DENSIFICATION PROCESS AND PROPERTIES OF DIAMOND/SiC COMPOSITES BY PRESSURELESS VAPOUR INFILTRATION

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Diamond/silicon carbide (SiC) composites with different diamond contents were prepared by pressureless silicon (Si) vapour infiltration. The densification process of the Si infiltration of the composites was analysed. Three densification process were put forward. The densification degree of the composites was determined by the concentration of the Si vapour. The three-dimensional skeleton of the SiC composite embedded with diamond constitutes the best path for the heat conduction of composites. With an increase of diamond content, the thermal conductivity (TC) of the composites increases at first and then decreases, reaching a maximum value at a diamond 60 vol. %, with the TC of 536 W·m⁻¹·K⁻¹. In the temperature range of 50 ~ 500 °C, the thermal expansion coefficient of the composite varies from 1.0 to 3.25 ppm·K⁻¹. The bending strength of the composite reached a maximum value of 334.52 MPa. The composite has a low thermal expansion coefficient, superior thermal conductivity and bending strength, and can be used as an alternative thermal management material.

INTRODUCTION

With the rapid development of the electronics industry, electronic products have become widely used and have considerably facilitated people's daily life and work. People use electronic products more and more frequently, and their requirements and expectations for their performance are also increasing. In addition, military radar, lasers, high-power microwaves and other devices, as well as civil 5G communication, new energy vehicles and other functional units tend to be miniaturised and highly integrated, and heat dissipation has become the technical bottleneck for the further improvement of their performance. Thermal management and thermal design pay special attention to the heat dissipation performance of materials. High thermal conductivity electronic packaging materials are the key to solving the heat dissipation problem.

Diamonds have the highest thermal conductivity among naturally occurring materials. The thermal conductivity of a diamond (2000 W·m⁻¹·K⁻¹) is five times that of copper (400 W·m⁻¹·K⁻¹) at room temperature. Therefore, it is frequently used as a reinforcement to prepare composite materials. Silicon carbide (SiC) has high thermal conductivity, a low linear thermal expansion coefficient, and stable chemical properties. It can be used to manufacture heat exchangers, power electronic components and large blast furnace linings. Diamonds, as a reinforcing phase of high thermal conductivity, can be used to prepare diamond/SiC

composites, which will further improve the thermophysical properties of a composite. Besides, they are also a candidate material for semiconductor materials.

The early opinion of preparing diamond/SiC composites is to use the high-temperature and high-pressure sintering method [1-3], which aims to ensure that the diamond is not graphitised or trace graphitised. With the development of research, the subsequent preparation methods include the infiltration method, precursor conversion method [4], vacuum discharge plasma sintering method [5] and hot isostatic pressing sintering method [6, 7], etc. Among them, the infiltration method includes pressure infiltration [8, 9] and pressureless infiltration [10]. Pressureless vapour infiltration has many advantages, such as being a simple process, having a low cost, can accommodate an unlimited shape of parts, is an easy industrial production application and so on, which is favoured by researchers. Zheng Wei [11] used the silicon vapour reaction infiltration method to prepare diamond/SiC composites, and studied the thermal expansion coefficient of diamond/SiC composites. The effect of the infiltration temperature on the microstructure and properties of specimens has also been studied. Zhenliang Yang [12, 13] prepared diamond/SiC composites by pressureless silicon vapour infiltration and studied the thermophysical properties, thermal expansion behaviour and graphitisation behaviour. However, the densification mechanism of diamond/SiC composites is rarely reported upon.

In this paper, high-density diamond/SiC composites were successfully prepared by pressureless Si vapour infiltration. A fresh idea was used to explain the mechanism of the densification during the infiltration process. The dual effect of molecular motion and capillary force is the mechanism of the sample infiltration. The morphology of the SiC composite is determined by the concentration of the Si vapour. The microstructural and thermophysical properties of the diamond/SiC composites were investigated

