Carbon nanotubes formation by short-time ball milling and annealing of graphite

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In this study, carbon nanotubes were synthesized by mechano-thermal process from elemental graphite powders. Initially, high ultra-active amorphous carbon was obtained by short time milling process from graphite under inert atmosphere. Then, isothermal annealing of milled graphite powders was conducted at 1600^{o}C for 6 h in Ar gas. From the investigations of Transmission electron microscopy and Scanning electron microscopy, it was revealed that bamboo and cylindrical nanotubes were formed after isothermal annealing. In this study, nanotubes which have the diameters between 50 and 200 nm were produced at a short time ball milling process and a lower annealing temperature of 1600 ^{o}C although bamboo and cylindrical nanotubes are reported to be produced after ball milling of graphite for 150 h and then annealing amorphous graphite at least 1800 ^{o}C.

(Received November 24, 2011; accepted February 20, 2012)

Keywords: Carbon Nanotube, Ball milling

1. Introduction

Carbon nanotubes (CNTs) are crystalline graphitic sheets rolled up into a seamless cylindrical shape. Since carbon nanotubes were discovered by Iijima in 1991, they have attracted wide attention all over the world because of their extraordinary chemical, electronic, thermal and mechanical properties [1]. Their special properties make CNTs potential candidates for many application areas such as field emission devices, scanning probes, nanoscale electronic devices, hydrogen storages, chemical sensors and composite reinforcing materials [1,2]. Many methods have been developed to manufacture CNTs, such as electric arc discharge, laser ablation of a carbon target, and chemical vapor deposition (CVD), as well as electrochemical synthesis and pyrolysis of benzene in the presence of hydrogen [2]. Recently, Manafi et.al [3] and Y. Chen et al. [4] reported that CNTs could be synthesized by annealing of ball milled graphite powder. An understanding of the formation mechanism is crucial in order to control the growth process, and to optimize the production of high quality nanotubes. The common character of the current preparation methods is that CNTs are produced by assembling single carbon atoms to form nanotubes. The changes in the crystallinity of graphite during milling have been examined on several occasions [5,6,7] and the general conclusion is that graphite passes through a nanocrystalline phase prior to amorphization.

X.H. Chen et al. [7] found that the crumpled graphite layers led to various nanostructures, such as bended or curved graphite sheets at various angles after 150 h of ball milling. In addition, it was reported by Y. Chen et al. that milled graphite were turned into thin multi-walled carbon nanotubes (MWNTs) by milling for 150h and then annealing in a temperature range of 1000-1500 °C. No nanotubes were found below 1000 °C because the annealing temperature is too low for the crystallization. In contrast, only thick bamboo tubes and large crystals were formed after heating at 1800 °C [4,7,8].

In this paper, the synthesis of carbon nanotubes are achieved by short time high-energy ball milling and then annealing at 1600 ^{o}C for 6 h. Ball milling and thermal annealing are caused nucleation and growth of nanotubes which have diameters between 50 and 200 nm

2. Experimental

In this study, milling process was performed in dry and wet conditions. The dry and wet ball milling experiments were carried out at the room temperature, and the commercial hexagonal graphite powders which are thermodynamically too stable to be converted to a different structure were used as the starting material (Merck kGAA, 99.5%, <50 μm). A high energy planetary ball mill (Fritsch Pulverisette 7) was used for milling process, and a rotational speed of the vial at 900 RPM which means 78 times the force of gravity (78G) was chosen. Hardened steel vials and balls were used in experiments. The ball milling was carried out with 8 mm balls, and the ball-to-powder weight ratio (BPR) was 8:1. Iron of 4 at.% was added as a catalyst for nucleation of CNTs. Pure graphite powder was dry milled for 1/4, 2, 3,

4, 5 h. The milling process was executed under the 400 kPa high purity (99,996%) argon gas to prevent oxidation during ball milling.

Wet milled graphite powders were also examined in this study. BPR, ball diameter, milling atmosphere were maintained the same as the dry milling parameters, and only 10 ml ethanol (96 vol.%) was added to the graphite powders for decreasing agglomeration during milling. Graphite powder was wet milled for 5h. Then, the milled samples (wet and dry milled) were isothermally annealed separately in an alumina-tube furnace under the Ar gas flow about $5x10^{-2}$ l/min at 1600 ^{o}C for 6 h. The structural changes of the milled samples were investigated by using Rigaku X-ray diffractometer (XRD) with CuKα radiation. Annealed samples were investigated via Carl Zeiss Evo 40 model Scanning Electron Microscopy (SEM), JEOL JEM 2100F model High-Resolution Transmission Electron Microscopy (HR-TEM). Chemical compositions were examined by using Oxford instrument Energy dispersive X-ray (EDX) attached to the TEM.

