Synthesis of diamond from carbon nanotubes under high pressure and high temperature

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The investigation on elemental carbon has long been of considerable interest because of its great importance in both science and technology. One of the most outstanding achievements which occurred in carbon science was the synthesis of diamond under high-pressure–high-temperature (HPHT) conditions [1,2]. Now, man-made diamond is commercially available and plays an indispensable role in modern industry for abrasives, tool coatings, microelectronics, optics and other applications. Another important advance in carbon science was the discovery of fullerenes and carbon nanotubes [3,4]. These novel carbon phases have gained high visibility because they have the potential to exhibit unique structural variety and extraordinary optical, mechanical, and electronic properties [5]. Recently, a number of studies relating to the behaviors of fullerenes under high pressure have been reported which were focused on probing the cage structure stability and looking for new novel structures [6–8]. Moreover, it has been demonstrated that fullerenes can convert to diamond by applying high pressure at either room temperature [9] or high temperature [10]. However, only a few works have been so far focused on the structural stability and phase transformation of carbon nanotubes at high pressure [11,12]. As we know, the transformation of graphite or graphite-like materials to diamond is of great technological importance and therefore remains an exciting field in both experimental and theoretical studies. Therefore, a detailed study of the behaviors of carbon nanotubes at high pressure is very necessary for further understanding their structures and properties and comparing with that of graphite.

In the present work we report the conversion of carbon nanotubes to diamond at 4.5 GPa and 1300°C using a six-anvil high pressure apparatus with the existence of NiMnCo catalyst. The detailed characterization conducted shows that carbon nanotubes transform to quasi-spherical onion-like structures first and then to diamond crystals. It is different from the phase transformation behavior of graphite to diamond under high pressure and high temperature conditions.

For the experiments presented here, multiwalled carbon nanotubes with diameters of 20–50 nm produced by catalytic chemical vapor deposition (CCVD) were used as starting material (Fig. 1). A 6×600 ton six-anvil high pressure apparatus with an electric current heating device was employed for the high pressure experiments. In each experiment, about 50 mg of carbon nanotubes placed between two NiMnCo alloy flakes were put into the high pressure cavity and a cubic body with a cylinder sample chamber of pyrophyllite was used as pressure seal and transmitting medium. Before and after high pressure runs, the samples were monitored by transmission electron microscopy (TEM; H8100), scanning electron microscopy (SEM; S-4200) and Raman spectroscopy (T64000). High-resolution transmission electron microscopy (HRTEM) investigations were carried out using a JEOL2010 microscope operating at 200 kV.

Fig. 1 shows the representative morphology of carbon nanotubes in the starting material. The carbon nanotubes exhibit typical concentric graphitic shell structure with a hollow core. The diameters of most carbon nanotubes in our sample are around 30–40 nm uniformly. No other forms of carbon can be detected in the sample by TEM study.

Before annealing carbon nanotubes under high pressure, we pressed the carbon nanotubes up to a hydrostatic pressure of 6 GPa for 4 h at room temperature. After removal from the high pressure cell, some of the samples were dispersed in alcohol, placed on a holey carbon
microgrid and then observed directly with TEM. No structural changes were found and all the nanotubes kept their hollow one-dimensional cylinders as the original. According to previous reports, after the graphitization at 2800°C under ambient pressure as well as argon protection or high vacuum, the structural characteristics of carbon nanotubes may be not only kept but also improved [13]. Monthioux also predicted that the structure of nanotubes may not be lost under 3000°C [14]. All of these prove that carbon nanotubes are stable under a pressure below 6.0 GPa or a temperature below 2800°C, respectively.

When the samples were annealed at 1300°C for 12 min under 4.5 GPa, we found some diamond crystals grown on the NiMnCo flake. Fig. 2 shows a characteristic SEM image of the diamond crystals which are 0.1–0.5 mm in size and with the shapes of cubes, cubo-octahedra or octahedra. Energy-dispersive X-ray analysis (EDX) with these crystals showed the carbon K\textsubscript{α} line as the only relevant peak in the spectrum, indicating that these crystals are made of pure carbon.

