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Scanning electron microscope observation of the purification behaviour of carbon nanotubes

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Carbon nanotubes, with their unique structure, are expected to have a variety of applications as industrial materials. However, carbon nanotubes synthesized using the laser ablation method or arc discharge evaporation method always include other carbonaceous materials. Purification is a very important step in the use of carbon nanotubes as industrial materials. For the efficient recovery of nanotubes it is very important to clarify the gasification behaviour of the nanotube-containing material during the purification step. In this study, the gasification behaviour of a nanotube-containing material with various gasification agents was investigated in detail using a fixed-point observation technique and scanning electron microscopy. The gasification manner of the carbon nanotube-containing material was clarified using oxygen, carbon dioxide and hydrogen plasma as the gasifying agents. The gasification behaviour of the sample depended on the kind of reactant gas. In hydrogen plasma, carbon nanotubes were partly purified. Under the experimental conditions examined, oxygen gasification at 1023 K was the most effective method for purification of carbon nanotubes, and nanotubes were recovered selectively. © *1999 Kluwer Academic Publishers*

1. Introduction

Carbon nanotubes [1] with their unique structure are expected to be used as catalyst supports, molecular sieves, semiconductors and nanoprobes. Recently, a method of large-scale synthesis using laser ablation and arc discharge evaporation has been developed [2–4] and single-wall nanotubes have been synthesized for new applications of carbon materials.

Carbon nanotubes synthesized using the laser ablation method or arc discharge evaporation method always include other carbonaceous materials. Purification is a very important step in the use of carbon nanotubes as industrial materials. Purification of nanotubes by gasification with oxygen or carbon dioxide has been investigated previously [5–7]. However, few studies on the gasification behaviour of nanotube-containing materials have been reported and the gasification mechanism has not been clarified in detail. It is very important for the efficient recovery of nanotubes to clarify the gasification behaviour of nanotubes during the purification step. We investigated the gasification mechanism of the nanotube itself by observing the same area of the sample before and after gasification with transmission electron microscopy (TEM) [8]. We also found that the effect of gasification on the purification of carbon nanotubes was dependent on the kind of reactant gas used [9]. It is very important for the efficient recovery of nanotubes to clarify the gasification behaviour of the nanotube-containing material during the purification step.

In this study, the gasification behaviour of a nanotube-containing material with various gasification agents was investigated in detail using a scanning electron microscope (SEM); fixed-point observation technique i.e. the same area of the sample before and after gasification was observed with SEM for each gasification step.

2. Experimental procedure

2.1. Sample

Raw samples were synthesized from graphitic rods by the arc discharge evaporation method using a carbon cluster fabrication instrument (Vacuum Metallurgical Co., Ltd, Type-3) at the National Institute of Materials and Chemical Research. The conditions of synthesis were: d.c. voltage, 18 V; helium pressure, 67 kPa; helium flow rate, 5000 $\text{cm}^3\,\text{min}^{-1}$. An inner black core was picked up from the cathode product in which a large amount of nanotubes was included. Then, the core was ground to less than 100 μm and dispersed in methanol with the use of an ultrasonicator for 1 h. After decantation, the suspended matter was dried at 393 K for 2 h. The original sample was put on a $5 \times 5\ \text{mm}^2$ silicon wafer and marked with small silicon wafer pieces for fixed-point observation with SEM.

2.2. Gasification, with oxygen, and carbon dioxide

Gasification of the silicon wafer sample was carried out in a thermobalance (Shinku Riko, TGD-7000). Oxygen and carbon dioxide were used as the reactants. After the system was evacuated and completely substituted with nitrogen gas, the sample was heated up to a desired temperature at 100 K min^{-1} and held in nitrogen flow. Then, the reactant gas was introduced into the reactor and gasification of the sample was initiated. After the sample was gasified for the desired reaction time, the reactor was cooled down to room temperature in a nitrogen stream. Oxygen gasification was carried out at 1023 K and at an oxygen concentration of 10 vol % (N_2 base). Gasification with carbon dioxide was carried out at 1473 K. Gasification was ended by stopping the reactant gas supply.

