SYNTHESIS OF CARBON NANOTUBE REINFORCEMENT IN ALUMINUM POWDER BY IN SITU CHEMICAL VAPOR DEPOSITION

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1 Introduction

Since their discovery by Iijima [1], carbon nanotubes (CNTs) have been expected as ideal reinforcements for composite materials, arising from their excellent mechanical, thermal, and electrical properties, as well as low density. However, the researches on CNT-reinforced metal matrix composites are few as compared with those on CNT-reinforced polymer composites [2, 3], which is attributed to the difficulties in achieving CNT/metal composites with homogeneously dispersed CNTs in the metal matrix and strong interfacial bonding between the CNTs and the matrix. To solve these problems, high energy ball milling was usually applied to disperse CNTs in the metal powders [4-12]. While the morphology and structural integrity of the CNTs are often damaged by the impacting of the milling media under the harsh milling conditions, and thus degrading the reinforcing effect of CNTs [11, 13].

On the other hand, it is well known that CNTs with smaller diameter possess more excellent properties, but until now the diameter of CNTs as reinforcement used in metal matrix composite was mainly larger than 15 nm [4-11]. Few researches have been carried out by using CNTs reinforcement with smaller diameter. Recently, Choi et al. [12] reported that the addition of single-walled CNTs to aluminum matrix resulted in a significant improvement in the overall mechanical performances such as tensile strength and ductility.

In this paper, we report a novel method to prepare homogeneously dispersed CNTs with a small diameter (～10 nm) in Al matrix, which is expected to overcome the limits of traditional mixing method. This process involves depositing the Co catalyst evenly onto the Al powder surface by impregnation route and in-situ synthesis of CNT/Al composite powders by CVD. The dispersion and structure of CNTs in Al powder are investigated.

2 Experimental

2.1 Preparation of the catalyst precursor

The right amounts of $Co(NO)_3 \cdot 6H_2O$ and Al powder (-200 mesh, 99.0% purity) were mixed in 100 ml ethanol to yield a mass ratio of Co:Al=1:99. The mixture was sonicated for 20 min then heated at 60 ^oC under constant magnetic stirring until the ethanol was vaporized completely. After drying in the air, the mixed powders as catalyst precursor was obtained, which was employed in the following synthesis experiments.

2.2 Production of CNT/Al composite powders

Firstly, the as-prepared catalyst precursor was kept in a quartz boat and placed in horizontal quartz tube reactor. To gain Co/Al catalyst, the mixed powders were heated to 250 ^oC in an argon atmosphere, then the hydrogen (150 ml/min) was introduced instead of the argon and kept at 250 ^oC and 450 ^oC for 1h, sequentially. After that, CNTs were synthesized at 600 ^oC for 30 min by introducing a mixture flow of C_2H_2/Ar (20/240 ml/min) into the reactor. Finally, the system was cooled to room temperature under argon atmosphere and CNT/Al composite powders were obtained. The content of CNTs was calculated as follows:

$$\text{CNT (wt.\%)} = (M_1-M_2)/M_1 \times 100\%$$

where M_1 is the weight of the CNT/Al composite powders obtained by CVD and M_2 is the weight of the Ni/Al catalyst.

2.3 Characterization

Field emission scanning electron microscope (FE-SEM) (Hitachi, S4800), transmission electron microscope (TEM) (Philips Tecnai G^2 F20, 200kV) and X-ray diffractometer (XRD) (Rigaku D/MAX-2500) were employed to characterize the samples. Raman spectroscopy of the composite powders was performed by using the 514 nm line of an Ar^+ laser

as the excitation source to validate the quality of the CNTs.

3 Results and discussion

The content of CNTs in the CNT/Al composite powders is 2.7 wt.% for a reaction time of 30 min, indicating that Ni/Al catalyst with low Ni content has a high catalytic activity. Fig. 1a shows the distribution of CNTs in Al powder. A mass of CNTs with average length of 2 μm are homogeneously dispersed on the surface of the Al powder like a web. A more detail investigation of CNTs are preformed by SEM at high magnification, as presented in Fig. 1b. It can be seen that the diameter distribution of CNTs is narrow in the range of 8-13 nm. Moreover, some ends of the separate CNTs implant into the surface crack of Al powder, which improves the bond between CNTs and Al matrix and is helpful to load transfer. In addition, it should be noted that the content of CNTs in CNT/Al composites can be adjusted by changing reaction time.

