Journal of Alloys and Compounds 737 (2018) 21–30

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Study on microstructure and thermal properties of a CNF/Cu nanocomposite fabricated using chemical mixing

Ari Shin [a], Yong-In Kim [b], Se-Hyun Ko [b], Jun Hyun Han [a, *]

[a] Department of Materials Science and Engineering, Chungnam National University, Daejeon 305-764, Republic of Korea
[b] Advanced Process and Materials R&BD Group, Korea Institute of Industrial Technology, Incheon 404-254, Republic of Korea

ARTICLE INFO

Article history:
Received 30 September 2017
Received in revised form
30 November 2017
Accepted 4 December 2017
Available online 7 December 2017

Keywords:
CNF/Cu composite
Microstructure
Thermal analysis
Electroless plating
Chemical mixing

ABSTRACT

The microstructure and thermal properties of a carbon nanofiber reinforced copper matrix (CNF/Cu) nanocomposite processed by chemical mixing, with an electroless plated copper coating on the CNFs, were analyzed in depth and compared with those of nanocomposites processed by conventional mechanical powder mixing and wet powder mixing. The electroless copper plating on the surfaces of the individual CNFs enabled them to become embedded inside copper particles, which successfully solved the non-uniform dispersion of CNFs in Cu matrix, the most important problem in CNF/Cu nanocomposite manufacturing. The CNF/Cu nanocomposite prepared by chemical mixing had well dispersed CNFs, no pores, and no intermediate phase which can be a cause of thermal resistance. Its thermal conductivity was accordingly much higher (435 W/mK) than the nanocomposites processed by mechanical powder mixing and wet powder mixing, as well as the theoretical thermal conductivity of copper (398 W/mK).

1. Introduction

As microelectronic devices continue to evolve toward further miniaturization and higher component density, the power the compact devices consume has been significantly increasing. Since most of that power is converted to heat, efficient dissipation of the heat generated in the compact devices during operation has become an important issue, which affects their reliability and lifetime. Heat dissipation can be achieved by employing a heat sink made of thermally conductive materials. Metals such as aluminum and copper have been widely used as heat management materials in many electronic systems. In particular, copper, which has a higher thermal conductivity and a lower coefficient of thermal expansion (CTE) than aluminum, is an excellent material for a heat sink or heat spreader [1,2]. However, typically there is a large difference in CTE between the ceramic substrate of the devices and the copper heat sink, and this mismatch results in thermal stress which can lead to the thermal failure of solder joints or the ceramic substrate. In addition, the thermal stress can produce local gaps in the contact plane between the heat sink and the ceramic substrate, which hinders effective heat dissipation. To address these problems, it is necessary to design novel heat dissipation materials which have a high thermal conductivity, comparable to that of copper, and a low CTE, comparable to the CTE of ceramics [3].

In efforts to fabricate advanced materials having low CTE and high thermal conductivity, many investigations have focused on metal matrix composites such as SiC/Al [4–6] and W/Cu [7,8]. While these developed composites have been shown to reduce the difference in CTE between the ceramic substrate and composite heat sink, the thermal conductivities of the composites are generally reduced as the amount of reinforcement materials in the composites is increased [9,10]. In recent studies, copper composite materials reinforced with carbonaceous nanomaterials such as carbon nanofibers (CNFs), carbon nanotubes (CNTs), and graphene have appeared to be promising candidates as heat management materials, due to the high thermal conductivities and very low CTEs of the carbonaceous nanomaterials [9,11–16]. However, the addition of carbonaceous nanomaterials also causes a significant decrease in the thermal conductivity of the composites, which is largely due to the difficulty of achieving homogeneous dispersion of the nanomaterials. Therefore, developing C/Cu composites which have a low CTE without degrading their thermal conductivity has been a very important goal [17].

In general, metal matrix composites have been fabricated using liquid metallurgy and powder metallurgy. Liquid metallurgy processes such as liquid infiltration or melt stirring have a number of

---

[*] Corresponding author.
E-mail address: jhhan@cnu.ac.kr (J.H. Han).

https://doi.org/10.1016/j.jallcom.2017.12.034
0925-8388/

problems, including issues with wettability, solubility, and reactivity between the copper and carbon, which make it challenging to fabricate C/Cu nanocomposites with good quality [18,19]. In contrast, with powder metallurgy processes there is no need to consider the difference in specific gravity between carbon and copper, or the wettability.

For these reasons, powder metallurgy has been widely used for fabricating C/Cu nanocomposites [20]. Chu et al. [21,22] fabricated CNT/Cu nanocomposites by mechanical powder blending using a high speed air flow. However, the nanocomposites' thermal conductivities and densities were significantly reduced, due to thermal resistance at the interface between the copper matrix and the CNT reinforcement, the presence of CNT clusters, and large porosity. The primary problems with C/Cu composites fabricated by conventional powder metallurgy are the non-homogeneous dispersion of carbon, and the absence of chemical bonding between the copper and carbon.

Cho et al. [23,24] fabricated a CNT/Cu nanocomposite using a new process known as wet powder mixing to enhance the dispersion of the CNTs in the copper matrix. In this process, acid-treated CNTs and copper powders were initially mixed in organic solvents such as ethanol or acetone. The mixed powders were dried in an oven and then solidified using spark plasma sintering (SPS). The fabricated nanocomposites exhibited a higher thermal conductivity (359 W/mK) than the copper matrix (349 W/mK). However, the increase in thermal conductivity was not practically significant (~10 W/mK) and beyond 1 vol% of CNT, the thermal conductivity was reduced.

