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Short communication

Fabrication of diamond/SiC composites by Si-vapor vacuum reactive infiltration

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Abstract

Diamond/SiC composites were fabricated by a rapid gaseous Si vacuum reactive infiltration of porous carbon-containing diamond preforms at 1600 °C for 1 h. The obtained composites consisted of diamond, β-SiC and a small fraction of residual unreacted Si; nearly fully dense composites were achieved. Graphitization of diamond did not occur during the infiltration at 1600 °C under vacuum. The transgranular fracture mode of diamond crystals and the perfect interface between diamond and SiC suggested a strong interfacial bonding strength. Relatively-low coefficient of thermal expansion (3.6×10^{-6}/K, 50–400 °C) and high thermal conductivity (562 W/m K) of diamond/SiC composites showed great potential for thermal management applications.

Keywords: A. Powders: gas phase reaction; B. Composites; C. Thermal properties; D. SiC

1. Introduction

Miniaturization and higher functionality is becoming a major trend in power electronics packaging currently. This will unquestionably drive a more critical need for improved thermal management materials to ensure more efficient heat transfer and dissipation, so as to prevent the circuit and substrate from overheating [1]. Diamond/SiC composite is deemed one of the most potential packaging materials for high-performance electronic equipment because of its outstanding properties such as ultrahigh thermal conductivity (TC), tailorable coefficient of thermal expansion (CTE), low density, high corrosion resistance and wear resistance [2]. However, diamond is an unstable form of carbon under pressures lower than 5 GPa. Spontaneous graphitization of diamond took place at low pressure in the case of temperature exceeding 1500 °C [3]. Therefore, the most common methods for the preparation of this composite are high pressure high temperature (HPHT) sintering by infiltration of diamond crystals with melt Si [4] and HPHT sintering from a mixture of diamond and Si powders [4]. But the HPHT techniques are unsuitable for low-cost production of complex shaped composites with large dimension [5]. Owing to the excellent mechanical properties of diamond and SiC, the expense of further machining amounts to more than 50% of the production costs according to the shape, surface quality and component size of the diamond composites [6]. Therefore, a cost-effective process for preparing large size and complex shape diamond/SiC composites is urgently needed. The reactive infiltration process is confirmed to be a low-cost and highly efficient route, which is favorable for the preparation of high performance SiC-based composites with near net shape [6,7]. Because of good wettability between molten silicon and carbon [8], the liquid Si reactive infiltration process was widely used to produce SiC composites [9–11]. Gaseous Si reactive infiltration techniques were generally employed to prepare biomorphic SiC ceramics [12,13]. The reaction between Si and C is exothermic with an enthalpy of $H^0=-117.77\ \mathrm{kJ\ mol^{-1}}$

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[14]. In comparison to liquid infiltration, the reaction during the vapor infiltration is more moderate. As a result, the reactive infiltration is easier to be controlled, the microstructure of the resultant materials is more uniform, and a high relative density is more likely to be achieved. Moreover, explosive reaction results in sharp rising of temperature localized in the sample. This will accelerate the erosion of diamond by Si [15], and even lead to graphitization of diamond, both of which are harmful to the thermal properties of the composites. Besides, the Si-vapor infiltration is preferable for near-net-shape manufacturing of diamond/SiC composites compared to the liquid Si method. As the preforms are separated from molten Si during the vapor infiltration, the surface quality of the infiltrated samples was better than that of the samples immersed in molten Si. The machining cost was much lower for the former method. Therefore the Si vapor infiltration method was likely to produce diamond/SiC composites with high performance and low cost.

Up until now, there is little report on the fabrication of dense SiC composites by Si-vapor vacuum reactive infiltration. In this paper, diamond/SiC composites were rapidly produced by the Si-vapor vacuum reactive infiltration process. The microstructure and thermal properties of the composites were investigated.