TEM images of the typical CNTs synthesized at 600 ^{o}C for 30 min are presented in Fig. 2. It is visible from Fig. 2a that the crooked CNTs with well graphitized multi-walled structure have a diameter of about 10 nm, and none amorphous carbon is found in sight. The catalyst particles exist at one end of the CNTs, which is accordant with SEM observation (see Fig.1). EDX results (as seen in Fig. 3) have proved that these catalytic particles are Co, in which the copper peaks should be ignored because they originate from the sample holder. HRTEM image of CNTs is presented in Fig. 2b, it can be found that the wall surfaces of CNTs seem relatively clean and smooth. The graphitic sheets of the CNT are apparent, and the interlayer spacing between graphitic sheets is 0.34 nm, consistent with the ideal graphitic interlayer space (0.34nm).

The as-obtained composite powders are also characterized by Raman spectrum, as seen in Fig. 4. This Raman spectrum distinctly exhibits two peaks (1339.0 and 1605.3 cm^{-1}) corresponding to multi-walled CNTs, which are related to the vibrations of carbon atoms with dangling bonds for the in-plane terminations of disordered graphite (D) and the vibration in all sp^2 bonded carbon atoms in a 2D hexagonal lattice (G), respectively. The intensity ratio of D to G band (I_D/I_G) is calculated to be 0.80. The low relative intensity of D to G-band implies that the obtained CNTs in Al powder are mainly composed of well-crystallized graphite, in good agreement with the above SEM and TEM observations.

Fig. 5 shows the XRD patterns of the as-obtained composite powders. It can be observed that the strongest peaks are ascribed to Al, and very few CNTs and Co catalyst are detected, resulting from their small content. While no any peaks of alumina were observed, indicating that the success of this process in fabricating CNTs/Al composite powders for avoiding oxidation of Al powder.

According to the above illustration, the as-obtained CNTs/Al composite powders are beneficial for fabricating CNT-reinforced composites with high properties. Such work is in progress.

4 Conclusions

Homogeneously dispersed CNTs reinforcement with the average diameter of 10 nm was fabricated in Al powders via in-situ chemical vapor deposition by using Co catalyst. The as-obtained composite powders with well-crystallized CNTs may pave a new way to prepare CNTs/Al composite with high properties.

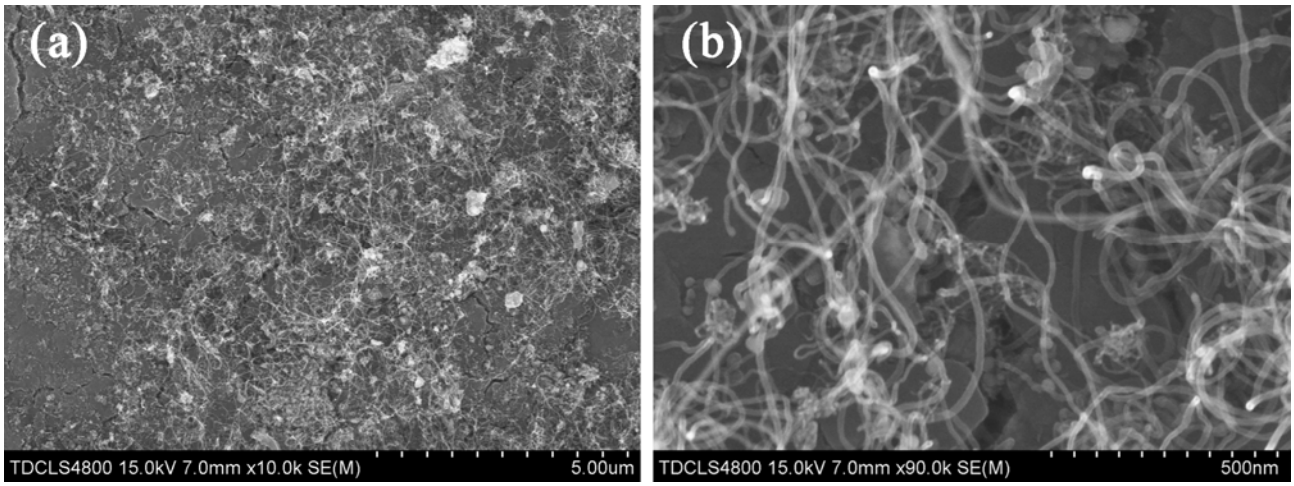

Fig. 1. SEM images of CNT/Al composite powders.

