Preparation of copper–diamond composites with chromium carbide coatings on diamond particles for heat sink applications ☆

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HIGHLIGHTS

- Cr_7C_3 coatings were successfully formed on diamond particles in molten salt.
- Cr_7C_3 coatings obviously promoted the wettability of diamond and copper matrix.
- Cr_7C_3 coatings greatly enhanced thermal conductivity of Cu–diamond composites.
- The composites are suitable candidates for being heat sink applications.

ARTICLE INFO

ABSTRACT

Cr_7C_3 coatings were formed on diamond particles for improving the wettability between diamond particles and copper. The coatings were formed with a reaction medium of chromium in mixed molten salt. Copper–diamond composites with Cr_7C_3 coatings on diamond particles have been fabricated by vacuum pressure infiltration method. The microstructure of interfacial bonding between diamond and copper was discussed. Thermal conductivity and thermal expansion behavior of the obtained copper–diamond composites with various fractions of diamond particles were investigated. The as-fabricated composite exhibit a thermal conductivity of 562 W m^{-1} K^{-1} associated with coefficient of thermal expansion of 7.8 × 10^{-6} K^{-1} with a Cr_7C_3-coated diamond volume fraction of 65%. These results indicate that the obtained composites are suitable for being heat sink applications.

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1. Introduction

Thermal considerations in power electronic devices have become extremely important with the continuing miniaturization and integration of microelectronics, requiring ever more efficient heat dissipation. Metal matrix composites (MMCs) offer the possibility to tailor the properties of a metal by adding an appropriate reinforcement phase and to meet the demand for thermal management. The ideal thermal management materials working as heat sink applications should have thermal conductivity above 300 W m^{-1} K^{-1} with a low and tailorable coefficient of thermal expansion (CTE) of 4–9 × 10^{-6} K^{-1} for future electronic component, such as microprocessors, LED, laser diodes or high power [1,2]. Traditional heat sink materials such as Mo/Cu, W/Cu, SiC/Al or SiC/Cu, however, despite featuring matched CTEs, have thermal conductivities lower than 300 W m^{-1} K^{-1}.

Diamond has the highest thermal conductivity in nature, ~2200 W m^{-1} K^{-1}, as well as an appropriate coefficient of thermal expansion (CTE) of 2.3 × 10^{-6} K^{-1}. These properties make diamond an ideal reinforcement in metal matrix composites for heat sink applications. Copper is widely used as heat-spreading material because it exhibits high thermal conductivity (400 W m^{-1} K^{-1}). However, it presents a large CTE (17.0 × 10^{-6} K^{-1}) which is too high as heat sink applications. Therefore, in recently, the copper matrix composites reinforced with diamond particles have been extensively investigated [3–6].

Unfortunately, copper is known to be naturally non-wetting with diamond due to chemical incompatibility, leading to weak interfacial bonding and high thermal resistance. The interface plays a crucial role in determining thermal conductivity and CTE of copper/diamond composites [7–9]. At present, the ways to improve the interfacial bonding include metal matrix alloying and modification of diamond particles. The addition of Zr to copper matrix has a thermal conductivity of 533 W m^{-1} K^{-1} in Cu–Zr/diamond composites [10]. Zhang et al. [9] have reported a thermal

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conductivity of 493 W m^{-1} K^{-1} using Ti-coated diamond particles to reinforce copper matrix.

The present study focuses on copper matrix composites reinforced with Cr$_7$C$_3$-coated diamond particles, and the composites are fabricated by vacuum pressure infiltration method. The Cr$_7$C$_3$ coatings were successfully synthesized on diamond particles surfaces using molten salt method for the first time. It is revealed that the Cr$_7$C$_3$ coatings on diamond particles have good wettability with copper, and metallurgical interfacial bonding was formed to decrease the interfacial thermal resistance of composites. The intrinsic contribution of the Cr$_7$C$_3$ coatings to enhance the thermal conductivity of copper–diamond composites has been discussed. Microstructure, interfaces, thermal conductivity and thermal expansion behavior of the obtained composites were further investigated.

2. Experimental

The infiltrated oxygen free copper with purity more than 99.99% was used as matrix. Diamond particles used in this study are synthetic MBD8 grade diamond with nitrogen content of 230 ppm, purchased from Polaris Diamond Powder Co. Ltd., China. The thermal conductivity is estimated to be about 1500 W m^{-1} K^{-1} according to the level of nitrogen content. The diamond particles are faceted with hexagonal or octahedral shapes and diameters around 70 μm (Fig. 1(a)). The chromium powders of ∼30 μm with purity more than 99.8% were used as coating materials (Fig. 1(b)). The chromium carbide coatings were synthesized on diamond particles surfaces using the molten salt method. Diamond particles and chromium powders were mixed uniformly with molar ratio of 10:1 and then embedded in an alumina crucible with a mixture of chloride salt (mol ratio of NaCl:KCl = 1:1), heat-treated at 900 °C for 60 min in a tube furnace under high purity argon atmosphere and then cooled to room temperature. The processed powders were separated by ultrasonic wave with boiling distill water, and then the coated diamond particles were dried in the vacuum drying oven at 120 °C for 60 min.

