研 究

Preparation of Multi-Walled Carbon Nanotube Compact by the Spark Plasma System (SPS)

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Received September 30, 2004

SYNOPSIS

The multi-walled carbon nanotube (MWNT) was not consolidated without additives by the spark plasma system (SPS). The phenol resin of 33 wt% was added to promote the consolidation. The MWNTs were aligned perpendicular to pressing direction of SPS in the consolidated compact. Bulk density and Young's modulus were more than 1.7 g/cm³ and 10 GPa for the MWNT consolidated at 120 MPa at 1200 °C and 1400 °C. The fracture behavior on bending test was a kind of quasiplastic deformation and was based on pull out of the MWNTs.

KEY WORDS

Carbon nanotube, multi-walled carbon nanotube, consolidation of multi-walled carbon nanotube, multi-walled carbon nanotube compact

1 Introduction

Carbon nanotubes (CNTs), which were discovered in 1991¹⁾, are long, slender fullerenes where the walls of the tubes are hexagonal carbon (graphene layer) and often capped at each end. A lot of investigations have been shown that CNTs exhibit many superior mechanical, electric and electronic properties over any other known material and hold substantial promise as high-strength composites, energy storage and energy conversion devices, sensors, field emission displays and radiation sources, hydrogen storage media and nanometer-sized semiconductor devices²⁾. CNT consists of single-walled carbon nanotube (SWNT)^{3,4)}, double-walled carbon nanotube (DWNT)⁵⁾ and multi-walled carbon nanotube (MWNT)¹⁾. One of interests arises from their formidable mechanical properties, i.e. Young's modulus up to 640 GPa for SWNT⁶⁾ and up to 1800 GPa for MWNT⁷⁾ and strength up to 45 GPa for SWNT⁸⁾. CNT is expensive these days, but the cost of its fabrication will surely decrease in near future. Low-cost CNTs will be useful for fillers of composites and starting materials to produce structural and/or functional compacts. Graphite is a hard-to-sinter material, and its powder can only be sintered at very high temperatures under pressing⁹⁾. The sintering ability of CNT is the same as that of graphite, and advanced techniques are needed to consolidate it at lower temperatures before transforming into graphite. The spark plasma system (SPS) has been developed for sintering of

metal and ceramics in the plasma and electric field¹⁰⁾, and it has been used for consolidation of various kinds of materials such as metals, ceramics and polymers¹¹⁾.

In this paper, the MWNT was mixed with phenol resin in ethanol. After removing the ethanol and decomposing the phenol resin by heating, the mixture of the MWNT and the amorphous carbon transformed from the phenol resin was consolidated by SPS. Bulk density, Young's modulus, and Poisson's ratio were determined for the consolidated MWNT.

2 Experimental Procedures

CNT used for the consolidation was MWNT (NanoLab Inc., USA). Purity of the MWNT is more than 80%, and most of impurities are amorphous carbon. The MWNT was purified to remove metal catalysts by using 50% HNO₃ solution. The novolak type of phenol resin was dissolved in ethanol. The MWNTs were put in the ethanol solution. After evaporating ethanol, the phenol resin film on the MWNT was decomposed at about 200 °C in air. The coated MWNTs were put in a graphite die and set in the spark plasma system (SPS) (Sumitomo Coal Mining Co. Ltd., SPS-1050). The consolidation was carried out between 1000 °C and 1600 °C at 120 MPa in a vacuum. In case of the consolidation at 1000 °C, the consolidation temperature was raised as follows: heating rate from 0 °C to 900 °C at 100 °C/min, from 900 °C to 980 °C at 20 °C/min, from 980 °C

to 1000 °C at 5 °C/min and holding time at 1000 °C for 5 min.

The microstructure of the consolidated MWNT was analyzed by a transmission electron microscope (JEOL, JT-007). The polished surface of the consolidated MWNT was observed with an optical microscope (Nikon, N-01). X-ray diffraction (XRD) was carried out on the MWNT and the consolidated one using Cu K α line by an X-ray diffractometer (Rigaku, Rotaflex, RU-200B). Density of the consolidated disk was determined based on Archimedes' principle using water. Elastic modulus of disk samples (3 mm in thickness and 20 mm in diameter) was measured by a pulse-echo overlap ultrasonic technique, using an ultrasonic detector (Hitachi Kenki Co. Ltd., ATS-100) and a storage oscilloscope (Iwasaki Tsushinki Co. Ltd., DS6411).

