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Ceramics International 38 (2012) 6131–6136

CERAMICS INTERNATIONAL

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Preparation of Si–diamond–SiC composites by in-situ reactive sintering and their thermal properties

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Received 12 March 2012; received in revised form 23 April 2012; accepted 26 April 2012
Available online 3 May 2012

Abstract

This article described a novel method of preparation of Si–diamond–SiC composites by in-situ reactive spark plasma sintering (SPS) process. The relative packing density of Si–diamond–SiC composite was 98.5% or higher in a volume fraction range of diamond between 20% and 60%. Si–diamond–SiC composites containing 60 vol% diamond particles yielded a thermal conductivity of 392 W/m K, higher than 95% the theoretical thermal conductivity calculated by Maxwell–Eucken's equation. Coefficients of thermal expansion (CTEs) of the composites are lower than the values of theoretical models, indicating strong bonding between the diamond particle and the Si matrix in the composite. The microstructures of these materials were studied by field emission scanning electron microscope (FE-SEM) and X-ray diffraction (XRD). As a result of reaction between diamond and silicon, SiC phase formed.

Keywords: C. Thermal properties; Ceramic-matrix composites; Particle-reinforcement; Microstructures

1. Introduction

With booming electronic industry and growing requirement for highly integrated devices, diamond composites became hot spots in the new material research field for their high thermal conductivity and low coefficient of thermal expansion. Within the past years there was a significant increase on publications related to diamond grains reinforced composites. Most of these publications are related to metallic matrix materials (Al, Cu and Ag). Up to now there has been a limited number of publications and especially of success stories, where diamond grains have been successfully introduced in silicon matrix materials resulting in significant improvements of the properties of the matrix material.

The reason why metallic matrix materials resulted in a faster success compared with silicon based materials, is of course related to the fact that a metallic matrix is in general characterized by rather poor thermal expansion performance (mainly refers to Al, Cu and Ag) and the relative high density (mainly refers to Cu and Ag). By introduction of diamond grains, which are characterized by better/higher properties than the matrix, it is easier to generate benefits through the reinforcement. The situation is quite different when speaking about reinforcing silicon matrix. Here the matrix material itself exhibits good material properties already, which hampers significant improvement through the reinforcement. To take advantage of the promising properties of diamond grains, many aspects related to the processing of materials have to be considered.

Compared with the traditional packaging materials, Such as AlN [1,2] or SiC [3,4], diamond–silicon matrix composites have higher thermal conductivity and lower coefficient of thermal expansion. Development of diamond–silicon matrix composites is very important from both scientific and practical points of view. This is because diamond–silicon matrix composites combine fine thermal properties with excellent mechanical characteristics.

The mechanical properties of Si–diamond–SiC composites were reported to have an average Vickers hardness of

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http://dx.doi.org/10.1016/j.ceramint.2012.04.062

about 31–100 GPa and the fracture toughness is on the order of 7.8 ± 1.3 [5,6]. The average bending strength of these composites was measured at 400–750 MPa [7]. However, until now, only a limited number of studies have been addressed on thermal properties of Si–diamond–SiC composites. For example, Si–diamond–SiC composites with high diamond volume fractions, which could be produced by infiltration of diamond performs with molten silicon or silicon alloy, yielded the thermal conductivity of at least 400 W/m K in a volume fraction range of diamond between 58% and 81% [8]. Thermal conductivity up to 600 W/m K was measured for diamond composites obtained at high pressures (2 GPa) by sintering diamond grains in the presence of silicon [9]. However, these methods are high-cost and time-consuming process. In addition, it is difficult to make the composite with homogeneously dispersed diamond particles when fabricated by infiltration techniques or high pressure high temperature sintering.

Recently, an increasing interest has been focused on the research of diamond reinforced ceramic matrix materials synthesized by in-situ reactive spark plasma sintering method that can efficiently improve the interfacial bonding strength between the matrix and reinforcements [10,11]. What is more, SPS is a very effective technique to promote the densification of diamond-particle-filled composites [12]. In this paper, we reported Si–diamond–SiC composites produced by in-situ reactive spark plasma sintering technique. With this method, the sintering temperature was well controlled below the melting point of Si (1693 K), which made the whole Si–diamond–SiC composites preparation process more energy-efficient and low cost. In this work, we focused on the preparation of Si–diamond–SiC composites and their thermal properties. Moreover, the influence of interface on thermal properties of Si–diamond–SiC composites was specifically discussed.

