The influence of substrate grain size on carbon nanotube growth

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Effect of grain size on the formation of carbon nanotubes (CNTs) is investigated. As a basic metallurgical parameter, grain size insinuates the proportion of grain boundary to the entire materials. 99.9%wt Ni substrates with four different grain sizes were prepared by typical thermomechanical treatment. CNTs were synthesized on polished Ni surfaces by chemical vapor deposition process (CVD) at 600°C, using ethanol as a carbon gaseous source and argon as a carrier gas. Under scanning electron microscopy, it was found that specimen with smaller grain size was prone to yield denser CNTs bundles. This may substantiate a hypothesis that the planar defects, namely grain boundary, could act as the major nucleation sites for CNTs growth. However, Raman spectrum indicated the independency of CNTs purity on substrate grain size.

Key words: Carbon nanotube, Grain size, Nickel, Ethanol, Chemical vapor deposition

Introduction

Despite the fact that the synthesis of carbon nanotubes (CNTs) may date back more than half a century by carbon materials scientist community but unknown to them until the advent of transmission electron microscope when hollow structure was revealed and published by *Radushkevich et al.* in 1952, the major achievement took place in 1991 when single-wall carbon nanotubes were synthesized by *Iijima et al.* and simultaneously by *Bethune et al.* [1]. Since then national laboratories worldwide have directed themselves into the realm of Nanotechnology and Nanoscience. Soon after, unique property of CNTs has been explored leading to countless applications as field emission-base devices [2], chemical sensors [3], electrodes for supercapacitors [4], nanoelectronic devices [5], nanocomposite strengtheners [6, 7], etc.

CNT, a single molecule of bended sp^2 hybridization carbon atoms, is an allotropic phase of carbon formed when 1) no O_2 environment 2) high enough temperature and 3) suitable catalysts. It is easy to imagine single-wall (SWNT) and multi-wall (MWNT) carbon nanotubes by rolling single or multiple graphene sheets into tubular morphology. For SWNT, typical diameter is in the range of 0.4-2.5 nm but energetically favorable at 1.4 nm[8].

Among a variety of recent CNTs manufacturing methods, arc discharge and laser ablation processes, using graphite rods containing catalyst particles as a solid carbon source, can produce selective CNTs with less structural defects than other methods. However, high purified CNTs have no use if there is no way to assemble them into a practical structure. The two-fold advantages are gained by using Catalyst Chemical Vapor Deposition (CCVD) methods whereby not only CNTs can be synthesized but they can also arrange themselves onto patterned substrates. Such the structure is suitable for fabricating a superior field emitter tip in X-ray sources and an electrode in supercapacitors. Nevertheless, electrical contact and sound mechanical bonding of CNTs to metallic substrate is prerequisite. This couldn't attainable without sophisticate and laborious task. In searching for more effective route, some research group runs into studying to grow CNTs directly on metallic substrate without deposition of transition metallic catalysts (Fe, Ni, Co, Mo, and their alloys). The study of Nickel [9-12] and SS304 [13] as bulk catalyst materials has been reported. Still, some basic metallurgical parameters are overlooked.

In this work, we study the impact of grain sizes of bulk catalyst Ni on the formation of CNTs. Ni with purity 99.9 wt% of grade N1000 is chosen otherwise the complicate interference of alloys and precipitate particles. Using ethanol alcohol as gaseous carbon source with Ar as the carrier gas can synthesize CNT at lower reaction temperature it promises a scalable production at lower cost. Consequently, we follow the method

here, the same process as in our previous works [9, 10]. Finally, quantitative and qualitative results are interpreted from electron micrograph and Raman spectra.

Experimental

Nickel of grade N1000 (99.9 wt% Ni) conforming to ASTM B39-79 was used as active catalytic substrates. Table 1 shows N1000 major chemical composition. Four different grain sizes were prepared by metallurgical heat treatment on the bulk materials. Their surfaces were mechanically ground and polished until the final step at 1 µm diamond suspension. They then were ultrasonically degreased in acetone for 30 seconds and blown dried in jet air. All specimens were placed at the end of heating zone inside a tube furnace (Fig.1).

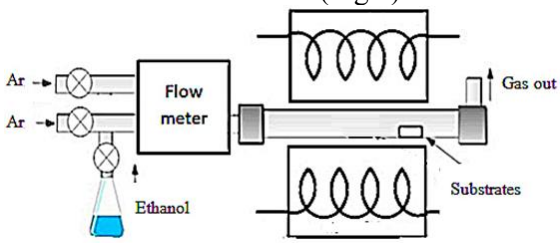


Fig.1 Schematic diagram of tube furnace reactor with gas flow controller for CNTs growth.

