Applied Thermal Engineering 73 (2014) 739–744

Contents lists available at ScienceDirect

Applied Thermal Engineering

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

Microstructure and thermal properties of copper matrix composites reinforced by chromium-coated discontinuous graphite fibers

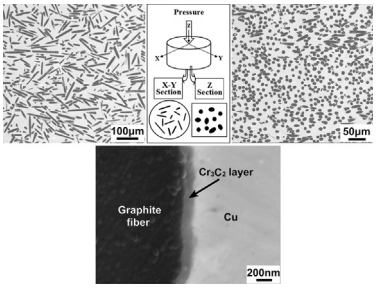
Haoming Zhang [a, b, *], Mingju Chao [a], Hongsong Zhang [b], An Tang [b], Bo Ren [b], Xinbo He [c]

[a] Key Laboratory of Materials Physics of Ministry of Education, Zhengzhou University, Zhengzhou 450001, China
[b] Department of Mechanical Engineering, Henan Institute of Engineering, Zhengzhou 450007, China
[c] School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China

HIGHLIGHTS

- Discontinuous graphite fiber/Cu composites for heat sink applications are developed.
- The Cr element is pre-coated on graphite fiber to improve interfacial bonding.
- The formed Cr_3C_2 layer helps to enhance thermal conductivity and reduce CTE.
- The composites have high thermal conductivity, low CTE and good machinability.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 14 November 2013
Accepted 17 August 2014
Available online 23 August 2014

Keywords:
Metal matrix composites
Microstructure
Heat conduction
Thermal expansion

ABSTRACT

Discontinuous mesophase pitch-based graphite fibers were coated with chromium via chemical vapor deposition technique and Cr-coated graphite fiber/Cu composites were fabricated by hot-pressing sintering. Their microstructure and thermal properties, including thermal conductivity and coefficient of thermal expansion (CTE), were investigated. Results show that the fabrication process led to the fibers with a 2-D random arrangement in Cu matrix, resulting in anisotropic thermal properties of the composites. The Cr coating reacted with graphite fiber and formed a thin and continuous Cr_3C_2 layer. This Cr_3C_2 layer established a good metallurgical interfacial bonding between the fiber and Cu matrix, which helps to enhance the thermal properties and to reduce the CTEs of the composites. The composites with 35–50 vol% content of fibers achieved the relative densities of >98%, the in-plane thermal conductivities of 380–412 W/mK and the in-plane CTEs of 6.1–9.4 $\times$ 10^{-6}/K. Due to the high thermal conductivity, low CTE and good machinability, the composites are promising materials for heat sink applications.

1. Introduction

Heat removal from ever smaller and more strongly heat dissipating electronic devices has become a serious concern in today's electronics. Materials serving as heat sinks of such electronic devices should have a high thermal conductivity to rapidly dissipate heat and a low coefficient of thermal expansion (CTE) to effectively minimize thermal stresses [1]. This is of vital importance to enhance the performance, life cycle and the reliability of electronic devices. Traditional heat sink materials like Kovar, W(Mo)–Cu or SiC/Al(Cu), which suffer of certain limitations of their relatively low thermal conductivities (no more than 250 W/mK), are no longer sufficient to fulfill the requirements of heat removal of the most recent power electronic components, such as microprocessors, LED,

* Corresponding author. Key Laboratory of Materials Physics of Ministry of Education, Zhengzhou University, Zhengzhou 450001, China. Tel.: +86 371 67767838; fax: +86 371 67767758.
E-mail address: zjpzhm@sina.com (H. Zhang).

http://dx.doi.org/10.1016/j.applthermaleng.2014.08.034
1359-4311/

laser diodes or high power [2–5]. Recent developed diamond/metal (Cu, Al or Ag) composites family, despite featuring very high thermal conductivity [6–8], has so far been limited to niche markets, due to its poor machinability and high cost [9,10].

With the advancement of graphite fiber technology, the discontinuous, milled form of mesophase pitch-based graphite fibers can offer a high thermal conductivity in excess of 900 W/mK, a negative CTE to -1.45×10^{-6}/K as well as a low price. Combining such graphite fibers with high thermal conductive copper in an appropriate way, it is expected to obtain the graphite fiber/Cu composites with high thermal conductivity, low CTE, good machinability and reasonable cost. It has been suggested that the major problem in the development of Cu matrix composites containing carbon-based fillers is the absence of chemical reaction between carbon and copper, which will lead to a weak interface and a bad transfer of properties between reinforcement and matrix [11–14]. In the present work, such milled graphite fibers are compounded with Cu powders by hot-pressing sintering. In order to improve the interfacial bonding, chromium, a carbide-forming element, is coated on the surface of these fibers through chemical vapor deposition (CVD) technique. The microstructure of the resultant Cr-coated graphite fiber/Cu composites are examined by X-ray diffraction, scanning/transmission electron microscopes, and the effects of arrangement, chromium metallization and content of the fiber on the thermal properties in terms of thermal conductivity and CTE are discussed.