2. Experimental procedures and theoretical models

2.1. Materials

Si 99.96% (purity in wt%) was used as matrix base material for all samples. The diamonds used were 100 μm (the average particle diameter) synthetic monocrystals of the type FDP from Henan Union Abrasives Corp. The diamond volume fraction amounted to approximately from 20% to 60%.

2.2. Spark plasma sintering

The SPS system (Mod. 1050, Sumitomo Coal Mining Co. Ltd., Japan) was used to synthesize Si/diamond composites. The powders were mixed in methanol using a magnetic stirrer. The mixing time was 30 h. The goal of this process was to obtain a uniform mixture of diamond and silicon matrix powders. After mixing, methanol was removed by evaporation. The mixtures of diamond and Si powders were sintered between 1523 and 1643 K for 5 min in argon (0.03 Mpa). The heating rate was 50 K/min and a pressure of 50Mpa was applied throughout the sintering process.

2.3. Analysis of composites

Field emission scanning electron microscope (Sirion 200, FEI, Holland) was used to examine the microstructure of samples and energy dispersive X-ray (EDX) was used to analyze the elements of the samples.

X-ray diffraction (X'Pert PRO, PANalytical B.V, Holland) with monochromatic CuKα radiation source was used to get the diffraction patterns of the samples, which identified the phases present.

Thermal conductivity of the samples was measured at 50 °C by a laser flash apparatus (TC-7000, SINKU-RIKO.INC., Japan) with an international standard [13]. This system directly measured the thermal diffusivity (α) and specific heat capacity (Cp). The density (ρ) of the samples was measured by Archimedes method. The thermal conductivity could be derived from the equation: thermal conductivity $(\lambda)=\alpha\times Cp\times\rho$.

The coefficient of thermal expansion was measured from room temperature to 375 K at a rate of 5 K/min for both heating and cooling in an argon atmosphere by using a dilatometer (DIL 403PC, NETZSCH, Germany), with an international standard [14].

2.4. Theoretical models of thermal properties

In order to explore the effect of interface on thermal conductivity, we used a theoretical model proposed by Hasselman and Johnson to deduce interfacial thermal conductance [15]:

$$\lambda=\lambda_m\times\frac{2(\lambda_d/\lambda_m-\lambda_d/\alpha h-1)V_d+\lambda_d/\lambda_m+2\lambda_d/\alpha h+2}{(1-\lambda_d/\lambda_m+\lambda_d/\alpha h)V_d+\lambda_d/\lambda_m+2\lambda_d/\alpha h+2} \tag{1}$$

where λ_m, λ_d and λ are the thermal conductivity of the matrix, reinforced particles and composite, respectively. V_d and α represent the volume fraction and radius of the reinforcement particles, respectively. The thermal boundary conductance h will be used to quantitatively assess the efficiency of heat transfer in composites. h is the inverse of interface thermal resistance (ITR). The interface thermal resistance can be explained as the discontinuity in the temperature when heat flows between two dissimilar elements. Assuming the perfect bonding between the diamond particle and the Si-matrix in the composite, the h value become ∞ and Eq. (1) is simplified to Maxwell–Eucken proposed by Eucken [16]:

$$\lambda=\lambda_m\times\frac{2(\lambda_d/\lambda_m-1)V_d+\lambda_d/\lambda_m+2}{(1-\lambda_d/\lambda_m)V_d+\lambda_d/\lambda_m+2} \tag{2}$$

In the present study, this Eq. (2) is also utilized to evaluate the effect of consolidation for Si-matrix composite containing diamond particle made by SPS process.Kerner model [17] and Rose–Hashin Bounds model (R–H model) [18] have been used widely to predict theoretical coefficients of thermal expansion of composites. They take shear effects into account at the boundaries between particles and the matrix. Hence, we utilized Kerner model and Rose–Hashin Bounds model in the present study to evaluate CTEs of the samples. Kerner model can be expressed by the following equation:

$$\alpha_c = \alpha_m V_m + \alpha_d V_d + V_d V_m(\alpha_d - \alpha_m) \times \frac{K_d - K_m}{V_m K_m + V_d K_d + (3K_d K_m / 4G_m)} \tag{3}$$

and Rose–Hashin Bounds model can be expressed by the following equation:

