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Microstructure evolution and mechanical properties of carbon nanotubes reinforced Al matrix composites

Xiaoqing Liu[a], Caiju Li[a,*], Jürgen Eckert[b,c], Konda Gokuldoss Prashanth[b,d], Oliver Renk[b], Long Teng[a], Yichun Liu[a], Rui Bao[a], Jingmei Tao[a], Tao Shen[a], Jianhong Yi[a,*]

[a] Faculty of Materials Science and Engineering, Kunming University of Science and Technology, Kunming 650093, China
[b] ErichSchmid Institute of Materials Science, Austrian Academy of Sciences, Jahnstraße 12, A-8700 Leoben, Austria
[c] Department Materials Physics, MontanuniversitätLeoben, Jahnstraße 12, A-8700 Leoben, Austria
[d] Department of Manufacturing and Civil Engineering, Norwegian University of Science and Technology, Teknologivegen 22, 2815 Gjovik, Norway

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ABSTRACT

Carbon nanotubes reinforced pure aluminum (CNT/Al) composites were fabricated by combined ball milling and powder metallurgy (PM) techniques. The distribution of CNTs, the evolution of the average Al grain size of the powder mixtures and as-prepared composite bulks were investigated, and the mechanical properties of the composites were also tested. With increasing ball milling time, the entangled CNTs were broken, gradually achieving a uniform dispersion within the Al matrix. The microstructure became denser and the Al grains in the powder mixture and extruded composites got significantly refined. Some small-sized Al_4C_3 needles along the Al grain boundaries were observed using transmission electron microscopy (TEM). The in-situ formed Al_4C_3 rods have an orientation relation with the Al matrix as Al_4C_3 [110]//Al [$\bar{1}$12], which strongly improved the Al-CNT interface bonding. The yield and the ultimate tensile strength of the composites significantly increased, when the ball milling time increased from 2 to 12 h, finally reaching about 210 ± 4.2 MPa and 253 ± 3.7 MPa, respectively, for the composite milled for 12 h. The enhancement of mechanical properties mainly stems from the uniform distribution of CNTs, the grain refinement of the Al matrix and the in-situ formed Al_4C_3.

1. Introduction

Carbon nanotubes (CNTs) since discovered by Iijima [1], their excellent strength (up to ∼100 GPa), ultrahigh Young's modulus (∼1 TPa) along with large aspect ratios (up to ∼1000) and surface area have rendered CNTs the first choice as reinforcement for composites [2].Among the metal matrix composites (MMCs) reinforced with CNTs [3–6], CNT/Al composites have been regarded preferentially as promising structural materials for light weight, high strength and anti-corrosion, which can be widely applied in the automotive and aerospace industries [7].

It is well known that the major challenges in the fabrication of CNTs reinforced Al matrix composites are the difficulty of evenly incorporating and distributing CNTs in the matrix due to the possibility of CNTs agglomeration caused by the Van der Waals forces. To solve this problem, so far, methods such as molecular level mixing [8], nanoscale dispersion [9], in situ synthesis [10], flake powder metallurgy [11],friction stirring [12], high energy ball milling [13] and solution coating [14] have been adopted to improve the distribution of CNTs in the metal matrix. Among these synthesis techniques, high energy ball milling is a type of grinding method, which is widely applied to break up the entangled CNTs. Thus, it is regarded as an effective approach to prepare well-dispersed multi-walled carbon nanotubes (MWCNTs) reinforced metal matrix composite powders for subsequent processing, although it may simultaneously produce structural damages of CNTs [15,16]. Jagannatham et al. [17] produced CNT(Cu) reinforced Al composites by combined ball milling and spark plasma sintering (SPS). It was found that the CNTs were uniformly dispersed in the matrix when ball milling was performed at 300 rpm for 2 h. Liu et al. [18] studied the effect of ball milling time on the mechanical properties of 0.5 wt% MWCNTs reinforced pure Al composites, and observed CNTs singly dispersed in the matrix after 6 h of ball milling, which resulted in optimal enhancement of the mechanical properties. In order to limit the damage and keep the integrity of CNTs during ball milling, Carvalho et al. [19]employed low-energy ball milling at 40 rpm for six days and hot pressing to successfully fabricate 2 wt% Ni-coated MWCNTs reinforced AlSi alloy composites. Meanwhile, due to the typical process characteristics of ball milling, which involves repeated deformation,

* Corresponding authors.
E-mail addresses: lcj@kmust.edu.cn (C. Li), yijianhong@kmust.edu.cn (J. Yi).

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cold welding and fragmentation of particles, a fine and uniform dispersion of the reinforcement in a grain-refined soft matrix was expected and observed [20,21]. Regarding the effect of interfacial reaction, it is constantly a critical issue, which can't be neglected. In the past decade, a large number of researchers dedicated to reveal the influence of interfacial reaction product (Al_4C_3) to the mechanical properties of CNT/Al composites [12,22,23]. To the best of our knowledge, appropriate quantity of Al_4C_3 is beneficial to the load transfer efficiency [24].

Until now, some published reports are available concerning the effect of processing parameters, such as ball milling time and sintering temperature, on the microstructure evolution of CNT/Al composites [18,25–27]. However, not enough studies have been done to fully clarify the effect of microstructure evolution, such as grain refinement of soft matrices like an Al matrix during fabrication, on the mechanical properties of the composites. Kim et al. [28] studied the grain refinement assisted strengthening of CNTs reinforced copper matrix nanocomposites. It was demonstrated that the enhanced yield strength stems from the reinforcing effect of CNTs and additional hardening of the matrix by refining the Cu grain size. Deng et al. [29] fabricated CNT/Al-2024 composites with 0–2 wt% CNTs addition by isostatic pressing and observed some fine, nano-sized grains in TEM images, which further contributed to the enhanced mechanical properties of the consolidated composites.

