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Length effect of carbon nanotubes on the strengthening mechanisms in metal matrix composites

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ABSTRACT

In the present work, we studied the effect of the aspect ratio of carbon nanotubes (CNTs) on strengthening aluminum metal matrix composites (Al MMCs). To this end, Al samples reinforced with CNTs of various aspect ratios were produced via three different powder metallurgy methods. Microstructural examination revealed that the CNTs were uniformly dispersed in the materials with a range of aspect ratios from 6.5 to 55. The tensile results showed that the CNTs exhibited a strong strengthening effect in the composites regardless of their aspect ratios. However, the post-loading examination and quantitative analysis indicated that there was a strengthening mechanism transition for CNTs, which was closely associated with the aspect ratio or length of CNTs. The origin of such transition was explored from the viewpoint of dislocation-CNTs interaction under loading. The findings may provide a new insight in understanding the strengthening behaviors of CNT-reinforced MMCs.

1. Introduction

Carbon nanotubes (CNTs) have attracted great attention in materials science and technology because of their super-high strength (up to ~100 GPa), super-high elastic modulus (~1 TPa) and other extraordinary physical properties [1–3]. Interest in using CNTs as a reinforcement in metal matrix composites (MMCs) was encouraged by the successful application of nanotubes in producing high-performance polymer-based composites [4,5]. MMCs reinforced with CNTs offer several distinct advantages over their polymeric counterparts such as inherent stability at elevated temperatures, high strength and stiffness, and superior electrical and thermal conductivity derived from metal matrices. However, it is rather difficult to uniformly disperse CNTs in metals due to the propensity of CNTs to agglomerate into clusters [6]. As such, to develop an effective approach for homogeneous dispersion of a high volume fraction CNTs was regarded as the most significant challenge in the field of CNT-MMCs in the past decade [6–10].

To overcome the dispersion problem, various methods have been developed in metal and alloy matrix systems [7]. The molecular-level mixing process in Cu-CNTs [11] and in-situ grown method in Al-CNTs [12] were two outstanding examples that produce MMCs with over 5 vol.% CNTs and high composite strengths, approximately triple those of unreinforced metals. Out of all dispersion methods, high energy ball milling (HEBM) still remains the most popular because it is simple, easy to control, and applicable to almost all metal matrices. Extensive studies have applied HEBM to the fabrication of MMCs using matrix materials of Al [13–18], Mg [19–21], Ti [22,23], and Cu [24,25]. For example, Esawi et al. [13,26,27] used an HEBM process to disperse 2 wt.% multi-walled CNTs in Al powder. Conditions that achieved good dispersion, however, also led to the breakage of CNTs during the HEBM process. As a result, a reduction of CNT length in MMCs processed by HEBM seems inevitable as reported in a vast number of studies [13–27]. One interesting phenomenon is that the metal-CNTs composites dispersed by HEBM usually possess high strengths. For example, Choi et al. reported that Al MMCs reinforced with 4.5 vol.% CNTs had a tensile strength over 600 MPa under suitable milling conditions [28]. Wang et al. reported that Ti MMCs composites exhibited a compressive yield strength of ~900 MPa with 0.4 wt.% CNTs [22]. However, the strengthening effects from the shortened CNTs have not been clearly demonstrated in these works.

The CNT-related strengthening in CNT-MMCs is usually complex due to multiple potential mechanisms. The possible mechanisms include: (1) load transfer from matrix to CNTs [29,30]; (2) grain

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refinement caused by CNTs' pinning [31]; (3) Orowan looping by CNTs [29]; (4) solid solution strengthening by carbon atoms from CNTs diffused into metal matrices [32]; (5) particle strengthening induced by the in-situ formed or precipitated carbide from the reaction between the matrix and CNTs [33]; (6) work hardening of the matrix due to dislocation multiplication as a result of thermal mismatch between the matrix and CNTs at the interfaces [29]; (7) strengthening by impurities introduced when mixing CNTs into matrices [34]. Among these, load transfer is the most desired because it makes the best use of the outstanding mechanical properties of CNTs. However, the prevailing mechanism is still yet to be identified unequivocally [7]. This is partially because all the above mechanisms are associated with the microstructure of composites, which varies greatly with the dispersion and consolidation processes in different studies. Due to the influence from other mechanisms, the efficiency of load transfer is rather difficult to evaluate in MMCs via experiments. For example, a large number of dislocations and impurities have been reported in metal matrices processed by HEBM [26,34], which no doubt have a great contribution to the strength improvement in MMCs.