EXPERIMENTAL

Raw materials

Single crystal diamonds (-100 mesh, average particle size of 148 µm, purchased from Henan Famous Diamond Industrial Co., Ltd, China) constitutes the skeleton of the infiltration body. The nitrogen concentration in the diamond particles measured by an American LECO ONH 863 elemental analyser was 140 ppm. According to the relationship curve between the thermal conductivity of the diamond and nitrogen concentration [14], the actual thermal conductivity of the diamond was 1738 W·m^{-1}·K^{-1}. Phenolic resin powder (purity 99.99 %, 2123#-1 type, purchased from Henan Zhengzhou Hengtong Chemical Co. Ltd., China) was used as the binder phase and one of the carbon sources for the silicon-carbon reaction. In addition, silicon powder (< 10 µm) and graphite powder (< 50 µm) were used as additives, whose purity was 99.98 %, which were purchased from Xing Rong Yuan Technology Co., Ltd., Beijing, China. The raw materials were calculated according to the volume fraction, weighed, wet-mixed and formed under 30 MPa pressure. The forming size of the blank is $\Phi = 30 \times 3$ mm^2. Composite green bodies with a diamond content of 40, 50, 60, 70 and 80 vol. % were prepared and labelled as D40-SiC, D50-SiC, D60-SiC, D70-SiC and D80-SiC, respectively. After treating the composite bodies at a high temperature of 1100 °C, the Si infiltration process could be performed. The heat treatment was carried out under high purity argon protection.

Characterisation

Pressureless Si vapour infiltration was carried out in a vacuum furnace with an ultimate vacuum of 1 Pa. In order to observe and analyse the pressureless vapour phase Si infiltration process, the Si infiltration was performed at 1650 °C. The Si infiltration time of the diamond/SiC composites was set to 30 and 60 minutes. The infiltration time of 60 minutes guaranteed the complete infiltration of the composite. Scanning electron microscopy (SEM, JEOL JSM-6510A, Japan) and a supplementary energy dispersive spectrometer (EDS) were employed to observe and analyse the microstructure, morphology, and components of the diamond/SiC composites. The

thermal conductivity of the composites (λ) is determined by the equation: $\lambda = \rho \cdot \alpha \cdot C_P$, where ρ, α, and C_P are the density, thermal diffusivity coefficient, and specific heat capacity of the composite, respectively. The ρ was determined based on Archimedes drainage method, α was measured at room temperature by a Netzsch LFA 467 HyperFlash® (sample size: $\Phi = 10 \times 2$ mm^2). The specific heat capacity (C_P) of the composites was calculated by the compound rule as $C_P = (C_D \cdot \rho_D \cdot V_D + C_{SiC} \cdot \rho_{SiC} \cdot V_{SiC} + C_{Si} \cdot \rho_{Si} \cdot V_{Si}) / \rho_t$, where V is the volume fraction of each component, ρ_t is the theoretical density of the composite calculated by the rule of mixture using $\rho_t = \rho_D \cdot V_D + \rho_{SiC} \cdot V_{SiC} + \rho_{Si} \cdot V_{Si}$. The average of three experimental values implied the final examination result. The thermal expansion coefficient was measured by a DIL 802 produced by TA Instruments (USA). The size of the samples was $25 \times 3 \times 4$ mm^3. The test temperature range was from 50 to 500 °C, and the heating rate was 5 °C·min^{-1} using high-purity nitrogen protection. The bending strength of the composite materials was measured by a microcomputer control electron universal testing machine (model: WDW-100), with a sample size of $20 \times 2 \times 3$ mm^3.

RESULTS AND DISCUSSION

Densification mechanism and microstructure

The X-ray diffraction (XRD) patterns of the high-density diamond/SiC composites prepared by pressureless vapour Si infiltration after the complicated fabrica-tion process exploration are shown in Figure 1. The yellow, black and blue lines are the standard XRD patterns for the diamond, SiC and Si phases, respectively. Through the calibration analysis, the composites consist of three phases - diamond, SiC and Si. No graphite phase peaks were found in the XRD diffraction results, indicating that the optimisation of the experimental design process is a favourable solution to the diamond graphitisation problem in the process of pressureless vapour Si infiltration.

