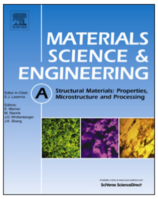
Materials Science & Engineering A 670 (2016) 205–216

Contents lists available at ScienceDirect

Materials Science & Engineering A

journal homepage: www.elsevier.com/locate/msea



Microstructure and mechanical properties of carbon nanotubes reinforced aluminum matrix composites synthesized via equal-channel angular pressing

Hassan Zare [a], Mohammad Jahedi [b,*], Mohammad Reza Toroghinejad [a],
Mahmoud Meratian [a], Marko Knezevic [b]

[a] Department of Materials Engineering, Isfahan University of Technology, Isfahan 84156-83111, Iran
[b] Department of Mechanical Engineering, University of New Hampshire, Durham, NH 03824, USA

ARTICLE INFO

Article history:
Received 3 March 2016
Received in revised form
30 April 2016
Accepted 11 June 2016
Available online 14 June 2016

Keywords:
Metal matrix composites
Powder processing
Severe plastic deformation
Particle distribution
Consolidation

ABSTRACT

In this work, 2 vol% carbon nanotubes (CNTs) reinforced aluminum (Al) matrix composites of superior microstructural homogeneity are successfully synthesized using Bc equal-channel angular extrusion (ECAP) route. The key step in arriving at high level of homogeneous distribution of CNTs within Al was preparation of the powder using simultaneous attrition milling and ultra-sonication processes. Microstructure as revealed by electron microscopy and absence of Vickers hardness gradients across the material demonstrate that the material reached the homogeneous state in terms of CNT distribution, porosity distribution, and grain structure after eight ECAP passes. To facilitate comparison of microstructure and hardness, samples of Al were processed under the same ECAP conditions. Significantly, the composite containing only 2 vol% exhibits 20% increase in hardness relative to the Al samples.

1. Introduction

Carbon nanotube (CNT) reinforced metallic matrix composites are being increasingly explored to enhance various properties of the matrix materials such as strength [1–4], conductivity [5], corrosion resistance [6,7], and magnetic properties [8–10]. Critical to the realization of such materials with improved properties is the development of fabrication techniques providing a homogeneous dispersion of nanotubes in the metallic matrix. As a result of fabrication, these materials are usually nanostructured in terms of not only CNTs distribution but also in terms of grain size distribution, which provides another strengthening mechanism originating from large content of grain boundary area defects and dislocation substructures [11–14]. To date, a number of nano-materials have been synthesized to exit in the form of atomic clusters or nano-particles [15–17], nano-crystallines [18–20], nano-rods [21–23], nano-tubes [24,25], and nano-layers [26–28]. These nanomaterials are used as a constituent in creating nano-composites. By definition, nano-composites consist of two or more components, where one or more of the constituents have less than 100 nm in a length scale. Structurally, particles and reinforcing fibers or layers are enhancing the strength in the matrix of the composite. Most generally, nano-composites can be classified based on the matrix material as: the polymer matrix nano-composites [29,30], nano-composites with ceramic matrix [31,32], and metal matrix nano-composites [3,33]. This study is focused on the metal matrix nano-composite (MMNC). MMNCs have wide applications in the automotive and aerospace industries due to the lightweight, high strength, and stiffness. Applications include: automotive like disk brakes [34–37], cutting tools such as tungsten carbide cutting tools [38,39], and aerospace like monofilament silicon carbide fibers in a titanium matrix for jet's landing gear [40–42].

CNT as one of the carbon allotropy has unique properties arising from their symmetric crystal structure. Mechanical properties of CNTs are far beyond the mechanical properties of any matrix material rising an exciting opportunity of using them as a reinforcing material within a given matrix material. Single-walled CNTs possess theoretical Young's modulus of approximately 5 TPa. The average Young's modulus of multi-walled CNTs is reported to be around 1.8 TPa and its flexural strength is 14.2 GPa [43,44]. Not only mechanical properties but also light weight, high length to diameter ratio, excellent electrical and thermal properties make CNTs be well-suited to be used as reinforcements in a number of materials.

Compared to the other reinforcements like SiC, B_4C, and Al_2O_3, CNTs have not been widely used in the metal-reinforced nano-composites mainly due to difficulties in achieving dispersion of the

---

[*] Corresponding author.
E-mail address: mohammad.jahedi@unh.edu (M. Jahedi).

http://dx.doi.org/10.1016/j.msea.2016.06.027
0921-5093/

CNTs in the metallic matrix. Additionally, interfacial chemical reaction of CNTs with a metal within the composite is usually weak even at high temperature and pressure, which typically reduces the efficiency of the CNTs reinforcements in nano-composites [24,25,45,46]. To overcome this issue, researchers have explored several advanced methods to enhance dispersion of CNTs within a metal matrix. For example, Noguchi et al. [47] utilized a nano-scale dispersion method in Al-CNT composites by setting up an elastomer precursor, Cha et al. [48] took an action into a molecular level in the copper matrix composites by means of a salt containing Cu ions, and Hu et al. [49] suggested an in-situ reduction approach in Au-CNT composites.

