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### **Preparation and characterization of diamond– silicon carbide–silicon composites by gaseous silicon vacuum infiltration process**

*Diamond–SiC–Si composites have been prepared using gaseous silicon vacuum infiltration. The evolution of the phases and microstructures of the composites have been analyzed using X-ray diffraction technique and scanning electron microscopy. It has been found that the diamond–SiC–Si composite is composed of  $\beta$ -SiC, diamond, and residual Si. The diamond particles were distributed homogeneously in the dense matrix of the composites. Besides, the effects of particle size and content of diamond on the properties of diamond–SiC–Si composites have been analyzed. The thermal conductivity of the composites increases with particle size and content of diamond. When the particle size and content of diamond are 300  $\mu\text{m}$  and 80 wt %, respectively, the thermal conductivity of the composites approaches the value of 280  $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ .*

**Keywords:** *diamond–SiC–Si composites, microstructure, evolution of phases, vacuum infiltration, thermal conductivity, XRD, scanning electron microscopy.*

#### **INTRODUCTION**

A diamond/SiC composite possesses many key physical properties such as the high thermal conductivity, exceptional hardness, and excellent wear resistance. The characteristic of high thermal conductivity of the diamond/SiC composite makes it promising for many industrial applications such as heat spreaders and heat transfer rig, as more demanding thermal management issues arise in the microelectronics industry [1–3]. Such diamond/SiC composites are usually prepared by gaseous/liquid silicon vacuum infiltration of diamond compacts, which inevitably results in the residual silicon. Therefore, to be more exact, the produced composite should be denoted as diamond–SiC–Si composite.

The diamond–SiC–Si composites produced by the liquid silicon infiltration typically need high pressure and high temperature (HPHT) [4–8], and is usually done at pressures of 6–10 GPa and temperatures of 1700–2100 K. SiC matrix phase is formed as a result of the reaction between diamond and silicon. However, there exist several drawbacks in HPHT liquid silicon infiltration method. Firstly, HPHT method can only produce samples with simple shape, besides, it has a high preparation cost. Secondly, liquid silicon infiltration cannot fully penetrate diamond compact [5, 6]. This restriction is caused by the closure of pores in the diamond compact due to the sealing effect of the initial formation of silicon carbide on the surface of the compact. Moreover, it can be anticipated that this effect becomes increasingly pronounced with decreasing size of diamond particles [7, 8]. Recently there are a few reports on the preparation of diamond–SiC–Si composites by the liquid silicon infiltration under a low pressure condition, where the

diamond–SiC–Si composites were successfully fabricated under ambient pressure or vacuum condition [9–11]. However, the liquid silicon infiltration not only gives rise to the postprocessing problems, but also increases the tendency of cracks occurrence in the composites. Therefore, a new method of gaseous silicon vacuum infiltration is put forward to solve these problems.

The purpose of the present work is to propose a new method to prepare diamond–SiC–Si composite, i.e., gaseous silicon vacuum infiltration [12–14]. This process does not need high pressure, so it avoids high preparation costs. Furthermore, gaseous silicon infiltration is a gentle reaction, thus it can avoid self-quenching phenomenon occurred in a liquid silicon infiltration by the rapid reaction between liquid Si and C. In this paper, the evolution of phase and microstructure of the composites were analyzed using X-ray diffraction technique and scanning electron microscopy. Besides, the effects of a particle size and diamond content on properties of diamond–SiC–Si composites were studied.

### EXPERIMENTAL

Diamond preforms were produced using phenolic resins and commercial diamond powders with four different particle sizes, e.g., 37.5, 75, 150, and 300  $\mu\text{m}$ . The composition of the diamond preforms was modified by changing contents of a diamond powder and phenolic resin, and the weight percent of diamond particles varied in the range of 40 to 80 wt %. The roles of the phenolic resin included two aspects: first of all, it acted as a binder during the hot mould process used for forming a diamond compact; secondly, the phenolic resin provided carbon source for Si–C reaction to form SiC matrix and prevented the diamond from reacting with silicon.

For the preparation of diamond preforms, diamond powder was mixed with phenolic resin solution (anhydrous alcohol was used as the solvent) to form slurry, then the slurry was dried in drying oven to obtain the phenolic resin modified diamond powder. The resulting powder was compacted to shape with dimension of 35 mm in length, 30 mm in width and 5 mm in thickness under pressure of 40 MPa and temperature of 200  $^{\circ}\text{C}$ . The compacts were then pyrolyzed at 1000  $^{\circ}\text{C}$  for 1 h in flowing argon to form the preforms for gaseous silicon vacuum infiltration. At last, the obtained diamond preforms (green body) and silicon powders were loaded into a graphite crucible (schematically shown in Fig. 1). The green body was located on the top of silicon powders with a certain distance between silicon powders and green body to avoid liquid silicon infiltration at high temperature. Subsequently, the crucible was placed in a graphite furnace and heated to 1600  $^{\circ}\text{C}$  (10  $^{\circ}\text{C min}^{-1}$  heating rate) in vacuum. Finally, Si vapor produced by melting Si penetrated into a perform and reacted with carbon at 1600  $^{\circ}\text{C}$  for 1 h in vacuum ( $\sim 20$  Pa).