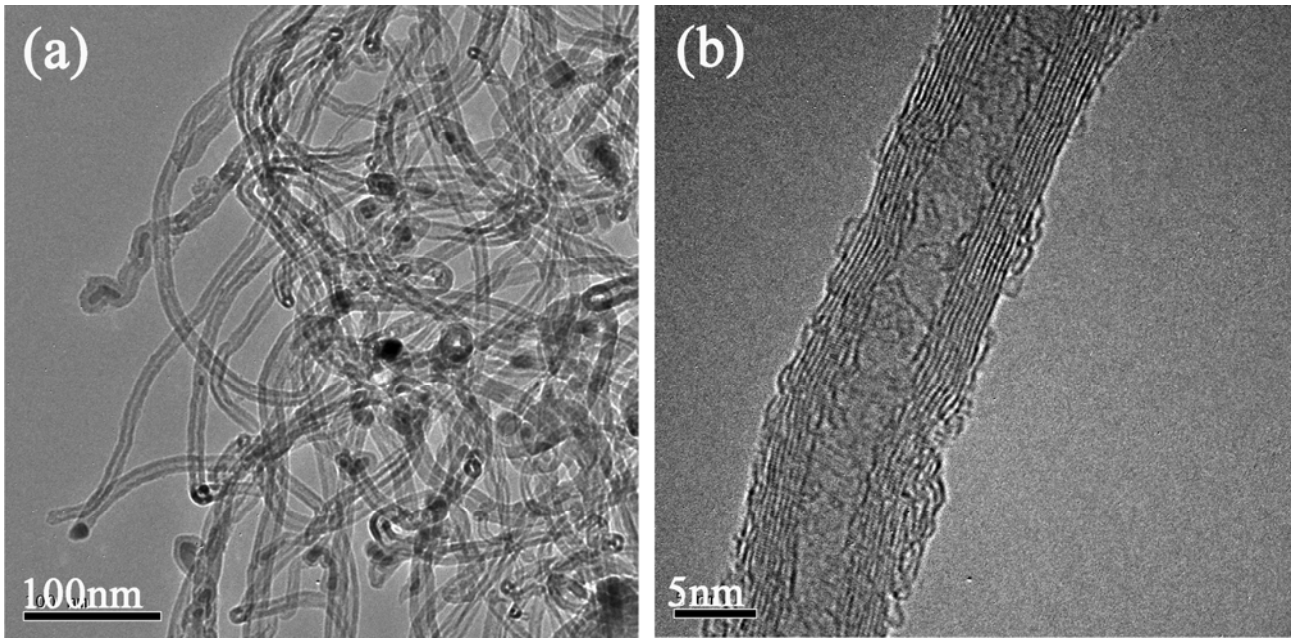

Fig. 2. TEM images of CNTs synthesized at 600 ^{o}C for 30 min.

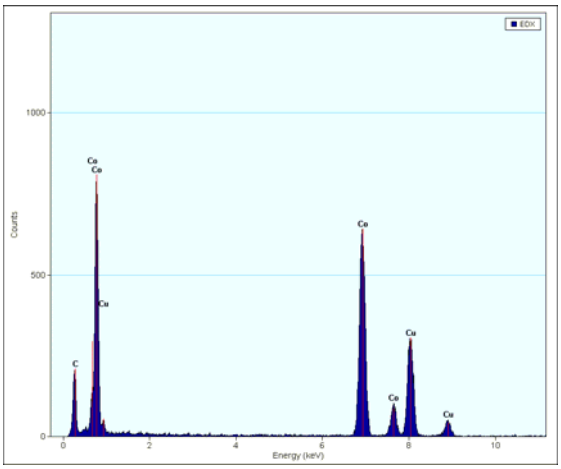

Fig. 3. EDX spectrum of the catalytic particle encapsulated at the end of CNT.

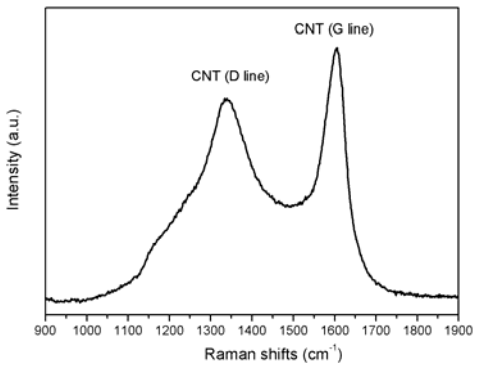

Fig. 4. Raman spectrum of the as-obtained composite powders.

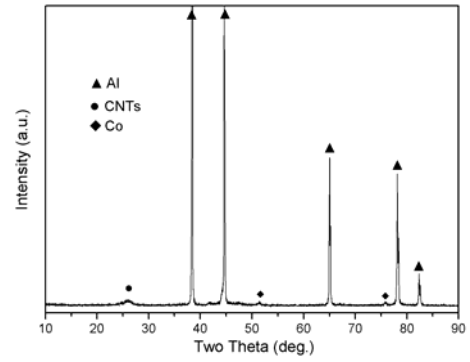

Fig. 5. XRD pattern of the as-obtained composite powders.

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