3. Results and discussion

Although nanotube has not been formed during the ball milling process, the high energy ball milling treatment is an essential step to form the nanotubes during subsequent annealing. Direct heating of the graphite powders without milling treatment does not cause any nanotube structures because graphite is very stable. To provide the different structure formation of graphite (such as nanotube), either high temperature (above 3000 ^{o}C) is required or covalent bonds within the graphite must be deformed by the other methods. The role of ball milling treatment is to create precursor containing nucleation structures and free carbons atoms [4]. In addition, the size of the carbon particles is one of the important factors for the formation of the CNTs [3].

In this paper, ball milling process was chosen as the first step in order to form free carbon atoms and nucleation structure, which have an important role for CNTs formation. The milling process having two different types (wet and dry milling) was applied to the graphite powders. Wet milling process was applied to the graphite powders so that Fe contaminations occurred due to abrasion of balls and vial were decreased during milling process. Wet milling process was performed for 5 h. Ball milled powders were examined by XRD.

The XRD spectra of graphite powders milled (dry and wet) for 5 h were shown in Fig. 1.a. From XRD spectra, the intensity of characteristic (002) peak was decreased, but not fully disappeared after wet milling process. It means that hexagonal graphite structure was remained stable even after 5 h milling and no amorphous phases were produced after wet milling. In the wet milling condition, powders and balls agglomerate and rotate together during milling. Due to the reduction of the impact force of the colliding balls, the milling intensity is reduced. The milling intensity is an important parameter for mechanical milling (MM) and reactive milling (RM). Maurice and Courtney reported in a computational modeling of milling that deformation in one powder particle which is trapped between balls can be expressed as;

$$\alpha(r) = R.v\left(\frac{\rho_B}{H_v}\right)^{1/2} - \frac{r^2}{R} \qquad (1)$$

Where v is the relative impact speed, r is the distance of the powder to contact center, R is the diameter of the ball, ρ_B is the density of the ball, and H_v is the hardness of the powder [9]. It can be denoted for equation (1) that a decrease in the relative impact factor lowers the deformation of the powder particle which results in a reduction of amorphization. Concurrently, it was reported that in case of wet milling with ethanol, the hexagonal graphite structure remained stable and the untransformed structure after MM was similar to the crumpled papers [10]. Thus, bended and/or crumpled graphite layers after milling process do not participate in nanotube formation as a carbon source in case of low energy intensities at the MM.

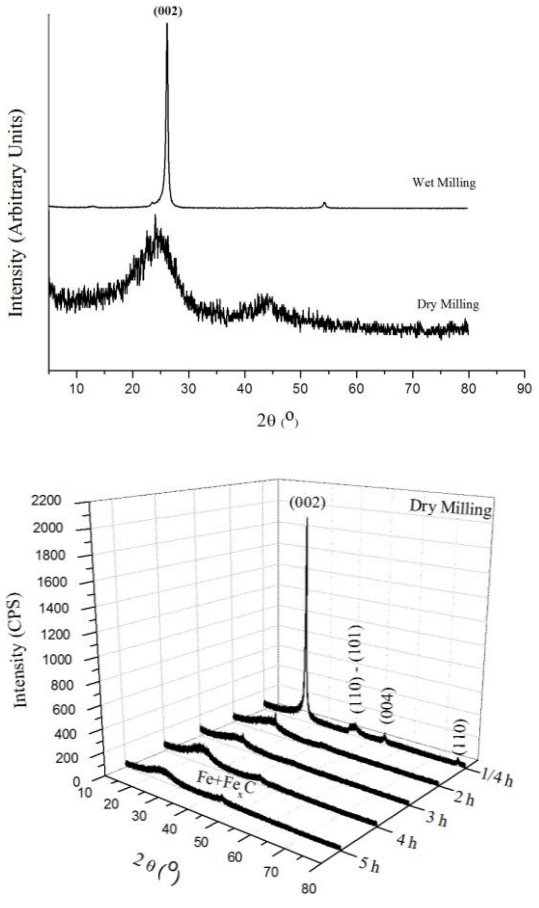

Fig. 1. XRD patterns of a) dry and wet milled powders for 5 h, b) dry milling for 1/4, 2, 3, 4, 5 h.

