A novel method for fabrication of Fe catalyst used for the synthesis of carbon nanotubes

E Z KARIMI^{a,*}, J VAHDATI-KHAKI^a, S M ZEBARJAD^a, I A BATAEV^b and A G BANNOV^c

^aDepartment of Materials and Metallurgical Engineering, Faculty of Engineering, Ferdowsi University of Mashhad, Mashhad, Iran

^bDepartment of Mechanical Engineering, Novosibirsk State Technical University, Pr. K. Marksa 20, 630092 Novosibirsk, Russia

^cDepartment of Chemical Engineering, Novosibirsk State Technical University, Pr. K. Marksa 20, 630092 Novosibirsk, Russia

MS received 15 April 2013; revised 6 June 2013

Abstract. Carbon nanotubes (CNTs) have been grown by decomposition of propane over a nanocomposite catalyst by chemical vapour deposition (CVD). The catalyst was prepared from an aluminum/iron oxide/graphite mixture milled in a high-energy ball-milling equipment. Scanning and transmission electron microscopies, Raman spectroscopy and X-ray diffraction measurements have been carried out in order to investigate the catalyst and synthesized CNTs. The results show that iron nanoparticles are produced in an alumina and ball-milled graphite matrix. This produced nanocomposite is used as a catalyst to synthesize CNTs via CVD successfully. The yield of CNTs formation was greatly influenced by the milling time and deposition temperature.

Keywords. Iron catalyst; mechanochemical; chemical vapour deposition; carbon nanotubes.

1. Introduction

Single-wall and multi-wall carbon nanotubes (CNTs) are currently the subject of an intense research effort owing to the outstanding properties that they may possess. Many methods have been used to produce CNTs, but they mainly fall into the main categories such as arc discharge in the absence or presence of metal (Journet *et al* 1997), laser vapourization of a metal–graphite composite target (Thess *et al* 1996), carbon monoxide disproportionation on a metal catalyst and hydrocarbon pyrolysis (Dai 2002; Magrez *et al* 2010), using a metal nanocatalyst (Laurent *et al* 1998). Indeed, in many mentioned synthesis methods, fabrication of CNTs need nanometric metal particles (Laurent *et al* 1998). Transition metals (Fe, Co, Ni, etc) are used as catalysts, which provide both nucleation and growth sites for CNTs (Yunyu *et al* 2007; Paul and Samdarshi 2011). It has been found that the catalyst plays an important role in the rate of growth, purity and structural properties of the resulting nanotubes (Alexiadisa and Verykiosa 2009). In this case, Rummeli *et al* (2007), for example, showed that both the diameter and number of walls of the resultant CNTs increase proportionally to the size of the catalyst particle. Also, Jianwei *et al* (2005), through using the layer-by-layer assembly

method, fabricated catalyst particles of a controlled size distribution for CNT growth and showed a reasonably graphitized structure with an outer diameter of 15 nm. Formation of non-selective forms of carbon was also observed by Perez-Cabero *et al* (2003) with the iron–silica catalysts with higher iron content. They explained this result by the fact that the degree to which metallic iron aggregates upon reduction into metallic particles depends on the iron content. Thus, catalysts with higher iron content exhibit larger metallic iron particles, leading to other forms of carbon than nanotubes.

It is worth noting that the catalyst particle size is an important factor in CNT growth and catalysts with large particle sizes have been claimed to be ineffective (Nerushev *et al* 2003; Ajayan 2004). The increase of mean crystallite size led to a decrease of the surface area. Lower surface area, more effective encapsulation with carbon, resulted in a decrease of number of free active sites for hydrocarbon decomposition (Narkiewicz *et al* 2010). The graphene shell at the surface of the particle immediately deactivates their catalytic role by inhibiting incorporation of the carbon species from the carbonaceous gas and stops nucleation and growth from the particle (Parka *et al* 2002). A crucial point is to control the synthesis of metal particles with desired sizes that are stable at the high temperatures required for the CNT formation (Yu *et al* 2005). Various processing routes have been developed for the synthesis and commercial

