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Mechanical Properties of Aluminium-Based Nanocomposite Reinforced with Fullerenes

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Abstract

Aluminum has been spot-lighted due to its earth-abundant and light-weight nature. However, usages of aluminum as an engineering material have been limited by its low strength compared to other engineering metals such as steel and titanium. One possible way to strengthen aluminum is reinforcing it with carbon-based nano-materials, which exhibits superior elastic modulus and yield strength. Here, we develop aluminum-based composite, in which each of fullerenes are intended to be uniformly dispersed via three-step ball-milling processes: first, using a planetary-milling process the fullerene particles were shattered into smaller particles by shear force with two different control agents of stearic acid and ethyl alcohol, respectively; second, planetary milling process was repeated to mix the primarily ball-milled fullerenes and pure aluminum powder; third, attrition milling process was carried out for grain refinement of aluminum as well as further dispersion of fullerenes. Finally, the composite powder was consolidated using hot-pressing or hot-rolling. The composite, containing 2vol% fullerenes milled with stearic acid, shows ~220 Hv in Vickers' hardness.

Introduction

Constant efforts are being made to develop new structural materials with high specific mechanical performances. Aluminum has been considered as a good candidate for the light-weight structural materials, due to its low density and consequently weight-saving potential [1–3]. In this context, various efforts have been undertaken to develop aluminum matrix composites with these advantages, but also making up for its low strength/stiffness limitations [4–11].

Carbon nano-materials, such as fullerenes [4, 5], carbon nanotubes [6–9], and graphenes [10, 11], have so far been considered as attractive reinforcing agents for light-metal matrix composites, due to their high stiffness/strength (i.e., ~1 TPa of stiffness and ~30 GPa of yield strength) as well as low density. To exploit these superior properties of carbon nano-materials into bulk composites, several important factors should be achieved such as homogeneous dispersion of each reinforcement, preservation of molecular structure of the reinforcement, sufficient interfacial bonding and absence of cavity/defects/artifacts in bulk specimens [6, 7].

A powder metallurgy (P/M) route is one of promising techniques, since it enables fairly uniform dispersion of carbon nano-materials and its low processing temperature minimizes thermal damages to the carbon nano-materials [6–9]. However, it has been reported that the severe damage of carbon nano-materials, particularly for carbon nanotubes, induced by high impact energy of balls [6] results in unfavorable chemical interfacial reactions between the damaged carbon nano-materials and the metal matrix during high-temperature consolidation processes [7]. Without solving this critical problem in dispersion, therefore, the giga-Pascal-level strength of the carbon nano-materials would not be beneficial for any structural composite applications [6–9].

Regarding these technical hurdles, fullerenes with a spherical structure may be considered as a more fascinating reinforcing agent compared to carbon nanotubes or graphenes, due to their zero-dimensional geometric characteristics. They would be readily dispersed and rarely destroyed during severe mechanical dispersion processes in the metal matrix. Previously, the improvement of yield strength of aluminum from 150 to 250 MPa has been reported by reinforcing fullerenes via severe plastic deformation techniques [4]. Furthermore, aluminum-based composites, fabricated via liquid metal infiltration techniques, have been introduced, where the composite shows good interfacial bonding between aluminum and fullerenes [5]. However, the mechanical properties of the composites are still below the theoretical expectation based on the superior stiffness/strength of fullerenes.

In this study, we employ three-step ball-milling processes to disperse fullerenes into the aluminum matrix. Microstructures and mechanical properties of the composite, varied according to the type of control agents and hot working processes, are discussed.

Experimental

Aluminum – based composites containing fullerenes were fabricated by hot-pressing or hot-rolling of ball-milled powder. Aluminum powder (150 μm, 99.5% purity, Changsung Co. Ltd.) and fullerene soot (Sigma Aldrich Korea Co. Ltd.,) were used as starting materials.

