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Effect of processing route on mechanical and thermal properties of few-layered graphene (FLG)-reinforced copper matrix composites

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ABSTRACT

In this study, copper/few-layered graphene (Cu/FLG) composite powder is prepared using two different approaches, chemical synthesis and mechanical milling, and the effect of the processing routes on the mechanical and thermal behaviors of hot-pressed pallets is examined. With both processing routes, the strength of the matrix is increased ~3.90 and ~2.82 times by grain refinement, and is further increased 1.14 times by incorporating 0.5 vol.% FLG. In addition, for both processing routes, the coefficient of thermal expansion is reduced from ~17.07 to ~15.15 (ppm/K) by incorporating 0.5 vol.% of FLG in both composites. Considering its cost-effectiveness, simplicity, and potential for mass-production, the mechanical process demonstrates the ability to produce Cu/FLG composites with a high mechanical and thermal performance that is comparable to solution-based chemical synthesis routes.

1. Introduction

Copper has excellent mechanical, electrical, and thermal properties and thus is widely used as a key material in structural, electronic, and thermal applications [1]. However, the coefficient of thermal expansion (CTE) of copper (~16.9 ppm/K) is approximately four times higher than that of commercial semiconducting materials (4–7 ppm/K) such as GaAs, AlN, and Si [2], which leads to the generation of thermal cracks at the interface between Cu and semiconducting materials. In this respect, copper-based composites have been developed to improve mechanical properties and to reduce the CTE of copper, with the aim of minimizing thermal stress and damage generated during the operation of electronic devices. Although materials such as SiC, AlN, Diamond, Mo, and Kovar are used as reinforcement in copper matrix composites, these have respective disadvantages such as bad machinability (SiC, AlN), high cost (Diamond), high density (Mo), and low thermal conductivity (Kovar) [2,3].

Graphene is a potentially good candidate for use in reinforcing copper matrix composites, owing to its excellent mechanical properties such as high tensile strength (130 GPa) and high Young's modulus (0.5–1 TPa) [4], electrical (5×10^{-1} S/m) [5] and thermal conductivities ($4.8–5.3 \times 10^{3}$ W/mK) [6], and negative in-plane CTE (−0.71 ppm/K) [7]. Since the discovery of graphene in this respect, a number of studies have been conducted on graphene reinforced metal-matrix composites (MMCs) with the aim of improving their mechanical and thermal properties. For example, Wang et al. reported that the tensile strength of Al/graphene composites with only 0.3 wt.% graphene is 1.61 times higher than that of pure Al [8], and it has been determined that the yield strength of Mg–Al alloy containing 0.6 wt.% of graphene nanoplatelets (GNPs) is 1.31 times higher than that of Mg–Al alloy [9]. Furthermore, it has been found that the strengthening effects of graphene on pure Mg are high compared to other reinforcements such as SiC, Al_2O_3, Y_2O_3, and SiO_2 [10]. However, only a few reports have demonstrated the remarkable improvements related to the properties of metal/graphene composites. The lack of studies in this regard is attributed mainly to two problems: firstly, it is very difficult to disperse graphene uniformly in highly packed metallic atoms due to its 2-D structure, and secondly, metallic matrices usually form weak interfaces with graphene due to their poor affinity.

To solve these issues, a number of researchers have developed a variety of processing route to produce high performance metal/graphene composites such as casting [11], electro-deposition [12], differential speed rolling [13,14], powder metallurgy [4,14–16], and

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chemical synthesis [17–19]. The casting method has the advantage of enabling mass-production and a reduction in costs. However, graphene tends to easily react with metals at high processing temperatures (i.e., above the melting point of matrix metals), resulting in the formation of unfavorable products that deteriorate the mechanical properties of the composites. The advantages of electro-deposition are that it can produce nano-grained materials with full density and homogeneous distribution of graphene into the matrix, although it is not possible to produce large-scale bulky specimens due to the slow processing speed, and it is also not possible to precisely control the fraction of graphene and metals [20,21]. Powder metallurgy has frequently been employed because it enables the uniform distribution of graphene into the metal matrix though a repeated procedure of cold welding, fracturing, and re-welding. However, with an increase in the graphene content, graphene has a tendency to agglomerate in the metal matrix, indicating that it can only be uniformly distributed when a low content is added. Furthermore, graphene can be easily destroyed because of the high impact generated during the mechanical milling process. Graphene can be uniformly dispersed in wet processes and has a tight ionic or hydrogen bonding with metals, and therefore to secure a tight interface between graphene and metals, in addition to a uniform dispersion of graphene, a number of researchers have used chemical synthesis methods [17–19]. However, chemical synthesis method has several disadvantages, such as high process costs, difficulties in mass production, and a lack of precise control in the composition of composites.

Therefore, in spite of the large number of studies undertaken, the effects of the various processing routes have not been well determined. To further investigations, in this study we produce Cu matrix composites containing few-layered graphene (Cu/FLG) using two different processing methods, chemical synthesis and powder metallurgy, and then compare the effect of the processing routes on the mechanical/thermal behaviors of the composites.

2. Experimental

2.1. Fabrication of Cu/FLG composites

The Cu-based composite containing few-layered graphene (Cu/FLG) was fabricated by hot pressing the Cu/FLG composite powders, which were produced via two different approaches of solution and mechanical processes, as illustrated in Fig. 1. Pure copper powder (99.9% purity, 180 μm diameter, Kojundo Korea Co. Ltd., Japan) and graphite (99.5% purity, 5–10 μm diameter, 1–20 nm thickness, XG Sciences Inc., USA) were used as starting materials.

