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Effect of milling time on the formation of carbon nanotube by mechano-thermal method

ERTAN EVİN[1], ÖMER GÜLER[1,*], MUSTAFA AKSOY[1] and SEVAL HALE GÜLER[1,2]
[1]Department of Metallurgy and Materials Engineering, Fırat University, Elazığ 23119, Turkey
[2]Department of Metallurgy Engineering, Mersin University, Mersin, Turkey

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Abstract. **Mechano-thermal method was used for synthesizing the carbon nanotubes (CNTs) in this study. In this method, graphite powders in the elemental form were firstly exposed to milling process in high-energy ball milling and then the milled powders were annealed at high temperatures. As a result of milling of the graphite, ultra-active disordered carbon structures were obtained. This structure serves as a carbon source for the formation of nanotubes during the annealing process. This study investigated the effect of the milling process. For this purpose, graphite powders were milled at different periods such as 5 and 150 h and then annealed at 1600°C. The transmission electron microscopy and scanning electron microscopy examinations demonstrated that CNTs formed in samples milled both for 5 and 150 h. However, the difference in the milling time influenced the amount of CNTs, their size and the formation of other structures except from nanotubes.**

Keywords. **Carbon nanotubes; mechano-thermal process; ball milling time.**

1. Introduction

Since the discovery of carbon nanotubes (CNTs) by Iijima,[1] many researchers have devoted to understand their properties and to produce high-quality nanotubes. Many methods have been developed to fabricate CNTs, such as electric arc discharge, laser ablation of a carbon target and chemical vapour deposition (CVD), as well as electrochemical synthesis and pyrolysis of benzene in the presence of hydrogen.[2] Alternatively, Chen *et al*[3] reported that CNTs could be synthesized by annealing of ball-milled graphite powder. Chen *et al* preferred the mechano-thermal method for CNT's synthesis because this method is one of the new potential industrial methods owing to advantages of large-quantity production and low cost. 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[4–6] and the general conclusion is that graphite passes through a nanocrystalline phase prior to amorphization.

In the production of CNTs by the mechano-thermal method, one of the most important parameters is milling process of graphite powders. Quality and quantity of formed nanotubes were affected by milling process. Many researchers investigate the milling of graphite powders and character of milled powders. Although the obtained results contain some similar milling parameters, such as used mill, milling atmosphere, milling time, but there are changes in the properties and characters of obtained structure after milling process.[7–11]

In this paper, the effect of ball milling time on the formation of CNTs by the mechano-thermal process was investigated by using different milling times (short times and long times). After high-energy ball milling process, powders (both short-time milled and long-time milled) were annealed at high temperature in the same conditions. Ball milling and thermal annealing cause nucleation and growth of nanotubes and carbon nano-structures having different forms.

2. Experimental

In this study, ball milling process was performed at different milling times, from short-milling time (5 h) to long-milling time (150 h). The ball milling was carried out at room temperature and commercial hexagonal graphite powders were used as starting material (Merck kGAA, 99.5%, <50 μm) which are thermodynamically too stable to be converted to a different structure. A high-energy planetary ball mill (Fritsch Pulverisette 7 Premium Line) was used for milling process and a rotational speed of the vial at 900 RPM was chosen. Hardened steel vials and balls were used in the experiments. The ball milling was carried out with 8 mm balls and ball-to-powder weight ratio (BPR) 8 : 1. Iron was added as a catalyst at 4 at%. The milling process was executed under the 400 kPa high-purity (99.996%) argon gas to prevent oxidation during ball milling. Graphite powder was milled for 2, 3, 4, 5, 50, 100 and 150 h.

Subsequently, the milled samples were isothermally annealed separately in an alumina-tube furnace under the Ar gas flow of about 5×10^{-2} l min^{-1} at 1600°C for 6 h. The structural changes of the milled samples were investigated

*Author for correspondence (oguler@firat.edu.tr)

using Rigaku X-ray diffractometer (XRD) with CuKα radiation. Annealed samples were investigated via scanning electron microscopy (SEM) (Carl Zeiss Evo 40 instrument) and high-resolution transmission electron microscopy (HR-TEM) (JEOL JEM 2100F instrument). Chemical compositions were examined using energy-dispersive X-ray (EDX) (Oxford Instrument) which was attached to the TEM.

