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Production of carbon nanotubes using mechanical milling in the presence of an exothermic reaction

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ABSTRACT

Carbon nanotubes (CNTs) have shown promising potential for many applications in field of engineering due to their unusual significant properties. A major challenge for the industrial applications of CNTs is the large-quantity production. In this field, one new method for CNT production is annealing the ball milled graphite powder. The annealing process should be done in high temperature (1200–1400 °C) and needs time more than 6 h. The novel process introduced in this paper is elimination the annealing stage thorough a thermite reaction. The necessity heat for the conversion of milling products to CNTs was generated in the milling chamber by an exothermic reaction. In addition, the reaction products acted as catalysts to the CNT formation process. The adiabatic temperatures of 1809, 2000 and 2325 K were selected according to balancing graphite and thermite mixture (Aluminum + Iron oxide powders) for exothermic reaction. The results of thermo gravimetric analysis (TGA) test proved that CNT formation strongly depends on adiabatic temperature. The results of microscopic evaluation done by transition electron microscope (TEM) showed that at higher adiabatic temperature CNTs could be produced.

1. Introduction

Since the time of discovery by Iijima, many researchers have devoted their efforts to studying Carbon Nanotubes (CNTs) due to their important applications [1–5]. The demand market of CNTs is increasing because of its vast applications, especially for electrochemical devices [6], field emission devices [7,8], hydrogen storage [9], composites [10,11], and nanoelectronic and optoelectronic devices [12,13]. There are some developed synthesis methods for fabrication of both single-walled nanotubes (SWCNTs) and multi-walled nanotubes (MWCNTs). The popular processes include electric arc discharge, laser ablation, chemical vapor deposition (CVD), electrochemical synthesis, and ball milling–annealing methods [14–16]. Among them, the ball milling–annealing method, consisting of a pre-ball milling and a subsequent thermal annealing process, can produce much larger quantities of both SWCNTs and MWCNTs due to a solid-state process [14–16]. In addition, the method has a capability to produce other nanotubes and even nanowires such as boron nitride (BN) $TiTe_2$ and $TiSe_2$ [17–22]. Also, controlled reactive ball milling has produced nano particles of metal oxides [23], nitrides [24], hydrides [25], and carbides [26] at room temperature. According to literature survey done by the authors using ball milling along with annealing include with some limitations. For example, annealing treatment needs to a high temperature resistant furnace and furthermore long period of times to do annealing. For the reasons mentioned above the main goal of current research is to compensate the effect of annealing appeared after ball milling. To do so the authors attempt to fabricate CNTs using a new method. As a matter of fact in this new method it has been tried to eliminate the subsequent annealing of ball milling–annealing technique. For this purpose, the released heat from a thermite reaction during ball milling process has been substituted with annealing after ball milling.

2. Experimental procedure

Crystalline graphite powder with a high purity (>99.9%) was used as the starting carbonaceous material. Thermite powder mixture (Aluminum + Iron oxide powders) was also used as reacting agent. The amounts of Al and Fe_2O_3 powders were chosen based on calculation of theoretical adiabatic temperature of $C + Al + Fe_2O_3$ powder mixture. Al powder purity was about 99.5% with a mean size of 45 micron and the purity of used Fe_2O_3 was about 98% with average particle size of 1 micron. Ball milling process was performed at room temperature in a planetary ball mill using hardened steel balls with a diameter of 10 mm. The instrument contained stainless steel vial with an internal diameter of 50 mm and height of 80 mm. The ball to powder weight ratio was kept constant 40:1 and the rotation speed of the vial was 300 rpm. The vial was loaded with four grams of the $C + Al + Fe_2O_3$ mixture with steel balls. The adiabatic temperature (T_{ad}), defined as the theoretical temperature rise during the reaction under adiabatic conditions, was calculated considering following reaction:

$$2Al + Fe_2O_3 + xC = Al_2O_3 + 2Fe + xC \quad (1)$$

These calculations were based on the total change in enthalpy during the chemical reaction that will raise the temperature of the product in the adiabatic condition.

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Table 1
The amount of powders and related adiabatic temperatures.