*Author for correspondence (ebrahimzk88@gmail.com)

production of nanocatalysts. The most usual methods to prepare nanocatalysts are mechanical milling (Muñoz *et al* 2007), impregnation (Takenaka *et al* 2003), co-precipitation (Narkiewicz *et al* 2007) and sol-gel (Luisetto *et al* 2008). Among these methods, mechanochemical synthesis, that is, chemical reactions induced by high-energy ball milling (HEBM), is a well-known method for fabrication of novel materials such as nanocomposites. High-energy ball milling can enhance the kinetics of reactions of components and results to induce chemical reactions in powder mixtures at lower temperatures or even at room temperature. This technique can lead to the formation of interpenetrating phase composites with nanosized microstructures. One of the most important specifications of such phases is better performance rather than that of conventional microcrystalline counterparts (Suryanarayana 2001). In fact, in mechanochemical approach, the nanostructured crystalline will be produced by the structural decomposition of coarser-grained structures as the result of severe plastic deformation during HEBM. This has become a popular method to make nanocrystalline materials because of its simplicity, the relative inexpensive equipment and the applicability to essentially all classes of materials. In the past decades, mechanochemical approach has been successfully applied to the synthesis of ultrafine metals (Ding *et al* 1995).

Based on a literature survey done by the authors, using mechanochemical process for fabrication of catalysts needed for CNTs growth has not received much attention. For example, Ding *et al* (2004) used this method to make $\text{Al}_2\text{O}_3/\text{Fe}(\text{Co}, \text{Ni})$ nanocomposites for MWCNTs and SWCNTs growth. Liu *et al* (2006) synthesized MgO/Fe nanocomposite using ball milling. For this purpose, they mixed Mg and Fe_2O_3 along with Mg powder for 24 h. Using ball milling for production of metal oxide is very common. For example, Xiaomei *et al* (2003) produced aluminum hydroxide and iron oxide powders after 24 h milling to obtain nanocrystals of size ~ 20 nm. They used the material as a catalyst for preparing CNTs. Perhaps the most important limitation of the methods proposed by previous researchers is attributed to two or three steps of their processes. We believe that by our new method, nanocomposite catalyst can be produced in just one step, besides decreasing the milling time up to 15 min.

2. Methods

2.1 Materials

Commercially pure Al (purity more than 99%, $< 100 \mu\text{m}$), Fe_2O_3 (purity more than 99%, $< 100 \mu\text{m}$) and graphite (purity of 99.9%, $< 200 \mu\text{m}$) powders, all from Sigma-Aldrich Co., were used as raw materials in this study. SEM micrographs of the starting powders are shown in figure 1.

2.2 Catalyst synthesis

Several mixtures of iron oxide and aluminum powders along with 10 wt% of graphite powder were mechanically milled for different times. Experiments were conducted in a centrifugal planetary mill AGO-2S with two 150 mL steel barrels filled with 10 mm zirconium oxide balls. A 2 g sample of $\text{Al}-\text{Fe}_2\text{O}_3$ -10 wt% graphite mixture and 150 g balls was put in barrels. The molar ratio of Al to Fe_2O_3 was kept constant at 2 : 1, according to stoichiometry of thermite reaction (1):

Ball milling was carried out at a rotation speed of 1000 rpm under air atmosphere and the milling time was varied from 2.5 to 15 min. The vials were cooled by circulating water around them.

The adiabatic temperature and the heat released from exothermic reaction during milling can be controlled by varying the percentage of graphite (table 1). This is because the formation of Fe and Al_2O_3 from the reactants is a severely exothermic reaction. Here, only 10 wt% of graphite was selected.

2.3 CNTs synthesis

The synthesis of CNTs was carried out by a CVD method using nanocomposite powders obtained by ball milling ($\text{Fe}/\text{Al}_2\text{O}_3/\text{C}$) mentioned in detail before and the so-called catalyst. As much as 0.15 g of catalyst was spread over a ceramic boat and placed in a tubular reactor. Propane (C_3H_8) was used as the carbon source and carbonization was performed at a temperature range of 625–850 °C in $\text{Ar}-\text{C}_3\text{H}_8$ mixture for 30 min. Propane was introduced into the gas stream at a flow rate of 30 mL/min diluted with 200 mL/min argon carrier. After reaction, the system was cooled down to room temperature and the products were characterized by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). The effect of growth temperature on the formation yield of CNTs was also examined by carrying out the propane decomposition reaction at different temperatures, i.e. 625, 700 and 850 °C. The synthesized CNTs were cooled in Ar flow and the weight of the deposited CNTs was measured.