In the following experiments, graphite powders were milled as dry because structural change and full amorphization was not provided by 5 h wet milling process. Fig. 1.b shows XRD analysis of the dry milled graphite powders. (002) peak intensity was severely reduced by dry milled for 1/4 h. This peak was nearly disappeared after 2 h milling time and the structure was transformed to fully amorphous phase after 3 h milling. In this study, although full amorphization was almost provided milling for 3 h, the ball milling process was carried out 5 h to reduce the particle sizes of the amorphous carbon since the size of the carbon particles is one of the important factors for the formation of the CNTs [3].

Broadening of the (002) peak indicates that the interlayer distance of graphite increased during milling process, and the full amorphization process was completed, as reported by other researchers [5,6,11]. During milling, the severe plastic deformation and fracturing of particles were caused, and particle size continuously reduced. İt was revealed by using Raman spectroscopy [12] that, previous to amorphization of graphite, the grain size was reduced to an ultimate value of about 3 nm by fracturing along the basal plane and subsequent fracturing of the hexagonal network. Thus, the hexagonal phase gradually transforms to a mixture of the amorphous phase and nanosized crystallites via turbostratic structure [10].

In recent reports, as described previously, amorphization of graphite was performed by long milling times as 15, 24 and even 100 hours [13,14,15]. In addition, some reports indicate that graphite powders were milled even for 150 h to form carbon nanotubes by mechano-thermal methods [4,10]. But in this study, we reached the amorphization of hexagonal graphite with the 5 hours milling time. A series of milling experiments were made for the optimization of milling parameters e.g. ball to powder ratio, ball diameter and charging volume of vials for the shortening of the milling time. Amorphization of graphite powders was obtained with optimum milling parameters. The high rotational speed of the milling device was also effective for transforming graphite powders to amorphous nano carbon powders. The reason for this state is thought to be the high energy input to the powders for amorphization at the milling process since centrifugal acceleration was 78G. The higher energy intensities during the milling cause higher amorphization rates because of the high impact force which transforms the structure to the amorphous phase.

Crystallization of the amorphous carbon takes place during the annealing. Newly shaped (002) layers form with different morphologies, including nanotubes, nanocells, nano onions and flat sheets, possibly depending on nature of the nucleation regions [4]. The dry and wet milled powders are exposed to the isothermal annealing at 1600^{o}C for nanotube formation. Fig. 2 shows SEM image of wet milled (5 h) and then annealed (1600 ^{o}C for 6 h) samples. Hexagonal graphite layers exist in structure. Graphite layers were partially broken due to both much reduced plastic deformation and agglomeration of particles during the wet milling process, and these broken layers remain without changing during annealing process. During wet milling process, partial amorphous occur in powders, but this amorphous phase was not crystallized during annealing process. Because, this amorphous phase was not sufficiently activated during the wet milling process and the annealing temperature applied is very low for graphitization of amorphous carbon. That also shows that no further changes even after heat treatment of the wet milled powders were observed to form nanotubes.

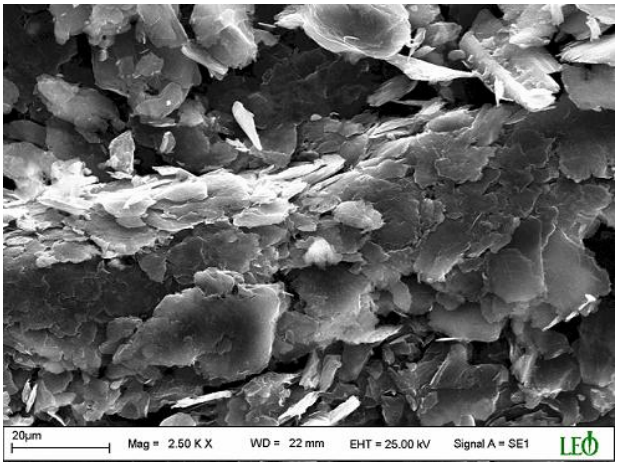

Fig. 2. SEM image of powders wet milled and then annealed at 1600 ^{o}C for 6 h.

Since CNTs were not obtained by wet milling process, graphite powders were milled for 5 h and then milled powders annealed at 1600 ^{o}C for 6 h. Fig. 3 shows SEM images of the dry milled (for 5 h) and then annealed (at 1600 ^{o}C for 6 h) samples. SEM investigations clearly showed that the structure of the annealed sample contains yield carbon nanotubes (Fig. 3a, b). Nanotubes are consisted of both cylindrical and bamboo type nanotubes in Fig. 3a,b. In Fig. 3a, the arrow indicates bamboo type carbon nanotube. Diameters of the nanotubes are between 70 and 200 nm, and lengths of tubes are several micrometers. Chen et al. report that diameter of nanotubes is related to the diameter of the metal particle [8]. So, nanotubes with metal catalyst (in cylindrical or bamboo structures) in this study have relatively large diameters ranging from 70 to 200 nm [8].