2.3. Hydrogen plasma etching

It has been reported that hydrogen plasma is effective against etching graphitic carbon in diamond synthesized using the chemical vapour deposition method. The reactivity of graphitic carbon is generally higher than that of diamond in hydrogen plasma. In this work, hydrogen plasma gasification was applied for purification of the nanotubes.

Plasma etching of the sample was carried out using a microwave plasma reactor. The experimental apparatus used is described elsewhere [10]. Microwaves (2.45 GHz) generated by the magnetron were supplied to the quartz tube through a set of guide tubes, an isolator, a tuner and power monitor. The sample, set on a silicon wafer, was placed on a quartz holder. The reactor was evacuated up to 13.4 Pa using a rotary vacuum pump. Then, hydrogen gas was introduced into the reactor, and plasma was generated. The experimental conditions were a microwave input power of 100 W and a reaction pressure of 268 Pa. The surface temperature of the sample was tentatively measured with an optical pyrometer (MODEL IR-U). The temperature of the sample was around 1220 K under these condition.

2.4. Fixed-point observation with SEM

The purification behaviour of the sample was observed using a fixed-point observation method with SEM (Jeol JSM-5300LV).

A series of SEM observations and purification of the sample were carried out as follows. At first, the original sample, set on a silicon wafer, was observed by SEM. To avoid prejudice, more than 20 fields were observed for each sample and photographs were taken at the desired magnification for comparison. The silicon wafer sample was set in the thermobalance or microwave plasma reactor and was reacted for a desired time. After reaction, the area selected for the previous observation was observed with SEM, again. These procedures were repeated several times.

3. Results and discussion

3.1. Oxygen gasification

Fig. 1a shows an SEM image of the raw material. Many lumps of carbonaceous materials 2–5 μm in size and a few nanotubes were observed. Several nanotubes were bundled.

