Development of New Carbon Nanotube Production Technique "Carbon Transmission Method"

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The authors propose a novel carbon nanotube (CNT) production technique called Carbon Transmission Method (CTM) that uses fibrous catalyst. The supply of carbon source and the growth of CNT can be independently controlled in different atmospheres at each end of a fibrous catalyst. The authors demonstrated that by diffusion of carbon from the one end of a Fe fibrous catalyst in CO gas, the growth of CNT can be observed on the other end of the catalyst in an isolated state in Ar gas. The use of the CTM technique allows the fabrication of high quality CNT that can be used for electric wire and cable applications.

1. Introduction

Various types of wires and cables have been used for electric power transmission and telecommunication applications. **Figure 1** shows the history of the development of conductive materials for power transmission lines and telecommunication lines. In the beginning, copper (Cu) electric wires were used for supplying electricity to electric lights and industrial machineries and for telecommunication purposes, because Cu has excellent properties such as low resistivity, ease of forming into wire and relative cheapness due to its abundance. With the increase of electric power consumption and telecommunication traffic, other conductive materials have been developed. In the information and communication area, the amount of information being transmitted exploded after optical glass fiber has been developed. As the result of the expansion of world-wide information communication networks, wide-scale social change has occurred. In contrast to optical glass fiber, Cu has been used mainly for electric power transmission to this day. In recent years, however, the copper price is going up drastically along with the development of the global economy and the increase in world-wide energy consumption. Moreover, growing awareness of global warming has impelled the society to place more importance on sustainability and eco-friendliness than on convenience and comfort. As an answer to the world-wide demand for innovative energy-saving and eco-friendly technologies, carbon nanotube (CNT) is being proposed.

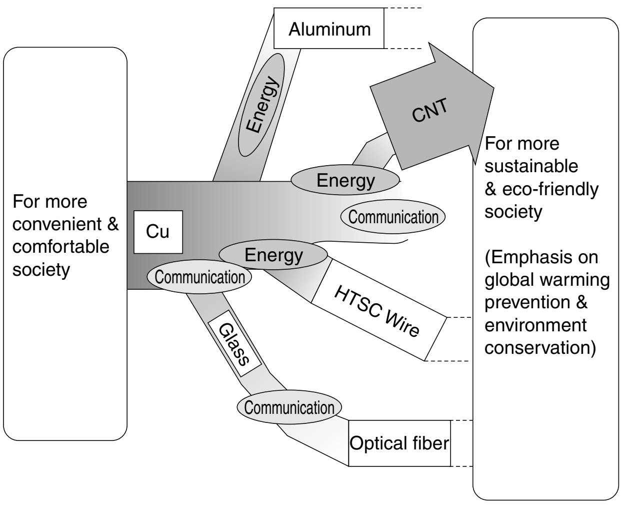

Fig. 1. History of development of conductive materials for electric power line and communication line applications

2. Comparison between Thermal CVD Method and Carbon Transmission Method

Carbon nanotube (CNT) has excellent properties such as lighter weight than aluminum and much higher strength than steel. Because of its one-dimensional conductivity due to the cylindrical graphene structure, CNT exhibits a low resistivity. Much efforts have been made to achieve the continuous growth of high-quality CNTs [(1)-(4)]. For example, it was found that the growth of CNT is enhanced by adding water to carbon source gas in the thermal CVD process [(4)], thereby enabling the growth of CNT approximately 10 mm in length. However, CNT has so far reached only the initial stage of practical application as electric wires. This is because, for practical use, electric wires are usually required to have meters or kilo-

