The effect of CSL boundary on Carbon Nanostructure Synthesis

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Keywords: Carbon nanotubes, Coincidence site lattice, Nickel, Chemical vapor deposition

The effect of surface crystallographic orientation on the formation of carbon nanotubes was investigated. Chemical vapor deposition (CVD), having ethanol as carbon source under the atmospheric pressure in argon, was the method to synthesize carbon nanotubes (CNTs) directly on Ni substrates of grade N1000. The substrates were first grain boundary engineered to achieve two different proportions of ∑3-∑27 CSLBs at 45% for H-CSL and 25% for L-CSL samples. EBSD technique was used to evaluate the proportion. The analysis of synthesized products revealed a good accumulation of carbon as well as the growth CNTs within the early 10 minutes on the H-CSL specimen. There was also a discovery of CNTs on the substrate within merely 1 minute of the synthesis time. The different factors of the proportion of CSLs which collectively represented surface crystal orientation other than surface texture could affect the role of Ni substrate to the decomposition rate of carbon containing gas or the absorption rate of decomposed carbon atoms; thus, controlled the kinetics of CNT formation.

Introduction

Since the visually proofs of carbon nanotubes (CNTs) in 1991 [1], there had existed increasing eagerness in Nanotechnology to apply their later found superior properties to real life applications. The unique characteristics include mechanical properties (tolerance against strain, stress and possesses high modulus), chemical properties, and electronical properties (high conductivity) and that qualify CNTs ideal materials for high performance filed emission-substrate devices [2], chemical sensors [3], nanoelectronic devices [4], electrodes for supercapacitors [5], nanocomposite strengtheners [6] etc.

Nevertheless, the production of CNTs themselves is as challenging as assembling them into usable equipment. Ideal electrodes for supercapacitor application require electrical conduction and the mechanical strength between carbon nanotube and the substrate. Among the present synthesis methods of CNTs [7], only Chemical Vapor Deposition (CVD) offers such the potential in two fold benefits. Not only carbon nanotubes could be synthesized but also simultaneously grown directly onto conductive substrates. Still low purity and less selective products retard the progression. As such, certain researches aim on the direct synthesis of carbon nanotubes on metallic substrates. Surface condition is among the process parameters in CVD. Parameters could be classified by components they involve 1) carbon sources including gas type, mixing ratio, gas flow rate, initial temperature, 2) substrates including catalyst type, chemical composition, surface condition, 3) environment including process temperature and pressure.

Recent aspects of the studying of surface reactivity are metallurgy, texture, and atomic. In the previous researches [10] of a synthesis of carbon nanotube using ethanol on nickel grade N1000, it indicated that the structure of grain and grain boundary did influence the synthesis of carbon nanotubes. Intergranular area promoted chemical decomposition growth before subsequent inward into the grains or even the other ways around. Both mechanisms yielded the same conclusion of the faster reaction rate for the small grain size substrates. Sequential study therefore aimed to study effect of CSLBs towards the growth. of carbon nanotubes using the method of chemical vapor deposition on Nickel grade N1000, which has different proportions of CSLBs, albeit with similar size of grains. The research was to study the effect of CSLBs has towards the growth of carbon nanotubes, using ethanol vapor to be the source of carbon combined with argon gas. The growth of carbon nanotubes is investigated by field-emission scanning electron microscope. The CSLBs and crystal orientation of the substrate were analyzed with EBSD technique installed in the scanning electron microscope.

Experimental

Thermo-mechanical processing, namely grain boundary engineering (GBE), was applied to specimens originating from as-received Ni electrodes of grade N1000 (99.9 wt.% Ni). Our previous works of the GBE on the substrates [11] yielded 2 separated groups according to the proportion of the CSLBs. The first being the substrate with the high proportion of the special grain boundary (H-CSL); there were 4 samples prepared by the grain boundary engineering method mentioned previously work [11]. The preparation could be concluded as follows.

1) The preparation of Nickel substrate

This experiment used the substrate which is a nickel substrate grade N1000, there were 8 samples in total. The chemical components are shown in Table 1. The substrate were Separated according to the proportion of the CSLBs into 2 groups. The first being the substrate with the high proportion of the special grain boundary (H-CSL); there were 4 samples prepared by the grain boundary engineering method mentioned previously work [11]. The preparation could be concluded as follows. First, brought the sample to go through being heated under a state of argon gas at the temperature of 650ºC, with the rate of temperature increase being 10ºC per minute. Afterwards, brought the sample to hastily reduce the temperature in room-temperature water, then the sample was cold rolled at room temperature by 40% thickness reduction (40%TR), followed by annealed at 600ºC for 60 minutes under flowing argon. Then brought the sample of quickly decreased its temperature in room-temperature water, followed by 40%TR, then annealed it at 600ºC for 5 minutes, and reduce the temperature it quickly, once again, in room-temperature water.