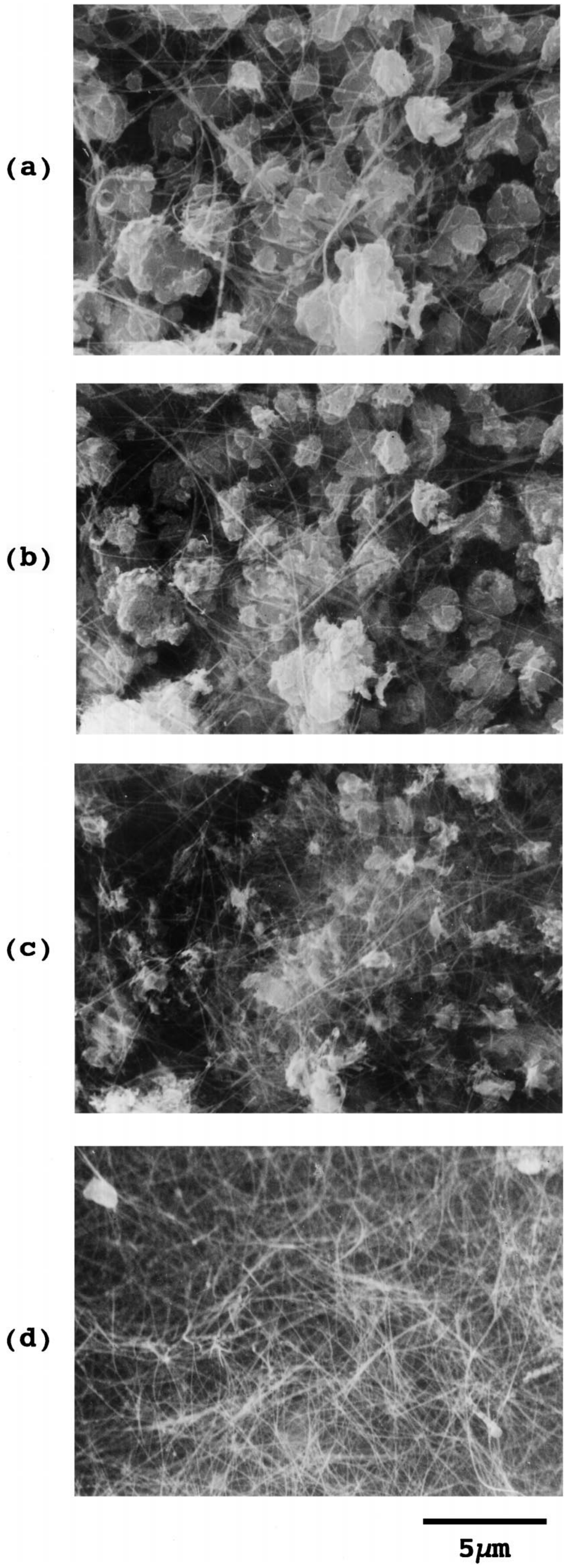

Figure 1 SEM images of carbon nanotube-containing material before and after gasification with oxygen gas: (a) raw material, and at a reaction time of 1 min (b), 3 min (c), and 5 min (d).

The sample was gasified at 1023 K because oxygen gasification of the nanotube-containing sample at 1023 K was more effective for purification of carbon nanotubes than that at lower temperatures [8, 9]. The gasification behaviour of the sample with oxygen at 1023 K is shown in Fig. 1. An SEM image of the sample gasified with oxygen for 1 min is shown in Fig. 1b. The size of the lumps was gradually reduced, and the surface became rough and porous during gasification. In some cases, it was observed that the lumps broke down to small particles. Some nanotubes were released from lumps and tubes bundled. As a result, many tubes appear in the photograph of the sample after gasification. Fig. 1c shows an SEM image of the sample after gasification for 3 min. As the reaction progressed, many lump-shaped carbonaceous materials disappeared and carbonaceous materials less than 1–2 μm in size remained. After 5 min of reaction time, carbon nanotubes remained selectively (Fig. 1d). Similar gasification behaviour to that mentioned above, was observed for other fields. The selective recovery of carbon nanotubes is due to the difference in reactivity between the carbon nanotube and other carbonaceous materials. The reactivity of amorphous carbon towards oxygen is higher than that of graphitic carbon. Besides, it is considered that the reactivity of the carbon nanotube is lower than that of graphitic carbon because a nanotube has no doungling bond. We evaluated the gasification behaviour of the sample by the change of apparent cross-sectional areas of the nanotubes and other carbonaceous materials determined from Fig. 1, semiquantitatively. Figs 2 and 3 show the apparent cross-sectional areas

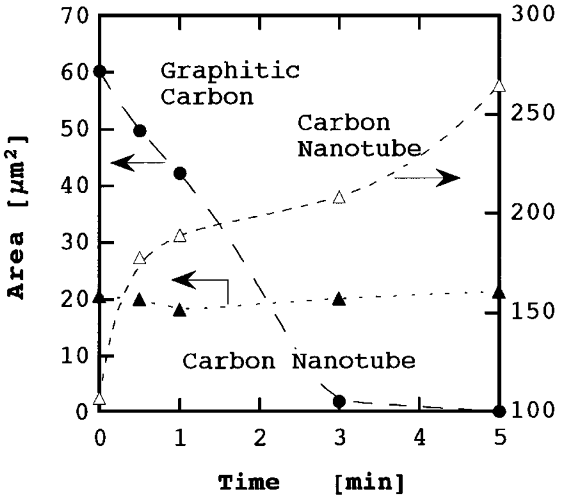

Figure 2 Relation between apparent areas of other carbonaceous materials and nanotubes and total length of nanotubes.