Enhanced mechanical and functional properties have been achieved using CNTs reinforced metallic matrix composites synthesized with variable content of CNTs. For example, substantial improvements in fracture toughness, wear resistance, and hardness were obtained with 10–15 vol% CNTs in Cu-CNT composites fabricated by hot pressing sintering [50]. A 70% increase in microhardness was reported in Al6061-CNT composites made by plasma spray forming when 10 wt% CNTs was added to Al matrix [51] while a 65% decrease in coefficient of thermal expansion (CTE) was found when 15 vol% CNTs were added to the nano-Al matrix [52]. An addition of 4 vol% CNTs [53] was observed to yield more grain refinement than non-reinforced copper via high pressure torsion (HPT) process as well as a 1 vol% CNTs to the copper matrix to achieve full density after 8 passes of equal channel angular pressing (ECAP) [54]. It has also been observed that at higher CNT (more than 5 vol%) [55], loading properties such as yield and tensile strengths tend to degrade. This is due to the inability of most of the processes to homogeneously distribute CNTs or to obtain dense components at high CNT content as well as improper bonding could lead to inefficient load transfer to the CNTs. Optimal content of CNTs in metal matrix composites enhancing the mechanical properties was reviewed in [55–57] and it was found to be the most effective when the content is 2 vol%.

Conventional deformation processes such as rolling and extrusion have been utilized extensively in the consolidation of the powders [33,58]. It was found that improving the consolidation and homogeneity requires very high strains (> 4), especially for composites containing fine particles. The processes of severe plastic deformation (SPD) have attracted much attention due to their ability to impart large plastic strains and thus substantially improve the homogeneity of particle distribution. While SPD processes such as equal channel angular pressing (ECAP) [54,59], accumulative roll bonding (ARB) [60–62], and high-pressure torsion (HPT) [53,63,64] have been extensively utilized for improving the consolidation process and distribution of the particles, several other innovative methods such as torsion extrusion (TE) [65], forward extrusion follows by equal channel angular pressing (ECAP-FE) [66], ECAP with back pressure [67,68], and high pressure double torsion (HPDT) [69,70] have even been more effective. In particular, HPDT was found to enhance distribution of SiC in a Cu matrix [69] as well as to improve crystallographic texture homogeneity [71]. Among these bulk SPD processes enhancing particle distribution and ensure consolidation, ECAP is the most attractive one due to its simplicity and ability to impair the most homogeneous strain distribution of all.

In general, ECAP process has two channels with the same cross-sectional area. Samples are usually circular or square according to the dimensions of the channels. After applying the appropriate lubricants, the sample is placed in the inlet channel and extruded through the outlet channel using a punch under pressure. The deformation mode in the ECAP process is a simple shear.

In this paper, Al-CNT composites are fabricated using multi-pass ECAP processing method. The content of CNTs was 2 vol%, which was added into pure Al matrix. To disperse the CNTs in the matrix, we utilized a combination of attrition milling and ultrasonic waves. The material was characterized in terms of microstructure and mechanical properties. To this end, we performed density measurements using Archimedes method, grain structure characterization using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) characterization, and Vickers hardness tests. The microstructural examinations show that ECAP can synthesize the composites with high degree of microstructural homogeneity. We find that CNTs are effective in improving grain boundary properties by linking the grains via the grain boundaries. This is due to their large aspect ratio. The hardness tests reveal the significant role of CNTs on enhancing the mechanical properties. To facilitate the comparison of enhancement in terms of hardness, Al samples are also processed in the same way. Smaller grain size was obtained in the Al matrix after the addition of CNTs into the composite. We rationalize that this is due to increased dislocation activity over shorter mean free path than in pure Al without CNTs leading to enhanced grain fragmentation and potentially reduced amount of grain growth hindered by CNT links.

2. Materials and experimental procedures

In this work, the Al- 2 vol% CNT composite samples were successfully fabricated using ECAP. Fig. 1 shows steps involved in the process of making Al-CNT composites. Microstructure and mechanical properties of the material are studied and critically compared with the Al samples in the same condition.

2.1. Starting materials

Commercially pure aluminum powders with average particle size of 30 μm and multi-walled carbon nanotubes (CNTs) with a diameter of 10–30 nm and a length of 5–15 μm are used as the starting materials. CNTs are produced with catalytic chemical vapor deposition (CCVD) method which revealed 95% purity and density of 1 g cm^{-3}. To investigate the chemical composition of Al powders as well as CNTs, the spectroscopy method is utilized. The results are shown in Table 1. In order to remove catalytic impurities from the CNT powders, which mainly consist of nickel and cobalt, an acidic treatment was performed. The acidic treatment consists of treating the CNTs in a solution of nitric acid of 68% purity for 12 h which is following by washing the CNTs with distilled water for several times to reach pH equals to 7. The SEM images of CNTs after acidic treatment and initial morphology of Al powders are shown in Fig. 2a and b, respectively. The large diameter to length aspect ratio of CNTs ensures a high magnitude of surface energy between the branches of CNTs [72]. As a result, there are many agglomerations in the starting material. In order to reduce these undesirable agglomerations, we have explored several methods including treating the CNTs in an acetone solution and/or imposing the ultrasonic waves as described in the next section. We selected acetone because it evaporates quickly, which essential for shortening the time involved in attrition is milling. The short time for attrition milling is important for not existing the flow properties of the material. Additionally, acetone introduces no contamination in the mixture after evaporation.

2.2. Mixing starting materials

To assure initial dispersion of CNT particles within the Al matrix, several procedures were explored. The procedures consist of attrition milling process and ultrasonication (see Fig. 1). In the attrition milling, the ball to powder ratio (BPR) was approximately 15 and the milling speed was 500 rpm. The milling and ultrasonic