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# Microstructure, microhardness and thermal expansion of CNT/Al composites prepared by flake powder metallurgy

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ABSTRACT

Carbon nanotube/aluminum (CNT/Al) composites are prepared by a combination of flake powder metallurgy and hot-isostatic-pressing. The specimens are investigated by several techniques including Raman spectroscopy, optical microscopy, scanning- and transmission electron microscopy. The composites show a layered-microstructure with a stacking of CNT/Al flakes with a CNT-rich layer between two flakes. The individual Al grains forming the flakes are about 500 nm in size. The CNTs are well dispersed within a flake and they bridge the micro-cracks. The results reveal that the coefficient of thermal expansion (CTE) decreases markedly upon the increase in carbon content, reaching $15.4 \times 10^{-6}\,K^{-1}$ for the specimen with a carbon content of 2.0 wt% (2.9 vol%), i.e. a 30% decrease compared to the CTE of pure Al. This could arise from the layered-microstructure resulting from the utilization of Al flakes as opposed to rounded particles.



## 1. Introduction

Silicon, the material at the basis of the semiconductor devices, shows a low coefficient of thermal expansion (CTE) ($5 \times 10^{-6}\,K^{-1}$) in comparison with the common packaging materials like copper ($17 \times 10^{-6}\,K^{-1}$) and aluminum ($21–26 \times 10^{-6}\,K^{-1}$) [1,2]. The CTE difference will cause distortions at the interface upon repeated changes in temperature, which ultimately will lead to failure of the device. Aluminum-matrix composites with a lower CTE than pure Al have been prepared by adding some low CTE materials such as Si, SiC, AlN and diamond [2,3]. Carbon nanotubes (CNTs) have been become an attractive additive material for reducing the CTE of the aluminum-matrix composites [4–13] because of a very low or even negative CTE, in the range $-2 \times 10^{-5}$–$0.5 \times 10^{-5}\,K^{-1}$ depending on the CNT characteristics [14]. The end results however depend on many materials- or process-parameters, including the precise nature of the matrix (pure or alloyed Al), of its grain size (nano-, micrometric), of the carbon content and of the kind of CNTs (single-wall, double-walled, multi-walled) and of the consolidation route (hot-pressing, hot extrusion…) and atmosphere (vacuum, $N_2$, Ar) (Table 1). CTE as low as $10 \times 10^{-6}\,K^{-1}$ have been reported when using nanometric-sized Al with either single-wall CNTs [7] or multi-walled CNTs (MWCNTs) [12]. Many techniques have been developed to prepare CNT/Al composite powders with a uniform dispersion of the CNTs [4,5,13,15,16]. However, high-energy ball-milling [13] tends to damage the CNTs whereas molecular-level mixing [15] and *in situ* synthesis of CNTs in metallic powders [16] may lead to oxide impurities. Besides these techniques, the so-called polyester binder-assisted (PBA) mixing technique has been reported for dispersing CNTs in a metallic powder, without damaging them, with the support of polyesters such as polyvinyl alcohol (PVA), natural rubber and ethylene glycol [17–23]. Moreover, it seems that using Al in the form of flakes, as opposed to isotropic grains, to prepare CNT/Al composites, is beneficial, at least to increase tensile strength without losing too much plasticity [19,20,24–26]. The aim of this study is to investigate the CTE of MWCNT/Al composites prepared by a combination of flake powder metallurgy, PBA mixing technique and hot-isostatic-pressing.

## 2. Experimental

### 2.1. Composite preparation

A commercial Al powder (Hunan Jinhao Aluminum Industrial Co., Ltd., 99.5%, average diameter 24 μm) was selected for the

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**Table 1**
Consolidation method, relative density (ρ ± 1%), microhardness and CTEs of CNT/Al composites with different carbon contents ($C_n$, wt% or $C_v$, vol%).