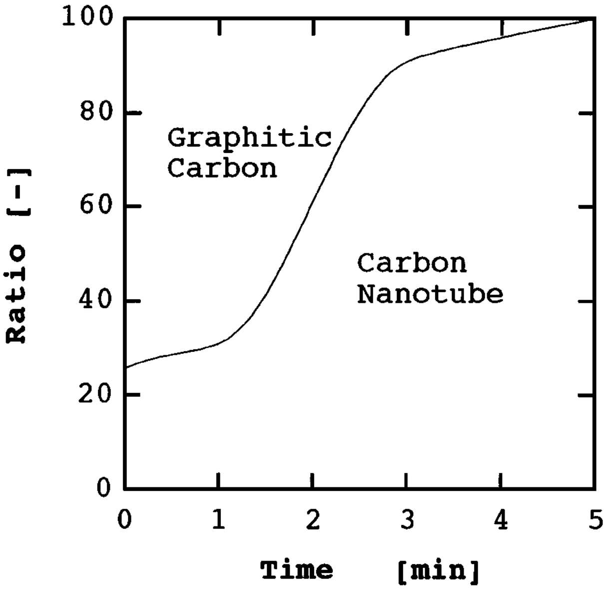

Figure 3 The ratio of the area of nanotubes to that of other carbonaceous materials.

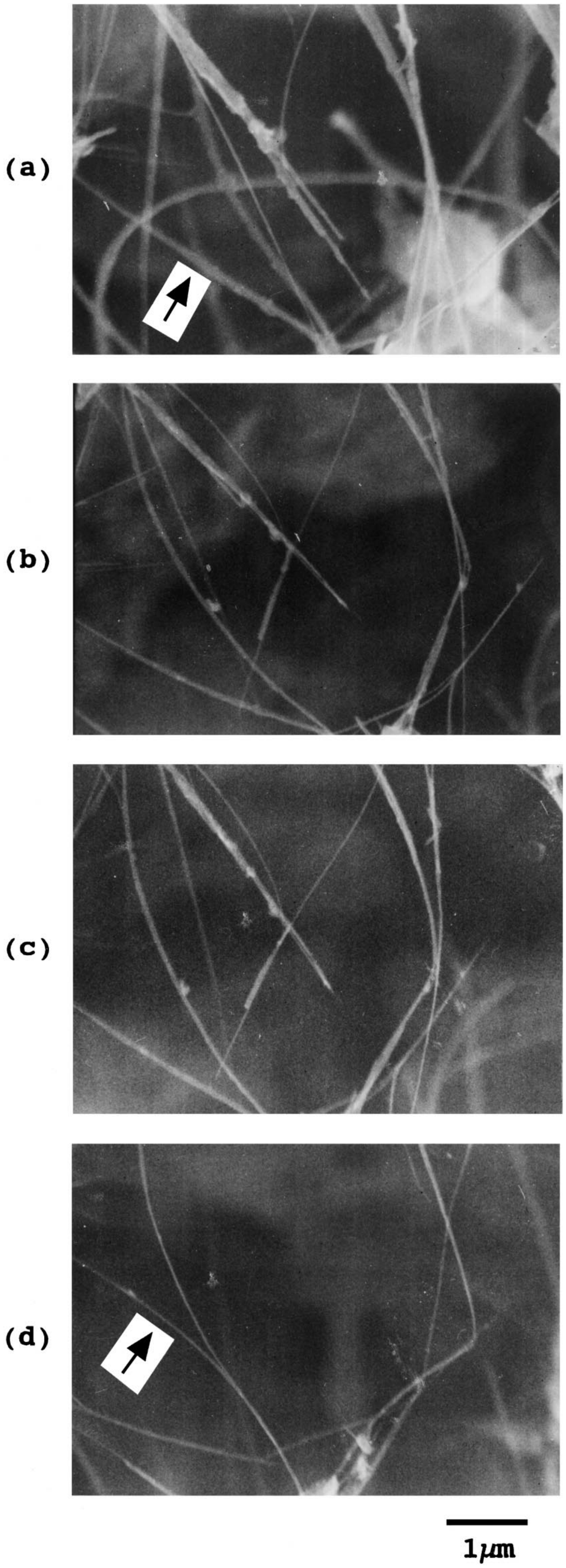

Figure 4 SEM images of carbon nanotube-containing material before and after gasification with oxygen gas: (a) raw material, and at a reaction time of 0.5 min (b), 1 min (c), and 3 min (d).

of other carbonaceous materials and nanotubes and the total length of nanotubes, and the ratio of the area of other carbonaceous materials to that of the nanotubes, respectively. Large carbonaceous particles were monotonically gasified up to 3 minutes of gasification time (Fig. 2). As a result, the area of nanotubes reached over 90% of the sample in 3 min (Fig. 3).

