J Mater Sci (2011) 46:3862–3867
DOI 10.1007/s10853-011-5307-0

Fabrication and thermal conductivity of near-net-shaped diamond/copper composites by pressureless infiltration

Ying-Hu Dong · Xin-Bo He · Rafi-ud-din · Liang Xu · Xuan-Hui Qu

Received: 21 November 2010 / Accepted: 18 January 2011 / Published online: 29 January 2011

Abstract Near-net-shaped diamond/copper composites with a relative density of over 99% and thermal conductivity of over 350 $\mathrm{Wm^{-1}\,K^{-1}}$ are successfully fabricated by powder press-pressureless infiltration processing. The effects of infiltration temperature, infiltration time, interfacial thickness, and type of protective atmosphere on the thermal conductivity of the diamond/copper composites were investigated. The results showed that the diamond-copper composites with complicated shape exhibited better thermal properties, which can be widely used in electronic packaging field. It was found that the properties of diamond-copper composites infiltrated in high vacuum atmosphere were better than that of composites infiltrated in other atmospheres. The thickness of interface showed great effects on the properties of composites. The carbide interfaces were attributed to the decrease of interfacial thermal resistance and enhancement of wetting properties between the diamonds and copper.

Introduction

Diamond/metal composites can be widely used as electrical contact, wear resistant, heat management materials and machining tools [1–3] due to their high hardness, wear resistance, thermal conductivity (TC) and low coefficient of thermal expansion (CTE). Meanwhile, increase in properties and decrease in price of synthetic diamond in recent years bring the diamond/metal composites a tremendous and promising future both in researches and applications. Many researchers have done a great deal of researches on manufacturing techniques as powder metallurgy (PM), hot pressing (HP), high-temperature high-pressure (HTHP), squeeze casting, gas pressure infiltration and chemical vapor co-deposition (CVD), etc. Great efforts to mechanism and performances of diamond/metal composites were also made [4–7]. However, acting as heat managing materials, the diamond-copper composites must be further studied in order to improve the TC property and economically fabricate heat managing parts with complicated shape.

It is well known that the wettability shows great effects on the performances of composites. The wettability between liquid copper and carbon (including graphite and diamond) are very poor [8], therefore, researchers added carbonization easily form elements as Cr, B, Ti into copper to form copper alloys to enhance the wetting performance efficiently [9, 10]. In addition, because of the hard-to-work, the composites were usually prepared as simple-shape materials as cylinder, cube or slice, which can hardly meet the complicated shape requirements of electronic packaging parts. As a near-net-shape forming processing and pressureless infiltration technique, which has been widely used to form SiC/metal, Mo/metal, W/metal and AlN/metal composite parts with complicated shape, did not be applied

---

Y.-H. Dong (✉) · X.-B. He · Rafi-ud-din · L. Xu · X.-H. Qu
School of Materials Science and Engineering, University
of Science and Technology Beijing, 100083 Beijing,
People's Republic of China
e-mail: niatdyh1@163.com

Y.-H. Dong
School of Materials Science and Engineering, Nanchang
Hangkong University, 330063 Nanchang,
People's Republic of China

Rafi-ud-din
Division of Chemistry, Pakistan Institute of Nuclear Science
and Technology, P.O. Nilore, Islamabad, Pakistan

to prepare diamond/metal composites. In this study, diamond-copper composites with complicated shape were made through powder press-pressureless infiltration successfully, and the performances of composites were measured and the effects of infiltration parameters (such as infiltration time, temperature, interfacial carbides, and protect atmospheres) on TC were studied.

Experimental

The synthetic diamond (MDG400) with mean particle size of 115 μm applied in this study was supplied by Henan Famous Diamond Industrial Co., Ltd of China. The high purity copper (99.999%) was offered by GRIPM Advanced Materials Co., Ltd, Beijing, China. The Cu-11Ni-3Cr (wt%) alloys was prepared in vacuum arc melting furnace.