3. Results and discussion

Although the previous studies reported that long milling times such as 150 h are required in synthesizing the CNTs using the mechano-thermal method, our previous study reported that the production of CNTs were successfully synthesized after short milling process such as 5 h.[9] In this study, the changes in the nanotubes formed after the 5- and 150-h milling process and in other carbon structures were determined.

3.1 *Short-milling time results*

Synthesis of CNTs by the mechano-thermal method composed of two basic step. Milling of the graphite powder is first step. Milling process provides the formation of precursor structure.[3,7,8,10] Also, the decrease of the particle size of the powder is provided because of milling process. Second step is annealing process. This process provides CNTs transformation of milled graphite structures. Without milling process, as a result of heating the graphite powders at temperatures such as 1600°C, nanotube formation is not observed in the structure. This is because graphite is very stable and it must either be heated to very high temperatures (above 3000°C) or the strong C–C covalent bonds inside the graphite must be deformed by use of different methods in order to be able to transform into different structures such as nanotube and onion.

Previous studies reported that graphite powder was subjected to 150-h milling process for CNT formation by the mechano-thermal method.[7,8,10] In this study, graphite powders were milled for 2, 3, 4, and 5 h in order to determine the effect of short milling times on the CNT formation. Milled powders were subjected to XRD examination. Figure 1a illustrates the XRD pattern of the graphite powders which were unmilled and were subjected to 5-h milling process. Unmilled graphite powder has a hexagonal structure and consists of a series of stacked parallel layer planes. As also seen from the figure, the XRD patterns of the hexagonal graphite consist of the characteristic (002) peak and other peaks (004, 110). After 5-h milling process, these peaks have completely become lost, i.e., the structure has completely amorphized. Figure 1b illustrates the increasing milling time and structural changes in the graphite. As seen from the figure, after 2-h milling process important degrees of amorphization occurred in the structure, however characteristic (002) peak did not completely disappear. After 3-h milling process, characteristic (002) peak completely disappeared

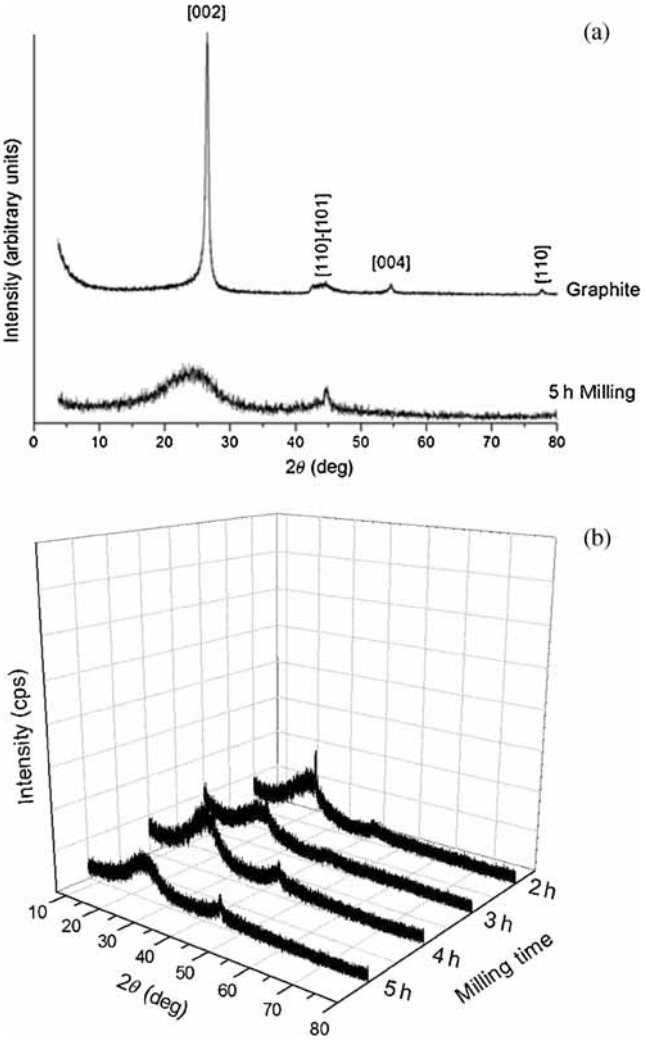

Figure 1. (**a**) XRD spectra of unmilled graphite and 5 h milled graphite and (**b**) XRD spectra of structural change of graphite by increasing milling time .

