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Synthesis and characterization of alumina/carbon nanotube composite powders

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Synthesis and characterization of alumina/carbon nanotube (CNT) composite powders have been investigated for production of nanotube reinforced ceramic composites. The alumina/CNT powder was prepared by catalytic decomposition of acetylene gas with iron supported on alumina. The catalyst source was iron nitrate and the iron content was controlled up to 5.0 mol % to change the CNT compositions in the composite powders. The nanotube content in the powders was determined by an elemental analyzer. The quantity and quality of the CNT in the powders have been investigated with SEM, TEM, XRD and BET. The content of CNT was increased up to 12.5 wt. % and the CNT diameter increased with increasing iron catalyst content. The surface area and carbon content analysis shows that the quality of CNT is highest at 1.0 mol % iron catalyst loading. The synthesized CNT was fairly well-dispersed in the alumina powder.

Key words: Carbon nanotube (CNT), Alumina/CNT composite, Surface area.

Introduction

Since carbon nanotubes (CNTs) were discovered by Iijima nearly a decade ago, extensive theoretical and experimental research has been carried out to identify the structural characteristics and various properties of CNTs [1]. They have many remarkable physical characteristics such as novel electronic properties, exceptionally high axial strength and Young's modulus of the order of a terra pascal [2-5]. Due to their unique mechanical properties, CNTs have recently been considered as reinforcing elements in ceramic matrix composites [6-8].

Catalytic decomposition of hydrocarbons seems to be a more effective CNT production method compared to electric arc discharge and laser ablation methods because it has the potential for large scale CNT production and control of size and growth density [9, 10]. The catalytic decomposition of hydrocarbons in the presence of different supported transition metal catalysts has already been investigated [11-13]. Supported Co, Ni and Fe catalysts were found to be the most active in the catalytic decomposition. For the fabrication of bulk ceramic/CNT composites, relatively low iron concentration was chosen, compared to other research, in order to minimize the iron content in the bulk composites. In the present paper, the influence of the iron content in the starting materials on the microstructure, quantity and quality of CNTs has been investigated, prior to reporting the fabrication and characterization of the bulk alumina/CNT composite.

Experimental Procedure

Alumina/CNT composite powders were synthesized by the catalytic decomposition of acetylene over alumina powders impregnated with iron catalysts. To prepare the alumina powder impregnated with iron catalysts, alumina (AKP-30, Sumitomo Chemical, Osaka, Japan) and iron catalyst (Fe(NO₃)₃·9H₂O, Fluka Chemie GmbH, Buchs, Switzerland) were mixed in ethanol in a planetary ball mill for 12h using alumina balls 10 mm in diameter. After ball milling, the ethanol solution was removed via rotary evaporation at 80°C. The materials were then heated at 150°C overnight followed by grinding into a fine powder.

For the CNT synthesis, alumina powder having four different iron catalyst contents (0.1, 0.5, 1.0 and 5.0 mol %) was placed in an alumina boat mounted in a tube furnace. Details of the experimental setup are described elsewhere [14]. The production of CNTs was carried out at 750°C with two hour reaction time under $C_2H_2:H_2:N_2$ gas flow in the ratio 20:100:400 sccm respectively.

After the synthesis, the composite powders were examined by a SEM (S-4300, Hitachi, Japan) to measure the length, diameter and uniformity. Samples were dispersed in a carbon tetrachloride (CCl_4) solution, and then scooped up onto a perforated carbon microgrid. For TEM observations, these specimens were examined with a side-entry type HRTEM (H9000-NAR, Hitachi, Japan) operating at 300 kV with a point resolution of 0.18 nm. HRTEM was used to determine the wall

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structure of individual carbon nanotubes. X-ray diffraction analysis was carried on the synthesized alumina/ CNT composite powders. The weight percent carbon in the composite powder was obtained by an elemental analyzer (Flash EA 1112 series, CE Instruments, Italy). A surface area and pore size analyzer (ASAP 2010, Micromeritics, USA) was used to study the N2 adsorption-desorption isotherm at 77 K. The difference between the specific surface area of the composite powder and that of the same powder after oxidation in air at 850°C (carbon-free powder) was obtained from the BET equation. The pore size distributions of the composite powders and the carbon-free powders were calculated from the adsorption branch of the isotherms by the BJH (Barret-Joyner-Hallenda) method. The BJH method is based on the Kelvin equation, which relates the relative pressure of nitrogen in equilibrium with the porous solid to the size of the pores where capillary condensation takes place.

Results and Discussion

Figure 1 shows micrographs of the prepared alumina powders and alumina/CNT composite materials. Aver-



Fig. 1. SEM micrographs of (a) the prepared alumina powders and (b) alumina/CNT composite materials.