Adiabatic temperature (K)	Graphite (g)	Aluminum (g)	Iron oxide (g)
1809	2	0.52	1.48
2000	1.75	0.56	1.65
2325	1.4	0.60	2

The released energy from thermite reaction was considered to provide the needed heat for increasing the temperature of products up to T_{ad} as shown in Eq. (2). This equation applies to a phase change occurring between the initial temperature and T_{ad}

$$-\Delta H_{298} = \int_{298}^{T} (C_p(Al_2O_3))dT + 2\int_{298}^{T} (C_p(Fe))dT + x\int_{298}^{T} (C_p(C))dT \quad (2)$$

where, ΔH_{298} is the enthalpy of the reaction, C_p is the specific heat capacity, and T is the adiabatic temperature. Three different amounts of x were chosen, so that adiabatic temperatures of 1809, 2000 and 2325 K to be achieved. In fabrication of carbon nanotubes through ball milling followed by annealing, the annealing temperatures reported in literature are in the range of 1450–1700 K [14–19]. In the above procedure, annealing duration is around 6 hours. But, in new route introduced in present paper the time interval during which the sample remains in high temperature is very short. This is why higher temperatures (1809, 2000, and 2325 K) have been selected. Therefore the masses of graphite, Al and Iron oxide mixture were calculated in basis of selected adiabatic temperatures. Table 1 shows the weight of used materials for ball milling.

The milling runs were interrupted for 0.5 h to cool chambers whenever the powder was milled for 5 h. Milling was carried out after desired period (100 h). Then the milled powders were characterized using various techniques. The carbon types of samples were investigated by means of thermo gravimetric analysis (TGA) and also microscopic evaluation was performed using a LEO Zeiss 912 AB-120Kv transmission electron microscopy (TEM).

3. Results and discussion

It is well known that different structural forms of carbon have different oxidation behaviors. In other words, they exhibit different reactivity with oxygen which is dependent on the available reactive sites. As a result, TGA and DTG (differential thermo gravimetric) studies have been found to be useful to understand the nature and structure of carbons present in the carbonaceous material. Fig. 1 shows the TGA and DTG graphs for 100 h milled graphite subjected to TGA experiment under air conditions. The weight loss observed in the curve is due to carbon oxidation.

Amorphous carbons tend to oxidize at lower temperature because of their lower activation energies for oxidation and/or due to the presence of large number of active sites as well as dangling bonds. It leads the system to increasing specific surface area to over 600 m^2/g [27–32]. For example, Welham and Williams [28] proved that the milled graphite was shown a large reduction in the onset temperature for oxidation, indicating that it was considerably activated by milling. Furthermore, Fukunag et al. [29], suggested that bonding between the C atoms was broken during milling and

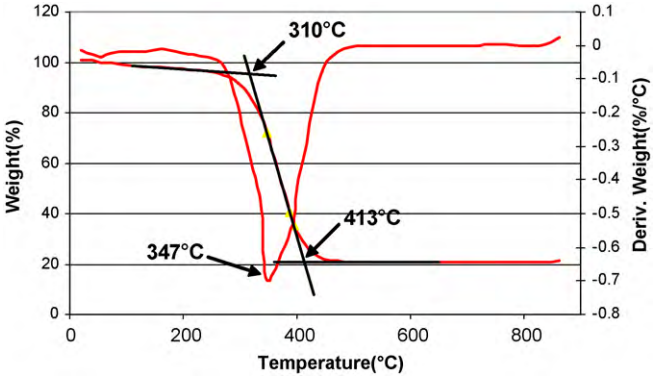

Fig. 1. Thermogravimetric analysis of 100 h milled graphite.

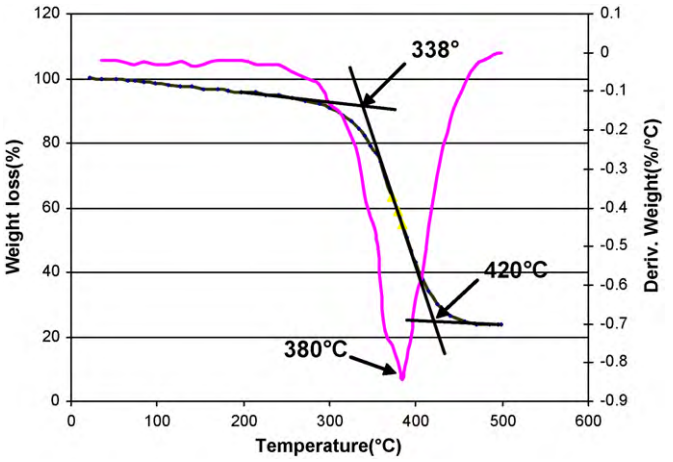

Fig. 2. Thermogravimetric analysis of 100 h milled mixture of graphite + Al + Fe_2O_3 with T_{ad} = 1809 K.