and a completely amorphous structure was obtained. In the experiments made in this study; although a full amorphization was obtained after 3-h milling process, milling time was prolonged up to 5 h in order to decrease the particle size of the amorphous carbon. After 5 h milling process, formed particles cause positive effect on the nanotube formation. They assist in the graphitization of nano-sized iron amorphous carbon and ensure that the tube maintains its shape during the enlargement of the nanotube.[3,10]

The crystallization of the amorphous carbon occurs during the annealing process performed at high temperature. Recrystallization (002) layers may occur in different morphologies. These structures formed may be in the form of nanotubes, nano-cells, nano-onions, flat layers and the formation of these structures depends on the nature of the nucleation zone.[3] Figure 2 illustrates SEM images of the sample which was milled for 5 h and then subjected to 6-h annealing process at 1600°C. From SEM images, it is seen that CNTs exist in the sample (figure 2a and b). These obtained tubes consist of both cylindrical- and bamboo-type nanotubes. With

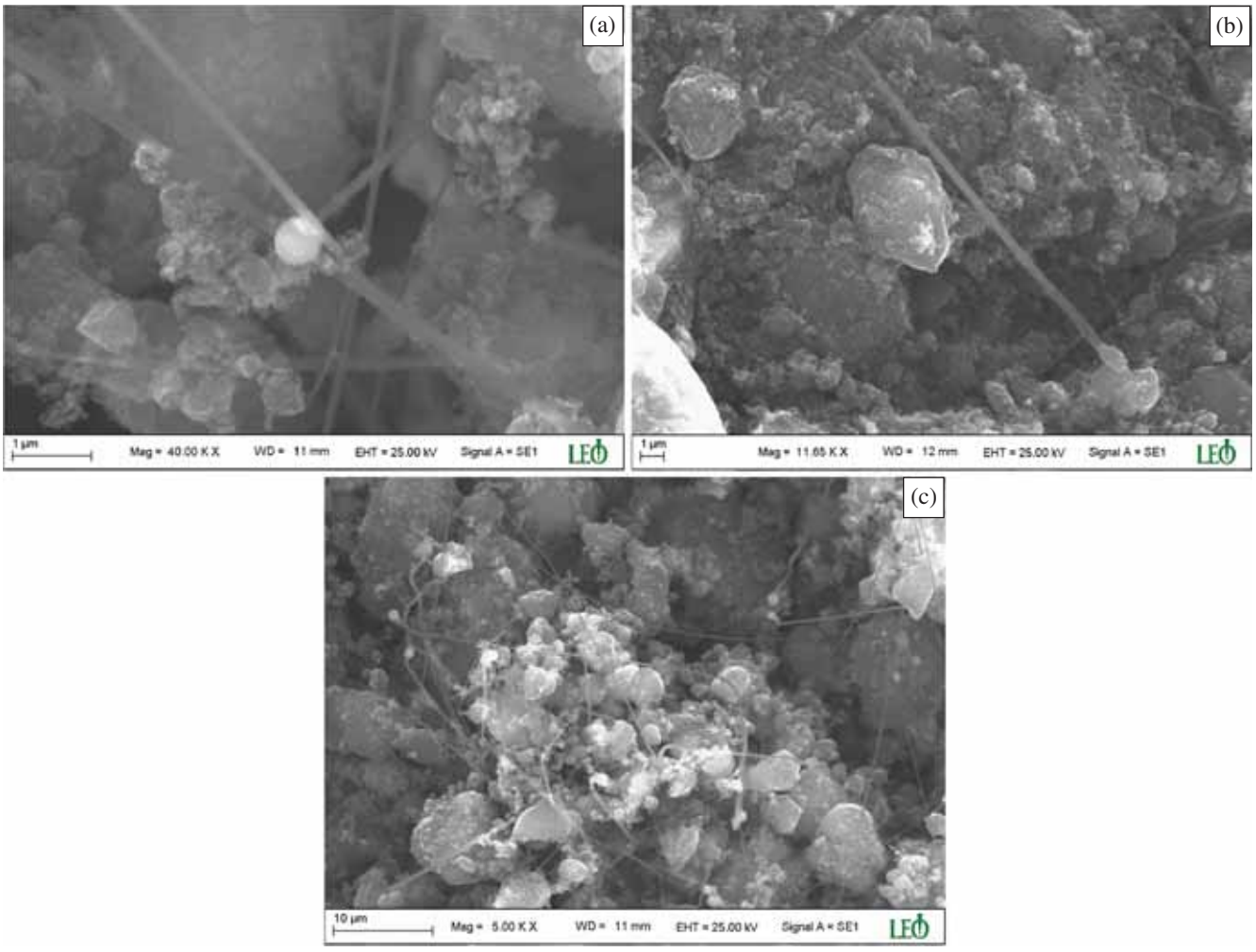

Figure 2. SEM image of sample after milling for 5 h followed by annealing at 1600°C for 6 h. (**a** and **b**) Bamboo and cylindrical type CNTs, (**c**) metal based various structures at the end of the CNTs.

