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Load-bearing contribution of multi-walled carbon nanotubes on tensile response of aluminum

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ABSTRACT

We fabricated a uniformly dispersed and aligned multi-walled carbon nanotube reinforced aluminum matrix (Al–MWCNT) composite with minimal work hardening and without interfacial chemical compounds. In this paper, the direct load-bearing contribution of MWCNTs on the Al–MWCNT composite was investigated in detail for various volume fractions of MWCNTs. For up to 0.6 vol% of MWCNTs, the ultimate tensile strength (UTS) of the Al–MWCNT composite increased with the conservation of the remarkable failure elongation of Al. These UTS values are consistent with shear lag model. We also observed an uncommon multi-wall-type failure of MWCNTs during the hot extrusion process. However, owing to the agglomeration of MWCNTs in the Al matrix, the UTS deviated significantly from the shear lag model and the remarkable failure elongation of Al decreased. The possibility of strengthening, without degrading ductility, was demonstrated by exploiting directly the load-bearing ability of individually and uniformly dispersed aligned MWCNTs.

1. Introduction

Inexpensive and mass-producible carbon nanotubes (CNTs) with their light weight, remarkable mechanical responses (e.g., multi-walled carbon nanotubes (MWCNTs) have young's modulus of ~1 TPa and strength of ~200 GPa with outstanding energy-absorbing capability and flexibility), and thermal/chemical stability [1,2], could quite possibly be the perfect candidates for enhancing significantly the strength and stiffness of structural metal-based systems. They can improve energy efficiency in many industries that place demands on metals, such as the aerospace and automobile industries. Therefore, CNT reinforced aluminum (Al) matrix (Al–CNT) composite is expected to be a new high specific strength material, and powder metallurgical processing is attracting attention for its fabrication process for Al–CNT composite, which helps to avoid the excess reaction at Al/CNT interface. In this regard, powder metallurgical processing and mechanical properties of carbon nanotube (CNT) reinforced aluminum (Al) matrix (Al–CNT) composites have been investigated in recent years [3–7].

Processing of Al–CNT composites has faced great challenges in dispersing undamaged CNTs uniformly within the Al matrix and in achieving intimate Al/CNT interfaces [3,4,8]. These two issues are vital prerequisites for the effective and realistic exploitation of the remarkable load-bearing capability of CNTs in a host metal matrix. In this regard, high-energy mechanical mixing/milling has been used widely [6] (despite dealing with lightweight, flexible, and highly entangled nanostructures with the high possibility of damaging the CNTs structure) to break the CNT aggregates, address the dispersion issue, and somehow improve the final densification and Al/CNT interfacial connections. The final consolidation of the mixed powders has been performed mainly using the powder metallurgical process, such as hot pressing and spark plasma sintering (SPS) [5]. In some studies, these have been followed by a secondary process, mainly hot extrusion, for possible CNT alignment with better densification [3,4,8]. Despite the strengthening reported in many of these studies, it is still not clear whether it was caused directly by the load transfer to the CNTs (via

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high interfacial interlocking resistance [9–12], which is caused either by an intimate clean interface or an interfacial impurity such as aluminum carbide (Al_4C_3) [3,4,13]), and/or the processing-induced work hardening of the Al matrix, and/or dislocation generation at the interfaces (due to different elastic moduli and coefficients of thermal expansion of the CNTs and the Al matrix) [14,15]. Furthermore, ultimately, the intrinsic ductility of the Al matrix became severely degraded. In brief, the direct load-bearing contribution of CNTs on the tensile response of the Al matrix, in a clean system in the absence of process-induced work hardening, dislocations, defects, and interfacial impurities (e.g., Al/CNT reaction products, etc.) has, as far as we know, never been demonstrated previously.

Recently, we succeeded in fabricating a fully dense Al–MWCNT composite by combining a colloidal mixing approach, and SPS followed by hot extrusion [8]. It seems that this Al–MWCNT composite has little residual strain, and contacted the Al/MWCNT interface directly without any interfacial chemical compound, and with the MWCNTs aligned mostly in the extrusion direction [8]. In this paper, we investigate the tensile response of this Al–MWCNT composite with various MWCNT volume fractions, and discuss the results with the use of transmission electron microscopy (TEM) micrographs and Kelly–Tyson's shear lag model [16]. This Al–MWCNT composite is a unique clean system, by which we could eventually demonstrate the contribution of load transfer to the MWCNTs (if any) on the tensile response of the Al, in the absence of processing-induced work hardening, and interfacial impurities (Al_4C_3).

