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Strong, ductile, and thermally conductive carbon nanotube-reinforced aluminum matrix composites fabricated by ball-milling and hot extrusion of powders encapsulated in aluminum containers

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A B S T R A C T

Aluminum matrix composites reinforced by carbon nanotubes (CNTs) were fabricated by ball-milling (with aluminum powder; average diameter 30 μm), followed by hot extrusion of the powders encapsulated in aluminum containers (at 550° with an extrusion ratio of 9). The CNTs were intended to improve the mechanical properties and thermal conductivity of the aluminum composites formed by powder metallurgy. The CNTs were of two types—vapor-grown carbon fibers (VGCFs) with a diameter of 150 nm and multiwalled CNTs (MWCNTs) with a diameter of 65 nm. The composites were evaluated by their Vickers microhardness, tensile strength, and thermal conductivity. The microhardness exceeded 100 HV and increased with increasing volume fraction of reinforcement. The MWCNT-reinforced composites were harder than the VGCF-reinforced composites and exhibited higher ultimate tensile strength (over 450 MPa). The maximum fracture strain (37.2%, observed at a volume fraction of 0.5%) is the highest reported in the literature. Conversely, the VGCF-reinforced composites exhibited higher thermal conductivity than the MWCNT-reinforced composites. The thermal conductivity of the 0.5% VGCF-reinforced composites (203.7 W/m K) also exceeds any previously reported value. In summary, composites with unprecedentedly high ultimate tensile strength, fracture strain, and thermal conductivity were fabricated by a simple process that minimized damage to the CNTs during mixing, protected them from oxidation and excessive reaction with the aluminum matrix and effectively densified composites by hot extrusion.

1. Introduction

Carbon nanotubes (CNTs) are attractive reinforcements for composite materials owing to their light weight, extraordinarily high Young's modulus, tensile strength, and thermal conductivity [1–3]. CNT-reinforced aluminum matrix composites are expected to realize structural parts with superior properties in automobiles and aircrafts [4–20]. Recently, researchers have reinforced aluminum matrix composites with CNTs and reported their results. The strengths of light metals incorporating nanomaterials are thought to exceed the highest possible strength of composites incorporating macrosized reinforcements [21,22]. Hence, such composites are expected as next-generation aerospace structural materials. Most previous reports have focused on solid state fabrication because it avoids the poor wettability of CNTs in molten aluminum [23,24]. Among the various reported methods are plasma spraying fabrication of composites [8], composite fabrication by nanoscale dispersion (NSD) [9], surfactant-aided dispersion of CNTs in aluminum matrix [10], fabrication of nanolaminates of CNTs-reinforced aluminum composites by flake powder metallurgy [11], in-situ chemical vapor deposition (CVD) growth of CNTs on aluminum powders [12], mixing of CNTs and aluminum powder by high energy ball-milling (HEBM) [13,14], and a strengthening mechanism [15,16]. However, because the plasma-spray technique does not refine the aluminum grain size, the resulting composites have low strength [8]. Kwon [9] reinforced aluminum matrix composites with vapor-grown carbon fibers (VGCFs). They applied the NSD method, which uniformly disperses the CNTs in aluminum powder using natural rubber. The mixed VGCFs and aluminum powder was consolidated by spark plasma sintering (SPS) at 600 °C and hot-extruded at 400 °C. The tensile strength and fracture strain were approximately 180 MPa and 10.5%, respectively. Again, the fabricated composites were not accompanied by grain refinement. Although CNTs and aluminum strongly interact owing to aluminum carbide (Al_4C_3) formed at the interface, the CNTs tend to convert to Al_4C_3 nanorods, which decrease the ductility of the

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composites [17,18]. Chen et al. fabricated composites by the surfactant-assisted ball-milling method [10]. They coated aluminum powder particles with unbundled CNTs, obtaining composites with intermediate tensile strength (192 MPa) and high fracture strain (~20%). Jiang et al. fabricated CNTs-reinforced aluminum composites with a nanolaminate architecture in a three-step process—preparation of nanoflake aluminum powder by ball-milling, adsorption of CNTs on the nanoflake powder, and alignment and consolidation of the nanoflakes [11]. Their composites achieved a tensile strength of 375 MPa and a fracture strain of 12%. The high strength and ductility of their composites were attributed to the nanolaminate structure, which enabled the CNTs to retain the aluminum grains and maintain the dislocations. He et al. [12] fabricated CNT-reinforced aluminum composites by direct synthesis of the CNTs on aluminum powder. The CNTs were well-dispersed in the aluminum matrix and the composites exhibited high tensile strength (398 MPa). However, although the abovementioned methods are effective for composite fabrication, they are experimentally expensive. In contrast, Choi et al. successfully fabricated high-strength composites by HEBM, which is cost-effective [13,14]. The strength of the composites containing 4.5 vol% CNTs reached 629 MPa owing to the high refinement of the aluminum grains (< 200 nm), while the fracture strain decreased with increasing strength. Choi et al. reported the highest-strength composites in the contemporary literature. The ductility of composites is also expected to be improved by optimizing the mixing conditions, consolidation temperature, and interfacial structure. Therefore, ball-milling and HEBM are promising methods for obtaining high-strength CNT-reinforced aluminum matrix composites.

