Revelation of catalytic reduction process affecting the morphology and properties of CNTs/carbon fabrics and their composites

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Abstract. Carbon nanotubes/carbon fabrics and their reinforced resin matrix composites were manufactured by chemical vapor deposition and molding method, respectively. Different catalytic reduction processes with different catalyst types and reduction temperatures had different effects on their morphology and properties. It was found by a series of characterization methods that the catalytic activity of the bimetallic catalyst was higher than that of the single metal, and the surface uniformity of CNTs catalyzed by Fe-Co was the best. When the reduction temperature reached the growth temperature, the uniformity of CNTs and the interlaminar shear strength of composites increased obviously. The influence mechanism of these parameters was discussed in depth, which provided a fundamental engineering basis for understanding of catalytic reduction process, optimizing of CNTs growth process and the application of high-performance composite materials.

1. Introduction
Carbon fabrics reinforced polymer matrix composite is a special class of high-performance materials that has received extensive research attention in recent decades [1]. Due to its unique combination of properties, such as high specific strength, high specific stiffness, excellent corrosion resistance [2], and excellent designability [3], it has become an ideal choice for structural materials in many fields, such as aerospace [4], automobile and ship [5], weapon equipment and civil infrastructure [6]. However, the surface inertness of the carbon fabric itself [7] causes a weak bond with the matrix [8], resulting in the low interface strength [9, 10] and the damaged mechanical properties of the composite. Therefore, many experimental studies have been devoted to the surface modification of carbon fabrics and the interfacial optimization of their composites [11]. One of the most competitive and promising methods is the direct growth of Carbon nanotubes (CNTs) on the surface of carbon fabrics by chemical vapor deposition (CVD), which aims to improve the interface bonding and the overall mechanical properties of the composites on the nanometer scale.

In the whole process of CNTs growth by CVD, the catalytic reduction process is considered to play an important role. In this process, the catalyst provides the initial carbon cap for CNTs nucleation, and catalyzes the cracking of carbon source, continuously supplying activated carbon atoms to the roots of
the CNTs, so as to promote their growth [12]. Different catalyst types and catalytic reduction temperatures will cause the catalyst particles to have different crystal structures, different particle sizes, and different catalytic activities, which will have different effects on the growth of CNTs. However, there are few researches focusing on the catalytic reduction process. In this paper, the effects of catalyst types and catalytic reduction temperatures on the morphology and the mechanical properties of carbon fabrics and their composites were studied, and the mechanism was discussed.

2. Experimental

2.1. Preparation of CNTs/carbon fabrics reinforcements
The commercial carbon fabrics from Zhongjian Company were cut into a suitable size and laid on a graphite frame. It was put into a \( \phi 40 \) vertical CVD furnace, and kept at 450°C for 1.5h to remove the surface sizing agent. Then, the ethanol solutions of 0.05mol/L \( \text{Fe(NO}_3\text{)}_2 \cdot 9\text{H}_2\text{O} \) and 0.05mol/L \( \text{Co(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} \) were prepared, and the two were mixed at a ratio of 1:0, 0:1, 1:1, and 2:1, respectively. The desized carbon fabrics were immersed in the different solutions mentioned above respectively, taken out and placed in the CVD furnace after 10min. Keeping the furnace pressure at 0.01MPa, the reactor was heated to 450°C, 500°C, 550°C, or 600°C, and then the temperature was maintained for 0.5h with \( \text{H}_2 \) being passed in. During the process, the catalyst's nitrate precursors were reduced to metal nanoparticles, labeled as \( \text{Fe, Co, Fe-Co, and Fe}_2\text{-Co} \), respectively. The temperature of reactor was subsequently raised to 600°C, and CNTs were synthesized directly on the surface of carbon fabrics by introducing a mixture of \( \text{H}_2 \), \( \text{C}_2\text{H}_2 \), and \( \text{N}_2 \) for 10 min, obtaining the CNTs/carbon fabrics reinforcements. The feeding rates of these gases were set to 6, 6, and 12L/min, separately. The specific sample parameters are shown in table 1.

| Sample | Catalyst type | Reduction temperature(°C) |
|--------|---------------|---------------------------|
| 1#     | Fe            | 450                       |
| 2#     | Co            | 450                       |
| 3#     | Fe-Co         | 450                       |
| 4#     | Fe-Co         | 450                       |
| 5#     | Fe-Co         | 500                       |
| 6#     | Fe-Co         | 550                       |
| 7#     | Fe-Co         | 600                       |