$$\begin{cases} a_c^u = \dfrac{4V_m V_d G_d (K_m - K_d)(a_m - a_d)}{3K_m K_d + (4G_d(K_m + K_d)/2)} + (a_m V_m + a_d V_d) \\ a_c^l = \dfrac{4V_m V_d G_m (K_m - K_d)(a_m - a_d)}{3K_m K_d + (4G_m(K_m + K_d)/2)} + (a_m V_m + a_d V_d) \end{cases} \tag{4}$$

where α_c is the coefficient of thermal expansion of the composite, α_d is the coefficient of thermal expansion of the dispersions, α_m is the coefficient of thermal expansion of the matrix, V_d is the volume fraction of the dispersions in the composites, V_m is the volume fraction of the matrix in the composites, K_d is the bulk modulus of the dispersions, K_m is the bulk modulus of the matrix, G_m is the shear modulus of the matrix, G_d is the shear modulus of the dispersions, the superscript u represents upper bound and l signifies lower bound.

3. Results and discussion

3.1. Sintering temperature and relative packing density of composites

The relative packing density and sintering temperature of Si–diamond–SiC composites are shown in Table 1. As a matter of fact, SPS is a very effective technique to promote the densification of Si–diamond–SiC composites. In this work, the relative packing density of Si–diamond–SiC composites was 98.5% or higher in a volume percentage range of diamond between 20% and 60%. Additionally, the increase of silicon content in samples decreased the sintering temperatures and increased the relative packing density obviously.

Table 1
Sintering temperature and relative density of Si/diamond composites.

Diamond volume fraction (%)	Relative density (%)	Sintering temperature (K)
60	98.5	1643
50	99.0	1623
40	99.1	1593
30	99.4	1563
20	99.7	1523

3.2. In-situ reaction

The X-ray diffraction patterns of sintered samples are shown in Fig. 1. From this result, we can only find out peaks that correspond to Si, SiC and diamond (C) in the pattern of sintered samples. From the XRD patterns of sintered samples, we can infer that the following chemical reaction has taken place during the sintering process and its corresponding Gibbs free-energy function is given as follows:

$$\mathrm{Si}(s) + \mathrm{C}(s) = \mathrm{SiC}(s, \beta)$$

$$\Delta G^0 = -73,050 + 7.66T$$

Micron-grade diamond particles are susceptible to allotropic reconversion to graphitic sp^2 or amorphous carbon during isothermal exposure in non-oxidizing atmospheres at temperatures as low as 750 °C [19]. It is noteworthy that the X-ray diffraction patterns of sintered samples do not show any peaks corresponding to graphite peaks. The possible explanation can be offered for this. Silicon acts as oxygen scavenger and by reducing concentration surface absorbed oxygen and free oxygen inside the pores, it significantly decreases the catalytic effect of oxygen on diamond graphitization [20].

3.3. Microscopy analysis

FE-SEM micrographs of the fracture surface of samples are shown in Fig. 2. The light-gray regions are continuous silicon matrix. Diamond particles that appear as deep-gray are observed to be well embedded in the silicon matrix. No evidence of either porosity or any other obvious defects was found in the materials. The matrix adheres on some diamond particle surfaces, indicating that in these cases, interfacial bonding was stronger than the matrix tensile

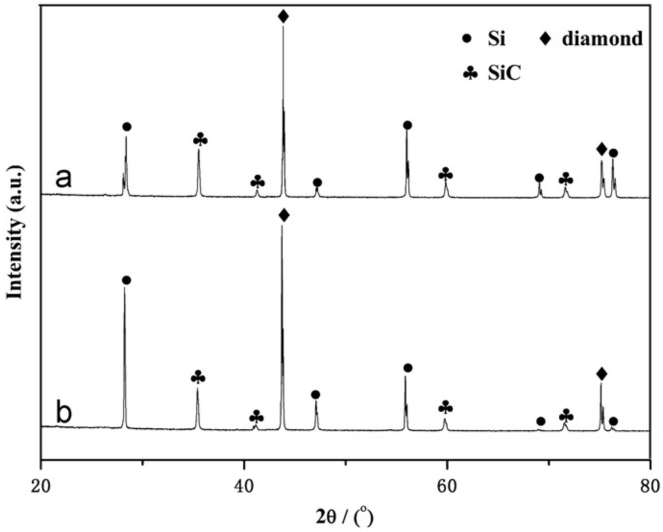

Fig. 1. X-ray diffraction patterns: (a) Si–20 vol% diamond (sintering temperature of 1523 K); (b) Si–60 vol% diamond (sintering temperature of 1643 K).

