Novel Bridged Carbon Nanofibers Grown by Cleaving Carburized Iron Substrates

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We developed a novel growth method for carbon nanofibers (CNFs), such as carbon nanotubes (CNTs), and multi-layered graphene sheets, where the metal nanoparticle catalyst and template substrates were not used for growth of the CNFs. The CNFs were grown with the bridge formation between the cleaved crack walls through the carburizing heat treatment of the high purity iron oxide foils in an acetylene gas flow. We indicate a possibility that the bridging growth CNFs (BG-CNFs) are formed by division of an unknown novel iron phase including a large amount of carbon as a solid solution. We introduce the new fabrication process of BG-CNFs and possibility for the practical use.

Keywords: carbon nanotube, graphene, iron, carburize, bridge, carbon nanofiber, oxide

1. Introduction

Carbon nanotubes (CNTs) and graphene are expected as industrial materials for future electric wires and devices. They have excellent properties, with lighter weight, higher strength and high conductivity, compared with conventional metals\(^1\)-(\(^7\)). For practical applications, the primary properties of these carbon nanomaterials should be reflected in the scale of each application, and we have studied and developed CNT growth methods for electric wire applications\(^8\), \(^9\). In this report, we introduce the novel growth method of CNFs, and show possibilities for applications.

2. Problems of the Present Growth Method for CNTs and Graphene Sheets

CNTs are generally grown on a metal nanoparticle catalyst by providing a carbon source gas as shown in Fig. 1\(^{11\text{--}15}\). The nanoparticles have a diameter of a few nm, and CNTs are grown in harmony with the diameters of the nanoparticles. It is difficult to keep stable conditions on the tiny metal nanoparticles for the carbon source supply and the growth of CNTs. Thus, novel control methods for a more stable growth of CNTs are desired.

Recently, graphene has been researched actively for such as transparent conductive films and electronic devices\(^6\), \(^17\). Figure 2 shows the multi-layered graphene sheet on a template substrate, such as copper or silicon. The graphene sheets have defects and kinks by mismatching between the graphene sheet and the template substrate. Therefore, the mismatching problems need to be solved.

3. Bridge Grown Method

In this report, we introduce a novel growth method of CNTs and multi-graphene sheets without using the metal nanoparticles and template substrates\(^10\).

The bridge grown method has novel features that the bridging growth CNFs (BG-CNFs) are grown in the cracks of the cleaved substrates as shown in Fig. 3.
4. Experimental and Results

High-purity electrolytic iron foils (purity of 4-5N), were used as the starting material with a thickness of 50–80 µm. The iron sample was placed at the center bottom of a quartz glass tube in an electric tubular furnace. Heat treatment was performed at two steps: oxidation and carburization (including reduction). First, the iron foil was oxidized by heat treatment for 1 min. at 850˚C in air. Oxidation doubled the thickness of the iron foil from 50 µm to about 100 µm. We analyzed the oxidized iron samples by X-ray diffraction (XRD) and identified them as iron oxide composed of hematite (Fe₂O₃) and magnetite (Fe₃O₄).

Next, we heated the iron oxide samples to 850 ˚C at a rate of 10 ˚C/ min and maintained this temperature for 10 min. under nitrogen (N₂) gas with a flow rate of 700 mL/ min. The gas flow was changed to a mixture of 5% acetylene (C₂H₂) in N₂ with a flow rate of 740 mL/ min. Samples were heat treated at 850˚C under the acetylene gas flow. A N₂ gas flow was then used to decrease the temperature in the furnace.

Samples were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), XRD and Raman spectroscopy. Samples for TEM were prepared by dividing the sample at a crack with BG-CNFS by bonding it to a TEM grid and then removing part of the heat-treated sample. Raman spectra were acquired using a laser excitation of 532 nm with an incident power of 0.4 mW and spot size of 1 µm.

Photo 1 shows an SEM photograph of the surface of a carburized sample with BG-CNFS in the cracks. Almost all the BG-CNFSs were formed linearly to the bridged direction between the cleaved cracks as shown in Photo 2. The ends of the BG-CNFSs were connected completely to the walls in the cracks.

We observed the structure of the BG-CNFSs by TEM, and confirmed that the BG-CNFSs were composed of carbon through energy dispersive X-ray spectroscopy (EDX) and electron diffraction (ED) analysis. TEM images revealed that the BG-CNFSs had two shapes, tubular, bridging growth carbon nanotubes (BG-CNTs), and sheets, bridging growth carbon nanosheets (BG-CNSs).

Photo 3 shows a BG-CNF with a root connected to a cracked wall and the opposite side was free and a broken end. The broken end indicates the tubular shape as shown in Fig. 4. The ED pattern obtained around the top end indicates that the BG-CNT is composed of multi-layered graphene layers as shown in Fig. 4 (2).
**Photo 4** shows a BG-CNS with flat and scrolled structures. The top end was cleaved with a horizontal straight line, as shown in **Fig. 5**. The ED analysis on the flat area of the top end of the BG-CNS indicated it was composed of multi-layered graphene.