The ideal composition of the diamond/SiC composites is expected to only contain diamond and SiC. However, it is difficult to control the amount of Si in the experiment so that it can completely react to form SiC. Therefore, the existence of free Si in the composite is unavoidable in the vapour Si infiltration preparation method. At the same time, the successful preparation of the diamond/SiC composites with a low free Si content or even without free Si residue is also the direction of our efforts in the next stage. In addition, the diffraction peaks of the diamond, SiC, and Si are sharper and the peak width is narrower, indicating that the three phases have better crystallinity, a better crystal form and a smaller particle size under the optimisation of the design process parameters.
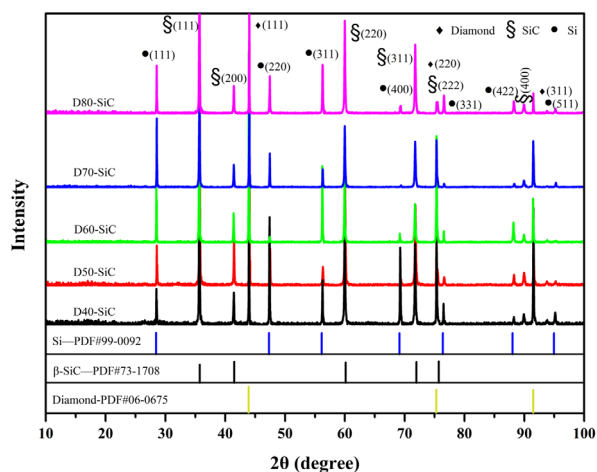
Figure 1. The XRD diffraction pattern of the diamond/SiC composites prepared by pressureless vapour Si infiltration.

of SiC was fast at first and then slow. In order to realise the densification of composites, the Si vapour will nucleate and crystallise on the surface of the SiC phase and fill the pores between the diamond particles quickly.

Pressureless Si vapour infiltration is related to Si vapour concentration distribution, silicon-carbon reaction and molecular motion, etc. The densification process of the composites is more complicated. According to the microscopic observation of the incompletely reacted composites, a new view on the densification mechanism was put forward. Figure 2 shows typical Field Emission Scanning Electron Microscope (FE-SEM) images of the diamond/SiC composite after 30 minutes of Si vapour infiltration. According to the reaction level, the Si infiltration densification of the composites can be divided into three processes: Firstly, the silicon-carbon reaction on the diamond surface; Secondly, the filling between diamond particles; Lastly, the growth and accumulation of nanowires. Red box No. 2 in Figure 2a shows the silicon-carbon reaction on the diamond surface during the Si infiltration process. Composite porous green body additives (Si, graphite and phenolic resin pyrolysis products) adhered to the diamond surface. Based on the conclusions of previous studies, the SiC-axis nanowires produced by the pyrolysis of the composite green body, on the one hand, enhance the strength of the green body, on the other hand, lay the foundation for the subsequent green body densification process [15]. During the infiltration process, the nucleation and growth of SiC grains randomly occurred on the surface of the diamond. As the silicon-carbon reaction progressed, the isolated SiC particles fused and covered the diamond surface. The SiC grains preferentially nucleated and grew on the (100) diamond crystal plane. Red box No. 1 directly shows the densification form between the diamond particles during the Si infiltration. The diffusion coefficient of the Si in the SiC is 4.2×10^{-10} cm^2·s^{-1} (1600 °C), 9.5×10^{-10} cm^2·s^{-1} (1800 °C), and the effective diffusion coefficient of the carbon in the SiC is 8.86×10^{-9} cm^2·s^{-1} (1600 °C), 2.9×10^{-7} cm^2·s^{-1} (1800 °C), it can be seen that the diffusion process is extremely slow [16]. The formation rate
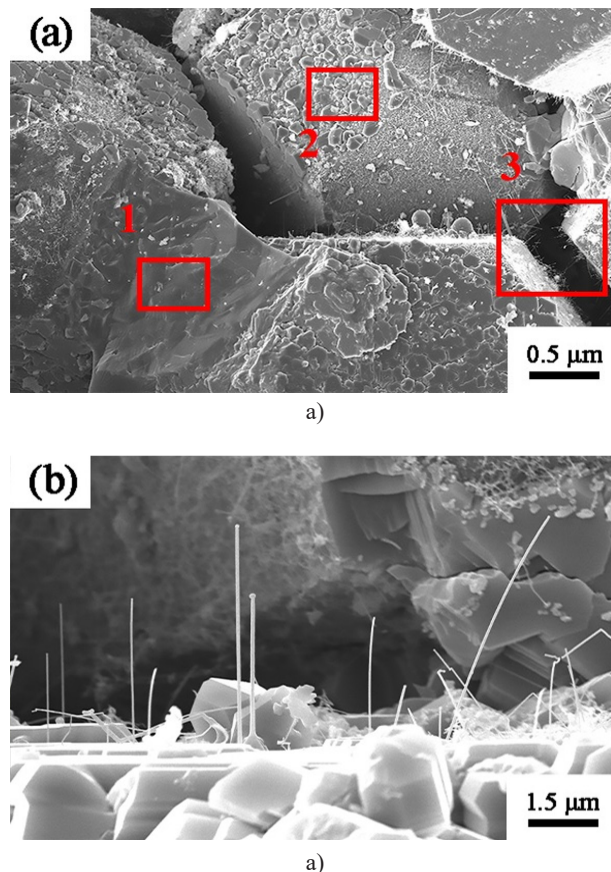
Figure 2. Typical FE-SEM images of the diamond/SiC composite after 30 minutes of Si vapour infiltration.

