Investigating the effects of CVD reaction time on the growth of carbon nanotubes

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Ethanol has been found superior precursor for carbon nanotubes growth with lesser amount of amorphous carbon impurities. In this study, attention has been focused to determine the influence of Alcoholic Catalytic Chemical Vapor Deposition (ACCVD) reaction time on the growth and quality of CNTs via cobalt based catalyst. Effects of different reaction times on synthesis of CNTs were investigated by using characterization techniques like Scanning Electron Microscopy, EDX, X-Ray Diffraction and Raman Spectroscopy. Our results demonstrated that higher reaction times had significant enhancing effects on the yield of grown CNTs up to a critical reaction time and after that CNTs yield decreased. Quality of grown CNTs for 60 minutes was better than other reaction times. ACCVD reaction times also had a noticeable effect on the diameter of grown CNTs. Diameter of grown CNT has decreased continuously with the increase of reaction time from 60 to 150 minutes. The synthesized CNTs were a mixture of SWCNTs and MWCNTs.

(Received August 1, 2012; accepted September 18, 2013)

Keywords: Alcoholic catalytic chemical Vapor deposition (ACCVD), Ball milling, Ethanol, Carbon nanotubes (CNTs)

1. Introduction

Since the discovery of carbon nanotubes in 1991 by Iijima [1], CNTs have attracted researchers a lot to create new fields for applications, because of their outstanding physical, mechanical and electronic properties [2-6]. In comparison with conventional reinforcing materials, addition of carbon nanotubes have developed nanocomposites with better mechanical properties due to their highly appreciated properties like stiffness, yield strength and modulus of elasticity [7-8]. There are three main well recognized techniques to synthesize carbon nanotubes [9-12]: electric arc, laser ablation and chemical vapor deposition. Among these listed CNTs growth techniques, CVD [13-15] is considered superior because of its simplicity in operation, high yield of CNTs, low operational cost and low temperature of reaction.

Chemical vapor deposition process provides an opportunity to use carbon precursor in liquid, solid or gaseous form for carbon nanotubes growth [16]. In 2002, Maruyama et al**.** synthesized high quality SWCNTs using liquid precursors (methanol and ethanol) over Fe-Co catalyst supported on zeolite [17]. Shinohara et al. were also successful in the synthesis of high quality SWCNTs through alcoholic catalytic Chemical Vapor Deposition process [18]. Lopez et al. synthesized CNTs over the conducting glass, nickel plates and porous alumina substrate using Fe and Co acetates as a catalyst by ethanol decomposition [19]. Investigations of Marion et al. in the synthesis of high quality MWCNTs over pre-deposited Fe-catalyst thin film (5nm) by ethanol decomposition [20] were also successful. All results of carbon nanotubes synthesized by ethanol decomposition showed quality superiority. Reason for the better quality of carbon nanotubes synthesized by ethanol decomposition is due to the availability of OH^- radicals released after the decomposition of ethanol vapors. OH^- radicals are beneficial for the removal of amorphous carbon impurities [17, 21-22].

Stellite-6 is a cobalt based alloy and exhibits outstanding mechanical and oxidation resistance properties for wear applications at high temperatures in powder and bulk form [23-24]. No systematical parametric study has reported the synthesis of CNTs on nano-particles of cobalt based catalyst "stellite-6" under different reaction times by ACCVD process.

The main purpose of this study was to investigate the effects of different ACCVD reaction times on yield, quality and diameter of the grown CNTs. In order to find optimal ACCVD reaction time, grown CNTs were characterized by SEM and Raman Spectroscopy.

2. Experimental procedure

Stellite-6 is cobalt based alloy used as a catalyst for CNTs growth and was provided by Sterlo Co. Particle size of provided stellite-6 powder was in the range of 20-200 µm. For the growth of CNTs, µm sized range stellite-6 powder was converted to nano-sized by ball milling. The conditions for ball milling are given in Table 1. Absolute ethanol (99.99 % pure provided by Labscan Asia Co) was used as a carbon source for CNTs growth.