Ball milling was conducted via three steps; first, using a planetary-milling process the fullerene particles were shattered into smaller particles with two different control agents; second, planetary milling process was repeated to mix the primarily ball-milled fullerenes and pure aluminum powder; third, attrition milling process was carried out for grain refinement of aluminum as well as further dispersion of fullerenes. Specifically, a planetary mill (Fritsch Co. Ltd., Pulverisette 5, Germany) was employed to shatter fullerene aggregates where fullerenes are initially agglomerated via Van der Waals bonding. The effect of two different control agents on this shattering operation was compared: 10 wt% stearic acid as a solid control agent was employed to prevent agglomeration among fullerenes (designated "dry-milled fullerenes); and 95.0% ethyl alcohol as a liquid control agent was used to weaken the bonds among fullerenes as well as to prevent agglomeration (designated "wet-milled fullerenes). A stainless chamber (500ml) was charged with 1 g of fullerenes and 800 g of 5 mm–diameter–stainless balls with a control agent. Then, a cycle of 200–RPM–milling for 15 min and pausing for 75 minute was repeated 8 times. To mix the pre-milled fullerenes and aluminum, a planetary mill was repeated 8 times under the same condition (a cycle of 200–RPM–milling for

15 min and pausing for 75 minute). An attrition mill (KMC Co. Ltd., KMC-1BV, Korea) was used for dispersing shattered fullerenes into aluminum powder. A stainless chamber was charged with fullerenes, aluminum powder, and 5 mm–diameter–stainless balls, where the ball–to–powder weight ratio was 15:1. Attritor was operated at 500 RPM for 24 hours in argon atmosphere. To avoid the excessive cold welding, stearic acid was used as a process control agent. Three different Al-2vol% fullerenes composite powders were finally prepared: (i) attrition-milled powder without the pre-mixing process; (ii) attrition-milled powder with dry-milled fullerenes; and (iii) attrition-milled powder with wet-milled fullerenes. For the third case (wet-milled fullerenes), ethyl alcohol was evaporated before attrition milling.

Flowingly, the composite powder was consolidated via two different processes of hot rolling and hot-pressing. Prior to hot-rolling, the ball-milled powder was heat-treated at 500℃ in vacuum for 20 minutes to remove stearic acid. A copper tube was used as a container of powder during rolling and was then mechanically peeled off after rolling. Hot rolling was performed at 480℃ with every 12% of reduction per pass until thickness of the sample reaches 1.8 mm. For hot-pressing, ball-milled powder was packed into a stainless steel mold and was then consolidated under a pressure of ~210 MPa at 500℃ for 1 h. Boron nitride was used as a lubricant to minimize the effect of friction during hot-pressing.

The morphology of fullerenes and aluminum powder was observed by scanning electron microscope (SEM, JEOL, JSM 2001F, Japan). The microstructure of the bulk Al/CNTs composite was observed examined using a high -resolution transmission electron microscope (HRTEM, JEOL 2000). Thin foil specimens from the sheets were carefully prepared by an ion-beam milling method (Gatan, Model 600, Oxford, UK). The density of the hot-rolled sheets and hot-pressed pellets was determined using the Archimedes method. The Vickers hardness of the specimens was measured using a micro Vickers' hardness testing machine with an indenter load of 300 gf.

Results and discussion

Planetary milling is found to be effective to shatter the giant fullerene particles (~200 μm in diameter), which was initially agglomerated via Van der Waals bonding during manufacture, into smaller ones. Dry-milled fullerenes (Fig. 1 (a)) exhibit a wide size distribution from ~0.1 to 8 μm while wet-milled fullerenes (Fig. 1 (b)) are mostly segmented into tiny particles with sizes less than 500 nm. Ethyl alcohol has been reported to be effective to weaken the van der Waals force among fullerenes [12], thereby stimulating de-bonding of fullerenes. Their mixtures with aluminum powder are shown in Figs. 1 (c) and (d), respectively, where fullerenes are marked by arrows. Dry-milled fullerenes are visible on the aluminum powder surface (Fig. 1 (c)) whereas wet-milled fullerenes are considered to be embedded insider the aluminum powder (Fig. 1 (d)).

