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# Fabrication of 2014 aluminum matrix composites reinforced with untreated and carboxyl-functionalized carbon nanotubes

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ABSTRACT

2014 aluminum matrix composites reinforced with untreated (P-CNTs) and carboxyl-functionalized carbon nanotubes (C-CNTs) were successfully fabricated by the combination of sintering and hot extrusion. It is revealed that the C-CNTs are easier to disperse compared to the P-CNTs. Interfacial analysis indicated that a thin layer of aluminum carbide ($Al_4C_3$) exists at the interface between the matrix and the P-CNTs. However, no obvious transition layers of $Al_4C_3$ were observed at the interface of C-CNTs and 2014Al matrix in composites. Also, no preferred interfacial crystallographic orientation relationship between the C-CNTs and aluminum matrix was observed. Furthermore, C-CNTs have a larger effective interfacial contact with aluminum matrix compared to the untreated CNTs, due to large amount of −COOH group and defects on the surface of the C-CNTs interacting with Al by strong chemical and physical interactions. These aspects in turn affect the mechanical properties of the composites. The ultimate tensile strength of the composites were raised from 530 to 600 and 630 MPa with 0.5 wt.% of P-CNTs and C-CNTs, respectively. It reveals that the C-CNTs are more effective in strengthening the aluminum matrix than the P-CNTs.



## 1. Introduction

Metal matrix composites (MMCs) have been receiving great attention due to their high tensile strength, hardness and modulus, as well as their high wear resistance compared to the matrix [1–4]. Carbon nanotubes (CNTs) are considered to be ideal reinforcements of composites due to their exceptional strength, modulus and heat conductivity [5–7]. However, because CNTs have tremendous specific surface area and very strong van der Waal's force attraction between them which lead to the formation of CNTs clusters. How to homogeneously disperse the CNTs in a metal matrix and achieve excellent interfacial bonding between the CNTs and metal matrix are still unsolved problems [2,8–11]. Therefore, only limited studies have been reported on MMCs. The metal matrix of the reported CNTs-MMCs which mainly focused on the dispersion and alignment in matrix of CNTs, were essentially limited to pure aluminum [3,4,9,11–13]. However, pure aluminum matrix is usually not eligible for applications due to its low mechanical strength.

Al-Cu based 2014Al alloy is heat treatable aluminum alloy, which offers high strength at low specific weight and are extensively employed as structural components, particularly in the aircraft industry [14,15]. CNTs reinforced 2014Al composites are thus be considered to have more application potential. However, homogeneously disperse the CNTs in the matrix and achieve excellent interfacial bonding between the CNTs and the matrix are still needed to be addressed.

The functionalized treatment is a common way to obtain a homogeneous dispersion of CNTs by introducing carboxyl or hydroxyl groups on the surface of the CNTs. Calculations show that the addition of carboxyl or hydroxyl groups adds around 0.2 nm to the graphitic layer roughness [16]. Higher roughness engenders lower van der waal's force by reducing the proximity of interacting surfaces and by increasing the distance between their atoms [17,18]. In the case of interfacial bonding, the amorphous carbon generated during the chemical vapor deposition [19] could affect the interfacial bonding status between CNTs and Al matrix to some extent, because the amorphous carbon tends to react with aluminum to form aluminum carbide [20]. Meanwhile, the carboxyl treatment could remove carbon impurities and introduce defects on the surface of the CNTs [21]. However, the influence of the surface characteristic on the strengthening of CNTs in MMCs has not been well

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studied.

In view of these facts, in the present work, the 2014Al matrix composites reinforced with untreated carbon nanotubes (P-CNTs) and carboxyl-functionalized carbon nanotubes (C-CNTs) by the combination of sintering and hot extrusion were fabricated to clarify the influence of surface characteristic on the dispersion of the CNTs and the interfacial bonding status between the CNTs and the 2014Al matrix.

## 2. Experimental details

CNTs (with an average diameter of ~25 nm and length of ~1.25 μm) synthesized by a chemical vapor deposition (CVD) method were selected as the reinforcements (Fig. 1a). Carboxyl functional treated CNTs (C-CNTs) (with an average diameter and length of ~25 nm and ~1.25 μm) were provided by Chengdu Organic Chemistry Co., Ltd., China. 2014 aluminum alloy powders with an average powder size of about 10 μm were employed as the matrix (Fig. 1b).

The experiment process was illustrated in Fig. 2. Firstly, the two kinds of CNTs (0.25 g) were dispersed in 250 ml ethanol, sonicated for 60 min, and then poured into 200 ml ethanol solution that contained 49.75 g 2014Al alloy powders, respectively. Secondly, the composite mixtures were then vigorously stirred by magnetic stirring for 30 min followed by drying at 333 K for 24 h in an oven. Thirdly, ball milling were performed in a planetary ball mill at a constant speed of 300 rpm for 6 h under argon atmosphere with ball to power ratio of 8:1 with 0.5 g stearic acid addition into the dried mixture as process control agent. Finally, the ball-milled powders were packed and cold compacted at a pressure of 50 MPa for 2 min, and subsequently the compacts were hot vacuum sintered for 50 min under 793 K and then pressed at a pressure of 50 MPa for 10 min in a self-made vessel, with furnace cooling to room temperature. Hot extrusion was conducted at 693 K with an extrusion ratio of about 15:1. The extrudates were then solution treated at 775 K in air for 2 h and naturally aged for more than 96 h before test.