2. Experimental

2.1. Raw materials

The milled form of mesophase pitch-based graphite fibers (XN100 type) used in this work was purchased from Nippon Graphite Fiber Corporation. Their basic parameters and thermal properties taken from the data sheet of the manufacturer were listed in Table 1. The Cu powders used are the gas-atomized spherical Cu powders, having a mean particle size of 14 μm and a purity >99.9%, supplied by General Research Institute for Nonferrous Metals, Beijing, China.

2.2. Chromium metallization of graphite fibers

The surface of graphite fibers were coated with chromium via CVD technique. Generally, the CVD technique is based on a chemical reaction leading to the deposition of metallic elements on the surface of target substance [15]. In this case, $CrCl_3$ powders were selected to provide chromium resource, and CrH_3 powders were chosen as reducing agent. After mixing graphite fibers with $CrCl_3$ and CrH_3 powders at a weight ratio of 100:15:4, the mixture was placed into a deposition chamber of CVD apparatus. Then, the vacuum in the chamber was pumped to a level of 1×10^{-2} Pa. The deposition temperature and time were set to 690 °C and 100 min, respectively. After deposition, the vacuum was pumped to 1×10^{-2} Pa again. Finally, the Cr-coated graphite fibers were sieved from the resulting mixture using a shaking-sieve machine. The main reaction in current CVD process can be expressed as $CrCl_3(g) + CrH_3(s) \rightarrow Cr(s) + 3HCl(g)$. With the increase of temperature, $CrCl_3$ gasified and reduced to Cr atoms by reacting with CrH_3. These generated reactive gaseous Cr atoms deposited on the surface of the graphite fibers, forming Cr coating. The average thickness of the Cr coating on the fibers is about 150 nm, which is examined by scanning electron microscopy (SEM) method. The SEM images of the as-received and Cr-coated graphite fibers are given in Fig. 1. It is seen that the Cr coating is successfully deposited on the surface of the graphite fibers forming a continuous coverage.

Table 1
Parameters and thermal properties of the as-received milled mesophase pitch-based graphite fibers.

Density (g/cm^3)	Diameter (μm)	Length (μm)	Thermal conductivity (W/mK)		CTE (10^{-6}/K)	
2.225	10	100–200	Axial 900–960	Radial 5–10	Axial −1.45	Radial 4–6

2.3. Consolidation of composites

The Cu powders with varying contents of Cr-coated graphite fibers (35, 40, 45, 50 and 55 vol%) were dry mixed at room temperature by using a 3-D vibratory mill for 8 h with rotary speed of 2500 rpm. Vacuum hot-pressing sintering system (Model Hi-Multi 5000, Fujidempa Kogyo Co. Ltd., Japan) was used to synthesize the Cr-coated graphite fiber/Cu composites. The powder mixture was compacted into a cylindrical graphite die with an inner diameter of 30 mm. A sheet of graphite felt was placed between the punch and the powders as well as between the die and the powders for easy removal. The compact powders were sintered at 940 °C under a uniaxial pressure of 35 MPa for 40 min in high vacuum (1×10^{-3} Pa). The heating/cooling rates were about 10 °C/min. After sintering, the samples with diameter about 28 mm and thickness about 12–14 mm were obtained after getting rid of the graphite felt left on the surface of the composites. For comparison purposes, a sintered copper sample and an uncoated graphite fiber (50 vol%)/Cu composite sample were also fabricated under the same conditions.

2.4. Characterization

The bulk density of the composites was measured by the water immersion method based on Archimedes' law and compared with the theoretical density. The morphology and fracture surface of the composites were observed on LEO-1450 SEM. The phases in composite were determined by X-ray diffraction (XRD) conducted on Siemens D5000 diffractometer using Cu Kα radiation. The observation for interface area was carried out on LEO JSM-7001F field emission (FE)-SEM and JEM-2100 transmission electron microscopy (TEM).

The thermal conductivity, λ, of the composites was determined from measurements of composite density, ρ, thermal diffusivity, α, and specific heat capacity, C, using the relationship $\lambda = \alpha\rho C$ [16]. Specific heat capacity was measured using differential scanning calorimetry (TA-Instruments Q100) on cylindrical discs 4 mm in diameter and 0.5 mm thick. Thermal diffusivity was measured at room temperature by a laser flash apparatus (LFA447, Netzsch, Germany) on disc-shaped specimens with a diameter of 10 mm and a thickness of 2.5 mm. In order to obtain reliable results, seven tests were performed on each specimen and the mean value was chosen for calculations throughout this paper.

The CTE of the composites was measured by a Perkin–Elmer TMA7 dilatometer in temperature range 20–250 °C at a nominal heating and cooling rate of 5 °C/min. The dimension of the specimens was 5 × 5 × 2.5 mm. To diminish systematic errors, the dilatometer was calibrated by measuring an alumina specimen under identical conditions. The reported CTE was an average value in the temperature range between 25 and 100 °C.

3. Results and discussion

3.1. Microstructure of the composites

Density measurements show a post-sintering densification of >96.5% for all prepared Cr-coated graphite fiber/Cu composites samples. Typical SEM morphologies of the composites in perpendicular and parallel to hot-pressing direction are shown in Fig. 2.