Thermal Expansion Coefficient of Cr(Ti)-Diamond/Copper Composites Prepared by Pressureless Infiltration

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Abstract. Ti(Cr)-diamond/copper composites were fabricated by infiltrating liquid copper into porous diamond preforms without pressure. Thermal expansion properties were measured from 50 to 500 °C by high-precision thermomechanical analyzer. The examination results were analyzed and compared to the predictions of theoretical models. The results indicate that the CTE of Cr(Ti)-diamond/copper composites are among 2-8×10^{-6}k^{-1}, and the increase trend of CTE of Cr-diamond/copper composites is slower than that of Ti-diamond/copper composites with an increase of temperature. The Turner or German theoretical model are more suitable for designing and evaluating the CTEs of Ti(Cr)-diamond/copper composites.

Introduction

Diamond/copper composites (DCC) are attached great importance due to its excellent thermal conductivity (TC) and lower coefficient of thermal expansion (CTE)[1-3]. At present, the popular fabrication methods of DCC mainly include high temperature-high pressure (HTHP) technique[4-5], pressure infiltration[6], spark plasma sintering (SPS)[7] and composite electrodeposition[8]. Thereamong, the TC of DCC fabricated by HTHP has surpassed 900 W.m\(^{-1}\).K\(^{-1}\), and it can meet all kinds of thermal management of modern electronic devices. However, these existing fabricating techniques can only fabricate DCC with simple shape, and the most of them must assisted by extra pressure equipments with high costs. Moreover, the difficulty of machining also restricts the fabrication and application of DCC. Therefore, the novel fabricating methods must be selected to meet the requirements of high TC as well as complicated shape. In our earlier research, the near-net-shape forming and pressureless infiltration has been provided as a novel method[9,10]. In this paper, the CTEs of the composites were examined and analyzed, and the efficient theoretical mode for forecasting the CTE of DCC was also proposed.

Experimental

The diamond with mean size of 110µm is supplied by Henan Famous Diamond Industrial Co., Ltd. Ti(Cr)-coated diamond is prepared by salt-bath method. The high purity copper (99.999%) is offered by GRIPM Advanced Materials Co., Ltd, Beijing. Firstly, the Ti(Cr)-coated diamond powder were compacted into cylinder (Ø10×5mm).Thereafter, the porous diamond preforms were covered by copper blocks and put into atmosphere sintering furnace, and the molten copper was infiltrated into diamond preforms for 30-90 minutes at temperature of 1250-1450°C. The CTE were determined by DIL402PC-type thermal dilatometer.

Results and discussion

Effect of temperature on CTEs of DCC

The values of Ti(Cr)-coated DCC are indicated in Fig.1. The CTEs of Cr (Ti)-coated DCC both enhance with an increase of temperature within the measure temperature range. The mean CTEs of
the two composites are \(3.91 \times 10^{-6} \text{k}^{-1}\) and \(6.41 \times 10^{-6} \text{k}^{-1}\), respectively. They can matched with the ceramic substrates and the chip of integrated circuit well. Comparing with Ti-coated DCC, the CTEs of Cr-coated DCC are lower at the same temperature. Maybe it is because that the infiltration temperature of Cr-coated DCC is lower.

![Fig. 1 CTE of Cr-coated (a) and Ti-coated (b) DCC](image)

**Numerical results of theoretical model and comparison with experiments**

The numerical results of the CTEs of composites were calculated by Kerner Model[11,12], Mixing Rule, Turner Model[11,13] and German Model[14], respectively. The Kerner model assumes that the reinforce particles are spherical and surrounded by a uniform layer of matrix, and give a equation for calculating the CTE of composites as follow:

\[
\alpha = \frac{\alpha_c + \alpha_v V_c (\alpha_c - \alpha_v)}{1 - V_c}
\]

where \(\alpha\) is the thermal expansion, \(V\) is the volume fraction of diamond, \(\alpha\) is the coefficient of thermal expansion, \(G\) is the shear modulus, and the subscripts c, m and p refer to composite, matrix and reinforcement particles, respectively. \(\alpha\) is the thermal expansion given by rule of mixtures. \(E\) is the modulus of elasticity.

