



Simulation of catalyst behavior during chemical vapor deposition processing of carbon nanotubes



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ABSTRACT

Nucleation of carbon nanotubes is considered to start with the supersaturation of carbon atoms dissolved in a catalyst. In chemical vapor deposition synthesis, it is believed that condensation of the source gas terminates the growth. However, some experimental studies have suggested that termination is primarily affected by catalyst behavior. We modified the potential functions and observed the behavior of carbon–iron mixed nanoparticles by a molecular dynamics method and found that the iron fraction melted at the equivalent temperature of growth termination. Thus, we concluded that the catalyst fusion prevented nucleation that would normally occur as a consequence of solution supersaturation.

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1. Introduction

The growth mechanism of carbon nanotubes (CNTs) [1,2] has been discussed since its landmark discovery in 1991 and 1993. In the early stages of its development, CNTs were synthesized by laser furnace methods [3] or arc discharge techniques [4]. We do not know for certain whether the existing growth models [5–10] were affected by these earlier synthesis methods. The present growth models are based on the idea that for growing CNTs, isolated carbon atoms should be continuously supplied to the catalyst. At present, one of the most recognized models is the nanoparticle model. In this model, the nucleation process starts with the supersaturation of carbon atoms dissolved in the metal catalyst. Saturated carbon atoms form cap-like structures on the catalyst surface and grow longitudinally. In this growth model, a variety of metal catalysts are examined in terms of the crystal surface structure of catalyst nanoparticle [11].

Following these early synthesis methods, some catalytic chemical vapor deposition (CVD) processes [12–22] were developed. Unlike the arc discharge and laser furnace methods where elemental carbon is the precursor, carbon atoms are supplied in the form of a chemical such as carbon monoxide, methane, and alcohol so that the growth process becomes complicated. Though some radical approaches have been attempted to include these complicated decomposition processes in the existing growth models [23–25], it is considered that the behavior after the decomposition stage should follow the present model. Among the CVD methods, alcohol catalytic CVD [25] is an ideal one, because it affords a pure single-walled CNT

without the need for any posttreatment. Generally, the purity and crystallinity of single-walled CNTs increase as the reaction temperature increases. However, at around 950 °C, the growth suddenly terminates. Regarding this phenomena, it is speculated that condensation or supersaturation of the carbon-source gas results in the nanotube-growth termination. Some FT-IR experiments have indicated the existence of a carbon–carbon double bond; thus, condensation was considered to be a viable explanation for nanotube growth termination.

With respect to this problem, we performed in situ observation of reaction products [26,27] in the reactor using a quadrupole mass spectrometer. As a result, we determined two key products with water as a by-product. As shown in Figure 1, the amounts of these key products increase as the temperature increases, and we do not detect any other products. In this figure, the amounts of the key products seem to exhibit a positive correlation with the G/D ratio, which approximately expresses the purity and crystallinity of a single-walled CNT. At temperatures greater than 900 °C, the G/D ratio becomes zero; thus, the growth is considered to be terminated. Nevertheless, the amounts of the two above-mentioned key products and water still increase as the temperature increases. Hence, we conclude that the reaction proceeded in the preferred direction. On the other hand, the mean diameter of the single-walled CNTs was affected by the catalyst size [27–33], and as the growth model suggested, the catalyst nanoparticle retained its structure. The melting temperature of the nanoparticles is known to become lower than that of the bulk material, which is a theoretically predicted observation [33].

In this study, we focused on the catalyst behavior during the CVD process. We modified the existing potential function to reproduce the bulk melting point and applied the modified model to a

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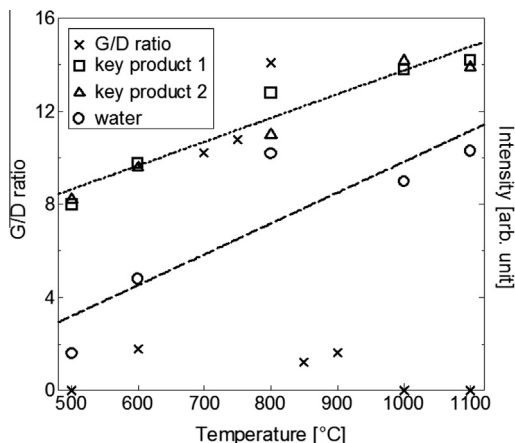


Figure 1. Experimental results measured by quadrupole mass spectrometer. After the growth of carbon nanotube terminates, the amount of two key products and water increase. We inferred that these two key products were ethylene and acetylene owing to their fragments shown in mass spectroscopy [27]. This result suggested that the reaction proceeded preferable direction even at high temperature.

carbon–iron mixed nanocluster by observing its behavior using the molecular dynamics method. Consequently, we found that the iron fraction of the mixture melted at a temperature equivalent to that required for the growth termination of CNTs.