Recently, strengthening via the load transfer mechanism in MMCs has been verified by in-situ tensile tests on an Al-CNTs composite [30]. The load transfer effect of CNTs was found to obey the Kelly-Tyson model [35] derived from the shear lag theory [36] of plastic matrices. According to the model, a large length or aspect ratio of CNTs is required to achieve the CNT fracture mode during composite failure, which corresponds to load transfer and high strengthening efficiency [30]. A significant implication is that for HEBM-dispersed composites with small CNT lengths, the load transfer mechanism alone may fail to explain the high strength of the composite. On the other hand, in MMCs reinforced with relatively long CNTs, the strengthening effect is often explained by the load transfer mechanism only [9,11,37]. However, part of the strengthening effect may be attributed to the Orowan mechanism. Considering CNTs with a nanometer level diameter and sub-micrometer length, they still have a small volume-equivalent diameter. It is then expected that the inter-CNT distance can be small [38]. A strengthening prediction using the Orowan model is large enough to compete with that via the load transfer mechanism. Therefore, to identify the dominant strengthening mechanism in MMCs reinforced by CNTs of various lengths, the contribution from each mechanism has to be clarified.

In this study, an attempt was made to reveal the role of the length or aspect ratio of CNTs in strengthening MMCs. CNTs with various lengths or aspect ratios were incorporated into pure Al powders by three dispersion methods. The HEBM method was applied at varying milling times of 2–48 h. These Al-CNTs powder mixtures were consolidated to fabricate Al-CNTs composites through spark plasma sintering and subsequent hot-extrusion. The CNT-induced strengthening effect was evaluated by examining the mechanical properties of the composites under tension. Microstructural examinations were performed for the powders, as-extruded composites and post tensile testing specimens to pin down the possible strengthening mechanisms. It was revealed that CNTs showed a strong length-dependent strengthening effect. A transition of the primary strengthening mode was observed when CNT length is changed. The underlying mechanisms were discussed from the viewpoint of the interaction between matrix dislocations and CNTs with specific lengths.

2. Experimental

2.1. Powder production

In the present work, pure Al (~20 μm powder size, 99.9% in purity, Kojundo Chemical Laboratory CO., Japan) and CNT powders (Baytubes C150P, multi-walled CNTs, supplied by Bayer Material Science, Japan) were used as raw materials to produce Al-CNTs composite samples containing a wide range of aspect ratios. To achieve a homogeneous dispersion of CNTs in the composites, three dispersion methods were employed. The first was a dry process using high energy ball milling (HEBM). Mixtures of Al powder, CNTs (1 wt.% or 1.3 vol.%) and stearic acid (process control agent, 1 wt.%, or ~2.7 vol.%) were sealed into a 500 mL volume zirconia jar together with ZrO_2 milling balls (ball to powder mass ratio of 5) for HEBM. The jar was aerated with argon gas to protect the powder from excessive oxidation during milling. HEBM was carried out on a planetary ball milling machine at 200 rpm for 2–48 h. For comparison and production of flaky powder, Al powders without CNTs were processed under the same milling conditions. After milling, the stearic acid was burned off in a vacuum furnace (~50 Pa) at 450 °C for 30 min.

The second dispersion method was the solution ball milling (SBM) method recently developed in our group [39]. A slurry of a 160 g isopropyl alcohol (IPA) based solution with ~1 wt.% zwitterionic surfactants, 1 wt.% CNTs solution, and 160 g Al powders was mixed using the planetary ball milling machine. The slurry was sealed into the ZrO_2 jar together with ZrO_2 milling balls (640 g for of 10 mm diameter and 160 g for 5 mm diameter). The revolution speed was 200 rpm and the milling time was 1 h.

The third dispersion technique was a two-step wet method known as mechanical coating (MC) [40]. The first step was to produce flaky Al powder using the aforementioned dry method with a milling time of 4 h. The second step was to coat the surface of the flaky Al powders with CNTs. Flaky Al powders were bathed in an IPA based solution with ~1 wt.% zwitterionic surfactants and 1 wt.% CNTs. The mixture was contained in a plastic bottle and set on a rocking milling machine for 120 min. 30 g of zirconia balls were added to assist the coating process.

Both the powder slurries produced by SBM and MC were dried in ambient conditions for 24 h and then burned in a vacuum furnace (~50 Pa) at 450 °C for 30 min to remove the remaining surfactants. Details about the two processes can be found in previous studies [39,40].

2.2. Composite fabrication

The Al-CNTs powder mixtures produced by HEBM, SBM, and MC were all consolidated by the same combination of spark plasma sintering (SPS, SPS-1030S, SPS Syntex) followed by hot-extrusion. SPS was conducted at a sintering temperature of 600 °C with a heating rate of 20 °C·min^{-1} and a holding time of 60 min. The hot-extrusion was carried out at a temperature of 500 °C with an extrusion ratio of ~37. After extrusion, the samples were cooled down to room temperature in air. For comparison, reference specimens made of both pure flaky and starting Al powders were also sintered and then hot-extruded with the same parameters. Details about the consolidation process can be found in a previous study [41].

2.3. Microstructure characterization

A field emission scanning electron microscope (FE-SEM, JEM-6500F, JEOL, Japan) was used to characterize the morphology of the Al powders, the Al-CNTs powders and the composites. In addition, a high resolution transmission electron microscope (HR-TEM, JEM-2010, JEOL, Japan) operated at 200 kV was used to examine the microstructure characteristics of the starting CNT powder, the Al-CNTs powder, and the Al-CNTs composites. TEM samples of the composites were prepared using a focused ion beam