Journal of Alloys and Compounds 587 (2014) 255–259

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Thermophysical properties and microstructure of graphite flake/copper composites processed by electroless copper coating

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ARTICLE INFO

Article history:
Received 17 August 2013
Received in revised form 29 September 2013
Accepted 30 September 2013
Available online 14 October 2013

Keywords:
Metal matrix composites
Heat conduction
Microstructure
Thermal expansion

ABSTRACT

This study focuses on the fabrication of thermal management material for power electronics applications using graphite flake reinforced copper composites. The manufacturing route involved electroless plating of copper on the graphite flake and further spark plasma sintering of composite powders. The relative density of the composites with 44–71 vol.% flakes achieved up to 98%. Measured thermal conductivities and coefficients of thermal expansion of composites ranged from 455–565 $W\,m^{-1}\,K^{-1}$ and 8 to 5 ppm K^{-1}, respectively. Obtained graphite flake–copper composites exhibit excellent thermophysical properties to meet the heat dispersion and matching requirements of power electronic devices to the packaging materials.

1. Introduction

Effective thermal management in modern power electronics requires a heat sink material with high thermal conductivity (TC) and low coefficient of thermal expansion (CTE). The carbon family, which has a variety of allotropes, is the most promising materials in the area of advanced composite in terms of their excellent thermal properties [1–4]. Many investigations have been made on the diamond/metal composites family, which exhibits high performance with TC ranging from 350 $W\,m^{-1}\,K^{-1}$ to 700 $W\,m^{-1}\,K^{-1}$ [5–8]. However, the high price and the poor machinability limit their wide application. Today, with the development of more sophisticated and miniaturized electronic devices, the ease of machinability is clearly one of the most advantageous factors that may push the materials up to the commercialization state [9]. Carbon fiber/metal composites have a well machinability, while it suffers from the low TC of fiber [10–12]. Even the carbon nanotube with the TC as high as 3000 $W\,m^{-1}\,K^{-1}$ has been used as the reinforcement [13–15]. Unfortunately the result is not ideal. One of the important bottlenecks is that the carbon nanotubes perform high TC in only one direction (axial direction), as well as carbon fiber.

Recently, the high quality graphite flake (GF) with high TC in basal plane, low density and cheap price is receiving increasing attention [16]. Both binary and ternary aluminum based composites containing the GF have been investigated and show remarkable thermal properties [17,18]. Copper, with a higher TC and a lower CTE than aluminum, is an ideal matrix material for the heat sink applications. However, there are few studies on composites combined with graphite flake and copper. As we known, the wettability between Cu and graphite is poor and flakes are tended to lie on the top of each other in the fabricating process. Thus, it is difficult to fabricate dense composite with homogeneously distributed GF through infiltration method and conventional powder metallurgy process. However, it is anticipated the problem mentioned above could be overcome by coating the GF with copper, which has been successfully used in fabricating CNT/Cu composites [19,20].

In addition, the sparking plasma sintering (SPS), which is characterized by a lower sintering temperature, a higher heating rate and the application of the current, has been applied in the development of high performance metal matrix composites. In SPS process, the die and sample are heated by Joule heating from a current passing through them. During a current pulse, spark discharges are ignited in the pores, which can efficiently remove adsorbed gases and oxides from the powder particle surfaces leading to sintering enhancement.

In the present study, the GF–copper composites were fabricated using a SPS, which involves coating GF with copper, using electroless plating technique. The relative density of the composites up to 98% was achieved and GF homogeneous dispersion in composites was obtained.

2. Experimental procedure

The GF (density of 2.231 g cm^{-3}, Q-carbon Material Co., Ltd., China) was used as starting material. Fig. 1 shows the scanning electron microscopy (SEM) images of the as-received GF. The diameter of the GF ranges from 20 μm to 70 μm with the thickness of about 1 μm. It can be observed that the edges of some flakes are bent or curled.

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http://dx.doi.org/10.1016/j.jallcom.2013.09.207

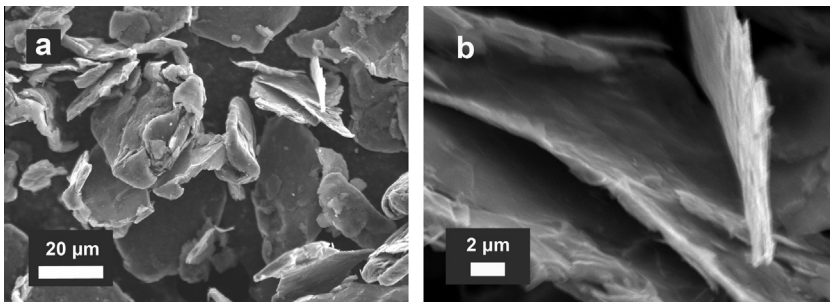

Fig. 1. SEM morphologies of as-received graphite flakes: (a) overall view and (b) high magnification.