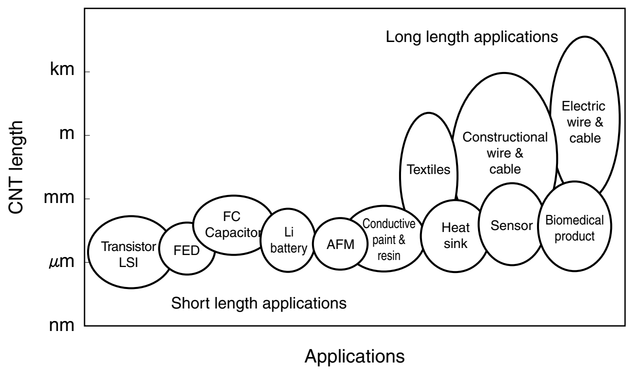

Fig. 2. Required CNT lengths for various applications

meters lengths, as shown in **Fig. 2**. **Figure 3** shows the growth mechanism of CNT in the thermal CVD process. The growth rate of CNT slows down with reaction time and eventually stops in the thermal CVD process [(5)], because unnecessary inhibitory carbon covers the nano-sized catalyst particles as the result of the decomposition of carbon source gas. It is difficult to maintain the continuous growth of CNT in the CNT growth process that uses particle catalyst. In the thermal CVD process, removing unnecessary inhibitory carbon by adding water to nano-particle catalyst leads to the destruction of CNT. To solve this problem, breakthrough techniques that do not use nano-particle catalyst must be created. The author proposes a novel CNT growth technique named Carbon Transmission Method (CTM) that separates the two functions of catalyst, which are supplying carbon source gas and growing CNT [(6)]. The structure of the catalyst for the CTM process is composed of a fibrous catalyst and a non-catalytic separator foil, as shown in **Fig. 4**. The carbon source supply function and the CNT growth function of the catalyst can be separately controlled in different atmospheres at each end of the fibrous catalyst. The mechanism of CNT growth by the CTM process is as follows. The carbon source gas is provided without the formation of inhibiting carbon layers on the end of the Fe fibers. The dissolved carbon diffused from one end of the Fe fibers to the other end through the Ag foil separator. The CNTs grow continuously on the ends of Fe fibers that reside in an inactive gas such as Ar. It is known that the diffusivity of carbon in immediate vicinity area along Fe grain boundary is about 10^3 to 10^4 times higher than in bulk Fe [(7), (8)]. Therefore, faster CNT growth rate can be achieved when source carbon is provided quickly by fast diffusion along the sub-μm diameter fibrous catalyst.

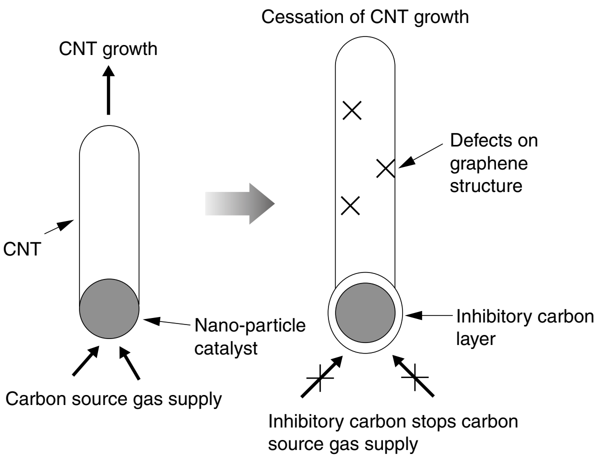

Fig. 3. Mechanism of growth and cessation of growth of CNT in thermal CVD process

