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Strengthening and toughening mechanisms in graphene-Al nanolaminated composite micro-pillars

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ABSTRACT

Uniaxial compression tests were carried out on micro-pillars fabricated from nanolaminated graphene (reduced graphene oxide, RGO)-Al composites of different RGO concentrations and laminate orientations (the angle between laminate planes and the pillar axis). It was found that the strengthening capability of RGO can be enhanced by either orienting the RGO layers parallel with the loading direction or raising the RGO concentration. The stress–strain response of the micro-pillars was populated with discrete bursts, and the stress increments of the bursts scaled with the RGO concentration, regardless of the laminate orientation relative to the loading direction. These observations were interpreted by the variation in the load-bearing capacity of RGO in different laminate orientations, the dislocation annihilation at the RGO/Al interface, and a crack deflection mechanism provided by the robust RGO/Al interface that toughened the composites. This work underscores the importance of structural design and control in the stiffening, strengthening, and toughening of metal matrix composites, and the methodology developed may be applied to other composites with microstructural heterogeneity to probe their specific mechanical behaviors and structure-property correlations.

1. Introduction

In metal matrix composites (MMCs), a uniform distribution of the reinforcements in the metal matrix is often desired, as microstructrual homogeneity may prevent severe stress concentration and the ensuing premature failure of the composites that are frequently caused by reinforcement agglomeration. However, in spite of many improved mechanical properties such as strength, stiffness and wear resistance [1], these MMCs with uniformly distributed reinforcements usually make a compromise between strength and toughness, which greatly hinders their broad engineering applications, and suggests that a new approach of microstructure design is needed. To achieve balanced mechanical properties in MMCs, there has lately been a variety of research efforts dedicated to the fabrication and characterization of composites with heterogeneous microstructures, such as hybrid [2,3], gradient [4], interpenetrating network [5,6], and ring-like structures [7], among which MMCs having a nanolaminated structure attract a lot of recent interests. The nanolaminated structure is widely adopted by hard biological materials [8–10], which, by taking advantage of the high strength of nano-scaled constituent phases and the various toughening mechanisms provided by the laminated structure, are shown to be both strong and damage-tolerant [10–12].

The excellent mechanical properties and exquisite microstructure of hard biological materials have inspired studies on developing MMCs with a nanolaminated structure. For example, carbon nanotube (CNT)-metal composites with sandwiched structure were fabricated, where improvements in mechanical strength and toughness were reported [13–15]. Compared to the one-dimensional CNT, the two-dimensional geometry of graphene is intrinsically more compatible with the planar laminated structure, and it has been proposed that graphene may give more effective load transfer between the reinforcement and matrix in the composites [16], making it an ideal reinforcement in nanolaminated MMCs [17–19]. Until now, however, most of the studies on graphene-metal composites are focused on the homogeneous distribution of graphene and the suppression of its agglomeration, and there have been limited attempts in careful microstructure design for graphene-metal composites [20,21]. Co-milling of metal

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powders (such as Al powders) with graphene is an effective and extensively adopted way to disperse graphene uniformly in the metal matrix, while the high energy milling process would seriously damage the integrity of graphene and promote interfacial reactions, resulting in a marginal or even a negative strengthening effect of graphene in the metal matrix [22,23]. Moreover, the distribution of graphene in co-milled composites is usually random, which is unfavorable for fully realizing its strengthening capability due to the strong anisotropy of its properties, and may also cause a poor match between strength and ductility in the as-fabricated composites [21]. By employing a molecular-level mixing process, Hwang et al. [24] fabricated millimeter-sized graphene-Cu composite samples and explained the good strengthening effect of graphene by the strong adhesion between graphene and Cu. However, the as-fabricated composite still suffered from a random distribution of graphene in the Cu matrix, and experimental evidence and associated analysis on possible deformation mechanism were lacking. By alternately evaporating metal thin films and transferring monolayer or bilayer graphene onto metal-deposited substrates, Kim et al. [18] fabricated graphene-Cu and graphene-Ni nanolaminated composite films. Uniaxial compression tests carried out on nano-pillars milled from these films showed a considerable enhancement in mechanical strength of the composites over their monolithic metal counterparts, which was attributed to dislocation blockade at the graphene/metal interface. Nevertheless, the fabrication method adopted in this work is time-consuming and only applicable for thin films, making it difficult to scale-up.

