

GASIFICATION OF CARBON NANOTUBE-CONTAINING MATERIAL

K. Morishita and T. Takarada

Faculty of Engineering, Gunma University
1-5-1, Tenjin-cho, Kiryu, Gunma, Japan 376

Keywords: carbon nanotubes, gasification, microscopic observation

Introduction

Carbon nanotubes synthesized using arc discharge evaporation method always include graphitic carbon, amorphous carbon and carbon nanoparticles. The purification step is needed to precisely characterize the physical and chemical properties of nanotubes and to study the application of those. Recently, the purification of nanotubes by the gasification with oxygen^{1, 2)} or carbon dioxide³⁾ was carried out. However, few studies on the mechanisms of gasification of carbon nanotube-containing materials have been reported. In this study, the gasification behaviors of nanotube-containing materials and nanotubes were investigated by fixed point observation techniques with scanning electron microscope (SEM) and transmission electron microscope (TEM).

Experimental

Materials

Samples synthesized by arc-discharge evaporation method (Vacuum Metallurgical Co., Ltd., Type-3) in National Institute of Materials and Chemical Research were used. The conditions of synthesis were DC voltage of 18V and He pressure of 500 Torr. An inner black core of the cathode product was picked up. Then, the core was crushed and dispersed in methanol with the use of a sonicator. The sample recovered as a float was used as raw materials in this study.

Gasification

The gasification of sample was carried out in a thermo-balance (Shinku Riko; TGD-7000). After evacuation and substitution with N₂ gas, sample was heated up to a desired temperature with N₂ flow. Then, reaction gas was introduced into the reactor and the gasification of sample was initiated. The experimental conditions were as follows: oxygen (1, 10vol%) 773K, 823K, 1023K, 1073K; carbon dioxide (100vol%) 1173K.

SEM and TEM observations

A series of SEM observation and gasification of sample was carried out as follows. The raw materials put on Si wafer was observed with SEM and then set in the thermo-balance. After the sample was gasified for a desired reaction time, the area selected by the previous observation was observed with SEM, again. These procedures were repeated several times. The SEM used was JEOL JSM-5300. In the case of TEM observation, sample was put on copper grid (400mesh). A series of TEM observation and gasification of sample was essentially similar to the case with SEM mentioned above. TEM observations were carried out using JEOL 1200EX at ACCV of 100kV. In these experiments, more than 10 fields were observed and more than 50 photographs were taken for each sample. It is very important to observe many fields because microscopic observations are apt to give prejudiced informations.

Results & Discussions

Reactivity

Nanotube-containing materials were gasified in a thermo-balance. Figure 1 shows the gasification profiles obtained under various conditions. The reactivity of sample toward oxygen was so high that about 90wt% of sample was gasified in 5min at conditions of 1023K and 10vol% of oxygen. The activation energy for oxygen gasification was estimated as about 140kJ/mol. The gasification profile of sample in carbon dioxide was somewhat peculiar. The conversion was smoothly increased up to around 70wt%, and the gasification was seemed to be

saturated after that.

Gasification behaviors of nanotube-containing materials

A series of SEM observation and gasification of sample was repeated several times. Figure 2 shows the SEM photographs of raw material and the samples partially gasified. The gasification temperature was 1023K. Besides carbon nanotubes, many large lumps of carbon and many carbon nanoparticles were observed in the raw material. As the reaction progressed, other carbonaceous materials were gradually consumed and only carbon nanotubes were remained at 5min of reaction time. This is due to the difference in the reactivity between carbon nanotubes and other carbon materials. In the course of gasification, many tubes were newly appeared from lumps of carbon materials. Careful observations revealed that not only other carbonaceous materials but also carbon nanotubes were damaged by oxygen gasification. Figure 3 shows the results obtained at 823K. The total conversion was about 90wt%. No remarkable difference in the gasification rate between other carbon materials and nanotubes was observed. Therefore, considerable amount of other carbon materials were remained in the sample gasified. It may safely be said that it is better for the efficient recovery of nanotubes to gasify raw material with oxygen at a high temperature such as 1023K than at a low temperature of 823K. In the case of CO₂ gasification at 1173K, as the reaction progressed, large lumps of carbonaceous materials were gradually gasified just like the case of oxygen gasification. A number of carbon nanoparticles, however, were remained in the sample. Further purification step will be needed.