We analyzed the structure of the BG-CNFs by Raman spectroscopy, as shown in **Fig. 6**. In the Raman spectra of BG-CNFs in the cracks, the G- and D-bands that are related to graphite structure and defects, respectively, can be used to evaluate crystal phase and defect concentration. This data indicates that BG-CNFs are composed of crystal of multi-layered graphene structure, rather than amorphous carbon.

Tension experiments for the carburizing samples in the heat treatment furnace were performed by Professor Jun-ichi Fujita’s group of Tsukuba University. They demonstrated that the BG-CNFs were formed on the cleaved surface of the sample by tension deformation in carburizing heat treatment with acetylene gas flow.

### 5. Growth Mechanism of BG-CNFs

We considered the growth mechanism of BG-CNFs. We paid attention to BG-CNFs in a sector shaped crack, as shown in **Photo 5**. BG-CNFs were formed along the opened trajectory into a sector form. It indicates that BG-CNFs were grown with each speed at different places according to the cleaving motion with the sector form.

In the conventional growth process of CNTs, a carbon source gas decomposes and shifts to solid carbon (CNTs) on a metal nanoparticle catalyst. Therefore, the CNTs grow with the speed in accordance with the supplied carbon quantity.
On the other hand, BG-CNFs grow according to the spreading speed at the cleaved crack walls. Therefore, it seems that the growth mechanism of the BG-CNFs is different from the conventional CNT growth on metal nanoparticles.

At the phase diagram of Fe-C, carbon concentration of atomic ratio is less than 25% of Fe3C. Therefore, it is difficult to explain the growth of BG-CNFs by cleaving iron substrates according to the conventional Fe-C phase diagram. Photo 1 shows that the BG-CNFs have grown in the cleaved cracks of the carburized iron substrate. This result suggests the possibility that an unknown special iron phase has appeared by the heat treatment.

We observed the inside structure in the heat treated samples for clarifying the mechanism of the formation of BG-CNFs through heat treatment of iron oxide in acetylene. Figure 7 shows a SEM photograph of the polished cross section of the heat treated sample for 2 minutes at 850°C in a 5% acetylene gas flow. The structure is composed of porous iron, and the precipitated carbon in the pores. Therefore, the carbon is deposited in pores of the iron, as shown in the pattern diagram at the upper right of Fig. 7. On the other hand, Fig. 8 shows a SEM photograph of the polished cross section of the heat treated sample for 10 minutes at 850°C in a 5% acetylene gas flow. The iron is broken into small particles dispersed in the carbon matrix. Therefore, the pattern of iron and carbon is reversed, as shown in comparison of the pattern diagrams in Figs. 7 and 8. It indicates that the iron substrate was broken into small pieces by the precipitation of the inside carbon as the carburizing progressed. Generally, it is known that precipitated material is cementite (Fe3C) from Fe-C alloy, according to the Fe-C phase diagram. Therefore, it is difficult that this carbon precipitation phenomenon is explained by the usual Fe-C phase diagram.

Thus, we paid attention to the iron oxide used as a starting material, and supposed the mechanism as follows. The dense iron oxide (Fe3O4, Fe2O3) is reduced to a porous iron oxide (Fe1-xO) and then the porous iron, includes a large amount of the atom vacancy through the secession of the oxygen by heat treatment in the acetylene gas flow. Next, the atomic vacancy is filled by the penetration of the carbon atom, and then the carbon is precipitated with breakup into smaller pieces of iron, as shown in Fig. 8. Therefore, we consider the possibility of a special iron phase, including much amount of carbon to be associated with the growth of BG-CNFs.

On the other hand, when we used the iron samples with the lower purity of 3N, the carburized samples could not be kept in a sheet form, and broke into fine powder. This experiment demonstrates the use of high purity iron over 4N is essential for the BG-CNF growth by cleaving the iron substrates.

6. Possibility of BG-CNFs for Applications

BG-CNFs have novel features in the growth process and mechanism compared with general CNT and graphene growth methods. CNT growth does not need to use metal nanoparticles involved with handling difficulty. Multi-layered graphene growth does not need the template substrates involved with the surface mismatching problems. BG-CNFs are grown directly by tension in midair between the cleaved separated substrates. Therefore, it can be easily moved to arbitrary places after the growth of BG-CNFs.

For practical use, form control of BG-CNFs is required. However, current growth processes have a difficulty in controlling the cross section of BG-CNFs because the cross section shape of a BG-CNF is configured by the uncontrollable cleaved surface of the carburized iron. We will research the processes to form the controllable cleaved points for BG-CNFs.
7. Conclusion

We have heretofore recognized the CNT growth on a metal nano-particle as a limited phenomenon in nano-scale. However, we discovered BG-CNFs grown by cleaving the carburized iron substrates as a bulky scale phenomenon.

BG-CNFs have been grown by cleaving the carburized iron substrates. We suppose the possibility that the special iron structure including extra-large amounts of carbon has been formed by reducing and carburizing the iron oxide.

The mechanism of these phenomena is not clear related to the growth of BG-CNFs. We will seek to solve the mechanism, which could lead to the development of a novel fabrication process for long CNT and graphene wires.

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References

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