Molecular Dynamics in Formation Process of SWNTs

SHIGEO MARUYAMA and YASUSHI SHIBUTA
Department of Mechanical Engineering, The University of Tokyo,
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, JAPAN

The formation mechanism of single-walled carbon nanotubes (SWNTs) was studied with the molecular dynamics simulation. Starting from randomly distributed carbon and Ni atoms, random cage structures of carbon atoms with a few Ni atoms were obtained after 6 ns simulation. Ni atoms on the random cage prohibited the complete closure and anneal of the cage structure into the fullerene structure. In the next stage the simulation cell size was artificially shrunk for realization of proceeding collisions of precursor clusters within the computational time limit. Collisions of such imperfect random-cage clusters lead to an elongated tubular cage structure, which can be regarded as an imperfect SWNT.

Keywords Molecular Dynamics Simulation; Growth Mechanism; SWNTs; Brenner Potential; Ni Atom; Fullerene

INTRODUCTION

Discoveries of multi-walled carbon nanotubes (MWNTs)[1] and single walled carbon nanotubes (SWNTs)[2] have opened new research and application fields with the carbon material. Even though the macroscopic generation of SWNTs with the laser-furnace technique[3], the arc-discharge technique[4], and the catalytic chemical vapor deposition (CCVD) technique[5] has been demonstrated, the formation mechanism of SWNTs is still not clear. Besides the theoretical interest of the self-assembly formation of such elongated perfect structure of

carbon, understandings of the formation mechanism are crucial for the development of purer and larger amount and hopefully chirality-controlled generation technique.

Theoretical contributions to the formation mechanism of carbon nanotubes were limited since the system size and time scale were far beyond the simple simulation of the whole process. Several previous classical molecular dynamics calculations [6,7] examined the specific points of generation mechanism with Brenner potential [8] for carbon only system. However the roles of metal catalysis were not fully discussed since a reliable classical potential function between metal and carbon was not known. We had constructed the classical potential function between carbon clusters and several metal atoms (La, Sc and Ni) based on DFT calculations of small metal-carbon binary clusters for the simulation of the formation process of the endohedral metallofullerene[9]. Using these potential functions, molecular dynamics simulations were performed with carbon and Ni system for the precursor clusters of SWNTs. Furthermore, by compressing the calculation cell to enhance the collision of those precursor clusters, the possible structure as the result of successive collisions was explored.

SIMULATION TECHNIQUES

Generation conditions of SWNTs by the laser-furnace[3] or by the arc discharge techniques[4] are exactly the same as for fullerene and endohedral metallofullerene except for the doped metal species. Hence the same molecular dynamics simulation condition as for our previous empty fullerene[10,11] and for endohedral metallofullerene[9] except for the catalytic Ni atoms was employed. The Brenner potential[8] in its simplified form[10] was used for the carbon-carbon interaction. The metal-carbon potential was constructed with the covalent term based on the coordination number of metal atom and the Coulomb term due to the charge transfer from metal to carbon cluster[9]. In the case of Ni-carbon potential the charge transfer was relatively small and the Coulomb term was neglected. Ni-Ni interaction potential was expressed in the similar fashion[9].

As the initial condition, the completely random vapor mixture of 2500 carbon and 25 Ni atoms were allocated in a 585 Å cubic fully-periodic simulation cell. The high density of the system was compensated with the special temperature control method[10,11] at 3000 K. In order to examine the side-effect of this acceleration, separate

annealing simulations of cluster structures were performed. In the later stage, the periodic cell size was slowly reduced to enhance the collision events in order to further accelerate the simulation.

RESULTS AND DISCUSSIONS

Initial Clustering Stage

Figure 1 shows a snapshot after 6 ns molecular dynamics calculation at 3000 K starting from the random gas phase initial condition. Many relatively large clusters up to about 200 carbon atoms and a few metal atoms were observed. Carbon clusters tended to be spherical random cage structure with a few metal atoms at around the defect vacancy, which prevented the cage structure from the complete closure.