| Ref. | Consolidation method | Sample | $C_n$ (wt%) | $C_v$ (vol%) | ρ (%) | H (HV) | CTE ( $\times 10^{-6}$ $K^{-1}$) |
|---|---|---|---|---|---|---|---|
| [39] | SPS | Al | 0 | – | – | 45 | – |
| | | MWCNT/Al | 0.5 | – | – | 50 | – |
| [40] | SPS | MWCNT/Al | 2 | – | 99 | 88 | – |
| [34] | SPS | MWCNT/Al | 1 | – | – | 44 | – |
| | | | 3 | – | – | 55 | – |
| | | | 5 | | – | 54.5 | – |
| [18] | SPS + Hot extrusion | MWCNT/Al | 2 | | 98 | 52 | – |
| [32,35] | Vacuum sintering | Al | 0 | | – | 34 | – |
| | | MWCNT/Al | 0.75 | | – | 50 | |
| [36] | Hot-extrusion | Al | 0 | | 99 | 39.4 | – |
| | | MWCNT/Al | 2.5 | | 99 | 84.5 | – |
| | | | 5 | | 99 | 95.2 | – |
| [37] | Hot-extrusion | MWCNT/Al | 6 | | 97 | 151 | – |
| [6] | Hot-pressing | Al | 0 | | – | – | 26.1 |
| | | MWCNT/Al | 4 | | – | – | 23.2 |
| | | SWCNT/Al | 3 | | – | – | 20.4 |
| [7] | Vacuum sintering | n-Al | | 0 | – | – | 26.2 |
| | | SWCNT/n-Al | | 10 | – | – | 14.8 |
| | | | | 15 | – | – | 9.8 |
| [8] | Hot-extrusion | 2024 Al | 0 | | – | – | 26.3 |
| | | MWCNT/2024Al | 1 | | | | 22.5 |
| [9] | Hot-pressing | 2009Al | | 0 | – | – | 23.6 |
| | | MWCNT/2009Al | | 1.5 | – | – | 21.3 |
| | | MWCNT/2009Al | | 4.5 | – | – | 17.5 |
| [11] | Hot-pressing + Vacuum sintering | MWCNT/2024Al | | 3 | – | – | 19.2 |
| | | MWCNT/2024Al | | 5 | – | – | 17.9 |
| [12] | Sintering in $N_2$ | n-Al | 0 | – | 90 | – | 80.1 |
| | | MWCNT/n-Al | 1 | | 92 | – | 54.4 |
| | | MWCNT/n-Al | 3 | | 94 | – | 10.5 |
| | | MWCNT/n-Al | 5 | | 92 | – | 23.2 |
| [13] | Sintering in Air + Hot-extrusion | Al | 0 | | – | 64 | 26.0 |
| | | MWCNT/Al | 1.5 | | – | 81 | 24.8 |
| | | MWCNT/Al | 2.5 | | – | 95 | 24.0 |
| | | MWCNT/Al | 3.5 | | – | 115 | 22.5 |
| | | MWCNT/Al | 4.5 | | – | 130 | 21.5 |
| This work | HIP | S0 | 0 | 0 | 98 | 44 | 22.0 |
| | | S0.5 | 0.5 | 0.7 | 96 | 55 | 19.5 |
| | | S1 | 1.0 | 1.5 | 96 | 69 | 18.0 |
| | | S1.5 | 1.5 | 2.2 | 95 | 83 | 16.4 |
| | | S2 | 2.0 | 2.9 | 94 | 62 | 15.4 |

study. Commercial carboxyl-functionalized MWCNTs (Chengdu Organic Chemicals Co. Ltd.) were used. The details of the functionalization process are not known to the authors. The carbon content in the MWCNT specimen is equal to 95 wt%, the balance probably corresponding to some residual metal catalysts. The key characteristics of the MWCNTs (number of walls, outer and inner diameters, length and presence of defects) are determined later in the paper. MWCNT/Al composite powders with a carbon content ($C_n$) equal to 0, 0.5, 1, 1.5 and 2 wt% were prepared by a PBA mixing route. They will be noted as P0, P0.5, P1, P1.5 and P2 hereafter. First, the Al powder was ball-milled (200 rpm, 2 h, ball-to-powder weight ratio of 10:1, $N_2$ atmosphere). The so-obtained Al flakes were slowly added to ethylene glycol under magnetic stirring (400 rpm, 2 h), forming the Al slurry. The appropriate amount of MWCNTs was dispersed in ethanol as reported earlier [27,28] and the so-obtained suspension was mixed with the Al slurry under magnetic stirring (400 rpm, 2–3 h) at 80 °C in order to evaporate ethanol. Finally, the resulting slurry was ball-milled (150 rpm, 2 h, ball-to-powder weight ratio of 10:1, $N_2$ atmosphere) and heated at 220 °C for 24 h in vacuum (residual pressure 200 MPa) to remove ethylene glycol. The MWCNT/Al powders were consolidated by cold uniaxial compaction (200 MPa, 5 s) followed by capsule-free hot-isostatic-pressing (HIP, AIP6-30H, Isostatic Press Inc's, US). The specimens were heated (10 °C/min) up to 620 °C, applying a 1 h dwell at this temperature for the pressing process (100 MPa). A natural cooling down to room temperature was performed. The sintered specimens, in the form of pellets 10 mm in diameter and about 5 mm thick, were polished down to 1 μm using diamond slurries. The sintered specimens are noted S0, S0.5, S1, S1.5 and S2 hereafter.

### 2.2. Characterization

The MWCNTs were observed by high-resolution transmission electron microscopy (HRTEM, JEOL JEM 2100F operated at 200 kV). Their length was evaluated from field-emission-gun scanning electron microscopy images (FESEM, Hitachi S-4800 operated at 5 kV). The Raman spectra of the CNTs, powders and sintered specimens were recorded with a confocal RAMAN Microscope (Labram HR 800 Jobin Yvon) using 632 nm laser excitation. For each specimen, the spectra were averaged from five areas. The pellet density was measured by Archimedes method. X-ray diffraction (XRD) patterns of powders and sintered specimens were recorded using a Rigaku Rint Ultima diffractometer with Cu $K_\alpha$ radiation. The Al grain size in sintered specimens was determined by optical microscopy (3D KEYENCE VHX-1000) on surfaces chemically etched by a weak reagent (mixture of 0.25 mol $L^{-1}$ $KMnO_4$ and 0.25 mol $L^{-1}$ NaOH) at room temperature for 6 s. The Al powders and flakes as well as the sintered specimens were observed by FESEM (JEOL JSM 6700F operated at 5 kV and Hitachi S-4800 operated at 5