dangling bonds were created, which increased in number with an increase of milling time; the structural change led them to imagine that the milling may result in a decreasing size of the crystallites of graphite [30,31].

3.1. Role of adiabatic temperature on CNT formation

In Fig. 1, a sharp weight loss is appeared around 350 °C which corresponds to oxidation of amorphous carbonaceous material [30–33]. Here, milling process was performed using graphite only and no detectable reaction was occurred during milling. It can be concluded that 100 h milling of graphite in the absence of thermite mixture resulted in refining and amorphization of carbon. Figs. 2–4 show the TGA and DTG graphs of 100 h milled graphite in the presence of various amounts of thermite mixtures resulted in different adiabatic temperatures in the system. T_{onset} (The temperature in which oxidation just begins) of sample having adiabatic temperature of 1809 K (Fig. 2) is almost the same as T_{onset} of 100 h milled graphite (Fig. 1). It means that here also amorphous carbon is formed during milling. This is similar to Manafi et al. report [32] who proposed that the crystallite sizes of the graphite decreased gradually as milling time increased resulted in the increasing the microstrain. This leads them to suggest the formation of an amorphous-like phase or very fine particles (~10 nm). In the curve shown in Fig. 3, belonging to the sample with T_{ad} of 2000 K, two steps can be observed in TGA and DTG curves. It

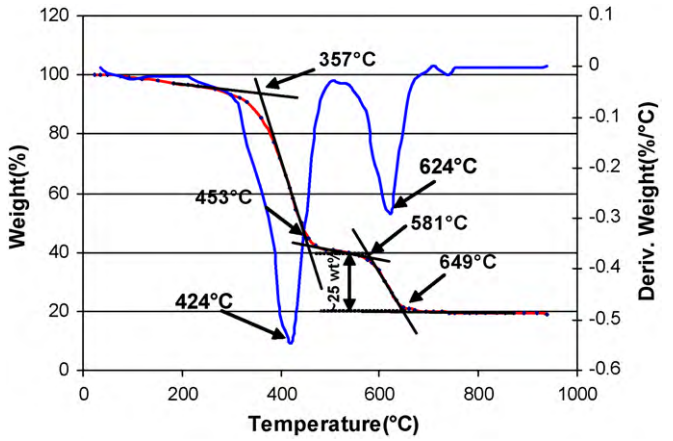

Fig. 3. Thermogravimetric analysis of 100 h milled mixture of graphite + Al + Fe_2O_3 with T_{ad} = 2000 K.

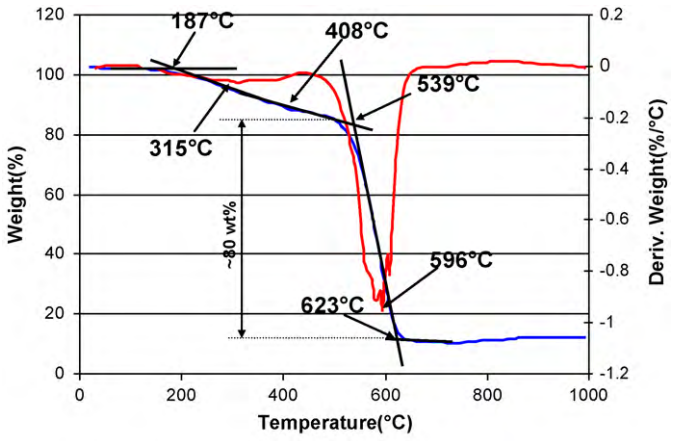

Fig. 4. Thermogravimetric analysis of 100 h milled mixture of graphite + Al + Fe_2O_3 with T_{ad} = 2325 K.