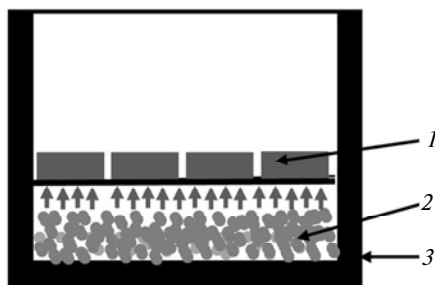


Fig. 1. Set-up for the gaseous silicon infiltration: diamond preform (1), Si powder (2), graphite crucible (3).

The samples were cut into 3×4×35 mm specimens and polished for three-point bending test in a WDW-100 (Changchun Research Institute of Testing Machines, Jilin, China) universal testing machine, with a crosshead speed of 0.5 mm/min and a span of 30 mm. The phase compositions of the composites were characterized by X-ray diffraction (XRD, D8 Advance, Bruker/Axs Corp., Germany) with Cu K $\alpha$  radiation. The thermal conductivity was calculated from the measured thermal diffusivity determined using a NETZSCH LFA 427 flash thermal conductivity meter, the measured density, and an estimated value of the specific heat of the composites. The microstructures of the composites were studied by scanning electron microscopy (SEM, S4800 Hitachi, Japan).

## RESULTS AND DISCUSSION

The XRD patterns of a green diamond compact and diamond–SiC–Si composite are shown in Fig. 2. The diamond compact is composed of diamond particles and pyrolytic carbon derived from phenolic resin. However, only diamond peaks are shown in the XRD patterns for diamond compact, indicating the amorphous state of the pyrolytic carbon. It can be observed from XRD patterns of diamond–SiC–Si composite (see Fig. 2, 2) that the obtained composite consists of diamond,  $\beta$ -SiC, and Si after gaseous silicon infiltration. The peaks of Si exist and are strong, indicating that the Si remains in the composite despite reaction of carbon and Si leading to formation of  $\beta$ -SiC [15]. As far as the free silicon is concerned, unreacted Si vapour recondenses as liquid on the wall surface of pore channels and fills in the pores of the preform to form a dense composite; as a result, the remnant Si appears in the final composite. Meanwhile, the diamond phase remains in the composites; however, this can not rule out that a few diamonds reacted with Si.

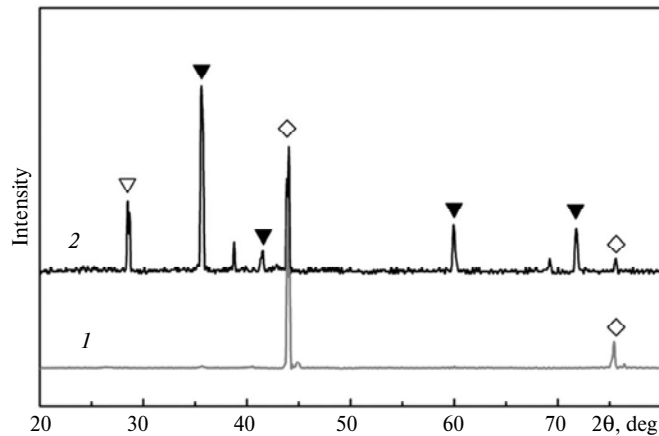


Fig. 2. XRD patterns of (1) diamond compact and (2) diamond–SiC–Si composite: diamond (◇), SiC (▼), Si (▽).

Figure 3 shows the effects of the mean particle size of diamond on the bending strength and thermal conductivity of diamond–SiC–Si composites. All the samples have the same diamond content of 40 wt %, and the particle size of diamond ranges from 37.5 to 300  $\mu\text{m}$ . The thermal conductivity of the composites increases with diamond particle size, and approaches a maximum value of 138.1  $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  at the diamond particle size of 300  $\mu\text{m}$ . The increase of the thermal conductivity with diamond grain size increasing from 37.5 to 300  $\mu\text{m}$  can be explained based on a “two-zone” microstructure model [1] of diamond grain (schematically shown in

Fig. 4). According to this model, the diamond particles in the composites are comprised of two zones: an eroded surface layer of a certain thickness with a moderate thermal conductivity and a core of pristine diamond with undisturbed high thermal conductivity. The grain size of diamond particles will become smaller for surface SiC layer induced by the Si–C reaction after silicon infiltration. Because the surface SiC layer thickness is considered to be dependent on diamond grain sizes, thus the diamond particles with smaller size have a thicker eroded SiC layer. Therefore, the composites with a larger size of diamond particles maintain more volume percent of pristine diamond and show high thermal conductivity.