The two kinds of CNTs were characterized by X-ray diffraction (XRD) (D/Max 2500 PC, Rigaku, Japan) using Cu Kα radiation in the range of 20°~80° with a scanning speed of 4 deg/min and an acquisition step of 0.02° (2θ). Raman spectroscopy was obtained by REINSHAW in Via Raman spectroscope with an excitation laser wavelength of 633 nm in the range of 1000–2000 $cm^{-1}$. X-ray photoelectron spectroscopy (XPS) was conducted on a VG ESCALAB MK IIsystem. Different CNTs samples for Transmission electron microscopy (TEM) observation were prepared by dispersing the corresponding CNTs in ethanol, sonicating for several minutes, and subsequently dripping one drop of the liquid on a holey carbon TEM support grid. After dried overnight, the samples are observed by TEM (TEM; JEM-2100F, Japan and Tecnai $G^2$ 20 American) at an acceleration voltage of 200 KV. Samples for interface observation were prepared by ion beam thinner (Leica, EMRES101), then studied by TEM. The pre-mixed composite powders as well as fractured surface were characterized by a Field emission scanning electron microscopy (FESEM) (JSM-6700F, Japan). Tensile specimens with a gauge length of 10 mm, a width of 4.0 mm, and a thickness of about 1 mm were wire-cut from the extruded composites parallel to the extrusion direction. Tensile tests were conducted at a strain rate of $3 \times 10^{-4}s^{-1}$ at room temperature using a MTS 810 (American) system.

## 3. Results and discussion

The surface of the pristine CNT (P-CNT) is partially covered with 1–2 nm thick amorphous carbon layer, as shown in Fig. 3a, while for the carboxyl-functionalized CNT (C-CNT), no amorphous carbon was observed on the surface. In addition, there are a lot of defects on the surface of the C-CNT, as shown in Fig. 3b. These defects increase the roughness of the surface [16], which is believed to be beneficial for stress transfer from the matrix to the CNTs. This will be meticulously investigated hereinafter.

The crystallinities of the P-CNTs and the C-CNTs were analyzed using XRD. Fig. 4 presents the XRD patterns of P-CNTs and the C-CNTs. The four peaks are related to graphitic characteristic in CNTs, corresponding to the (002), (100), (004), and (110) reflection planes. The (002) and (004) peaks denote interlayer spacing between adjacent graphene layers, while the (100) and (110) peaks indicate the in-planar graphitic structure [21]. Compared with the XRD pattern of the P-CNTs, the (002) peak of the carboxyl treated CNTs is slightly shifted to lower angles, whereas the (004), (100) and (110) peaks remain at a position similar to that of the pristine CNTs. The nearly identical (004) peaks indicate that the C-CNTs maintain a highly ordered tube structure and the similar (100) and (110) peaks suggest negligible damage of the in-plane graphene structure of the C-CNTs [21].

As Raman spectrum is sensitive to the disordered graphite structure, raman spectroscopy was obtained to estimate the quality of the P-CNTs and the C-CNTs. There are two important bands of raman spectrum, ie. the D band (at about 1350 $cm^{-1}$) and the G band (at about 1580 $cm^{-1}$) [22]. The D band corresponds to the $A_{1g}$ breathing mode of $sp^3$-hybridized carbon atoms of defects or amorphous carbon atoms in CNTs, while the G band corresponds to

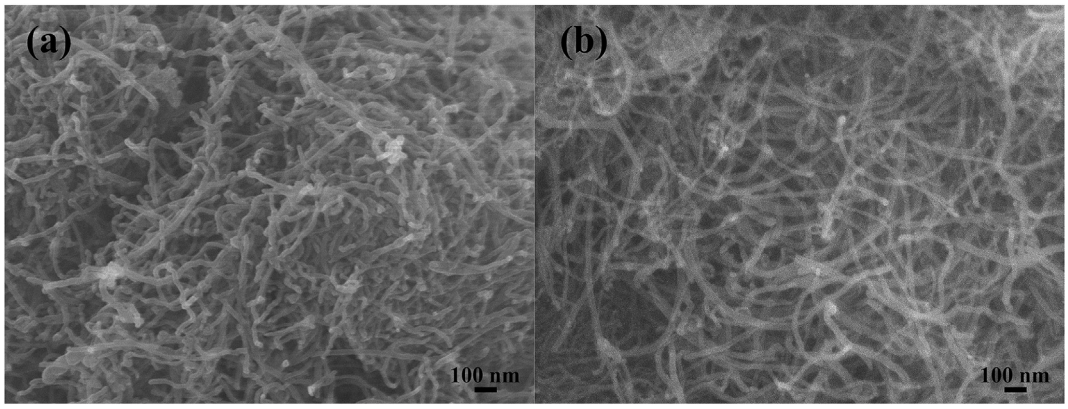


**Fig. 1.** FESEM micrographs of the as-received carbon nanotubes (a) and the 2014 aluminum alloy powders (b).