The set-up used for CNTs growth was available at Processing Labs (*FMSE, GIKI).* It consists of a tube furnace with the diameter and length of 25 and 100 cm respectively. Other accessories of CVD set-up consist of quartz tube, ceramics boat, heating chamber to vaporize ethanol, heating plate, vapor pressure gauge and argon cylinder. The schematic of ACCVD set-up is shown in Fig. 1.

Table 1. Ball milling conditions for the conversion of micron to nano-size of stellite-6 powder.

Mill type	Ball to powder weight ratio	RPM	No. of balls	Balls Dia. (mm)	Time (hours)
PM 400 Planetary ball mill	10:1	200	5	15	100

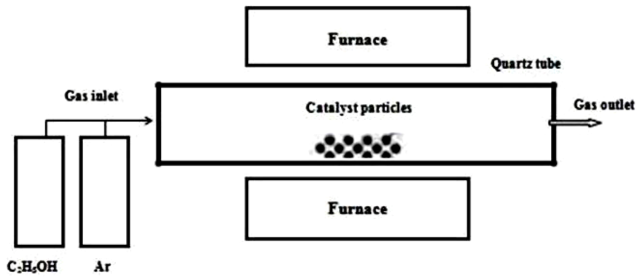

Fig. 1. Schematic of ACCVD apparatus used for CNTs growth.

Nano-scale stellite-6 powder (1-gram in quantity) was placed in ceramic boat. Ceramic boat was arranged right in the center of quartz tube placed in tube furnace. Initially quartz tube was evacuated at 10^{-3} mbar to avoid oxidation of catalyst particles at high reaction temperature. After evacuation, tube furnace was raised to 850 °C in the presence of Ar gas. Attaining certain ACCVD reaction temperature (850 °C), the ethanol vapors at particular vapor pressure of 25 mbar were allowed to flow in the quartz tube for different reaction times like 60, 90, 120 and 150 minutes. After the completion of CVD reaction, the tube furnace was shut down, and ACCVD treated catalyst nano-particles were allowed to cool at room temperature. By varying reaction time from 60-150 minutes, other parameters were kept constant (vapor pressure of ethanol 25 mbar, ACCVD reaction temperature 850 °C).

Grown carbon nanotubes on particles of stellite-6 were characterized by scanning electronic microscopy (SEM), energy dispersive spectroscopy (EDS) and X-Ray Diffraction (XRD). Quality of grown CNTs for different reaction times was estimated by Raman Spectroscopic analysis. Raman analysis was performed at room temperature in the range of 150-1800 cm^{-1} using He-Cd laser (442 nm excitation).

3. Results and discussion

We have observed CNTs growth on nano-particles of stellite-6 at different reaction times like 60, 90, 120 and 150 minutes by keeping other parameters constant (ACCVD reaction temperature 850 °C and vapor pressure of ethanol 25 mbar). The SEM images for catalyst particles treated under different reaction times are shown in Fig. 2. To make ensure the presence of grown CNTs phase, XRD results are demonstrated in figure 5. Quality of grown CNTs was investigated by Raman Analysis, and the results are displayed in Fig. 6.

SEM images for grown CNTs shown in Fig. 2 (a-d) reveal that CNTs clearly vary from one-another with respect to their lengths and morphologies, it means that different ACCVD reaction times have great influence on the final appearance of grown CNTs. Researchers have explained the impact of CVD reaction time on the yield, diameter and length of grown CNTs in different ways. S. Maruyama et al. have reported the decreased yield of grown CNTs because for longer ACCVD reaction times, the survival of smaller diameter CNTs is difficult [10]. Rodney Andrews et al. and H. E. Unalan et al. have shown the increased density of CNTs with the increase of CVD reaction time [25, 29]. S. Chaisitsak et al. have reported the decreased crystalline growth of CNTs with the increase of CVD reaction time [26]. J. L. Kang et al. [27] have explained an interesting effect of CVD reaction time on the morphologies of grown CNTs. CNTs change from an onion like shape to longer CNTs with the increase of CVD reaction time**.** M. A. Azam et al. [28] research results show that CVD reaction time on yield and crystalline structure of CNTs are effective up to certain reaction time after that amorphous regions are prominent due to poisoning of catalyst particles and also due to the burning of grown CNTs by oxidation.