3 Results and Discussion

The TEM image of the MWNT is shown in Fig. 1. The major part of tube diameters was 20–40 nm, and the biggest one rarely observed in the TEM photograph was about 200 nm. Amorphous carbon was identified by TEM and estimated less than 20 %.

The MWNTs consisting of amorphous carbon were not consolidated by SPS, which was not activated by SPS and did not play a role to combine each MWNT. The phenol

resin was added to achieve the consolidation, and its carbon residue was of about 20%. The optical micrograph revealed that the MWNT consolidated with the 23% phenol resin contained coarse pores, as shown in Fig. 2. Much of the phenol resin promoted to get rid of the pores, and coarse pore was not produced in the MWNT consolidated with 33% phenol resin. Fig. 3 shows that there was no coarse pore on the polished surface of the consolidated MWNT. Block patterns were observed in these photographs and indicated a structural regularity. The MWNTs were very roughly aligned in the block, and direction of the alignment was different in each one. The reason why the MWNT was ordered by SPS was not clear, but the ordered alignment might be due to the weak interaction between MWNTs, SWNT forming the bundle structure by strong interaction.

TEM image of the MWNT consolidated at 1400 °C is shown in Fig. 4. The MWNTs were aligned in the plane perpendicular to the pressing direction of SPS. The same alignment was observed for the MWNT consolidated at 1000 °C and 1200 °C. The alignment was not random in

Fig.1 TEM image of MWNT.

Fig.2 Optical micrograph of the MWNT consolidated with 23 wt% of phenol resin at 1000 °C at 120 MPa for 5 min.

Fig.3 Optical micrograph of the MWNT consolidated with 33 wt% of phenol resin consolidated at 1200 °C at 120 MPa for 5 min.

Fig.4 TEM image of the MWNT consolidated at 1400°C at 120 MPa for 5 min.

Fig.5 TEM image of the MWNT consolidated at 1600°C at 120 MPa for 5 min.

this plane, and some regularity was found in it. The MWNTs tended to be in line each other in the small area. When the regularity expanded to the large area, the block pattern may be formed. The diameter of the consolidated MWNT was more than 100 nm and larger than that of the starting MWNT. This growth did not occur during the consolidation but was caused during the ion thinning process for TEM, where argon plasma being used. The structure of the MWNT was partially decomposed at 1600°C by SPS, and graphite-like materials were formed, as shown in Fig. 5. However, the tube structure persisted in this consolidated MWNT.

Fig. 6 shows X-ray diffraction patterns of the MWNT consolidated with the phenol resin of 33% at 1000°C–1600°C at 120 MPa. The diffraction pattern of the MWNT was measured at the same time. Diffraction angle and intensity of graphite were pointed by open circle in Fig. 6. The diffraction pattern of MWNT was different from that of graphite, as shown in Fig. 6a. Several diffraction peaks not assigned to graphite were at about $2\theta = 38^\circ$ and between $2\theta = 42^\circ$ and $2\theta = 47^\circ$, and all of them was based on the tube structure. The diffraction pattern of the MWNT consolidated at 1000°C, which is shown in Fig. 6b, was

Fig.6 X-ray diffraction pattern of MWNT and the consolidated one.

slightly different from that of the MWNT. The difference was that a small peak appeared near $2\theta = 36^\circ$, and it was not found in the diffraction pattern of graphite. When the consolidation temperature was raised higher than 1200°C,

the (101) peak of graphite was strong compared with others. X-ray diffraction patterns of the MWNT consolidated at 1200 °C, 1400 °C and 1600 °C are shown in Figs. 6c, 6d and 6e, respectively. The X-ray diffraction was measured on the plane perpendicular to the pressing direction, and the MWNTs were parallel aligned in it. It was revealed that the tube of the MWNT was made of rolled-up sheets of the (101) plane. The (101) peak was not clear on the MWNTs which were not consolidated. On the other hand, the MWNTs were closely connected in the dense MWNT, and X-ray diffracted through the several MWNTs. The difference from graphite was emphasized on the diffraction pattern of the MWNT consolidated at 1400 °C, as shown in Fig. 6e. New diffraction peaks, which were not assigned to graphite, appeared between $2\theta = 30^\circ$ and $2\theta = 42^\circ$. It is obvious that decomposition of the MWNT started at 1400 °C. The intensity of new peaks became strong for the MWNT consolidated at 1600 °C, and the decomposition progressed further. The MWNT was converted into different compounds from graphite. MWNT is not decomposed until 2400 °C by heating¹²⁾. The SPS process consists of some effects such as the spark plasma, electric field and others, and carbon fibers are sectioned into powders by the SPS treatment⁹⁾. Graphen layer of the MWNT was decomposed by the spark plasma and resulted in structures different from graphite.