The infiltration densification of the vapour-phase Si depended strictly on the concentration of the Si vapour in the system. Red box No. 3 in Figure 2a shows the SiC nanowire on the diamond surface. Figure 2b is an enlarged view of the nanowire. The silicon-carbon reaction SiC on the diamond surface acts as the crystal nucleus, and the subsequent SiC is grown along the (111) crystal surface to form SiC nanowires with various scales. A different carbon to silicon ratio (molar ratio) will affect the morphology of the SiC. When the carbon-silicon ratio is relatively low, the Si vapour tends to react with the added carbon source in situ to form flaky or blocky SiC. On the contrary, when the carbon-silicon ratio is high, nanowires were generated. When the concentration of the Si vapour in the system was low, a large number of nanowires were generated on the diamond surface. If the Si vapour could be continuously replenished, the nanowires will grow, stack and fill the porous area between the diamond particles quickly.

Under the premise of sufficient Si vapour, the porous diamond green bodies can be infiltrated at 1650 °C for 60 minutes to achieve densification. The typical cross-sectional morphology of the sample after 60 minutes of Si vapour penetration is shown in Figure 3. The diamond/SiC composite achieved densification under experimental conditions (Figure 3a). The diamond shape remains relatively intact without any obvious graphitisation. The diamond on the cross section of the composite exhibits a cleavage fracture, indicating the superior bonding strength between the diamond and the SiC (Figure 3b). The diamond surface was severely corroded by the Si vapour, and pits of varying sizes occurred (Figure 3a). The appearance of the lunar-like surface (erosion pit) is caused by the different states of free carbon, the uneven distribution of the impurity defects and the difference in the uniformity of the additive coverage on the surface of the diamond grains. Figure 3c is an enlarged view of the pit region on the surface of the diamond. From the inside to the outside of the pit interface, there are diamond phases, nano-crystalline SiC phases and micro-crystalline SiC phases. Due to the existence of the Si and carbon additives, a violent reaction takes place at high temperatures to generate the SiC. The