2. Experimental

Synthetic diamond powders (Henan Famous Diamond Industries Co., Ltd.) with crystal size of 50–60 μm, phenolic resin powder (Henan Zhenzhou Hengtong Chemical Co., Ltd.) of the type 2123#-1, and silicon and graphite with particle sizes less than 10 and 50 μm, respectively, were used. Diamond particles were washed with hydrochloric acid for 0.5 h to remove impurities. The powders of diamond, phenolic resin, silicon and graphite were mixed with tungsten carbide balls of size 5 mm using a planetary ball mill. The wet mixing in ethanol continued for 16 h, and the rotation speed was 30 rpm. Phenolic resin acts as a binder for the green compacts and carbon sources for the porous preforms after pyrolysis. Green compacts with the dimension of Φ20 mm × 5 mm were obtained by compacting the powder mixture at a pressure of 30 MPa. Afterwards, the specimens were pyrolyzed at 1100 °C for 16 h under argon atmosphere in a graphite heated furnace. Heating rate of 1 °C/min was applied up to 700 °C to avoid distortion of samples. Holding time of 2 h was applied at the peak temperature to ensure the complete carbonization of the resin. The porous preforms were placed above a graphite crucible which was filled with excess Si powder, and they were heated rapidly to 1600 °C in a vacuum furnace. Subsequently, Si vapor produced by molten Si penetrated into the pore channels of the preforms, and reacted with carbon to form SiC, promoting densification of the diamond/SiC composites. Due to the good chemical stability, it was difficult to determine the contents of diamond, SiC and Si in the composites directly. It is assumed that the total volume of the diamond particles added in the green compact was constant during the pyrolysis and infiltration processes. As a result, the volume of diamond in the infiltrated sample was calculated from the mass of the green compact. The volume fractions of SiC and Si in the resultant materials were calculated according to the rule of mixture. The calculated phase composition, porosity and density of the samples are given in Table 1.

Porosity and density of the samples were measured by Archimedes' principle. The XRD patterns of porous preforms and diamond/SiC composites were recorded using an X-ray diffractometer (XRD, Siemens D 5000 X). Raman spectra were obtained at room temperature using a Raman Microimaging System Lab (Ram HR 800). The 514 nm incident laser wavelength of an Ar^+ laser was used as the excitation line, and the spectral resolution was approximately $1.0\,cm^{-1}$. The microstructures were observed by Field-Emission Scanning Electron Microscopy (FE-SEM, ZEISS ULTRA 55). The TC was calculated from density, thermal diffusivity, and specific heat of the composites. The thermal diffusivity was measured using a NETZSCH LFA 427 flash thermal conductivity meter. Specific heat was derived from the theoretical value calculated by the rule of mixture. The CTEs (50–400 °C) were measured by a NETZSCH DIL 402C dilatometer with the heating rate of 5 °C/min.

3. Results and discussion

The XRD patterns of the samples after pyrolysis and infiltration were shown in Fig. 1. It was observed that the porous preforms were composed of diamond (JCPDS no.06-0675), Si (JCPDS no.27-1402), and graphite (JCPDS no.89-8487). The absence of SiC suggests that Si did not react with carbon source at 1100 °C. In addition, weak diffraction peaks of tungsten carbide (JCPDS no.25-1047) appeared in the samples due to the contamination of WC balls during mixing. For the infiltrated samples, peaks

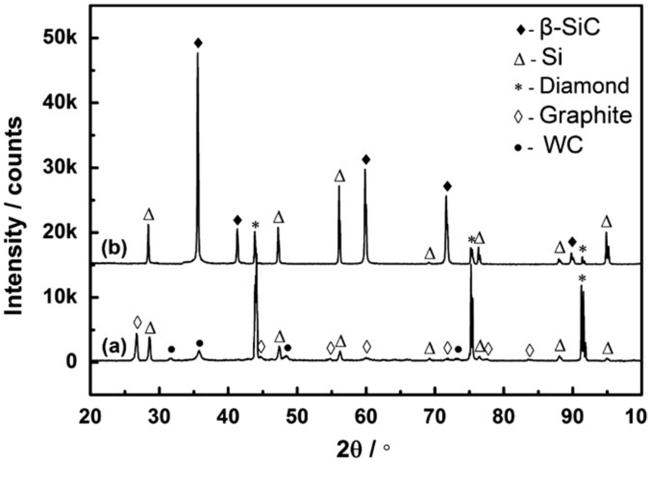

Fig. 1. XRD patterns of the samples: (a) pyrolyzed specimens, and (b) infiltrated specimens.