To prevent the oxidation, Ar gas flow rate was kept at 500 sccm while heating the samples up from room temperature to 600°C. The samples were left at this temperature for 10 min to attain a uniform temperature before commencing CVD process by feeding Ar gas through a liquid ethanol containing flask heated at about 80°C on a hot plate. Ar flow rate at 1000 sccm is chosen to convey the ethanol vapor inside to the reactor. After a predetermined reaction time of 20 min, the supply of ethanol vapor stopped and the system was allowed to cool down to 300°C under 500 sccm Ar flow and from 300°C to room temperature in still air. Fig.2 shows the time-temperature diagram. The specimen yielding the densest CNTs out of three was selected for further analysis of time evolution by stopping dwelling time at 5 and 10 minutes. The morphology and purity of the synthesized CNTs were assessed by a field-emission scanning electron microscope (FE-SEM; Hitachi model S-4700) and by Raman spectra (Perkin Elmer model Spectrum GX) with laser at 1064 nm, respectively.

Table1 N1000 major chemical composition (wt%)

Ni	Co	Fe	Cu	Cr	S	C	Sb
99.9	0.0396	0.0002	0.0005	0.0008	0.0017	0.0009	0.0004

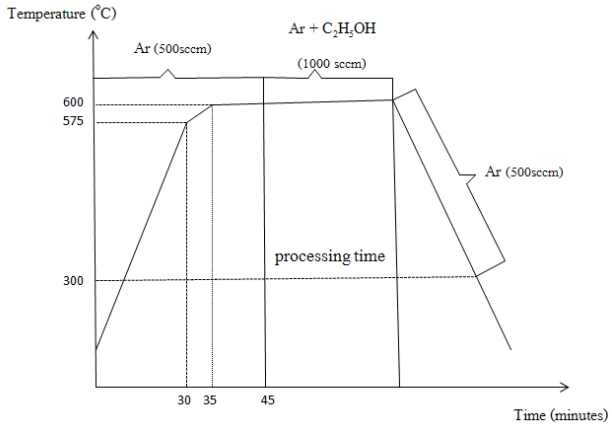
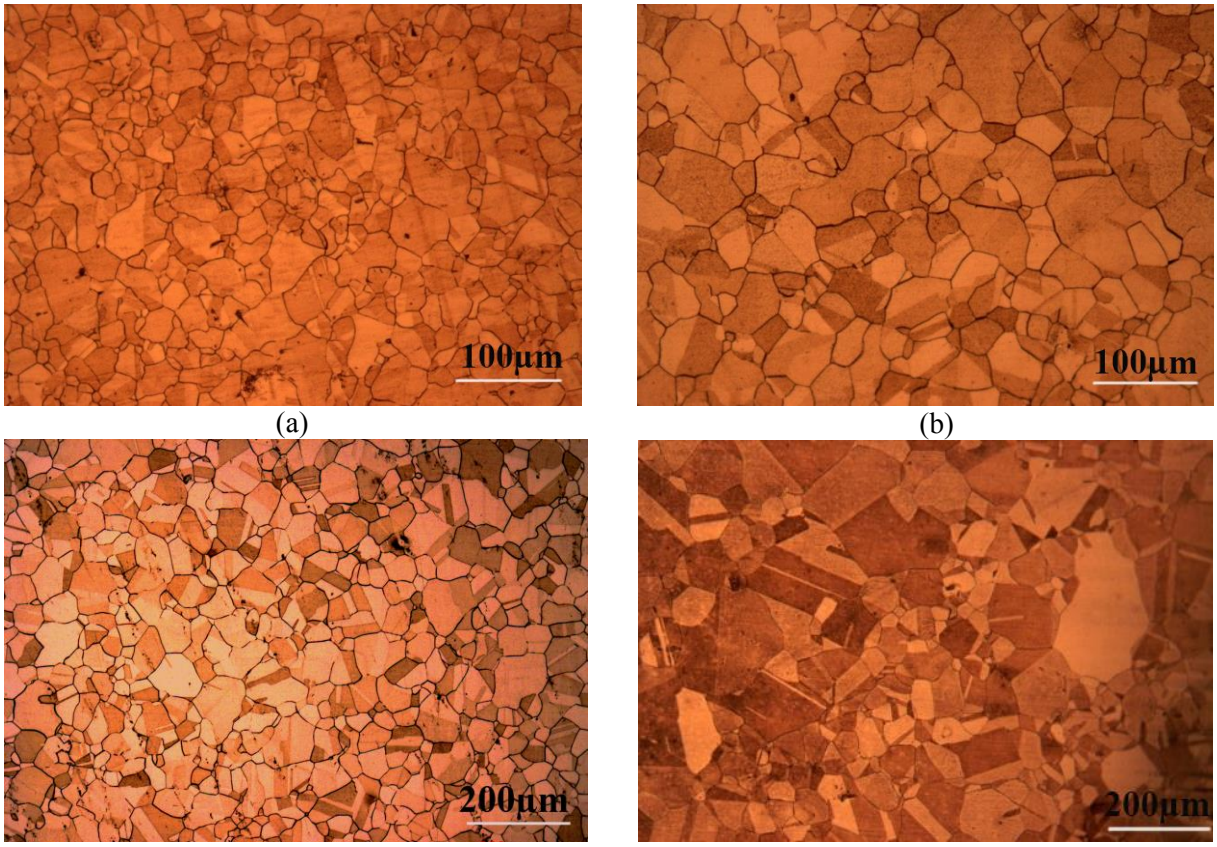


