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Fabrication of carbon nanotube reinforced Al composites with well-balanced strength and ductility

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ABSTRACT

An approach was developed to fabricate carbon nanotube (CNT)-reinforced Al composites. In a typical process, the Co catalyst was evenly deposited on the surface of Al powder by impregnation route, and then the CNTs were grown in the Al powder by chemical vapor deposition to obtain CNT/Al powders. After ball-milling of the obtained powders for a short time, the CNT/Al composites were fabricated by compacting, sintering and hot extrusion of the ball-milled powders. During this process, the well dispersed CNT reinforcement is deeply embedded in the Al powder forming an effective interface bonding with matrix. As a result, the CNT/Al composites containing 2.5 wt.% CNTs exhibit the ultimate tensile strength of 334 MPa which is 1.7 times higher than that of unreinforced Al, and good ductility of ~18% elongation to failure. Thus, well-balanced strength and ductility are achieved in CNT-reinforced Al composites.

1. Introduction

In order to improve energy efficiency through the weight reduction of automobiles and aircraft, it has been attracted a growing attention to develop metal matrix composites (MMCs) with lightweight and high-strength. Due to the low density and the remarkable mechanical, thermal, and electrical properties, carbon nanotubes (CNTs) have been regarded as the ideal reinforcement for composite materials to increase both stiffness and strength, meanwhile also contributing to weight saving [1,2]. The applications of CNTs in MMCs for overcoming the performance limits of conventional materials have been increasingly reported in recent years [3]. However, up to now there are a limited number of publications about the successful introduction of CNT resulting in significant improvement of the mechanical properties, especially the tensile strength, of the metallic matrix [4–7]. Furthermore, it is difficult to get a well-balanced strength and ductility for CNT-reinforced MMCs, namely, the reported results obtained the enhanced tensile strength by addition of CNTs while the ductility of composites decreased dramatically [4–6], which cannot meet the requirements for industrial applications. These are primarily attributed to the difficulties in achieving CNT/metal composites with uniform dispersion of CNTs in the matrix and the strong interfacial bonding between the CNTs and the metallic matrix.

So far, among the various CNT dispersion methods reported [4–11], high-energy ball milling [12–20] is used most commonly. However, there is a large size and density discrepancy between the metallic matrix powders and the CNTs, and the CNTs supplied on the market are in the form of entangled bundles. As a result, it needs a long milling time i.e. severe mechanical working process for CNT dispersion, which easily leads to the destruction of the molecular structure of CNTs [21,22]. In order to weaken the van der Waals forces between CNTs, the preliminary treatment of the pristine CNT by using the strong acids or other chemical materials before ball milling is needed [12–15], during which the length of CNTs is shortened and the structure of CNTs is damaged. As a result, the reinforcement effect of CNTs in MMCs by using ball milling dispersion is not noticeable.

In this study, we reported a novel approach to prepare the CNT-reinforced Al composites with both good strength and ductility. In this process, the in situ chemical vapor deposition (CVD) combined with ball milling for a short time are used to synthesize CNT/Al composites. The well dispersion of CNTs on the surface of Al powder can be obtained by using the in situ CVD method, then the execution of ball milling for a short time can further improve the dispersion of CNTs, and meanwhile, implant the CNTs deeply into the matrix particle forming a strong interface bonding between

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CNTs and Al matrix. Compared with other mixing methods, the important feature of the process is that no pretreatment of the CNTs is required and their original structure is well reserved.

2. Experimental

2.1. Fabrication of CNT/Al composites

Fig. 1 illustrates the fabrication procedure of the CNT/Al composite powders used in this investigation. In a typical synthesis process of the experiment, four steps were involved.

2.1.1. Preparation of Co/Al catalyst

The right amounts of $Co(NO_3)_2{\cdot}6H_2O$ and Al powder (−200 mesh, 99.0% purity, purchased from Tianjin Fengchuan Co., Ltd.) were mixed in 120 ml ethanol to yield a mass ratio of Co:Al = 1:199. The mixture was sonicated for 20 min and then heated at 60 °C under constant magnetic stirring until the ethanol was vaporized completely. After drying at 80 °C for 6 h, the as-prepared powder was reduced in hydrogen atmosphere at 250 °C for 1 h and sequentially at 450 °C for 1 h. Thus, Al powder with Co nanoparticles homogeneously spreading on [23], namely, Co/Al catalyst was obtained (Fig. 1a).

2.1.2. In situ synthesis of CNTs in Al powder by CVD

CNTs were synthesized at 600 °C using Co/Al catalyst with the reaction time of 20 min by introducing a mixture flow of C_2H_2/Ar (20/240 ml/min) into the reactor. Then the system was cooled down to room temperature under argon atmosphere, and the CNT/Al composite powders containing 2.5 wt.% CNTs were obtained (Fig. 1b). The content of CNTs was calculated as follows:

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

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

2.1.3. Ball milling of the in situ synthesized CNT/Al powders

The as-prepared 2.5 wt.%-CNT/Al powders were placed in 250 ml stainless steel mixing jars containing stainless steel milling balls of 6 mm diameter (ball-to-powder ratio = 10:1). The jars were filled with argon and were then agitated using planetary ball mill (QM-3SP4, purchased from Nanjing Nanda Instrument Plant) at 500 rpm for 30 and 90 min, respectively (Fig. 1c).