As in our empty fullerene and metallofullerene studies[9,11], cluster structures in Figure 1 were not well annealed. An example of the annealing simulation of the Ni-attached carbon cluster is shown in Figure 2. Picking up a NiC_{60} cluster in Figure 1, vibrational annealing process was simulated for 200 ns without additional collisions at 2500 K. As clearly seen in Figure 2, quasi-periodic motion of the Ni atom

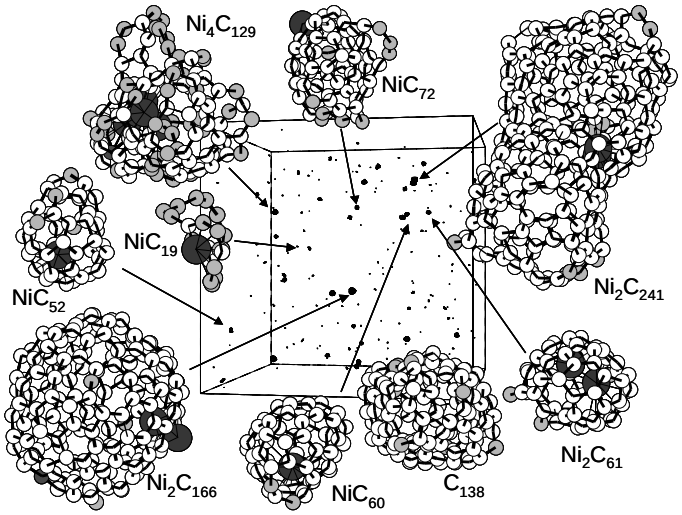

FIGURE 1 A snapshot of the clustering molecular dynamics simulation at 6 ns from initial random gas phase configuration. Large solid circles, empty circles, and gray circles represent Ni atoms, threehold-coordinated carbon atoms, other carbon atoms, respectively.

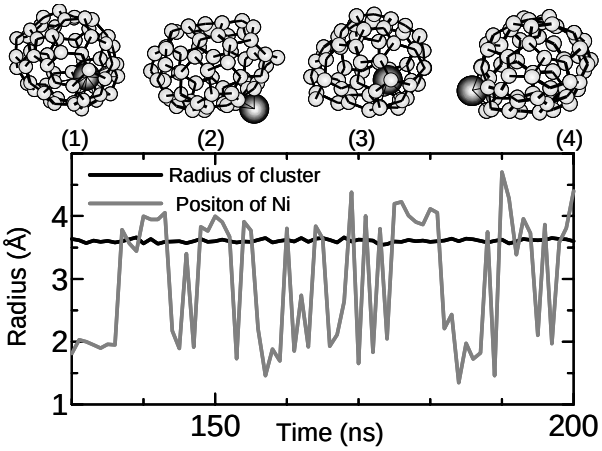

FIGURE 2 Long time annealing at 2500 K of NiC_{60} cluster appeared in Figure 1. The radial position of Ni atom compared to the average radius of carbon cage in the bottom panel shows the repetitions of flipping motion.

flipping inside and outside of the carbon cage were observed. The possibility of this meta-stable structure should be confirmed with more accurate *ab initio* level calculations. These imperfect carbon cage structure with several metal atoms outside were partially confirmed by the FT-ICR reaction experiments of laser vaporized clusters[13].

Collisions of Cage-Carbon Clusters Leading to the Tubular Structure

In the real generation situation of SWNTs, it is expected that those clusters experience later collisions at lower temperature and lower frequency as they expand. However, because of the computational limitations, we had to slowly shrink the simulation cell to enhance the collisions. The shrinking rate was set as 6×10^{-5} Å per time step (about 12 m/s), which was much slower than the typical translational velocity of clusters. The large particle with some tubular structure was obtained after collisions of clusters.

