

Influence of metal coating on single-walled carbon nanotube: Molecular dynamics approach to determine tensile strength

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ABSTRACT

The physical strength of a metal-coated single-walled carbon nanotube (SWCNT) is derived in terms of a stress–strain curve by molecular dynamics simulation. The breaking stress of a metal-coated SWCNT was lower than that of an uncoated SWCNT; however, the force constant increased by 17%, which can be attributed to the effect of the metal coating on the SWCNT. With regard to the rupture phenomena, it was observed that the uncoated SWCNT yielded more easily than the metal-coated SWCNT at the yield point. The rupture phenomenon was initiated by a local distortion of the metal atoms of the SWCNT.

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1. Introduction

Among various types of carbon nanotubes [1,2], single-walled carbon nanotube (SWCNT) [3] has been attracting considerable attention since their discovery in 1993. An SWCNT exhibits several useful properties such as high thermal conductivity due to its unique quasi-one-dimensional structure. It can be synthesized using different techniques such as a laser furnace technique [4], arc discharge technique [5,6], and various chemical vapor deposition (CVD) techniques [7–13]. A large number of SWCNT can be grown inexpensively using a super growth technique [14]; however, their growth mechanism has not yet been elucidated completely. Each of the abovementioned techniques involves a different growth mechanism of SWCNT; however, a well-established and acceptable growth model does not exist. Thus far, several theoretical and practical growth models have been introduced [7,15–21]. Modifying the properties of SWCNT can enhance their applicability in various engineering fields. Recently, Ishikawa et al. [22] deposited metal species onto a vertically aligned SWCNT (VA-SWCNT) film, and Zhang et al. [23] coated an isolated SWCNT with several metal species. Such experiments are very interesting because it is known that the SWCNT exhibits high thermal conductivity; thus, the VA-SWCNT is also expected to exhibit high thermal conductivity; however, it should be conjugated with a metal species before use. Inappropriate conjugation would decrease the efficiency of the SWCNT; however, a suitable metal species coated on the SWCNT would enhance its efficiency. The electrical properties of SWCNT are strongly dependent on its chirality, which we cannot control at present. By coating the SWCNT with metal species, we can prepare a metallic SWCNT whose electrical properties are independent of chirality. However, this may affect the original

properties of SWCNT, such as high thermal conductivity and high physical strength.

In this study, we determined the stress–strain curve of SWCNT and observed their rupture phenomena by molecular dynamics simulation. It was observed that the breaking stress of the metal-coated SWCNT was lower than that of the uncoated SWCNT; however, there was an increase of 17% in the force constant, which was caused by the incorporation of the coating metal. With regard to the rupture phenomena, it was observed that the uncoated SWCNT yielded more easily than the metal-coated SWCNT due to yield stress. The rupturing phenomena are initiated by amplifying the local distortion for the uncoated SWCNT and by the metal atoms tear the C–C bond at the local distortion for the metal-coated SWCNT.

2. Methods

An isolated SWCNT with (5, 5) chirality is used as an object whose carbon–carbon interaction parameters are determined using a simplified Brenner–Tersoff potential [24,25]. The carbon–metal and metal–metal interaction parameters of the isolated SWCNT are also determined using the Brenner type potential, and its potential parameters are employed from the results of Shibuta and Maruyama [26]. The metal-coated SWCNT is prepared by metal cluster deposition onto the isolated SWCNT, as described in our previous study [27]; therefore, we explain its condition briefly. In this study to simulate the rupture phenomena of metal-coated SWCNT, we employed 250 nickel atoms which can smoothly attached on SWCNT surroundings unlike gold atoms. To reduce the calculation load, the chiral index of (5, 5) was employed. The surroundings of SWCNT is smoothly coated by nickel atoms at least one layer without both ends and the equilibrium position for nickel in the first layer is the center of hexagon of carbon atoms. The equilibrium position for the nickel atoms in the second