In the solution process (S.P.), 30 mg of graphite and 10 mg of sodium dodecyl sulfate (SDS, Sigma-Aldrich Korea, Korea) were dispersed into 50 mL of distilled water with sonication for 1 h. The FLG suspension was then dried in an oven (natural convection oven ON-01E, Jeio Tech Co., Ltd., Korea) at 110 °C for 10 h. In the next step, 40 mg of FLG powder was dispersed into 20 mL of absolute ethanol with sonication for 1 h, and then 1.5 g of copper (II) acetate monohydrate powder ($Cu(OAc)_2{\cdot}H_2O$, Daejung Chemical Co., Korea) was added to the FLG suspension, which was then dispersed by sonication for 1 h. The FLG/$Cu(OAc)_2$ solution was dried in an oven at 80 °C for 4 h, and the dried powder was then calcinated at 300 °C for 3 h under vacuum to precipitate Cu_2O and Cu on the FLG. The obtained FLG/Cu_2O/Cu powder was ball-milled with pure Cu powder, using a planetary mill (Pulverisette 5, FRITSCH Inc., Germany), to disperse the FLG/Cu_2O/Cu into the Cu powder. The Cu powder and FLG/Cu_2O/Cu powder (0, 0.2 and 0.5 vol.%) were put into a stainless steel chamber (500 mL) with 5 mm diameter stainless steel balls at a powder-to-ball weight ratio of 1:15. Furthermore, stearic acid (1 wt.%) was added as a processing control agent to prevent excessive cold welding among the powders. The milling cycle consisted of a 1-h-pause subsequent to 1-h-milling at 200 rpm, and was repeated 24 times in Ar. This solution-processed composite powder was then referred to as S.P. Cu/FLG.

In the mechanical process (M.P.), an attrition mill (KMC-2BV, KMC Inc., Korea) was used for dispersing graphite into the Cu powder. A stainless chamber was then charged with Cu, graphite (0, 0.2 and 0.5 vol.%), stearic acid powders (1 g), and 5-mm-diameter stainless steel balls at a powder-to-ball weight ratio of 1:15. Following this, the attrition mill was operated at 600 rpm milling speed for 6 h in Ar. The mechanical-processed composite powder was then referred to as M.P. Cu/FLG.

After conducting the ball milling process, the stearic acid was removed by heat-treatment of the composite powder at 500 °C for 20 min in vacuum. Finally, the powder was hot-pressed at 500 °C for 1 h under a pressure of ~255 MPa to produce a composite pellet.

2.2. Characterization

Powder morphology was observed using a scanning electron microscope (SEM, JEM-7610F, JEOL Ltd., Japan), where the powder was coated with Pt to improve the image quality during SEM analysis. The crystal structure of the powder and composite pellet was examined by X-ray diffraction (XRD, CN2301, Rigaku, Japan) analysis with a Cu radiation source ($\lambda = 0.15405$ nm) at a scan speed of 2°/min. The microstructures of the hot-pressed samples were analyzed using transmission electron microscopy (TEM, JEM-2100F, JEOL Ltd., Japan). The grain size distributions of the hot-pressed samples were determined by the linear intercept method based on TEM images. In addition, the structure of graphite and FLG was investigated by Raman spectroscopy (Raman, LabRam HR, HORIBA Jobin Yvon Co. Ltd., France). The spectra were collected under ambient conditions using the 532 nm line of an argon-ion laser at 0.5 mW power. The compressive test was conducted using a universal testing machine (UTM, RB Model 301 Unitec TTm, R&B Inc., Korea) with a constant strain rate of $1 \times 10^{-4}\,s^{-1}$. A rectangular specimen with a width–length–height ratio of 1:1:1.5 was prepared by cutting and mechanical polishing of the Cu/FLG composite pellet. In addition, the coefficient of thermal expansion (CTE) of Cu/FLG composites were measured using a thermo mechanical analyzer (TMA, TMA-Q400, TA instruments Co., Ltd, USA) at a heating rate of 5 °C/min from 25 to 200 °C.

3. Results

Fig. 2 shows the morphology of (a) FLG/Cu_2O/Cu, (b) S.P. Cu/FLG 0.5 vol.%, (c) graphite, and (d) M.P. Cu/FLG 0.5 vol.% powders. The graphite were exfoliated during repeated sonication and were then covered by the flower-like Cu_2O and Cu particles (with diameters of 200–400 nm) after calcination in vacuum, as shown in Fig. 2 (a). These particles were formed by agglomeration of smaller particles with sizes of ~20 nm (see inset of Fig. 2 (a)). During the solution process, Cu ions tended to nucleate at the defects or functional groups of the FLG, and they aggregated to lower the surface energy [16]. Fig. 2 (b) shows the morphology of S.P. Cu/FLG 0.5 vol.%. The Cu powder was significantly refined (from ~180 to ~2 μm in average diameter) and flattened by severe plastic deformation during the planetary milling. The FLG were also shattered and embedded inside the Cu powder in relation to strong shear stress applied during milling. However, during the mechanical process (attrition milling process), the initially agglomerated graphite (shown in Fig. 2 (c)) also became fragmented and embedded inside the flattened Cu powder, as shown in Fig. 2 (d). This is considered to occur because both Cu powder and graphite were subjected to significant impact energy by the balls during attrition milling.