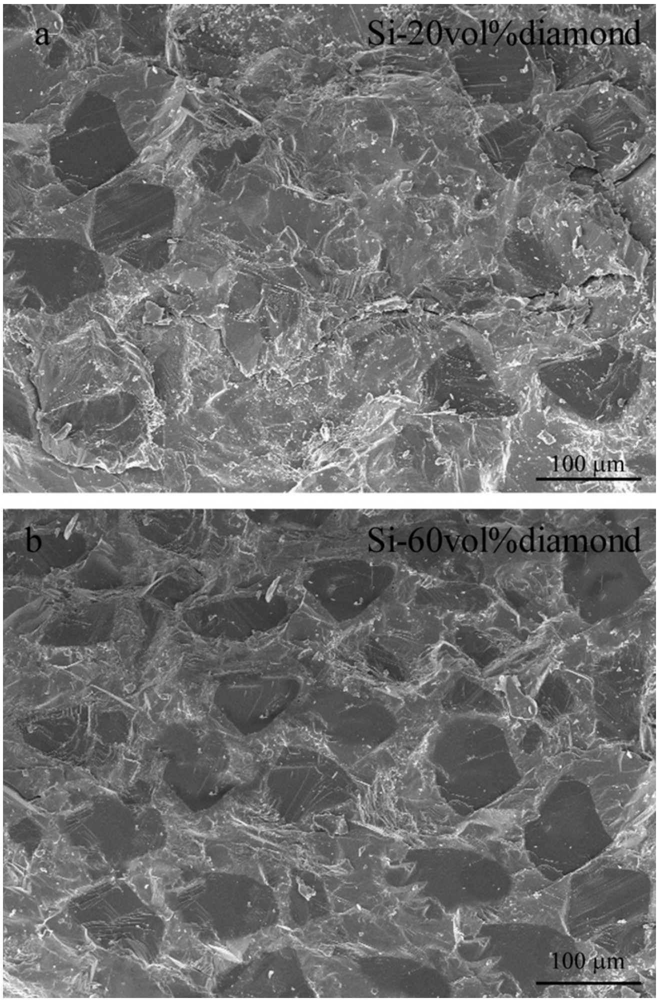

Fig. 2. Microstructures of fracture surfaces of the composites: (a) Si–20 vol% diamond (sintering temperature of 1523 K); (b) Si–60 vol% diamond (sintering temperature of 1643 K).

strength. The chemical composition of the interface area has been indicated by EDX line scanning, and the result is presented in Fig. 3. Following the scan path of Fig. 3b, first a diamond grain is crossed, followed by the interface layer that reveals distinct signals for diamond (C) and a slowly increasing signal for silicon (Si) before entering the silicon matrix layer. As our expectation, samples do not display any other phase besides diamond, Si and SiC in Fig. 1.

3.4. Thermal conductivity and coefficients of thermal expansion

Thermal conductivity values for Si/diamond composites are summarized in Table 2. It infers that the sample properties mainly depend on the volume fraction of diamond. Thermal conductivity of samples sintered increases obviously with the increase of diamond content. The enhancement of thermal conductivity in Si–diamond–SiC composites can be explained as follows. The interface plays a critical role in determining both microstructure and thermal conducting behavior of the composites. The interface acts as a bridge between diamond reinforcements and silicon matrix. Combined with the EDX analysis (Fig. 3) and the XRD analysis (Fig. 1) of samples, we can find the evidence of interfacial silicon carbide, which formed as a result of the reaction between diamond and silicon. Interfacial silicon carbide has a high thermal conductivity,