The fabrication of composites with both high strength and high ductility is strongly anticipated and has been achieved to some extent. However, existing fabrication methods are excessively expensive and cannot easily fabricate the composites that constitute the actual structures. Fabrication methods that extend the cost-effective ball-milling and/or HEBM methods are anticipated. Recently, we reinforced aluminum matrix composites by VGCFs, large-diameter CNTs that are also known as carbon nanofibers [16]. The VGCFs and aluminum powder were mixed by ball-milling, and the mixture was subsequently encapsulated in an aluminum container. The mixing condition was carefully determined to minimize the fracture and shortening of VGCFs during the mixing to homogenize the dispersion of VGCFs in the aluminum matrix and to minimize the powder particle size. Minimizing damage to the VGCFs was a top priority. Next, the container was machined and subjected to hot extrusion, yielding dense composites with partially aligned VGCFs. The VGCFs were well-dispersed through the aluminum matrix. The tensile strength of 0.5% VGCF-reinforced aluminum matrix composites was 427.1 MPa, and the fracture strain exceeded 30%. These values were higher than previously reported values for VGCF-reinforced aluminum matrix composites [9]. The reinforcing mechanism of the composites was also discussed. The composites were found to be strengthened by load bearing of the VGCFs, aluminum grain refinement after VGCF addition, thermal mismatch of the constituents, and the Orowan strengthening effect. However, in the previous study, the amount of VGCF incorporated into the aluminum matrix was small (< 1.0 vol%). To investigate the effect of volume fraction on the mechanical properties of the composites, we here fabricate VGCF-reinforced aluminum composites with volume fractions up to 5 vol% by ball-milling and hot extrusion of the powder-encapsulated aluminum container. We also reinforce composites by small-diameter CNTs (65 nm) under the same mixing and extrusion conditions. The mechanical properties of composites reinforced by both types of CNTs were compared, and the thermal conductivities were evaluated. The effects of CNT diameter and volume fraction on the microstructures of the composites (aluminum grains, CNT shape, and orientation) are also observed. The mechanical properties and thermal conductivities are compared with the literature values [8–14,20,34] and discussed in relation to the fabrication process and microstructures.

Table 1
Properties of the CNTs.

Property	CNT1 (VGCF)	CNT2 (MWNT-7)
Geometry	Average diameter 150 nm Average length 15 μm	Average diameter 65 nm Average length 7.5 μm
Density	2.0 g/cm^3	2.1 g/cm^3
Young's modulus	516.5 GPa [16]	850 GPa [25]
Tensile strength	3100 MPa [16]	1.5*10^5 MPa [25]

2. Materials and methods

2.1. Fabrication of composites

CNTs were mixed with aluminum powder with an average diameter of 30 μm (Kojundo Chemical Laboratory). Two types of CNTs were used—VGCFs (Showa Denko Co. Ltd, Japan; average diameter: 150 nm, average length: 15 μm) and MWNT-7 (Hodogaya Co. Ltd, Japan; average diameter: 65 nm, average length: 7.5 μm). Both CNTs have fiber-like structures with rolled graphitic sheets (transmission electron microscopy images of the CNTs are shown in [25]). Their sizes and mechanical and thermal properties are listed in Table 1 [16,25].

Hereafter, VGCF and MWNT-7 CNTs are referred to as CNT1 and CNT2, respectively. The mixing condition of CNT1 with aluminum was reported in our previous study [16]. The CNT1 and aluminum powder were mixed in a planetary ball-mill (Fritsch Pulverisette 5). Stainless jars containing CNT1, aluminum powder, stainless-steel balls, and stearic acid ($C_{17}H_{35}COOH$) were rotated at 200 rpm for 3 h. The stearic acid was a control agent that prevented excessive cold welding of the powder. The stainless balls were 8 mm in diameter, and their weight fraction (relative to the CNT–aluminum powder mixture) was 20:1. To prevent excessive cold welding of the powder, rotation for 20 min followed by suspension for 40 min was repeated nine times. Under this condition, CNT1 can be dispersed in the aluminum matrix without excessive fracture and shortening. Under the same conditions, CNT2 was also mixed with aluminum powder to minimize the damage induced by ball-milling.

The interior of the particles in the powders after mixing was observed before fabrication of composites, using scanning electron microscopy (SEM). To prepare the SEM samples, the powders were embedded in an epoxy resin and then polished and etched using nitric acid. Further, aluminum grain structures inside the mixed powders were observed using field emission scanning electron microscopy (FESEM). The FESEM sample was prepared by polishing and finishing the surface of the epoxy resin embedding the mixed powder using a cross-section polisher (CP; JEOL).

The mixed CNTs and aluminum powders were encapsulated in aluminum A1050 containers. Powders were compressed in a vacuum (10^{-5} Torr) using the SPS system (Dr. Sinter; SPS Syntex) and capped by an aluminum lid applied under a force. The SPS system was used only for creating the vacuum, compressing the powders, and installing a lid. Pores in the compressed powders and oxidation of the powders during heating in the extrusion process were carefully avoided. Oxidation can result from residual air in the container. The containers were then machined into extrusion billets with a diameter and height of 30 mm and 45 mm, respectively. The extrusion used a conical die with a 60° angle and was performed at 550 °C with an extrusion ratio of 9 and an extrusion rate of 20 mm/min. Prior to extrusion, the temperature was raised to 500 °C for 0.5 h, raised to 550 °C for the next 0.5 h, and held at 550 °C for 0.5 h. This heating condition was carefully based on the following considerations: (i) the interfacial reaction of CNTs and aluminum rapidly proceeds around 600 °C [26], and high extrusion temperature is preferred for consolidating the composites. Therefore, to avoid extensive reaction of the CNTs and the aluminum matrix and to obtain densified composites, the extrusion temperature was set to