If each of the carbonaceous nano-particles had a coating of copper on their surface, the carbonaceous nano-particles could be separated with good dispersion, and the problems with the non-homogeneous dispersion of the carbonaceous nanomaterials, large porosity, and the interfacial thermal resistance between copper and carbon could all be solved at the same time [19,25,26]. Kim et al. [27] suggested a C/Cu composite powder synthesis process, called the molecular level mixing process, which introduced copper salt onto the surface of CNTs. This process induces ionic bonding between the acid treated CNTs and copper ions, and is effective in creating a homogeneous dispersion of CNTs. However, it was found that excessive oxygen atoms originating from the functionalized CNTs acted as a thermal barrier, resulting in degradation of the thermal conductivity of the CNT/Cu composites.

Silvain et al. [28,29] coated copper onto the surfaces of CNFs using a salt decomposition process, and in the composites that were fabricated using the salt decomposition process, they obtained thermal conductivities higher than that of the copper matrix. However, the salt decomposition process is complex and requires multiple heating steps.

As reported by many researchers, therefore, the composite powder fabrication method has been considered crucial to achieving the desirable microstructure and thermal properties of C/Cu composites.

In this work, the potential of an electroless plating process for enhancing the thermal conductivity of a C/Cu composite was examined. Vapor grown carbon nanofiber (VGCNF) was chosen as a reinforcement material because CNFs can be more easily dispersed, due to their superior straightness, than CNTs [30].

In order to avoid agglomeration of the CNFs, and to effectively improve the weak interfacial bonding between the copper and CNFs [31,32], the surfaces of each CNF were acid-treated and then coated with copper atoms directly, using electroless plating. These copper plated CNFs were then used to produce CNF/Cu nanocomposite powders. (This process is hereafter called (1) chemical mixing).

The microstructure and thermal properties of the CNF/Cu nanocomposites processed by chemical mixing were subsequently analyzed, and compared with those of CNF/Cu nanocomposites fabricated by two other fabrication methods. These were (2) conventional mechanical powder mixing of the CNFs and copper powders, and (3) wet powder mixing using a dispersing agent solution.

The three types of CNF/Cu nanocomposite powders were solidified using vacuum hot-pressing with the same densification conditions. Microstructures of the fabricated CNF/Cu nanocomposites were observed using a scanning electron microscope (SEM) and transmission electron microscopy (TEM). Their thermal conductivities and CTEs were also analyzed and compared with those of the copper matrix.

2. Experimental details

2.1. Surface modification of CNF

Vapor grown carbon nanofibers (VGCNFs, Showa Denko Co. Ltd., Japan) with average diameters of 15 nm were prepared. In order to ensure clean surfaces and improve the dispersion of the CNFs, the CNFs were inserted into a 3:1 (v/v) mixture of H_2SO_4 (95%) and HNO_3 (70%) and then ultrasonicated at 323 K for 2 h. The acid-treated CNFs were washed in distilled water and filtered using a centrifugal separator and then dried in a vacuum oven at 353 K for 24 h. The dried CNFs were added to a surfactant solution of 0.06 M sodium dodecylbenzenesulfonate (NaDDBS) and ultrasonicated for 3 h with a horn dismembrator (700 W, 20 kHz) for uniform dispersion of CNFs.

2.2. Three kinds of composite powder fabrication processes

Three kinds of CNF/Cu composite powders were fabricated: (1) by chemical mixing using electroless copper plating of the CNFs (CM), (2) by conventional mechanical powder mixing (MM), and (3) by wet powder mixing (WM). The volume fraction of CNFs in the composite powders was calculated by measuring the weight gain of the composite powders fabricated by electroless plating after the addition of CNFs, and then that value was used as the fill ratio for the composite powders fabricated by the mechanical and wet powder mixings.

2.2.1. Chemical mixing using electroless plaiting

The acid- and surfactant-treated CNFs were inserted into a sensitization solution (20 g/L $SnCl_2$, 80 ml/L HCl) and stirred using ultrasonication for 30 min. The sensitized CNFs were filtered off and successively stirred in activation solutions (1 g/L $PdCl_2$, 20 ml/L HCl) for 30 min under ultrasonication. After each pre-treatment step (sensitization and activation), the CNFs were separated from the solutions and rinsed with distilled water and then filtered using a centrifugal separator. After inserting the pre-treated CNFs into a plating bath including 30 g/L $CuSO_4 \cdot 5H_2O$, 150 g/L $NaKC_4H_4O_6 \cdot 4H2O$, and 45 ml/L 36 wt% HCHO aqueous solution, a Cu layer was coated on the surfaces of the CNFs. During this process the temperature and pH were kept at 33 °C and 12.8, respectively, to ensure a uniform copper coating on the CNFs. The thickness of the copper coating layer can be controlled by plating time. After electroless plating for 5 min, CNF/Cu composite powders having 3.4 ± 0.17 vol% of CNF were prepared. The CNF/Cu nanocomposite powders were rinsed with distilled water and ethanol, and then dried in a vacuum oven.

2.2.2. Conventional mechanical powder mixing

The acid-treated CNFs were mechanically mixed with copper powders (99.9% purity, 3.25–4.75 μm in diameter, Alfa Aesar Co.