Fig.2 CVD processing time-temperature diagram.

Results and discussions

Light optical micrographs revealed grain structure of the Ni substrates (Fig.3). By linear intercept method, average grain size of sample No.1, 2, 3, 4 were 31, 39, 57 and 82.5 µm, respectively. Fig 4a-h shows the SEM images of synthesized CNT on each substrate under the same CVD process parameters at 600°C for 20 min. It is evidence that less CNTs and CNFs were generated on the substrate with larger grain size (Fig. 4.e-h). This result suggests that the density of CNTs reduces as substrate grain size becomes larger.

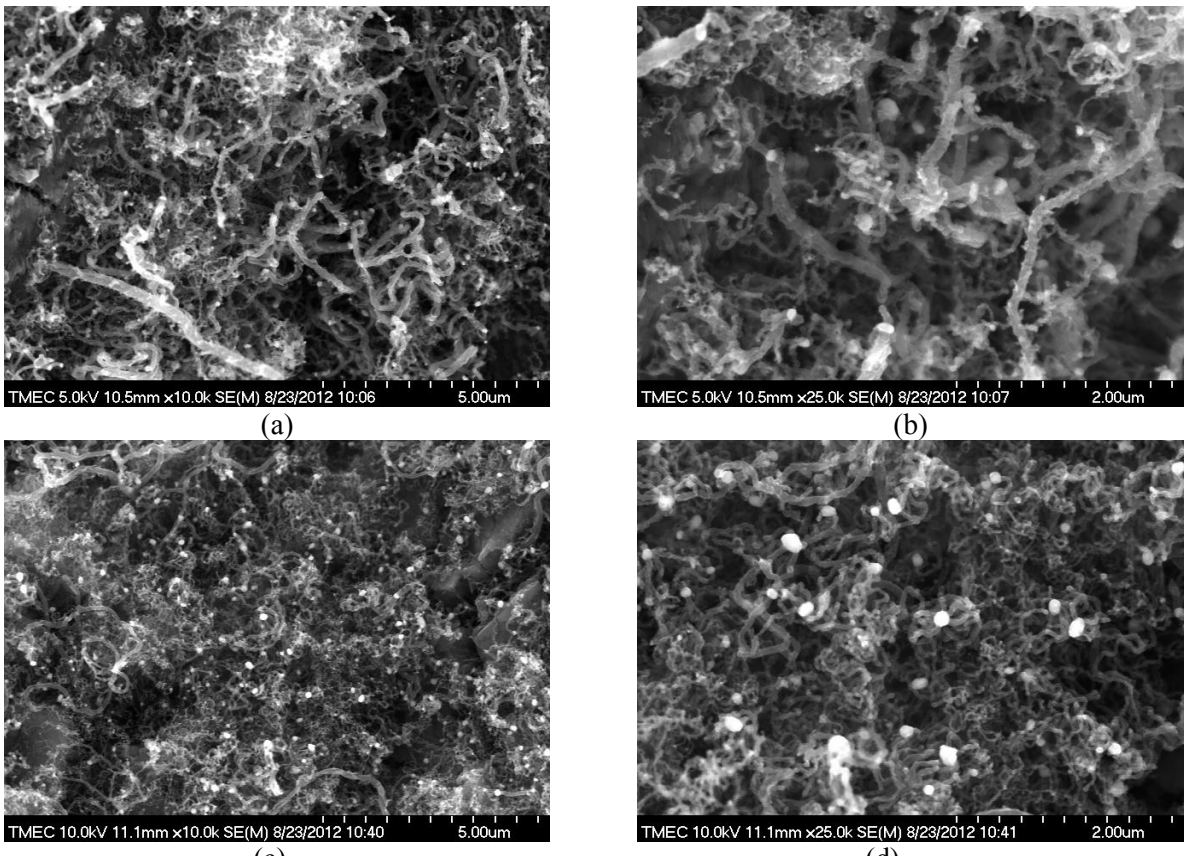
Due to the fact that grain boundary acts as the active nucleation sites for CNTs is evident from the works of *C. Du and N. Pan* [14] on Ni grid substrate and *L. Huang et al.* [15] on Si coated by Fe-N film, the consequent result is reported here that smaller grain size, i.e. sample No.1, yield denser CNT forest. Grain boundary (GB) may be defined as interfacial area between misoriented adjacent crystals. Atomic misfit at GB increases its energy higher than perfect lattices. Such the open site makes it prone to chemical reaction; thus, suitable for CNTs to nucleate. The smaller the grain size means the higher contribution of the grain boundary area to the system. That provides more active areas for decomposition of carbon from gaseous carbon source. Interestingly, the GB thickness is 0.5-1 nm [16] which is comparable of CNTs' diameter. As noticed in Fig. 4.b, d, g, i , some CNTs actually grew on CNF instead of Ni substrate. This means too long processing time.