2.2. Preparation of CNTs/carbon fabrics reinforced composites
TDE-85 epoxy resin and DDS curing agent were selected as the resin mixture, and the prepreg was prepared after it was completely wetted with CNTs/carbon fabrics. Put it into the hot press, adopt the method of sectional pressurization: keep the temperature at 120°C, 150°C and 180°C for 1h respectively, and apply the pressure of 60-80kg/cm² at the pressurization point, then the CNTs/carbon fabrics reinforced composite was made by post-treatment.

2.3. Characterization
The surface morphology of CNTs/carbon fabrics were characterized by Field emission scanning electron microscope (FESEM), and the graphitization order of CNTs/carbon fabrics were characterized by Raman spectroscopy.

According to the national standard GB/T3362-2005, the monofilament strength of carbon fabrics under different process conditions were tested. A monofilament with appropriate length was cut out from the carbon fabric, fixed on a paper frame, and tested for tensile strength with XQ-1 tensile tester from Donghua University. At least 30 monofilaments were tested for each sample.

According to the standard JC/T773-2010, the interlaminar shear strength (ILSS) of carbon fabrics/epoxy resin composites under different process conditions were tested. The laminates were cut
into 20×10×2mm rectangular strips as test specimens, and tested with universal testing machine. It is then calculated by subsequent formulas to finally obtain the ILSS value. Each sample was tested at least 5 times, and the average value was taken.

3. Results and Discussion

3.1. Effect of catalyst types on CNTs loading on the surface of carbon fabrics
Figure 1 shows SEM images of CNTs/carbon fabrics obtained after using different catalyst types. The comparison of the corresponding CNTs yield is shown in figure 2. When Fe is used as catalyst, the yield of CNTs loaded on the surface of carbon fabric is only 3.16%, the length is short and the diameter is small. There are still small carbon shells on the surface of carbon fabrics which could not grow in time. Fe has a high melting point and low catalytic efficiency at 600°C. Therefore, Fe nanoparticles have a small number and a small size after reduction. Compared with Fe, Co has a larger particle size and is more likely to adsorb and crack more carbon source gases at 600°C, resulting the diameter of CNTs is larger and the yield is higher. When Fe-Co catalyst with the same concentration is used, the adsorption rate of carbon source is more matched with the diffusion rate of active carbon atom. CNTs grown are longer, without impurities. They have the best surface uniformity and the highest yield. This indicates that the catalytic activity of the bimetal catalyst is higher than that of the single metal. In this process, both Fe and Co catalysts play an important role, balancing their catalytic efficiency to a certain extent, which is conducive to the increase of CNTs yield and purity. The catalytic activity of Fe₂-Co is higher than that of Fe-Co, and the adsorption cracking rate of carbon source is faster than the diffusion rate of active carbon atom, which makes it easy to deposit a thick graphite layer on the surface of catalyst and deactivate it, resulting in poor surface uniformity of CNTs and increase of impurity particles, such as amorphous carbon.

![Figure 1](Image 1.png)

**Figure 1.** Surface morphology of CNTs/carbon fabrics under different catalyst types.

![Figure 2](Image 2.png)

**Figure 2.** Yield of CNTs under different catalyst types.

3.2. Effect of catalyst types on the graphitization degree of CNTs/carbon fabrics
The CNTs/carbon fabrics catalyzed with different catalysts were characterized by Raman spectroscopy, and the results are shown in figure 3. There are only two Raman peaks in the four spectra, namely 1360cm⁻¹ (D peak) and 1600cm⁻¹ (G peak). The G peak represents the graphitization and crystallization of CNTs, and the D peak represents the disordered carbon structures or the structural defects of CNTs [13]. The intensity ratio of G peak to D peak (I_G/I_D) is considered as a rough measurement of the quality and crystallinity of CNTs. The lowest R value when Fe is used as catalyst indicates that the CNTs catalyzed by Fe have the best quality and the highest crystallinity. In contrast, Co has the worst catalytic effect. The graphitization degree of CNTs catalyzed by Fe-Co and Fe₂-Co is
between that catalyzed by Fe and Co, and because of the more Fe content in Fe\textsubscript{2}-Co, the quality of CNTs catalyzed is closer to that catalyzed by Fe.