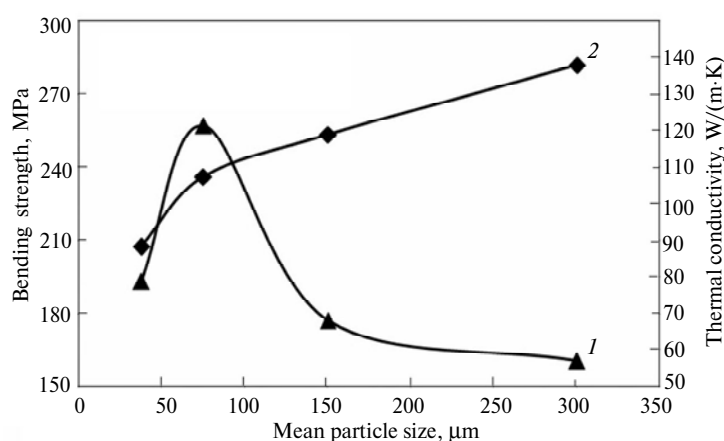


Fig. 3. Effects of a mean particle size of diamond on the bending strength (1) and thermal conductivity (2) of diamond–SiC–Si composites.

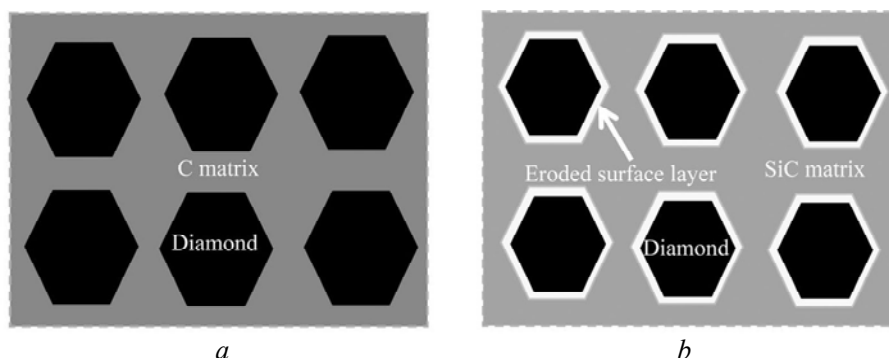


Fig. 4. Diagram of (a) green body before Si infiltration and (b) composite after Si infiltration (diamond/SiC composite).

The bending strength of the composites increases when the particle size of diamond increases from 37.5 to 75  $\mu\text{m}$ , and then decreases with the further increase of diamond particle size. The diamond–SiC–Si composite reaches the maximum value of 256.8 MPa at the diamond particle size of 75  $\mu\text{m}$ . As far as particles of reinforced ceramic matrix composite are concerned, the reinforced particles with too large size are likely to break, which will lead the prepared composites to possess low bending strength. Meanwhile, the reinforced particle with too small size is easy to be eroded in the silicon infiltration, thus the strengthening effect of the particles becomes weaker and the composite also shows a poor mechanical property. As a result, a moderate particle size of diamond is a guarantee to the improved mechanical property.

Figure 5 shows the effects of diamond content on the bending strength and thermal conductivity of diamond–SiC–Si composites. The result shows that the thermal conductivity of the composites increases with the diamond content. In our experiment, the maximum content of diamond is 80 wt %, and the corresponding thermal conductivity reaches a maximum value of  $280 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ . On the other hand, the bending strength decreases with the increase of the diamond content. With the increase of the diamond content, the corresponding carbon from the phenolic resin decreases, thus the content of formed SiC matrix is reduced, which results in a less bonding between the diamond particles and has a negative effect on the bending strength of diamond–SiC–Si composite.

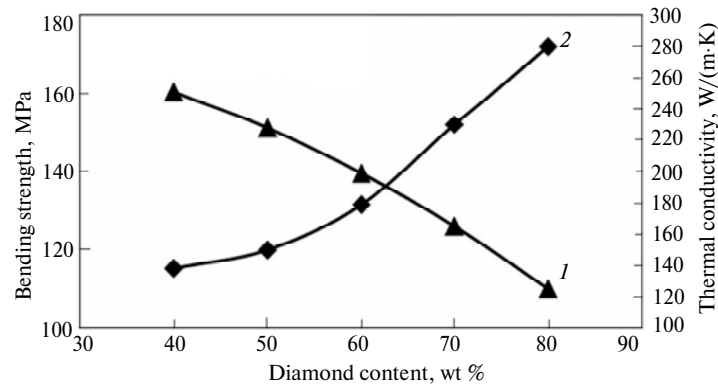


Fig. 5. Effects of diamond content on the bending strength (1) and thermal conductivity (2) of diamond–SiC–Si composites (all the samples have the same mean diamond particle size of  $300 \mu\text{m}$ ).

