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Enhanced mechanical properties of aluminum based composites reinforced by chemically oxidized carbon nanotubes

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ABSTRACT

Uniform dispersion and suitable interface are two critical issues to realize the high strengthening potential of carbon nanotubes (CNTs) in metal based composites. In this work, surface modification of CNTs was applied to simultaneously overcome these two challenges in Al matrix composites by a chemical oxidization method. It was found that the functional groups, such as hydroxyl and carboxyl groups, can be successfully decorated on the surface of CNTs by chemical oxidization, thus improving the dispersion of CNTs in ethanol. Concurrently, the morphology of oxidized CNTs and the Al-CNTs interface depend strongly on the activity of the applied oxidants. The mixture of sulphuric acid and hydrogen peroxide can slightly etch the outer walls of CNTs, which benefits the anchoring bonding between the CNTs inner walls and Al matrix, and improves the interface stability, hence exploits the load bearing capacity of the CNTs inner walls and eventually leads to the effective load transfer between Al and CNTs. The outstanding reinforcing effect of surface-modified CNTs was investigated and discussed by the strengthening models. This work provides a new approach to uniformly disperse CNTs and improve interfacial bonding for CNTs reinforced composites simultaneously.

1. Introduction

With extremely high strength (up to ~100 GPa) and Young's modulus (~1 TPa), as well as low density (~2.1 g/cm^3) [1–4], carbon nanotubes (CNTs) have been expected as a type of promising reinforcements for high performance composites [5]. Reinforcing CNTs into light metals, such as aluminum (Al), has opened the way to make light but strong composites, which has great potential applications in aerospace industries [6]. As for the Al/CNTs composites fabrication, powder metallurgy (PM) route has been commonly used due to its controllability, flexibility and simplicity [7–10]. A critical step in PM route is to uniformly disperse the CNTs in Al powders, which strongly affects the distribution of CNTs in composites and eventually determine the mechanical properties of Al/CNTs composites [9]. The existence of CNTs clusters will degrade the mechanical properties of bulk composites and the strengthening efficiency of CNTs [11]. However, the uniformly dispersed CNTs in Al powders is hard to achieve, since the entangled or bundled CNTs clusters are easily induced due to Van der Vaals force between CNTs, large specific surface area and aspect ratio of CNTs [12].

Up to the present, the high energy ball milling (HEBM) was commonly applied to disperse CNTs in the Al powders [11,13–15]. Although uniform dispersion of CNTs can be obtained by optimizing ball milling parameters, the mechanical performance of these fabricated Al/CNTs composites were still below the expected values, because the impact of milling balls on CNTs often greatly damaged their structural integrity, which lower the strengthening efficiency of CNTs [16]. To relieve such structural damage, solution-assisted wet mixing process has been developed in the past decade [17–20]. Prior to these wet mixing processes, the pristine CNTs were commonly chemically oxidized. For examples, in the study of Deng et al. [18], concentrated nitric acid was used to oxidize the CNTs before mixing with Al powders, which contributed to a homogenous distribution of CNTs in Al/CNTs composite. Zhou et al.

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[20] also resorted a two-step oxidization process to promote the CNTs dispersion in Al powders, by using concentrated nitric acid and a sulphuric acid/nitric acid mixture. In these studies, the oxidization of CNTs aimed to acquire a stable dispersion of CNTs in ethanol as well as Al powders during subsequent wet mixing process.

It has been widely acknowledged that chemical oxidization can improve dispersion of CNTs in polar mediums (ethanol, methanol, isopropanol and water, etc.) through decorating the graphitic surface of CNTs with functional groups, such as hydroxyl and carboxyl groups [21–23]. In addition to surface modification, the chemical oxidization of CNTs also leads to the sidewalls exfoliation and etching [24–27]. In other words, the chemical oxidization of CNTs not only promotes the dispersion of CNTs, but also affects their morphology. With respect to Al/CNTs composites, the smooth walls of CNTs make it difficult to form a strong interfacial bonding with Al matrix, and the slippage of CNTs under tension along Al-CNTs interface occurs easily [28]. If the sidewalls of CNTs can be slightly etched at the same time of promoting their dispersion, the altered morphology might help to increase the interfacial shear strength between Al matrix and CNTs, and exploit the load bearing capacity of inner walls. However, most attention was focused on the role of chemical oxidization in the dispersion of CNTs [18,19,29], and its possible effects on the interface bonding and strengthening efficiency of CNTs in Al/CNTs composites were rarely reported.

In the present work, the CNTs were treated by different oxidizing reagents. The dispersion in ethanol and the morphology alteration after different treatments were investigated. Furthermore, these chemically oxidized CNTs were incorporated into Al powders to fabricating Al/CNTs composites. The effects of chemical oxidization on the Al-CNTs interface and mechanical properties of Al/CNTs composites were studied. The mechanisms that uniform dispersion and surface modification of CNTs can improve the mechanical properties were also discussed.

2. Experimental

2.1. Chemical oxidization of CNTs

The employed pristine CNTs fabricated by catalytically chemical vapor deposition (CVD) using metal oxide as catalyst were purchased from Sigma-Aldrich Co. LLC. The average diameter and length of CNTs are about 10 nm and 3 μm, respectively. Chemical reagents were supplied by Sinopharm Chemical Reagent Co., Ltd. The pristine CNTs were oxidized through three different processes.

