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In-situ homogeneous synthesis of carbon nanotubes on aluminum matrix and properties of their composites

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Abstract: Using nickel catalyst supported on aluminum powders, carbon nanotubes (CNTs) were successfully synthesized in aluminum powders by in-situ chemical vapor deposition at 650 °C. Structural characterization revealed that the as-grown CNTs possessed higher graphitization degree and straight graphite shell. By this approach, more homogeneous dispersion of CNTs in aluminum powders was achieved compared with the traditional mechanical mixture methods. Using the in-situ synthesized CNTs/Al composite powders and powder metallurgy process, CNTs/Al bulk composites were prepared. Performance testing showed that the mechanical properties and dimensional stability of the composites were improved obviously, which was attributed to the superior dispersion of CNTs in aluminum matrix and the strong interfacial bonding between CNTs and matrix.

Key words: aluminum matrix composites; carbon nanotubes; chemical vapor deposition; in-situ synthesis

1 Introduction

Since the discovery in 1991 by IIJIMA [1], carbon nanotubes (CNTs) with unique structure have been the focus of numerous investigations because of their fascinating properties and application potentials. They are regarded as excellent reinforcements for composites to overcome the performance limits of conventional materials [2]. Many research efforts have dealt with CNTs/polymer, CNTs/ceramic and CNTs/metal composites [3−5]. Most researches in this field have dealt with CNT/polymer composites, which show obvious property enhancement [6,7]. However, compared with polymer matrix composite, the agglomeration of CNTs in metal or ceramic composites is more severe and the interfacial wettability between matrix and reinforcement is far from satisfaction, due to the strong van der Waal's force among CNTs caused by their small scale and large specific surface area. Thus, the reinforcement effect of CNTs is not fully exploited. In order to remedy those problems, some researchers tried the methods, such as ball milling, plasma spraying, to achieve the homogenous dispersion of CNTs in the composites. However, the perfect structure of CNTs may be destroyed, and the dispersion of CNTs as well as the properties of the composites is still not ideal.

With the development of in-situ synthesis technique in CNTs/ceramic composites [8,9], some researchers paid particular attention to its application in CNTs/metal composites. CNTs have been successfully synthesized in Cu, Mg, Ag and Al matrixes by in-situ chemical vapor deposition (CVD) [10−13], which demonstrated the feasibility of in-situ synthesis of CNTs in metal matrixes. However, the low melting point and active chemical property of the metals, such as Al and Mg, restrict the reaction temperature of CNTs growth by CVD in these metals, resulting in the poor graphitization degree and aggregation of CNTs. Accordingly, the properties of CNTs/metal composites are still not satisfactory. And the in-situ synthesis of CNTs in low-melting-point metals is still under discussion.

In our previous work, the feasibility of in-situ synthesis of CNTs in aluminum powders was confirmed

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[10] and aluminum matrix composite reinforced by CNTs with diverse structures was fabricated by in-situ synthesis process [14]. However, it is still unclear that which type of transitional metal catalyst is more suitable to prepare CNTs/Al matrix composites with superior performance. In this work, the synthesis effects of CNTs, using different transition metal (Fe, Co and Ni) catalysts supported on aluminum powders at the critical temperature approaching the melting point of aluminum, were first investigated. The transitional metal catalyst suitable to in-situ synthesis of CNTs in low-melting-point metal was determined. The yield, graphitization degree and dispersion of CNTs in aluminum powders were analyzed. CNTs/Al in-situ composites were prepared and characterized. By this work, the in-situ synthesis process of CNTs/Al composite powders was optimized and the performance improvement of aluminum matrix composite was realized.