diameters ranging between 70 and 200 nm, the lengths of these tubes are around a few micrometres. Chen *et al* reported that the diameters of the nanotubes vary based on the diameters of the metal particles acting as catalyst.[7] The fact that the diameters of the nanotubes obtained in this study are relatively large is due to the metal particles. Since the milling time is 5 h, the size of the iron powders which were added at the beginning of the experiment in order to act as a catalyst, did not decrease sufficiently. During the annealing process, CNTs have developed on these particles which have relatively big size and therefore their diameters were relatively big. Furthermore, examining the SEM images; it is also seen that the amount of the amorphous carbon is high in the structure.

Figure 3 illustrates TEM images of the sample which was milled for 5 h and then subjected to 6-h annealing process at 1600°C. In the figure, a cylindrical nanotube with an iron particle is seen at the end part. This nanotube is a multi-walled CNT and has an external diameter of approximately 80 nm and an internal space of 60 nm. Consequently, at the end of 5-h milling process and 6-h annealing process at 1600°C, it was determined that CNTs were formed in the structure. The diameters of the nanotubes are between 70 and 200 nm and it could be asserted that they have relatively large diameters. Given that the diameters of the CNTs vary with the diameter of the metal catalyst, the reason of this situation can be short milling time. The size of the 30 µm pure iron powders which were added at the beginning of the experiment could diminish to 50 nm at most at the end of 5-h milling process. Due to the difficulty in controlling the milling process, there was no homogeneity in the structure. Namely, at the end of 5-h milling, the size of all iron particles in the structure did not have the same diameter but had diameters ranging between 50 and 200 nm. This situation also influenced diameters of the occurring nanotubes. Apart from this, amorphous carbon structures were observed in the structure, as well. Figure 4 illustrates diameter and length distributions of the formed nanotubes in which was milled for 5 h and then subjected to 6-h annealing process at 1600°C. Then, length and diameter of nanotubes were calculated by using similar to mean linear intercept (MLI) method. For this calculation, the length and diameter of nanotubes in unit area were measured by using five different TEM images.

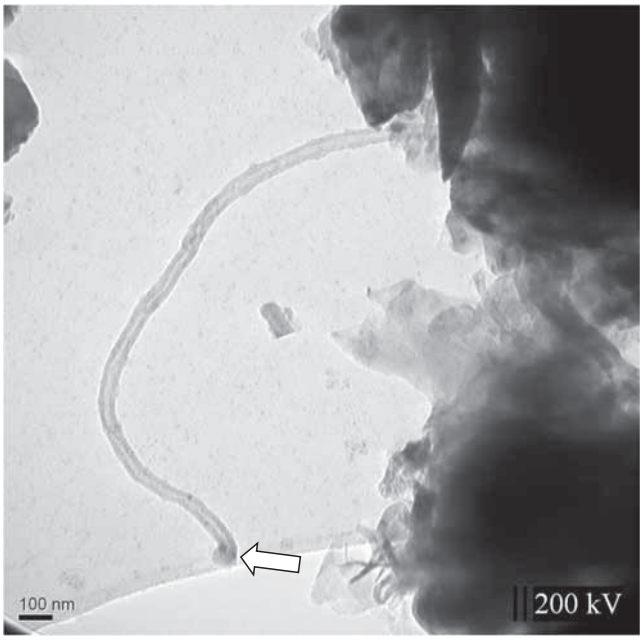

Figure 3. TEM image of sample after milling for 5 h followed by annealing at 1600°C for 6 h.