Prior to electroless copper plating, the GFs were heat treated at 400 °C in air for 15 min to remove the surface adhesive, then ultrasonic treated in the alcoholic solution for 15 min. After this treatment, the GFs were filtered off and then stirred in sensitisation solution (30 g L^{-1} $SnCl_2$, 60 ml L^{-1} HCl) for 15 min. The sensitized GFs were filtered off, then transferred to the activation solution (0.25 g L^{-1} $PdCl_2$, 10 ml L^{-1} HCl) and stirred in the bath for 15 min. After each step, GF were filtered and rinsed in distilled water carefully. Copper was deposited on the GF in a coating bath involving 15 g L^{-1} $CuSO_4{\cdot}5H_2O$, 14.5 g L^{-1} EDTA, 14 g L^{-1} $C_4O_6H_4KNa$ and 10 ml L^{-1} 36 wt.% HCHO aqueous solution at 45 °C under pH value of 12.5–13 (adjusted using NaOH). The thickness of coating can be controlled by the amount of GF in the plating bath. Finally, after rinsed in distilled water several times and dried in vacuum drier, the coated GF was reduced under hydrogen atmosphere for 2 h at 250 °C. The final volume fraction of GF could be estimated by the weight gain of coated GF. The consolidation of the copper coated GF was as follows: the coated GF were loaded into a cylindrical graphite die with an inner diameter for 30 mm in several batches. Then, the GF–copper composites were fabricated by Spark plasma sintering (mod. 1050, Cumitomo Coal Mining Co., Ltd., Japan) with a sintering pressure of 35 MPa and a sintering temperature of 985 °C.The phases of the products were determined using an X-ray diffraction spectrometer (XRD, Rigaku RINT-2000, Japan). The observation for interface area was carried out on JEM-2100 transmission electron microscopy (TEM). The density of powder and composites was measured by TD-2200 true density analyzer (Builder Electroing Technology Co., Ltd., China). The TC of composites was calculated as product of thermal diffusivity, density and specific heat. The thermal diffusivity C_p was calculated by the following expression: $C_p = (V^f\rho^fC^f + V^m\rho^mC^m)/\rho$, where V, ρ and C were the volume content, density and specific heat of each component, and superscripts f and m stand for the properties of flake and matrix. Thermal diffusivity was measured by JR-3 thermal physical testing instrument (Changsha Yin Shen Research Instrument, China). The sample size for the thermal diffusivity measurement was 3.8 mm × 3.8 mm × 10 mm. Oxygen-free high purity copper (99.999%) with a TC of 400 W m^{-1} K^{-1} was used as reference. The CTE was measured from room temperature to 100 °C by NETZSCH DIL 402C dilatometer in temperature range 25–100 °C under argon atmosphere and the heating rate was 10 °C min^{-1}. The dimension of the specimens was 25 mm × 3 mm × 3 mm. Due to the sample size limitation, the CTE in perpendicular pressing direction (X–Y plane) was measured. Fig. 2 shows the schematic view of three-dimensional volume of the fabricated composite, indicating the direction along which a given property was measured (parallel or perpendicular to the graphite basal planes).

3. Results and discussion

3.1. Study of phase-identification and composite microstructure

Fig. 3 shows the XRD patterns of GFs as received (Fig. 3 pattern a) and the coated GF after hydrogen heat treatment (Fig. 3 pattern b), respectively. As is shown in Fig. 3, two peaks at $2\theta = 26.44°$ and 54.78° correspond to the 002 and 004 crystal planes of the graphite phase, respectively. It should be mentioned that the (002) d-spacings of the as-received GF is 3.368 Å, which compares with 3.353 Å for the single crystal graphite. The low d-spacing and narrow peaks of GF indicate that the starting material is highly graphitic with a high TC in basal plane. Adams et al. [21] reported that the thermal conductivities of carbon fibers correlate best with the graphite inter-basal-plane spacing (d_{002}). The flakes used in this work can be seen as an expanded fiber. Thus, according to the relation between the TC and spacing (d_{002}) in Ref. [21], the estimated TC of the GF is about 880 W m^{-1} K^{-1}. In the case of coated GF with the hydrogen treatment, the peaks of both graphite and copper are obtained as shown in pattern b, indicating that the copper layer is obtained after coating process.

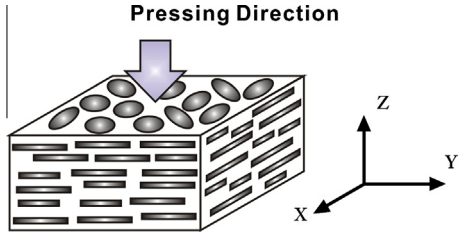

Fig. 2. The schematic view of three-dimensional volume of the fabricated composite, indicating the direction along which a given property was measured (parallel or perpendicular to the graphite basal planes).

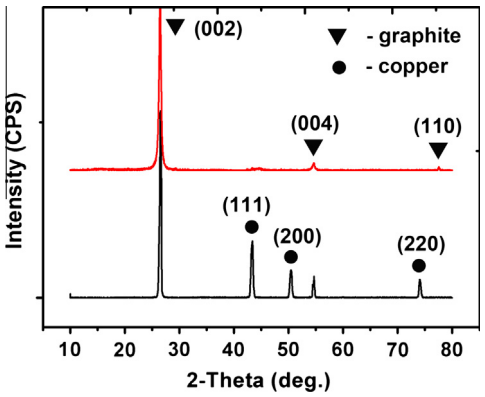

Fig. 3. XRD patterns of the (a) as-received and (b) coated graphite flakes.

The morphology of copper coated GF after hydrogen heat treatment is presented in Fig. 4. All the flakes are observed to be uniformly coated after electroless plating. The coating layer was seen to be compact and homogeneous at high magnification.

After the SPS processing, the relative densities of the final composites are up to 98.3%. Fig. 5 shows the typical microstructures of the 51 vol.% GF/Cu composite. The GFs (black gray) are uniformly dispersed in the Cu matrix (light gray) and no obvious gaps are observed as shown in Fig. 5a. Owing to the processing method, GFs are basically oriented in the plane perpendicular to the pressing direction. However, some flakes are bent or curled, particularly on the edge, which is relevant to their original morphology. Fig. 5b shows the TEM image of the interface structure of GF and copper matrix. Despite the absence of wetting between copper and graphite, the observed interface is quite continuous and no obvious gaps have been observed at nanometer resolution. The energy dispersive spectroscopy is used to analyze the elements at the interface region (position A, B and C), as shown in Fig. 5b. The regions A, B and C correspond to the Cu matrix, GF–Cu interface