CNTs have grown (Fig. 2a) on nano-particles of stellite-6 treated for 60 minutes CVD reaction time. CNTs are shorter in length but are healthy in number. As the ACCVD reaction was increased up to 90 minutes, the length of grown CNTs was also enhanced as shown in Fig. 2(b). Further increase in reaction time up to 120 minutes, should be beneficial for CNTs growth as it was for 90 minutes but SEM images shown in figure 2(c) do not support the theory for enhanced length of CNTs for longer reaction times and CNTs appeared in short length for 120 minutes reaction time. For longer reaction conditions, CNTs at their point of growth were burnt and also not flourished on cooling to room temperature due to catalyst poisoning. The burning effects of grown CNTs for 120 minutes reaction time can be visualized in SEM image 2(c) by the appearance of badly shaped, weaker and shorter length CNTs. Final increment in the ACCVD reaction time up to 150 minutes also verified the burning of CNTs. The SEM image shown in Fig. 2(d) indicates the growth of smaller and weaker CNTs. Besides the growth of shorter length CNTs for 150 minutes, the presence of large number of white colored CNTs can also be seen. White cap formation has enhanced with the increase of CVD reaction time and it is called soot. Simple conclusion for increased CVD reaction time (60-150 minutes) on the morphology of grown CNTs is summarized as: grown CNTs had lost shape, length and diameter for longer CVD reaction times.

The effects of CVD reaction time (60-150 mins.) on yield of grown CNTs are very interesting and the trend is shown in Fig. 3(a). Favorable growth conditions, like 60 and 90 minutes reaction time, have increased the yield (denser length and healthy number of grown CNTs) of grown CNTs. Yield at 120 minutes had decreased as compared to the yield at 90 minutes. The decreased yield for 120 minutes is verified by SEM image (Fig. 2c), whereby the appearances of burnt and weaker CNTs are evident. CNTs yield has increased for 150 minutes because of deposition of amorphous carbon for such longer reaction condition. Deposition of amorphous carbon is obvious in Fig. 2 (d). Effect of different ACCVD reaction times on the diameter of CNTs was also noticed and the results are displayed in Fig. 3(b). Diameter of grown CNTs has decreased continuously with the increase of ACCVD reaction time from 60 to 150 minutes. From our results, in case of reduced CNTs diameter with the increase of ACCVD reaction time, it was concluded that increased reaction time has stronger burning effects on the diameter of grown CNTs.

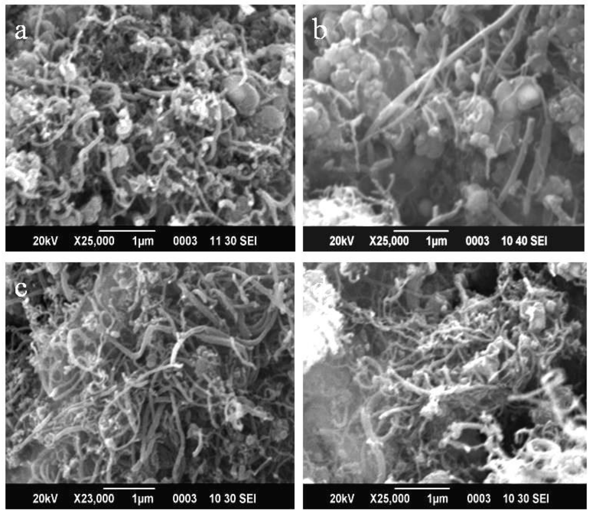

Fig. 2. SEM images showing CNTs growth at (a) 60 minutes, (b) 90 minutes, (c) 120 minutes, (d) 150 minutes.