However, careful observation showed that nanotubes were also gasified during the gasification experiment. Fig. 4 shows the gasification behaviour of nanotubes and other carbonaceous materials. The carbonaceous particles were gasified easily (see their central parts). As gasification progressed, almost all the nanotubes became thinner, and a few tubes disappeared after gasification. We have already reported that carbon nanotubes were gasified from the tip of the tubes and were peeled off [8]. The diameter of the tube, indicated by the point of the arrow in Fig. 4, decreased from approximately 250 to approximately 100 nm.

3.2. Carbon dioxide gasification

The gasification of nanotube-containing materials with carbon dioxide was carried out at 1473 K. The concentration of carbon dioxide was 100 vol %. The gasification behaviour of nanotube-containing material with carbon dioxide is shown in Fig. 5. Fig. 5a and b shows SEM photographs of the raw material and the sample gasified with carbon dioxide for 1 min, respectively. In the raw sample before gasification, many lumps several micro metres in size and nanotubes were observed. After 1 min gasification, many nanotubes were plainly observed in the same field. It seems that nanotubes buried in the carbon lumps were released. As the reaction progressed, large lumps of other carbonaceous materials were gradually gasified and subdivided into smaller particles. For example, a 3.5 μm lump, indicated by the circle in Fig. 5, transformed to the aggregate of small particles of approximately 300–450 nm in diameter within 30 min (See Fig. 5a and e). Moreover,