The bulk density and mechanical properties are shown in Table 1. The low bulk density of the MWNT consolidated at 1000 °C indicated that the consolidation was not accomplished. The bulk density of 1.74 g/cm³ was not high and depended on the tube structure because there was no coarse pore. The apparent porosity was almost the same for all consolidated MWNT. The closed porosity was calculated from the apparent porosity and theoretical density of graphite (2.266 g/cm³). Since the theoretical density of the MWNT must be lower than that of graphite, the closed porosity should decrease less than the values indicated in Table 1. Young's modulus and Poisson's ratio were measured on the surface where the MWNT was aligned parallel to the pressing direction of SPS. Young's modulus

of the MWNT consolidated at 1000 °C was less than that of the ones consolidated 1200 °C and 1400 °C. The Young's modulus of 11.1 GPa of the consolidated MWNT was not little, considering 16 GPa of a commercial graphite product with high density of 2.0 g/cm³. Poisson's ratio was negative for the MWNT consolidated at 1000 °C, and was very little for the one consolidated at 1200 °C and 1400 °C. The negative Poisson's ratio explained that the bond between the MWNTs was not completed at 1000 °C, which is consistent with the Young's modulus of 3.05 GPa. The little Poisson's ratio was explainable that the MWNTs were not tightly connected each other by the amorphous carbon, which being converted from the phenol resin and did not result in strong graphite at 1000 °C–1600 °C.

Bending strength of the consolidated MWNT was measured by a three-point bending test method but was not obtained. The sample for the bending test was curved by stress at first, and then it was fractured. This behavior was a kind of quasiplastic deformation. The consolidated MWNT behaved in the same way as plastic deformation of metal.

SEM image of the fractured surface of the MWNT consolidated at 1000 °C is shown in Fig. 7. Most diameter of the MWNTs was not larger than 20–40 nm, and the growth of them did not occur during the SPS consolidation. The majority of the MWNTs were pulled out, and it was hard to find cross sections of the MWNTs which were

Table 1 Bulk density and properties of the MWNT consolidated at 120 MPa for 5 min.

Consolidation temperature (°C)	Bulk density (g/cm ³)	Apparent porosity (%)	Closed porosity (%)	Young's modulus (GPa)	Poisson's ratio
1000	1.67	16.7	9.6	3.05	-0.62
1200	1.74	16.8	6.4	11.1	0.074
1400	1.73	15.6	8.1	10.1	0.034

Fig.7 SEM image of the MWNT consolidated at 1000 °C at 120 MPa for 5 min.

Fig.8 SEM image of the MWNT consolidated at 1200 °C at 120 MPa for 5 min.

ruptured during the bending test. The consolidation at 1200 °C resulted in a different fractured pattern. The fractured smooth surface and cross section were observed in Fig. 8. The MWNTs were connected more tightly at 1200 °C than at 1000 °C, and some of them were cut. The similar SEM image was given by the MWNT consolidated at 1400 °C. There were a lot of pulled-out MWNTs in these two fractured surfaces, because the bonding amorphous carbon was weak compared with the MWNT. The pull out phenomenon corresponded to the quasiplastic deformation on the three point bending test.

4 Summary

The MWNT was consolidated with the amorphous carbon converted from the phenol resin by SPS. The consolidated MWNTs were aligned in the plane perpendicular to the press direction of SPS in the consolidated compact. The alignment was not random in the plane, but the MWNTs tended to be in line in small area. The tube was rolled up with the (101) plane of graphite, being conformed by X-ray diffraction pattern of the consolidated MWNT. Bulk density and Young's modulus were more than 1.74 g/cm³ and 11.1 GPa for the MWNT consolidated at 1200 °C at 120 MPa. The fracture behavior on the bending test was a kind of quasiplastic deformation and based on pull out of the MWNTs.

Acknowledgment

This study is supported by Research on Advanced Medical Technology in Health and Labour Sciences Research Grants from Ministry of Health, Labour and Welfare of Japan. The authors are thankful to Yoshihiro Murakami, Shun Ito, Yuichiro Hayasaka and Yoshiyuki Sato for the measurements of X-ray diffraction patterns and observations of transmission electron microscope and optical microscope.

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