Firstly, diamond powders were coated by Ti or Cr using melting salt bath. Metal-coated diamond and proper binders were fully mixed and compacted into special shape preforms with sizes of $30 \times 18 \times 9\ \mathrm{mm}^3$ as shown in Fig. 1a. Then, the binders in preforms were removed by debinding of the preforms, and the porous diamond performs with porosity of 36–44 vol.% were put into infiltration furnace and covered by pure copper or copper alloys. The liquid copper was infiltrated into diamond performs at temperature of 1250–1450 °C for 30–110 min under different protect atmospheres. After being cooled, removed the redundant copper on surfaces and polished, the diamond-copper composites parts with near-net-shape were obtained (shown in Fig. 1b).

The bulk density of composites was measured according to Archimedes' principle. The microstructure was analyzed by scanning electron microscopy (SEM). Thermal diffusivity, α, was examined by laser flash technique, and the specific heat capacity, C_p, was derived from the rule of mixture:

$$C_{\mathrm{p}} = \frac{C_{\mathrm{d}} \cdot V_{\mathrm{d}} \cdot \rho_{\mathrm{d}} + C_{\mathrm{Cu}} \cdot V_{\mathrm{Cu}} \cdot \rho_{\mathrm{Cu}}}{\rho_{\mathrm{A}}} \tag{1}$$

Where C_{d} and C_{Cu} are the specific heat capacities of diamond and copper, V_{d} and V_{Cu} are the volume fractions of diamond and copper, and ρ_{A} is the density of composites. Thermal conductivity, K, was calculated from the Eq. 2:

$$K = \alpha \cdot C_{\mathrm{p}} \cdot \rho \tag{2}$$

where ρ is the density of composites.

Results and discussion

Microstructure and properties

The experimental results indicate that the wettability between Ti- or Cr-coated diamond and liquid copper, at high temperature, can be enhanced owing to the formation of carbide interfacial layer on the diamond surface (Ti or Cr can react with carbon atoms). The microstructure of the composites is shown in Fig. 2. The results display the uniform distribution of the Ti-coated diamond particles in Cu matrix exhibiting high bond strength between diamond and Cu (see Fig. 2a). On the contrary, the liquid copper can not be infiltrated into the diamond preforms without any coatings. The relative density of Ti-coated diamond/copper composites is about 96%. In order to further improve the relative density, the Cu alloys was selected in filtration which has been fabricated by the addition of 11 wt% of Ni and 3 wt% of Cr into copper by vacuum arc melting technique. The relative density of diamond/Cu-11Ni-3Cr composites reached 99.3%. Therefore, the TC of diamond/Cu-11Ni-3Cr composites was as high or a trifle higher than that of diamond/Cu composite due to its higher relative density. Figure 2b indicates that diamond particles are more uniformly distributed in the matrix and exhibits more excellent bond strength than that of Fig. 2a. A Comparison

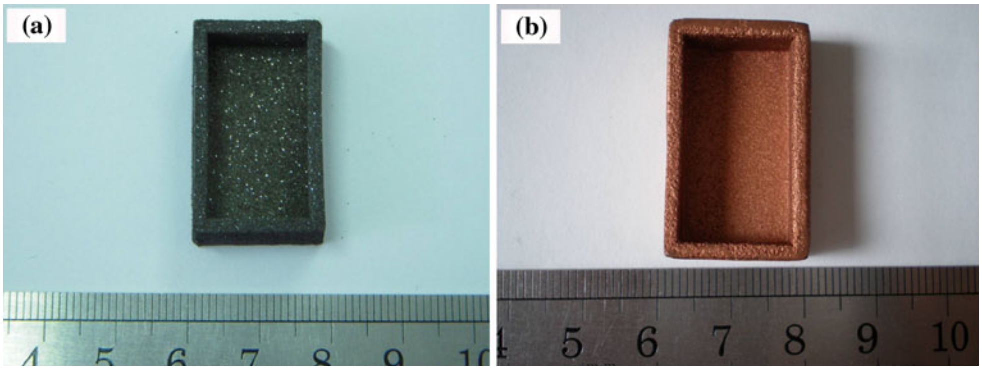

Fig. 1 Pressureless infiltration of near-net-shape diamond-copper composites: **a** porous diamond preform; **b** diamond-copper composite parts