silicon carbide grains do not have time to grow and subsequently form nanocrystals. The subsequent silicon-carbon reaction needs to be completed under atomic diffusion, which provides ample time for grain growth. Consequently, a microcrystalline SiC is formed. Nano-SiC and diamonds have the same grain orientation [10]. The generation of the nano-SiC can improve the bonding strength of the interface, which we would like to see. However, nanocrystalline SiC increases the number of grain boundaries, and its effect on the thermophysical properties of the composite needs further investigation. It can be seen from Figure 3c that the diamond is tightly bound to the SiC without any obvious pores and cracks, and the diamond has no graphitisation transformation, which confirms the XRD results in Figure 1. Under the experimental conditions, there is no graphitisation phase transition in the diamond particles. Due to the reaction at a higher temperature, the thin SiC layer has limited protection, which reduces the strength of the diamond particles, and the cross-crystal fracture of the diamonds occurs in the cross-section morphology of the composite.
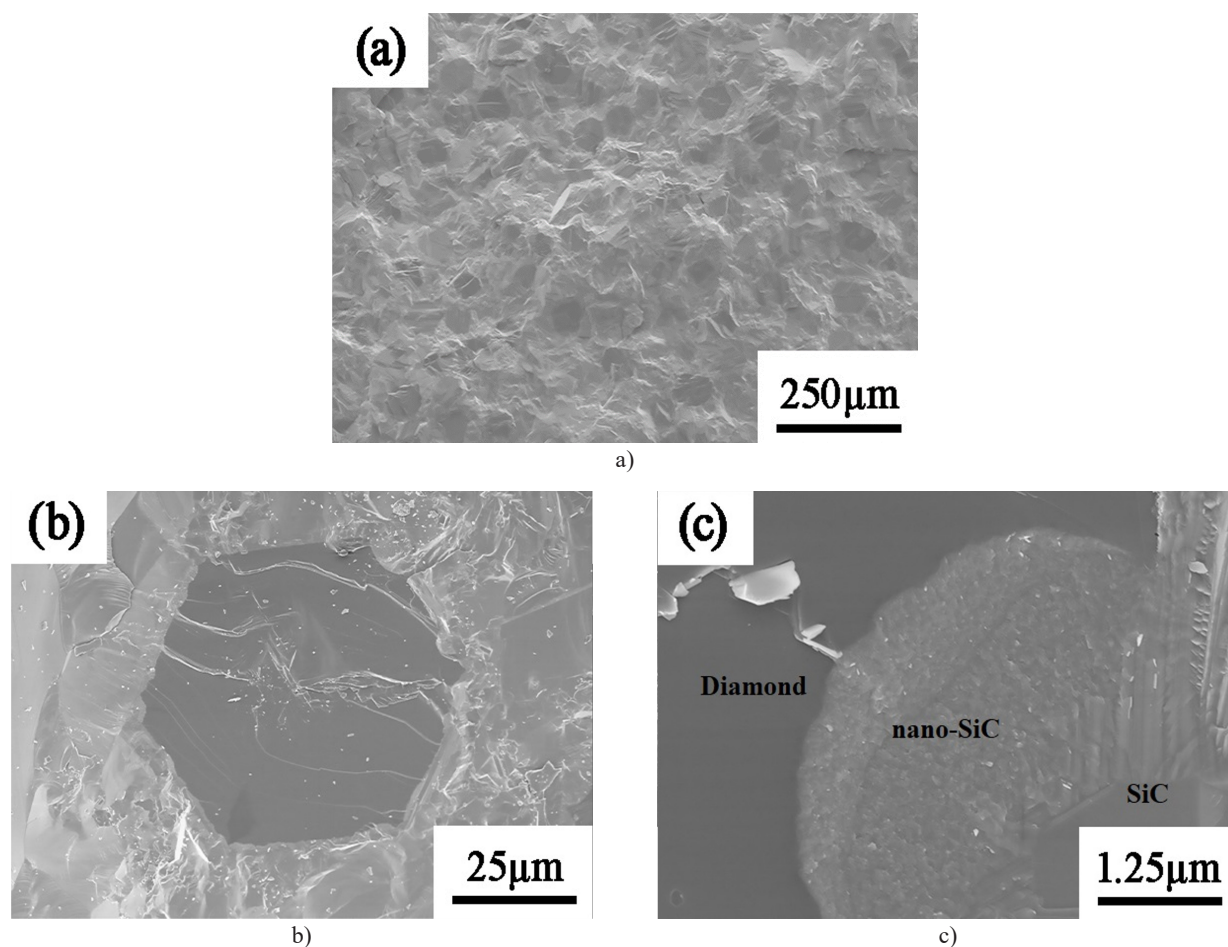

Figure 3. Typical cross-sectional morphology of the sample after 60 minutes of Si vapour infiltration.

The SiC is randomly distributed among the diamond particles. It typically presents an "island type" and "island chain type" distribution. This phenomenon was determined by the distribution of additives, such as graphite powder, Si powder and phenolic resin. In addition, the crystallisation contingency of the SiC and Si phase also plays an essential role. Figure 4 shows a typical cross-sectional SEM image and the element mappings of the diamond/SiC composite. The composite took the silicon carbide phase as the three-dimensional skeleton, where the diamond was embedded in the nodes of the skeleton, and the free Si filled the holes of the skeleton. As shown in Figure 4a, the microstructure of the composite can clearly distinguish three different phases: the diamond phase is black, the SiC phase is grey, and the rest is the free Si phase. The diamond phase and the SiC phase form the preferred three-dimensional heat conduction path. The high thermal conductivity diamond phase can improve the thermal conductivity of the SiC matrix.

