The Influence of the Density of CNT Arrays on Their Atomic Oxygen Erosion Effects

Man Li, Yuming Liu, Yu Li, Qiang Yu, Yongtai Zhang, Chong Liu

a Beijing Institute of Spacecraft Environment Engineering, Beijing, P. R. China;
b Science and Technology on Reliability and Environment Engineering Laboratory, Beijing, P. R. China.

Abstract. To investigate the characteristic of carbon nanotube (CNT) arrays with high resistance to the hazardous conditions of atomic oxygen in space environment, the erosion effects of atomic oxygen on CNT arrays with different density have been studied by atomic oxygen simulation equipment. To characterizing the change of the surface morphologies of CNT arrays before and after atomic oxygen exposition, A scanning electron microscope (SEM) analysis method have been used. The SEM images shows that the morphologies of the surface of CNT arrays after atomic oxygen experiment are quite different from those before atomic oxygen experiment. The higher density CNT arrays are etched away more uniformly. The erosion yield of the CNT arrays with higher density is much less than that with lower density, which means that the CNT materials have different atomic oxygen erosion yield. The resistance ability of CNT materials to atomic oxygen is depending on their density.

1. Introduction
Carbon nanotubes (CNTs) are outstanding materials for space application due to their unique properties with high thermal and electrical conductivities, low density, good chemical stability, extremely high strength, and high stiffness [1, 2]. In space application, the CNT materials will be exposed in space environments. The suffer extreme space environments will greatly affect the properties of CNTs. Atomic oxygen in space environment is one of the most dangerous environments for space materials. Atomic oxygen is energetic particle and can etch most space materials. So before the application of carbon nanotubes in aerospace, the resistance ability of CNTs to atomic oxygen must be obtained to assuring that CNTs is suitable for using in atomic oxygen environment [3].

To present the atomic oxygen effects on CNTs, A few studies had been carried out [4-7], such as CNT wires, CNT films CNT composites. To present the atomic oxygen effects, the atomic oxygen erosion yields ($E_y$, volume of material removed per oxygen atom arriving) had been measured. Their results showed that different CNT materials had different atomic oxygen erosion yields. It presented that CNT-Polymer matrix had higher resistance against the atomic oxygen environment than polymer, which meant adding CNTs into polymer matrix could improve the resistance of polymer matrix composites against the atomic oxygen environment [4]. For pure CNT materials, the erosion yields were quite different. The CNT wires and carbon nanotube films have the erosion yields about 2.64×10$^{-25}$ cm$^3$/atom and 6.6×10$^{-25}$ cm$^3$/atom respectively [5,6]. But the erosion yields of CNT arrays were very high about (6×10$^{-23}$ - 17×10$^{-23}$) cm$^3$/atom [7]. We had supposed that the density of CNT arrays might
influence the atomic oxygen effects of CNT array. Here the atomic oxygen effects of CNT arrays with higher density than before have been studied. The experimental results will be presented.

2. Experimental method
Well aligned CNT arrays with different density were synthesized by chemical vapor deposition methods. An atomic oxygen simulation facility was used to produces a 5 eV neutral atomic oxygen beam to simulate the atomic oxygen environment. The sample of CNT array was placed on a holder in the atomic oxygen simulation facility. The atomic oxygen exposure test is carried out under vacuum condition. After the vacuum degree was superior to 0.001Pa, a directed atomic oxygen beam was produced and impacted the CNT arrays.

The morphologies of CNT arrays before and after atomic oxygen exposure were studied by scanning electron microscopy (SEM, S-4800, Japan).

According to Eq. (1) as reported before [9], the erosion yield of CNT arrays could be calculated by:

\[ E_y = \frac{\Delta L}{F} \]  

Where \( \Delta L \) is the height loss of the CNT arrays (cm) which can be calculated from their SEM images, \( F \) is the atomic oxygen fluence (atoms/cm²).

3. Result and discussion
Figure 1 shows the surface morphologies of CNT arrays with different density before atomic oxygen exposure. On the surface of both CNT arrays, the carbon nanotubes are tangled in each other. The density of CNT arrays synthesized by depositing acetylene (Figure 1 b) is at least twice than that synthesized by depositing ethylene (Figure 1 a).

![Figure 1 The surface morphologies of CNT arrays before atomic oxygen exposure with lower density (a) and higher density (b)](image)
After atomic oxygen exposure with the atomic oxygen fluence $0.5 \times 10^{20} \text{atom/cm}^2$, the surface of the CNT arrays with lower density isn’t flat any more according to Figure 2. Many needle-shaped bundle structures have been obtained (Figure 2 a and c). Each needle-shaped bundle contains both carbon nanotubes and amorphous carbon (Circled in Figure 2a).

The surface morphology of the CNT arrays with higher density after atomic oxygen exposure is quite different from those with lower density (Figure 2 b and d). Abundant amorphous carbon is produced after atomic oxygen exposure (Figure 2 b). The amorphous carbon and the carbon nanotubes are twined and formed net-structure on the surface of the CNT arrays (Figure 2 d). The surface of the CNT arrays isn’t continuous, on which there are many lines. None needle-shaped bundle has been formed on the CNT arrays with higher density.

![Figure 2](image)

**Figure 2** Different magnified SEM images of CNT arrays after atomic oxygen exposure with nominal fluence of $0.5 \times 10^{20} \text{atom/cm}^2$. (a) (c) CNT arrays with lower density; (b) (d) CNT arrays with higher density

If the atomic oxygen exposure test is continuing, the surface of CNT array with lower density isn’t flat and continuous any more. CNTs are completely etched away in some regions as was reported before [7] (Figure 3 a).