can be seen that in first step, the oxidation begins at 357 °C and ends at temperature 453 °C. As discussed above, these temperature ranges including the first sharp DTG peak (424 °C) can be assigned to amorphous carbon which is more susceptible to air oxidation. In the second step, the oxidation begins at 581 °C and terminates at 649 °C. The second peak (624 °C) which is located around 600 °C is due to oxidation of carbon nanotubes. The same results are obtained for sample having T_{ad} of 2325 K whose oxidation has been started and ended at 539 and 623 °C, respectively (Fig. 4). The first peak of DTG at T_{ad} of 2325 K is about 315 and starts at 187 °C and ends at 408 °C. In both Figs. 3 and 4, the second peaks (539 and 624 °C), are due to oxidation of carbon nanotubes [33–35]. Since the induced weight losses in each step are related to amorphous carbon or CNT oxidation, as shown in Figs. 3 and 4, one may calculate the weight percent of them using TGA curve as mentioned in [27]. Therefore, for the sample having T_{ad} of 2325 K, the amount of carbon nanotubes, understood from TGA curves, is about 80 wt%; while, the sample having T_{ad} of 2000 K contains 25 wt% carbon nanotubes.

3.2. Microscopic evaluation

The results are verified by TEM micrographs, which will be presented in the following. It maybe concluded that the adiabatic temperature has a significant influence on nanotube formation during milling process. Moreover, it is well known that iron has a catalytic effect on carbon nanotubes formation [35,36]. As mentioned in experimental section, three different amounts of Al and Fe_2O_3 were chosen, so that adiabatic temperatures of 1809, 2000 and 2325 K to be achieved. As a result, the higher adiabatic temperature that can be attained is due to the more amounts of thermite mixture chosen initially. Consequently, the more product of reaction including iron will be achieved. Therefore, more iron particles can potentially be produced in the thermite reaction in the case of samples having T_{ad} of 2325 K. The Presence of iron particles plays a positive role in carbon nanotubes formation and promotes the process. Here, it should be noted that, the metals used to catalyze CNT