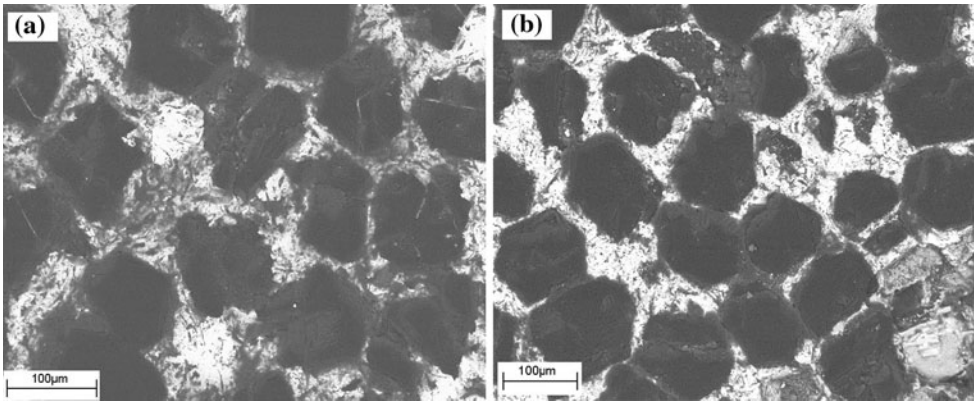

Fig. 2 SEM micrographs of diamond-copper composites: **a** diamond + pure copper; **b** diamond + Cu-11Ni-3Cr alloys

of the spreading ability of the pure Cu and Cu alloys following the pressureless infiltration reveals that the residual pure Cu piles up at one place of the surface of composites, while the residual Cu alloys spread smoothly and uniformly all over the surface of the composites. It is visible that the diamond particles are wetted efficiently by Cu alloys containing Ni and Cr as compared to the pure Cu. Furthermore, thermal conductivity of diamond/Cu (or Cu alloys) composites, manufactured by pressureless technique, is estimated to be over 350 $\mathrm{Wm^{-1}\,K^{-1}}$ which is higher than that of AlN, W/Cu, and SiC/Al composites. Therefore, the diamond/Cu (or Cu alloys) composites are more appropriate for heat sink parts in high power electronic components or integrated circuits.

Effect of infiltration temperature on thermal conductivity

The effect of infiltration temperature on TC is shown in Fig. 3. The volume fraction of diamond is about 56% and the composites (In order to investigate the influence factors on diamond/copper composites directly and credibly, this article just selected pure copper to infiltrate diamond performs.) are infiltrated for 90 min under argon atmosphere. Thermal conductivity of the Cr-coated diamond preforms enhances with an increase in the infiltration temperature and finally culminates at 1350 °C. Thermal conductivity of Ti-coated diamond preforms exhibits the similar trend but the infiltration of the preforms with copper cannot be performed below 1200 °C. Hence, it is obvious that the Cr coatings are more beneficial in ameliorating the wetting characteristics than that of the Ti coatings below 1200 °C. In addition, thermal conductivity of Ti-coated diamond–copper composites have not exhibited any inflexion in the experimental temperature range, which indicates that the mean infiltration temperature of Ti-coated diamond is higher than that of Cr-coated diamond.