The diamond porous preforms used for the fabrication of copper–diamond composites were prepared by two-step procedure: that is, pressing the mixture of coated diamond particles with various fractions (50–70 vol.%) and organic binder into a cylindrical mold; then degreasing the binder in high purity hydrogen atmosphere at 400 °C for 1 h. Copper–diamond composites with chromium carbide coating on diamond particles were fabricated by vacuum pressure infiltration. The diamond preform and copper were positioned in graphite die, and then heated at 1150 °C for 10 min. After that, a pressure of 20 MPa was applied to infiltrate the molten copper into the diamond preform for 5 min. The heating was switched off and the system was cooled down in the furnace. The copper–diamond composites with uncoated diamond particles were also fabricated for comparison.

The phase structures and microstructure of coated diamond particles were characterized by Siemens D5000 X-ray diffraction (XRD) using Cu radiation and LEO1450 scanning electron microscopy (SEM). The interface area on the composites fracture surfaces and energy disperse spectroscopy (EDS) element line scanning across the interface was characterized by ZEISS ULTRA 55 SEM. The bulk densities of the composites were measured using Archimedes' method and compared with the theoretical densities. The theoretical density (ρ_t) of Cu–diamond (carbide-coated) was calculated using the rule of mixture:

$$\rho_t = \rho_d \cdot V_d + \rho_i \cdot V_i + \rho_m \cdot V_m \tag{1}$$

where ρ is density, and V is volume fraction. The subscript "d", "i" and "m" refer to diamond, interfacial coating and copper matrix, respectively. Samples were machined by laser processing. The specific heat capacity was derived from the theoretical value calculated by rule of mixture:

a) Composites with uncoated diamonds

$$C_c = \frac{C_d \cdot V_d \cdot \rho_d + C_m \cdot V_m \cdot \rho_m}{\rho_c} \tag{2}$$

b) Composites with carbide-coated diamonds

$$C_c = \frac{C_d \cdot V_d \cdot \rho_d + C_i \cdot V_i \cdot \rho_i + C_m \cdot V_m \cdot \rho_m}{\rho_c} \tag{3}$$

where C is specific heat capacity. The subscript "c" refers to composite.

Thermal diffusivity (α) of the sample (sample size: Φ10 mm × 3 mm) was measured by Netzsch LFA427 Laser Flash machine at room temperature. Thermal conductivity, λ, was calculated from thermal diffusivity measurement using the following formula:

$$\lambda_c = \alpha \cdot C_c \cdot \rho_c \tag{4}$$

The CTEs of composites were measured by a dilatometer (DIL 402 C NETZSCH, sample size: 3 mm × 4 mm × 25 mm), and the device was calibrated using an alumina sample. The test temperature ranged from 25 to 100 °C at a heating rate of 3 °C/min. The CTE was evaluated according to the relationship of CTE = $\Delta l/(l\Delta T)$, where Δl, l and ΔT are the thermal expansion displacement, the original dimension of sample, and the temperature change, respectively. The uncertainty in the thermal measurements was ±5%.
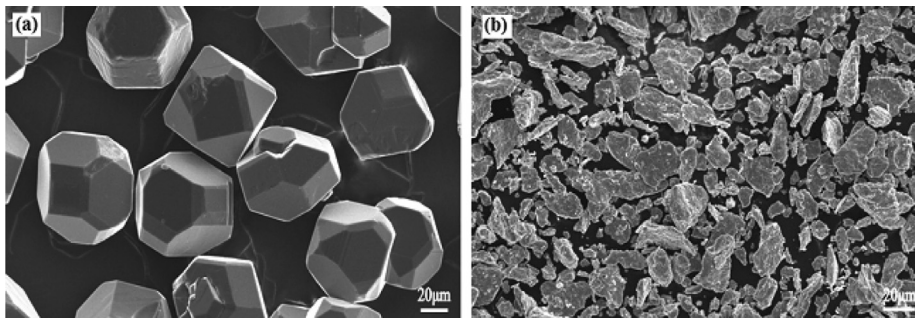

Fig. 1. SEM images of (a) the diamond particles and (b) the chromium powders.