Figure 6 shows SEM micrographs of a green body and diamond–SiC–Si composite with a diamond particle size of  $300 \mu\text{m}$ . It can be seen from the SEM micrographs of the green body that the pyrolytic carbon distributes homogeneously around the diamond (see Fig. 6, *a*). Moreover, the diamond and pyrolytic carbon are loosely distributed in the green body, which provides the infiltration channel for the gaseous silicon infiltration. Diamond was surrounded with pyrolytic carbon derived from phenolic resin, so gaseous Si will firstly react with pyrolytic carbon to form a compact SiC coating around diamond [13]. As shown in Fig. 6, *b*, the diamond particles are distributed homogeneously in the composites. Besides, the composite has a dense matrix between the particles, indicating the effective densification of the gaseous Si infiltration. It is also observed that the surfaces of a few diamond particles are eroded slightly despite the protection from the compact SiC coating, because the loose structure between diamond particles and the pyrolytic carbon provide the interstices for the Si vapor infiltration.

## CONCLUSIONS

Diamond–SiC–Si composites with high thermal conductivity have been prepared by gaseous silicon vacuum infiltration process. The obtained diamond–SiC–Si composite is composed of  $\beta$ -SiC, diamond, and residual Si. The particle size and content of diamond have strong effects on the properties of diamond–SiC–Si composites. The thermal conductivity of the composites increases with the increase of particle size and content of diamond. On the other hand, a moderate particle size and relatively lower content of diamond is beneficial to the bending strength. When the particle size and content of diamond are  $300 \mu\text{m}$  and 80 wt %, the thermal conductivity of the composite reaches a maximum value of  $280 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ .

respectively, the composite has a thermal conductivity of  $280 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  and a bending strength of 107 MPa. The diamond–SiC–Si composite has a homogeneous distribution of diamond in the dense matrix. Moreover, the diamond is not severely eroded due to the protection of pyrolytic carbon.

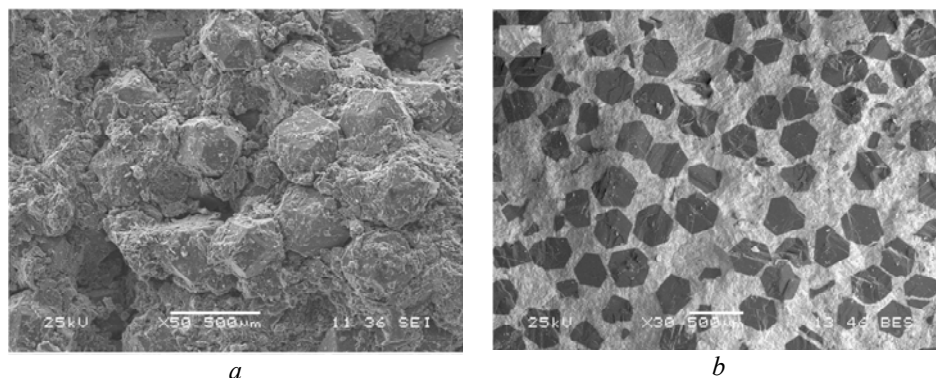


Fig. 6. Typical cross-sectional SEM micrographs of (a) green body and (b) diamond–SiC–Si composite.

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*Проведен анализ еволюції фаз і мікроструктури композитів алмаз–SiC–Si, виготовлених з використанням процесу вакуумної інфільтрації газоподібного кремнію. Дослідження виконано за допомогою дифракції рентгеновських променів і скануючої електронної мікроскопії. Встановлено, що композит алмаз–SiC–Si складається з  $\beta$ -SiC, алмазу і залишкового Si. Алмазні частинки розподілені однорідно в щільній матриці композитів. Також проаналізовано вплив розміру частинок і вмісту алмазів на властивості композитів алмаз–SiC–Si. Показано, що теплопровідність композитів зростає зі збільшенням розміру частинок і вмісту алмазів. Теплопровідність композитів наближається до значення  $280 \text{ Вт}\cdot\text{м}^{-1}\cdot\text{К}^{-1}$  при розмірі частинок і вмісту алмазу 300 мкм і 80 % (за масою), відповідно.*

**Ключевые слова:** композиты алмаз–SiC–Si, мікроструктура, еволюція фаз, вакуумна інфільтрація, теплопровідність, дифракція рентгеновських променів, скануюча електронна мікроскопія.

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