2. Experimental details

Gas-atomized Al powder (Ecka Granules Japan Co., Ltd.) with 99.85% purity and average particle size of 6.19 μm, and pristine MWCNTs (Hodogaya Chemical Co., Ltd.) with average diameter of 50 nm and length of 10–20 μm were used as starting materials. The pristine MWCNTs were acid-treated in an ultrasonicated mixture of H_2SO_4 98%/HNO_3 68% (3:1 v/v) at 50 °C for 24 h to break their agglomeration and to functionalize their surface with carboxylic groups. Predetermined amounts of Al powder and surface-functionalized MWCNTs were dispersed separately in ethanol by performing bath-sonication for 3 h before the final mixing of their dispersions [8–12]. The MWCNT volume fraction of the final composites was controlled to be 0.2, 0.4, 0.6, 0.8, 1.0, 1.5, 2.0, 3.0, and 5.0 vol%. Next, the dried mixed powder was consolidated into fully dense bulks by using SPS (Dr. Sinter S511, SPS Syntex Inc.). SPS was performed at 600 °C with a heating rate of 40 °C/min for 20 min, under a compressive stress below 50 MPa [3,8]. The sintered bulks were then extruded in a 60° conical die at 550 °C by a universal Instron tester (UH-500kN1, Shimadzu Corporation, Japan). The extrusion experiments were performed under the extrusion rate of 20 and speed of 1 mm/min.

The relative density of the Al–MWCNT composites was measured by the Archimedes principle. Microstructural characterization was performed using a field-emission scanning electron microscope (FE-SEM; JSM-6500F, JEOL, Japan) and a high-resolution transmission electron microscope (HR-TEM; HF-200EDX, Hitachi, Japan). For the TEM observations, the thin films of Al–MWCNT composites were prepared by the ion milling method (GATAN PIPS Model 691, Gatan Inc.) The crystallinities of pristine and functionalized MWCNTs were evaluated by Raman spectroscopy (SOLAR TII Nanofinder, Tokyo Instruments Co. Ltd., Japan). The grain size of Al was evaluated by electron back scatter diffraction method (EBSD; Orientation imaging microscope, TexSEM Laboratories Inc., Japan). The extruded composites were machined for tensile testing in accordance with the JIS Z 2201 standard. Tensile tests were conducted using the universal testing machine (AUTOGRAPH AG-I 50 kN, Shimadzu Co., Ltd., Japan) under the crosshead speed of 1 mm/min.

3. Results and discussion

Table 1 shows the relative densities of the Al–MWCNT composites. In this study, Al powder and MWCNTs were mixed together by a colloidal process (not mechanical mixing such as the ball milling method) and SPS was carried out in solid state (i.e., the SPS temperature was lower than the melting point of Al). Therefore, it seems that MWCNTs are not incorporated into Al particles and the relative density should be low. Nevertheless, the relative densities were higher than 97.5%, despite the volume fractions from the MWCNTs. Although they decreased slightly when the volume fractions of MWCNTs were high. Thus, TEM observation was conducted to understand this phenomenon. Fig. 1 shows the microstructure of the Al-MWCNT composite after SPS. MWCNTs were observed between two thin layers in the Al matrix. It has been reported that Al particles are covered with a thin alumina (Al_2O_3) layer, which shows at the particle boundary of Al after SPS in Carbon fiber reinforced Al matrix composite [17]. Therefore, it seems that the observed thin layers are the Al_2O_3, and it shows that MWCNTs have intervened at Al particle boundaries, not inside of Al particles (see Fig. 1b). This microstructure is consistent with the hypothesis mentioned above; SPS were carried out in a solid state in this study, thus MWCNTs are not incorporated into Al particles. However, the gaps at the Al particle boundaries created by the existence of the MWCNTs were filled up with Al. It has been reported that and the thin Al_2O_3 layer on Al particle can be fractured by the surface cleaning effect in SPS [17–20]. Moreover, Lalet et al. have suggested that the local temperature in SPS and reported the infiltration of Al into the triple point of Al particle boundaries through the fractured the Al_2O_3 layer [17]. Therefore, it seems that Al has transformed to liquid phase in SPS, and infiltrated into the gap through the fractured Al_2O_3 layer as can be seen by the white broken arrows in Fig. 1b. This result shows clearly why a fully-dense Al–MWCNT composite can be fabricated by SPS, and supports the hypothesis we have proposed; the infiltration of momentarily appearing liquid phase Al into defects on the surface of the MWCNTs, and the formation of directly contacted Al/MWCNT interfaces [8]. It was observed that there was no chemical compound (i.e., aluminum carbide (Al_4C_3)) at the Al/MWCNT interfaces, although Al_4C_3 could easily be formed at the directly contacted Al with the defects on the surface of the MWCNTs. Therefore, it seems that the appearance time of the liquid phase of Al is insufficient for interfacial reaction.

The relative densities achieved 99.9% after hot extrusion on each volume fraction of the MWCNTs (see Table 1). Fig. 2 shows the microstructure of the Al–MWCNT composite after hot extrusion. The MWCNTs were individually and uniformly dispersed in the Al matrix without contact among them, and they were mostly aligned to the extrusion direction. Then, the result of EBSD mapping

Table 1
Relative densities of Al–MWCNT composites fabricated by SPS, and SPS followed by hot extrusion.

MWCNT (vol%)	Relative density of spark plasma sintered bulk (%)	Relative density of hot extruded bulk (%)
0.0	99.7	99.9
0.2	99.5	99.9
0.4	99.4	99.9
0.6	99.3	99.9
0.8	99.3	99.9
1.0	99.1	99.9
1.5	98.8	99.9
2.0	98.3	99.9
3.0	98.0	99.9
5.0	97.5	99.9