Figure 2 shows TEM image of Al-2vol% fullerenes composite, fabricated using dry-milled fullerenes. Fullerenes, mark by arrows, exhibit a mean diameter of ~10 nm. As compared to fullerenes right after planetary milling (Fig. 1 (a)), the size of fullerenes decreases extremely after attrition milling and hence the attrition mill is thought to be very powerful for further fragmentation of fullerenes. Based on statistical analysis using TEM images, the grain size of composites is estimated to ~40 nm (not shown here).

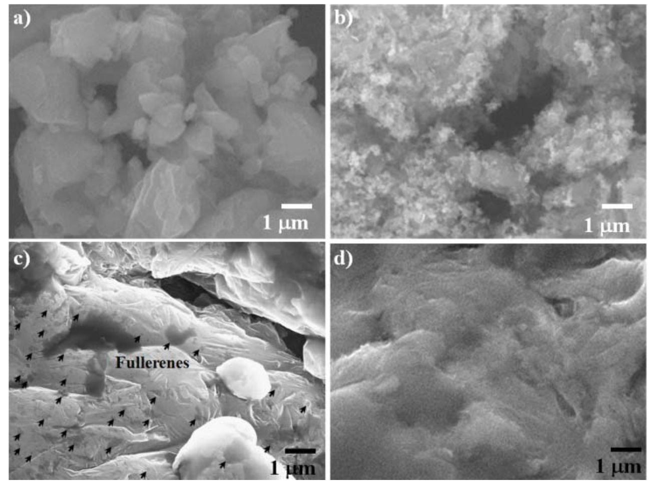

Figure 1 SEM images of **(a)** dry-milled fullerenes, **(b)** wet-milled fullerenes, **(c)** ball-milled mixture of aluminum powder and dry-milled fullerenes, and **(d)** ball-milled mixture of aluminum powder and wet-milled fullerenes.

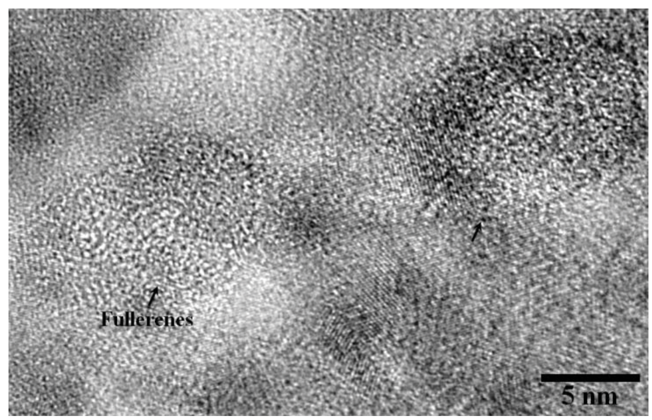

Figure 2 TEM image of Al-2vol% fullerenes composite, fabricated using dry-milled fullerenes.

Figure 3 shows density (Fig. 3 (a)) and Vickers' hardness (Fig. 3(b)) data for the hot-rolled and hot-pressed composites, where the composite containing un-pretreated fullerenes is designated "No Premix", that containing dry-milled fullerenes "Dry P", and that containing wet-milled fullerenes "Wet P", respectively. The density of the composites is in the range of ~2.57 to 2.63 g/cc, which is ~96.5 to ~98.5% of the theoretical density. The theoretical density is calculated using the rule of mixture as follows [13]

$$\rho_{com} = \rho_f V_f + \rho_m V_m \qquad (1)$$

where ρ_{com} is the density of the composite, and ρ_f and ρ_m are the densities of the fullerenes (1.3 g/cc), and the aluminum matrix (2.7 g/cc), respectively. Furthermore, V_f and V_m are the volume fraction of the fullerenes (0.02) and the aluminum matrix (0.98), respectively. The rule of mixtures is considered to be valid when aluminum is physically mixed with fullerenes, and no reaction occurs between the aluminum and carbon (e.g., formation of aluminum carbides). Since the density of the composites is higher than 96% of the theoretical value and is not significantly varied according to the milling and hot-working types and it is, it is considered not to significantly affect the mechanical properties of the composite.

