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Microstructure and thermal behavior of diamond/Cu composites: Effects of surface modification

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ABSTRACT

Copper matrix composites reinforced with dual-metal-layer coated diamond particles were prepared via hot-press sintering. The effects of W-Ni and W-Cu coatings on the microstructure and thermo-physical properties of the composites were analyzed. The thermal behavior of the composites was simulated using finite element models based on the experimental microstructure images. The results show that the dual-layer coatings not only favor the densification of the composites but also benefit the formation of excellent interfacial bonding. The thermal conductivity of the composites reinforced with 45 vol% W-Cu and W-Ni coated diamond particles reaches 661 and 563 W/mK, respectively. The simulation of the thermal behavior of the composites with dual-layer coatings shows that a temperature drop occurs when heat flows through the boundary between the diamond and copper. The heat flux transmits from one diamond to the nearest one and forms a heat transfer channel along the direction of the temperature gradient.

1. Introduction

Nowadays, heat dissipation has become a critical issue for the reliability and efficiency of modern electronic devices. Electronic packaging materials with high performance and long-term reliability are essential owing to the requirements of high power density and miniaturization of electronic components [1,2]. Especially, in the field of aerospace engineering, the demand for high-performance materials used in micro-electronics and semiconductors has increased considerably [3]. Therefore, the electronic packaging materials with excellent thermo-physical properties incorporated into devices as heat spreaders is an effective way of addressing the heat problem [4].

For such application, diamond particles-reinforced copper matrix (diamond/Cu) composites have been promising candidate as they achieve excellent thermo-physical properties from the well combination of properties of their constituents [5,6]. In the composites, both the reinforcement and matrix have high thermal conductivity and the coefficient of thermal expansion (CTE) can vary between those of diamond and copper (1.5 to 17 $\times 10^{-6}$/K) [7]. Accordingly, the diamond/Cu composites offer extremely high thermal conductivity for efficient heat transfer as well as adjustable low CTE matching the semiconductor chips or laser diode bases [8].

It is known that the interface between the reinforcement and matrix plays a vital role in determining the performance of metal matrix composites (MMCs) [9,10]. However, the poor wetting ability between diamond and copper results in weak interface bonding in diamond/Cu composites. This weak diamond/Cu interface bonding leads to high interface thermal resistance. To prepare diamond/Cu composites with high interfacial bonding strength under conventional conditions, two widely used methods are: (i) Introduction of alloy elements into the copper matrix to promote carbide formation at the interface [11–14] and (ii) Surface modification of the diamond particles to improve the wetting ability [15,16]. Both methods have been studied widely in recent years, and the diamond/Cu composites with outstanding thermal properties have been obtained. In the alloying method, the carbide-forming elements, such as Cr [17,18], B [11], Zr [19] or Ti [20], were introduced. It was demonstrated that, with these elements alloyed into the matrix, the diamond/Cu composites with improved interface bonding were obtained [21,22]. However, it is difficult to control the amount of additives and the redundant additives in matrix will deteriorate the thermal properties of the composite.

When the surface modification is applied, the effect of coating elements such as Cr [23], Ti [24], W [25], and Mo [26] are studied widely. The research of Abyzov et al. [27] showed that when the thickness of tungsten layer on diamond was 110 nm, the composite achieved a thermal conductivity of 900 W/mK. Moreover, a chromium layer containing Cr_3C_2 was applied in the preparation of diamond/Cu composites using spark plasma sintering [28,29]. Owing to the application of B_4C

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layers with a thickness of 1 μm, the diamond/Cu composites prepared using powder metallurgy reached a thermal conductivity of 687 W/mK [30]. Therefore, the surface modification of diamond is an effective method to improve the interface bonding. However, the more economical methods to prepare the diamond/Cu composites with excellent thermal properties need to find for the engineering application.

For the overall thermal properties of MMCs, the introduction of thin layer at the interface plays a major effect. Theoretical understanding is vital to guide the design and fabrication of better composite material for thermal application. Several analytical models are effective for performing thermal analysis of diamond/Cu composites with the introduced interface layer. The Hasselman-Johnson (H-J) model is widely used because it takes the particle size, volume fraction and interfacial thermal resistance into consideration. However, without consideration of the shape of diamond and the interface structure, the simulation results always deviate from the experimental values. Finite element method (FEM) is a popular and widely used practical method for analyzing the mechanical, thermal and electromagnetic properties of materials [31]. Especially, it is used to describe the thermal properties of anisotropic composites [32]. Yang et al. [33] and Muhammad et al. [34] have successfully employed FEM models for diamond/Al and diamond/Cu composites. Thus, the FEM analysis of thermal behavior of diamond/Cu composites can help to develop a better understanding of the heat transfer mechanism in the composite and to validate the numerous models that have been proposed in literature.

In the present work, dual-layer coatings were deposited on diamond particles to improve the interface bonding and the thermal properties the diamond/Cu composites. It also aims at the development of highly property-controlled diamond/Cu composites by hot pressing method. The effects of the dual-layer coated diamond on the densification and thermal properties of the composites were analyzed. To incorporate the detailed information of the microstructure, scanning electron microscopy (SEM) images of the diamond/Cu composites were used to simulate the thermal behavior of the composites, and the effective thermal conductivity of the composites was estimated.

