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Direct measurements of the mechanical strength of carbon nanotube - Aluminum interfaces

Chenglin Yi [a], Xiaoming Chen [a, b], Feilin Gou [a], Christopher M. Dmuchowski [a, c], Anju Sharma [d], Cheol Park [e], Changhong Ke [a, c, *]

[a] Department of Mechanical Engineering, State University of New York at Binghamton, Binghamton, NY 13902, USA
[b] Micro- and Nanotechnology Research Center, State Key Laboratory for Manufacturing Systems Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, China
[c] Materials Science and Engineering Program, State University of New York at Binghamton, Binghamton, NY 13902, USA
[d] Small Scale Systems Integration and Packaging Center, State University of New York at Binghamton, Binghamton, NY 13902, USA
[e] Advanced Materials and Processing Branch, NASA Langley Research Center, Hampton, VA 23681, USA

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A B S T R A C T

Interfacial load transfer plays a critical role in the bulk mechanical performance of nanofiber-reinforced metallic-matrix nanocomposites (MMNC). In this paper, we investigate the mechanical strength of interfaces in double-walled carbon nanotube (CNT)-reinforced aluminum (Al) nanocomposites by using *in situ* electron microscopy nanomechanical single-tube pull-out techniques. The nanomechanical measurements reveal the shear lag effect on the CNT-Al interface that is found to possess an average interfacial shear strength (IFSS) of about 28.7 MPa. The study also shows that thermal annealing results in substantially higher binding strength interfaces between CNTs and Al matrices. The average IFSS of CNT-Al interfaces that were thermally annealed at 400 °C is found to reach about 35.3 MPa, a 23% increase from that of the non-annealed interfaces. The maximum load bearing capacity of the annealed interfaces reaches about 304 nN, a 40.1% increase from that of the non-annealed ones (about 217 nN). The findings are useful to better understand the load transfer mechanism in CNT-reinforced MMNC and the tuning and optimization of the reinforcing performance through thermal processing.

1. Introduction

The light, strong and durable characteristics of nanofiber-reinforced metal-matrix nanocomposites (MMNC) are attractive to a number of industries such as the aerospace and automotive industries [1–3]. The nanofiber's extraordinary mechanical properties and high surface-to-volume ratio characteristics enable a substantial property enhancement of bulk metal matrix with a small amount of additive nanofibers. An adequate load transfer on the nanofiber-metal interface is essential in order to take advantage of the extraordinary mechanical properties of the reinforcing nanofibers, which is the core reinforcing mechanism in nanofiber-reinforced MMNC or nanocomposites in general [4–6]. Carbon nanotubes (CNTs) [7] are one of the most promising reinforcing fibers for disruptive MMNC technologies due to their ultra-strong, resilient and low density properties [8]. The research of CNT-reinforced MMNC first emerged in the late 1990s [9–11], and substantial advances have been achieved during the past two decades. However, the understanding of the interfacial load transfer on CNT-metal interfaces remains elusive, which has been a major scientific obstacle in the development of the CNT-reinforced MMNC technology. The underlying challenges behind the lack of such critical knowledgebase include two parts. *First*, the load transfer on CNT-metal interfaces is governed by sophisticated physical and even chemical phenomena, which possess comparable or even higher complexities compared to those involved on CNT-polymer interfaces. For examples, metal grains in direct contact with CNT lattices may yield under the shear force on the CNT-metal interface. The size/shape of metal grains and their mechanical properties are sensitive to processing conditions [12–15], which affects their contacts and interfacial interactions with CNT surfaces and thus the interfacial load transfer capacity. In addition, reaction products may form on CNT-metal interfaces at elevated processing temperatures

* Corresponding author. Department of Mechanical Engineering, State University of New York at Binghamton, Binghamton, NY 13902, USA.
E-mail address: cke@binghamton.edu (C. Ke).

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[16–21], and their impacts on CNT-metal bonding interactions and the interfacial load transfer remain not well-understood. The interfacial interaction is also substantially affected by the residue thermal stress on the CNT-metal interface [22–24], which is due to the fact that CNTs usually possess much lower coefficients of thermal expansion (CTEs) than metal materials. Dislocation plays an important role in metal strengthening, which are substantially affected by the residue thermal stress as well as the Orowan looping effect due to the small size of CNTs [25]. *Second,* it is technically challenging to directly and quantitatively characterize the interfacial load transfer on CNT-metal interfaces at an *individual* tube level. Direct quantitative measurements of the interfacial strength of individual nanotubes with metal matrices are essential for a complete understanding of the interfacial stress transfer and their reinforcing mechanisms. However, a vast majority of the reported studies on CNT-reinforced MMNC in the literature were carried out at a macroscopic level, which can at most be used to evaluate interfacial strength properties indirectly and qualitatively [21,23,26–29]. Reports on direct, quantitative, and microscopic measurements of the interfaces formed by individual nanotubes with metal matrices remain scarce [16,30]. This is ascribed to the challenges in the nanomechanical characterization that requires precise nano positioning and manipulation with adequate spatial resolutions, applying and sensing loads with adequate force resolutions, and real-time observation of the mechanical response of nanostructures that typically demands *in situ* electron microscopy techniques [31,32]. The preference of using small diameter nanotubes (e.g., single or double-walled nanotubes) for MMNC applications tends to add an additional degree of challenges in the nanomechanical measurement of tube-metal interfaces in MMNC. This is because in nanotube-reinforced MMNC, only the outermost shell of a tube makes contacts with metal matrices and contributes to effective load transfer, and thus the property enhancement of the matrix.