For the second group, which are the substrate with the low proportion of CSLBs (L-CSL), 4 samples prepared by being annealed at 700ºC for 160 minutes ,with the rate of temperature increase at 10ºC per minute, under flowing argon; then bring it to reduce the temperature quickly in water of room-temperature. Before the synthesis of carbon nanotubes, the two group of substrates both have its sample's preparation of surface; starting from polishing the substrate with mechanical ground and polished until the final step at 1 μm diamond suspension. After, the samples were an ultrasonically degreased in acetone for 30 seconds and blown dried in jet air.

As for the preparation of work for an analysis via EBSD technique. Each sample were polished down to 0.05 μm colloidal silica suspension for GBCD evaluation using EBSD technique in a scanning electron microscope of Hitachi model S3400N equipped with TSL (EDAX) orientation imaging microscopy data collection 5, software version 5.3.2.Operating parameter was 20 KV using a square grid with a step size of 3.2 μm. The Brandon deviation criterionwas used to classify grain boundaries by CSL description. The equation 1 is allowed.

$$\Delta\theta = 15^{o}\Sigma^{-\frac{1}{2}} \quad (1)$$

All grain boundary types were reported as length fractions. Grain size measurements were performed by optical microscopy using the linear intersection method.

2.The synthesis of carbon nanotubes

All specimens were placed at the end of heating zone inside a tube furnace (Fig.1). To prevent the oxidation, Ar gas flow rate was kept at 500 sccm while heating the samples up from room temperature to 600º 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 80oC 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 (1,5, 10, 15 minute) the supply of ethanol vapor stopped and the system was allowed to cool down to 300º C under 500 sccm Ar flow and from 300º C to room temperature in still air. Fig.2 shows CVD processing the time-temperature. The morphology of synthesized carbonnanotubes were invitigated by field-emission scanning electron microscope (FE-SEM; Hitachi model S-4700).

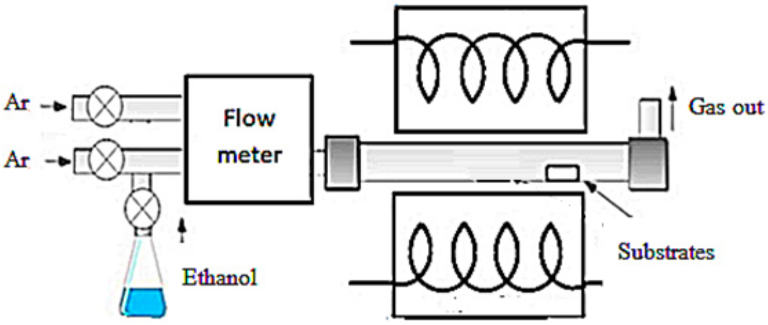


Fig.1 Schematic Fig. of tube furnace reactor with gas flow controller for carbon nanotubes growth.