Thermophysical properties

The histogram of the relationship between the thermal conductivity of the diamond/SiC composite and the diamond content is shown in Figure 5. As the diamond content increases, the thermal conducti-vity of the composites first increases and then decreases. The diamond content is less than 60 vol. % and the thermal conductivity of the composites increases at a faster rate. On the contrary, if the diamond content is greater than 60 vol. % and the thermal conductivity of the composites decreases at a slower rate. The highest thermal conductivity of the composite is 536 $W \cdot m^{-1} \cdot K^{-1}$ (60 vol. % diamond). The high rigidity of the diamonds makes the volume expansion of the high-volume fraction diamond composites bigger under the pressure of 30 MPa, and the content of the free Si in the composites increases. The free Si is harmful to the thermal conductivity of the composite. A further analysis shows that the SiC content in the composite with q high volume fraction of diamond decreases, forming an "island" distribution,
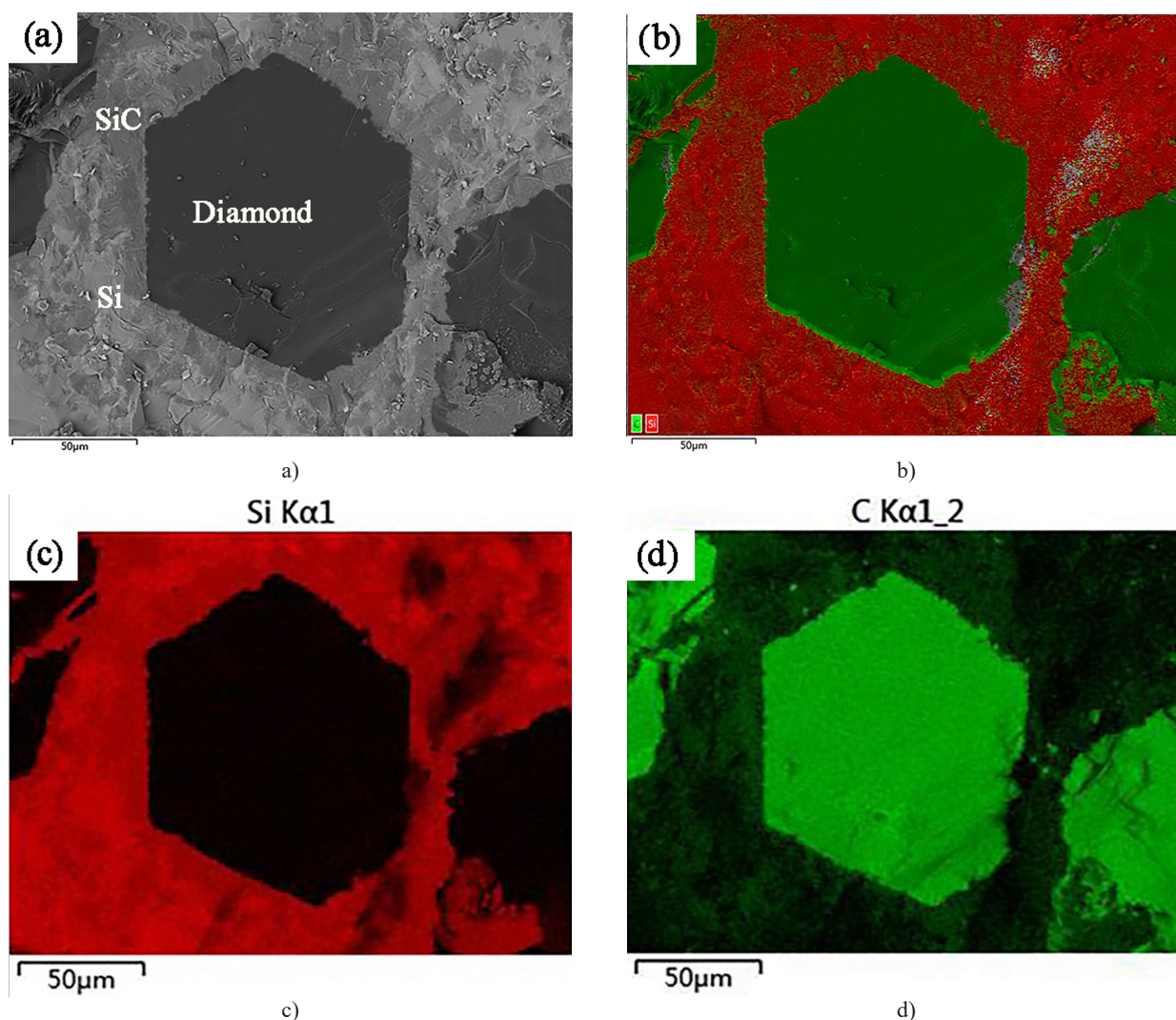