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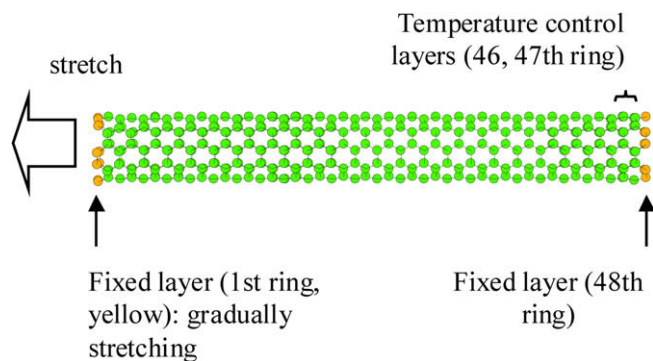


Fig. 1. Calculated system. SWCNT with (5, 5) chirality consists of 480 carbon atoms. The right end ring (48th ring) is fixed and the next two layers (46th, 47th rings) work to control the temperature. The left end ring (1st ring) is also fixed by their *y* and *z* directions, but gradually expands with a certain displacement in each step.

layer was the center of the nickel atoms in the first layer. The isolated SWCNT consists of 480 carbon atoms, and its one side (48th ring in Fig. 1) is fixed. The SWCNT is stretched by gradually pulling the other side (1st ring). The temperature is controlled by only the next two layers (46th, 47th rings) on the fixed side as shown in Fig. 1. To avoid from unintentional sudden relaxation, we did not control the other end. Each stretch step should take an enough relaxation time; otherwise, there may arise an unrealistic distortion and that results in unreliable rupture. Fig. 2 shows the propagation of displacements of the 10th, 25th, and 40th rings at 0 K and 300 K. After the first ring is displaced by 0.1 Å and 0.5 Å at $t = 0$, the displacement propagates toward the opposite direction. The veloc-

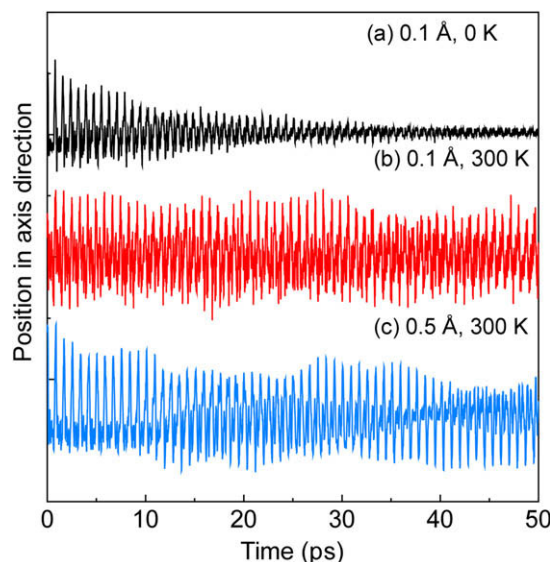


Fig. 3. The relaxation of stretch. The thermal fluctuation is comparable to the displacement that results in difficulty in discriminating the fluctuation and vibration in 300 K, but in 0 K the relaxation can be seen. These vibration period is approximately 785 fs in 0 K and 835 fs in 300 K.

ity of propagation does not depend on the initial displacement length in this study. Each displacement value is expressed as an average of 10 atoms in each ring. At 300 K, the displacement length is too small to be observed, due to the thermal vibration of each atom. If there is sufficient relaxation time, each atom or ring will be restored to its original position. The time profile of the 10th ring is shown in Fig. 3. At 300 K (Fig. 3b and c), an obvious convergence of the rings is not observed because the displacement length of the rings is smaller than that obtained due to thermal fluctuation; in contrast, at 0 K (Fig. 3a), an obvious convergence of the rings is observed. The atoms constantly vibrate around the equilibrium position, where vibrations are roughly equal to 785 fs at 0 K and 835 fs at 300 K. Even though 20 ps appears to be a sufficient relaxation time after each instance of stretching by 0.1 Å.