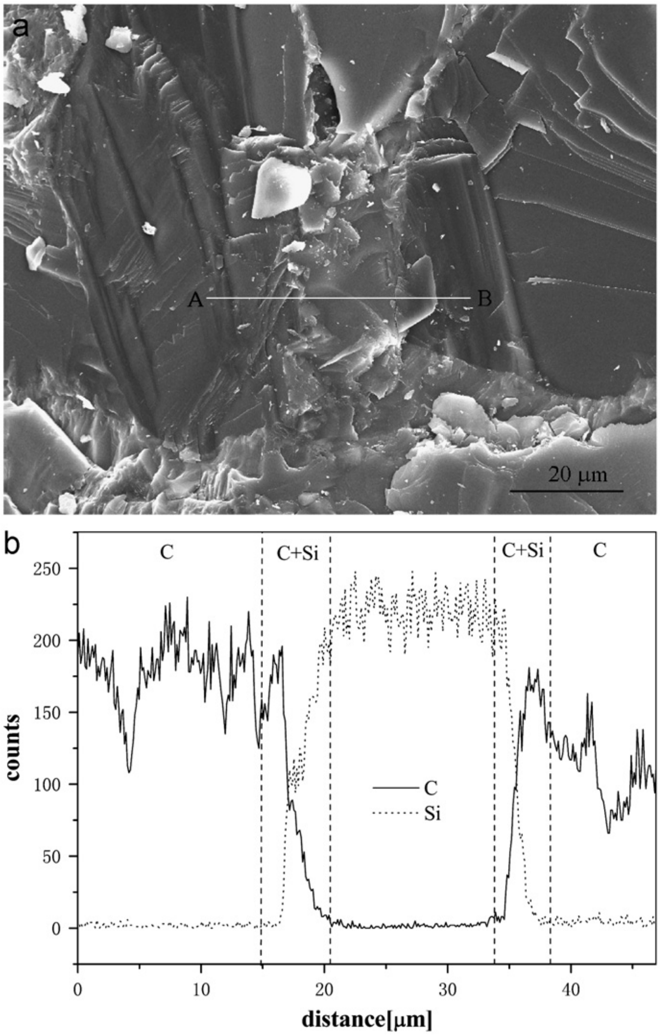

Fig. 3. EDX interface line scan between sites A and B, i.e., fracture surfaces of Si–60 vol% diamond (sintering temperature of 1643 K) (a) and element concentration profile from sites A to B (b).

Table 2
Measured thermal conductivity λ of Si/diamond composites.

Diamond volume fraction (%)	λ (W/m K)
60	392 ± 0.85
50	320 ± 0.87
40	268 ± 0.96
30	223 ± 0.79
20	185 ± 0.89

which is good for heat transfer to occur across silicon–diamond interfaces.

Using the values measured for λ in this study (Table 2) and using the materials data compiled in Table 3, h can be back-calculated for composites using the equation of H–J model. The thermal boundary conductance h for the composites fabricated in our present work was calculated using Eq. (1) and the h values obtained were 3.0–5.08×10^8 W/m^2 K in a volume fraction range of diamond between 20% and 60%. In Fig. 4 depicted also are theoretically calculated values of thermal conductivity for Si–diamond–SiC composites using the Maxwell–Eucken equation for cases with various percentages of conductivity as opposed to 100% theoretical values. As seen in Fig. 4, the experimental values are much higher than 95% the theoretical value calculated using Maxwell–Eucken equation. It should be emphasized that this result indicates that the bonding between the diamond particles and the Si-matrix is strong. As shown in Table 2, thermal conductivity values of Si–diamond–SiC composites, which prepared by in-situ reactive spark plasma sintering, cannot be compared with those fabricated by infiltration techniques [8] or high pressure high temperature sintering [9]. This is mainly because of the reason of three respects. First of all, the high volume fraction of diamond (58–81% [8], 80% [9]) has remarkable influence that cannot be ignored on improving thermal conductivity of samples. Secondly, it can be seen from Maxwell–Eucken model that thermal conductivity of composites would be improved by higher-quality diamond (the thermal conductivity is about 2000 W/m K [8]) if the volume fraction and matrix properties of invariants are taken into account. Finally, the actual ideal thermal boundary conductance of Si–diamond–SiC composites may be achieved by the formation of partial grain-to-grain diamond contacts at higher pressure and more complete reaction of Si with diamond [8,9]. Hence, by choosing higher-quality diamond (the thermal conductivity is around 2000 W/m K [21]) or reaching the actual ideal thermal boundary conductance of the system, thermal conductivity values exceeding 500 W/m K may be expected from Si–diamond–SiC composites prepared by SPS.

Table 3
Properties of diamond and Si assumed for calculation of thermal expansion α and thermal conductivity λ.

Material	λ (W/m K)	α (10^{-6}/K)	K^c (10^{10} Pa)	G^e (10^{10} Pa)
Si (matrix)	125[a]	3.6[a]	9.8[b]	5.2[b]
Diamond	1000[b]	1.2[b]	36[d]	50[b]

[a] Measured.
[b] Provided by the manufacturer.
[c] Bulk modulus.
[d] From [12].
[e] Shear modulus.

