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Synergistic strengthening effect of graphene-carbon nanotube hybrid structure in aluminum matrix composites

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ABSTRACT

High-performance reinforcement and tailored architecture are currently explored to develop advanced metal matrix composites. In this work, aluminum (Al) matrix composite reinforced by hybrid carbon nanofillers was fabricated by a composite flake assembly process. It was found that for various carbon nanofiller volume fractions, a striking synergistic strengthening effect was achieved by employing graphene (reduced graphene oxide, RGO) and carbon nanotube (CNT) hybrid structure as reinforcement in the Al matrix. Particularly, a tensile strength of 415 MPa was achieved with the addition of 1.5 vol.% of RGO-CNT hybrid, which is significantly higher than those reinforced by individual CNT or RGO (326 and 331 MPa, respectively). The synergistic strengthening effect was attributed to the formation of a planar network of RGO and CNT, which improves the load transfer efficiency between the matrix and the reinforcement in composites. Our study highlights the importance of reinforcement architecture for enhancing the strengthening ability in composites, and provides an effective route to fully take the advantage of the superior properties of various reinforcements.

1. Introduction

The properties of materials are largely dependent on the microstructure of their components. For example, steels would become stronger and tougher by modifying their hard phase microstructures, and properly adjusted structure of the precipitated phase would help achieve the optimal properties of alloys. Similarly, in the field of composites, in addition to the constant pursuit of reinforcements with better properties, another possible route to obtain superior performance is to tailor the reinforcement architecture [1,2]. In recent years, efforts have been made to fabricate composites with non-uniform microstructures, such as the formation of reinforcements network and braid structure. Those studies reveal that a carefully designed reinforcement distribution may contribute favorably to composite properties such as their tensile strength [3,4], thermal expansion behavior [5] and toughness [6].

The one-dimensional carbon nanotube (CNT) and two-dimensional graphene with high Young's modulus (~1 TPa) and tensile strength (~100 GPa) are considered ideal reinforcements for composites [7,8], and enhanced properties have been demonstrated in the field of composites reinforced by individual graphene or CNT [9–11]. On the other hand, the dimensional difference as well as the strong interaction force through $\pi-\pi$ interactions promotes spontaneous formation of a network between graphene and CNT [12,13], making the graphene-CNT hybrid viable co-reinforcements for composites. Recently, by employing graphene-CNT hybrid as fillers, excellent performances have been achieved in the field of supercapacitor, electrocatalyst, lithium ion battery, photocatalyst [14–17], and etc. What's more, the enhancing effect of hybrid graphene-CNT filler was also found in mechanical properties, particularly in polymer matrix composites. For instance, polyvinyl alcohol (PVA) fibers reinforced with graphene-CNT hybrid exhibits an ultimate tensile strength of nearly 600 MPa and a toughness as high as 970 J g^{-1} [18], which exceeds the toughness of most polymer matrix composites reported so far. In addition, considerably enhanced mechanical properties of epoxy-based composite were obtained at ultralow graphene-CNT hybrid concentration [19]. The potential of graphene-CNT used as co-reinforcements in composites has also induced a broad interest in metal matrix composites (MMCs), to meet the soaring demand of lighter, stronger and stiffer structural materials from the field of transportation, aerospace, and military applications [20]; however, in the case of

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metal matrix composites, unlike the polymer matrix that has rich functional groups at its interface with the reinforcement, the metal matrix is intrinsically incompatible with nano-sized fillers in terms of both surface properties and geometries [21], so agglomeration of the reinforcements in composites during processing is often observed. Recently, an attempt has been made to fabricate (graphene–CNT)–Mg composites by stirring the metal powder with ultra-sonicated dispersion of hybrid reinforcement [22]. Unfortunately, synergetic strengthening was not obtained, probably due to the lack of uniform distribution of the hybrid reinforcement.

In this work, a composite flake assembly process was developed to fabricate aluminum (Al) matrix composite reinforced by uniformly dispersed graphene-CNT hybrid. In our recent work, we demonstrated that graphene oxide (GO), a variant of graphene, can be uniformly adsorbed on aluminum (Al) powder surface via electrostatic interactions [23]. Due to the existence of carboxyl (-COOH) and other ionogenic groups, the GO sheets are negatively charged in aqueous media, while the fresh surface of Al flakes becomes ionized and positively charged once they contact water. Thus, GO sheet can be uniformly adsorbed onto the Al flakes simply by electrostatic attractions. In this work, we will further show that by the same adsorption mechanism, hybrid graphene-CNT reinforcement can be uniformly distributed in the Al matrix. The spontaneously formed GO-CNT hybrid (Fig. 1a) is negatively charged due to the carboxyl-like functional groups on both GO and carboxylated CNT, promoting a spontaneous adsorption of the hybrid on Al surface, and subsequent thermal reduction process can convert most GO to graphene (reduced graphene oxide, RGO), as verified by Raman and XPS spectrums [23], leading to uniform distribution of RGO-CNT hybrid reinforcement on flake Al powders (Fig. 1b). We investigated the controllable dispersion of hybrid reinforcement in Al matrix and its advantage for strengthening over its individual components. It was found that 1.5 vol.% of hybrid reinforcement has an ability to increase the Young's modulus and tensile strength of Al matrix by over 18% and 60%, respectively, which outperform the strengthening effect of individual RGO or CNT with the same carbon volume fraction, indicating a strong synergistic strengthening effect. Planar interconnected network of RGO-CNT hybrid as well as their well-aligned distribution is considered to be responsible for the dramatically enhanced mechanical properties.