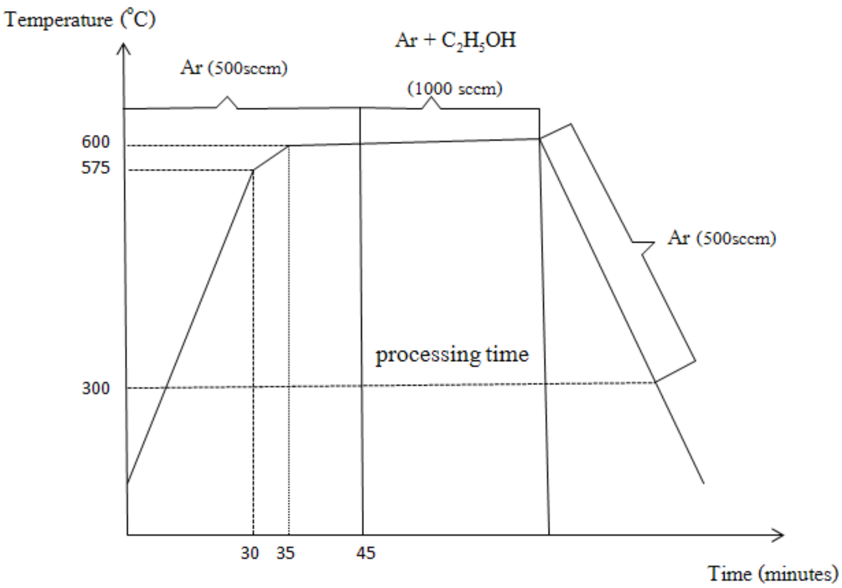


Fig.2 CVD processing time-temperature

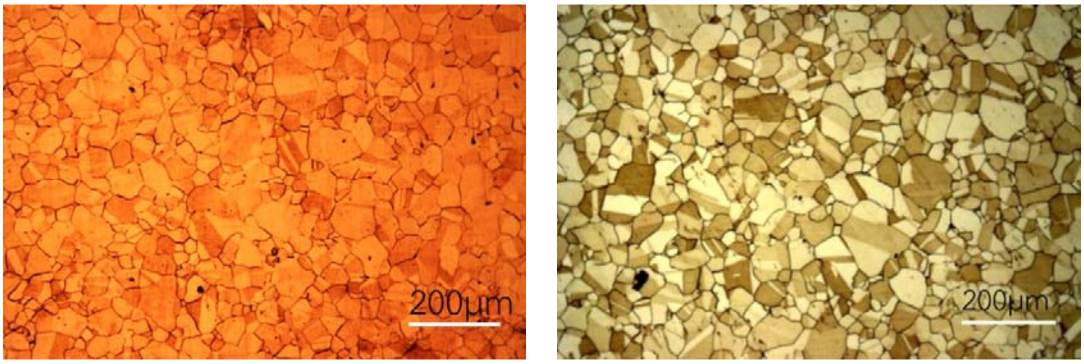
Result and discussions

Fig 3 shows optical micrographs of H-CSL and L-CSL samples of nickel with average grain size of 55 µm and 57 µm respectively while the proportion of special grain boundary (∑3-∑27) are 45.3% and 25.3% respectively. For the distribution of various types of grain boundary in the substrate, it is illustrated in Table 2. This result indicated that majority of grain boundary's type on the L-CSL substrate is ∑1, with the proportion of 38.4%; that is more than ∑1 in H-CSL substrate by approximately 1.9 times, Whereas the majority of the grain boundary type in the H-CSL substrate is ∑3, with the proportion of 37.8%, higher than ∑3 in the L-CSL substrate 1.7 times approximately. However, when added up altogether the proportion numbers of ∑1-∑27 on the L-CSL and H-CSL, the numbers are 63.7% and 65.5% respectively. They are of extremely similar values.

Fig 4-5 shows the SEM images of synthesized carbon nanotubes on each substrate under the same CVD process parameter at 600ºC for 1-15 minute. If one observe the synthesis of carbon nanotubes on the substrate for 1 minute, it was revealed that parts of H-CSL substrate started to have accumulation of carbon in the shape of ridge, the small carbon scales were also discovered on the substrate (Fig. 4a-b). When put in comparison with L-CSL substrate (Fig 5a-b), it becomes apparent that parts of the substrate were covered with carbon that accumulated until it becomes an undulated elevation. Only parts of the two substrates have an accumulation of carbon, this shows that the amount of carbon accumulated on the substrate is still not enough. That is, the amount of ethanol vapor which entered into the system were too little, hence the small amount of accumulation. In comparison to the synthesis of carbon nanotubes for 5 minutes (Fig. 4c-d, 5c-d), it appears that the majority of the H-CSL substrate's surface area had accumulation of carbon with the characteristics of ridges, as well as larger carbon scales. This is because the increased amount of ethanol vapor causes the accumulation of carbon to increase as well (Fig 4d). At the same time, the majority of the L-CSL substrate's surface had the accumulation of carbon with the characteristics of ridges, carbon scales were also discovered (Fig.5g).This type of carbon accumulation is similar to the synthesis of carbon nanotubes on the H-CSL

Table 2 grain boundary character distribution statics of each sample

Sample	Grain size(μm)	∑1	∑3	∑9	∑27	∑1-∑27	∑3-∑27
Low- CSL	57	38.4	22.5	2.3	0.5	63.7	25.3
High-CSL	55	20.2	37.8	5.6	1.9	65.5	45.3



(a) (b)

Fig. 3 Microstructure of Nickel grade N1000 (a) H-CSL (b) L-CSL

substrate at 1 minute. Afterwards, with an expansion of Fig.4d and 5d using higher magnifying power (Fig. 4e and 5e), it was revealed that bended carbon nanotubes were grown on the surface of H-CSL substrate and L-CSL substrate. This demonstrates that the synthesis time of 5 minutes is sufficient for the growth of carbon nanotubes, which is consistent with previous researches [10]. Afterwards, with the synthesis time increase to 10 minutes, carbon nanofiber and carbon nanotubes were grown on the amorphous carbon (Fig.4f).On the other hand, there were not many amorphous carbon created on the L-CSL substrate (Fig. 5e) , until the time synthesis reach the 15 minutes, it appears that carbon nanofiber and carbon nanotubes were being grown at a rate quite low, to the point that parts of surface area were actually apparent (Fig 4 g-h and 5 g-h) on both the H-CSL and L-CSL substrate. The most interesting point is that carbon nanotubes discovered growing on the H-CSL substrate (Fig 4b) at the 1 minute of the synthesis. This demonstrate that the H-CSL substrate will have an accumulation of carbon, as well as the growth of carbon nanotubes faster than L-CSL substrate in the early phrase of synthesis (1-10 minutes). This is because H-CSL substrate has better absorption rate, or a better distribution of carbon in the substrate than L-CSL.