3. Results and discussion

Fig. 4a shows the force–strain curve obtained by the molecular dynamics simulation. A suitable stress value is defined by assuming the SWCNT to be cylindrical, with the effective cross section as the diameter. In this study, diameters of the uncoated and metal-coated SWCNT are 6.93 Å and 8.32 Å, respectively. The value of the yield stress of the metal-coated SWCNT was approximately half that of the uncoated SWCNT as shown in Fig. 4b. This can be attributed partly to an increase in the cross sectional diameter of the SWCNT by coating metals; however, because the yield force also decreases, the physical strength certainly becomes weak by coating. It has been further observed that metal atoms tend to break carbon bonds. When the SWCNT exhibits local distortion due to stretching, metal atoms break the carbon bonds and stick to the defect. This breaking may be due to a difference in bond lengths. Assuming that the distortion of a hexagonal carbon network in the horizontal direction is negligible, the bond length of a C–C bond becomes 1.8 Å just prior to yield. In reality, the C–C bond length could be reduced from 1.8 Å to approximately 1.75 Å by the distortion of the carbon hexagonal network. According to the Brenner potential, the influence on binding energy suddenly reduces as expressed by an attenuation function f in Eq. (1), where

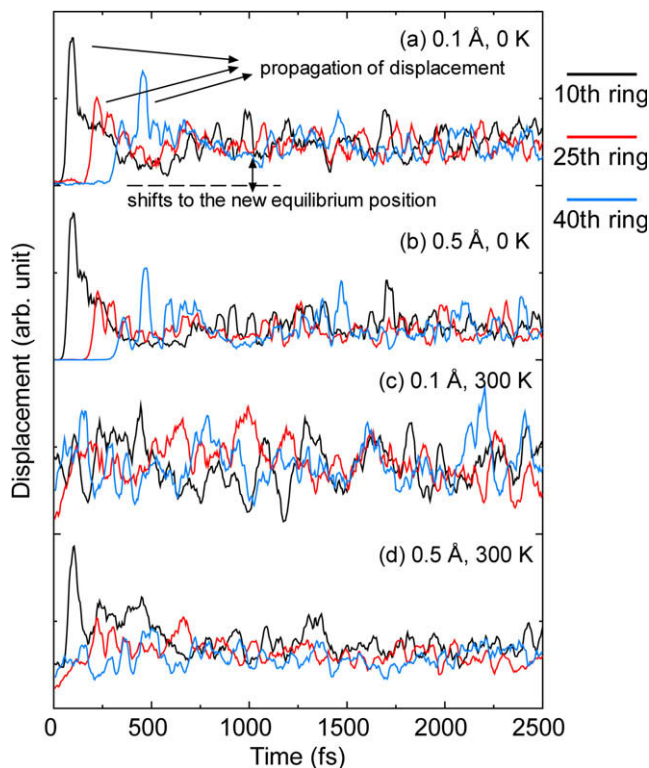


Fig. 2. The propagation of displacement. At time = 0 the first ring named in Fig. 1 is pulled from its equilibrium position by a certain length shown in this figure. The displacement propagates with some delay depends on the distance from the first ring and gradually converges to the new equilibrium position. The propagation delay does not depend on the displacement length in these range but depend on the temperature.

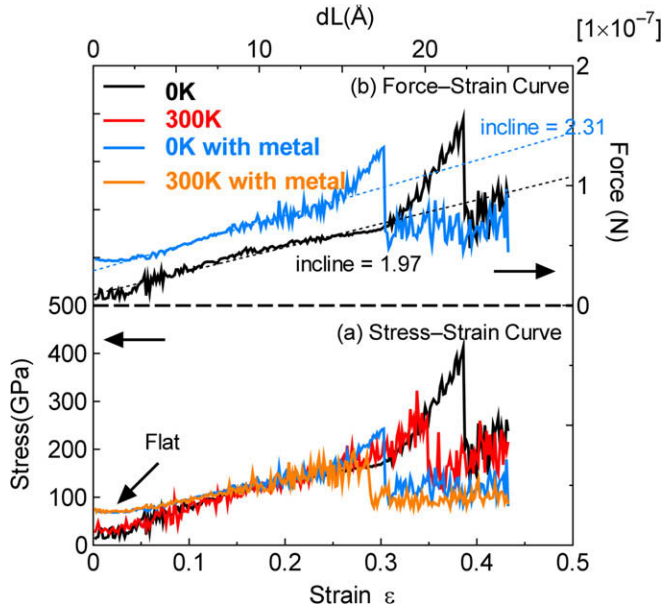


Fig. 4. The force-strain curve (a) and stress-strain curve (b). The stress is defined by assuming their cross section with 6.93 Å for the uncoated SWCNT and 8.32 Å for the metal-coated SWCNT in diameter. The metal-coated SWCNT meets earlier yield point that loses nanotube structure but has a larger force constant. The metal-coated SWCNT has a residual stress that makes the inclination flat in a small strain (displacement) range.