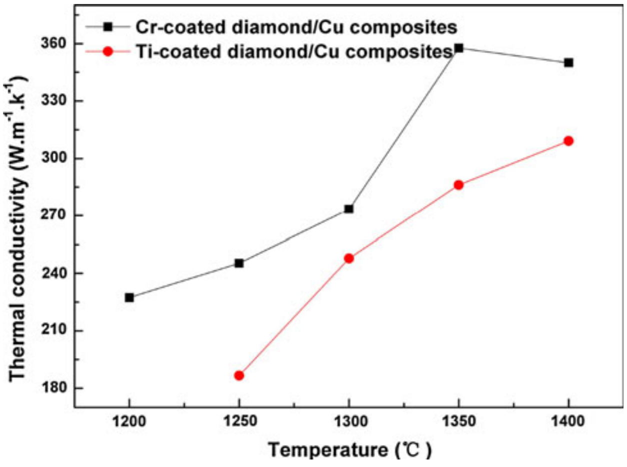

Fig. 3 Effect of temperature on TC of diamond/Cu composites

Actually, a rise in the temperature reduces in the viscosity of liquid copper. This lower viscosity facilitates the rapid compaction of the diamond preforms filled with liquid copper. In addition, the contact angle between the liquid copper and the Ti- or Cr-coated diamond depreciates with increasing temperature. This reduction in the contact angle facilitates the spreading of the liquid copper on diamond surface resulting in the reduction in the interfacial thermal resistance and eventually the enhancement in thermal conductivity of composites. However, with excessively high temperature, the density as well as thermal properties degrades owing to the various factors such as flowing out of the liquid copper from preforms, graphitization of the diamond, and hot corrosion [11, 12]. An increase in the temperature beyond 1450 °C results in the flowing out of a large quantity of copper from the Cr-coated diamond preforms leading to the reduction in its relative density and thermal conductivity down to 94.3% and 293 $\mathrm{Wm^{-1}\,K^{-1}}$, respectively.

Effect of infiltration time on thermal conductivity

Ti- and Cr-coated diamond preforms, covered with copper blocks, are infiltrated at 1350 and 1400 °C for 30–110 min under argon atmosphere. The thermal conductivity as a function of infiltration time is depicted in Fig. 4. An increase in the infiltration time results in a rapid enhancement in the thermal conductivity of the composites. However, as the infiltration time is higher than 90 min, the increment in the thermal conductivity becomes slow. An appropriate infiltration time leads to a uniform dispersion of liquid copper among diamond skeleton resulting in the amelioration of the relative density and the thermal conductivity of diamond-copper composites.

A direction correlation exists between the relative density and the porosity of materials. The effect of relative density, i.e., porosity on TC is mainly decided by pores in materials. In order to elucidate the effect of porosity on thermal conductivity, two kinds of models are adopted. Equation 3 is generally used to describe the conductivity of two phase composites [13]:

$$\lambda = \lambda_1\left(1 + \frac{\theta_2}{\frac{1-\theta_2}{3} + \frac{\lambda_1}{\lambda_2-\lambda_1}}\right) \tag{3}$$

Where λ_1 is the conductivity of continuous matrix, i.e., the first phase, λ_2 is the conductivity of isolated inclusions, i.e., the second phase, and θ_2 is the volume fraction of isolated inclusions. If pores are considered as the second phase, λ_2 becomes 0 and θ_2 is the porosity of composites. Therefore, Eq. 3 can be transformed into Eq. 4:

$$\lambda = \lambda_0\left(1 - \frac{3\theta}{2+\theta}\right) \tag{4}$$

Where λ_0 is the conductivity of materials without pores, θ is the porosity of materials.

As for the multiphase system with randomly distributed inclusions, it can be described by the following equation [13]:

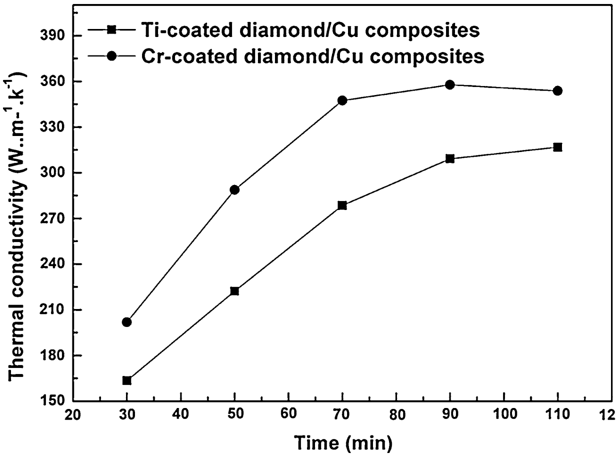

Fig. 4 Effect of infiltration time on TC of diamond/Cu composites

$$\sum_i \frac{\lambda_i - \lambda}{\lambda_i + 2\lambda}\theta_i = 0 \tag{5}$$

λ_i the conductivity of the ith phase, and θ_i is the volume fraction of the ith phase. If diamond and Cu in the composites are taken as one phase and pores as another phase, for the composite with porosity θ, the Eq. 5 can be written as:

$$\frac{\lambda_1 - \lambda}{\lambda_1 + 2\lambda}(1-\theta) + \frac{\lambda_2 - \lambda}{\lambda_2 + 2\lambda}\theta = 0 \tag{6}$$