Fig. 6 demonstrates the inverse pole figure of the H-CSL and L-CSL substrate. It is apparent that the two substrate have different crystal planes. In Fig.7 shows the distribution of crystal planes of the substrate. It appears that the majority of crystal planes of the H-CSL and L-CSL substrate, such as Plane 325, have the proportion of 20.3% and 28.8% respectively. Once include the proportion of all crystal planes of H-CSL and altogether, are 97.2% and 95.2% respectively. The most notable point of the two substrates is the difference of crystal plane of different planes, primarily are plane of 100 and 201. Whereas, the L-CSL substrate has the crystal plane of 111 and 325. This result shows that the surface structure of the two substrates are different, because there were crystal plane in difference; this affects the absorption of the distribution of carbon.

From the research by T.Hu and et.al [14], which studied the absorption of carbon atoms on nickel surface at the crystal plane of 100, 110 and 111. It was revealed that the surface plane of 100 is the most suitable area for carbon atom absorption; the second on is the surface plane of 110 and 111 respectively. Because of this, the H-CSL substrate has a better accumulation of carbon compares to the L-CSL substrate.

As for the growth of carbon nanotubes on the substrate, the crystal surface area is also of importance. Generally, in the formation phrase of carbon nanotubes, it will start from the carbon atom, which broke off from the carbon source, got absorbed on the surface; then the carbon atom enters the interstitial sites of the substrate, until there were sufficient in amount and suitable for the induction of grapheme sheets, which will become carbon nanotubes at further stages. Nowadays, there are researches on the formation of carbon nanotubes on nickel substrate's different planes; such as the research by H.Amara et al [15], which studied the formation of carbon nanotubes on nickel substrate's surface plane of 111; it was discovered that the carbon nanotubes will form interaction between carbon atoms (C-C bond), forming grapheme sheets. Before it is separated from the substrate's surface, formed into carbon nanotubes. The chemical potential and the adhesion energy are one of the factors to be considered.