![Figure 3](image)

**Figure 3.** Raman spectra of CNTs/carbon fabrics under different catalyst types.

### 3.3. Effect of catalyst types on tensile strength of CNTs/carbon fabrics

The tensile strength of CNT/carbon fabrics catalyzed by different catalysts was tested, and the comparison results are shown in figure 4. The change of carbon fabric strength during CVD mainly depends on two aspects [14]: the diffusion of catalyst particles into the carbon fabric and the repair of carbon fabric defects by CNTs [15]. Due to the low catalytic activity and the small particle size of Fe at 600°C, the diffusion degree to the graphite region of carbon fabric is low, and the damage to carbon fabric is not serious. However, the Fe nanoparticles that did not play a catalytic role remained on the surface of carbon fabrics, resulting in less CNTs yield and less defect repair. The catalytic activity of Co is higher than that of Fe, and a large number of active carbon atoms produced in CVD process can better repair the damage caused by catalysts, so that the tensile strength of CNTs/carbon fabrics is the highest under this condition. As Fe-Co has the catalytic properties of both Fe and Co, the CNTs catalyzed by it have good quality and high yield, but with the increase of its catalytic activity, the diffusion rate also accelerates accordingly, so that the tensile properties are impaired. The cracking rate of carbon source by Fe-Co is too fast, the catalyst particles are easy to be wrapped and inactivated, so the amount of diffusion and the yield of CNTs are reduced simultaneously, which results the damage and repair of CNTs/carbon fabrics tend to balance.

![Figure 4](image)

**Figure 4.** Tensile strength of CNTs/carbon fabrics under different catalyst types.
3.4. Effect of catalyst types on ILSS of CNTs/carbon fabrics reinforced composites

Figure 5 is the ILSS comparison of CNTs/carbon fabrics reinforced resin matrix composites. We can find that ILSS of the four composites are not much different. Uniform and high-quality CNTs will be beneficial to increase the resin wettability of carbon fabrics and the interlaminar properties of composites, such as Fe catalysis. The CNTs catalyzed by Co and Fe₂-Co are not uniform, which weakens the interlaminar bonding of composites and reduces the ILSS. For Fe-Co catalyst, the catalytic activity is the best and the catalyzed CNTs are uniform and pure, but the ILSS shows the lowest value. It is considered that the tensile strength of the CNTs/carbon fabric is the lowest under this condition, which results in the decrease of overall mechanical properties of the composites. Therefore, if the high catalytic activity of catalyst can be utilized, while the high tensile strength of reinforcement can be ensured, the interlaminar properties of the composite will be improved to a greater extent.

![Figure 5. ILSS of CNTs/carbon fabrics composites under different catalyst types.](image)

3.5. Effect of reduction temperatures on CNTs loading on the surface of carbon fabrics

The morphology of CNTs grown at different reduction temperature was analyzed by SEM, and the results are shown in figure 6. figure 7 shows the corresponding CNTs yield. CNTs reduced at 450°C and grown at 600°C have less yield and larger diameter. This is because when the temperature is raised from 450°C to 600°C, the nano-catalysts tend to aggregate in the direction of particle growth, that is, they mostly exist in the form of large particles. When the reduction temperature is set to 500°C, the activity of catalyst and the yield of CNTs are obviously increased, the entanglement of CNTs also increased accordingly. After reduction at 550°C, the fluidity of metal nanoparticles increased and the uniformity of CNTs decreased. When the temperature of reduction and growth is fixed at 600°C, the movement and aggregation of catalyst particles are reduced, so the uniformity and yield of CNTs are the highest.
3.6. Effect of reduction temperatures on the graphitization degree of CNTs/carbon fabrics

Figure 8 shows the Raman spectra of CNTs/carbon fabrics grown at different reduction temperatures. As the reduction temperature rises from 450°C to 550°C, the graphitization degree of CNTs increases slightly. However, after rising to 600°C, the crystallinity of the reduced metal catalyst increases, and the particle size is refined, resulting in the graphitization degree of CNTs being significantly increased, and the lowest R value in the corresponding Raman spectrum. This indicates that reduction at high temperatures and limiting the aggregation of catalyst particles are beneficial to the growth of high-quality CNTs.