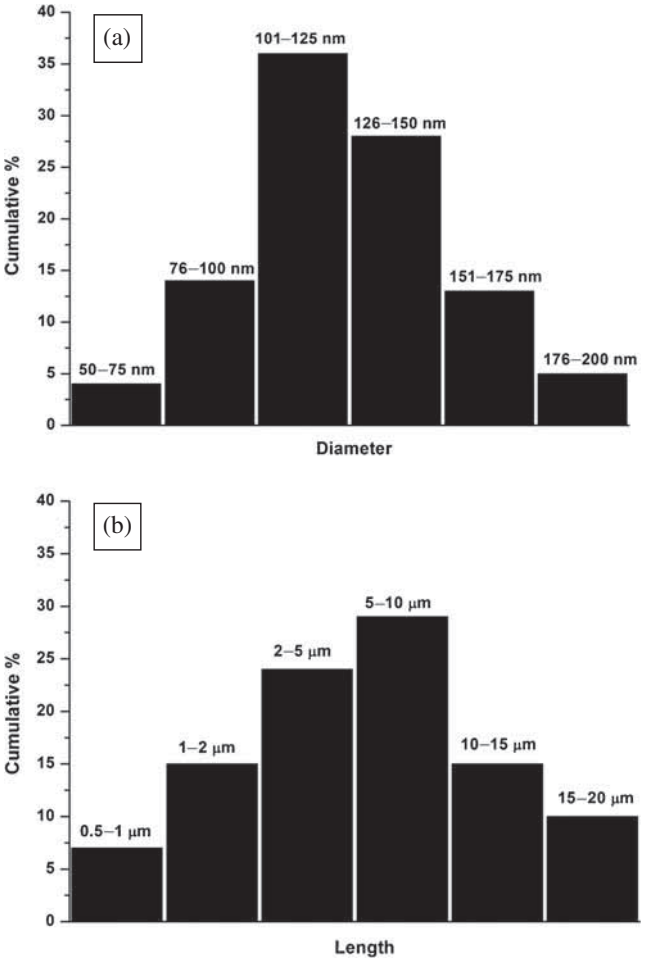

Figure 4. (**a**) Diameter distribution and (**b**) length distribution of formed carbon nanotubes after milling for 5 h followed by annealing at 1600°C for 6 h.

The crystallization temperature of the amorphous carbon is above 2000°C. However, the annealing temperature applied in this study is 1600°C. The relatively low annealing temperature, and a short milling time caused the amount of amorphous carbon which has again graphitized in other words converted into CNT, to be limited. Furthermore, although the graphitization of the amorphous carbon during the annealing process caused the formation of different structures other than CNT, the amount of such structures was scarce.

3.2 *Long milling time results*

In previous studies, graphite powder was milled for long milling times such as 150 h for the formation of CNT by