2. Experimental

The RGO-CNT hybrid reinforced Al were fabricated through a flake powder assembly process, which includes the following three processes:

2.1. Preparation of the GO-CNT hybrid

The 99% pure graphite oxide was offered by Nanjing XFNano Material Tech Co. Ltd, China, as determined from thermogravimetric analysis. It was added to deionized water and then ultrasonicated for 2 h to get fully exfoliated GO sheets. Multi-walled CNTs (30–50 nm in diameter, ~1 μm in length, carboxylated, 95% purity [21]) were supplied by Chengdu Organic Chemistry Co. Ltd., China and they were dispersed into deionized water by ultrasonication for 1 h. Suspensions of GO and CNT were then mixed together and mechanically stirred for 30 min to form GO-CNT hybrid suspension.

2.2. Adsorption of GO-CNT hybrid on Al flakes

Spherical Al powders (99.99% purity, average particle size ~10 μm, as shown in Fig. S1, provided by Henan Yuanyang Aluminum Industry Co. Ltd, China) were ball-milled in pure ethanol for 4 h to make Al flakes in a stainless steel mixing jar, with a mass ratio of the powder to milling balls of about 1:20. The as-prepared Al flakes have thicknesses ranging from 150 nm to 250 nm, with an average value of about 200 nm, which was measured by scanning electron microscopy (SEM) analysis. They were subsequently immersed in deionized water, after which the GO-CNT hybrid suspension were added and stirred until the hybrid was fully adsorbed onto the Al flakes [23]. After filtration, rinsing with ethanol, and vacuum drying, GO-CNT/Al composite powders were obtained.

2.3. Thermal reduction and composite consolidation

The GO-CNT/Al composite powders with three different carbon volume concentrations (0.5 vol. %, 1.5 vol. % and 3 vol. %) were thermally annealed in a tube furnace under H_2/Ar flow. The heating rate was 10 °C/min and the powders were kept at 500 °C for 2 h. GO can be sufficiently reduced and converted back to graphene (RGO) after this process. RGO-CNT/Al composite powders were first compacted into a billet (Φ 40 mm × 30 mm) under 500 MPa at room temperature. Then, vacuum hot pressing at 500 °C and 10^{-2} Pa for 1 h combined with hot extrusion at 440 °C (extrusion ratio 20:1) were employed to obtain highly densified bulk RGO-CNT/Al composite. For comparison purpose, RGO/Al and CNT/Al composites of the same carbon concentrations were fabricated by the same process.

2.4. Characterization

Field emission scanning electron microscopy (FESEM; FEI Quanta 250) and transmission electron microscopy (TEM; JEOL

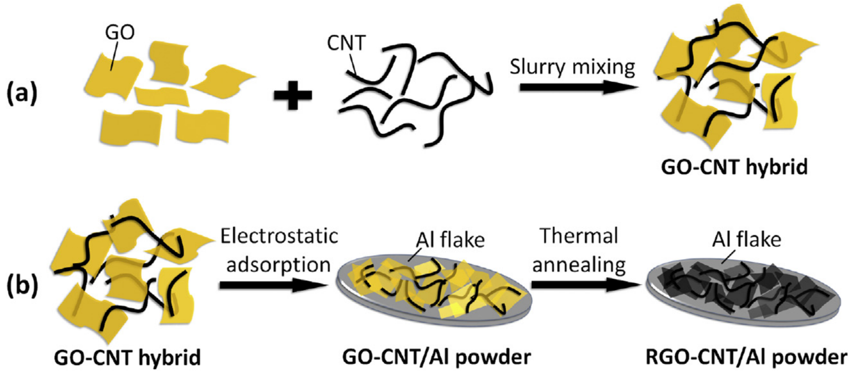

Fig. 1. Illustration of the fabrication procedure of RGO-CNT/Al composite powders. (a) The spontaneous formation of GO-CNT hybrid through π–π interactions. (b) Electrostatic adsorption of GO-CNT hybrid on Al flake and the reduction of GO to RGO through thermal annealing. (A colour version of this figure can be viewed online.)