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Strengthening and toughening of aluminum by single-walled carbon nanotubes

H.J. Choi, D.H. Bae*

Division of Materials Science and Engineering, Yonsei University, Shinchon-dong, Seodaemun-gu, Seoul 120-749, Republic of Korea

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ABSTRACT

Effects of single-walled carbon nanotubes (SWNTs) on strengthening and toughening behaviors of aluminum-based composites with grain sizes ranging from nano- to micrometer have been investigated. The strength of composites is enhanced as an increase in SWNT volume and a decrease in grain size. Nanocrystalline composite containing 3.5 vol.% SWNTs exhibits good ductility of ~5% tensile elongation to failure as well as superior yield stress of ~600 MPa. However, the strengthening efficiency of SWNTs becomes half of the theoretical prediction for nanocrystalline composites due to the recovery process around the interface. Nanocrystalline composite containing 2.0 vol.% SWNTs shows the fracture toughness of ~57 MPa mm$^{1/2}$, which is five times higher than that of starting aluminum. SWNTs may effectively block the propagation of necks and cracks, providing much improved ductility and toughness.

1. Introduction

The limited ductility of nanocrystalline (nc) metals has been concerned as crucial obstacles for applications [1–3] and therefore toughening of nc metals is emerging. The development of ultrafine- or microcrystalline- (mc) metal matrix composites has been considered to be one of breakthroughs that provide a desired combination of strength and ductility [4]. Recently, carbon nanotubes (CNTs) have been used to overcome engineering limits of materials by taking advantage of their exceptional mechanical properties [5–13]. Particularly, single-walled CNTs (SWNTs) with high aspect ratio beyond 1000 have been reported to show an elastic stiffness of ~1.5 TPa and a strength of ~30 GPa [5]. Hence, the development of the metal matrix composite containing CNTs has captured a growing attention [9–16].

An experimental study on the aluminum matrix composite containing 5 vol.% SWNTs revealed that the hardness value of the composite is around two times higher than that of monolithic aluminum [9]. The aluminum matrix composites containing multi-walled CNTs, which were fabricated by powder metallurgy routes involving ball-milling processes, also exhibited enhanced mechanical properties as compared to monolithic aluminum [10–16]. However, these experimental results were disappointing than theoretical expectations based on the superior properties of CNTs. It has been reported that critical reasons for the deteriorated mechanical properties of the composite are a weak interface and an inhomogeneous distribution of CNTs [12,13]. The recent review article on the metal matrix composites containing CNTs by Bakshi et al. also emphasized the importance of the dispersion of CNTs and the interface structure between CNTs and the matrix [14]. The weak interface stemming from the poor wettability between CNTs and the matrix might significantly deteriorate the mechanical performance of the composite. Dispersion of nano-materials in the metal matrix has still been challenging, particularly for CNTs which are supplied in the form of entangled bundles. Furthermore, severe mechanical working processes in powder metallurgy sometimes lead to the destruction of molecular structures of CNTs. In turn, detailed features of the role of the matrix (e.g. grain sizes nano over micro meter) on the mechanical behavior of such composites have not been evaluated.

Accordingly, the primary aim of this study is to synthesize the novel aluminum based composite containing SWNTs. The composite was fabricated using a mechanical milling followed by a hot extrusion. The strengthening and toughening behaviors of the composite are also examined in terms of the volume of SWNTs and the grain size of the matrix.

2. Experimental procedure

Monolithic aluminum and composite sheets were fabricated using a ball-milling technique followed by a hot-extrusion of ball-milled powder. To disperse SWNTs (diameter (d_o) ~2 nm, length (l_o) ~5 μm, and supplied from Iljin nanotech Co., Ltd.) in aluminum powder (99.5% in purity and <150 μm in diameter), the mixture of

* Corresponding author. Tel.: +82 2 2123 5831; fax: +82 2 312 5375.
E-mail address: donghyun@yonsei.ac.kr (D.H. Bae).

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SWNTs and aluminum powder was ball-milled using an attrition mill at 500 rpm in milling speed in a purified argon atmosphere for 24 h. Stainless steel balls with ~5 mm in diameter were used as milling media. The weight ratio of ball-to-powder was 15:1. Prior to milling, a control agent of 1 wt.% stearic acid ($CH_3(CH_2)_{16}CO_2H$) was added to prevent agglomeration among powder during milling.

To consolidate the ball-milled powder, hot extrusion was conducted with an extrusion ratio of 15:1. Prior to hot extrusion, the ball-milled powders were put into a copper container (ø30 mm × 70 mm), compacted under high pressure, degassed for 3 h at room temperature, and then sealed by welding. The sample was heated up to the pre-determined temperature of 470 °C with a heating rate of 20 °C/min. In this study, we produced five types of specimens, which vary according to the volume fraction of SWNTs (e.g. 0, 0.7, 1.5, 2.0 and 3.5 vol.%). All specimens were heat-treated at 600 °C for 6 h to produce the counterparts with larger grain sizes.

The grain size of the specimens was estimated using the X-ray diffraction (XRD, Rigaku, CN2301) patterns through the Scherrer formula [17]. Microstructures of the ball-milled powder and the extruded specimens were observed using transmission electron microscopy (TEM, JEOL 2000). Thin foil specimens from the rods were prepared using polishing followed by an ion beam milling method (Gatan, Model 600, Oxford, U.K.) for TEM analysis.