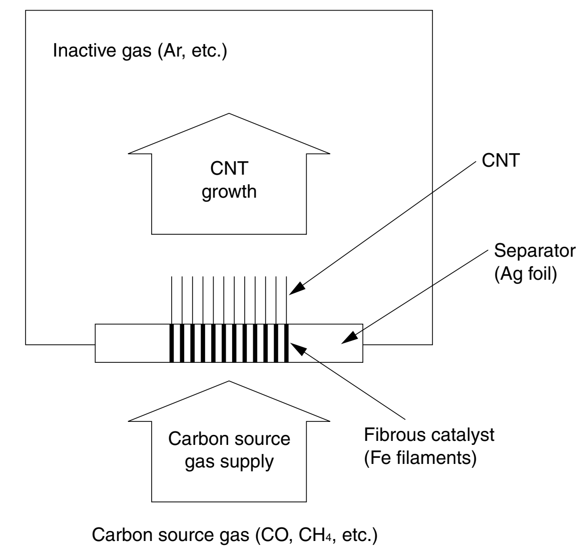

Fig. 4. Conceptual diagram of CNT growth by CTM process

3. Experimental Result and Discussion

Figure 5 shows the fabrication process of the catalyst for the CTM process. Fe was chosen as the fibrous catalyst and Ag was chosen as the separator. Pure Fe and Ag donot make alloy and can be easily deformed into fine wires. The CTM catalysts were fabricated by deforming the composite wire composed of Ag matrix and fine Fe fibers. High-purity Ag pipes (over 99.99 wt%) and high-purity Fe wires (99.998 wt%, RRR_H up to 2000) were prepared, and the composite wire was fabricated by performing the conventional techniques of metal wire drawing and stacking repeatedly in a similar way as the superconducting wires fabrication process [(9), (10)]. The fabricated composite wire made of Fe filaments and Ag matrix that has a diameter of 10 mm was cut into thin slices and polished until each slice becomes a foil-like specimen of about 50 μm in thickness. The both ends of Fe filaments were exposed over the surface Ag by chemical etching using a mixed aqueous solution of ammonia and hydrogen peroxide. The deformed Fe fibers were in various shapes, as shown in **Fig. 5**. One side of the catalyst foil specimens was sealed by Ag gaskets, and Ag holders were tightened by stainless bolts, as shown in **Fig. 6**. Ar gas was filled into the space in the Ag gasket between the two catalyst foil specimens. CO was applied as the carbon source gas to the outside of the Ar-gas filled catalyst foil specimens at 850˚C for 1 hour.

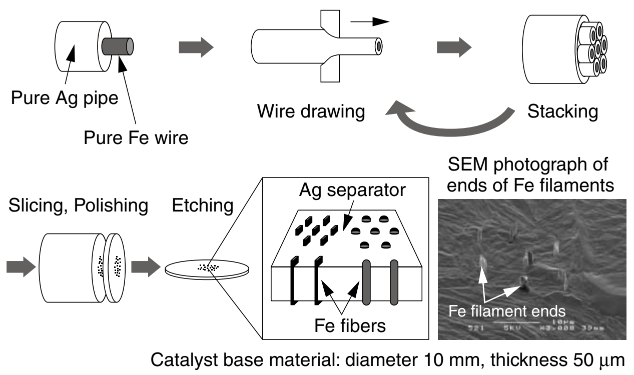

Fig. 5. Fabrication process of CTM catalyst

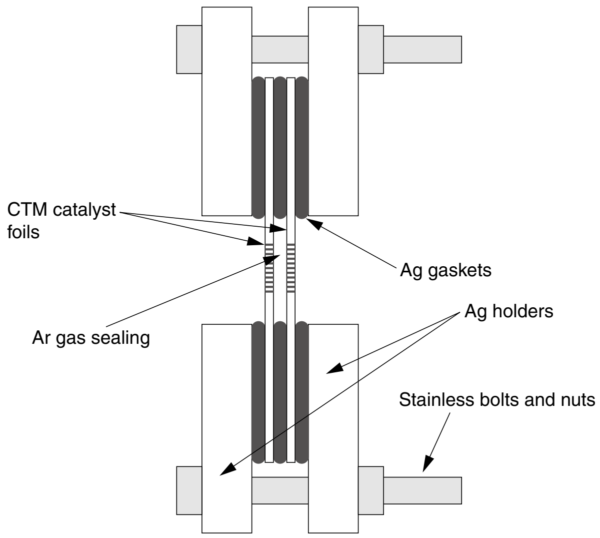

Fig. 6. Structure of specimen holder for CTM catalyst

After heat treatment, the lumps of carbon were observed on the carbon source gas supply side in CO gas as shown in **Fig. 7(a)**. The Fe spectrum was detected in the carbon lumps by EDX spectroscopy. The carbon filaments were observed on the side filled with Ar gas, as shown in **Fig. 7(b)**. No Fe spectrum was detected at the carbon filaments by EDX spectroscopy. These data indicate that the carbon filaments have grown on the end of Fe fibers. **Figure 8** shows a TEM photograph of a CNT grown on the end of a Fe fiber at the carbon transmission side in an Ar gas atmosphere. This CNT had a hollow structure and was grown at an end of the fibrous catalyst. **Figure 9** shows a TEM photograph of tape-like CNTs. These results indicate that CNTs can be grown by transmitting carbon through Fe nano-fibers.