Table 1. Weight percent of graphite in mixture and related adiabatic temperatures.

Graphite (wt%)	Adiabatic temperature (K)
5	3130
10	2922
15	2741

Figure 1. SEM images of initial materials: Al (a), Fe_2O_3 (b) and graphite (c).

The yield of deposited carbon was calculated from the following equation:

$$\text{Yield} = ((W_2 - W_1)/W_1)100\%, \quad (2)$$

where W_1 is the initial weight of the catalyst (milled products) and W_2 the weight of carbon deposited and catalyst.

2.4 Instrumental techniques

SEM observations were performed using a Zeiss EVO 50XVP at an accelerating voltage of 15 kV. For SEM analysis, a thin layer of powder was spread over the conductive adhesive tape. For better conductivity, a thin layer of gold (~10 nm) was deposited on the surface. The TEM analyses were carried out with a Tecnai 20 G2 model of FEI at an operating voltage of 200 kV. The obtained samples were dispersed ultrasonically in ethanol. A drop of the dispersed suspension was placed on a microgrid coated with thin layer of amorphous carbon and dried in air before fitting into the TEM apparatus. X-ray diffraction analysis performed by an ARL X'TRA advanced apparatus, using $\text{CuK}\alpha$ radiation. TGA was performed using a NETZSCH STA 449 C at a heating rate of 10 °C/min to warm the samples from room temperature up to 900 °C in a mixture of argon (20 mL/min) and

oxygen (10 mL/min) atmosphere. A Raman spectrometer (T64000 Horiba Jobin Yvon) was also used to identify the crystallinity of CNTs. The 514-nm line of an Ar-Kr laser was used for excitation. For purification, 1 g of synthesized CNTs was refluxed in 150 mL of concentrated nitric acid for 4 h. After refluxing, the mixture was cooled to room temperature, diluted with distilled water, and filtered through a 1.2 μm pore-sized membrane. The product on the membrane was washed thoroughly with distilled water and dried at oven (at 80 °C) overnight.

3. Results and discussion

3.1 XRD analysis

Figure 2 shows the XRD patterns of milled powder mixture containing Al- Fe_2O_3 -10% graphite after different milling times. The XRD pattern of powder mixture up to 2.5 min of milling time was identified as a mixture of iron oxide (Fe_2O_3) and aluminum. It means that this time is not enough for having a mechanical induced reaction and ball milling up to 2.5 min had no effect on as-received powder mixture except for the broadening of Bragg peaks, which is caused by reduction of the crystallite size as well as microstrain appeared in the powder particles (Fecht 1995). Perhaps the main reason for lack of reaction can be attributed to the kinetic. Indeed, decreasing particle

Figure 2. XRD patterns of mechanically-alloyed Al-Fe₂O₃-10% graphite powders after different times.

Figure 3. Scanning electron microscopy images in different magnifications showing the weblike net of carbon nanotube bundles covering the Fe-Al₂O₃-C grains.

size due to increasing milling time make a new condition for kinetic reactions. As a matter of fact, reducing the crystallite size to nanometer range and increasing the defect densities can promote the reaction kinetically by

providing short-circuit diffusion paths (Sheng *et al* 2002). Thus, one may conclude that increasing milling time for more than 2.5 min will cause to make a new phase such as Al₂O₃. Appearing of Al₂O₃ due to milling up to 5 min

Figure 4. SEM micrographs of CNTs synthesized at different temperatures.

is shown in figure 2, implying that the oxidation/reduction reaction has been induced by mechanochemical route. Consequently, during ball milling of Fe_2O_3 and Al, reaction (1) takes place and can be further promoted by the dynamically maintained high reaction interface areas, as well as the short-circuit diffusion path provided by the large number of defects such as dislocations and grain boundaries induced during ball milling (Sharifi *et al* 2009). The intensities of the peaks corresponding to alumina crystals decrease remarkably and have been disappeared as milling time increased up to 10 min. The formation of nanocrystalline materials during mechanical milling of ceramics or metallic powders is attributed to the intense cold working on the ball-milled powders. This leads to a dramatic increase in the number of imperfections (e.g., point and lattice defects), which leads to decrease in the thermodynamic stability of the starting materials (amorphization) (Eskandarany 2001). Therefore, the alumina peak could not appear in the spectrum and it means that it becomes amorphous or even nanocrystalline. With increasing milling time, the other interstitial compound (Fe_3C) appeared as well as AlFe_3 compound, while the intensity of iron peaks decreased slightly. This shows that continuing milling time may lead to formation of different intermetallic compounds. The lack of carbon peaks on XRD patterns is related to the lower intensity of carbon peaks compared with other materials.