The quasi-static uniaxial tension and compression tests were carried out using an Instron-type machine with an initial strain rate of $1 \times 10^{-4}\,s^{-1}$ at room temperature. For compression tests, rectangular specimens with 2:1 ratio of height-to-width were prepared from the hot-extruded rods. Two tungsten carbide plates, which were coated with a sprayed film of boron nitride, were used to minimize the effect of friction. All tests were conducted up to a strain of 0.1 and then interrupted. Tensile specimens (thickness: 1 mm, gauge length: 6 mm, gauge width: 3 mm, and effective grip length: 160 mm for both upper and lower grips) were prepared from the rods and loaded in the extrusion direction. Three-point bending tests were conducted according to ASTM E399-05 using an Instron-type machine with an initial strain rate of $5 \times 10^{-5}\,s^{-1}$ at room temperature. The hexahedral specimens (length (S): 15 mm, width (W): 3.75 mm, thickness (B): 1.88 mm) with an initial crack (length: 1.2 mm (a), width 0.25 mm) were prepared from the rods. To minimize other effects on crack propagation, the surfaces of the samples were polished mechanically using sand papers and buffers. The fracture toughness, K_{IC}, with the Mode I crack is calculated using fracture load (P) as:

$$K_{IC} = \frac{PS}{BW^{2/3}} \cdot f\left(\frac{a}{W}\right) \quad (1)$$

where

$$f\left(\frac{a}{W}\right) = \frac{3(a/W)^{1/2}1.99 - (a/W)(1-a/W)(2.15 - 3.93a/W + 2.7a^2/W^2)}{2(1+2a/W)(1-a/W)^{3/2}} \quad (2)$$

After the bending tests, crack profiles and fracture surfaces of the specimens were observed by optical microscopy (OM) and scanning electron microscopy (SEM), respectively.

3. Results and discussion

3.1. Microstructures

The dispersion procedure of CNTs in aluminum powder during a milling process has been reported in the previous studies [11,12]. Under the specific milling condition, a bundle of CNTs are firstly embedded within the aluminum powder as an entangled form, and then dispersed through the plastic deformation of the powder [12]. The morphology of the ball-milled powder, fabricated in the present study, is observed using TEM as shown in Fig. 1. SWNTs are found to be dispersed after milling.

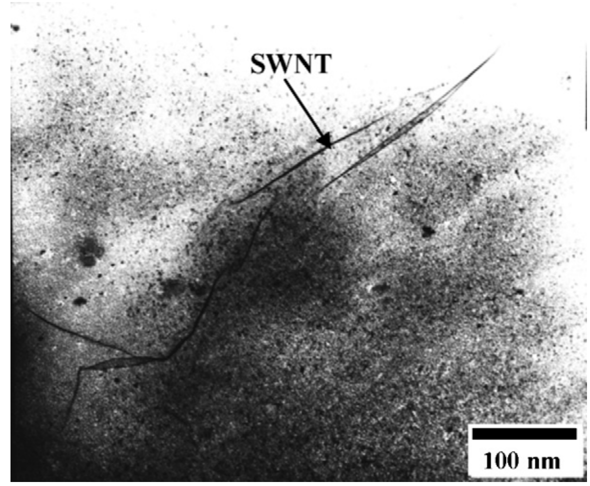

Fig. 1. TEM image of a ball-milled powder containing 0.7 vol.% SWNTs.

Fig. 2(a) shows TEM image of the hot-extruded composite containing 0.7 vol.% SWNTs, where SWNT is marked by an arrow. The grain size of powder was effectively reduced as milling was processed. Furthermore, hot-extrusion was conducted within 30 min at a relatively low temperature of 470 °C so that the grain growth was not significant [18]. The average grain size of the matrix was determined to be ~56 nm using XRD and TEM analysis. In Fig. 2(a), most grains seem to be smaller than 100 nm. Fig. 2(b) shows TEM image of the composite containing 0.7 vol.% SWNTs after heat-treatment at 600 °C for 6 h, where SWNT is also marked by an arrow. During heat-treatment, SWNTs seem not to be turned into carbides while the grain size is notably increased to be ~2.5 μm.

3.2. Mechanical properties

Compressive true stress vs. true strain curves of the nc and mc aluminum matrix composites are revealed in Fig. 3(a) and (b), respectively. As the grain size is reduced, the yield stress significantly increases; the monolithic mc and nc aluminum specimens exhibit yield stresses of ~200 and ~400 MPa, respectively. However, the work hardening capacity is significantly reduced as the grain size decreases. The yield stress also increases by incorporating SWNTs for both nc and mc composites. The strengthening effect of SWNTs is quite significant; e.g. an increment of ~300 MPa in strength is achieved with an addition of 3.5 vol.% SWNTs into mc aluminum. In Fig. 4, the compressive yield stress is plotted against the SWNT volume, loaded in both of the extrusion and transverse directions. The strengthening effect of SWNTs is more significant when the specimens are loaded in the extrusion direction whereas only a minor increment is observed when loaded in the transverse direction. This demonstrates the anisotropic properties of the composites, possibly due to the alignment of SWNTs along the extrusion direction.

Tensile true stress vs. true strain curves of the nc and mc aluminum matrix composites are shown in Fig. 5(a) and (b), where the curve for the mc composite containing 3.5 vol.% SWNTs is not included because the specimens were fractured before yielding. The yield stress is almost similar to that obtained from compression tests although significant differences between tension and compression have been reported in some nanocrystalline and submicron aluminum and aluminum alloys [19–21]. In general, this tension–compression asymmetry has been thought to be attributed to the residual stresses at grain boundaries in materials with binomial grain size distribution or processing defects such as pores and microcracks. The nc aluminum and the nc composite in the present