Journal of Alloys and Compounds 650 (2015) 217–223

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Reinforcement with in-situ synthesized carbon nano-onions in aluminum composites fabricated by flake powder metallurgy

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ARTICLE INFO

Article history:
Received 9 June 2015
Received in revised form
28 July 2015
Accepted 31 July 2015
Available online 5 August 2015

Keywords:
Carbon nano-onions
Polymer pyrolysis chemical vapor deposition
Flake powder metallurgy
Mechanical properties

ABSTRACT

Bulk aluminum matrix composites reinforced with carbon nano-onions (CNOs) were fabricated by a flake powder metallurgy route. Homogenous dispersion of CNOs (with an average size of ~20 nm) was guaranteed by *in situ* polymer pyrolysis chemical vapor deposition of the precursor on Al nanoflakes with high specific surface area, followed by consolidating the CNO/Al nanoflake powders and then hot extrusion. The uniformly dispersed CNOs in ultrafine grained Al matrix exhibited remarkable strengthening efficiency: the 1.2 wt.% CNO/Al composite had a yield strength of 268 MPa and an ultimate tensile strength of 384 MPa, improved by 77% and 56% as compared to the Al matrix without CNOs, respectively. The strength enhancement with the in-situ CNOs is mainly attributed to a combined mechanism of grain boundary strengthening and Orowan strengthening.

1. Introduction

Metal matrix nanocomposites (MMNCs) reinforced with nano-carbons have attracted growing research attention with the aim to develop new-generation of super-strong, stiff, tough and light-weight structural materials [1]. Among all the MMNCs under development, much progress has been achieved in aluminum composites reinforced with 1-D carbon nanotubes (CNTs) and 2-D graphene nanoplatelets (GNPs) [2,3]. However, because of the feature of very high aspect ratio, so far it still remains a great challenge to achieve uniform dispersion and good interfacial bonding without causing the damage to GNPs and CNTs during fabrication [4,5]. As an alternative, carbon nano-onions (CNOs) with concentric fullerene-like structures [6] could also serve as ideal reinforcements, because its 0-D morphology can avoid tangle of 1-D CNTs and restacking of 2-D GNPs.

Nevertheless, the dispersion of CNOs in metal matrix is by no means easy because of its nanosize and large surface area. Up to present, several "ex-situ" methods such as codeposition [7], squeeze casting [8] and high energy ball milling [9], have been adopted for the fabrication of MMNCs reinforced with CNOs or other spherical fullerene. However, in these methods, the spherical fullerene usually experienced severe mechanical processing and/or high temperature treatment. As results, the spherical fullerene were damaged and tended to react with the matrix to form brittle Al_4C_3, which was considered to be harmful in metal matrix composites [10].

Thus, "in-situ" growth has been developed with the aim to obtain well dispersed and undamaged nano-carbon within metal matrix. For example, Kang and co-workers applied chemical vapor deposition (CVD) to synthesize CNTs [11–13] on spherical Al powders with size of tens of micrometer, and then consolidate the composite powders with powder metallurgy (PM) techniques, but no mechanical properties was reported on the as-obtained CNOs reinforced composite. More recently, we developed an upgraded version of CVD-PM method to further improve the cost efficiency of in-situ method. By this method, CNTs [14,15] and CNOs [14] could be uniformly grown on the surface of Al nanoflakes within a closed batch reactor, with polyethylene glycol (PEG) as carbon precursors and cobalt nitrate as catalyst. The large specific surface area of Al nanoflakes provided more growing sites for catalyst nanoparticles, and thus greatly promoted the homogeneity and volume fraction of the in-situ CNTs and CNOs. Therefore, this novel method of polymer

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http://dx.doi.org/10.1016/j.jallcom.2015.07.294
0925-8388/

pyrolysis CVD (PPCVD) combined with flake powder metallurgy (Flake PM) provides a feasible way to fabricate CNO/Al composite and evaluate the strengthening effect of in-situ CNOs.

In the present study, 1.2 wt.% CNO/Al composite with well dispersed ~20 nm CNOs were successfully obtained by the PPCVD-Flake PM processes. The tensile test showed 77% enhancement in yield strength and 56% enhancement in ultimate tensile strength relative to the unreinforced ultrafine grained Al matrix. According to quantitative analysis, the major strengthening mechanisms of the in-situ CNOs were found to be grain boundary strengthening and Orowan strengthening.

2. Experimental

The PPCVD-Flake PM technique using to fabricate in-situ CNO/Al composites was illustrated in Fig. 1.

Three steps were involved in the PPCVD process of producing CNO/Al powder: (1) formation of a precursor film on the surface of Al nanoflakes by surface coating; (2) CoOx nanoparticle formation via low-temperature heating; (3) Co nanoparticle catalyst formation and CNO growth by high-temperature heating. In a typical experiment, 30 g PEG (MW: 1000), 100 g citric acid monohydrate (CA) and 50 g $Co(NO_3)_2 \cdot 5H_2O$ (denoted as Co(II) hereafter) were added into 200 ml absolute ethanol to make a precursor solution with the mass ratio of PEG:CA:Co(II) = 3:10:5. Then 100 g Al nanoflakes with average thickness of 500 nm (Fig. 2a) were dispersed into the precursor solution, filtered, and then vacuum dried to form a PEG-CA-Co(II) film on the surface of Al nanoflakes. Finally, the precursor film-cladded Al nanoflakes were sealed in the closed batch reactor [14], preheated at 230 °C for 2 h, and then was maintained at 470 °C for 2 h to decompose PEG and grow CNOs.