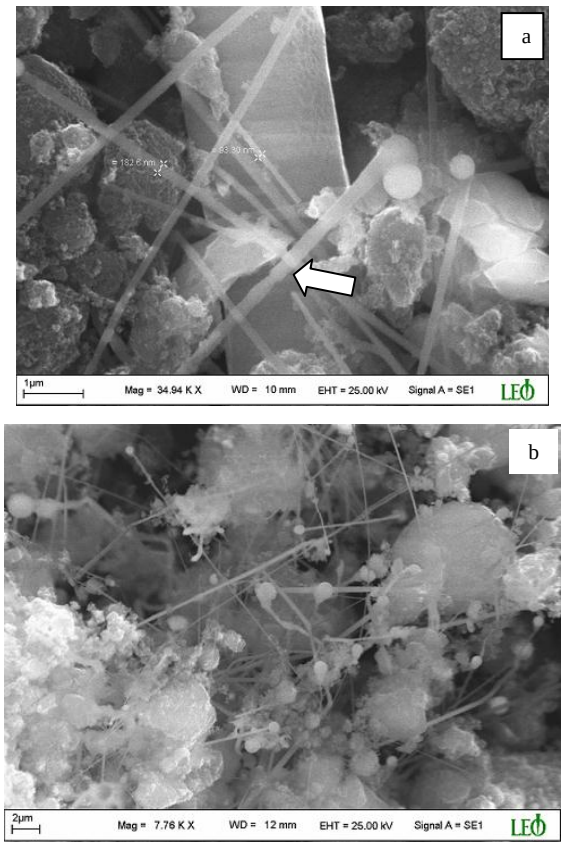

Fig. 3. SEM image of annealed graphite at 1600^{o}C for 6 h. a) Bamboo type CNTs, b) metal based various structures at the end of the CNTs.

The TEM image in Fig. 4a shows a cylindrical nanotube containing an iron particle (indicated by an arrow) at the tip. This carbon nanotube has large hollow core and an outer diameter about 80 nm. This nanotube is multiwall carbon nanotube and it consists of about 30 graphite layers with a hollow centre of 60 nm. TEM image of the MWNT in Fig.4a were shown in Fig.4b for different magnification. The nanotube was made of parallel graphene planes oriented along the tube axis. The interplanar distance between two adjacent graphene planes was about 0,34 nm which is close to that of the [002] interplanar distance in graphite i.e. 0,334 nm. The higher interplanar distance was attributed to the curved shape of their structure [16]. Both inside and outside of thewalls are terminated, leaving the structure defected. It is worth noting that walls on both sides of tube are partially broken, leading to the discontinuity of the graphitic planes (indicated by arrows at Fig. 4b). Besides, the catalyst encapsulated in the CNT is coated with parallel and continuous graphite sheets.

Both SEM and TEM images clearly show that non-recrystallization amorphous carbons were also existed together carbon nanotubes. Each region of powders can't be equally milled due to nature of milling process. So, sufficient activation was not provided in some region while some region of powders were sufficiently activated during milling process. Additionally, in these experiments, the annealing temperature (1600 ^{o}C) is lower than the crystallization temperature of amorphous carbon (i.e. activated carbon 2000 ^{o}C). Therefore, well-crystallization structure of the amorphous carbon is difficult to form if sufficient activation isn't provided during milling process. After annealing, the newly formed structures are composed of partial crystallization carbon and non-crystallization amorphous carbon (Fig. 3a,b and Fig. 4a). Partial crystallization carbon structure includes nanotubes, nanocells, nanoporous particles and these structures were formed by recrystallization of amorphous nano carbon which mechanically activated for sufficient level.

Fig. 4c shows the EDX analysis of catalytic particle encapsulated by carbon atoms at the tip of carbon nanotube (arrow in Fig.4.a). EDX results has shown that the catalytic particle is iron. The source of Fe content is the contaminations during milling process (because of colliding balls and vial) and also Fe is added as catalyst at the beginning of the milling process. Carbon atoms in iron particle are existed because carbon atoms diffuse in iron particle during the milling and annealing process. Copper in EDX analysis is because of grid which used in HR-TEM investigations.