3.2 SEM observation

Figure 3 shows the SEM images of a typical sample of carbon nanotubes with different lengths grown on mechanochemical products. The produced carbon nanotubes appear as spaghetti with disorder and random shape. Fabrication of CNTs due to mechanochemical method proves that the milled products (Fe) play as catalysts. This is because CNTs need a catalyst for nucleating and growing particularly in CVD method. Also, it is obvious that the large quantity of carbon nanotubes were achieved by

Figure 5. Yield of CNTs for samples milled at different times.

using this approach. As seen in the micrographs, each CNT nucleated and grew from a catalyst and since the quantity of Fe is much higher, the yield of CNTs formation can be high as well. So, this demonstrates that the mechanochemical method is a promising technique for the production of CNTs growth catalysts. In figure 4, it can be seen that the diameter of CNTs increases with increase in the annealing temperature.

The yield of CNTs is shown in figure 5. As it can be seen that the carbon yield increased with increase in milling time up to 10 min. The yield of CNTs formation at annealing temperature of 625 °C is low because of negligible decomposition of propane. The maximum value (490%) is related to a sample that milled for 10 min and annealed at 700 °C for 30 min. At longer milling times, the carbon yield decreased due to the decrease in catalytic activity. This seems to be related to producing cementite (Fe_3C), which consumes some amount of iron catalyst. For higher growth temperatures, the average size of the active catalytic particles increases due to coalescence. The yield of CNTs initially increases with the annealing temperature (from 625 to 700 °C) and then decreases at higher temperature (850 °C). By looking into more details on figure 5, it can be concluded that 700 °C is an optimum temperature for achieving the highest yield. This trend is similar to that found by Cui *et al* (2000) and Ducati

Figure 6. TEM micrographs showing the (a) as-grown CNTs synthesized by CVD at 700 °C over Fe/Al₂O₃/C catalyst and (b, c) nanoparticle at the tip of CNT and related analysis.

et al (2002). Perhaps the main reason of this variation is related to both hydrocarbon decomposition rate and grain-size growth as temperature increases. Indeed, the lower yield of CNTs at low temperature (lower than 700 °C) is due to the activation barrier for the surface-bulk penetration of carbon atoms at the catalyst particles (Juang *et al* 2004; Zhang *et al* 2008). The worse condition is whenever the temperature is higher than 700 °C. In this case, decreasing the yield of CNTs formation is referred to hydrocarbon decomposition rate. It leads to increase in the carbon supply rate, which results in exceeding the carbon diffusion rate. On the other hand, at high reaction temperatures, the decomposition rate of hydrocarbons is faster than the diffusion rate of carbon atoms, and, therefore, the catalyst can be encapsulated by excess carbon atoms and can deactivate. Finally, the carbon produced due to decomposition will accumulate on the catalysts and prevent their role in CNTs formation. In summary, the yield of CNTs depends on both hydrocarbon decomposition rate and carbon diffusion rate. At high temperature (>700 °C), the dominant mechanism is decomposition rate, while at lower temperature (<700 °C), the rate of diffusion is much higher than that of decomposition rate (Juang *et al* 2004).

3.3 TEM analysis

Figure 6 displays TEM micrographs of the as-grown CNT sample, which has been fabricated over Fe/Al₂O₃/C catalyst. From figure 6, it is evident that many CNTs are entangled with each other. As is shown with arrows (figure 6(a)), there are carbon nanotubes with different diameters ranging between 10 and 50 nm. Based on the TEM-EDX data, almost all the metal tips of the nanotubes formed on the particles were iron (Fe). Figure 6(b and c) demonstrate an iron nanoparticle at the tip of CNT. Therefore, it can be speculated that the growth mechanism of

carbon nanotubes is tip growth (Dupuis 2005). Indeed, in the tip growth model, the metal catalyst particle might remove from the surface and move at the top of the growing carbon nanotube. The interaction between the catalyst particle and support is stronger at base-growth mechanism than tip-growth mechanism. So catalyst particle remains attached to the support (Dupuis 2005).