2.1.4. Preparation of CNT/Al composites

The ball-milled composite powders were consolidated in a steel mold with 10 mm in diameter at 600 MPa. After sintered at 630 °C for 1 h in argon atmosphere, hot extrusion was conducted with an extrusion ratio of 16:1 at 500 °C to obtain the CNT/Al composites (Fig. 1d). After extrusion, the relative density of the composite bulk can be over 98%. The bulk samples made of starting Al powder and Al powder after 90 min of milling were both prepared under the same forming process for comparison.

2.2. Characterization

Field emission scanning electron microscope (SEM, Hitachi S4800) and high-resolution transmission electron microscope (TEM, Philips Tecnai G^2 F20, 200 kV) were employed to characterize the samples. The composition of catalyst particles was measured with an energy-dispersive X-ray spectroscope (EDS) attached to the Philips Tecnai G^2 F20. Raman spectroscopy of the composite powders was performed by using the 532 nm line of Ar^+ laser as the excitation source to validate the quality of the CNTs. For tensile testing, the dog-bone samples with gauge length of 20 mm and gauge diameter of 4 mm were machined. The tensile testing was conducted with a crosshead speed of 0.5 mm/min at room temperature.

3. Results and discussion

The distribution of Co catalyst in Al powder is shown in Fig. 2. The quasi-sphere Co nanoparticles (as denoted with arrows in Fig. 2) are uniformly dispersed on the surface of Al powder. The size of Co catalyst ranges between 8 and 14 nm, which is beneficial for producing CNTs with a narrow distribution of diameter [24].

Fig. 3a shows the SEM image of the in situ synthesized CNT/Al composite powders containing 2.5 wt.% CNTs by CVD, which indicates that the composite powders with the diameters of 50–80 μm are spherelike in shape. The surface of the Al powder is fully covered by homogeneously dispersed CNTs with the lengths in the range of 2–5 μm, as shown in Fig. 3d. Furthermore, from SEM observation, we can infer that the purity of as-synthesized CNTs with average diameter of 10 nm is very high, indicating that the obtained CNT/Al powders do not require further purification and can be directly used for the following fabrication process. It seems that the as-prepared CNT/Al powders by using in situ CVD show the good composite microstructure [4,23]. However, due to the uniform dispersion of in situ synthesized CNTs on the surface of Al powder, the diffusion bonding among Al powder is interrupted during the forming process of composite bulk, especially when the content of CNTs is larger than 2.0 wt.% [23], which leads to poor densification and the reduction of the composite properties.

Therefore, ball milling is used in order to further enhance the interface bonding between CNTs and Al matrix, and we find that the powder morphologies are significantly varied according to milling time. At the early stage of milling (30 min of milling), the composite powders get flattened by the ball-powder-ball collisions, as shown in Fig. 3b. The thickness of the flake powder is ~4 μm (see the inset of Fig. 3b), indicating that large plastic deformation is introduced in the powders. At the same time, the CNTs start to be separated and implanted into the Al matrix through the plastic deformation of the matrix, and some ends of CNTs with the length less than 200 nm are exposed on the surface of Al powder (Fig. 3e).

After ball milling for 90 min, the flake-like powders are fractured, and then the refined powders get cold-welded to each other, forming the spherical-shaped powders with the diameter ranged from 20 to 50 μm (Fig. 3c). During the repetitive process of fracturing and welding, the CNTs are deeply embedded inside the powders as shown in Fig. 3f. Only some ends of the separated CNTs are presented on the surface of Al powder (as indicated with arrows in Fig. 3f). Thus, the individually dispersed CNTs into Al matrix are achieved.

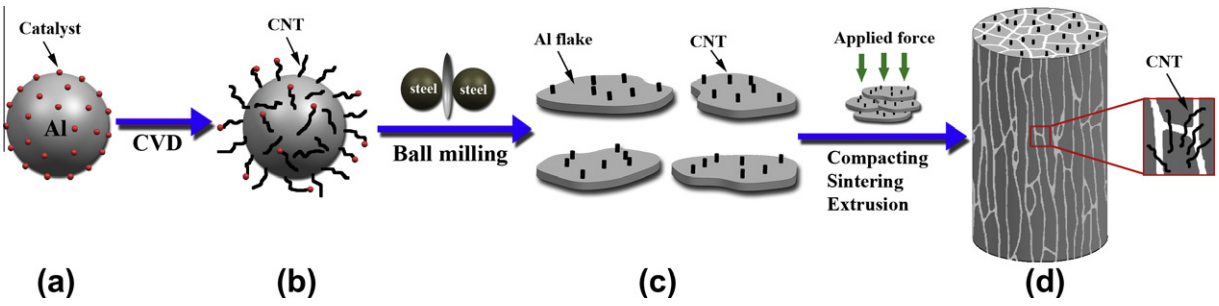

Fig. 1. Schematic illustration of the procedure to fabricate CNT/Al composites. (a) Preparation of Co catalyst spread homogeneously on the surface of Al powder, (b) in situ synthesis of CNTs in Al powder by CVD, (c) ball milling of the in situ synthesized CNT/Al powders, and (d) fabrication of CNT/Al composites by compacting, sintering and hot extrusion.