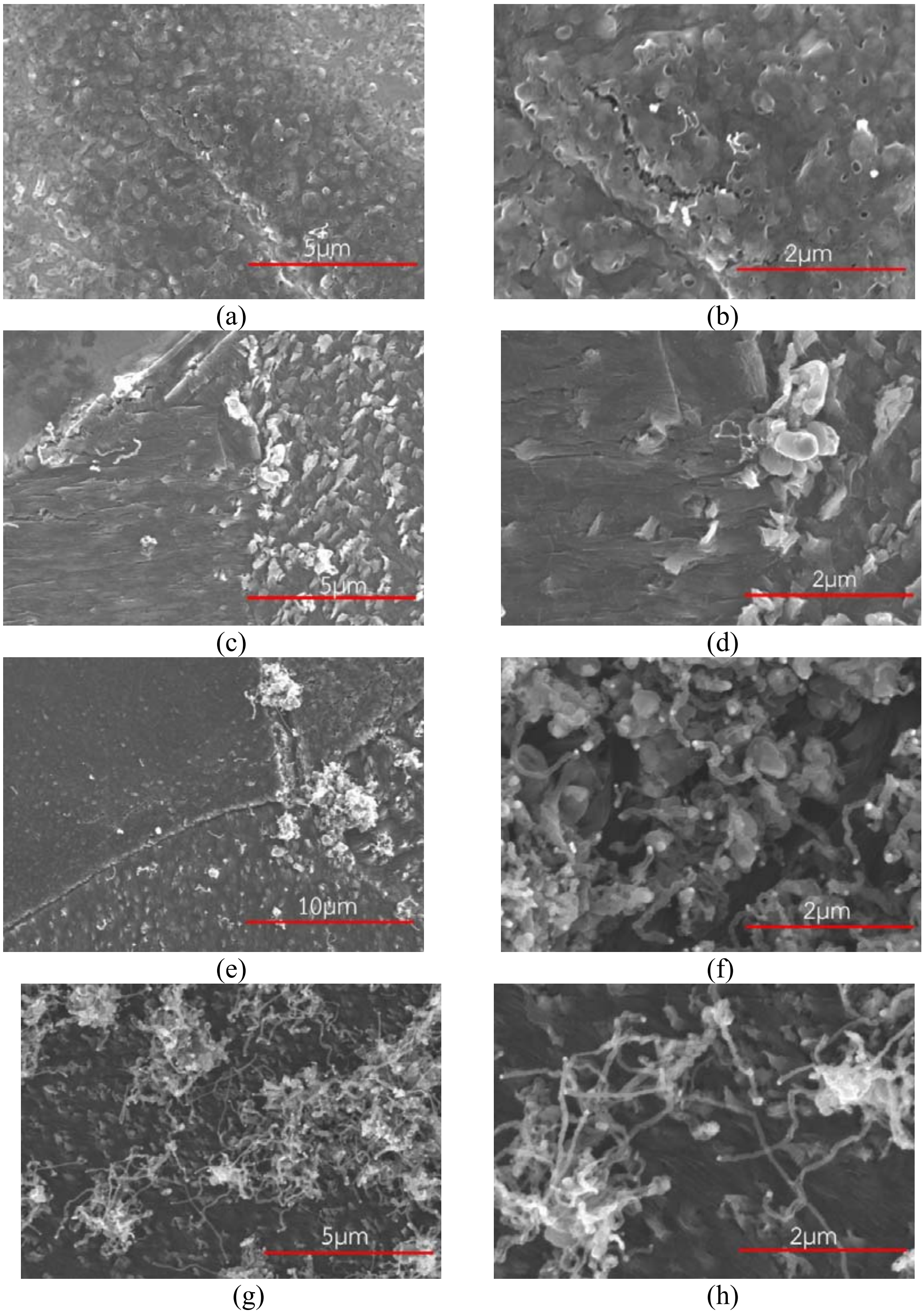


Fig. 4 SEM images of carbon nanofiber and CNTs grown on H-CSL substrate at 600°C (a-b) 1 min (c-d) 5 min (e-f) 10 min (g-h) 15min