Raman spectroscopy was used to further characterize these carbon crystals. We used a Jobin-Yvon T64000 micro-Raman system with the 514.5 nm line of an argon-ion laser for excitation at an output power of 200 mW. The measurement was performed at room temperature. The Raman spectrum, shown in Fig. 3, revealed the characteristic peak centered at 1332 cm\textsuperscript{-1}, which corresponds to cubic diamond. This analysis further demonstrates that these crystals are diamond rather than other carbon structures.

In order to investigate the growth mechanism of diamond from carbon nanotubes and compare with that of graphite, carbon nanotubes and graphite flakes were placed at the symmetric position of temperature and pressure between two NiMnCo catalyst flakes in the high pressure cell, and were subjected to high pressure and high temperature treatments. At 4.5 GPa and 1300°C, no conversion of graphite to diamond was observed. This suggests that the formation of diamond is favored if carbon nanotubes are used as starting material and there must be some differences in the process of transformation to diamond between graphite and carbon nanotubes.

For further study, small pieces taken off from the produced carbon nanotubes treated at 1300°C and 4.5 GPa were crushed into small chips and characterized by high-resolution transmission electron microscopy. Fig. 4a shows a characteristic TEM image of the products. It can be seen that the hollow long cylindrical structures of the carbon nanotubes disappear. Instead, some quasi-spherical carbon particles can be observed to form. High-resolution TEM image of the quasi-spherical carbon particle (Fig. 4b) indicates the formation of an onion-like graphitic structure which is composed of concentrically nested graphitic
closure of the graphene planes. The high curvature of the nested graphitic shells and cross-links between the layers in the onion-like structures formed lead to an increased fraction of sp³ bonds, which facilitates the formation of diamond.

Synthesis of sp³-bonded cubic diamond of high quality at high pressures and high temperatures with transition metal catalysts from sp²-bonded graphite-like carbon precursors is of great technical importance and considerable commercial interest. However, the mechanism by which transition metals catalyze the transformation from graphitic materials to diamond (and vice versa) is still obscure [21]. Diamond synthesis is sensitive to the nature of the starting carbon materials. In our experiments, no conversion to diamond was observed from graphite in the presence of NiMnCo catalyst or carbon nanotubes in the absence of NiMnCo catalyst at 4.5 GPa and 1300°C. Therefore, NiMnCo catalyst plays the key role for the transformation of carbon nanotubes to diamond. High-resolution transmission electron microscopy studies demonstrated that carbon nanotubes transformed into quasi-spherical onion-like particles first under high pressure and high temperature. We think that the diamond crystals could be nucleated from these onion-like particles with the aid of NiMnCo catalyst. In this process, the atoms of the metal catalyst diffuse into the onion-like graphitic particles, promote the deformation of graphene layers of the quasi-spherical shells, which are then converted into diamond layers. The increased fraction of sp³ bonds induced by the high curvature of the graphitic layers and cross-links between the graphitic shells might make the diamond formation favored from the quasi-spherical graphitic structures. Detailed studies of the transformation mechanism of nanotube-onion and onion-diamond are in progress.

In summary, we have synthesized diamond using carbon nanotubes as starting material at 4.5 GPa and 1300°C with the existence of NiMnCo catalyst. Under the same condition, no diamond crystals were obtained when graphite was used as the carbon source. The lower pressure and temperature in the current work suggests that carbon nanotubes can be used as another carbon source for the synthesis of high-quality diamond. It is expected that the pressure and temperature will be further reduced through the optimization of catalyst and technological process, which are of great importance from both basic and applied viewpoints.

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Mesostructure of polymer/carbon black composites observed by conductive probe atomic force microscopy

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The electric conductivity of random composites made of an insulating polymer matrix filled with conductive carbon black particles undergoes an insulator–conductor transition when the carbon black concentration increases. This transition is usually described by the percolation theory which predicts the emergence of an infinite cluster of connected particles [1]. The electrical transport properties of such disordered conductor–insulator composites are closely tied to their mesostructure, i.e. to the distribution of the carbon black aggregates in the matrix at every scale larger than the particle size. A better description of this mesostructure will help us understand the origin of their macroscopic properties, as some of them have important practical applications [2].

Previous experimental access to the microscopic structure was made using neutrons and X-ray diffraction [3] or TEM ImagE ANalysis and reconstruction using mathe-