In this work, we investigate the mechanical strength of interfaces in CNT-reinforced aluminum (Al) nanocomposites by using *in-situ* electron microscopy nanomechanical single-tube pull-out techniques. Aluminum is chosen as the model matrix material for this study due to its widespread usage in the aerospace and automotive industries. By pulling out individual double-walled CNTs of 3.1 nm in median diameter with different embedded lengths, the measurements reveal, *for the first time*, the shear lag effect on the CNT-Al interface and demonstrate that the effective interfacial load transfer occurs only within a certain embedded length. The nanomechanical study further reveals quantitatively that thermal post-processing leads to a substantial increase of the interfacial strength in CNT-Al nanocomposites, which is in part ascribed to a more intimate contact between CNT surfaces and Al grains that is caused by the residue thermal stress. The findings are useful to better understand the load transfer mechanism in CNT-reinforced MMNC and provide new insights into the reinforcing performance optimization through facile thermal treatments. The experimental methodologies established in this work can be readily extended to study the interfacial load transfer in other MMNCs that are composed of CNTs or other one-dimensional (1D) reinforcing fibers (e.g., boron nitride nanotubes) with a wide selection of metal matrices and their alloys.

2. Results and discussion

2.1. In situ electron microscopy nanomechanical single-tube pull-out measurements

Fig. 1(a) illustrates the employed *in situ* electron microscopy single-tube pull-out technique. In this testing scheme, the tested CNT-metal interface is formed inside a sandwiched metal/CNT/metal thin-film nanocomposite. A pre-calibrated atomic force microscopy (AFM) cantilever acts as a force sensor, and is mounted vertically to the stage of a 3D piezo nanomanipulator. The tip of the AFM probe is controlled to first grip the free-end of an identified protruding CNT cantilever with the aid of electron beam induced deposition (EBID) of Pt. Then, an incrementally increasing tensile force is applied to the tube through displacing the AFM cantilever until the nanotube is fully pulled out from the composite. The nanomechanical measurement is performed *in situ* inside a high resolution scanning electron microscope (HRSEM). The high resolution electron beam is used to control and monitor the whole manipulation process and the mechanical response of the tested tube during the pull-out process. This nanomechanical single-tube pull-out scheme is envisioned to be capable of testing tube-metal interfaces for a broad selection of metal materials and for tubes/fibers with a broad range of diameters (e.g., from a few to hundreds of nm). A similar version of this technique, in which metal matrices are replaced by polymer matrices, was demonstrated in the recent studies of the load transfer in nanotube-reinforced polymer nanocomposites [31,33,34].

Fig. 1(b) illustrates the main processes of manufacturing CNT-Al sandwiched thin nanocomposites with the engineered CNT-Al interfaces for the single-tube pull-out test as illustrated in Fig. 1(a). In brief, a thin layer of Al is first deposited on a clean silicon substrate (b-1), followed by the deposition of a well-dispersed CNT solution (b-2). Subsequently, a second Al layer is deposited on top to form an Al/CNT/Al thin-film nanocomposite (b-3). An optional step here is to have the thin-film nanocomposite thermally annealed in air at up to 400 °C. The thin-film nanocomposite is then fractured through cutting the substrate using a diamond cutter, and some of the embedded tubes are partially exposed as free-standing cantilevered structures (b-4). The advantage of this sample preparation approach is that a whole tube (including both the embedded and the protruding segments) stays in one horizontal plane, and is able to maintain its straightness if its length is controlled to be relatively short. It is noted that Al is an active material and reacts spontaneously with the contact of air and/or water. It is anticipated that a thin oxide layer is formed on the top surface of the first deposited Al film. Because the Al deposition is performed in an ultra-high vacuum environment. The oxide layer is not expected to appear in the contact between CNTs and the 2nd deposited Al film, which is considered as a contact between pure Al grains and CNTs. As displayed in the cross-section drawing in Fig. 1(b-4), the contact region between the CNT and the Al_2O_3 layer is expected to be much smaller than its contact with the surrounding Al grains. Therefore, the impact of the existence of the oxide layer on the overall load transfer on the CNT-Al interface is expected to be limited.

Fig. 2(a) shows an AFM image of a freshly deposited Al film of 100 nm in thickness on a silicon substrate by using electron beam evaporation deposition methods (see Materials and methods section for details). Fig. 2(b) shows an AFM image of a 100-nm-thick Al film that was thermally annealed at 400 °C for 2 h. The grain size of the annealed film is noticeably larger than that of the non-annealed one. For the grains shown in the two AFM images, the average grain size of the annealed film is estimated to be 32% larger than that of the non-annealed film. The X-ray photoelectron spectroscopy (XPS) characterization of the Al films, which is displayed in Fig. 2(c), shows that a thin-layer oxide of about 2 nm in thickness was formed on freshly deposited Al films, while a thicker oxide layer of about 7 nm was formed for thermally annealed Al films. XPS was employed to monitor changes in the surface aluminum oxide thickness between freshly deposited Al films with the ones thermally annealed at 400 °C for 2 h. The Al(2p) spectra shown in Fig. 2(c) clearly show an increase in the intensity of the oxide