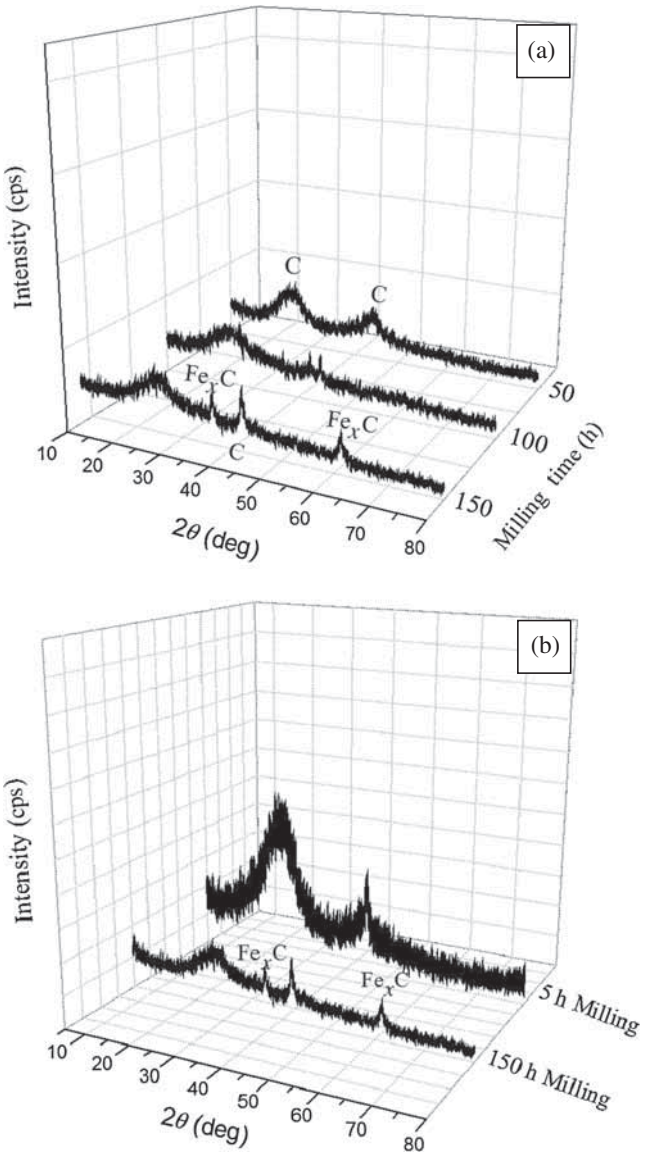

Figure 5. (**a**) XRD spectra of structural change of graphite by increasing milling times (50, 100, 150 h) and (**b**) XRD spectra of 5 and 150 h milled graphite.

using the mechano-thermal method.[7,8] In this study, CNT was obtained at the end of 5-h milling process applied on the graphite powder and the annealing process. However, in this study the graphite powder was also subjected to 150-h milling process in order to determine the effect of the long milling time on the structures to be obtained. Figure 5a illustrates the XRD pattern of the graphite milled for 50, 100 and 150 h. After 50-h milling process hexagonal structure completely transformed into an amorphous structure. An increase in the milling time did not cause any change in amorphous phase. However after 100-h milling process, iron carbide peaks started to form and as the milling time increased, the intensity of the iron carbide peaks also increased. The long milling time has increased the amount of iron which was worn from the balls and vials and mixed into the structure and caused the Fe in the structure to convert into iron carbide.

In consideration of the XRD pattern of unmilled graphite, (002) peak broadened after 150-h milling process. This broadening indicates that throughout the milling process, the distance between the graphite layers increased and full amorphization process occurred.[4,5,12] During the milling process, important plastic deformations and fractions in the particles lead the particle size to continuously decrease. After 150-h milling process, the intensity of the iron carbide peaks considerably increased. Figure 5b illustrates the XRD analyses of the powders which were milled for 5 h and 150 h for comparison purposes. Comparing XRD analyses of these two samples, it is seen that at the end of 5 h, (002) peak almost disappeared. However, when it is compared with the peak of the 150-h sample, one can mention the presence of a residual graphitic structure in the structure of the 5-h sample even if the amount is little.