The Turner model assumes that there is homogeneous strain throughout the composite and derives the calculation equation of the thermal expansion of the composite according to a balance of internal average stresses.

\[
\alpha = \frac{\alpha_m V_m \alpha_p V_p \alpha_p}{V_m \alpha_m + V_p \alpha_p}
\]

German researched the thermal expansion of some composites, such as W-Cu, Mo-Cu, TiC-Ni, SiC-Al and AlN-Al composites fabricated by liquid sintering. The results indicate that the microstructure of liquid and solid phases appears a three-dimensional network structure. Thus they provided a novel structure of liquid/solid phase-structure, tetrakaidecahedron model[14], and deduced the follow equation for calculating the CTE of composite by liquid sintering:

\[
\alpha = \alpha_1 + \frac{(\alpha_2 - \alpha_1)}{1 + B \frac{A_1}{A_2}}
\]

where \(B\) and \(A\) can be calculated by:

\[
B = \frac{3E}{(1-2\mu)} \quad \text{and} \quad A_1 = \frac{2R}{1+(1-2R)^2} = \frac{1-2R}{\pi R^2 (1-\pi R^2)}
\]

Where \(R\) is

\[
R = 0.0113 + 1.58V_1 - 1.83V_1^2 + 1.06V_1^3
\]

and \(\mu\) is Poisson’s ratio and \(V_1\) is the volume fraction of liquid phase (which is at range of 0-0.785).

The parameters needed for theoretical calculation are listed in table 1.

<table>
<thead>
<tr>
<th>Material</th>
<th>K/GPa</th>
<th>(\rho/g.cm^{-3})</th>
<th>E/GPa</th>
<th>G/GPa</th>
<th>(\mu)</th>
<th>(\alpha/10^{-6}.\text{k}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>140</td>
<td>8.96</td>
<td>110</td>
<td>46.0</td>
<td>0.34</td>
<td>16.4</td>
</tr>
<tr>
<td>Diamond</td>
<td>443</td>
<td>3.52</td>
<td>800-925</td>
<td>-</td>
<td>0.1-0.29</td>
<td>1.7</td>
</tr>
</tbody>
</table>
From the experimental results (see the EXP. datum in Fig.2 and Fig. 3), it can be found that the values of CTE of Ti(Cr)-DCC decline with an increase of volume fraction of diamond particles. The decline of CTE of composites is attributed to the fact that the diamond possesses very low CTE. This trend also can be deduced from all theoretical calculation equations mentioned above. Fig. 2 and Fig. 3 also show the comparison between predictions given by Mixing Rule, Kerner Model, Turner Model, German Model and experimental data for the coefficient of thermal expansion of the composites with various volume fractions of diamond particles. Although different in derivation procedures, in the present cases, it is obvious that the German Model and Turner Model give the very close predictions. Mixing Rule and Kerner Model give more emphasize to the original thermal expansion properties rather than the interaction and bond condition between copper phase and diamond phase. Therefore, the predictions of CTE of composites are higher than the experimental data obviously. The result of Turner Model is more close the experimental data in consideration of the symmetrical static stress among different phases in composites during the composites being heated. As an amelioration approach based on Kerner Model and Turner Model, German Model took more influence factor into account and established a novel liquid-solid structure model, tetrakaidecahedron model, which is more suitable for the prediction of diamond/metal composites (Because the crystal structure of polycrystalline diamond selected here is dodecahedron.). However, if just compare the experimental datum to the theoretical calculation results of Turner Model and German Model, it might seem that Turner Model is fit for the prediction of Ti-DCC otherwise German Model is suitable for Cr-DCC. It is mainly because that relative densities, the distribution of diamond particles, the interfacial bonding condition (shown in Fig. 6) as well as thermal conductivity of Cr-DCC are all superior than which of Ti-DCC fabricated by pressureless infiltration method. In conclusion, as for DCC by pressureless infiltration, the German Model is the most suitable way for predicting the thermal expansion properties of composites and the Turner Model can take the second place, and the experimental datum usually distribute within these two theoretical models.

Fig. 2 measured value and theoretical predictions of CTE of Cr-coated DCC

Fig. 3 measured value and theoretical predictions of CTE of Cr-coated DCC

Fig. 4 SEM of the fracture appearance of DCC: (a) Cr-coated diamond; (b) Ti-coated diamond
Conclusions

(1) The coefficient of thermal expansion (CTE) of Ti(Cr)-DCC fabricated by pressureless infiltration technique is at range of $2-8 \times 10^{-6} \ k^{-1}$, which can be tailored freely and well matched with the semiconductor materials such as Si, gallium arsenide (GaAs) or ceramic substrates.

(2) The CTEs of Cr (Ti)-DCC both enhance with an increase of temperature within the examining temperature range. Comparing with Ti-DCC, the average values of CTEs of Cr-DCC are lower at the same temperature.

(3) The present models can give prediction of CTEs for the DCC. The German model, on the other hand, provides quite closed predictions due to establishing a novel liquid-solid phase structure which is very similar with and suitable for the structure of diamond/copper.

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