Then Flake PM Process was applied to fabricate bulk materials. The as obtained CNO/Al composite powders were first compacted into Φ40 × 30 mm billets, which were consolidated by vacuum hot pressing at 500 °C and 500 MPa for 2 h, followed by hot extrusion at 440 °C with an extrusion ratio of 20:1. For comparison, unreinforced Al matrix specimen was also prepared by using the same pure Al nanoflakes. The morphology of CNO/Al composite powders was characterized on an FEI SIRION 200 SEM. High-resolution transmission-electron microscopy (HRTEM) analysis was carried out on a Philips Tecnai F20 S-Twin microscope at 200 kV for the morphologies and microstructure of the samples. Raman spectrum of the samples was recorded at room temperature on a HORIBA Jobin Yvon HR800 spectrometer, using the argon-ion laser beam as the excitation source at wavelength of 514.5 nm. Tensile tests were performed on the a rod sample of 5 mm in diameter and 25 mm in gauge length with a Zwick Z020 at a crosshead speed of 0.5 mm/min.

3. Result and discussion

The CNO/Al powders synthesized by PPCVD were characterized by SEM and TEM. Fig. 2b and c shows typical SEM images of the CNO/Al composite powders. It can be seen that the surface of Al nanoflakes were covered with a homogeneous, dense and thin layer of CNOs. In Fig. 2c, the diameter of the CNOs was measured to be 20 nm on average. The crystallinity degree of CNOs were examined by Raman spectroscopy. As shown in Fig. 2d, the spectra band at approximately 1598 cm^{-1} (G-band) is the characteristic of sp^2-hybridized carbon material and that at approximately 1358 cm^{-1} (D-band) is the characteristic of a disordered of carbon material [16]. Generally, the lower the D/G band intensity (I_D/I_G) is, the higher the degree of graphitization of the investigated carbonaceous materials. In this study, the I_D/I_G of CNO/Al composite was calculated to be 0.74, indicating a good degree of graphitization of the CNOs.

TEM observation (Fig. 3a) reveals that the CNO nanoparticles obtained on the Al nanoflakes are mainly spherical. Fig. 3b is the HRTEM image of a CNO, and the CNO shows a core–shell structure which consists of several concentric graphitic layers surrounding a

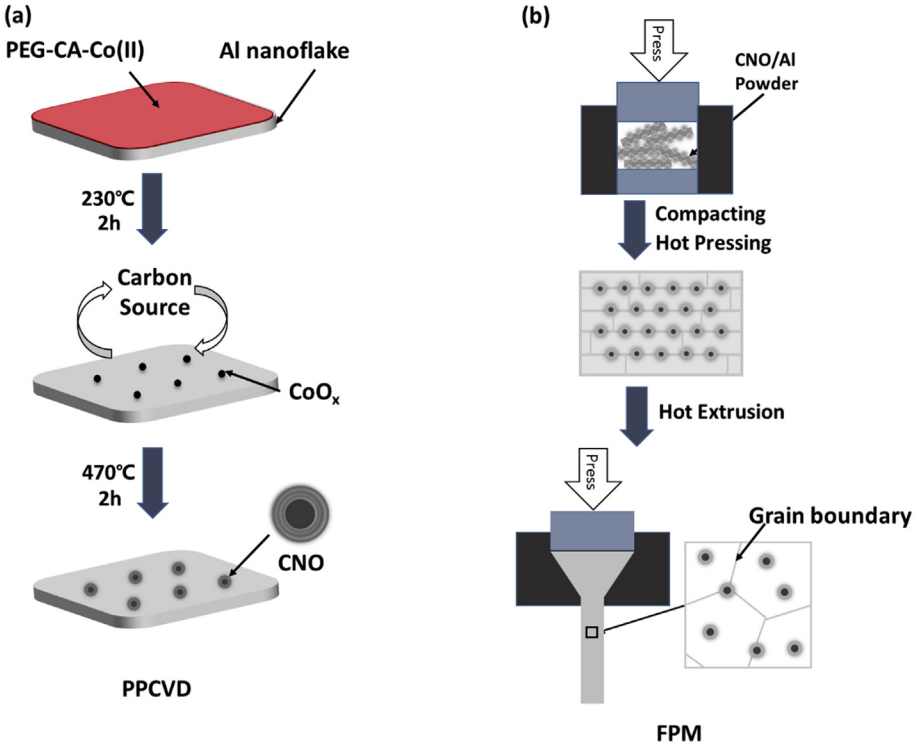

Fig. 1. Illustration of PPCVD (a) and Flake PM (b) processes for fabricating the bulk CNO/Al composite.