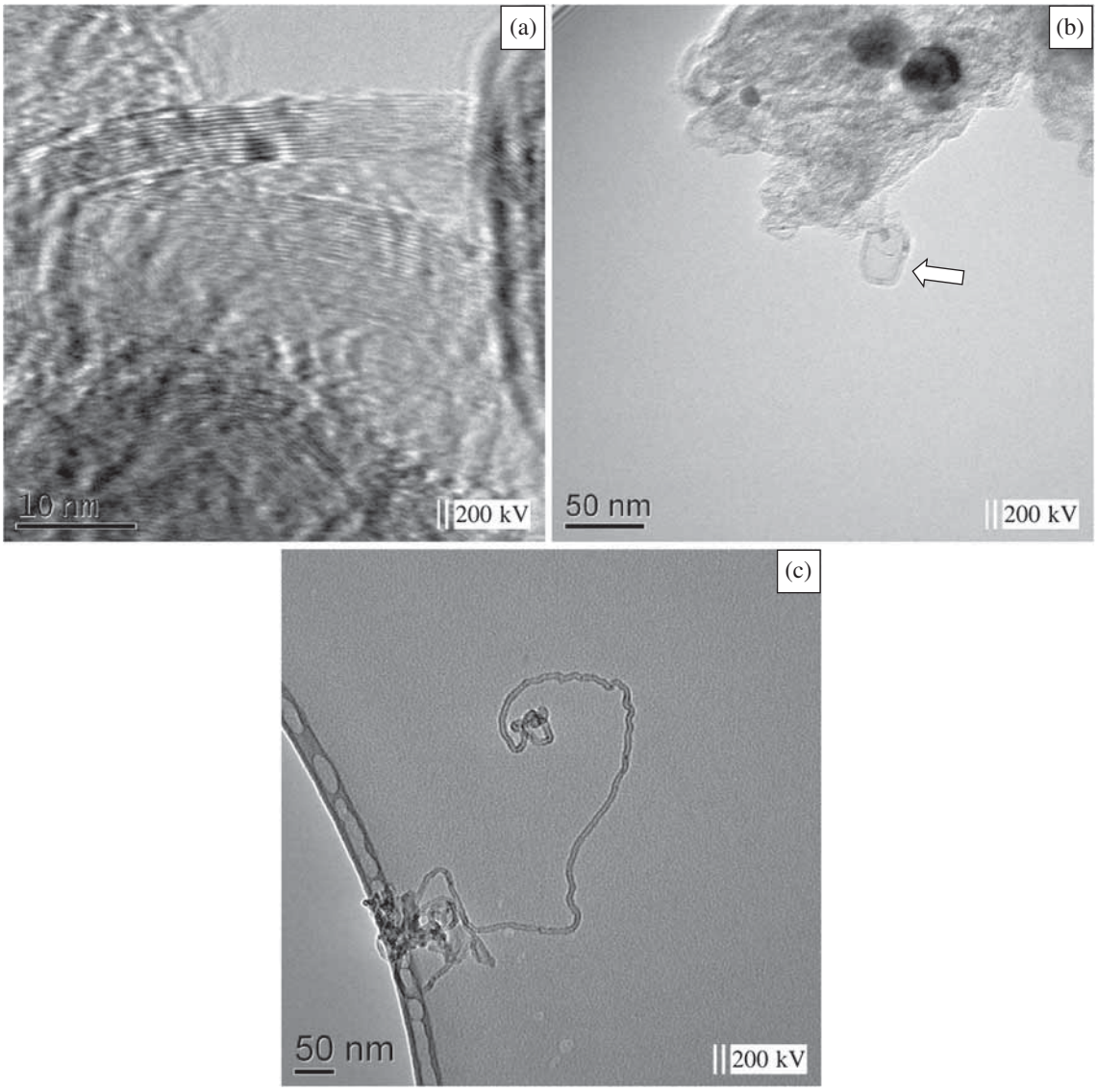

Figure 6. TEM image of sample after milling for 150 h followed by annealing at 1600°C for 6 h: (**a**) nano-arch structure, (**b**) nano-onion structure and (**c**) CNTs.

Although Chen *et al* stated that they obtained CNTs after 150-h milling process and then annealing process afterwards, high amount of different structures was observed except from the CNT in this study. Figure 6 illustrates the HR-TEM images of the structures which are obtained in this study by milling the graphite for 150 h and annealing it.

Figure 6a illustrates the high curved graphite sheets, namely, nano-arches. Figure 6b shows the HR-TEM images taken from a different region of the sample. As is seen, along with curved graphene layers, rolled graphene layers are seen in the structure as well. The structure shown with an arrow is a carbon nano-onion-type structure and inside of this structure is empty and its diameter is approximately 20 nm. The carbon nano-onion-type structures formed in high amounts adjacent to the big structure in the figure. Figure 6c illustrates the HR-TEM images of the CNTs which formed inside the structure. The diameters of the CNTs which formed within the structure are between 20 and 30 nm. Figure 7 illustrates diameter and length distributions of the formed nanotubes in which was milled for 150 h and than subjected to 6-h annealing process at 1600°C. Then, length and diameter of nanotubes were calculated by using similar to the mean linear intercept (MLI) method.