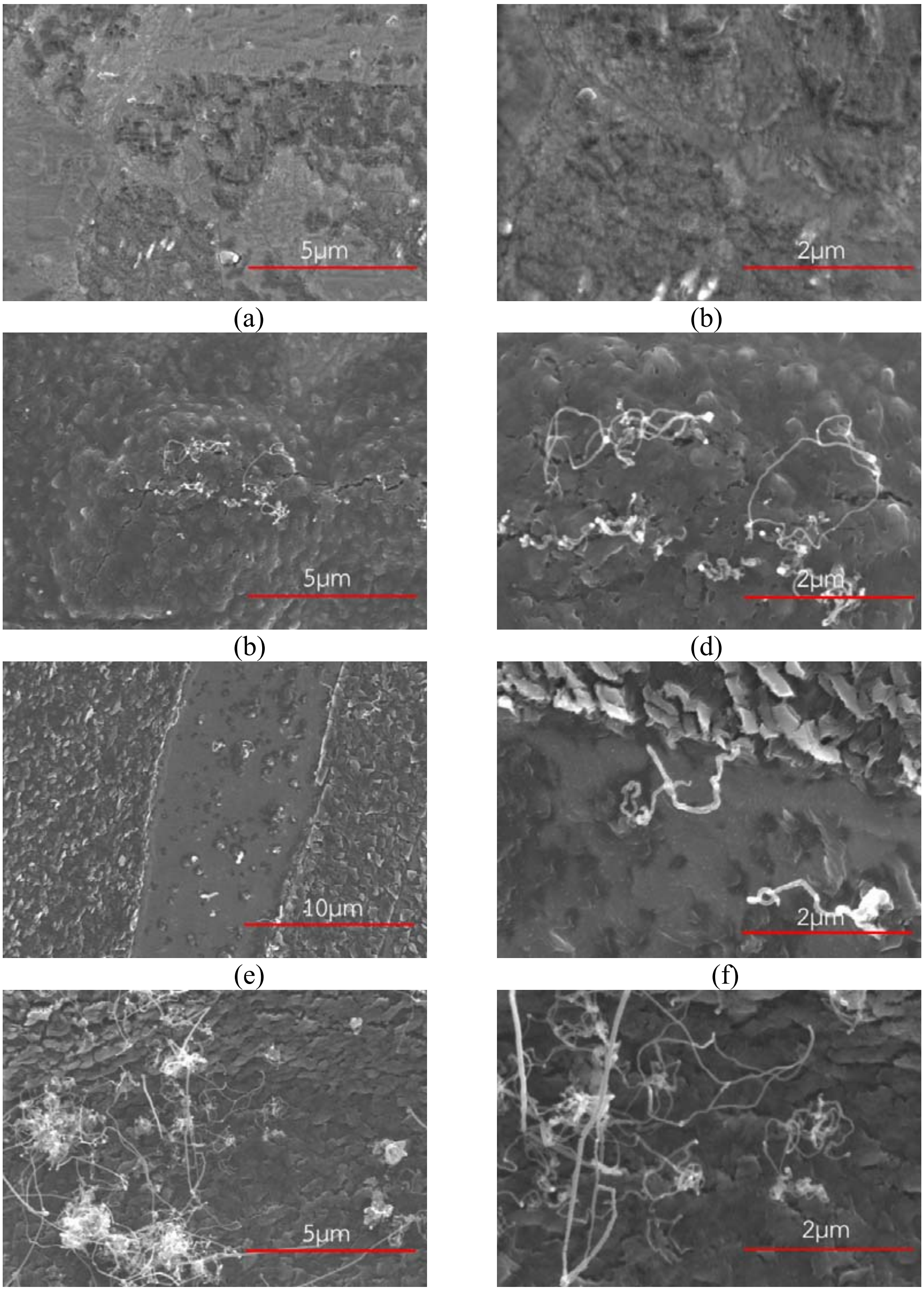
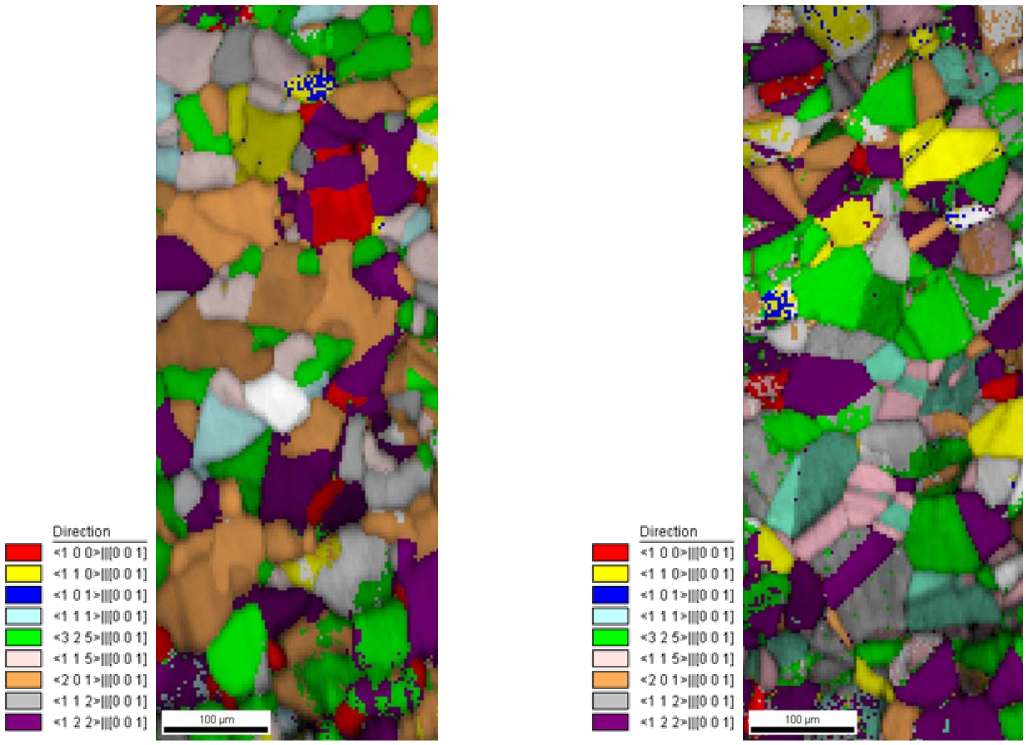


Fig. 5 SEM images of carbon nanofiber and CNTs grown on L-CSL substrate at 600^{o}C (a-b) 1 min (c-d) 5 min (e-f) 10 min (g-h) 15min

The chemical potential and the adhesion energy from the formation of grapheme sheets, and the formation of carbon nanotubes on nickel substrate's surface plane 111 is -5.00eV/atom, -0.03 eV respectively. As for the formation of carbon nanotubes on the nickel surface plane 100, there could be a formation of carbon nanotubes when there is chemical potential and adhesion energy [16], that is -4.62 eV/atom, - 0.26 eV respectively. This shows that the carbon nanotubes formed o the substrate, when there are low chemical potential and adhesion energy. The formation of the carbon nanotubes on plane 100 is a formation that is perpendicular with the nickel substrate's surface; this resulted from an interaction between nickel and carbon (Ni-C), with the carbon atom infiltrated in the void of octahedral site. Whereas the forming tendency of carbon nanotubes is an interaction caused between Ni-C at the area of substrate's surface when there is low amount of carbon [17]. Fig. 8 demonstrated the atom alignment of with the void of octahedral site and tetrahedral site of various surface planes; it appears that the surface plane 100 has a void of octahedral site type mainly (Fig. 8a-b). Whereas, the surface plane of 111 has the void of tetrahedral site (Fig. 8c-d),the surface planes 201 and 325 have voids both of octahedral site and tetrahedral site (Fig.9e-g). It is clear that the surface plane of 325 has the smallest number of voids; as such, the H-CSL substrate only has the carbon nanotubes formation within merely a minute of synthesis, because the voids are suitable areas for the growth of carbon nanotubes.