of Si and diamond were also found. Besides, sharp β-SiC (JCPDS no.29-1129) peaks were detected, and no graphite peaks existed in the specimens. It could be inferred that high crystallinity β-SiC (cubic type) was formed as a result of the reaction between carbon and silicon. Since Si was in excess relative to carbon (except diamond) during the Si-C reaction, both graphite and glassy carbon were exhausted. This is beneficial to the densification of the composites. The results presented in Table 1 indicate that the content of Si in the infiltrated samples decreased rapidly with increasing contents of diamond and resin in the green compact. It is supposed that graphitization of diamond did not take place due to the absence of graphite peaks. To verify this conjecture, Raman spectra of the infiltrated specimens were repeatedly measured in different areas. Fig. 2 shows the typical Raman spectra of the resultant materials. The sharp peak centered at 1332 cm^{-1} belongs to diamond [16], and the small peaks located at 520 and 795 cm^{-1} correspond to Si [17] and β-SiC [18] respectively. Typical graphite peaks located at 1350 cm^{-1} (D peak) and 1580 cm^{-1} (G peak) were not detected [19]. It was reported that obvious graphitization of diamond happened at 1600 °C under vacuum [20]. However, the Raman spectra and XRD results revealed that diamond graphitization did not occur. It is seen that the diamond was prevented from graphitization for some reason, which is favorable for the production of diamond/SiC composites with good properties under low pressure.

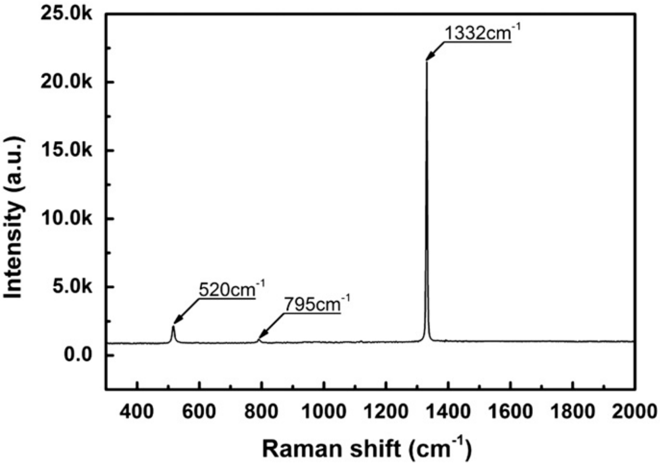

Fig. 2. Typical Raman spectra of the sample infiltrated at 1600 °C for 1 h.

Fig. 3 shows the microstructure of the infiltrated samples. Fig. 3(a) depicts that the composites consist of three phases, and the dark, gray and light gray phases were identified as diamond, SiC and residual silicon respectively [10]. Diamond particles with inerratic shape were uniformly dispersed in the SiC matrix. A little diamond powder was eroded by silicon, and only a little of free silicon was found. This suggests that diamond was prevented from eroding by silicon, and the SiC was mainly produced from graphite and pyrolytic carbon in the preforms. This was explained by the fact that gas–solid reaction is milder than liquid–solid reaction, and the Si–C reaction is faster for less crystalline carbon sources. Although a little Si (10–20 vol%) was added in the green