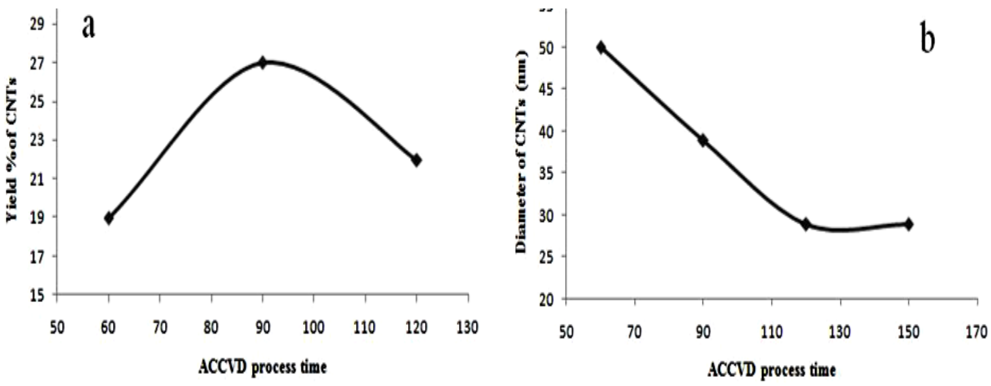

Fig. 3. (a) and (b) showing variation of yield and diameter of grown CNTs with different reaction times.

To display the enhanced carbon mass % after CVD treatment, EDS analysis for catalyst particles treated for 60 minutes is shown in Fig. 4b. EDS analysis showed the presence of all those elements of catalyst present before CVD treatment (Fig. 4a), except the enhanced carbon mass %, which confirms the growth of CNT. No contamination or other unwanted elements were detected after ACCVD treatment.

Phase comparisons before and after CNT growth are displayed in Fig. 5. When XRD patterns of ground stellite-6 (Fig. 5a) and catalyst particles treated for 60 and 90 minutes (Fig. 5b&c) are compared, the appearance of CNT peaks at 2-theta positions of 25, 44 and 74 are the major phase differences, confirm the growth of MWCNTs and SWCNTs. Some other phases appear at 2-theta positions of 34, 36.5, 42, 47, 55, 63.5, 65 and 67 respectively [30-33]. These phases are attributed to catalyst impurities, formed during CVD treatment.

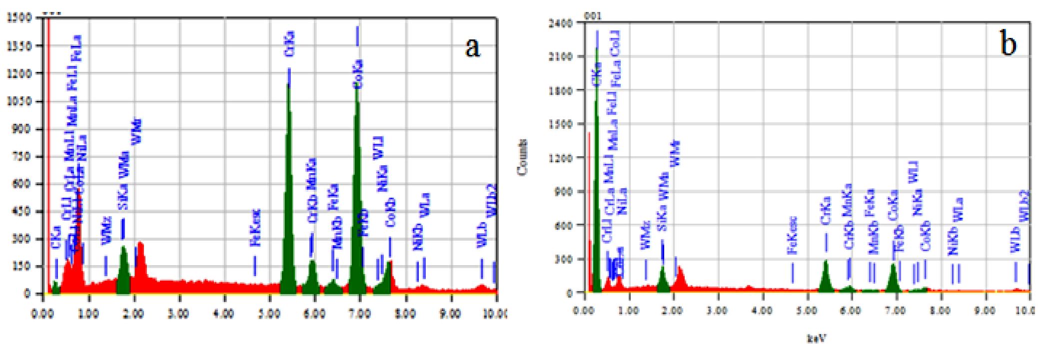

Fig. 4. Bulk EDX Analysis: (a) un-treated catalyst particles, (b) nano-particles of catalyst treated for 60 minutes.

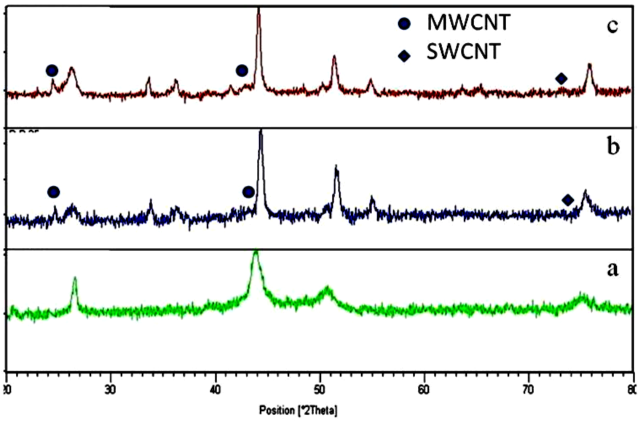

Fig. 5. Phase Analysis: (a) untreated stellite-6 particles, (b) 60 minutes (c) 90 minutes CVD treatment.