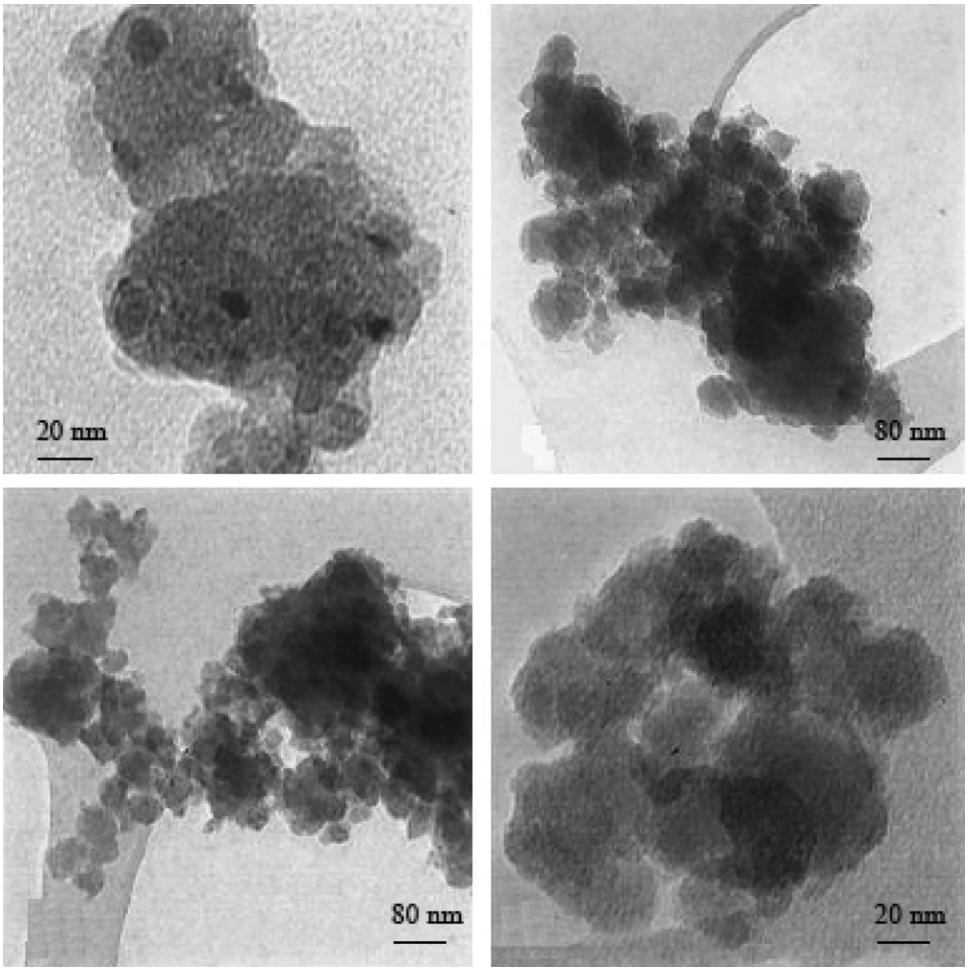

Fig. 5. TEM micrographs of 100 h milled mixture of graphite + Al + Fe_2O_3 with T_{ad} = 1809 K at different magnifications.

Table 2
The dependence of CNT% as a function of adiabatic temperatures.

		Oxidation start temp. (AC)	Oxidation end temp. (AC)	Oxidation start temp. (CNT)	Oxidation end temp. (CNT)	Temperature of the maximum rate of oxidation		CNT%
Graphite		310 °C	413 °C	–	–	347 °C		0
Graphite + Thermite mixture	T_{ad} = 1809 K	338 °C	420 °C	–	–	380 °C		0
	T_{ad} = 2000 K	357 °C	453 °C	581 °C	649 °C	AC 424 °C	CNT 624 °C	25
	T_{ad} = 2325 K	187 °C	408 °C	539 °C	623 °C	AC 315 °C	CNT 596 °C	80

formation are most often transition metals including iron, cobalt, and nickel. The special ability of these transition metals to catalyze CNT formation is mostly linked to their catalytic activity for the decomposition of carbon compounds, their ability to form carbides and the possibility for carbon to diffuse through and over the metals extremely rapidly. Herein, a very large number of papers concentrated on growth of CNTs can be found in literature reporting CNT growth [36,37].

The percentages of CNTs produced during each experiment calculated from the weight loss occurred around 600 °C, and the temperatures at which oxidation of each form of carbon begins and ends have been summarized in Table 2. As can be recognized from TGA and DTG curves, the maximum amount of carbon nanotubes belongs to sample having T_{ad} of 2325 K, while no carbon nanotube has been formed in sample with T_{ad} of 1809 K. TEM micrographs of milled mixture of $C + Fe_2O_3 + Al$ having T_{ad} of 1809 K shown in Fig. 5. As can be realized from this figure, there is no evidence of carbon nanotube formation.

It is clear from TGA graphs and TEM micrographs (Figs. 6 and 7) that the higher adiabatic temperature enhances the nanotube formation which can be associated with a faster reaction and growth rate. As could be observed, the average diameter of carbon nanotubes is about 8 nm (indicated in Fig. 7c). This is similar to what reported by other studies in which the dependency of