Gasification behaviors of nanotubes and nanoparticles

To clarify the gasification behaviors of nanotubes and nanoparticles, a series of TEM observation and gasification of sample was repeated several times. The gasification temperature was 1023K. A wide variety of gasification manners of carbon nanotubes were observed. It was often recognized that the gasification of nanotube was initiated from the cracks, defects and strains in nanotubes. Other typical gasification manner was shown in Figure 4. It can be seen that nanotube was gasified from the tip of the tube. This gasification manner was often observed in this study and reported by Tsang et al.³⁾ The diameter of tube was reduced from 18nm to 11nm near the tip (point-A) and from 20nm to 15nm at point-B in 5 seconds. From these results, the gasification rate of carbon nanotube is able to be measured directly. A careful observation showed that the tip angle of closed layer near the cap was enlarged as shown at point-C. Figure 5 shows the gasification manners of tubes and particles. In this field, many nanoparticles were observed as shown in Figure 5a. At 5sec of gasification time, some nanoparticles were considerably damaged and outer layers of some nanotubes were stripped off. Finally, almost all the nanoparticles were gasified at 10sec. The gasification rate of the irregular-shaped particles was higher than that of smooth-faced particles.

Similar experiments were carried out at 823K. The results obtained were shown in Figures 6 and 7. As the reaction progressed, the outer layers were transformed to amorphous and the spacing of the lattice was enlarged (Fig. 6). It was commonly observed that relatively thin tubes just as pointed by arrow in Figure 6 were swelled by the oxidation. The pitting formation by the oxygen gasification was sometimes recognized on the cylindrical outer surface of tubes (Figure 7). As a whole, no obvious difference in the gasification rate between nanotubes and nanoparticles was recognized at 873K. This is consistent with the results obtained with SEM observations.

Conclusions

The gasification behaviors of carbon nanotube-containing materials were clarified by SEM and TEM observations. The gasification rates of other carbonaceous materials were higher than those of nanotubes at 1023K. A wide variety of gasification manners of nanotubes were observed. The gasification manner of nanotubes strongly depended on the gasification temperature.

References

1. P. M. Ajayn et al., *Nature*, **362**, 522 (1993)
2. T. W. Ebbesen et al., *ibid.*, **367**, 519 (1994)
3. S. C. Tsang et al., *ibid.*, **362**, 520 (1993)

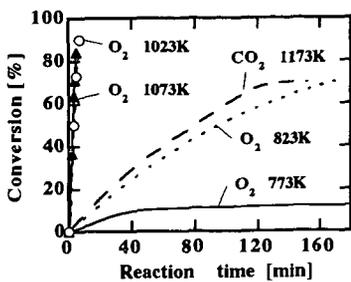


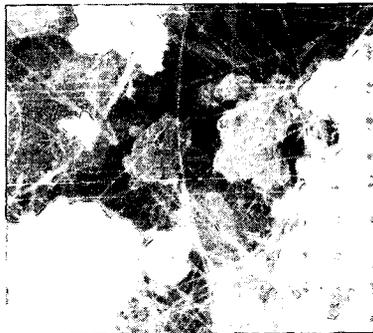
Fig. 1 Reaction profiles of samples



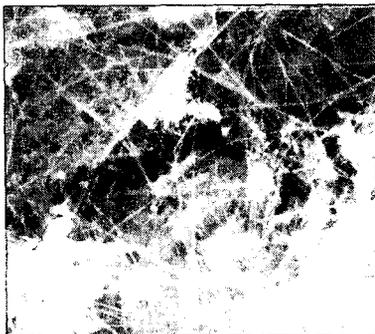
(a)



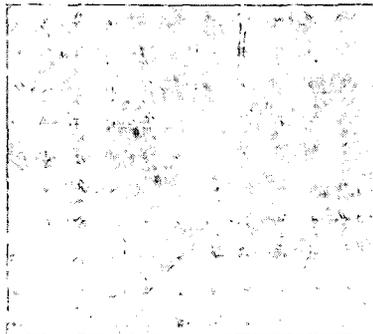
(b)



(c)



(d)



(e)

1μm

Fig. 2 SEM images of samples before and after O₂ gasification at 1023K

- (a) raw material
- (b) reaction time 0.5 min
- (c) reaction time 1 min
- (d) reaction time 3 min
- (e) reaction time 5 min

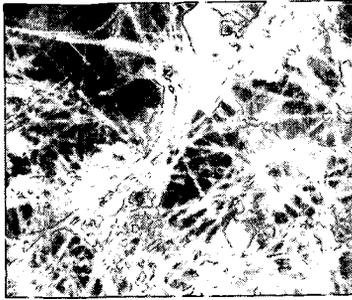
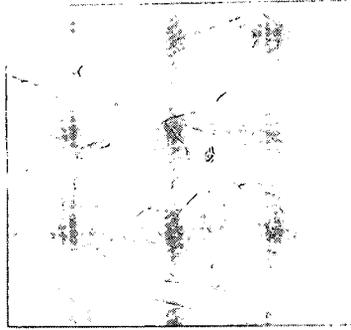
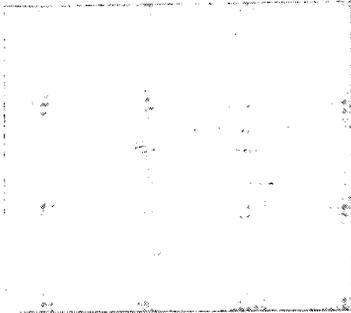