Properties of diamond and Si assumed for calculation of thermal expansion α are shown in Table 3. The comparison between the theoretically predicted and the experimentally obtained CTEs for Si–diamond–SiC composites is shown in Fig. 5. As shown, CTEs of the composites obtained experimentally are lower than the values of theoretical models (Kerner model and R–H model). This is a good indication in that the diamond particles have strongly bonded with the Si-matrix in the composite fabricated by SPS. Thermal expansion values for samples obtained in the present study are found to be in the range of 1.437–2.58×10^{-6}/K in a volume fraction range of diamond between 20% and 60%. On the other hand, diamond reinforced metallic matrix materials mainly include Al–diamond [12], Cu–diamond [22,23] and Ag–diamond [24], and their CTEs values are 10.4–12.5×10^{-6}/K, 6.9–8.3×10^{-6}/K and 8.6–9.7×10^{-6}/K, respectively. Thermal stress and warping arise from CTEs differences [25], which become significant in advanced electronic devices because

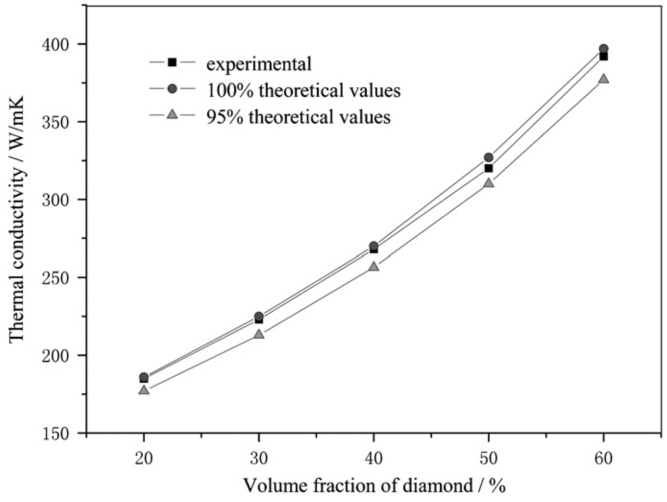

Fig. 4. Experimental data and theoretical predictions of thermal conductivity for Si–diamond–SiC composites with various volume fractions of diamond.

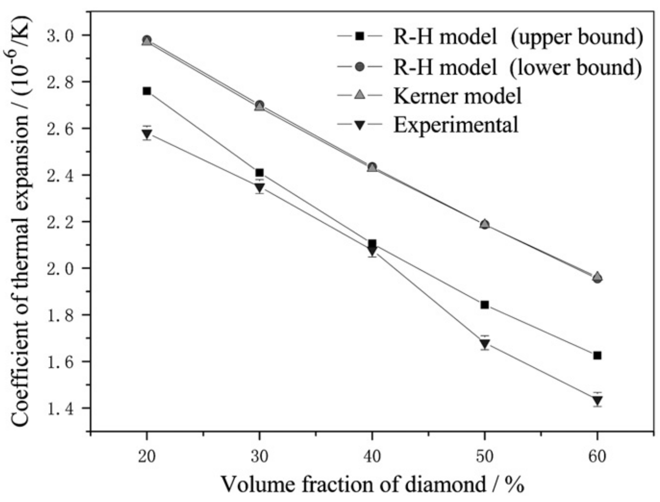

Fig. 5. Experimental data and theoretical predictions of coefficients of thermal expansion for Si–diamond–SiC composites with various volume fractions of diamond.

of high heat generated, for example, high-power laser diodes are in use. Therefore, Si–diamond–SiC composites would be more preferable than metallic-diamond composites in application.

4. Conclusions

The interfacial microstructures of Si–diamond–SiC composites fabricated by in-situ reactive spark plasma sintering process were examined. As a result of reaction between diamond and silicon, SiC phase formed. This study shows that silicon facilitates reduction of porosity and hinders diamond graphitization. The relative packing density of Si–diamond–SiC composites fabricated was 98.5% or higher in a volume fraction range of diamond between 20% and 60%. The increase of silicon content reduced the sintering temperatures and increased the relative packing density obviously. Thermal conductivity of samples sintered improved obviously with the increase of diamond content. Thermal conductivity and thermal expansion appear to be strongly related to interface microstructure, particularly to interfacial bonding between the silicon matrix and the diamond particles. Values of high thermal conductivity (392 W/m K) coupled with low thermal expansion (1.437×10^{-6}/K) as desirable for thermal management applications have been measured for Si/diamond composite with 60 vol% diamond particles.

Acknowledgments

This work was financially supported by the Independent Innovation Project of State Key Laboratory of Plastic Forming Simulation and Die and Mold Technology and technically supported by the Analysis and Testing Center of Huazhong University of Science and Technology.

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