Treatment 1: 0.36 g of the raw CNTs were dispersed in 120 ml mixed solution (NH_4OH-H_2O_2, mixture of NH_4OH (25 wt.%) and H_2O_2 (30 wt.%) with a volume ratio of 1:1) under 1 h ultrasonic stirring. The slurry was then kept at 80 °C for 10 h with mechanical stirring.

Treatment 2: 0.36 g of the raw CNTs were dispersed in 120 ml mixed solution (H_2SO_4-H_2O_2, mixture of H_2SO_4 (96 wt.%) and H_2O_2 (30 wt.%) with a volume ratio of 7:3) under 1 h ultrasonic stirring. The slurry was then kept at 50 °C for 5 h with mechanical stirring.

Treatment 3: 0.36 g of the raw CNTs were dispersed in 120 ml mixed solution (HNO_3-H_2SO_4, mixture of HNO_3 (68 wt.%) and H_2SO_4(96 wt.%) with a volume ratio of 2:1) under 1 h ultrasonic stirring. The slurry was kept at 50 °C for 4 h with mechanical stirring.

For each oxidization treatment, the 1 h ultrasonic stirring for the dispersion of CNTs in corresponding oxidants was conducted at room temperature in the ultrasonic cleaner (SB-5200DTD, 40 KHz, Ningbo Xinzhi Biotechnology Co., LTD). The oxidized slurry was diluted by 2000 ml deionized water and filtrated after chemical oxidization. Then the resulting CNTs were thoroughly washed until neutral pH and dried in vacuum at 85 °C overnight.

2.2. Fabrication of Al/CNTs composites

Owing to large curvatures and small surface areas of spherical Al particles which limit the attachment of CNTs with quite a large surface area and large aspect ratio, the as received spherical Al powders (2 μm in diameter) were firstly pre-milled into Al flakes with the same condition as reported in previous study to increase surface areas for absorbing CNTs [30]. In the meantime, chemical oxidized CNTs were dispersed in pure alcohol with the aid of 1 h ultrasonic stirring at room temperature, which was carried out by the same device as in the CNTs oxidization process. Then the CNTs slurry and the pre-milled Al powders were mixed by a planetary ball mill for 5 h. The rotation speed was 300 rpm and the ball to powder weight ratio was 5:1. In each 1000 ml ball milling jar, 250 ml CNTs slurry containing 0.39 g CNTs, 50 g pre-milled Al powders, 250 g stainless steel balls (about 500 balls) with 5 mm in diameter were included. The volume fractions of CNTs in the composite powders were maintained as 1 vol% by assuming the density of CNTs and Al powders as 2.1 g/cm^3, and 2.7 g/cm^3, respectively [31]. Then the ethanol was thoroughly removed in a vacuum drying oven. The dried composite powders were packed in a graphite mould and then sintered at 600 °C for 20 min in a spark plasma sintering (SPS) furnace (FCT HPD 25/3, Germany) under argon atmosphere. The heating and cooling rates were both 100 °C/min and the current at target temperature was about 1000 amps. During the whole sintering process, a mechanical pressure of 30 MPa was resorted to accelerate the densification process of specimens. After sintering 50 g composite powders, cylindrical samples with a height of 15 mm and a diameter of 40 mm can be obtained. To realize the full densification of the sintered composites, these bulks were hot rolled under the protection of stainless steel cans. The total height reduction was 30% through 6 passes. In order to avoid cracking, each sealed can was annealed at 450 °C for 0.5 h before hot rolling. In the end, the stainless steel coat attached on the hot rolled specimens was removed by machining. For comparison, reference specimen of Al based composite reinforced by pristine CNTs was also fabricated by the same process and parameters. The composite reinforced by pristine CNTs was referred to S1, and the composites reinforced by oxidized CNTs were named with the oxidants as S1@NH_4OH-H_2O_2, S1@H_2SO_4-H_2O_2 and S1@HNO_3-H_2SO_4, respectively.

2.3. Mechanical properties measurements

The room temperature tensile properties of these fabricated Al/CNTs composites were measured with a strain rate of 2.1×10^{-3} s^{-1} on a universal mechanical tester (Instron 3369). The dog-bone shaped tensile specimens with a gauge thickness of 3 mm, a width of 4 mm and a gauge length of 8 mm were cut from the rolled sheets by wire electrical discharge machining with the tensile axis parallel to the rolling direction [30]. For each type of the composites, the average tensile property values were obtained by three independent tests. Furthermore, the hardness of the produced Al/CNTs composites was evaluated by Vickers tester (HVS-50), using diamond indenter with loading weight of 10 kgf for 15 s holding time. The recorded hardness for each specimen was the average value of five independent measurements.

2.4. Microstructural characterization

A transmission electron microscope (TEM, Titan G2 60–300) operated at 300 KV was used to characterize the microstructures of the CNTs and the fabricated Al/CNTs composites. The TEM specimens of CNTs were fabricated through casting the dispersions of CNTs in ethanol on carbon grids. The accessory of focused ion beam