Fig. 2. Typical TEM micrograph of the CNT.

age particle size of the alumina powders is about 0.3 um and the CNTs have a diameter of about 10 to 50 nm, while their length is about 5 to 10 µm. In the synthesized composite powders (Fig. 1(b)), CNTs are relatively homogeneously dispersed in the powders. Figure 2 shows a typical TEM micrograph of the CNT. It clearly shows that the nanotube is a multi-walled hollow tube and not a solid fiber. The fringes on each side of the tube represent individual cylindrical graphitic layers. The CNT has approximately 15 to 20 walls of graphitized carbon. Figure 3 shows micrographs of the alumina/CNT composite materials with the different iron catalyst contents (0.1, 0.5, 1.0 and 5.0 mol %). The diameter of the CNTs tended to increase with increasing iron catalyst contents. Dai et al. reported that the diameter of CNTs could be determined by the size of the metal particle [15]. This result implies that the catalyst particle size depends on the amount of catalyst loading. Also, most of the closed tips are filled with catalyst particles (bright spot in SEM photographs, Fig. 3).

Figure 4 shows the XRD pattern of the alumina/CNT composite powder with 5.0 mol % iron catalyst. There are peaks corresponding to the (002) of graphite as well as the dominating sharp α -Al₂O₃ peaks. XRD analysis did not distinguish between graphite and CNTs. In addition, small α -Fe and Fe₂O₃ peaks were also detected. This shows that the iron nitrate converts to α -Fe and Fe₂O₃ in the tip of CNTs during the thermal processing.

The carbon content and the increase in specific surface area (Δ S) of composite powders are shown in Fig. 5. The carbon content and Δ S increase sharply as the iron catalyst content increased up to 1.0 mol %. There was a slight further increase in the carbon content and Δ S when the amount of iron catalyst was increased to 5.0 mol %. It shows that an increase in the amount of iron catalyst leads to an increase in the amount of carbon (CNTs). The increase in specific



Fig. 3. SEM micrographs of the alumina/CNT composite materials with the different iron catalyst content (a) 0.1 mol %, (b) 0.5 mol %, (c) 1.0 mol %, and (d) 5.0 mol %.



Fig. 4. The XRD pattern of the alumina/CNT composite powder with 5 mol % iron catalyst.

surface area per gram of carbon, $\Delta S/g_C$, is shown in Fig. 6. Peigney *et al.* suggested that ΔS is related to the quantity of nanotubes in the composite powders and that $\Delta S/g_C$ represents the quality of the nanotubes [8, 16]. The quality of CNT shows a maximum value at 1.0 mol % iron catalyst. The decrease in CNT quality at 5.0 mol % iron catalyst might be due to the generation of unwanted amorphous carbon or multishell carbon nanocapsules. Venegone *et al.* also reported that



Fig. 5. The carbon content and the specific surface area difference (ΔS) between composite powder and carbon-free powder as a function of the catalyst loading.

a higher loading of iron catalyst led to the encapsulation of the catalyst [17].

The pore size distribution calculated from the adsorption branch of the isotherms of the composite powder with 5.0 mol % iron catalyst loading and the carbonfree powder (heat treatment at 850°C) are shown in Fig. 7. The pore amount of the carbon-free powder is lower than that of the alumina/CNT composite powder in all



Fig. 6. The increase in specific surface area by gram of carbon, $\Delta S/g_C$, as a function of the catalyst content.



Fig. 7. BJH pore size distribution calculated from adsorption branch of the isotherms of the composite powder with 5 mol % iron catalyst loading and the carbon-free powder (heat treatment at 850°C).

pore size ranges because of the elimination of CNTs and other forms of carbon (amorphous carbon, multishell carbon nanocapsules). Especially, the composite powder shows major peak around 3 nm, corresponding to the diameter of the inner CNT cavity observed by TEM.

Conclusions

Alumina/CNT composite powders were synthesized by the catalytic decomposition of acetylene by iron catalyst supported on alumina powders. It was found that the synthesized powders have multi-walled CNTs (diameter: about 10 to 50 nm, length: about 5 to 10 μ m) and α -Fe and Fe₂O₃ particles were located at the tip of the CNTs. The carbon content of the synthesized powder increased up to 12.5 wt. % as the iron catalyst loading was increased up to 5.0 mol %. The diameter of CNTs was slightly increased as a result of the increase in the diameter of catalyst particles with increasing iron content. The surface area and carbon content analysis shows that the quality of CNT is highest at 1.0 mol % iron catalyst loading. The CNTs are relatively homogeneously dispersed in the alumina powders without any further mixing procedure. Therefore, the catalytic decomposition of hydrocarbon over iron catalyst supported on alumina is a suitable method for preparation of the composite powder.

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