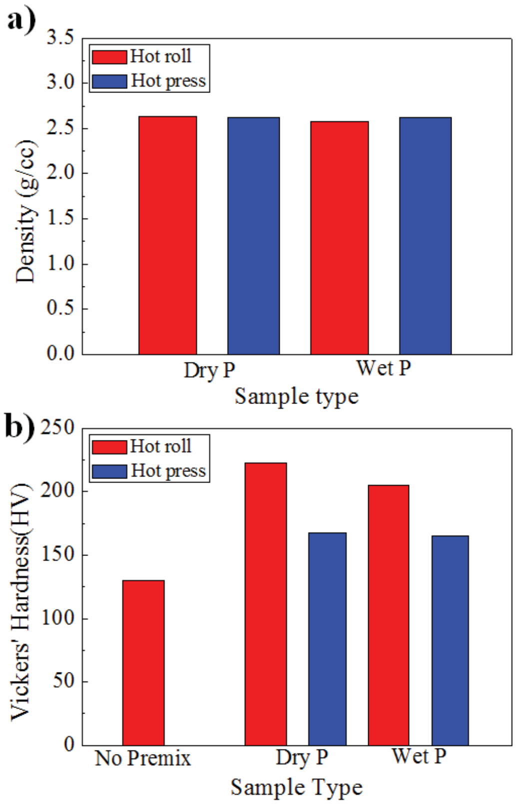

Figure 3 (a) Density and **(b)** Vickers' hardness for the hot-rolled and hot-pressed composites, where the composite containing un-pretreated fullerenes is designated "No Premix", that containing dry-milled fullerenes "Dry P", and that containing wet-milled fullerenes "Wet P", respectively.

The Vickers' hardness of the composites containing both of dry-milled fullerenes and wet-milled fullers is much higher than that of the composite containing un-pretreated fullerenes. It can be converted to the yield strength (σ_y), based on empirical equation of σ_y = ~ 3.3 HV for materials with negligible work hardening [13]; it is calculated to be ~430 MPa for "No Premix", ~734 MPa for hot-rolled "Dry P", ~555 MPa for hot-pressed "Dry P", ~680 MPa for hot-rolled "Wet P", and ~545 MPa for hot-pressed "Wet P", respectively. Regarding that the yield strength of monolithic cast aluminum is ~40 MPa [14], the strength of the composite is enhanced by ~18 times, with the help of grain refinement and incorporation of only 2vol% fullerenes. The first step to shatter fullerene aggregates using a planetary mill is found to be effective, providing better distribution of each fullerene and consequently leading to superior mechanical properties. Interestingly, the composite with dry-milled fullerenes exhibit higher Vickers' hardness that that with wet-milled fullerenes although the size of wet-milled fullerenes is much smaller after planetary milling. We hypothesize that the molecular structure of fullerenes may be destroyed by reacting with alcohol to some extent during planetary milling, deteriorating the mechanical properties. Furthermore, hot-rolled specimens show higher hardness as compared to hot-pressed pellets although their density is not varied significantly. It is thought to be a consequence of the considerable change in microstructures (e.g., grain growth or carbide formation), which may originate from the pre-longed exposure of the hot-pressed specimens to high-temperatures (i.e., 500^{o}C).

Conclusions

Al-2vol% fullerenes composite is produced by a powder processing route. 3-step ball milling processes are employed to effectively shatter fullerene aggregates and uniformly disperse each of fullerenes. Solid milling agent is found to lead to a higher hardness of the composite although liquid milling agent is more effective to shatter fullerene aggregates. Eventually, the composite containing dry-milled fullerenes, which was produced using hot-rolling, exhibits superior Vickers' hardness of ~220 Hv.

Acknowledgements

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