

Molecular Dynamics of Nucleation Process of Single-Walled Carbon Nanotubes*

Yasushi SHIBUTA[†] and Shigeo MARUYAMA[†]

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1. Introduction

The discovery of single-walled carbon nanotubes (SWNTs) [1] and the development of large-scale production techniques such as the laser-furnace [2] and arc-discharge [3] techniques have opened new research and application fields of nano-technology. Recently, catalytic chemical vapor deposition (CCVD) using alcohol as a carbon source [4,5] enabled the direct synthesis of vertically aligned SWNTs on quartz substrates. Mono-dispersed catalyst metal particles about 1-2 nm in diameter were observed on the quartz substrates [5]. Therefore, initial nucleation of carbon atoms on the catalytic metal clusters seems to be important in the formation process of SWNTs. In this study, interactions between catalytic metal clusters and carbon atoms in the nucleation process of SWNTs are studied using molecular dynamics (MD) simulations.

2. Formulation of multi-body potential functions

The Brenner potential [6] is used for the carbon-carbon covalent bond. For metal-carbon and metal-metal potentials, the homemade multi-body potential functions [7] are used. These functions have the

covalent term based on the Brenner potential; the parameters for three transition metals (Fe, Co and Ni) are re-constructed by fitting binding energies from Density Functional Theory (DFT) calculations to these functions using Gaussian 98 (B3LYP/LANL2DZ) [8].

Binding energies of small symmetrical clusters MC_n and M_n ($M = Fe, Co, Ni; n = 1-4$) with various bond lengths are calculated; the bond length is changed symmetrically at 0.05 Å intervals from 1.8 Å to 3.5 Å for metal-carbon clusters and from 1.5 Å to 3.0 Å for metal clusters. The obtained potential energy curves are fitted to following functions.

$$E = \frac{D_e}{S-1} \exp\left\{-\beta\sqrt{2S}(r-R_e)\right\} - B^* \frac{D_e \cdot S}{S-1} \exp\left\{-\sqrt{2/S}(r-R_e)\right\} \quad (1)$$

$$B^* = \left\{1 + b(N^C - 1)\right\}^\delta \quad (2)$$

For metal-carbon multi-body potential functions, multi-body effects are included by using the covalent factor B^* , which is expressed as a function of the carbon coordination number of a metal atom N^C . For metal-metal interaction, the equilibrium energy D_e and

Table 1 Formulation of potential function between transition metal atoms.

	S	$\beta(1/\text{Å})$	$D_{e1}(\text{eV})$	$D_{e2}(\text{eV})$	C_D	$R_{e1}(\text{Å})$	$R_{e2}(\text{Å})$	C_R	$R_1(\text{Å})$	$R_2(\text{Å})$
Fe-Fe	1.3	1.2173	0.4155	0.8392	0.8730	2.627	0	-	2.7	3.2
Co-Co	1.3	1.5552	0.4311	1.0230	0.6413	2.5087	0.1660	0.3770	2.7	3.2
Ni-Ni	1.3	1.5700	0.4217	1.0144	0.8268	2.4934	0.1096	0.3734	2.7	3.2
Ni-Ni ⁽⁷⁾	1.3	1.55	0.74	1.423	0.365	2.520	0.304	0.200	2.7	3.2

Table 2 Formation of potential function between a transition metal atom and carbon atoms.

	$D_e(\text{eV})$	S	$\beta(1/\text{Å})$	$R_e(\text{Å})$	$R_1(\text{Å})$	$R_2(\text{Å})$	b	δ
Fe-C	3.3249	1.3	1.5284	1.7304	2.7	3.0	0.0656	-0.4279
Co-C	3.7507	1.3	1.3513	1.6978	2.7	3.0	0.0889	-0.6256
Ni-C	2.4673	1.3	1.8706	1.7628	2.7	3.0	0.0688	-0.5351
Ni-C ⁽⁷⁾	3.02	1.3	1.8	1.70	2.7	3.0	0.0330	-0.8

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[†] Department of Mechanical Engineering, The University of Tokyo (7-3-1 Hongo, Bunkyo-ku, Tokyo, 113-8656, JAPAN)

the bond length R_e are expressed as direct functions of the metal coordination number N^M instead of the covalent factor B^* .

$$D_e = D_{e1} + D_{e2} \exp\{-C_D(N^M - 1)\} \quad (3)$$

$$R_e = R_{e1} - R_{e2} \exp\{-C_R(N^M - 1)\} \quad (4)$$

The coordination number N^C and N^M are defined using the cut-off function $f(r)$ [7]. The potential parameters are listed in Table 1 and Table 2.