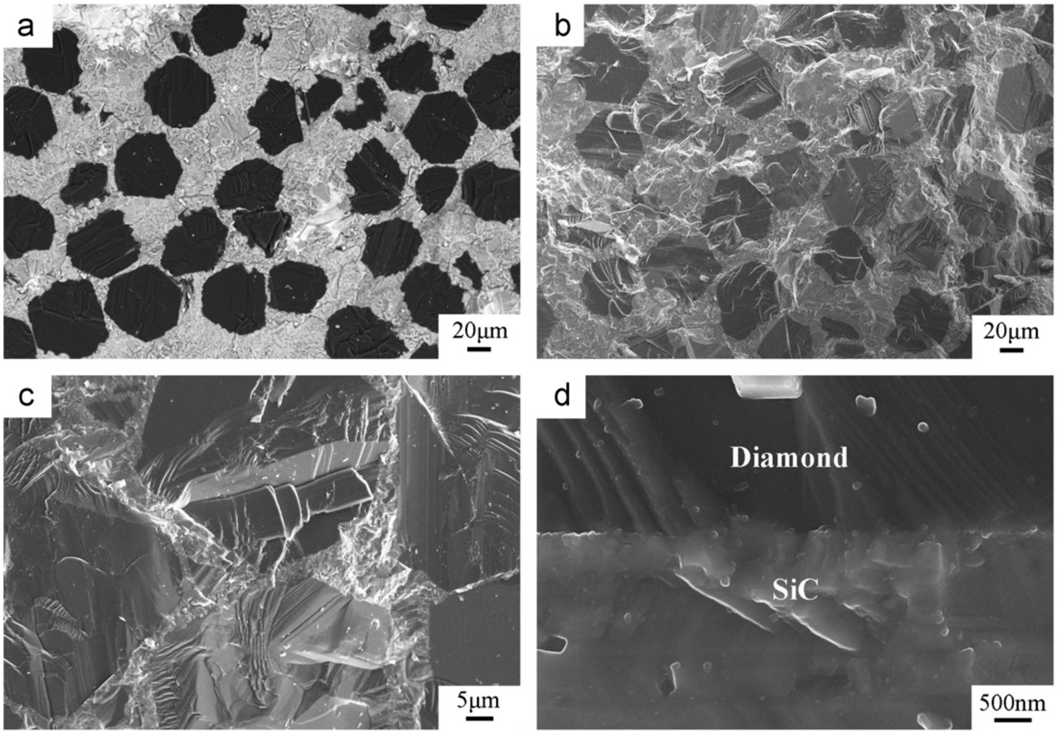

Fig. 3. SEM images of the infiltrated specimens: (a) backscattering image, (b) fractural surface, (c) high magnification image of (b), and (d) interfacial structure.

Table 1
Summary of the infiltration results of the preforms containing different amounts of silicon and resin.

Sample	Graphite content (vol%)	Silicon content (vol%)	Resin content (vol%)	Weight loss during pyrolysis (%)	Density (pyrolyzed state) (g/cm^3)	Porosity (%)	Calculated phase composition (vol%)		
							Diamond	SiC	Si
D4G1S2R3	10	20	30	7.71	2.01	28.63	35	42	23
D5G1S2R2	10	20	20	3.78	2.13	29.76	42	46	12
D6G1S1R2	10	10	20	3.82	2.09	31.46	46	52	2

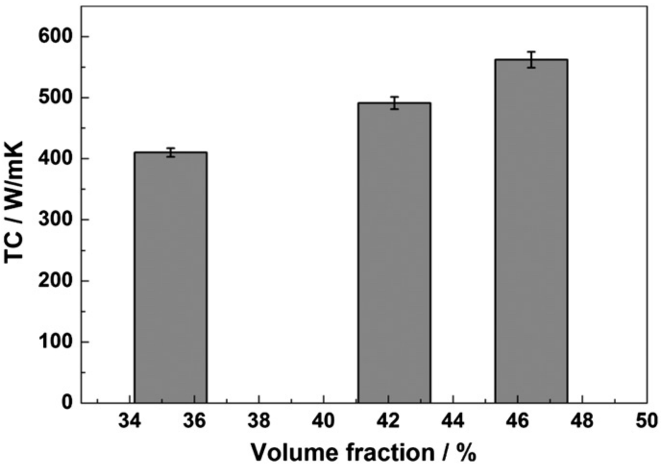

Fig. 4. TC of the diamond/SiC composite containing varied contents of diamond.

