Preparation of silicon carbide/copper composite by pressureless infiltration

Kezheng Sang, Linjie Liu, Xiaoheng Song, and Dejun Zeng

School of Materials Science and Engineering, Chang’an University, Xi’an 710064, P. R. China

*Corresponding author: zengdejun396@chd.edu.cn

Abstract. SiC/Cu composite was obtained by pressureless infiltrating Cu into porous SiC ceramic modified by W coating. The influence of W coating on the process of pressureless infiltration, composition, microstructure, thermal conductivity and bending strength of the composites were studied. The results show that the SiC ceramic is obtained by oxidation sintering. The Sol and hydrogen reduction methods can be used for W metallization on the surface of holes in porous SiC ceramic, and small W particles of about 1 μm are evenly distributed on the surface of SiC particles in the ceramic. After the modification of the W coating, a complete infiltration of the Cu melt into the porous SiC ceramic can be achieved under a vacuum of 10⁻¹Pa at 1350 °C. W particles react with SiC at high temperatures during the infiltration process, and WC particles are formed on the Cu-based alloy matrix. As the size of SiC particles increases from 10 μm to 150 μm, the thermal conductivity of the composite increases from 35 W / (m·K) to 45 W / (m·K), but the bending strength rapidly decreases from 200 MPa to 30 MPa.

1. Introduction

Metal matrix composites with high volume fraction of reinforcement are attractive in view of the possibility to further enhance thermal conductivity by the use of high thermal conductivity components and the flexibility to adjust the coefficient of thermal expansion by controlling the content of reinforcement. Among them, SiC/Cu composite is a typical one, where Cu used as high thermal conductivity components and SiC used as the reinforcement [1].

With a high volume fraction of reinforcement, this kind of MMCs can generally be achieved by infiltration of metal into reinforcement or porous ceramic [2–4]. A crucial problem of infiltration techniques concerns with the wetting behaviors in the system. In general, metal melts do not readily wet ceramics, especially covalently bonded ones. To improve the wettability, active elements are generally considered to be used. By adding Ti, Cr into the Cu to form alloy, SiC are well wetted by the alloy melt and the SiC/Cu composite is obtained [5]. However, the addition of alloy elements will cause the thermal conductivity of the metal to drop sharply [6]. For this reason, SiC surface metallization is often used to improve the wetting behavior between Cu melt and SiC. Yih, et al. [7] coated SiC particles with Cu by electroless plating, and the wetting of Cu melt was realized. Chmielewski et al. [8] formed W coating on the surface of SiC particles by plasma deposition method. The study showed that the wetting angle of W and Cu at 1350 °C was only about 30 °, indicating that the W coating and Cu melt had good wettability. W and SiC will react and generate WC at 1100 °C[9], however, the wetting angle between WC and Cu melt is even smaller (20 ° at 1100 °C), and the wettability remains[10].
In present study, W coating is prepared on the surface of holes in porous SiC ceramic by sol and hydrogen reduction methods, and then copper melt is pressureless infiltrated into the porous SiC ceramic to obtain SiC/Cu composite. The effects of W coating on the structure and properties of the composite are studied, which lays a foundation for the preparation and properties control of SiC/Cu composites with high volume fraction of reinforcement.

2. Experimental procedure

2.1. Porous SiC ceramic and modifying

SiC ceramic was prepared by dry pressing and oxidation sintering. Firstly, SiC powders with sizes of 10, 50 and 150 microns, respectively, were mixed with phenolic resin evenly, and then the mixtures were pressed with the pressure of 100 MPa to produce green bodies with sizes of 5 mm ×5 mm ×50 mm, and φ15 mm ×3 mm. The porous SiC ceramic was obtained by calcining the green body in muffle furnace at 600°C for 1h and followed by oxidizing sintering at 1350°C for 1h.

Ammonium metatungstate, citric acid and ethylene glycol were dissolved in deionized water according to the mass ratio of 6:3:2. The light yellow ammonium metatungstate sol was obtained by magnetic stirring in a water bath at 80°C for 2h. The Porous SiC ceramics were firstly dipped into the ammonium metatungstate sol and full of the sol in the pores by capillary action. Then they were dried in the drying box at 80°C for 12h. The dried samples were heated to 600°C for 3h in a muffle furnace. Finally, the W coating could be formed on the surface of holes in the porous SiC ceramic by reduction in hydrogen atmosphere at 800°C in a tubular furnace.

2.2. The composites

SiC/Cu composites were prepared by pressureless infiltration. The porous SiC ceramic modified by W coating were placed on pure copper blocks in a crucible, then they were heated at a rate of 10°C/min to 1350°C and hold for 1h under the vacuum less than 10⁻¹ MPa in a vacuum furnace.

2.3. Characterization

The porosity of the porous SiC ceramic was measured by Archimede’s method, and each value was calculated by averaging at least five data. The weights of samples were obtained by an electronic balance with the sensitivity of 0.1 mg. Phase composition of the ceramic and composite was analyzed by X-ray diffraction (XRD; D/max2200PC, Rigaku, Japan ) with Cu Kα radiation at 40 kV and 40 mA, and scanning velocity of 8°/min (DS=SS=1°; RS: 0.3mm ). Microstructure and fracture morphology were analyzed by scanning electron microscope (SEM; S-4800, Hitachi, Japan) equipped with energy dispersive spectrometer (EDS).

The bending strength was determined by three-point bending test, where the sample had the size of 4mm ×4 mm ×40 mm. The thermal conductivity was measured by a laser thermal conductivity instrument and the sample had the size of φ12.5 mm ×1mm.