3. Simulation Technique

The simulation technique is the same as in our previous report [9]. The Berendsen thermostat [10] is used to independently control translational, rotational, and vibrational temperatures of the system [7,9]. The relaxation time of the thermostat is set to 0.17 ps. The velocity Verlet method is employed to integrate the classical equation of motion with a time step of 0.5 fs.

4. Results and Discussion

We first prepare the initial transition metal clusters: Fe_{108} , Co_{108} and Ni_{108} by annealing face-centered cubic (fcc) crystal structures for 2 ns at 2000 K. The diameters of the obtained clusters are roughly 1.3 nm. As the initial condition, 500 carbon atoms and one of the annealed transition metal clusters are randomly allocated in a

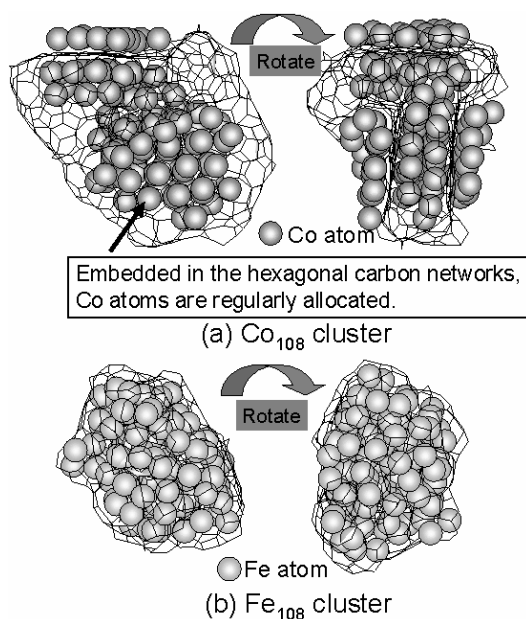


Fig. 1 Co_{108} and Fe_{108} clusters after 100 ns calculation.

cubic periodic cell of $(20 \text{ nm})^3$. The control temperature is set to 1500 K for subsequent simulations.

Figure 1 shows snapshots of Fe_{108} and Co_{108} clusters after 150 ns. The Co cluster has a partially crystal structure where metal atoms are regularly allocated and embedded in a hexagonal carbon network. This implies a strong interaction between the graphite lattice and the metal atoms. However, there is no allocated part in the Fe cluster. On the contrary, carbon atoms cover the entire surface of the Fe cluster. Figure 2 shows the number of hexagonal rings in these clusters over time. The number of hexagonal rings in the Co cluster increase about twice faster than in the Fe cluster. This shows the Co cluster has stronger graphitization action than the Fe cluster. It may be deduced that this difference of graphitization action reflects the ability as a catalyst on the formation of SWNTs.

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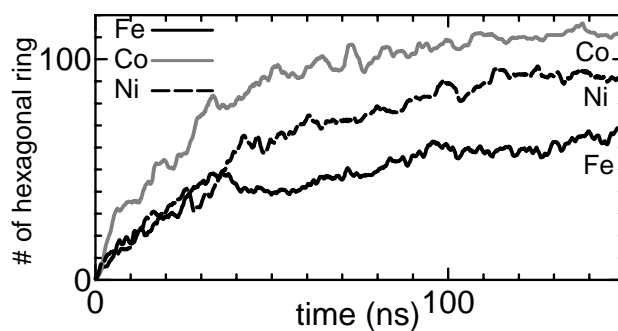


Fig. 2 Number of hexagonal rings in clusters.