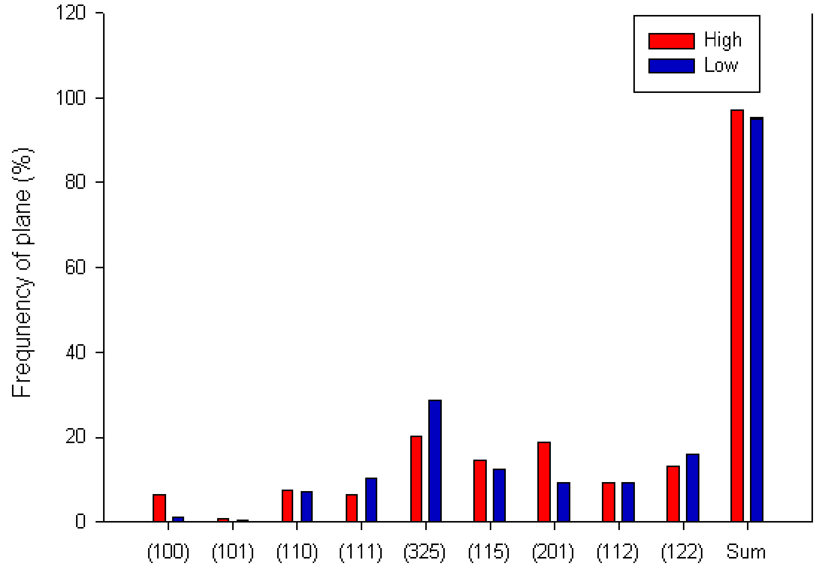


(a) (b)

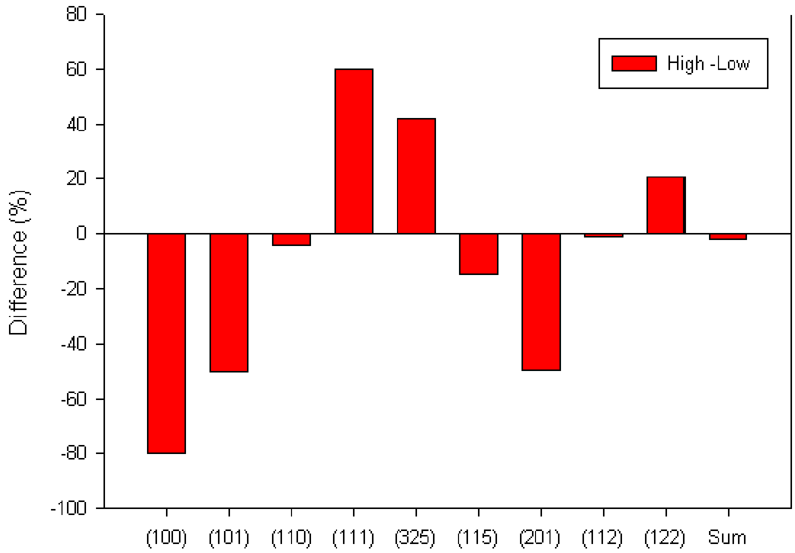
Fig. 6 the inverse pole figure of (a) H-CSL (b) L-CSL

Table 3 crystal plane distribution statics at surface of each sample

Sample	(100)	(110)	(101)	(111)	(325)	(115)	(201)	(112)	(122)	Total
High CSL	6.4	7.6	0.8	6.5	20.3	14.4	18.6	9.3	13.3	97.2
Low CSL	1.3	7.3	0.4	10.4	28.8	12.3	9.4	9.2	16.1	95.2



(a)



(b)

Fig.7 (a) The Fraction of crystal plane at surface of sample H-CSL and L-CSL (b) % difference of fraction of each processed sample

