which was suddenly fell down in the space and hanging by his slender string. This phenomena could be recognized nm-sized whiskers which may be sprouted suddenly very long, but we could not see it. There were some particularly numerous vortical or spiral whiskers when the middle substrate was removed and the space very wide, that means s vortex flow (Re = 15,421 at 1050 °C) of pyrolysis species (see. Fig. 5(a) and 5(b)). Fig. 6 shows a vortical whisker with diameter of 38 μm. In these whiskers both primary lengthening growth and secondary thickening growth have already began. Particularly in the vortical whisker the underpart of the growth was slender, but the upper part of

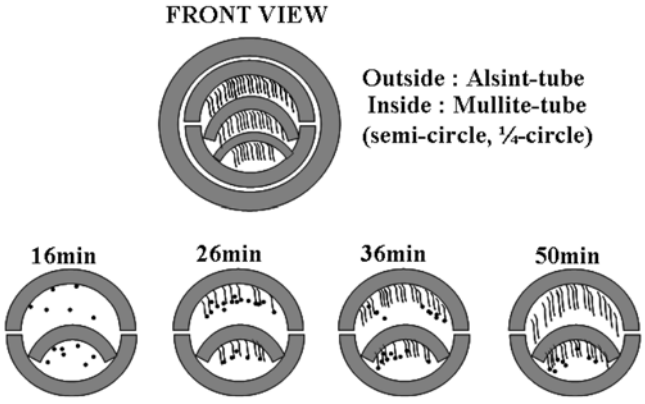

Fig. 4. progress views of μm- & nm sized pyrocarbon whisker growth on the substrate and its arrangements.

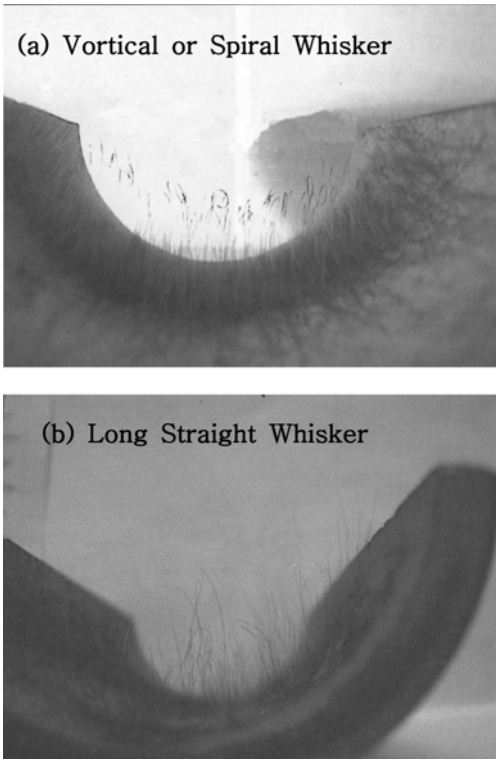

Fig. 5. Pyrocarbon whisker Growth in vortical or spiral (a) & straight forms (b).

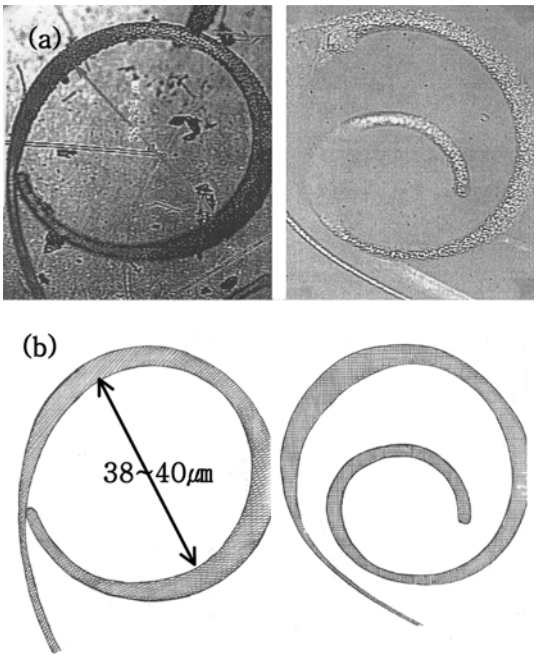

Fig. 6. Pyrocarbon whisker of spiral growth and sketches (b) of (a).

spiral was very thick through the more intensive secondary growth.