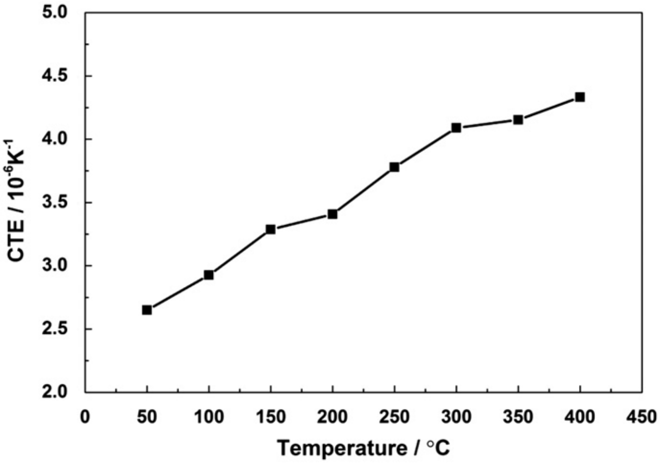

Fig. 5. CTEs of the diamond/SiC composite containing about 42 vol% of diamond.

body, it reacted with graphite and pyrolytic carbon preferentially. The aim of the addition of Si in the preform was to mitigate the expansive deformation of the samples during the in situ Si–C reaction. Fig. 3(b) shows that the microstructure of the composites was homogeneous and compact, and no pores were observed. It was reasonable to consider that the porous preforms were completely infiltrated by vapor Si, and full density was achieved after reactive infiltration at 1600 °C for 1 h, although the infiltration time is a little longer than that of the liquid infiltration. Indisputably, it was a high-efficiency and timesaving method compared with most of the other vapor infiltration processes [13,21,22]. Fig. 3(c) shows high magnification morphology of diamond particles. Apparently, all the diamond crystals in the composites correspond to transgranular fracture mode. The boundaries between diamond and SiC were clear and neat, and no microcracks or pores were detected. Fig. 3(d) shows the interfacial characteristics of diamond/SiC composite. Diamond and SiC were distinctly identified, and no intermediate phases existed. Moreover, no evidence of graphitization of the diamond particles was found in Fig. 3(b–d). The above results suggest a perfect interfacial bonding between diamond and SiC. As a result, excellent mechanical and thermal properties of diamond/SiC composites were expected.

The composition of the composites are given in Table 1, and the TC was calculated by the laser flash method. Fig.4 depicts the TC of diamond/SiC composites with varied contents of diamond. Owing to the good interfacial bonding, high relative density and excellent properties of diamond and SiC, TC of the diamond/SiC composites approaches 562 W/m K, while density of the specimen was 3.32 g/cm^3. The CTEs of diamond/SiC composite containing about 42 vol% of diamond were measured at the temperature ranging between 50 and 400 °C, as shown in Fig. 5. The average CTE was about 3.6×10^{-6}/K in the temperature range of 50–400 °C. Low values of CTEs were obtained due to the low CTEs of diamond and SiC. In comparison to the conventional thermal management materials, diamond/SiC composites have good thermal properties and low density, which is desirable for thermal management application.

4. Conclusions

Diamond/SiC composites were firstly produced through the Si vapor vacuum reactive infiltration process. This method is certified as a timesaving, high-efficiency and cost-effective fabrication technique in comparison to other CVI and CVI-R processes. Nearly fully dense diamond/SiC composites with homogeneous microstructure were obtained. The interfacial bonding between diamond and

SiC was strong, and no evidences of diamond graphitization were observed. In the case of diamond/SiC composites with 46 vol% diamond, the thermal conductivity reached up to 562 W/m K, and the density was only 3.32 g/cm^3. In the temperature range 50–400 °C, the average CTE was 3.6×10^{-6}/K for the composites containing 42 vol% diamond.

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