(a) (b)

(c) (d)

Fig. 3 Light optical micrograph of Ni substrates (a) sample No.1 (b) sample No.2 (c) sample No.3(d) sample No.4



(a) (b)

(c) (d)

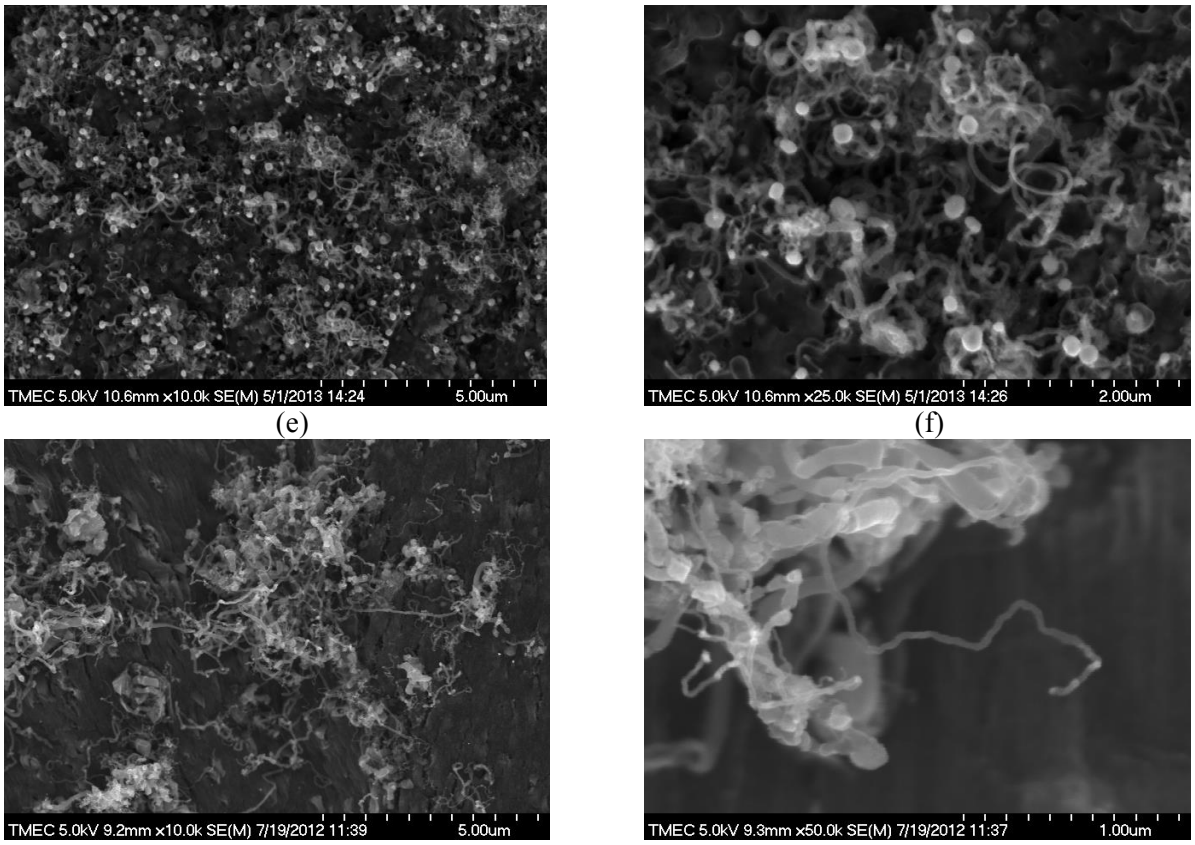


Fig.4 SEM images of carbon nanofibers and CNTs growth at 600^{o}C using different grain size of Ni substrates No.1 (a-b) No.2 (c-d) No.3(e-f),No.4 (g-h).

Raman spectra of CNTs grown on different grain size of Ni substrates are shown in Fig. 5. The D-band peak represents the extent of disorder in the sp^2 arrangement of carbon atoms. The G-band peak corresponds to the vibration of carbon atoms in the sp^2 graphite sheet. The intensity ratio of G-band to D-band (I_G/I_D) was measured to estimate the purity of nanotubes [17]. The Raman spectra showed the D-band peak around 1276-1283 cm^{-1} and the G-band peak at about 1589-1591 cm^{-1}. The I_G/I_D ratios are not much different, this indicates the purity of CNTs do not depend on the grain size of Ni substrates.

Whether the dense CNTs growth on small grain substrate is as a result of more nucleation sites or faster nucleation rate, it is worth further investigating for time evolution of the process. Fig 6 demonstrates SEM images of CNT grown on Ni substrates at 600^{o}C using different processing times. Fig.6 a, c show the size of the white regions increased as the ethanol flow time is increased while Fig 6e shows large amount of CNFs and CNTs was grown on substrate by CVD at 600^{o}C for 20 min. We notice that white line structure resembles to grain structure of as-received Ni. It is undetermined to us whether it is just coincident event or a profound theoretical background. However, the deposited carbon layer on Ni surface became smoother as ethanol flow time progressed (Fig. 6b,d,f).

Fig.6b found that the Ni surface is completely covered with deposited carbon where CNTs grown in bundles of curled CNTs. When the sublayer settled the growth of CNTs occurred really fast at sometimes during 10-20 minutes (Fig.6c,e). Raman spectra of CNTs at different growth time is shown in Fig.7. I_G/I_D ratio increases with time meaning that the purity of CNT is gradually improved.

