Advanced Materials Research Vol. 59 (2009) pp 120-124
online at http://www.scientific.net

Heat Sink Materials Processing by Pulse Plasma Sintering

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Keywords: diamond composite, thermal conductivity, interface structure, pulse plasma sintering

Abstract. A Pulse Plasma Sintering (PPS) process was employed to manufacture Cu-diamond composites with a 50% volume fraction of each constituent. Pure and Cr (0.8wt.%) alloyed copper matrices were used and commercial diamond powders. The composites were sintered at temperature of 900°C for 20 min and under pressure of 60 MPa. In these sintering conditions diamond becomes thermodynamically unstable. Cu0.8Cr-diamond and Cu-diamond composites with relative densities of 99,7% and 96% respectively were obtained. The thermal conductivity of Cu0.8Cr-diamond composite is equal to 640 $W(mK)^{-1}$ whereas that of Cu-diamond is 200 $W(mK)^{-1}$. The high thermal conductivity and relative density of Cu0.8Cr-diamond composite is due to the formation of a thin chromium carbide layer at the Cu-diamond interface.

Introduction

The miniaturisation of microelectronic devices results in dense packing of the electric circuits and increased heat generation. Dissipation and management of this heat requires material solutions, as the forecasts show, that already in the present decade, the heat dissipation limits of the currently used materials will be reached [1,2]. From all known materials diamond is the one with the highest thermal conductivity. The conductivity varies, depending on the impurity level, from 1500 to 2000$W(m\cdot K)^{-1}$ [3]. However, use of pure diamond is prohibited by high cost and technical constraints. Therefore, metal matrix diamond composites are considered as candidate materials for novel heat sink management applications. For microelectronic applications this composites must also meet requirements with regard to the coefficient of thermal expansion (CTE). As the heat sink is in a direct contact with the semiconductor, large differences in the CTE could lead to large stresses at the interface and break-down of the component [4,5]. As a result, materials with CTE close to that of Si are of special interest, among them Cu-diamond composites.

Diamond particles embedded in a copper matrix feature weak interfacial bonding [6], due to the poor wetting by liquid copper. The wetting can be improved by alloying copper with a strong carbide forming element such as e.g. Ti, Cr, B or Zr [7-9]. In order to obtain high values of thermal conductivity, the carbide interlayer has to be continuous and thin.

Under the sintering temperature in the range of 900-950°C diamond is metastable and can transform into graphite. However, the graphitisation of diamond in high vacuum (low partial pressure of oxygen) up to 1400°C is slow and restricted to the particle surface. Only above this temperature, the transformation proceeds quickly and occurs in the entire volume of the particle [10-12]. Therefore, to avoid diamond graphitization during composite fabrication, methods of rapid sintering conducted at relatively low temperature and under vacuum are needed.

Modern sintering methods, such as PAS (Plasma Assisted Sintering) [13], SPS (Spark Plasma Sintering) [14-16], FAST (Field Assisted Sintering) [17,18] and PPS (Pulse Plasma Sintering) [19-

21] feature lower temperatures and short processing times. A characteristic feature of these techniques is that a pulse current is used for heating the powders. During a current pulse, spark discharges are ignited in the pores, which remove adsorbed gases and oxides from the powder particle surfaces, thereby facilitating active contacts and accelerated sintering.

The present paper reports on properties of Cu-diamond composites sintered by PPS with two different matrices: pure and Cr-alloyed copper.

Experimental procedure

In the PPS apparatus, the material is placed in a graphite die between two graphite punches, as schematically shown in Fig.1a. Pulsed high electric current discharges, heating the pressed powder, are generated by a 300 μF capacitor, charged to a voltage of a maximum 10 kV. Thanks to the short duration of the electric pulses (500 μs) compared to the inter-pulse time (0.5 - 5 s), the average temperature of the sintered material is significantly lower than the instantaneous temperature during the current flow as schematically explained in Fig.1b.