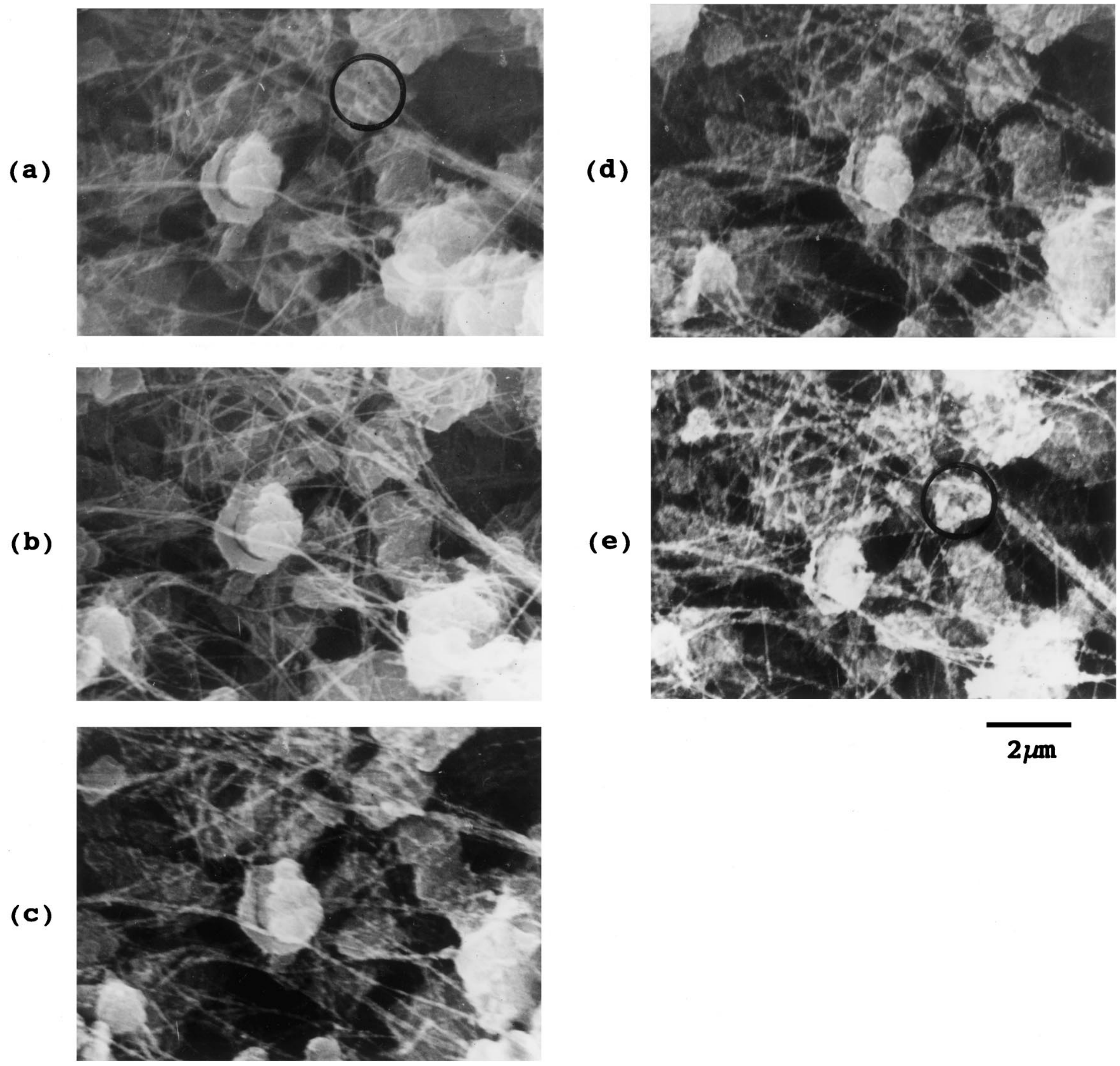

Figure 5 SEM images of carbon nanotube-containing material before and after gasification with carbon dioxide gas: (a) raw material, and at a reaction time of 1 min (b), 3 min (c), 5 min (d), and 30 min (e).

small particles were also observed on the surface of the nanotube. The sample was allowed to continue gasification for 3 h and the small particles still remained on the nanotube surface. Carbon nanotubes became thinner during the early period of carbon dioxide gasification; however, the tubes were not completely consumed. Under the reaction conditions used, conversion of the sample by weight basis levelled off after about 70 wt % conversion [9]. From the results it was concluded that large carbonaceous particles were easily gasified, and