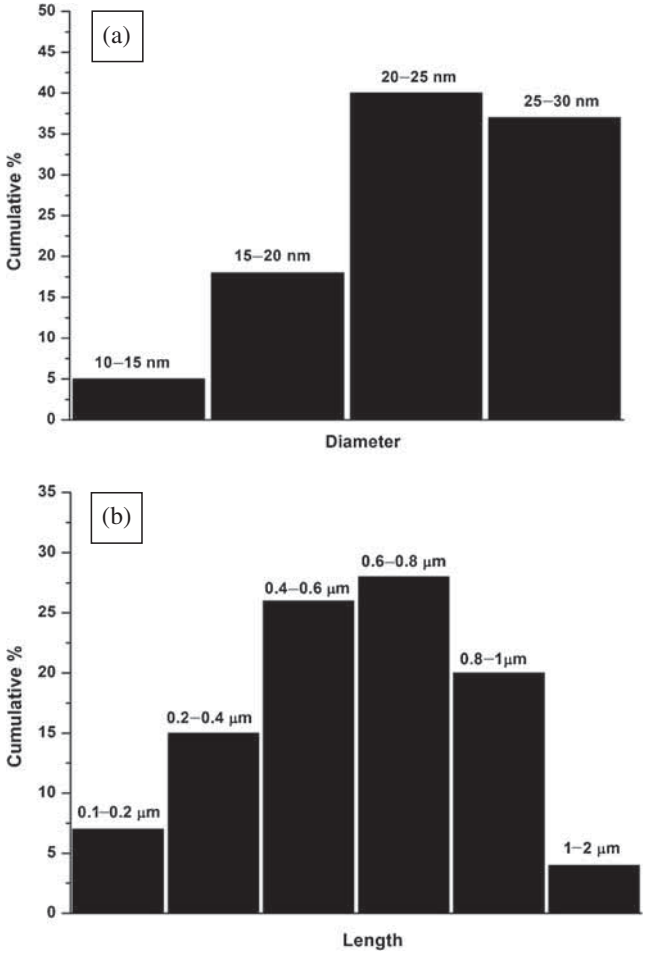

Figure 7. (**a**) Diameter distribution and (**b**) length distribution of formed carbon nanotubes after milling for 150 h followed by annealing at 1600°C for 6 h.

Many researchers studying on the milling of graphite have encountered some structures such as high curved graphite sheets, carbon nano-onion and carbon microspheres in their own studies.[6,13–16] In all of these mentioned studies, graphite was subjected to only milling process and powders were not subjected to the annealing process after the milling process. It was stated that these structures formed during the milling process. Furthermore, in these studies, CNTs did not occur after the milling process of the graphite. In the studies which achieved in producing CNT by using mechanothermal process, graphite powder was milled in high-energy ball mill and then annealing process was applied at high temperatures.[3,7,8] In this study, in the samples obtained at the end of 150-h milling process, both CNTs and other structures (nano-arches, carbon nano-onion, amorphous carbon) were encountered. Comparing to other studies conducted, the creation of structures which are so different from each other may be associated with the high milling rotation and long milling time. During the long milling process performed at high rotations, hexagonal graphite firstly became amorphized and then the nucleation of the structures such as nano-arches and nano-onion occurred. The annealing process performed after the milling process provided the growth of the structures like these nano-arches and nano-onion.

In addition, the nucleation and formation of the CNTs formed in the structure occurred as different from other structures which also formed. Milling process, due to its nature, is an uncontrolled and non-homogeneous process. During 150-h milling process; although in some part of the structure the nucleation occurred in the structures such as nano-arches and nano-onion, there have been still some amorphous carbon structures, which were not exposed to transformation, within the structure. During the annealing of the milled powders these amorphous carbon structures in the structure enlarge on proper iron cores and convert into CNTs. The structures, which nucleated during the milling process such as nano-arches and nano-onion cannot convert into CNTs during the annealing process. TEM examinations demonstrated that the amount of the CNTs in the structure is little. The formation of CNTs in small amounts in the structure proves that the core structures which have occurred during the milling did not convert into CNTs during the annealing process.

The fact that the amount of CNTs which formed at the end of the experiment is limited is thought to be caused by two reasons. As the first reason; CNTs are structures which nucleates and enlarges during the re-graphitization as a result of annealing excessive active amorphous carbon at high temperatures, and the fact that the small amount of amorphous carbon remained in the structure at the end of the milling process due to the long milling time decreased the amount of CNT formed. The other reason for the small amount of the CNTs is that CNTs enlarge on a catalyst during the annealing process. Iron powders, which were added at the beginning of the milling process in order to act as a catalyst, converted into iron carbides at the end of milling process.

Figure 4 illustrates this situation in the XRD pattern. The iron carbides occurring cause the catalyst rate in the structure to decrease and thereby to reduce the nanotubes occurring.

4. Conclusion

In case that the milling time selected is short in CNT production by the mechano-thermal process, there are CNTs, amorphous carbon and a small amount of other graphitic structures within the structure. The diameters of these nanotubes are relatively large. This situation is associated with the size of the catalyst. In case that the milling time is selected long, the structure contains CNTs and other graphitic structures. Amorphous carbon exists in a small amount. The graphitic structures other than CNT existing in the samples, which were subject to long-term milling, are in higher amounts compared with samples which were milled for shorter periods. The diameters of the CNTs, which were obtained at the end of long-term milling, are smaller than the diameters of the nanotubes in the samples which were milled for shorter periods.

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