Thermophysical properties of porous SiC ceramics fabricated by pressureless sintering

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Abstract

Highly porous SiC with approximately 30–41% porosity was fabricated by pressureless sintering without sintering additives at temperatures in the range 1700–2000 °C. Thermal diffusivities, specific heats, thermal conductivities and thermal resistivities of sintered samples are reported for temperatures from room temperature to 1000 °C. The thermal diffusivities and thermal conductivities of all samples decreased significantly with increasing temperature over this range, whereas specific heats and thermal resistivities increased. At any given temperature, the greater the porosity of the SiC, the lower the thermal conductivity.

Keywords: SiC; Laser flash method; Thermal diffusivity; Thermal conductivity; Porosity

1. Introduction

Silicon carbide (SiC) ceramics have been intensively studied for use in structural applications because of their excellent oxidation resistance, high mechanical strength at elevated temperature, high hardness, high corrosion resistance, high thermal conductivity and high thermal shock resistance imparted by the strong covalent Si–C bonds [1]. Examples of the applications in which SiC ceramics are used include seal pumps for automotive water pumps, composite armor protection, heat exchangers, bearings, abrasion-resistant components such as blast nozzles and centrifuge tiles, as well as furnace heating elements.

More recently, porous SiC ceramics have been proposed as replacement materials for cordierite in honeycomb and ceramic foams for ceramic monolithic catalyst supports because of their superior mechanical and thermo-chemical properties [2–5].

Several studies on the mechanical properties [6–9] and sintering behavior [10–12] of SiC have been reported, since the strong covalent bonds between Si and C make sintering difficult. Important factors governing the use of SiC at high operating temperatures or in severely fluctuating thermal environments include thermophysical properties such as thermal diffusivity, specific heat and thermal conductivity. Some measurements of thermal conductivity of dense SiC have already been reported [13–15], as has the fabrication of porous SiC ceramics [16–19]; however, the influence of microstructure and temperature on the thermophysical properties of porous SiC has not been investigated fully. To help fill this gap, in this paper we examine the influence of porosity and temperature on thermal diffusivity, specific heat, thermal conductivity and thermal resistivity of porous SiC ceramics fabricated at different sintering temperatures by pressureless sintering.

2. Experimental procedure

Fine SiC (ultra-fine degree, Ibiden Co.) with a mean particle size of 0.34 μm, specific surface area of 18.8 m²/g and composition shown in Table 1 was used as the starting powder. The powder was uniaxially pressed at 1 MPa to form rectangular prismatic samples 60 mm × 30 mm × 5 mm in size; these were further cold isostatically pressed at 200 MPa. Samples were then placed in a graphite crucible and sintered in a graphite-heating furnace at 1700–2000 °C for 2 h, under vacuum. Sintered samples were...
then cut and polished into disc shapes 10.0 mm in diameter and 2 mm thick. The relative density of the specimens was determined by the Archimedes method using water as the immersion medium. Phase analysis of the sintered samples was performed by X-ray diffraction (XRD, PW-1700, Philips Co.) using CuKα radiation. The microstructures were examined by scanning electron microscopy (SEM, S-4500, Hitachi Co.).

The porosities of the samples were obtained using the difference between the measured densities of the sintered samples and the theoretical density of SiC (3.16 g/cm³). Thermal diffusivity of the specimens was measured in a vacuum chamber over the temperature range 25–1000°C intervals by the laser flash technique [20] using a thermal analyzer (Kyoto Densi, LFA-501). The specimens were sputter coated with a thin layer of silver and colloidal graphite spraying to ensure complete and uniform absorption of the laser pulse prior to thermal diffusivity measurements.

The laser flash method involves heating one side of the sample with a laser pulse of short duration and measuring the temperature rise on the rear surface with an infrared detector. The thermal diffusivity is determined from the time required to reach half the maximum temperature of the resulting temperature rise curve for the rear surface [20]. The method is illustrated in Fig. 1.

The specific heat of the specimens was measured, also over the same temperature range during heating, using a differential scanning calorimeter (Netzsch, DSC 404C) with single-crystal alumina under argon gas used as a reference. The thermal conductivity (k) of each specimen was then obtained from the following relationship [20]:

\[ k = \alpha C \rho, \]  

where \( \alpha \) is the thermal diffusivity, \( C \) is the specific heat and \( \rho \) is the density of the specimen.

### 3. Results and discussion

#### 3.1. Microstructure

The relative porosity of sintered SiC samples as a function of sintering temperature is shown in Table 2. All samples had porosities in the range 30–41% of theoretical density. Porosity decreased with increasing sintering temperature, as expected, because of the higher sintering rates at higher temperature.

Fig. 2 shows typical microstructures of sintered SiC as a function of sintering temperature. All samples consisted of equiaxed grains approximately 1.2–3.3 μm in diameter, and were highly porous. The grain size of the samples increased with increasing sintering temperature, as the higher temperatures allow faster grain growth to occur.

In fact, the surface of SiC is easily oxidized so that a thin layer of silica sits on the SiC surface. A small amount of amorphous silicate-type phases are also formed in the present samples owing to reaction between silica on the SiC surface and oxide impurities present in the starting powder (see Table 1) [21]. Amorphous silicate phases act as sintering aids, accelerating the sintering of SiC at high temperature through a mechanism akin to liquid-phase sintering.

Fig. 3 shows XRD patterns of the sintered SiC samples. The XRD patterns indicate that the samples are predominantly β-SiC. It has previously been reported that the β-phase of SiC exhibits equiaxed grains [14].