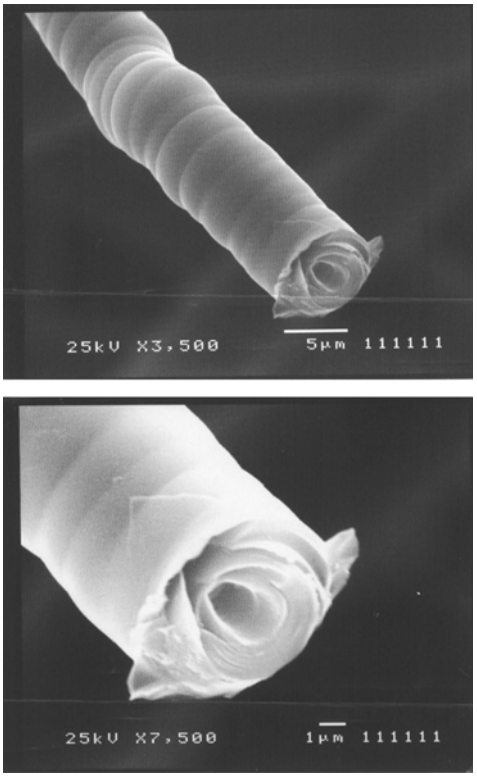

Fig. 7. SEM-photo of apyrocarbon whisker with a hollow axis and multiwallbag.

Fig. 7(a) shows SEM-photos of pyrocarbon whisker in the center of whisker there is to find a hollow tube, that is so called a subμm-hollow or so called nm-tube whisker. Fig. 7(b) shows a surface photo of subμm-whisker with the multiwallbag which could be interpreted by the screw and step dislocations.

4. Conclusion

It was concluded that with catalytic substrates, Fe-metal smeared Mullite-ceramics, through whose proper arrangement with spaces of 1 or 1.5 cm, methane pyrolysis has offered nice active screw and step dislocation for the accurate straight and vortical whiskers growth. It was recognized also the possibility of repeating whisker growth and crops of 2 or 3 cm long and slender μm- or subμm-sized pyrocarbon hollow whisker with the multiwall- bag which could be applied in the continuous process. Furthermore it was possible to identify the invisible nm-sized whisker growth by means of indirect methode, that is flakes hanging from the ceiling of Fe-smeared substrates. Such pyrocarbon whiskers may apply for the composite reinforcement and intercalation of Li++ or H_2-storage in the basal plane layers after the graphitization process.

References

[1] Mochida, I. "*Chemistry and Engineering of Carbon Materials*", Vol. 3, Asah Gura Publ. Co. Japan, 1990, 5.
[2] Delmonte, J. "*Technology of Carbon and Graphite Fiber Composites*", Van Nostrand Reinhold Co., New York, U.S.A. 1981, 45.
[3] Okuda, K. "*Carbon Fibers and Composites Materials*", Vol. 13, Koritz Publ. Co. Japan, 1988, 25.
[4] Turnbull, F.; Rappeneau, P. "*Growth and Perfection of Crystalls*", John Wiley & Sons, Inc., London, 1958, 47.
[5] Meyer, L.; Gomer, R. *Proceeding of the third Conference on Carbon*, Pergamon Press. 1957, 425.
[6] Bacon, R.; Bowman, J. C. *Bull. Am. Phys. Soc., Ser.* **1957**, *11*, 131.
[7] Fitzer, E.; Schlesinger, H. *Ber. Deut Kerm. Ges.* **1966**, *43*, 206.
[8] Fitzer, E.; Fritz, W.; Rhee, B. *High Temp- eratures-High Pressures* **1972**, *4*, 219.
[9] Rhee, B.; Kim, C. E. *J KICHE.* **1972**, *10*, 113.
[10] Rhee, B. *et al*., Extended Abstract Carbon '03 Conference, Oviedo, Spanish Carbon Group, 2003, 154.