3.4 Raman spectroscopy

Raman spectroscopy probes the lattice vibrations of ordered carbon materials and is, therefore, extremely sensitive to the graphitic character of these structures. Thus, Raman spectroscopy is widely employed for the characterization of carbon samples, and in particular for carbon nanomaterials like nanofibers and nanotubes (Tessonier *et al* 2009). The Raman spectra of CNT synthesized from 5 and 15 min milled powders are illustrated in figure 7(a and b), respectively. The centered peak at ~1330 cm⁻¹ is related to the band D, caused by the defects in the structure of the sp² carbon and can be due to the lattice defects in the graphite sheet that make up CNTs. Also, this band indicates deposition of amorphous carbon, or nanotubes with large diameters, or even nanofibers, which have more defects than nanotubes (Bonadiman *et al* 2006). The peak at around 1580 cm⁻¹ is related to the band G, which is generated by the tangential modes of vibration of carbon sp². Actually, it is intensified by the presence of nanotubes of small diameter, which have few defects, and demonstrates the presence of crystalline graphitic carbon (Bonadiman *et al* 2006). The ratio between the heights of the peaks D/G is 0.578 for 5 min and 0.676 for 15 min milled powders. It indicates that the degree of long-range ordered crystalline perfection of the CNTs grown using 5-min milled powder is higher than that of CNTs grown using 15-min milled powders. The lower frequencies, between 100 and 250 cm⁻¹, are denominated radial

breathing mode (RBM). Peaks in this band are detected only when SWCNT and DWCNT are present (Maschmann *et al* 2006). In our case, it seems that there are some amounts of these types of carbon, but because of low quantity we could not detect them.

3.5 Purification

Carbon nanotubes are usually contaminated with metal catalysts, amorphous carbon and graphitic nanoparticles and the presence of these impurities has hindered their

application. A large number of purification methods have been reported, but refluxing nitric acid has probably been the treatment that has been employed most often, at least as the initial step in purification (Hu *et al* 2003). The major function of nitric acid treatment is to remove metal catalysts, perhaps together with some of the amorphous carbon. Figure 8 shows the TGA analyses of the CNTs synthesized from 10-min milled powder and nitric acid-treated products. The weight loss curves directly reflect the occurrence of burning of carbon nanotubes. As it can be seen, the onset of burning is around 520 °C for both the samples. However, in the TGA curve of the nitric acid-treated products, the residual is lower than the non-purified sample. This amount is related to the amorphous carbon and iron catalyst, which were dissolved.

Figure 7. Raman spectra of CNTs synthesized using (a) 5-min and (b) 15-min milled powders.

Figure 8. TGA curves of CNTs synthesized using 10 min milled powder before and after purification.

4. Conclusions

In the current research, the authors present a new method for fabrication Fe nanocatalysts for synthesizing carbon nanotubes. For this purpose, aluminum/iron oxide/graphite mixtures were milled. The results remarked as follows:

- (I) Since the nanocomposite is attained after a short milling time (15 min), the process is claimed as an energy-saving process.
- (II) The produced nanocomposite included with iron nanoparticles in an alumina and ball-milled graphite.
- (III) The produced nanocomposite used as a catalyst to synthesize carbon nanotubes via chemical vapour deposition successfully.
- (IV) The CNTs were grown according to tip-growth mechanism.

Acknowledgements

The authors thank Dr S Veselov and Novosibirsk State Technical University for their support with various microscopy and XRD facilities. Valuable discussions with Prof Anatholy Bataev are gratefully acknowledged.

References

- Ajayan P M 2004 *Nature* **427** 402
- Alexiadisa V I and Verykiosa X E 2009 *Mater. Chem. Phys.* **117** 528
- Bonadiman R, Lima M D, Andrade M J and Bergmann C P 2006 *J. Mater. Sci.* **41** 7288
- Cui H, Zhou O and Stoner B R 2000 *J. Appl. Phys.* **88** 6072
- Dai H 2002 *Acc. Chem. Res.* **35** 1035
- Ding J, Miao W F, McCormick P G and Street R 1995 *Appl. Phys. Lett.* **67** 3804
- Ding J, Liu B H, Dong Z L, Zhong Z Y, Lin J Y and White T 2004 *Compos.* **B35** 103
- Ducati C, Alexandrou I, Chhowalla M, Amaratunga G A J and Robertson J 2002 *J. Appl. Phys.* **92** 3299
- Dupuis A C 2005 *Prog. Mater. Sci.* **50** 929