Because the conductivity of pores, i.e., λ_2 is 0, the Eq. 6 becomes as:

$$\lambda = \lambda_0(1 - 1.5\theta) \tag{7}$$

It can be deduced from both the Eqs. 4 and 7 that the pores exhibit a great influence on the thermal conductivity of materials. A small increase in the porosity results in a dramatic decrease of TC. Therefore, the better strategy should be the elimination of the pores during the course of manufacturing composites.

Effect of thickness of interfacial layer on thermal conductivity

Three batches of diamond with various thicknesses of Cr coatings are prepared by melting salt bath. The thickness range of three batches is 2–5, 4–7, and 6–9 μm, respectively. The Cr coated diamond/copper composites are also prepared by pressureless infiltration. TCs of these composites are 357.65, 309.12, and 246.27 $\mathrm{Wm^{-1}\,K^{-1}}$, respectively. It is found that the thermal conductivity of the composites decreases with an increase in the thickness of the Cr coatings. The interfacial carbides of Cr reduce the interfacial thermal resistance resulting in an improvement in the thermal conductivity of composites. As the thermal conductivity of carbides alone is much lower than that of diamond or copper, therefore, the existence of a thick carbide layer will degrade the thermal conductivity of the composites. Therefore, the most appropriate thickness of interfacial layer should just cover the surface of the diamond.

Effect of protective atmosphere on thermal conductivity

The diamond/copper composites are prepared by pressureless infiltration under various protective atmospheres such as high vacuum, high pure (HP) argon, pure argon, HP hydrogen, pure hydrogen, HP nitrogen, and pure nitrogen. The composition of each atmosphere is listed in Table 1, and the thermal conductivities of composites are displayed in Fig. 5. The results reveal that the Ti- or Cr-coated diamond preforms can not be infiltrated by liquid copper

Table 1 Specifications of protective atmosphere

Specification	Purity (%)	Impurity concentration (ppm(v/v))							
		O_2	N_2	CO	CO_2	CH_4	H_2O	H_2	THC
High pure H_2	99.999	≤1	≤5	≤1	≤1	≤1	≤3	–	–
Pure H_2	99.99	≤5	≤60	≤5	≤5	≤10	≤30	–	–
High pure Ar	99.999	≤2	≤5	–	–	–	≤4	≤1	≤2
Pure Ar	99.99	≤10	≤70	–	–	–	≤20	≤5	≤5
High pure N_2	99.999	≤3	–	–	–	–	≤5	≤1	≤3
Pure N_2	99.99	≤50	–	–	–	–	≤20	≤10	≤20

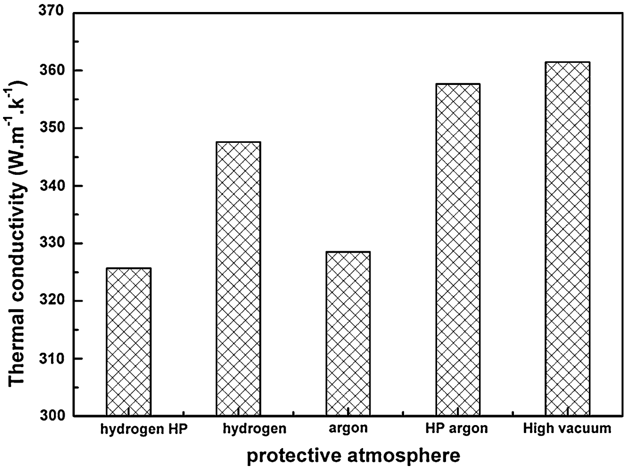

Fig. 5 Effects of protective atmosphere on the TC of diamond/Cu composites

under N_2 atmosphere owing to the reaction of Ti and Cr with N_2 as following:

$$\begin{aligned} 2Ti + N_2 &\xrightarrow{1200\,^{\circ}C} Ti_2N_2 \\ 2Cr + N_2 &\rightarrow 2CrN \end{aligned} \qquad (8)$$