R_1 is 1.7 Å and R_2 is 2.0 Å. On the other hand, the binding energy of a Ni–C bond, shows strongest between 1.76 Å and 2.0 Å that depends on the coordination number; therefore, nickel atoms tend to combine with carbon atoms firmly that results in the rupture of the SWCNT:

$$f(r) = \begin{cases} 1 & (r < R_1), \\ 0.5 \cdot \left(1 + \cos \frac{r-R_1}{R_2-R_1} \pi\right) & (R_1 < r < R_2), \\ 0 & (R_2 < r). \end{cases} \quad (1)$$

As to the force constant metal-coated SWCNT shows larger by 17% than that of uncoated one in Fig. 4b unlike the yield stress and/or force. It was speculated that the force constant of the metal-coated SWCNT should be decreased because the binding energy of the C–C bond became weaker by increasing the coordination number. On the contrary, the force constant increases owing to the metal contribution. When $\epsilon = 0$, stress (σ) is a nonzero value in the case of the metal-coated SWCNT. This is attributed to a residual stress, which is usually present on the conjugating surface of different species in a macroscopic model. According to our previous work the reason of realizing smooth coating on SWCNT was the coincidence of the bond length (Ni–Ni, with a infinite coordinating number) and the distance of the center of a hexagonal carbon network, which is the most stable position for the nickel atoms absorbed on SWCNT. However, strictly speaking, this distance is longer a little (approximately 0.05 Å) for the nickel atoms with practical coordination number; thus, the residual stress works toward the direction of shorten the SWCNT length. This residual stress is clearly seen at the beginning of stretch. The stress does not increase at the beginning of stretch until around $\epsilon = 0.05$ owing to the cancel of pulling stress and shorten stress. This stress remains constant until approximately $\epsilon = 0.05$ due to the absence of pulling stress and shortening stress.

In the uncoated SWCNT, the yield strain is approximately $\epsilon = 0.38$; however, this value itself is not essential for the molecular dynamics simulation. As mentioned by Agrawal et al. [28], the yield strain value is affected by the cutoff length at the Brenner po-

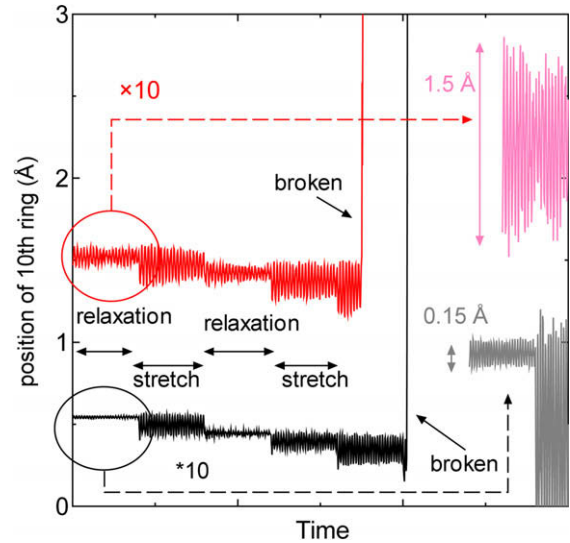


Fig. 5. The thermal fluctuation of the 10th ring in the axis direction in 0 K (bottom) and in 300 K (top). Usually, after each stretch the fluctuation converges to the new equilibrium position during the following relaxation time, but just before the amputation the fluctuation diverges.