The purpose of this study is to investigate the effect of ball milling time on the distribution and damage of the CNTs along with the changes of the Al grain size during preparation process, such as to better understand the strengthening effect of the CNTs assisted by grain refinement of the Al matrix on the mechanical properties of CNT/Al composites. In order to obtain homogeneous CNTs dispersion within the Al matrix and to limit the structural damages to the CNTs, a combination of ball milling with relatively low speed of 150 rpm and PM techniques were used to prepare Al matrix composites with a MWCNT content of 2 wt% (2.56 vol%). Subsequent hot extrusion was utilized to attain high-performance composites with higher relative density and good interface bonding. Long time ball milling and high temperature during PM processing leads to the formation of Al_4C_3, and the role of Al_4C_3 in improving the interface bonding is also discussed.

2. Experimental Procedure

2.1. Raw Materials

The pristine MWCNTs (Shenzhen Nanotech port Co. Ltd) with the diameter of 20–60 nm and length of 2 μm, were synthesized by means of chemical vapor deposition (CVD). Pure Al powders (Shanghai Aladdin biochemical Polytron Technologies) with average particle size of 25 μm were used in the present study. The morphologies of the starting materials are shown in Fig. 1: the Al powders were mainly spherical while MWCNTs were severely entangled.

2.2. Preparation of Composites

First, 29.4 g Al and 0.6 g CNT powders were placed into stainless steel vials and mixed with GCr15 steel balls in a glove box with purified argon atmosphere(purity: 99.999%). Subsequent ball milling was performed at room temperature using a planetary ball grinding machine run at a rotational speed of 150 rpm. The ball-to-powder weight ratio was 10:1 and the milling time was set to 0.5, 1, 2, 4, 6, 8, 10 and 12 h, respectively. No process control agent (PCA) was added during milling. Then, the as-milled powder mixtures were fed into a self-made die and cold compacted (pressure: about 187 MPa; holding time: 10 min) into cylinders with the diameter of 28 mm and height of about 15 mm. Subsequently, the composite cylinders were sintered at 833 K for 2 h under flowing argon gas (purity: 99.99%) and cooled to room temperature in the same furnace. Finally, the sintered bulks were gradually heated to 803 K and extruded into composite rods (CNT/Al-2 h to 12 h composites) with an applied pressure of about 735 MPa and an extrusion ratio of 36.

2.3. Characterization

The morphology of the as-milled powder mixture and the tensile fracture surfaces of the as-prepared composites were examined using scanning electron microscope (SEM, QUANTA 200) and field emission scanning electron microscopy (FESEM, Nova Nano 450). For analyzing the dispersion of the CNTs, the interfacial product (Al_4C_3) as well as the grain size of the Al matrix, the composite specimens were investigated by transmission electron microscopy (TEM, FEI G2 F30 S-TWIN). The TEM samples were prepared using a focused ion beam (FIB) system (GATAN PISP Model 691, Gatan Inc.) at a voltage of 4 kV. The damage extent of the CNTs during ball milling was evaluated by Raman spectroscopy using a LabRam HR Evolution device. The phases of powder mixtures and in the as-prepared composites were identified by X-ray diffraction (XRD, D/Max 2400) with Cu-K_α radiation source (λ = 1.54056 Å, with an operating voltage of 40 kV and current of 30 mA) and an image plate detector covering a 2θ range of 20°–120° scanned at 5°/min. The average grain size of milled powders and extruded composites were estimated from the Full-Width at Half Maxima (FWHM) of diffraction peaks, using Williamson and Hall method [30] after removing the instrumental broadening. The tensile tests were performed on an electronic universal material testing machine (Shimadzu, AG-X 100 kN) at a nominal strain rate of $1.0 \times 10^{-4}\ s^{-1}$. For these tests, the samples were cut and polished into dog-bone-shaped specimens with a gauge length of 16.5 mm and a cross section of 2 mm (width) × 3 mm (thickness). The average tensile strength of the extruded composites was measured from three specimens in order to have

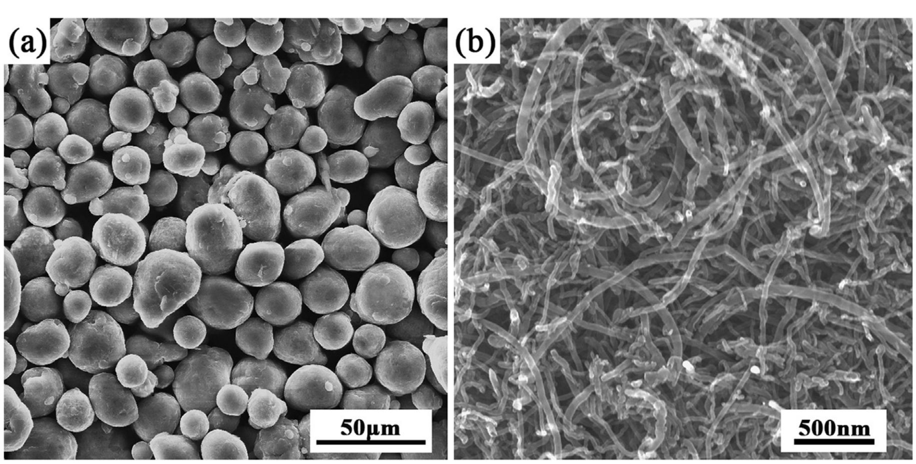

Fig. 1. Morphology of the as-received starting materials: (a) pure Al powder, and (b) purified MWCNTs.