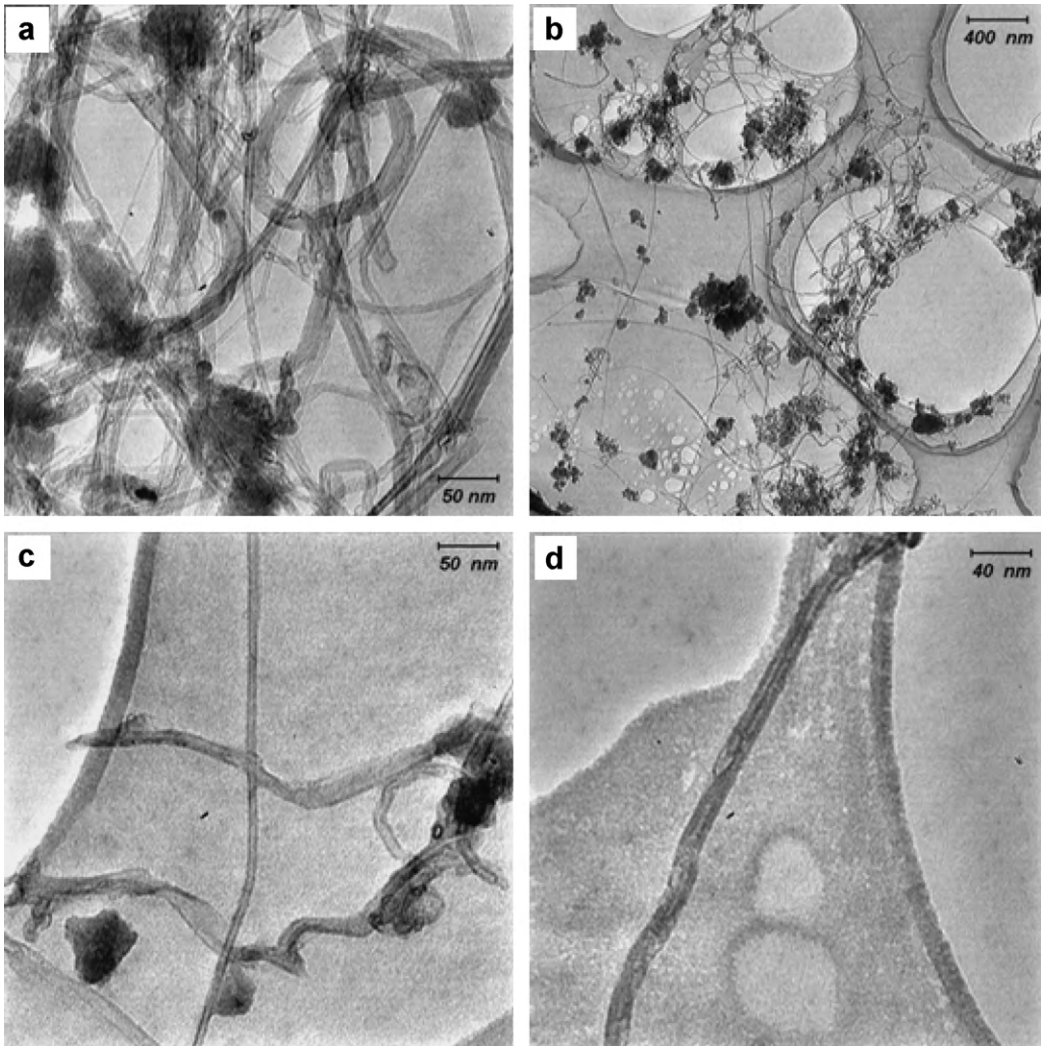

Fig. 6. TEM micrographs of 100 h milled mixture of graphite + Al + Fe_2O_3 (a and c) T_{ad} = 2000 K, (b and d) T_{ad} = 2325 K.

