

## The synthesis of carbon nanotubes on different type of stainless steels

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#### Abstract

Austenitic stainless steels of type AISI304, 316L, and 321 were examined as bulk metallic substrates for carbon nanotubes (CNTs) synthesis. Substrate surfaces were firstly mechanically ground and polished till 1 µm-diamond suspension step followed by the chemical vapor deposition process (CVD) using the mixing of ethanol vapor with Ar gas. One of the vital parameters for the selective growth of CNTs is substrate alloy composition. Many studies reported the successful use of various metals containing particles as catalyst particles for CNT growth. Nevertheless, the effect of carbide precipitates, already existing in stainless steels, on the growth has been investigated. According to published Time-Temperature Precipitate diagram (TTP), different grades of stainless steels possess different characteristics of carbide precipitates; thus, different impacts on CNT growth. Our results indicated that stainless steel of type 321 was preferable qualitatively to AISI 304 and 316L and the location of carbon nanofibers found was at grain boundary in all types of investigated stainless steels.

Keyword: Carbon nanotubes, Ethanol, Chemical vapor deposition, Hybrid steel-CNT materials

### 1. Introduction

At present, research works in the field of nanoscience and nanotechnology become highly active among scientists with high expectation that the outcome will change the way of life as semiconductor or polymer did in the last few decades. Since the first discovery of carbon nanotubes (CNTs) in 1991 [1, 2], researches in nanotechnology have been commence promptly in hi-tech countries with large amount of funding spend in hoping that they are the very first ones exploring benefits from such the nanothings. Soon after, unique physical and chemical properties of CNTs have been reported by national laboratories around the world leading to applications as potential an electron field emission source [3], chemical sensor [4], nanoelectronic device [5] electrode for supercapacitor [6], nanocomposite strengthener [7, 8], etc.

There are many methods to synthesize CNTs. Generally, we can classify them into two major classes depending on phases of carbon source i.e. solid carbon source and gaseous carbon source. After decomposition of the sources into elemental carbon atoms, they must arrange themselves into a thermodynamically stable form which possesses lowest free energy and CNT is the stable allotropic carbonaceous form when 1) no  $O_2$  environment 2) high temperature and 3) suitable catalysts [9]. Among the recent methods, arc-discharge or laserablation processes, using graphite rods containing catalyst particles as solid carbon sources, 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 piece of work. The two-fold advantages are gained using catalyst chemical vapor deposition (CCVD) methods whereby not only CNTs can be synthesized but they can also arrange themselves on patterned substrates. Such the structure, claiming for the new type of materials called hybrid nano-metal materials, is suitable for fabricating a superior field electron emitter and an electrode in supercapacitors.

Applications of the hybrid nano-metal materials for field electron emitters and supercapacitors need CNTs grown on metallic surfaces with additional requirement of electrical contact and sound mechanical bonding with the surfaces. This couldn't attainable without sophisticate and laborious procedures. In searching for more effective route, some research groups run into studying to implant CNTs directly on metallic substrate without a catalyst particle

layer. Their experiment parameters included process temperature, types of carbon sources, surface preparation methods, and alloying elements. Fe-Ni-Cr alloys [10-12], such as SS304 [13-16], Inconel [6, 17], and Nickel [18-20], were substrates on which CNTs could grow successfully. Even though they all concurred that it was metallic particles on which CNTs nucleated, no one concerned about optimum condition of the metallic precipitates as the embedded metallurgical microstructure of alloys. As a very first interest about the microstructure is the type of precipitation. Various metal carbide and intermetallic precipitates are possible depending on alloying other than heat treating. As a result, our preliminary objective of this work concerns about the impact of precipitates to CNT synthesis using different grade of stainless steels as the upstream parameters.

#### 2. Experimental Procedures

The stainless steels of grade AISI304, AISI316L, and AISI321 were used as bulk substrates with their chemical compositions in Table 1. Before starting the experiment, asreceived materials were solution treated at  $1100^{\circ}$ C for 1.5 h and quenched in water to room temperature. Samples of about 20 mm thick were cut followed by surface preparation of grinding and polishing until the final step of 1 µm diamond suspension. We then simply cleaned the surface ultrasonically in acetone for 30 s and blown dried in jet air.

Each specimen was located face up in the middle of heating zone inside a tube furnace





Type of SS	С	Mn	Si	Р	S	Cr	Мо	Ni	Ti
304	0.06	1.86	0.43	0.026	0.0236	18.56	-	8.05	-
316L	0.02	1.502	0.279	0.027	0.029	16.997	2.022	10.024	-
321	0.014	1.86	0.289	0.031	0.0045	17.00	0.223	10.024	0.2586

Table1 Element concentration (wt%) of different grade of stainless steels\*

\*Supplier certification

(Fig.1). While heating up from room temperature to 700°C, Ar flow rate at 500 sccm was kept to prevent oxidation at elevated temperature. The samples were hold at the temperature for 10 min to ensure a uniform temperature distribution before carbonaceous gas was introduced into the system with Ar at the total flow rate of 1000 sccm through an ethanol containing flask initially heated at 100°C. It took 20 min reaction time before the supply of ethanol vapor was shut down and the system was allowed to cool down to 300°C under 500 sccm of Ar and from 300°C to room processing temperature still The in air. temperature diagram is demonstrated in Fig. 2. The morphology of the synthesized carbon nanofibers was assessed in a field-emission scanning electron microscope (FE-SEM; Hitachi model S-4700).