tential In reality, at $\epsilon = 0.38$, the length of the C–C bond becomes 2.0 Å; this is equivalent to the cutoff length at the Brenner potential; thus, this value itself depends on the potential parameters but essentially the rupture phenomena occurred earlier in metal-coated SWCNT system. The yield strain at 300 K is less than that at 0 K. This difference in strains is attributed to the thermal fluctuations and not the decrease of binding energy due to the increase of the temperature. At high temperature, the velocity of the atoms increases, which results in a large fluctuation, as shown in Fig. 5. The upper part of this figure shows of the results obtained at 300 K, and the lower part shows those results obtained at 0 K. This figure shows that the thermal fluctuation is considerably larger in the case of 300 K. After each instance of stretching, there is a sufficient relaxation period during which the fluctuation decreases and the center of vibration shifts to the new equilibrium position. However, when the SWCNT yields, the fluctuation diverges and does not decrease during the relaxation period. At 300 K and approximately $\epsilon = 0.35$, the C–C bond length can exceed 2.0 Å due to the thermal fluctuation. It is speculated that the force constant should become smaller in 300 K than that in 0 K and the incline of the stress-strain curve should become smaller. This is not shown in Fig. 4. This reason is not clear but in this study the procedure is continuous stretch that may include any fluctuation that conceals the temperature effect; however, this effect is clearly confirmed in the simple harmonic oscillation shown in Fig. 3. As we mentioned above, the force constant estimated by the simple formulation shown in Eq. (2) becomes smaller by 13% (the harmonic period is 785 fs at 0 K, and 835 fs at 300 K):

$$T = 2\pi \sqrt{\frac{m}{k}}. \quad (2)$$

Fig. 6 shows images of the stretched SWCNT just before and after yield. In the case of the uncoated SWCNT, the nanotube easily yields after acquiring a string-like shape; however, in the case of the metal-coated SWCNT, the nanotube does not yield completely. These phenomena can be explained by the fact that the carbon atom prefers to exhibit an sp^2 structure or at least tends to maintain this structure at the Brenner potential; thus, once a particular bond is broken, all the carbon atoms saturate the dangling bonds by forming a spherical structure. This causes the SWCNT to rupture easily. On the other hand, in the case of the metal-coated SWCNT,