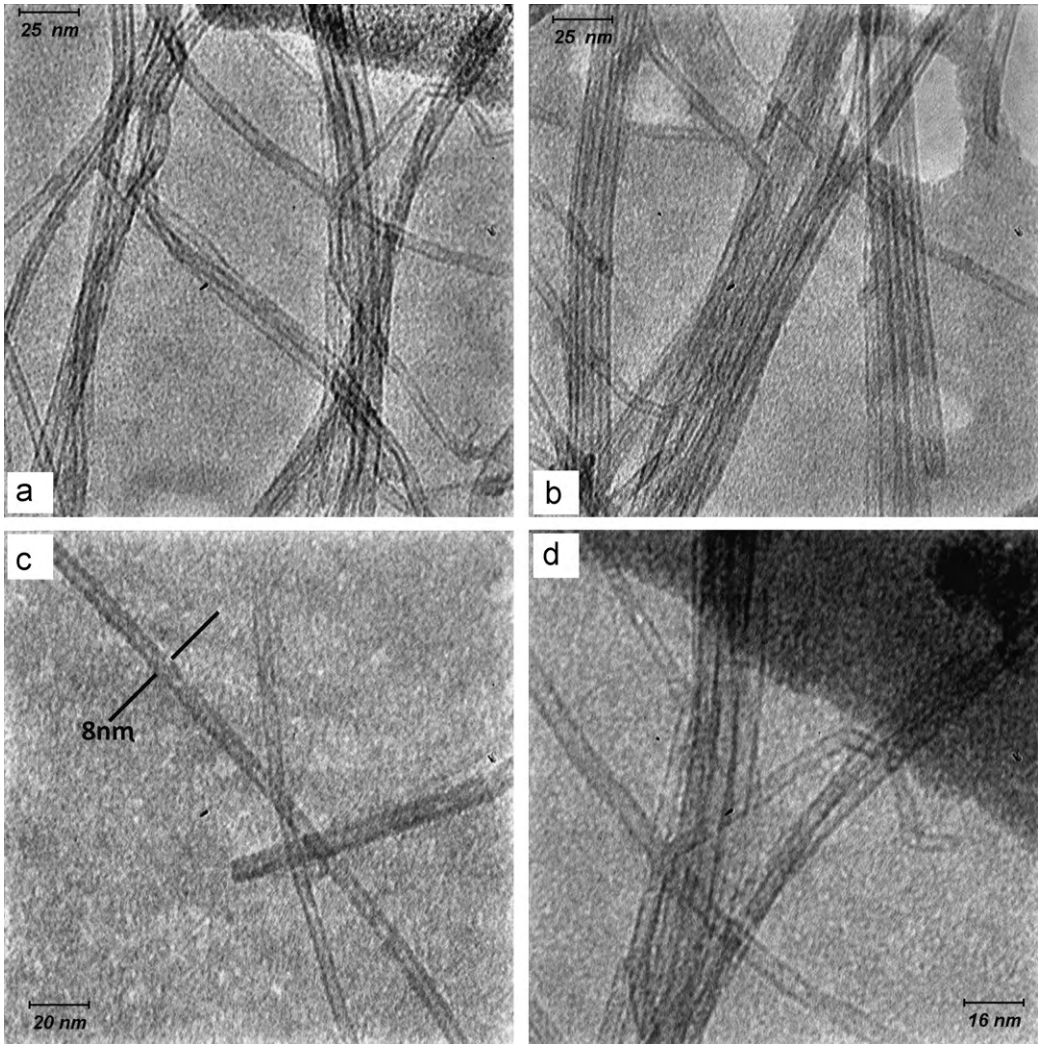

Fig. 7. TEM images of 100 h milled mixture of graphite + Al + Fe_2O_3, similar to Fig. 6. but at higher magnification, (a and c) T_{ad} = 2000 K, (b and d) T_{ad} = 2325 K

growth rate and coarsening on adiabatic temperature were shown [35–37].

3.3. The role of reactive milling on CNT formation

Understanding the role of reactive milling is critical for the CNT formation mechanisms. Collisions between steel balls or balls and vial mill, may cause trap some particles of (C + Al + Fe_2O_3) mixture between them. The heat released from exothermic reaction between Al and Fe_2O_3 due to high-energy impacts raises temperature and accelerates the diffusion process. Furthermore, deformation and fracturing of particles cause continuous size reduction and lead to shortening of diffusion distances. Furthermore, deformation and fracturing of particles cause continuous size reduction and lead to shortening of diffusion distances. Here, refining of particles, increasing of surface area, and amorphization of carbon occur during high-energy ball milling (Figs. 1–5). The nanometer-sized amorphous carbon is thermodynamically unstable, owing to a high surface free energy. All these phenomena lead to higher chemical reactivity of carbon. It is also well known that the mechanism of CNT formation is nucleation and growth [35–37]. It is thought that here also the same mechanism can be considered for carbon nanotube formation. The nucleation happens during ball milling process. Simultaneously, growth occurs because of the heat released by thermite reaction.

4. Conclusions

In the current research, a novel experimental approach that utilizes an exothermic reaction simultaneously ball milling of graphite as the starting carbonaceous material for the formation of carbon nanotubes has been investigated. The achieved results are remarked as below:

- The whole process of nucleation and growth of carbon nanotubes occurs during ball milling step because of the presence of exothermic agent.
- The heat released from exothermic reaction leads the system to be formed as carbon nanotube. This is because the growth of carbon nanotube depends strongly on carbon diffusion into the nanocatalyst (in the current study, iron particles achieved from byproduct of thermite reaction and somehow the abrasion of balls and vial).
- Milling assists to reduce the size of graphite particles as well as increasing the strain of their lattice and makes them to be disordered. These reasons cause them to become much more active for diffusion.

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