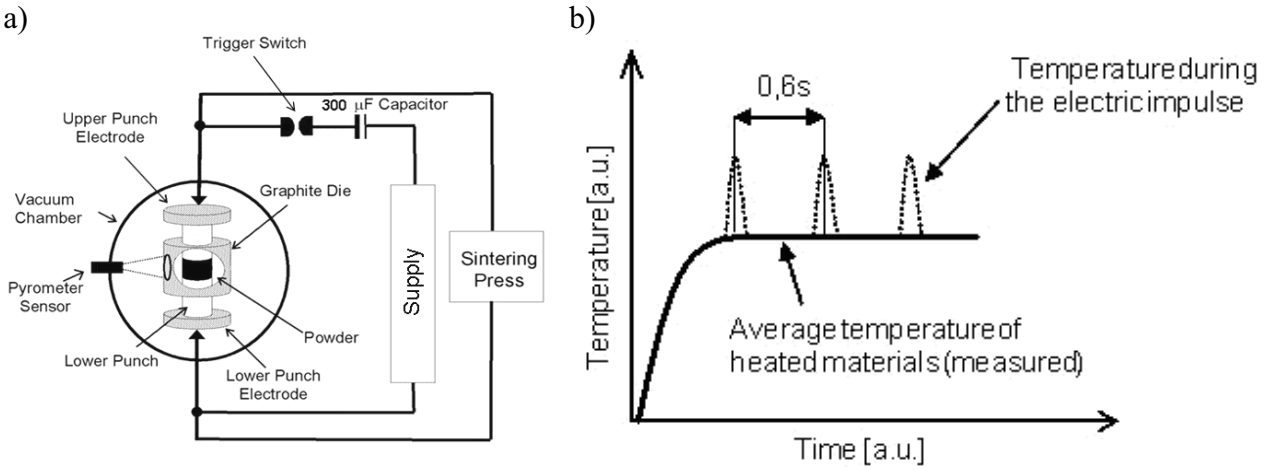

Fig.1. PPS equipment (a) and variation of the temperature during the sintering process (b)

The MBD4 type synthetic (Ib-)diamonds 70/80 from Luoyang High-Tech Qiming Superhard Materials Co. Ltd, Luoyang, Henan, China was used (see Fig.2) in our experiments. Two types of Cu powders were mixed with the diamond particles: (1) CuCr alloy with 0.8wt% chromium content and (2) electrolytic copper of technical purity (99.7%). The alloyed copper powder was prepared by gas atomisation and had an average particle size of 10-15 μm. Size of the electrolytic copper dendrites was up to 50 μm. The chromium content of the alloyed powder corresponded to the optimum required for a strong matrix/diamond bonding in CuCr/diamond composites [10]. Morphologies of powders used are shown in Fig.3. The copper and diamond powders were mixed in a horizontal blender for 100 h before sintering. The mixture was then annealed under hydrogen at 210°C for 1.5 h to reduce Cu_2O and sintered into cylindrical composite samples with 50% vol of diamond content.

In the final stage, the sample was cooled to room temperature still under a load of 60 MPa and in a vacuum of $5x10^{-2}$ Pa.

The phase composition of the sintered materials was determined with a PHILIPS PW 1140 X-ray diffractometer equipped with a PW 1050 goniometer using CoKα radiation. The microstructure and the chemical composition were examined in a HITACHI S 3500N scanning electron microscope equipped with a Noran Vantage EDS-Thermo system. The density was measured by the Archimedes method using a Gilbertini E154 balance. The thermal conductivity values were determined at Research Centre Seibersdorf in Austria by laser-flash method [22].

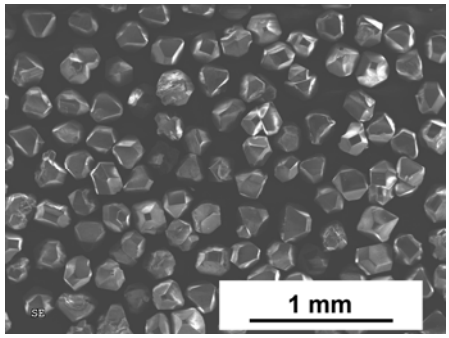

Fig.2. SEM micrograph of the used synthetic diamond powder

a) b)

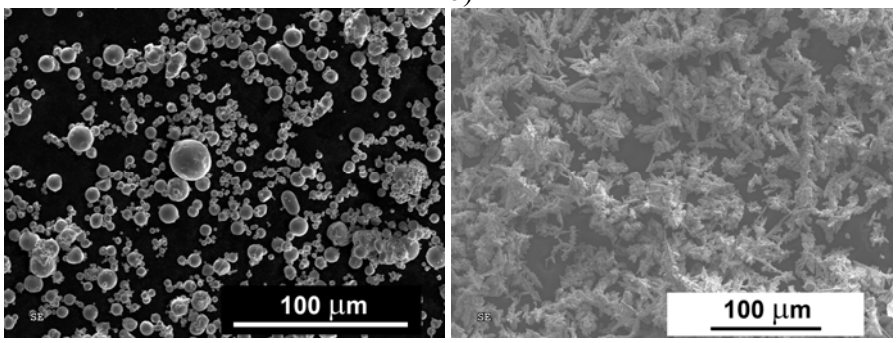

Fig.3. SEM micrographs of metal powders: a) atomized Cu0.8Cr alloy, b) electrolytic copper

Results and discussion

The phase composition studies of the Cu/diamond composite revealed only diamond and copper. Neither graphite nor any other phases were detected. The fracture surface of the Cu-diamond composite is shown in Fig.4. It can be noted that diamond particles have been detached from the copper matrix quite easily and that the fracture propagates either through diamond/copper interface or Cu matrix. The density of the obtained samples is equal to 96,9 % of the theoretical and its thermal conductivity is close to 200 W/mK. This is roughly half of the value for pure copper.