2. Experimental procedures

Commercial electrolytic copper powder (99.9 wt%) with an average size of 42 μm was used as the matrix, as shown in Fig. 1a. MBD6-type synthetic diamond particles with an average size of 400 μm (Henan Huanghe Whirlwind Co., Ltd. of China) were utilized as the reinforcing phase, as shown in Fig. 1b. Three types of diamonds were prepared for composite fabrication, one was the original synthetic diamond (Uncoated diamond), the others were W-Cu and W-Ni dual-layers deposited on the surface of diamond particles which were fabricated using a multi-step process. Diffusion method was applied to deposit the tungsten coating on diamond particles (diamond-W), as shown in Fig. 1c. After that, an outer copper or nickel coating was deposited on the tungsten coated diamond to form a W-Cu or W-Ni dual-layers using electroless plating method (diamond/W-Cu, diamond/W-Ni). The coating method was described in detail in the previous works [35,36]. The mass change of the diamond particles before and after coating was measured by gravimetric method, and the thicknesses of tungsten and nickel or copper coatings were then calculated based on the data of mass change. The average thickness of tungsten, copper, and nickel coating are about 420 nm, 2.8 μm, and 0.8 μm respectively.

Firstly, composite powders of UnDC-1#, NiDC-2# and CuDC-3#, as listed in Table 1, were mixed mechanically, respectively. Secondary, the mixed powders were carefully transferred into a carbide mold (ø10 mm) and compacted at first to avoid separation of the reinforcement and matrix. A pressure of 320 MPa was applied and held for 20 s, then the green compacts with relative densities of about 75% were obtained. After that, the green compacts were consolidated in a graphite mold by hot pressing at 920 °C under a pressure of 30 MPa for 2 h in nitrogen atmosphere. The hot-pressed samples were cooled in the furnace with pressure until 200 °C.

The X-ray diffraction meter (XRD) of the pre-coated diamond was recorded using a D/Max 2550 with Cu Ka radiation at a scan step of 0.08 (°) $*s^{-1}$ from 20 to 80 (°). The densities of the as-received composites were measured by the Archimedes method. The microstructures of the diamond and composites were examined by SEM (FEI SIRION 200) and energy dispersive spectrometer (EDS). The elemental distribution in the composite samples were analyzed using an electron probe micro-analyzer (EPMA, JXA-8230). The thermal diffusivities of the composites were measured using a JR-3 laser flash thermal analyzer by a heat flux technique. The thermal conductivity (λ) was calculated using $\lambda = \alpha \cdot \rho \cdot C_p$, as the product of the density (ρ), thermal diffusivity (α) and specific heat capacity (C_p), where C_p was calculated by the rule of mixture (ROM). To reduce testing errors of experimental data, three or more samples were tested. All the measured experiment value of the composite is obtained from the averages of four samples (every sample measured three times) under the same condition.

3. Finite element modelling

The FEM analysis was carried out using the commercial finite element software ANSYS. The microstructure of the diamond/Cu composites is imported via thresholding segmentation to develop a two-dimensional (2D) micro-scale model. The diamonds are assumed to be perfectly bonded to the matrix. The finite element mesh is generated from the SEM images. Additionally, an imposed temperature boundary condition in a steady-state heat transfer is defined to analyse the thermal behaviour of the composite. The thermal conductivities of the diamond, copper nickel alloy, and copper matrix were 1500 W/mK, 304 W/mK and 393 W/mK respectively. The model was analyzed to obtain the thermal flux and thermal gradients for each node. Subsequently, the heat flux components are defined using Fourier's law as follows:

$$q = -K \bigtriangledown T, \tag{1}$$

$$\bigtriangledown T = n_0 (\triangle T / h), \tag{2}$$

where q is the heat flux vector in W/m^2, K is the thermal conductivity of the composite in W/(mK), $\bigtriangledown T$ is the temperature gradient vector, $\triangle T$ is the temperature variate in K, h is the width between the two surfaces at different temperatures in m, and n_0 represents the vector.

In the FEM model, the top and bottom sides of the 2D model are remain insulated, and the right and left sides of the model are assigned constant temperature values of T and $T + \triangle T$, such that $\triangle T$ is the temperature difference across the 2D face. Under the steady-state condition, the total steady-state heat flux per unit thickness through any transverse cross-section of the model q_{ave} can be obtained via simulation. Subsequently, the effective thermal conductivity, K_{eff}, can be computed in the heat flow direction using the following equation:

$$K_{\text{eff}} = h q_{ave} / \triangle T. \tag{3}$$

4. Results and discussion

4.1. Microstructure of the pre-coated diamond

The SEM morphology of the diamond/W-Ni particles is presented in Fig. 2. Fig. 2a shows that the diamond particles still present their original shape, and the particle surface is densely and evenly covered by the nickel layers. The magnified images illustrate that the nickel coating consists of regular spherical particles of submicron size. However, some nickel particles grow faster than the others during the deposition and render the surface slightly coarser (Fig. 2b and c). Fig. 3 shows the SEM images of the diamond/W-Cu particles. The copper layer is continuously plated on the surface, as shown in Fig. 3a. Notably, in the process of plating, some copper particles grow faster to form micron-