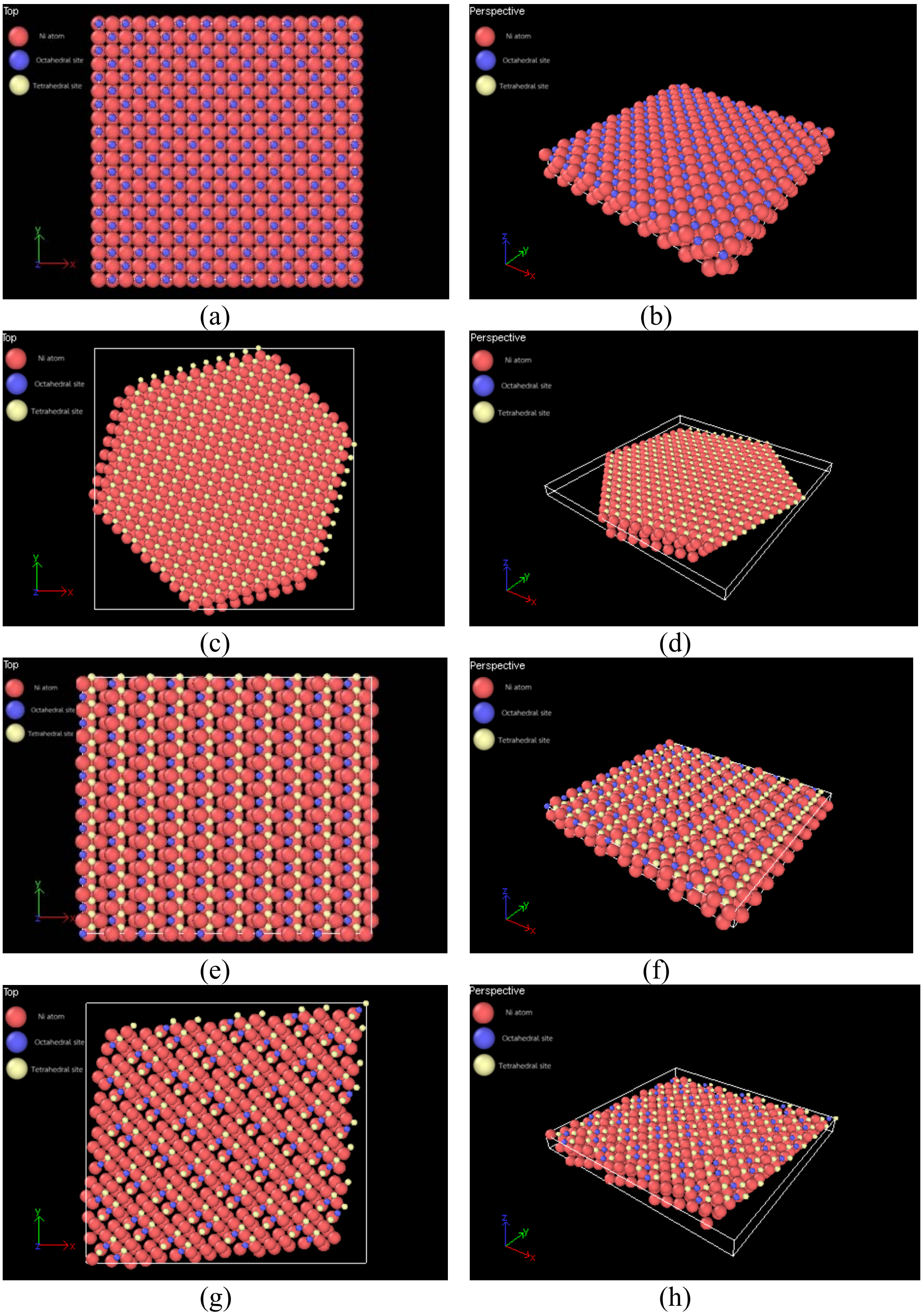


Fig. 8 the atom alignment of with the void of octahedral site and tetrahedral site of various surface planes (a-b) 100 (c-d)111 (e-f) 201 and (g-h) 325

Conclusion

This research studies the effect of CSL grain boundary on the growth of carbon nanotubes. The synthesis of carbon nanotubes is done via chemical vapor deposition from ethanol, on a nickel substrate with different proportions of the CSLBs, albeit with similar size of grains. From the synthesis, it appears that the H-CSL substrate has faster accumulation of carbon and growth of carbon nanotubes, compares to the L-CSL substrate, in the early phrase of synthesis. Furthermore, there were also discoveries of carbon nanotubes on the H-CSL substrates, with the synthesis period of only 1 minute. That is, because of the different factors of the CSL grain boundary's proportion, the two substrates have different surface plane; this impacts the rate of distribution or carbon atom absorption, as well as the formation of carbon nanotubes. The crystal plane of the substrate which are significantly different are plane 100, 111, 201 and 325. The H-CSL substrate has the crystal planes that are of difference: plane 100 and 201. As for the L-CSL substrate, the crystal surface planes differing are 111 and 325, which are the crystal surface plane of 100; that is the plane that can absorb the carbon atom the most at the void of octahedral type; there were many, hence the suitability in the formation of carbon nanotubes when there is low amount of carbon on the surface. As for the crystal surface plane 325, it was the plane with the lowest amount of octahedral site type and tetrahedral site type voids combined.

Acknowledgement

The authors would like to express our sincere gratitude to the financial funders, Coordinating Center for Thai Government Science and Technology Scholarship Students (CSTS) and National Science and Technology Development Agency (NSTDA) under the project name, A new researcher scholarship of CSTS, MOST. Certainly, this work couldn't be possible without their support.

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