#### 3.2. Thermophysical properties

Fig. 4 shows the thermal diffusivities of the present specimens as a function of temperature. At room temperature, the thermal diffusivity of sample A is slightly lower than those of samples B, C and D, but at higher temperature this difference disappears. It can therefore be concluded that the effect of microstructure on thermal diffusivity of SiC samples is negligible at elevated temperature, regardless of differences in porosity.

In addition, the thermal diffusivities of all samples decrease dramatically with increasing measurement temperature. The reason for this is the enhancement of phonon scattering at higher temperatures, which results in a

| Samples | Sintering temperature (°C) | Porosity (%) |
|---------|---------------------------|--------------|
| A       | 1700                      | 40.5         |
| B       | 1800                      | 39.6         |
| C       | 1900                      | 38.3         |
| D       | 2000                      | 30.4         |
decrease in thermal diffusivity. This observed temperature dependence is consistent with similar observations made on porous ZrO$_2$ coatings [22] and dense sintered SiC ceramics [15,16].

Fig. 5 compares the specific heats of all samples as a function of temperature. It can be seen that the specific heats for all specimens increase gradually with increasing temperature. This trend is similar to that found for dense SiC ceramics [16]. At any given temperature, there appears to be no distinct difference in specific heat between the four samples examined in this study. Consequently, these
suggestion that temperature is a predominant factor rather than microstructure on influence of thermal diffusivity and specific heat.

Fig. 6 shows thermal conductivities of sintered SiC samples from room temperature to 1000 °C. The thermal conductivities decrease significantly from 83 to 18 W/m K with increasing temperature over this temperature range. The thermal conductivities of the porous samples are well below that of fully dense SiC, namely 108–169 W/m K [15–17]. At room temperature, the thermal conductivity of SiC increases with decreasing porosity, i.e., increasing sintering temperature, as shown in Table 2. This indicates that porosity affects thermal conductivity. This result is consistent with studies showing that porosity and defects are a major factor in the reduction of the thermal conductivity of SiC coatings deposited by CVD [23], ZrO2 coatings deposited by EB-PVD [24], and Si/SiC composites [25]. Simulation studies have also shown that the thermal conductivity of a porous material strongly depends on the volume fraction, shape and spatial distribution of the pores [26].

These two factors affecting the thermal conductivity, namely temperature and porosity, can be discussed in terms of phonon-scattering theory. First, consider the influence of temperature on a body with constant porosity. The thermal conductivity of a solid can be expressed as [27]

\[ k_p = k_i \propto \frac{1}{T}, \]

where \( k_i \) is the intrinsic conductivity and \( T \) is the absolute temperature. It can easily be seen why thermal conductivity decreases with increasing temperature based on this equation. Second, consider the porosity of a material. Thermal conductivity through a solid is controlled largely by phonon transport; this relies on the propagation of thermal vibrations through the crystal lattice across a temperature gradient, and is dramatically reduced when large numbers of point defects and extended defects (e.g., dislocations) are present. Pores act as major disruptions to the crystal lattice (i.e., are large defects) and thus have a strong effect on thermal conductivity. When defects are present in a solid, the thermal conductivity is given by [28]

\[ k_p = k_i - \delta k_p, \]

where \( \delta k_p \) is the decrease in conductivity that results from phonon scattering by the defects. Put another way, the thermal conductivity is reduced because of a decreased mean free path for phonon transport as a result of phonon scattering at pores. In the first successful model for thermal conductivity, Debye used an analogy of the kinetic theory of gases to derive an expression for the thermal conductivity [29],

\[ k = \frac{1}{3} Cv\ell, \]

where \( C \) is the specific heat, \( v \) is the speed of sound in the object and \( \ell \) is the mean free path of a phonon. According to Eq. (4), if the mean free path is decreased, the thermal conductivity can also be seen to decrease. Together Eqs. (3) and (4) explain why the thermal conductivity of the highly porous sample A is less than that of samples B–D.

To analyze the thermal conductivity results more thoroughly, a quantitative evaluation of the phonon mean free path is necessary. The phonon mean free path is related directly to thermal diffusivity, \( \alpha \), and elastic wave velocity, \( v \), by [30]

\[ l = \frac{3\alpha}{v}, \]

where \( v \) is roughly constant with respect to temperature and can be obtained from the modulus and density of the solid, viz \( v = (E/r)^{1/2} \). The elastic wave velocity in SiC was determined to be \( 1.16 \times 10^6 \) cm/s [30].

Fig. 7 shows the temperature dependence of the phonon mean free path in porous SiC specimens. The phonon mean free path decreased with increasing temperature as well as increasing density.

To evaluate the heat transport behavior, the thermal resistivities of the specimens was obtained by taking the reciprocal of the thermal conductivities. Fig. 8 shows the thermal resistivities of porous SiC as a function of temperature. The thermal resistivities increase linearly with increasing temperature. This indicates that heat transport is indeed by lattice thermal conduction, i.e., phonon diffusion. It is known that even in a hypothetical, defect-free solid, the mean free path of a phonon decreases
and the intercept of imperfections in the solid. For an ideal dielectric solids increase in phonon scattering caused by a higher volume of defects and, in our case, pores. From our conductivity measurements, a value of $b = 1.55\text{–}1.73 \times 10^{-2}\text{m K/W}$ is obtained using Eq. (6).

4. Conclusions

Porous-sintered SiC samples were fabricated by pressureless sintering using only SiC powder without sintering additives. The sintered specimens had a highly porous microstructure (30–41% porosity) with equiaxed grains typical of β-SiC. The specific heats and thermal resistivities of the samples increased gradually with increasing temperature. This reveals a strong dependence of thermal diffusivity and thermal conductivity on porosity and temperature. The thermal resistivities of the SiC samples increased linearly with increasing temperature because as the fraction of pores, which decreases the mean free path of phonons diffusing through the solid.

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