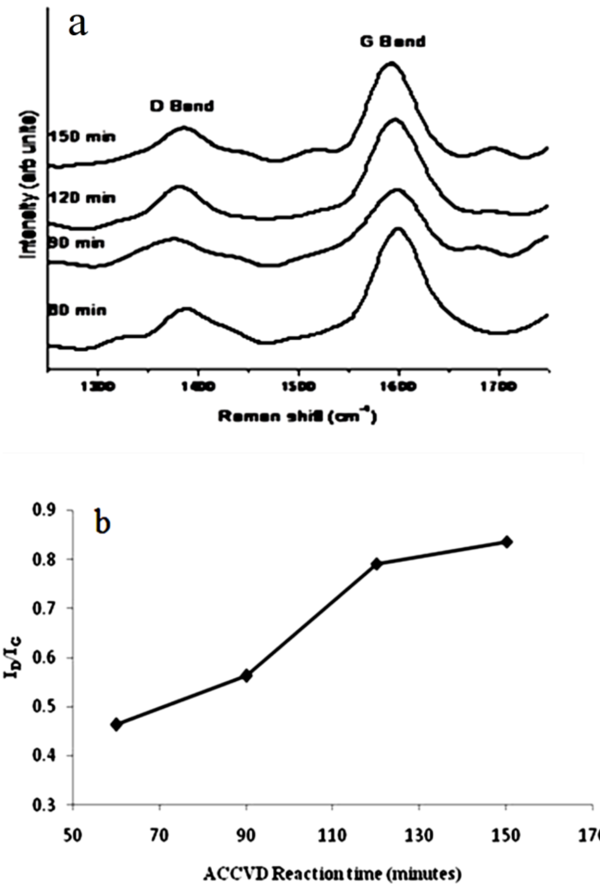

Fig. 6. (a) Raman spectroscopy analysis, (b) variation of I_D/I_G ratio with different ACCVD reaction times.

Quality of grown CNTs on stellite-6 nano-particles treated CNTs at different ACCVD reaction times was determined by Raman spectroscopy analysis (Fig. 6 a). Quality of grown CNTs was estimated by taking ratio between bands “D and G” after measuring their area under the curve of Raman spectrum [34]. Band appearing in Raman Spectrum at 1594 cm^{-1} called the G, corresponds to the well-ordered carbon atomic structure in a two-dimensional hexagonal lattice such as a graphite layer, while the band at 1390 cm^{-1} called the D and presents the amorphous carbon, impurities and defects in CNTs. A lower value (< 1) of the ratio between D and G band indicates better quality of grown CNTs.

It can be seen that I_D/I_G ratio is less for 60 minutes reaction time, and this is due to sufficient time for the decomposed carbon to saturate the catalyst particles. Another reason for better quality of grown CNTs is the lesser exposure of nucleated CNTs to available oxygen contents in CVD reactor. With the increase of CVD reaction time up to 90 minutes, I_D/I_G ratio is less than unit but slightly higher than 60 minutes. Further increase in reaction time up to 120 and 150 minutes, the ratio between D and G bands had further enhanced. The two solid reasons for the increased trend of I_D/I_G ratios for longer reaction times are the, burning of CNTs and poisoning of catalyst particles.

4. Conclusions

Purpose of this study was to investigate the effects of ACCVD reaction time on the growth of CNTs for hard alloy composites applications. Variations of reaction time from 60-150 minutes, it was found that 90 minutes was considered better from quantitative (27.65 %) point of view. Diameter of gown CNTs has decreased continuously with the increase of reaction time and minimum diameter was noticed for 150 minutes reaction time. Bulk EDS analyses performed after ACCVD treatment have shown enhanced carbon mass %, confirming the growth of CNTs. XRD analysis performed before and after the growth of CNTs has shown phase difference with the appearance of MWCNTs and SWCNTs at 2-theta positions of 25, 44 and 74 respectively. Qualitative effects show that the quality of grown CNTs (I_D/I_G=0.46) was superior for 60 minutes reaction time.

Acknowledgements

Author is thankful to *GIK Institute*, for providing laboratory assistance to complete this research work.

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