

저온에서 methane의 촉매적 열분해시 nanosized pyrolytic carbon whisker 성장의 발견

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Growth of Nanosized Pyrolytic Carbon Whisker by Catalytic Pyrolysis of Methane

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Abstracts

At the low temperature of 950°C the μm -sized whisker growth during the catalytic CVD of pyrolytic carbon from methane with H_2 - and Ar-gas on quartz substrate with NiO powder was found in this work. In the preliminary study it was observed from pure methane pyrolysis without catalyst at the high temperature 1500~1700°C. If the growth whisker should be stopped at initial stage, about 20 min. of the methane pyrolysis, it would be nanosized whisker growth. The screw growth mechanism and unique mechanical properties of whisker for composites were also recognized. If the pyrolysis would be continued, we could found also spiral growth of whiskers with diameter of about 1.5 μm . The large length of whisker was about 10 cm in 20 minute.

INTRODUCTION

More than 100 years ago was reported a nanosized feeble growth of graphite whisker with length of 1000Å and diameter of 10Å by Turnbull and Rappenauf[1], while a μm -sized formation of graphite whisker with length of 1.3 mm and diameter of 100 μm on the graphite fibers heated up 2500°C was found by Meyer[2] and a preparation of graphite whisker with length of 30 mm and diameter 0.5 - 5 μm from a graphite

vapor through a strong electric current discharge under inert atmosphere was succeeded by Bacon and Bowmann[3]. Late 1966 Fitzer and Schlesinger[4] and more late 1972 Fitzer and Rhee[5] have discovered the large polycrystalline carbon whisker growth on the Alsinted substrate during the pure methane pyrolysis at 1500 - 1700°C under normal atmosphere and vacuum of 50 - 200 Torr. The growth mechanism and rate were recognized by means of screw and step dislocation theories, primary length growth with 40 $\mu\text{m}/\text{s}$ by screw and secondary thick growth with 0.4 $\mu\text{m}/\text{s}$ by the step dislocation. Rhee has measured the thermal conductivity of 2000 w/m.K, stiffness with 500 GPa. But still recently there was no reports on the pyrolytic carbon growth in spite of such astonishing properties of carbon whisker.

In this study we have found again the perpendicular and straight growth of pyrolytic carbon whisker during the catalytic pyrolysis of methane by H_2 on the quartz substrate and NiO-powder but at lower temperature of 950 - 1050°C. This preparation of pyrolytic carbon whisker was quite reproduceable. The progression of pyrolysis could be observed and photographed through the looking glass. Under this temperature there was no deposition on the wall and obscure in the space of reactor, while above 950°C the space was bright, because the pyrolysis also takes place in the whole reactor volume. after the pyrolysis the reaction gas mixture was exhausted and photographed. One of the prepared carbon

whiskers could be picked up and applied on the observation under optical microscope, Ortholux, of Leitz Co. SEM and roentgenography. The density was measured with pycnometer and tensile strength with TM Instron.

EXPERIMENTAL

The tubular ceramic reactor has a length of 40 cm and a diameter of 3 cm with electric heating zone of 20 cm. Into the reaction zone a smaller half tube of quartz glass with length of 3 cm was inserted and on that wall was spreaded with nickelous oxide powder. The feed gases were supplied through three rotameters and during the heating Ar and H₂ gases were streaming, followed by feeding of methane gas. The optimum ratio was $P_{CH_4} : P_{H_2} : P_{Ar} = 0.5 : 0.1 : 0.4$ and residence time was about 1.5 sec. In front of inlet was adapted a looking glass through it observation was possible. Fig. 1 shows the observation of the pyrolysis progression. There were 3 feed inlet for Ar, H₂ and methane gas. Fig. 2 shows the bright inside of reactor on that grown many whiskers and Fig. 3 was the enlargement of the inserted half-quartz glass on that numerous whiskers were to observe. Fig. 4 shows the enlargement of a whisker with screw ring. Fig. 5 shows a cross section and Fig. 6 a Laue-photograph with distinct lattice plane 002, 004 and etc. which means a single crystal-like whisker-carbon growth.

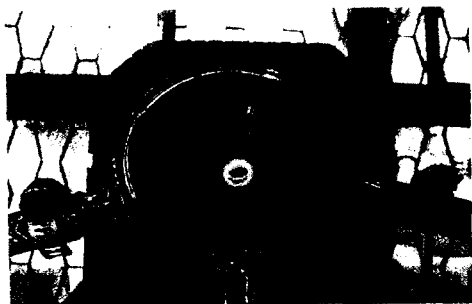


Fig.1. Pyrolysis reactor with looking glass and with three feed lines.



Fig. 2. Enlargement of the inside of reactor.



Fig. 3. Enlargement of the inserted half quartz glass on that numerous whisker growth..

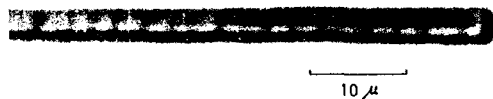


Fig. 4. Enlargement of a whisker with screw ring..

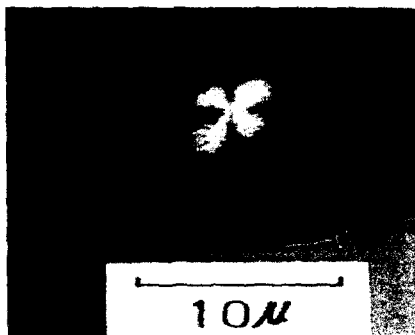


Fig. 5. Cross section of a whisker.



Fig. 8. Enlargement of a spiral carbon whisker.

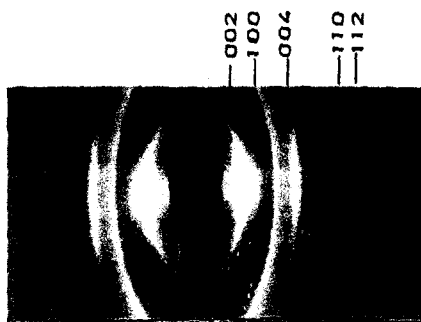


Fig. 6. Laue-Photograph of a whisker with lattice plane, 112, 110, 004, 100, 002..



Fig. 7. Spiral growth of pyrolytic carbon whisker.

RESULTS AND CONCLUSIONS

This study is recognizing that nanosized pyrolytic carbon-whiskers from methane pyrolysis with a catalyst NiO and H₂ on the quartz glass and mullite tube could grown at the lower temperature of 950°C than that of the former study[5]. The growth mechanism of a pyrolytic carbon whisker at the low temperature shows a screw dislocation and single crystal-like lattice planes. We found also spiral growth of pyrolytic carbon whisker(s. Fig. 7 and 8), when the pyrolysis continued long time, about more than 1 hour.

References

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