Fig.1 Schematic diagram of the reactor components.



Fig.2 CVD processing time-temperature diagram.

#### 3. Results and Discussion

Since precipitation reactions in austenitic stainless steels by thermomechanical treatment followed by thermal aging are complicated, only the guidance to precipitate forms can be consulted to interpret our results by reference to published TTP diagram of each grade of investigated steels. Initially, solution treated microstructure of the 300 series steels at 1100°C for 1.5 h was expected to be precipitate-free austenite which dissolved most former present carbide and intermetallic precipitates. Subsequent quenching substrates in promoted water metastable microstructure shown as metallographically in Fig. 3a-c for AISI304, 316L, and 321 with average grain size of 77, 103, and 123 µm, respectively. Some traces of remained

carbides still existed as pull outs which could be growth which relieved by using higher solution temperature or higher anne reducing applied pressure and time when period of polishing and grinding the samples. Even though substrates

polishing and grinding the samples. Even though the effect of grain size indicates inverse relationship to the quantity and growth rate of synthesized carbon nanofibers [21], we could ignore the factor in the intermediate step investigation.

Reheating the samples to 700°C allowed thermal energy to activate carbide nucleation and

growth while intermetallic precipitates required higher annealing temperature and a longer aging period of time. After 10 min pretreatment, substrates microstructures were assumed to develop according to TTP diagrams (Fig. 4). At this time, they suggested that  $M_{23}C_6$  were the predominant carbides present at grain boundary (GB) for 304 but still in incubation stage for 316L while MC dispersed within grains of 321. Simultaneously, ethanol vapor was carried into the reaction zone by inert Ar gas. To ensure

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Fig.3 Metallography and carbon nanofibers growth characteristics on AISI 304, 316L and 321.

continuous supply of carbon atoms, it is believed that the vapor can dissociate into many reactive reagents and the intermediate reaction involving methane as gaseous carbon source and OH free radical as etching reagent [22-25]. Indeed the reactions couldn't be possible without the presence of catalyst like Fe, Ni, Co, Mo, and their alloys which modifies kinetics by lowering reaction activation energy. Note that the smallest precipitates which could be identified depend on used equipment; thus, the TTP diagrams are the laborious pieces of works usually updated when more information is revealed by new techniques.

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It is well accepted that GB can be defined as a thin layer between misoriented crystals creating an open structure of atomic misfit layer about 2-3 atomic diameter thick with energy depending on its excess free volume and stress fields [26]. It provides high diffusivity path for carbon atoms to coalesce with various metals and become particles M<sub>23</sub>C<sub>6</sub> for SS304 and 316L and MC and  $M_{23}C_{6}$ for 321. As mention earlier, the





decomposition reaction of carbon containing gas couldn't be possible without catalyst. Only those carbides were present for the task leading to the assumption that the carbides were the catalyst particles by which activation energy decreased, in which carbon atoms dissolved and saturated, and finally on which nanofibers emerged.

Regarding to the assumption, the finer yields on the 321 substrate may be as a result of different major carbides, i.e. MC. In addition, we should account the disintegrated carbon atoms from gaseous source as addition carbon atoms on the substrate. They could increase carbon content on substrate and attract other metals to create more present carbides in all grades of steels or even new type  $M_7C_3$  in 304 and 316L. The less carbon in 316L to begin with should responsible for the less yields of nanofibers. As results shown in Fig. 3 are SEM images of synthesized carbon nanofibers on each substrate with different magnification under the same CVD process parameters at 700°C for 20 min. Agglomeration of carbon nanofibers were set outlining in patterns resemble to familiar grain structures where carbides were supposed to exist. If ones compare grain structure lineated by metallographic etching with that outlined by the bundles of nanofibers, they could convince themselves from the consistent structures that carbon nanofibers actually grown along grain boundaries (GBs) in addition to within grains. The finding should at least in part substantiate our stated assumption.

### 4. Conclusion

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We have grown carbon nanotubes on three types of austenitic stainless steels by CVD process using alcohol as carbon containing gas at 700°C. Different grades of the steels possess unique characteristics of carbide precipitates; thus, different effects on carbon nanofiber synthesis. In this research, we found that nanofiber nucleation sites were mostly at grain boundaries where M23C6 mostly precipitated for 304 and 316L. Disintegrated carbon may enhance  $M_7C_3$  or  $M_{23}C_6$  formation in 304 and 316L or accelerate MC or M23C6 at GB in 321. We anticipate the cleaner carbon nanofibers may result from different carbide catalyst in 321. Please keep in mind that our result is based on the guidance to precipitate forms as present in published time-temperature-precipitation diagrams (TTP). Further investigation and validation by TEM images is still needed. However, at least the prospective of embedded catalyst carbide in steels is vindicated. The promising application is the selective CNTs synthesis on embedded catalyst carbides in the various types of steel microstructure.

#### 5. Acknowledgement

We would like to express our sincere gratitude to the financial supporters, Thailand Graduate Institute of Science and Technology (TGIST) and National Science and Technology Development Agency (NSTDA). Also many thanks are given to Mr.Alongkot Treetong (Nanotec NSTDA) for the help of Raman Spectra analysis.



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