The reaction products of nitrides deteriorate the wettability between diamond and liquid copper. Figure 5 indicates that thermal conductivity of composites, prepared under vacuum, is superior to those under other protective atmospheres. In addition, kinetics of infiltration reveals that the driving force for the infiltration is the pressure gradient on fluid. It has been observed that the infiltration of the porous diamond preforms under the protective atmospheres such as H_2 or Ar results in the resistance pressure and the formation of close bubbles at the end of pores. These factors prevent the liquid copper from infiltrating into the diamond preforms expeditiously and consequently deteriorate the TC of composites. It is also visible in Fig. 5 that the thermal conductivities of the composites with highly pure atmospheres are better than those of with pure atmospheres. The less pure atmospheres contain more oxo-impurities such as O_2 and H_2O. The copper and diamond may be oxidized or hot eroded at high temperatures. Therefore, the enhanced purity of protective atmosphere is quite beneficial for the improvement in the thermal conductivity of diamond/copper composites.

Conclusions

1) The pressureless infiltration of the surface modified diamond with liquid copper results in the diamond/Cu composites exhibiting thermal conductivity of over 350 Wm^{-1} K^{-1} and relative density of 99.3%.
2) The enhanced infiltration temperature and the prolonged infiltration time are conducive to the amelioration of the thermal properties of diamond/copper composites. Various conditions for the pressureless infiltration of diamond/copper composites are optimized. The optimum infiltration temperature range is 1300–1400 °C, and the appropriate time range is 90–110 min. The existence of interfacial layers such as Ti or Cr carbides can accelerate the pressureless infiltration and enhance the thermal conductivity of diamond/copper composites.
3) Ti- or Cr-coated diamond preforms can be infiltrated without pressure under various protective atmospheres such as vacuum, H_2, and Ar. The suitability of protective effect follows as vacuum>HP Ar>HP H_2> pure Ar>pure H_2.

Acknowledgements This study is financial supported by the National Nature Science Foundation of China (no. 50774005) and the Fundamental Research Funds for the Central Universities.

References

1. Yoshida K, Morigami H (2004) Microelectron Reliab 44:303
2. Ge YF, Xu JH, Yang H (2009) Wear. doi:10.1016/j.wear.2009.09.002
3. Xu XP, Tie XR, Yu YQ, Mater J (2007) Process Technol 187–188:421
4. Ekimov EA, Suetin NV, Popovich AF, Ralchenko VG (2008) Diam Relat Mater 17:838
5. Battabyal M, Beffort O, Kleiner S, Vaucher S, Rohr L (2008) Diam Relat Mater 17:1438
6. Ruch PW, Beffort O, Kleiner S, Weber L, Uggowitzer PJ (2006) Compos Sci Technol 66:2677
7. Beffort O, Vaucher S, Khalid FA (2004) Diam Relat Mater 13:1834
8. Schubert T, Ciupiński Ł, Zieliński W, Michalski A, Weißgärber T, Kiebacka B (2008) Scripta Mater 58:263
9. Weber L, Tavangar R (2007) Scripta Mater 57:988

10. De Azevedo MG, Potemkin A, Skury ALD, De Azevedo Faria RN (2001) Diam Relat Mater 10:1607
11. Uspenskaya KC, Tormashev UN, Fedoceev DV (1982) J Phys Chem 56:495 (in Russian)
12. Shaoa WZ, Ivanov VV, Zhen L, Cui YS, Wang Y (2003) Mater Lett 58:146
13. Dong YH, Zhou XL, Hua XZ (2008) Hot Work Technol 37:1 (in chinese)