2. Methodology

The Brenner– Tersoff potential [34] was employed to model the carbon–carbon interaction. The bond-order potential [35] was applied to carbon–iron interactions, and the Finnis–Sinclair potential [36] was used for iron–iron interactions. The base parameter sets of bond-order potential used by Shibuta et al. [37] were adopted in this study. Though we focused on the behavior of the carbon–iron mixture, such as melting, nucleation, and dissolution, each potential function does not necessarily reproduce the physical properties. Among the various physical properties, the melting point is considered to be the most important property for observing the mixture behavior. We modified the potential depth by applying the scaling parameter to the Brenner–Tersoff, Finnis–Sinclair, and bond-order potentials for replicating the melting temperatures of graphite, iron, and cementite, respectively. Because the iron to carbon ratio in cementite is appropriate for the initial condition, we employed cementite as a model material for the carbon–iron mixture. The velocity Verlet algorithm is employed to integrate the Newton’s equation of motion, and the temperature is controlled by the Langevin method. To calculate the melting temperature, we gradually increased the temperature. It is difficult to simulate the realistic heating rate and bulk size in a molecular dynamics simulation; therefore, we examined different heating rates and different cluster sizes. Theoretically, in the case of an infinitely increasing rate and cluster size, the melting temperature should be equivalent to the actual value. The Lindemann index [38] shown in Eq. (1) is used for determining the melting point. If δ becomes greater than 0.1, the Lindemann index tends to diverge so that we consider the temperature for which $\delta = 0.1$ as the melting point.

$$\delta = \frac{2}{N(N-1)} \sum_{i < j} \sqrt{\frac{\langle r_{ij}^2 \rangle - \langle r_{ij}^2 \rangle}{\langle r_{ij}^2 \rangle}} \quad (1)$$

In Eq. (1), N indicates the number of atoms in the cluster, r_{ij} indicates the distance between the atoms of i and j , and the brackets stands for the ensemble average at the system temperature.

3. Results and discussion

3.1. Scaling parameters

We employed three types of potential function for each interaction. However, even if each potential function is developed with care, it is impossible to reproduce all the physical properties of the system. Among the system physical properties, the melting point is considered to be the most important in this study, as we are studying the nucleation and supersaturation of carbon atoms dissolved in the iron clusters. Therefore, we should use potential functions instead, with which can replicate the melting point of each material. In addition, if the heating rate is rapid, the melting temperature increases owing to overshooting and the apparent melting temperature becomes higher. Furthermore, if the cluster size is small, the melting temperature is also reduced. On the other hand, to minimize the calculation load, it is impossible to employ a realistic heating rate and cluster size (bulk, more than the Avogadro number). Thus, we estimate the melting temperature obtained by using our potential functions and apply the scaling factor to reproduce. The respective dependences of the melting point on the particle number and heating rate are shown in Figure 2. In this calculation, we screened the heating rate from 1×10^{11} to 2×10^{12} [K/s] for Fe_{686} , and we prepared several iron clusters

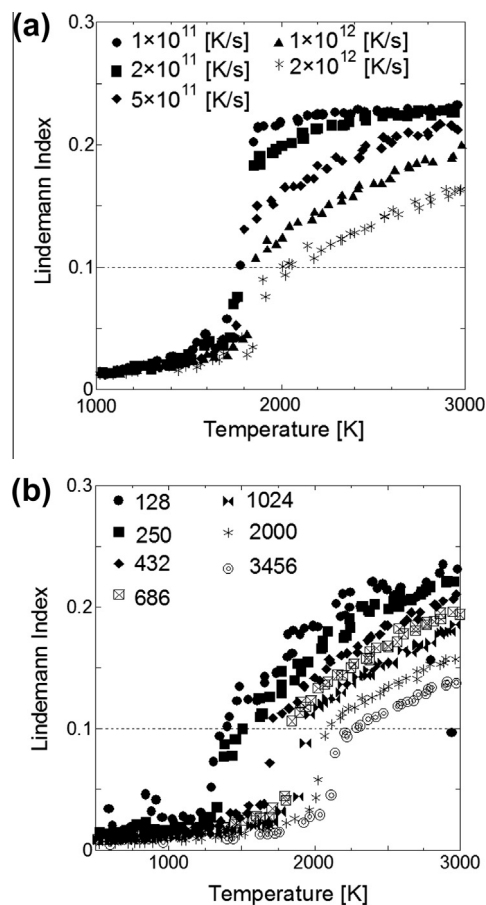


Figure 2. Effects of heating rate and cluster size on apparent melting point. Lindemann index indicates the phase of the material. Because Lindemann index shows sudden increase around at 0.1, this value is generally used to be threshold. Extremely slow increasing rate and large number of atom should show the melting point of the potential function. Owing to the calculation load, it is impossible to simulate under the ideal condition. Thus, the result gives an apparent melting point. In order to correct the difference, we screened the heating rate and cluster size. (a) Effect of heating rate on apparent melting point. (b) Effect of particle size on apparent melting point.

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