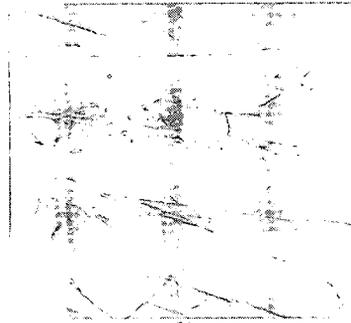
Fig. 3 SEM image of sample after O₂ gasification at 823K



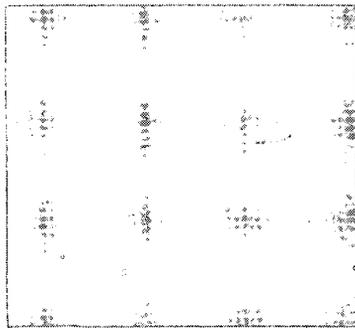
(a)



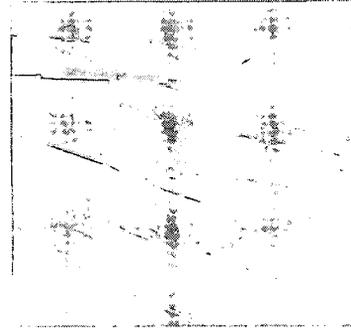
(a)



(b)



(b)



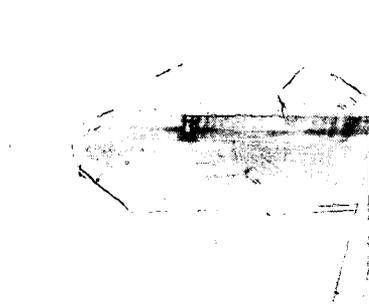
(c)

Fig. 4 TEM images before and after O₂ gasification at 1023K

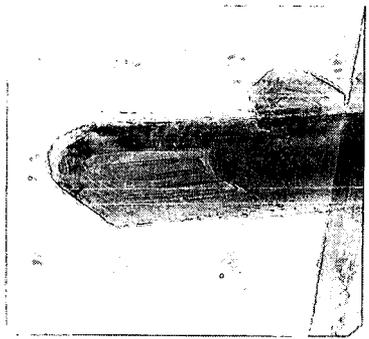
- (a) raw material
- (b) reaction time 5 s

Fig. 5 TEM images before and after O₂ gasification at 1023K

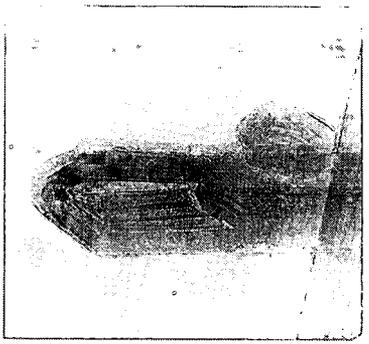
- (a) raw material
- (b) reaction time 5 s
- (c) reaction time 10 s



(a)



(b)

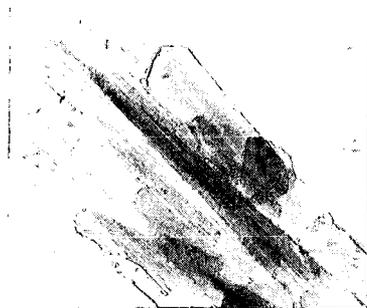


(c)

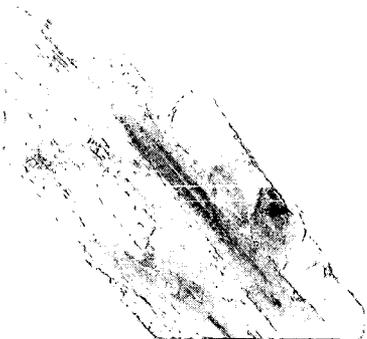
20nm

Fig. 6 TEM images of samples before and after O₂ gasification at 823K

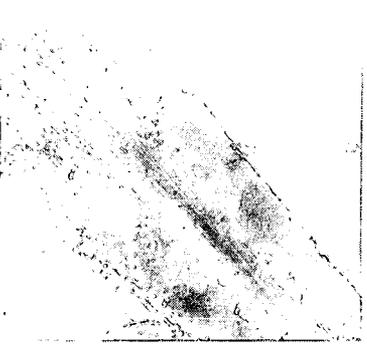
- (a) raw material
- (b) reaction time 20 s
- (c) reaction time 40 s



(a)



(b)



(c)

20nm

Fig.7 TEM images of samples before and after O₂ gasification at 823K

- (a) raw material
- (b) reaction time 10 s
- (c) reaction time 30 s