3. The results and discussion

3.1. Oxidation sintering and modification of the porous SiC ceramic

The porous SiC ceramic was prepared by oxidation sintering and further modified with W coating. Table 1 shows the weight changes and porosity of the porous SiC ceramic because of sintering and modifying. It can be seen that the weights of the samples increase after sintering, and the increase is considered to be due to the oxidation on the surface of SiC particles in the sintering procedure. SiO₂ could be formed on the surface of SiC particles due to oxidation and benefit to sintering of the SiC particles. The fracture morphology of the porous SiC ceramic is shown in figure 1. Some sintering neck can be observed in figure 1 and this result indicate the achievement of sintering under the present condition. The porous SiC ceramic with the particle size of 10μm has a bending strength of 30MPa.
Table 1. The weight changes and porosity of the porous SiC ceramic.

| SiC Particle Size (μm) | Weight Change of the SiC Ceramic after Sintering (wt %) | Porosity of the SiC Ceramic (%) | Weight Change of the SiC Ceramic after Modifying with W Coating (wt %) |
|-----------------------|------------------------------------------------------|---------------------------------|---------------------------------------------------------------|
| 10                    | 8.0                                                  | 39.6                            | 12.0                                                          |
| 50                    | 4.3                                                  | 40.1                            | 15.0                                                          |
| 150                   | 2.4                                                  | 40.5                            | 17.0                                                          |

Figure 1. The fracture morphology of porous SiC ceramic (SiC 10μm), a) morphology; b) details in a.

After modification by sol and hydrogen reduction, the weight of porous SiC ceramic increase to a certain extent (table 1). The modified SiC ceramic change from dark green to dark grey. Figure 2 shows the fracture morphology of the modified porous SiC ceramic. As can be seen from the figure, after modification by ammonium metatungstate sol, a large number of fine particles (about 1μm) are formed on the surface of SiC phase. These particles are evenly distributed on the surface of SiC phase and present a bright white color. The picture here is that because it is a morphological image obtained in backscattering mode, the brighter spot with larger atomic number should be the substance with larger atomic number. The XRD result reveal that the brighter spots should be the W particles (figure 2b).

3.2. Microstructures and properties of the SiC/Cu composites

Figure 3 is the XRD results of the composites with different sizes of SiC particles. It can be seen from the figure that the phases in the composites are WC, SiC, Cu and Cu-Si compounds. The formation of WC indicates that the W particles on the SiC phase react with SiC at high temperature in the infiltration procedure. The reaction is consistent with the results of Baud [9]. Meanwhile, the residual Si enters into the Cu melts, part of them form solid solution of Cu and the others form the Cu-Si compounds.
The microstructures of the composites with different size of SiC particles are shown in figure 4. It can be seen that a large number of gray particles and a small number of white bright spots are evenly distributed in the white matrix. Considering the backscattering mode of the SEM image, the SiC particles should be grey and the WC the bright. The matrix is Cu-Si alloys. It is noticed that the WC exists around the SiC particles in the composite with fine SiC particles (figure 4a), but at the boundaries between the SiC particles and the matrix in the composite with coarser SiC particles (figure 4c). What the SiC phase looks flat indicate that the interfacial reaction is restricted on the surface of SiC particles, and not take place inside the particles.

In present study, a pressureless infiltration of the porous SiC ceramic without W coating modification was also carried out but failed because of no infiltration of Cu taking place. However, the combination between the SiC and the matrix looks fine, as shown in figure 4. As a result, the wettability between the modified SiC ceramic and Cu melt is good, the modification of SiC ceramic by W is effective.
The thermal conductivity and bending strength of the composites with different size of SiC particles are shown in figure 5. It can be seen that the thermal conductivity increases from 35W/(m·K) to 45W/(m·K) with the increase of the size of SiC particles, but the bending strength decreases sharply from 200 MPa to 30 MPa. In composites, thermal conductivity is determined by the thermal conductivity of each phase and its interface structure. The thermal conductivity of pure copper is 398 W/(m·K) and that of SiC is 120 W/(m·K). So the actual thermal conductivity of the composites in present study are at a low level, but consistent with the results reported so far [6,11,12]. It is usually considered that the reduction of the thermal conductivity of the composites are due to the existence of the large number of interfaces in the composites. In fact, the present results show that the thermal conductivity of the composites increases with the increase of the size of SiC particles, accompanied with the reduction of the interface in the composites. In addition the reduction of the bending strength is due to the coarser SiC particles according to the theory of strength.

![Figure 5. Thermal conductivity and bending strength of the SiC/Cu composites](image)

4. Conclusion
The porous SiC ceramics with a porosity of about 40% are prepared by oxidation sintering at 1350°C for 1h. The Sol and hydrogen reduction methods are effective in W metallization on the surface of holes in porous SiC ceramic. After the metallization, small W particles of about 1 μm distribute evenly on the surface of SiC particles in the ceramic. Because of the modification of W, a complete infiltration of the Cu melt into the porous SiC ceramic is achieved under a vacuum of 10⁻¹Pa at 1350°C. W particles react with SiC at high temperatures during the infiltration process, and WC particles are formed on the Cu-based alloy matrix. As the size of SiC particles increases from 10 μm to 150 μm, the thermal conductivity of the composite increases from 35 W / (m·K) to 45 W / (m·K), but the bending strength rapidly decreases from 200 MPa to 30 MPa.

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