Figure 4. Typical cross-sectional SEM image and element mappings of the diamond/SiC composite.

and the optimal path of heat conduction is cut off. Therefore, the thermal conductivity of the composites with q high volume fraction of diamond decreases. As the diamond content increases, the SiC and free Si content decreases. The experimental results show that the SiC and Si content is not the less the better, only a reasonable content of the combination of the composite material (60 vol. % diamond), in the experimental diamond particle size, has the best thermal conductivity. The thermal conductivity of the diamond/SiC composites by the pressureless Si vapour infiltration is at a high level, which can meet the requirements of heat dissipation materials for electronic packaging.
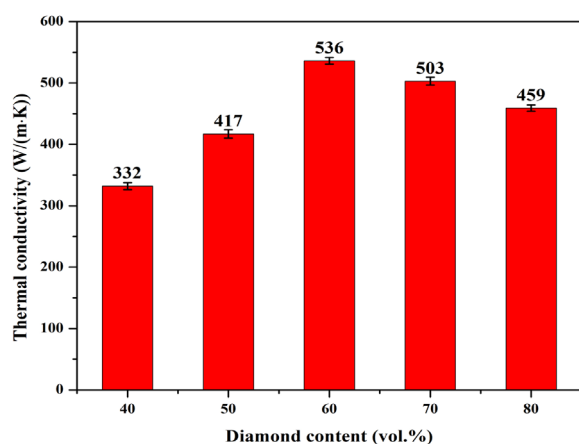

Figure 6. Curves of the thermal expansion coefficient of the composites with different diamond contents as a function of temperature.

Figure 5. Histogram of the relationship between the thermal conductivity of the diamond/SiC composites and the diamond content.

Figure 7. The relationship the bending strength of the diamond/ silicon carbide composite material and the diamond content.

Heat dissipation materials for electronic packaging must not only have excellent thermal conductivity, but must also have a certain degree of matching in the thermal expansion coefficient. The thermal expansion coefficient of a single-crystal Si is 2.5 ~ 2.6 ppm·K^{-1}, which corresponds to the area of the black parallel lines in Figure 6. The thermal expansion coefficient of SiC is 4.7 ppm·K^{-1} at 273 ~ 1273 K. As shown in Figure 6, the thermal expansion coefficient of the diamond/SiC composites increase with an increase in the temperature, and decrease gradually with an increase in the diamond content. The temperature range of the thermal expansion coefficient matching the composites and Si is 523 ~ 673 K. The higher the diamond content, the higher the applicable temperature of the composites. As a reinforcing phase, diamonds improve the thermal conductivity and reduce the thermal expansion coefficient of the matrix. Therefore, diamond/SiC composites can be used as a heat dissipation material for electronic packaging of high-power components.

