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Molecular Dynamics Simulation of Generation Process of SWNTs

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ABSTRACT

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. In the next process the cell size was artificially shrunk for realization of proceeding collisions of precursor clusters within the computational time limit. A Ni atom on the random cage prohibited the complete closure and anneal of the cage structure. Collisions of such imperfect random-cage clusters lead to an elongated cage structure, which can be regarded as an imperfect SWNT.

Keyword: Molecular Dynamics Simulation, Growth Mechanism, SWNTs,
Brenner Potential, Ni Atom

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Theoretical contributions to the generation mechanism of carbon nanotubes are not straightforward since the system size and time scale are far beyond the simple simulation of whole process. Several previous classical molecular dynamics calculations have examined the specific points of generation mechanism with Brenner potential [1] for carbon only system. However the roles of metal catalysis have not been discussed since a reliable classical potential function between metal and carbon has not been 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 [2]. In this paper, using these potential functions, molecular dynamics simulation was performed with carbon and Ni system for the precursor clusters of SWNTs. By compressing the calculation cell to enhance the collision of those clusters, the possible structure as the result of successive collisions was explored.

The growth process of metal-carbon binary clusters was simulated with the same technique as our previous simulation for endohedral metallofullerene [2]. 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 [2] at 3000 K. Figure 1 shows a snapshot after 6 ns molecular dynamics calculation starting from the random gas phase initial condition. Many relatively large clusters up to about 100 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.

In the next process, we slowly shrank the simulation cell to enhance the collisions. The shrinking rate was set as the 6×10^{-4} Å per time step (about 120 m/s) and the 6×10^{-5} Å per time step (about 12 m/s), which was much slower than the typical translational velocity of clusters. With the shrinking rate of 6×10^{-4} Å per time step, the large particle with some tubular structure was obtained after the collision of clusters. Figure 2 shows a snapshot before and after the 30 ns annealing of the imperfect tuber structure at 2000 K. The tubular structure became thick at the narrow part and most straight

due to annealing. With the shrinking rate of 6×10^{-5} Å per time step, clustering was much slower. Figure 3 shows the growth process of the typical tubular cluster from the slower shrinking cell at 2000K. 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. Since the narrow part of the tubular structure were usually Ni free, the tubular structure can be annealed to SWNT structure.

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 caged 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 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.

REFERENCE

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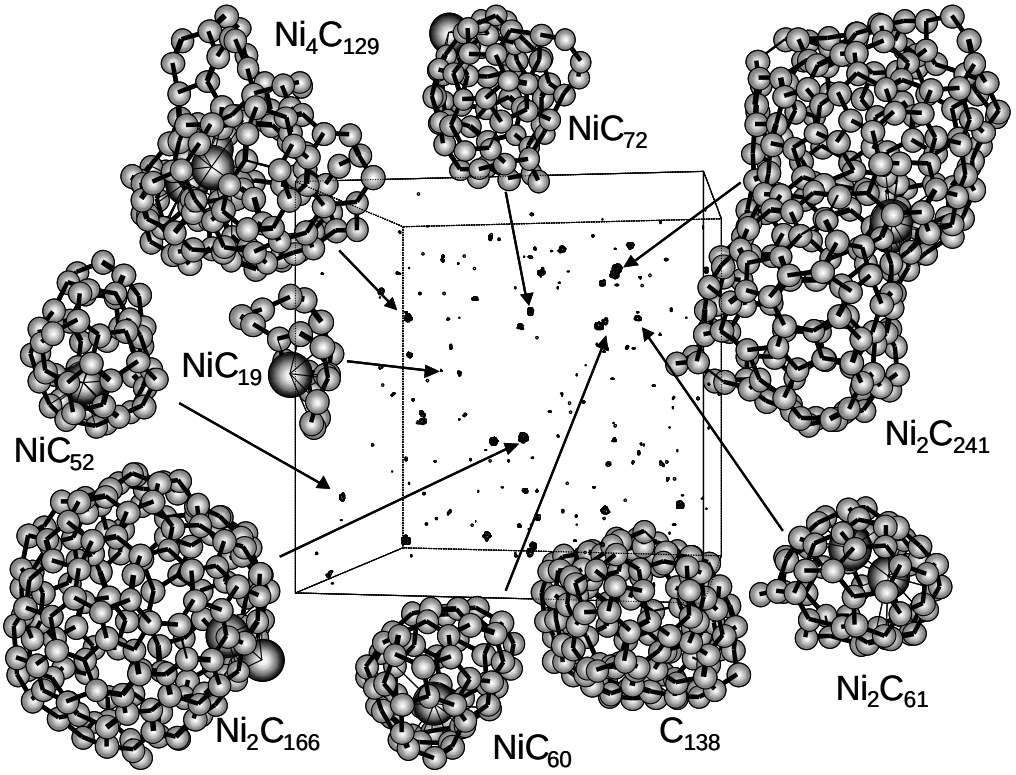
CAPTION TO FIGURES

Fig. 1 A snapshot of clustering simulation at 6 ns.
Fig. 2 Annealing of imperfect tubular structure at 2000K.
Fig. 3 Growth process of tubular cluster.