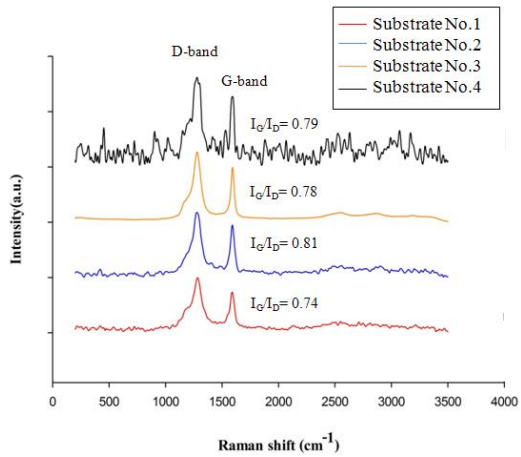


Fig.5 Raman spectra of CNT grown at different grain size of substrates

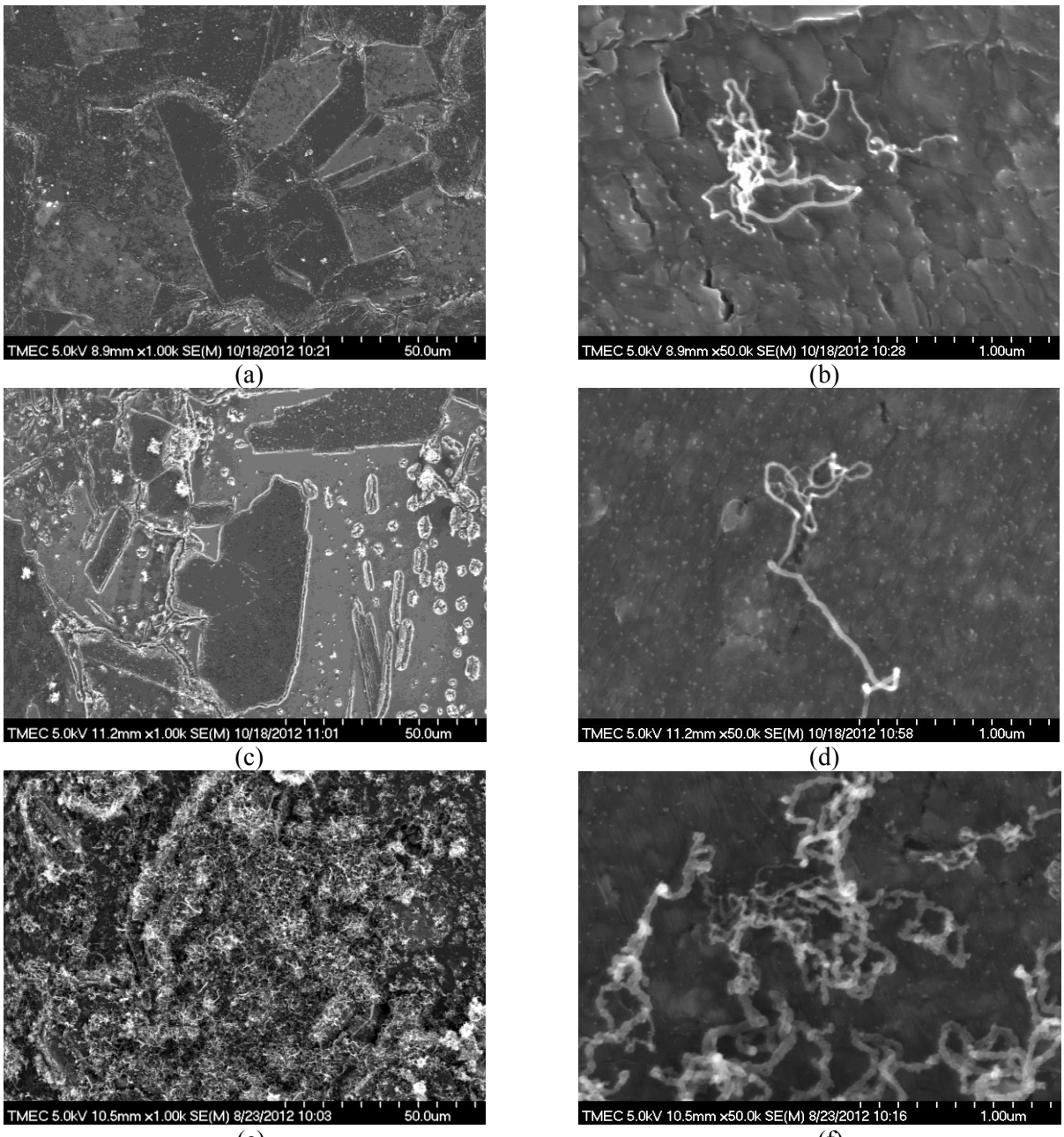


Fig. 6 SEM images of CNTs grown on substrates No.1 at 600°C (a,b) 5min (c,d) 10 min (e,f) 20min.

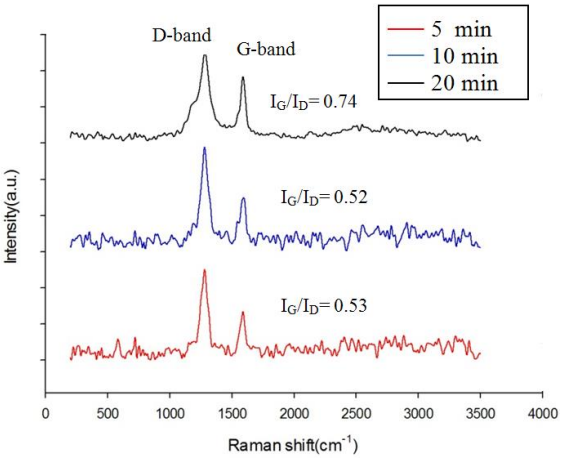


Fig.7 Raman spectra of CNT grown at different growth time ranges

Conclusion

We have grown carbon nanotubes on Ni substrates with four different grain sizes by CVD at 600°C. The effect of grain size and ethanol flow time on the formation of CNTs is investigated. It was found that densely packed carbon nanotubes and carbon nanofibers on the substrate are best at small grain size but the purity of CNTs isn't. The ethanol flow time is a significantly parameter for the growth of CNTs and the dissociation of carbon atom on Ni surface.

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