For continuous growth of CNT, carbon source gas must be provided continuously without depositing unnecessary inhibitory carbon on the carbon source gas supply side of the CTM catalyst. The conditions under which inhibitory carbon does not deposit on the carbon source gas supply side were investigated using pure Fe foils. The phenomenon of carbon deposition by carbon transmission was observed in the experiments with pure Fe foils. The heat treatment was performed through pure Fe foils (99.998 wt %) having thicknesses between 20 and 50 μm. In order to maintain sealing properties, Ag-coated stainless gaskets and tightly-bolted stainless holders were used.

CO and Ar gases were provided, respectively, as the carbon source supply gas and the inactive gas for each side of a Fe foil. After 1-hour heat treatment at 850˚C, carbon was observed on both sides of the Fe foil. Bulk carbon films of several-μm thickness covered with fine carbon filaments and particles were observed on the Fe

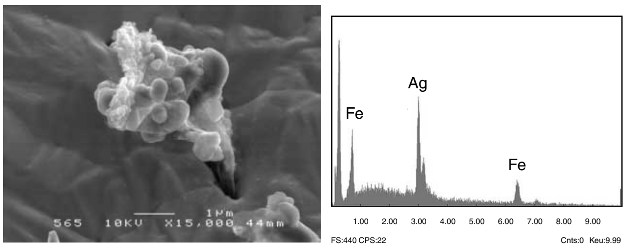

Fig. 7. (a) SEM image and EDX analysis of carbon substance

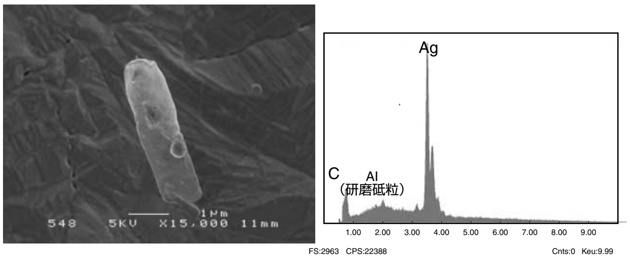

Fig. 7. (b) SEM image and EDX analysis of carbon nano-filament

Fig. 8. TEM photograph of CNT generated at end of Fe filament at carbon transmission side

Fig. 9. TEM photograph of CNTs generated at carbon transmission side

surface in the CO gas supply side. On the Fe surface of the CO gas supply side, fine carbon substances were formed by the decomposition and synthesis of CO gas on the Fe surface. On the other side in Ar gas, only bulk carbon films of several μm thicknesses were observed. It was found out that the bulk carbon films on the carbon transmission side of the Fe foil were graphite without defects, which are indicated as D-band peaks at the Raman spectrum. It is assumed that no defects were observed because these graphite films were grown from the inside of Fe in Ar gas.

Next, 1-hour heat treatment at 850°C was carried out in the methane (CH_4) gas flow supplied as carbon source gas. Deposited carbon was hardly observed at all on the CH4 gas supply side of the Fe foil. On the other hand, a lot of deposited graphite films were observed all over the surface at the carbon transmission side of the Fe foil in Ar gas. These results indicate that carbon transmission was carried out as the continuous supply of carbon source without depositing inhibitory carbon on the carbon source gas supply side.

4. Conclusions

The author proposes a novel CNT growth technique named CTM in order to realize CNT wires and cables. In the CTM process, different atmospheres were separately controlled at each end of a fibrous catalyst. The CNT growth demonstration was carried out on an end of the Fe filament catalyst in Ar gas by transmitting carbon along the catalyst from the other end in CO gas. The CTM process will enable the continuous growth of CNT without defects by controlling continuous carbon source gas supply so as to prevent inhibitory carbon from being deposited on the catalyst. The author believes that the CTM method has opened the door to the new generation of CNT growth techniques.

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