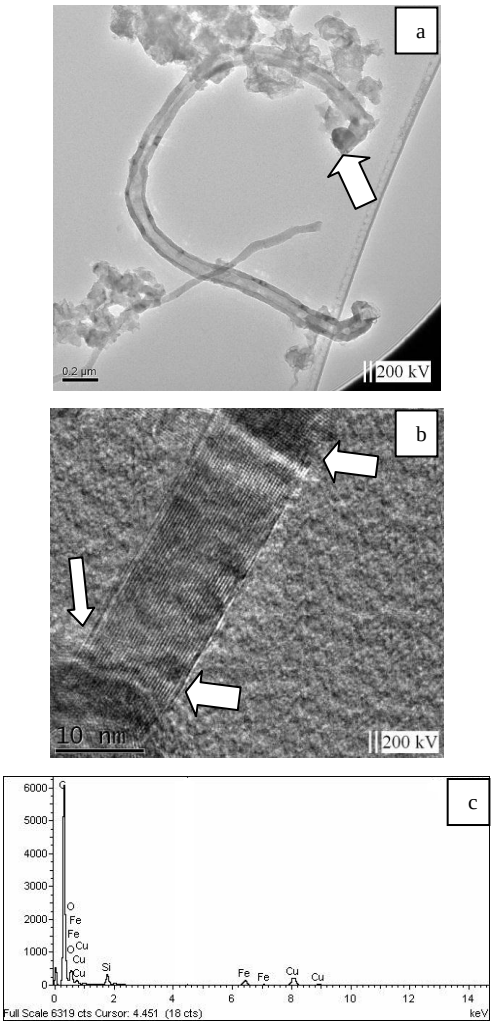

Fig. 4.TEM image of annealed graphite at 1600^{o}C for 6 h. a), b) CNTs, c) EDX of structure at the end of the CNTs.

The EDX results are supported by an opinion of Solid-Liquid-Solid (SLS) mechanism, reported by Chen, in the milling-annealing process [8]. According to the SLS mechanism, milled graphite powder turn into carbon nanotubes during annealing. The annealing temperature is much lower than the melting points of any known carbon materials. No vapor phase of carbon should be produced during the heating. As a consequence, the nanotube growth during the annealing should be a crystallization of the disordered phase, instead of condensation from carbon vapor phase.

Amorphous structures transform to a more stable shape and geometry such as nanotubes when high mobility becomes possible by annealing. The amorphous phase with the nanosized carbon atom clusters are carbon atom source for nanotube growth. Therefore, the ball milled graphite provides nanotube nuclei and is an available source of free carbon atoms, which is the ideal precursor for nanotube growth on a metal catalyst [8]. A schematic illustration of the growth mechanism is given in Fig. 5.

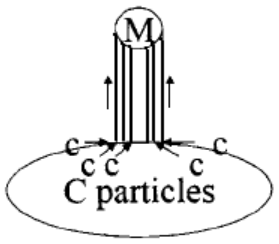

Fig. 5. Schematic illustrations of the growth mechanism proposed for solid-state formation [7].

In Fig. 4.a, dark colored particle (indicated by an arrow) is metal-based particle, and is encapsulated at the end of tube. In addition, it is responsible for the formation of embryo for this special structure. In fact, all iron particles with clean surfaces in the milled sample have been covered by graphitic layers during annealing. There is a strong catalytic effect of metal particles on the growth. The quantity and the diameter of tubes increase with increasing iron content and annealing time, respectively. It was reported that in the case of milling with agate vial, thin nanotubes were found after annealing at 1400 ^{o}C for 6 h in Ar gas. However, the nanotube yield is considerably lower when compared with the sample milled in a steel vial. No thick nanotube was found because of lack of catalyst particles [4]. The results of our study support these explanations about the formation of CNTs.

4. Conclusion

High energy ball milling was applied to the graphite powders for transformation to amorphous carbon so as to form nanotubes growth during subsequent annealing. XRD results showed that the amorphous carbon was observed in dry milling conditions while no structural changes were occurred in wet milled powders. Contrary to the previous literatures, the amorphization of graphite was completed at a shorter milling time for 5 h by means of high energy input about 78G. Moreover, in this study, carbon nanotubes were achieved by a shorter milling time of 5 h and of subsequent annealing even though graphite is milled for 150 h in previous literatures. Contaminants which arise from milling and the added Fe powders at the beginning milling were thought to play a major role for the nucleation of nanotubes. Although bamboo and cylindrical nanotubes are reported to be produced after annealing amorphous graphite at least 1800 ^{o}C, these nanotubes which have the diameters between 50 and 200 nm were observed after annealing about 1600 ^{o}C for 6 h in Argon in our study. Investigations are in progress on the formation of CNTs.

Although carbon nanotubes are successfully synthesized in this study, our studies continue to decrease diameter of the produced carbon nanotubes.

Acknowledgements

The authors would like to acknowledge for the financial support of Scientific and Technological Research Council of Turkey (TÜBİTAK, Project No.107M249).

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