Figure 3 shows the growth process of the typical tubular cluster from shrinking simulation at 2000 K. Again, in order to accelerate the simulation of annealing, we applied higher temperature than the typical experimental condition[3]. Even though the structure shown in Figure 3 is rather ugly, one can see that the tubular structure has grown longer by the collision and the coalescence. Ni atoms were slowly assembling to form Ni clusters, and they were diffusing around until finding the most stable position at the hemi-half-fullerene cap area.

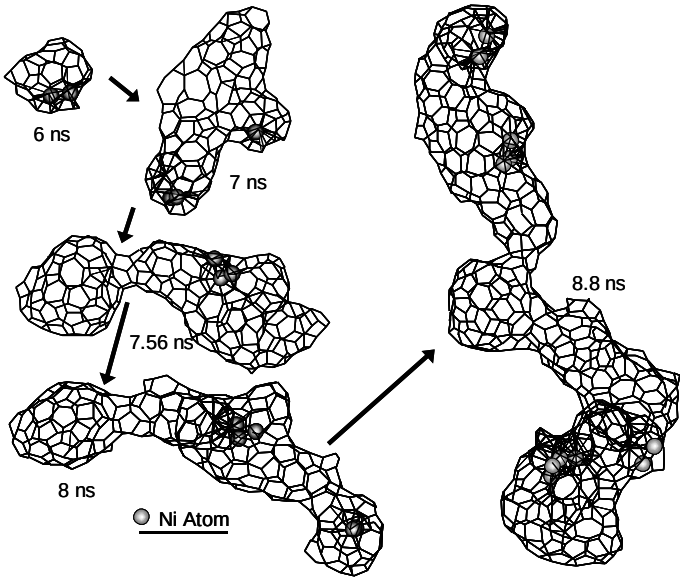

FIGURE 3 Growth process of a tubular structure by successive collisions of imperfect cage clusters..

Part of the annealing tendency was examined by separate simulations as shown in Figure 4. An intermediate structure appeared in Figure 3 (8 ns) was picked up for this annealing. Comparison of annealing effect with different temperatures (2000 K and 2500 K) for 50 ns is shown in Figure 4. The tubular structure became thick at the narrow part and most straight due to annealing. And, the clustering of Ni atoms was observed for 2500 K case. The metal cluster tended to come to the curved carbon area. Unfortunately, in the case of Figure 4, the metal cluster was trapped in curved defect part of the tubular structure. Since the narrow part of the tubular structure was usually Ni free, the tubular structure can be annealed to SWNT structure.

CONCLUSIONS

From the molecular dynamics simulation, the catalytic effect of Ni atoms on the formation of SWNT may be explained as follows. At the clustering stage, Ni atoms tend to stay at around the defect vacancy of carbon cage structure, and prevent the cage from closing to fullerene. Then, the random cage carbon clusters can make further growth by colliding with each other at the large defect area of the cage. The

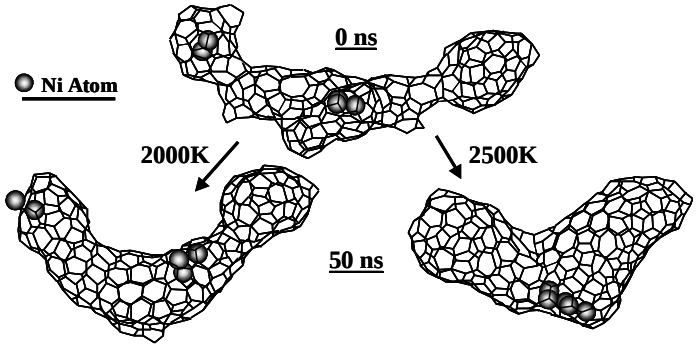

FIGURE 4 Annealing at 2000K and 2500 K of the intermediate structure at 8 ns in Figure 3.

collision leads to the elongated tubular structure as shown in Figure 3. Given the enough time for diffusion of metal atoms and network annealing, we expect that the structure becomes a straight SWNT with metal clusters at each end.

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