2 Experimental

2.1 Preparation of CNTs/Al in-situ composite powders

Right amount of pure Al powder was dissolved into $Fe(NO_3)_3{\cdot}9H_2O$, $Co(NO_3)_2{\cdot}6H_2O$ and $Ni(NO_3)_2{\cdot}6H_2O$ aqueous solutions with a concentration of 0.1 mol/L, respectively. Then 0.1 mol/L NaOH aqueous solution was dripped gradually into the above mixtures with constant stirring for 0.5 h. The co-precipitation was aged at room temperature for 12 h, filtrated and dried. Binary colloid $Me(OH)_x$/Al (Me represents Fe^{3+}, Co^{2+} or Ni^{2+}) was obtained. Then, the $Me(OH)_x$/Al powders were calcined in N_2 atmosphere at 450 °C for 2 h and the transition metal oxide/Al catalyst precursors were obtained. The catalyst precursors were put in quartz crucible and then placed into horizontal quartz tube reactor. The precursors were heated to 650 °C in N_2 atmosphere, and then reduced in a H_2 atmosphere for 2 h. Then CNTs growth was performed in a mixture gas of CH_4+N_2 ($V(CH_4)$=60 mL/min, $V(N_2)$=420 mL/min) at 650 °C for 60 min. Finally, the reactor was cooled to room temperature in N_2 atmosphere. The yield of the carbon nanostructure is defined as

$$\eta_{\text{Yield}} = \frac{m_{\text{a}} - m_{\text{b}}}{m_{\text{b}}} \times 100\% \quad (1)$$

where η_{Yield} is the yield of in-situ synthesized carbon nanostructure, m_{a} is the mass of as-grown composite powder, and m_{b} is the mass of catalyst precursor.

2.2 Preparation of CNTs/Al bulk composites

The CNTs/Al bulk composites were prepared by powder metallurgy process. The CNTs/Al in-situ composite powders were pressed in a mold of diameter 20 mm under a pressure of 450 MPa. Subsequently, the obtained bulk composites were sintered at 610 °C for 2 h in a vacuum sintering furnace. Then they were re-pressed by a hot-extrusion mold with an extrusion ratio of 10:1 under a pressure of 600 MPa at 450 °C. Pure Al bulk was prepared under the same processing conditions for comparison.

2.3 Characterization

Surface morphology and microstructure of the as-grown carbon nanostructures were examined by field emission scanning electron microscope (FESEM, Hitachi S-4800) and high-resolution transmission electron microscope (HRTEM, Philips TECNAI G^2 F20, 200 kV). X-ray diffractometer (XRD, Rigaku D/max 2000V/pc) was employed to detect the phase composition of the as-grown composite powders. The hardness of CNTs/Al composites was measured using a hardness testing device (Everone MH-6) operated at the load of 0.49 N and dwell time of 30 s. Tensile test of the round specimens of 2.5 mm in diameter was performed by a Shimadzu Universal Testing Machine model AG-50kNG (M/s Shimadzu, Kyoto, Japan). The thermal expansion of the composites was determined using NETZSCH DIL 402C thermo-mechanical analyzer at a heating rate of 5 °C/min within the temperature range from 50 to 300 °C.

3 Results and discussion

3.1 Characterization of CNTs/Al in-situ composite powders

The morphology and structure of the as-grown composite powders, synthesized by Fe, Co and Ni/Al catalysts with 10% transition metal content, were characterized by SEM and TEM, as shown in Fig. 1. Though the yield of the composite powders varied with various transition metal contents (5% and 15%), the type, morphology and structure of the as-grown carbon nanostructures were similar. Figure 1(a) shows the SEM image of the CNTs/Al composite powders prepared by Fe/Al catalyst. A mass of entangled CNTs could be observed and their diameters were not uniform, ranging from 10 to 30 nm. Their average length was about 1 μm. The surfaces of CNTs seemed not clean and smooth. When the reaction time was 60 min, the yield of CNTs was 2.7%. Due to the low yield, no obvious diffraction peaks of graphite appeared in the XRD pattern inserted in Fig. 1(a). TEM analysis revealed the microstructure of these CNTs, as shown in Fig. 1(d). The CNTs had relatively large hollowness and their wall thickness was 5−8 nm. Measured by Digital Micrograph software, the average interplanar spacing was 0.346 nm, which was far from the ideal (002) interplanar spacing (0.34 nm) of graphite carbon, which suggested that the CNTs possessed more defects and less crystallinity. Meanwhile,