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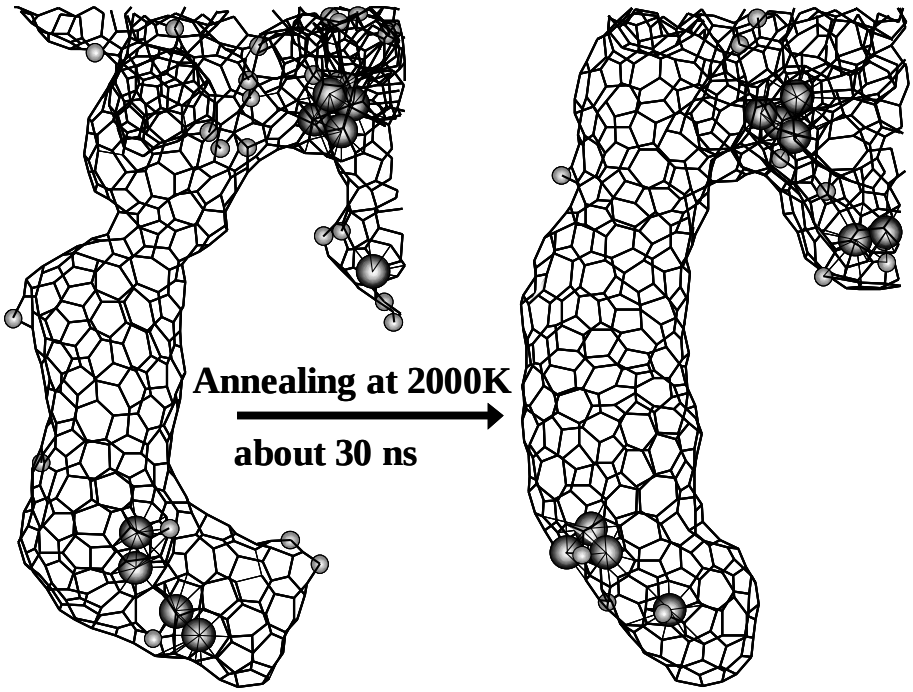
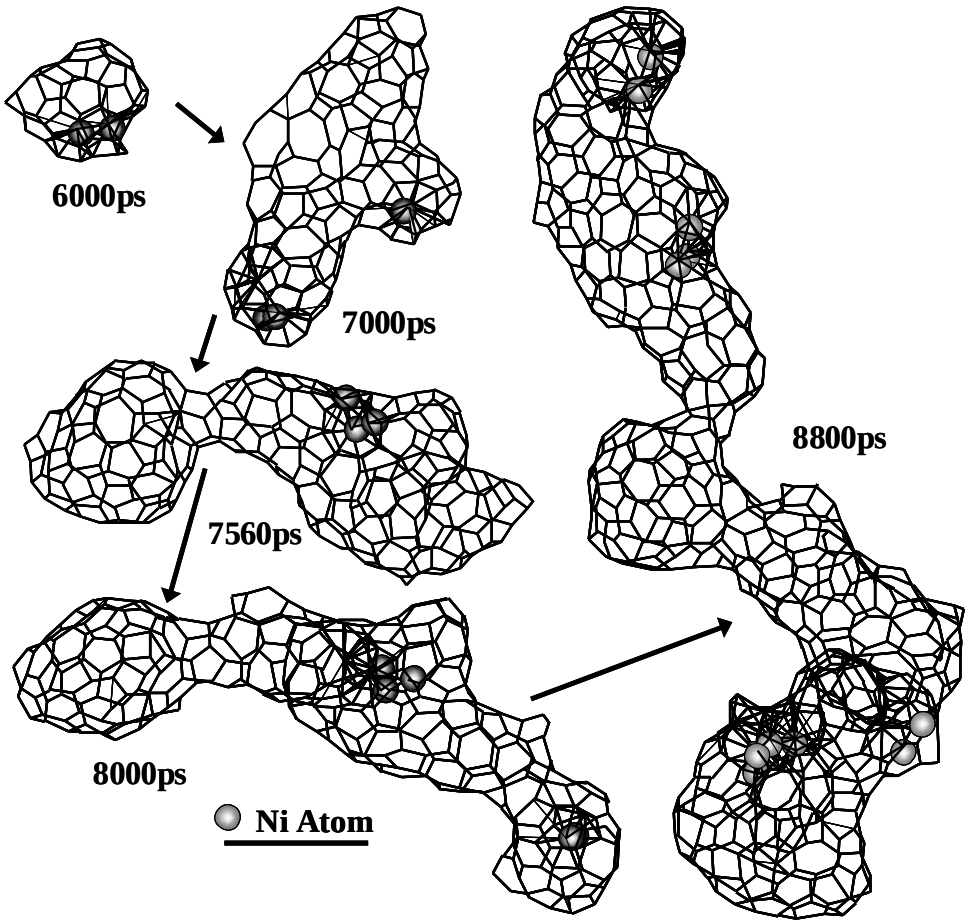


Fig. 2 Annealing of imperfect tubular structure at 2000K.



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