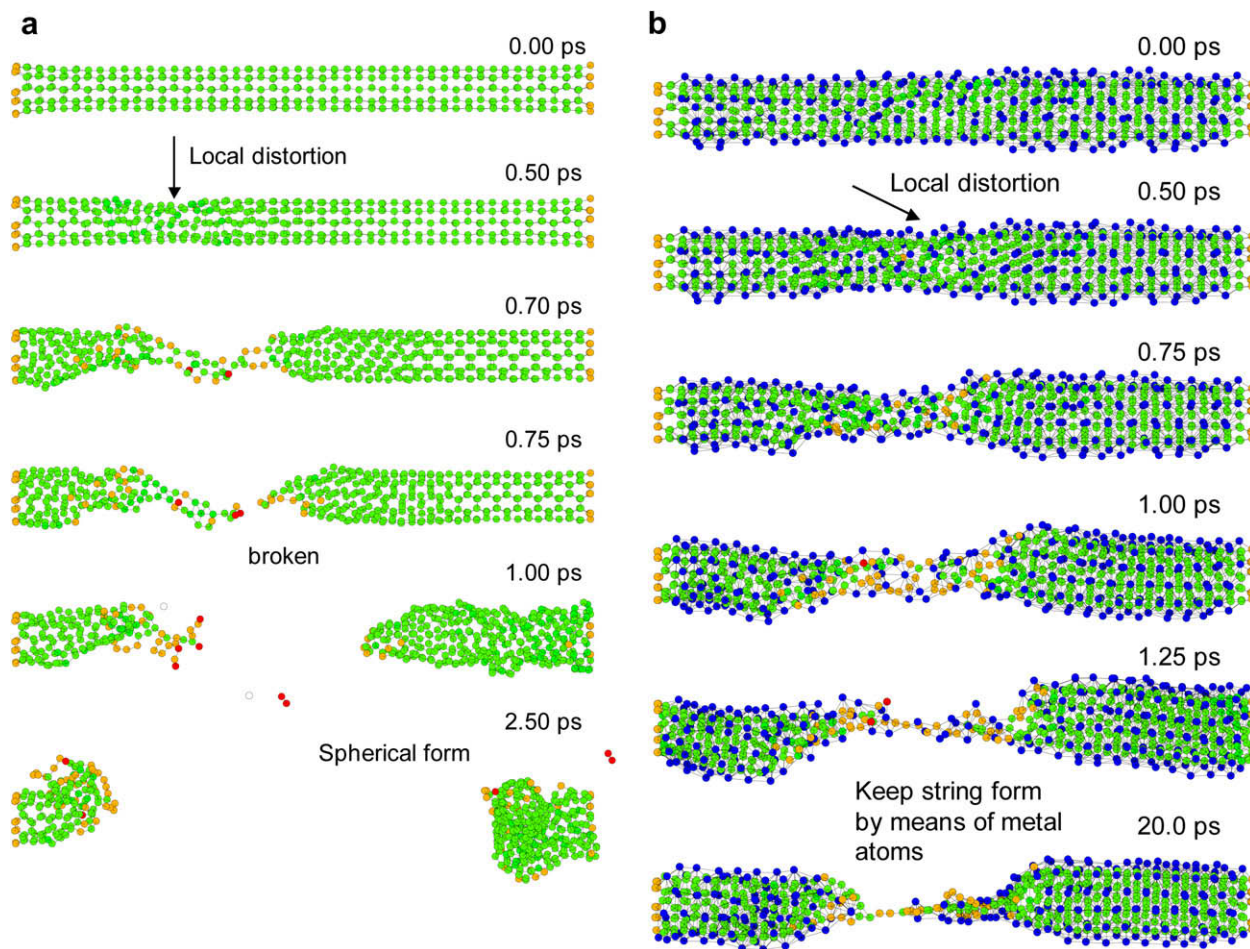


Fig. 6. The snap shots of stretches. The time shown in each figure denotes the time progress from the last stretch. The green, orange and red ball stands carbon atoms with 0, one, two dangling bonds, respectively. The blue ball stands metal atoms. The uncoated SWCNT is broken lightly broken but the metal-coated SWCNT is not completely broken, because the carbon atoms tend to take a spherical form after arising a local distortion and/or local defect to keep sp^2 structure; however, in case of the metal-coated SWCNT the metal atoms can terminate the dangling bonds of carbon atom that results in avoid or delay the complete amputation (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

numerous metal atoms, which are not strictly defined the coordination number like the carbon atoms are, can terminate the dangling bond of the carbon atoms and form bonds with each other. As a result, the SWCNT does not rupture completely because of the linking of the metal atoms; a subsequent annealing process could result in the formation of hexagonal or pentagonal carbon rings. If other metal species, which can coat SWCNT smoothly, are applied to this system, similar phenomena are expected; however, the binding energy between carbon and metal becomes stronger the yield point might come earlier because the C–C bond is broken by the metal atom earlier.

4. Conclusion

Molecular dynamics simulation of metal-coated and uncoated SWCNT was performed, and the stress–strain curves were derived. With regard to the yield point, the metal-coated SWCNT meets earlier yield point than uncoated SWCNT. This is not due to the binding energy of C–C but rather than interferences of the coating metal. The binding energy of C–C must be weakened by increasing the coordination number but the earlier rupture is caused by the coating metal atoms. When the strain becomes approximately 0.3, the binding energy of the C–C bond becomes extremely low; on the other hand, the binding energy of the Ni–C bond becomes nearly maximum. The metal atoms tend to combine with the car-

bon atoms by breaking C–C bond that results in the yield of SWCNT. Because the carbon atom prefers to keep sp^2 structure, the carbon atom whose pair is robbed by the metal atom forms a spherical structure to saturate its dangling bond.

The force constant of the metal-coated SWCNT increases by 17% due to the effect of the coating metal. The disadvantage of metal coating is that the yield stress becomes approximately half that of uncoated SWCNT and reduces by 25% in comparison with the yield force. This implies that the metal-coated SWCNT keeps still a higher tensile strength than conventional materials. The advantages of coating the SWCNT with a metal outweigh its disadvantages because a metal-coated SWCNT can exhibit novel properties, and its electrical properties could be controlled. With regard to the rupture phenomena, the uncoated SWCNT ruptures faster in order to maintain the carbon sp^2 structure by forming a spherical structure; on the other hand, the metal-coated SWCNT does not rupture completely because metal atoms that saturate the dangling bond of the carbon atoms and form bonds with each other are not clearly defined in terms of their coordination number in the potential function.

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