3.7. Effect of reduction temperatures on tensile strength of CNTs/carbon fabrics

Figure 9 is a comparison of the tensile strength of CNTs/carbon fabrics monofilaments grown at different reduction temperatures. There is no strict linear correlation between the tensile strength and the reduction temperature. If the reduction temperature is different from the growth temperature, for example, if the reduction temperature is set to 450°C or 500°C or 550°C, the catalytic activity of the metal will increase with rising temperature, and the amount of diffusion into the carbon fabric also increase. After rising to the growth temperature, the etching degree of the catalyst on the graphite crystal area of carbon fabric increases, resulting in the decrease of the final tensile strength. If the reduction and growth are at the same temperature, for example, catalyst reduction and CNTs growth
are completed at 600°C, the uniformly and high-quality CNTs will form cross-links with the surrounding carbon crystals, making up for the damaged surface microcrystals of carbon fabrics, which reduces the stress concentration under external forces, and improves the tensile strength of CNTs/carbon fabrics.

3.8. Effect of reduction temperatures on ILSS of CNTs/carbon fabrics reinforced composites

The change law of the composites ILSS shown in figure 10 and the tensile strength shown in figure 9 are consistent, and both show a maximum value when the reduction temperature is 600°C. This is due to the surface of CNTs/carbon fabrics is pure and free of impurities when the catalyst reduction and CNTs growth are carried out at 600°C, which is conducive to wetting with resin. In addition, the tensile strength of CNTs/carbon fabrics is the highest under this condition. Therefore, when CNTs transfers the shear stress from the matrix to the carbon fabric, the crack propagation is effectively prevented and the ILSS is maximized.

Figure 9. Tensile strength of CNTs/carbon fabrics at different reduction temperatures.

Figure 10. ILSS of CNTs/carbon fabrics composites at different reduction temperatures.

4. Conclusions

Through studying the influence of catalytic reduction process on the morphology and properties of CNTs/carbon fabrics and their composites, and in-depth discussing on the effect mechanism of catalyst types and reduction temperatures, we obtain the following conclusions:
Catalyst types affect their catalytic activity, as well as the synthesis quality and growth efficiency of CNTs, resulting in great differences in the properties of the final composites. The catalytic activity of the bimetallic catalyst is higher than that of the single metal, and the surface uniformity of CNTs catalyzed by Fe-Co is the best.

(ii) When the reduction and growth temperatures are set to 600°C, the uniformity of CNTs and the ILSS of composites increase obviously. In the process of rising temperature, the nano-catalysts tend to aggregate in the direction of particle growth, so removing this process will help to improve the overall performance of CNT/carbon fabrics and their composites.

References
[1] Sharma S P and Lakkad S C. 2015 Composites Part A 69 124-31
[2] Zhao Z B, Teng K Y, Li N, Li X J and Xu Z W. 2017 Composite Structures 159 761-72
[3] Lu R J, Wang C G and Wang Y X. 2018 Ecs. Journal of Solid State Science & Technology 7 49-53
[4] Liu B Y, Liu Z, Wang X J, Zhang G and Long S R. 2013 Polymer Testing 32 724-30
[5] An F, Lu C X, Li Y H, Guo J H and Lu X X. 2012 Materials & Design 33 197-202
[6] Fan W X, Wang Y X, Wang C G, Chen J Q and Wang Q F. 2016 Applied Surface Science 364(2) 539-51
[7] Gan Y X. 2009 Int. Journal of Molecular Sciences 10 5115-34
[8] Park S J and Kim B J. 2005 Materials Science & Engineering A 408 269-73
[9] Zhu Y, Bakis C E and Adair J H. Carbon 2012 50 1316-31
[10] Wu Q, Min L, Gu Y Z, Li Y X and Zhang Z G. 2014 Composites Part A 56 143-49
[11] Cheng Y, Xiao K Q, Lin Y and Mai Y W. 2002 Journal of Materials Science 37 921-27
[12] Rummeli M H, Schaffel F, Bachmatiuk A, Adebimpe D and Trotter G. 2010 ACS. Nano 4 1146-52
[13] Lee C J, Park J and Jeong A. 2002 Chemical Physics Letters 360 250-55
[14] Cartwright R, Esconjauregui S, Hardeman D, Bhardwaj S and Weatherup R. 2015 Carbon 81 639-49
[15] Naito K. 2014 Journal of Materials Engineering and Performance 23 3916-25