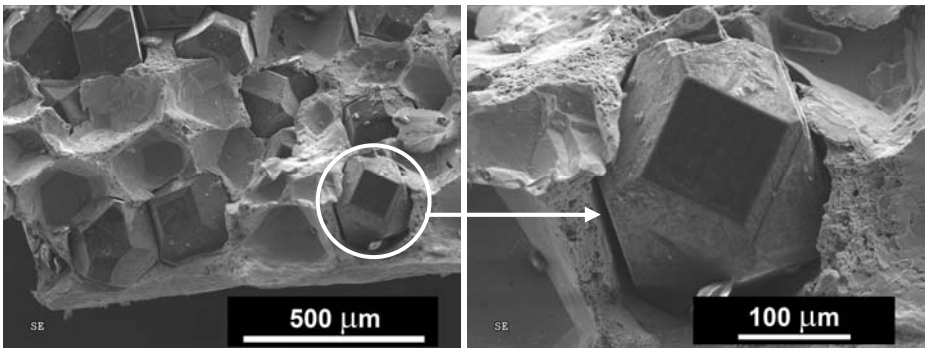

Fig.4. SEM images of the fracture surface of the Cu-diamond composite

The fracture surface of Cu0.8Cr- diamond composite is shown in Fig.5. Contrary to the fracture surface of pure copper matrix composite, delaminations at the matrix-filler interface are not observed and the interface bonding strength is good. Most of diamond particles are fractured. Only sporadically they are detached from the matrix. In the CuCr-diamond composites, the surface of diamond particles shows presence of well adhering pellets (see Fig.6).

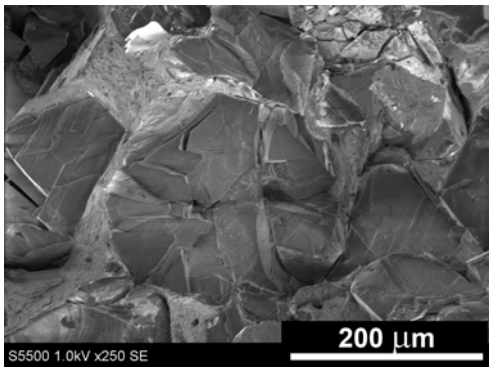

Fig.5. SEM image of the fracture surface in Cu0.8Cr-diamond composite

Chemical analysis of these pellets, performed using Energy Dispersive Spectroscope, revealed chromium. This suggests formation of chromium compounds at the interface, in particular formation of carbides. The formation of interfacial carbides in this type of materials was observed by Schubert et al. [9] who identified the carbide phase as Cr_3C_2. The density of the Cu0.8Cr-diamond composite was equal to 99.7% of the theoretical and its thermal conductivity amounted to 640W$(mK)^{-1}$.

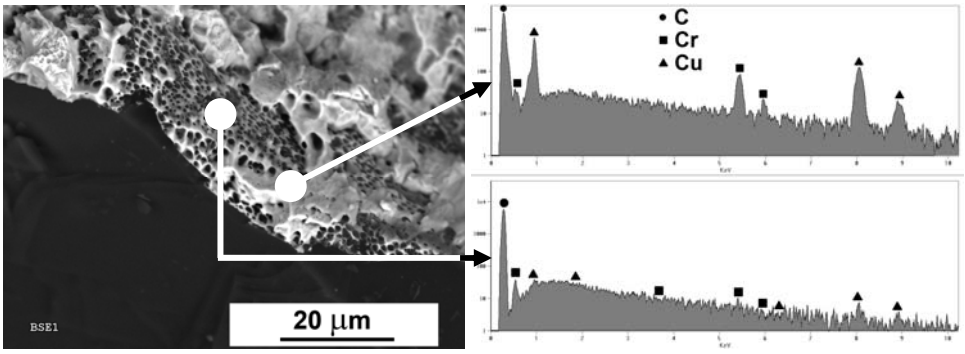

Fig.6. Pellets at the diamond particle surface

Conclusions

Pulse Plasma Sintering has been successfully used to fabricate Cu0.8Cr-diamond composites with high density (99.7% of theoretical) and thermal conductivity above 600 W/mK. The composite is characterized by uniform diamond particle distribution in the matrix and high strength bonding between the constituents. The good bonding is apparently obtained due to formation of chromium carbides at the CuCr-diamond interface. In spite of the fact that the composite is sintered at the temperature of 900°C, within the range of the thermo-dynamical instability of diamond, no graphite at the copper/diamond interface was found.

Acknowledgments

Part of this work has been performed within the framework of the Integrated European Project „ExtreMat“ (contract NMP-CT-2004-500253) with financial support by the European Community. It only reflects the view of the authors and the European Community is not liable for any use of the information contained therein.
The support by the Polish Ministry of Science and Higher Education is also acknowledged through the contract no. 506G/1090/9690/000.
Finally, the authors would like to thank the colleagues from ExtreMat consortium, especially dr. Th. Schubert from Fraunhofer Institute for Manufacturing and Advanced Materials and

dr. E. Neubauer from Austrian Research Centers GmbH for provision of primary powders and thermal conductivity measurements.

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