On the other hand, the CNT array with higher density is etched away relatively uniformly (Figure 3 b), the surface morphology of which nearly no change during the atomic oxygen exposure process (Figure 2d and Figure 3 b). Many nets composed of amorphous carbon and carbon nanotubes covers carbon nanotubes as shown in Figure 3 c and d. It seems that molecule structure of CNTs could be greatly destroyed by strong impact forces of high energy atomic oxygen, and then be turned into amorphous carbon or carbon particles. So amorphous carbon can be observed after atomic oxygen exposure. Due to the oxidation reaction, the amorphous carbon can react with atomic oxygen. The
amorphous carbon is formed and eliminated constantly and simultaneously, which lead to heigh of the CNT arrays decreasing gradually. The surface morphologies of different density CNT arrays are totally different though the atomic oxygen exposure condition is completely the same. The CNT arrays with lower density are etched away ununiformly, while the higher density CNT arrays are etched away much more uniformly. It is believed that the density of CNT arrays plays an important role for these phenomena. Although the CNT arrays are composed of condensed carbon nanotubes, there is narrow spacing between the CNTs [8]. The narrow space which depends on the density of CNT arrays results in different van der Waals forces between CNTs. The atomic oxygen can inject into the lower density CNT arrays, etch interior CNTs and press the CNTs on both sides, so a “V” shape structure can be observed after atomic oxygen exposure [7]. The CNTs can support each other strongly in higher density CNT arrays, so the atomic oxygen can’t cut CNT arrays apart and the CNT arrays are etched away much more uniformly.

![Figure 3](image-url)

**Figure 3** (a) Lower density CNT arrays after atomic oxygen test with fluence of $5.0 \times 10^{20}$ atom/cm$^2$. (b) (c) (d) Different magnified images of higher density CNT arrays after atomic oxygen test with fluence of $1.6 \times 10^{21}$ atom/cm$^2$.

The erosion yield of the CNT arrays with higher density were calculated. The height of CNT arrays is about 300 μm. When the atomic oxygen fluence is $1.6 \times 10^{21}$ atom/cm$^2$, the CNT arrays are almost etched away. So, the erosion yield of the CNT arrays is about $1.8 \times 10^{-23}$ cm$^3$/atom, which is much less than the lower density CNT arrays as reported before [7].

It had been studied that CNT wires was reported to erode at about $2.64 \times 10^{25}$ cm$^3$/atom [5], which means CNT wires are more resistant against atomic oxygen than CNT arrays. The reason may be due to the density of CNT too. The CNT wires are composed of CNT yarns, which means the density of CNT wires must be higher than the CNT arrays used here. The resistance of CNT based materials to
atomic oxygen must be related to the density of CNTs. It is very important to choose high density CNT-based materials when CNT-based materials is used in LEO applications.

4. Conclusions
The space atomic oxygen effects on CNT arrays with different density have been studied. The surface morphologies of CNT arrays with different density are also quite different after atomic oxygen exposure test. The CNT array with higher density is etched away relatively uniformly. The density of CNT arrays is related to the atomic oxygen erosion yields. A higher density CNT array can have better resistance to the hazardous conditions of atomic oxygen. So the CNTs materials with higher density may be more suitable for space application.

Acknowledgments
This work was funded by the Youth Program of National Natural Science Foundation of China (Grants No. 51902026) and the Basic Technology Research Project (No. JSHS2019203B001).

References
[1] O. Gohardani, M. C. Elola, C. Elizetxea. Potential and prospective implementation of carbon nanotubes on next generation aircraft and space vehicles: A review of current and expected applications in aerospace sciences, *Progress in Aerospace Sciences*, 2014, 70: 42-68
[2] M. B. Jakubinek, B. Ashrafi, Y. Zhang, Y. Martinez-Rubi, C. T. Kingston, A. Johnston, B. Simard, Single-walled carbon nanotube–epoxy composites for structural and conductive aerospace adhesives, *Composites Part B: Engineering*, 2015, 69: 87-93.
[3] S. L. Koontz, K. Allyn, L. J. Leger, Atomic oxygen testing with thermal atom systems: a critical evaluation. *J Spacecraft Rockets*, 1996, 33: 8-14
[4] S. B. Jin, G. S. Son, Y. H. Kim, C. G. Kim, Enhanced durability of silanized multi-walled carbon nanotube/epoxy nanocomposites under simulated low earth orbit space environment. *Composites Science and Technology*, 2013, 87: 224-231
[5] H. E. Misak, V. Sabelkin, S. Mall, P. E. Kladitis, Thermal fatigue and hypothermal atomic oxygen exposure behavior of carbon nanotube wire. *Carbon*, 2013, 57:42-49
[6] L. B. Jiao, Y. Z. Gu, S. K. Wang, Z. J. Yang, H. Wang, Q. W. Li, M. Li, Z. G. Zhang, Atomic oxygen exposure behaviors of CVD-grown arbon nanotube film and its polymer composite film. *Composites: Part A*, 2015, 71:116-125.
[7] Y. M. Liu, X. N. Yang, M. Li, Y. T. Zhang, C. Q. Zhao, W. Qin, Erosion effects of atomic oxygen on carbon nanotube arrays in different incidence direction. *Surface and Interface Analysis*, 2018, 50:592–598.
[8] B. Q. Wei, R. Vajtai, Y. Jung, J. Ward, Y. Zhang, G. Ramanath, P. M. Ajayan, *Nature*, 2002, 416: 495–496.