By using a modified powder metallurgy fabrication route, our research group developed bulk graphene (in the form of reduced graphene oxide, RGO)-Al composites with a bioinspired nanolaminated structure, while simultaneously keeping the structural integrity of graphene [19,25]. Macroscopic tensile tests revealed that the 1.50 vol % RGO-Al composites possess a Young's modulus of 87.1 ± 0.8 GPa and a tensile strength of 302 ± 3 MPa, 21% and 50% higher than those of the unreinforced Al matrix, respectively, without sacrificing the total elongation. These observations were rationalized in terms of the effective load transfer between RGO and the Al matrix as a result of the robust RGO/Al interface, and a crack deflection and bridging mechanism derived from the nanolaminated structure [25]. In this work, we extended our study by carrying out uniaxial compression tests on micro-pillars fabricated from the RGO-Al composites of different RGO concentrations and laminate orientations, with the aim of pinpointing their detailed strengthening and deformation mechanisms. In particular, the control of the angle that the laminates formed relative to the uniaxial loading axis enabled quantitative evaluation of the load-bearing capacity of RGO in the composites as well as the cohesive property of the RGO/Al interface. It was found that the strengthening effect and efficiency of RGO could be enhanced by either orienting the RGO layers parallel with the loading direction or raising the RGO concentration, and the robust RGO/Al interfaces provided a crack deflection mechanism that toughened the composites. This work underscores the importance of structural design and control in the stiffening, strengthening, and toughening of metal matrix composites, and the methodology developed may be applied to other composites with microstructural heterogeneity to probe their specific mechanical behaviors and structure-property correlations.

2. Experimental

Graphite oxide (GO, 99% purity, Nanjing XFNano Material Tech Co. Ltd., China [25]) was firstly sonicated in deionized water for 2 h to obtain an aqueous suspension with GO concentration of 1 mg/mL. 200 g of spherical Al powders (99.99% purity, 10 μm average particle size) were ball milled at a speed of 352 rpm in ethanol for 4 h to obtain flake Al powders, which were subsequently transferred to a beaker containing 500 mL pure ethanol. The GO suspension was blended with flake Al powders in the beaker and the mixed slurry was stirred at a speed of 400 rpm to make GO absorbed onto the flake Al powders. The mixed slurry was then filtered and the residue was rinsed with ethanol and vacuum-dried at 333 K for 24 h to obtain GO-Al composite powders. Subsequently, through thermal reduction at 500 °C for 2 h in a tube furnace under H_2/Ar flow, RGO-Al composite powders were obtained where GO was reduced to RGO. The RGO-Al composite powders were compacted under 500 MPa at room temperature and then hot pressed under 600 MPa at 530 °C for 1 h to obtain RGO-Al composite with a densification of 95%. Finally, through hot rolling at 350 °C, densified RGO-Al composite with a nanolaminated structure was obtained. The mass fraction of GO (and subsequently RGO) was controlled by the amount of GO mixed with flake Al powders, and the corresponding volume fraction of the reinforcement was estimated from the surface area covered by RGO layers in RGO-Al composite flakes [25], and the RGO thicknesses measured from high resolution transmission electron microscopy (HRTEM) images. 1.50 vol % was found to be the upper limit of the RGO concentration investigated in this work, as a higher RGO concentration would lead to the formation of macroscopic cracks during deformation processing, which made the fabrication of bulk composites unsuccessful using the present conditions. The structural integrity of RGO was almost fully kept during the rolling deformation process, as revealed by the Raman spectrums of RGO-Al composites before and after various rolling deformation steps (10%, 30%, 50%). (details can be found in the Supporting Information, Fig. S1) In addition to the composite samples, as-fabricated unreinforced Al samples (denoted by “Pure Al” hereafter) were also fabricated using nominally the same processing parameters for comparison. Details of the fabrication steps can be found in Refs. [19,25,26]. Focused ion beam (FIB, FEI Scios) was used to fabricate ~1.5 μm-diameter, 6–7 μm high micro-pillars from the polished surfaces of the bulk samples. The orientation of the laminates relative to the uniaxial loading axis was controlled by the angle between the ion beam and the rolling direction of the bulk sample [27]. The vertical taper of all pillars was controlled within 2° to ensure reliable interpretation of the mechanical test data [28,29]. Uniaxial compression tests on the pillars were conducted using an Agilent G200 Nanoindenter equipped with a 15 μm-diameter flat punch diamond tip at room temperature, and at a nominally constant strain rate of 0.005 s^{-1}. Continuous stiffness measurement (CSM) with 45 Hz harmonic oscillation frequency and 2 nm oscillation amplitude was applied to monitor the variation of contact stiffness during compression. Thereinto, the diameter was measured in the middle section of the pillar. Analysis of the compression data followed the methodology developed by Greer et al. [30] At least 10 pillars of each sample set were tested to get the statistics. The morphology of the pre- and post-compression pillars were studied by scanning electron microscope (SEM), and their microstructures were characterized by site-specific TEM analysis (JEOL 2100F) where the TEM specimens were prepared by the lift-out method using FIB [27].

3. Results

3.1. The microstructures of as-fabricated nanolaminated bulk RGO-Al composites

Bulk 1.50 vol % RGO-Al, 0.75 vol % RGO-Al and unreinforced Al samples were fabricated via the modified powder metallurgy fabrication route developed previously [19,25,26]. The representative TEM images of these three sets of samples before micro-