Electronic circuit substrates and packaging heat-dissipative materials carry a large number of components and chips. The used materials not only
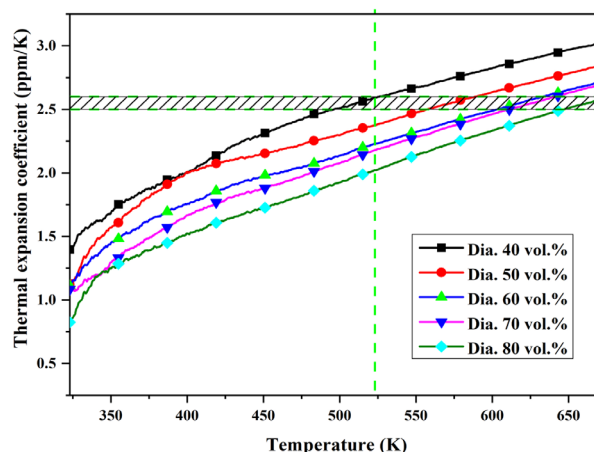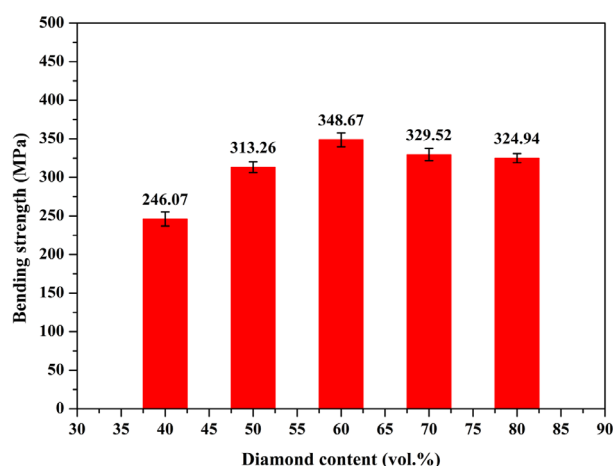
have certain heat dissipation functions, but also certain mechanical properties, in particular the bending strength. The high bending strength ensures the safe operation of the electronic circuits during transport, installation and vibration. Figure 7 shows the curve of the bending strength of the diamond/SiC composite as a function of the diamond content. The overall change in the trend of the composite bending strength is to first increase and then decrease. The maximum bending strength of the diamond/SiC composite is 348.67 MPa when the volume fraction of the diamond is 60 %.

When the volume fraction of the diamond is less than 60 %, the Si-C reaction in the densification process of the porous green body leads to the serious erosion of the diamond surface, which inevitably leads to poor interface bonding. As the diamond content increases, the amount of silicon and carbon additives with an initially high surface activity decreases. In the process of vapour phase Si infiltration, SiC nucleates, crystallises and grows along the diamond surface. The surface

SiC coating is tightly bound to the diamond, which belongs to the chemical bonding. The degree of erosion to the surface is weak, which can improve the bending strength of the composite. The SiC and free Si content in the high diamond volume fraction composites is low, and the actual diamond content reaches 70 %. In addition to the protective effect on the diamond surface, the SiC in the diamond/SiC composite extends to the free Si. The intrinsic bending strength of the Si phase is relatively low. The SiC phase and Si cross each other to form an "interlock", which has a positive effect on the bending strength of the composite. However, the erosion by the elevated temperature Si vapour and internal impurities reduces the intrinsic strength of the diamond particles, which is the main obstacle in improving the bending strength of diamond high volume fraction composites. Experimentally designed composites with 40 %, 50 %, 60 %, 70 % and 80 % diamond volume fraction have a bending strength above 200 MPa, which can meet the bending strength requirements of electronic packaging materials.

CONCLUSIONS

The densification mechanism of the diamond/SiC composites prepared by the pressureless Si vapour permeation method is still in the research stage. We think that molecular motion is the main factor affecting the densification. Three stages of the densification process of composites have been discussed: 1. The silicon-carbon reaction on the diamond surfaces; 2. Filling the pores between the diamond particles; 3. The formation and accumulation of SiC nanowires. The densification of the composites is determined by the Si vapour concentration. The SiC skeleton embedded with diamond constitutes the best three-dimensional heat transfer path. When the volume fraction of the diamond is 60 %, the thermal conductivity of the diamond/SiC composite prepared by pressureless vapour Si infiltration is 536 $W \cdot m^{-1} \cdot K^{-1}$, the thermal expansion coefficient is 1.0 ~ 3.25 $ppm \cdot K^{-1}$ (50 ~ 500 °C), and the bending strength is 334.52 MPa. The excellent thermal conductivity, high bending strength and matched thermal expansion coefficient of the composites can meet the requirements of electronic packaging heat dissipation materials.

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