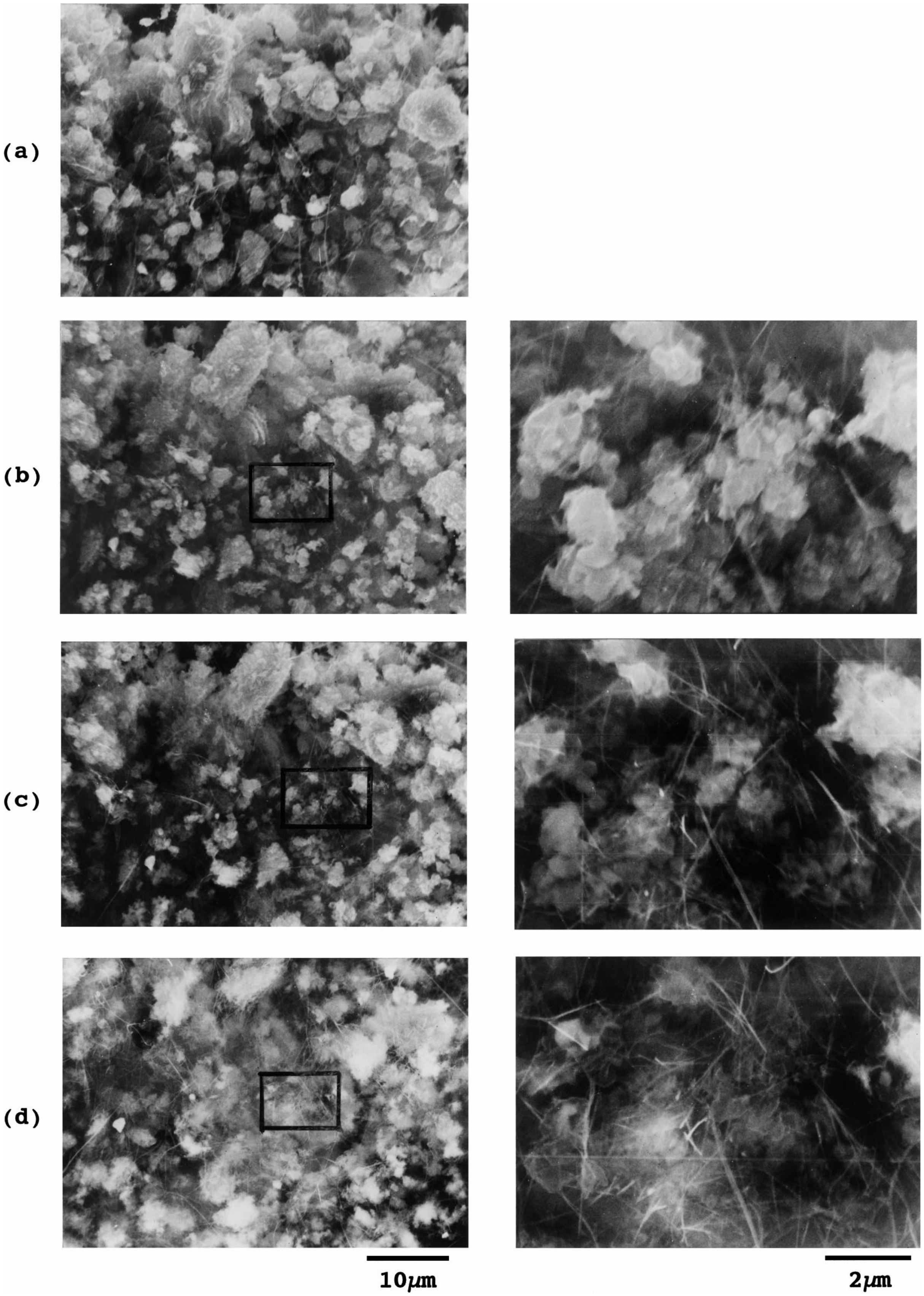

Figure 6 SEM images of carbon nanotube-containing material before and after gasification with hydrogen plasma: (a) raw material, and at a reaction time of 0.5 min (b, c) 1 min (d, e), and 2.5 min (f, g).

nanotubes and small particles were hardly gasified in a carbon dioxide atmosphere at 1473 K.

3.3. Hydrogen plasma gasification

The raw sample was treated in hydrogen plasma under the following experimental conditions: pressure, 268 Pa; input power, 100 W. SEM images before and after plasma gasification are shown in Fig. 6. Many carbonaceous lumps and some carbon nanotubes were observed in the raw sample, as shown in Fig. 6a. Gasification of the lumps initiated from their outside surface. As the gasification reaction progressed, the size of the lumps was reduced and several nanotubes were newly exposed. The nanotubes were partly damaged by the hydrogen plasma. In Fig. 6d, many straight nanotubes were observed; whereas the nanotubes were smoothly bonded in the case of oxygen gasification. The peculiar morphology of carbon nanotubes after treatment with hydrogen plasma may be due to etching of a particular part in the nanotubes.

It was found that carbon nanotubes were partly purified with hydrogen plasma from raw material synthesized by the arc discharge evaporation method. Further examination may be needed to purify the whole sample.

4. Conclusions

To investigate the purification of carbon nanotubes by gasification reactions in detail, select fields in the carbon nanotube-containing material were examined intermittently with SEM during reaction. The gasification behaviour of carbon nanotube-containing material was clarified by using oxygen, carbon dioxide and hydrogen plasma as the gasifying agents. The gasification behaviour of the sample depended on the kind of reactant gas. Under the experimental conditions examined, oxygen gasification at 1023 K was the most effective for purification of carbon nanotubes and nanotubes were recovered selectively. In the carbon dioxide atmosphere, large carbonaceous lumps included in the raw material were gradually reduced, but small particles remained. In the hydrogen plasma, carbon nanotubes were partly purified.

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