- Eskandarany M S E 2001 *Mechanical alloying for fabrication of advanced engineering materials* (New York: Noyes Publications/William Andrew Publishing) p. 37
- Fecht H J 1995 *NanoStruct. Mater.* **6** 33
- Hu H, Zhao B, Itkis M E and Haddon R C 2003 *J. Phys. Chem.* **B107** 13838
- Jianwei L, Xiaojun L, Amanda S, Toshiyuki O and Liming D 2005 *Chem. Mater.* **17** 6599
- Journet C, Maser W K, Bernier P, Loiseau A, de la Chapelle M L, Lefrant S, Deniard P, Lee R and Fischer J E 1997 *Nature* **388** 756
- Juang Z Y, Chien I P, Lai J F, Lai T S and Tsai C H 2004 *Diam. Relat. Mater.* **13** 1203
- Laurent C, Flahaut E, Peigney A and Rousset A 1998 *New J. Chem.* **22** 1229
- Liu B H, Ding J, Dong Z L, Zhong Z Y, Lin J Y and White T 2006 *Solid State Phenom.* **111** 183
- Luisetto I, Pepe F and Bemporad E 2008 *J. Nanopart. Res.* **10** 59
- Magrez A, Seo J W, Smajda R, Mionić M and Forró L 2010 *Mater.* **3** 4871
- Maschmann M T, Amama P B, Goyal A, Iqbal Z, Gat R and Fisher T S 2006 *Carbon* **44** 10
- Muñoz J, Cervantes J, Esparza R and Rosas G 2007 *J. Nanopart. Res.* **9** 945
- Narkiewicz U, Podsiadły M, Jedrzejewski R and Pelech I 2010 *Appl. Catal. A-Gen.* **384** 27
- Narkiewicz U, Podsiadły M, Arabczyk W, Wozniak M J and Kurzydłowski K J 2007 *Mater. Sci. Eng.* **C27** 1273
- Nerushev O A, Dittmar S, Morjan R E, Rohmund F and Campbell E E B 2003 *J. Appl. Phys.* **93** 4185
- Parka J B, Choia G S, Choa Y S, Honga S Y, Kima D, Choib S Y, Leeb J H and Cho K I 2002 *J. Cryst. Growth* **244** 211
- Paul S and Samdarshi S K 2011 *New Carbon Mater* **26** 85
- Perez-Cabero M, Rodriguez-Ramos I and Guerrero-Ruiz A 2003 *J. Catal.* **215** 305
- Rümmeli M H, Kramberger C, Schäffel F, Borowiak-Palen E, Gemming T, Rellinghaus B, Jost O, Löffler M, Ayala P, Pichler T and Kalenczuk R J 2007 *Phys. Status Solidi (B)* **244** 3911
- Sharifi E M, Karimzadeh F and Enayati M H 2009 *J. Alloys Compd.* **482** 110
- Sheng Y, Yonghe L and Hoyi L 2002 *Key Eng. Mater.* **217** 9
- Suryanarayana C 2001 *Prog. Mater. Sci.* **46** 1
- Takenaka S, Kobayashi S, Ogiwara H and Otsuka K 2003 *J. Catal.* **217** 79
- Tessonnier J P, Rosenthal D, Hansen T W, Hessl C, Schuster M E, Blume R, Girgsdies F, Pfander N, Timpe O, Su D S and Schlogl R 2009 *Carbon* **47** 1779
- Thess A et al 1996 *Science* **273** 483
- Xiaomei G, Jifa Q and Kenji S 2003 *Scr. Mater.* **48** 1185
- Yu Z, Chen D, Totdal B and Holmen A 2005 *Catal. Today* **100** 261
- Yunyu W, Zhiquan L, Bin L, Paul S H, Zhen Y, Li S, Eugene N B and Robert J N 2007 *J. Appl. Phys.* **101** 124310
- Zhang C, Pisana S, Wirth C T, Parvez A, Ducati C, Hofmann S and Robertson J 2008 *Diam. Relat. Mater.* **17** 1447