Journal of the European Ceramic Society 21 (2001) 2089–2093

www.elsevier.com/locate/jeurceramsoc

Electrical and thermal conductivity of liquid phase sintered SiC

Eduard Volz[a,*], Andreas Roosen[a], Wolfgang Hartung[b], Albrecht Winnacker[b]

[a]Institute of Glass and Ceramics, Department of Materials Science, University of Erlangen-Nuremberg, 91058 Erlangen, Germany
[b]Institute of Electrical Engineering Materials, Department of Materials Science, University of Erlangen-Nuremberg, 91058 Erlangen, Germany

Received 4 September 2000; received in revised form 21 November 2000; accepted 15 December 2000

Abstract

Commercial silicon carbide ceramics are semi-conductors. To obtain SiC ceramics with insulating properties, a synthesised SiC powder which was doped with vanadium and boron to get insulating behaviour due to compensating mechanism, and in addition a commercial powder was used. Both powders were pressureless sintered by liquid phase sintering. Different packing powders were used to influence the electrical behaviour of the dense SiC ceramics. The influence of these conditions on the electrical and thermal conductivity are described. Densification of SiC by a solution-precipitation mechanism in the temperature range around 1900°C results in a decrease of resistivity. The resistivity of the commercial powder could be improved by using a vanadium based packing powder. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Electrical conductivity; SiC; Sintering; Thermal conductivity

1. Introduction

Silicon carbide (SiC) is a structural material for high-temperature and mechanical applications due to its high oxidation resistance and fracture strength at elevated temperatures, excellent thermal conductivity and low coefficient of thermal expansion. These excellent properties have their origins in the strong covalent bonding character. The high covalency bonds and the low self-diffusion coefficient make pressureless sintering of SiC impossible without sintering additives. Prochazka[1] first sintered SiC pressureless with additions of boron and carbon via a solid-state-sintering mechanism up to 98% of theoretical density. In the early 1990s Mulla[2] showed the possibility of sintering SiC without pressure at temperatures between 1850 and 2000°C by the formation of a liquid-phase of Al_2O_3 and Y_2O_3 additions. After that, research has focused on improving the mechanical properties of SiC.[3,4] Also many investigations have been done to study coarsening of the microstructure in liquid-phase-sintered (LPS) SiC[5,6] and to understand the effect of different packing powders on the densification behaviour.[7,8]

The aim of this work is to improve the resistivity of LPS SiC. Due to its high thermal conductivity and low coefficient of thermal expansion, which is close to that of Si. SiC ceramics would be ideal substrates for microelectronic applications[9] if they were electrical insulating. The high bandgab of 3.3 eV and high breakdown strength of 3 MV/cm of SiC makes it of interest for electrical power devices. The resistivity of SiC single crystals can be adjusted up to 10^9 Ωcm at 200°C by doping with donors (nitrogen, phosphorus) and acceptors (aluminum, boron) during crystal growth.[10] Transition metals like V produce deep intrinsic electronic levels in the bandgap which makes it possible to produce SiC single crystals and wafers with a resistivity in the range of 10^{15} Ωcm at room temperature. This is the basis for the experimental approach to prepare intrinsic isolating SiC ceramics.

2. Powder synthesis

As starting powders for the SiC powder synthesis, high purity carbon (SGL Carbon, Germany) and silicon (MEMC, Pasadena, USA) in a molar ratio of 1:1 were blended in a mixer. In a graphite crucible the mixture was inductively heated in an evacuated furnace up to 1200°C. The synthesis took place under argon atmosphere

---

[*] Corresponding author. Tel.: +49-9131-8527554; fax: +49-9131-8528311.

E-mail address: volz@ww.uni-erlangen.de (E. Volz).

PII: S0955-2219(01)00178-9

and started above the melting point of silicon. The synthesis temperature reached 1900°C, because of the exothermic synthesis reaction and was aborted after 30 min. Different experiments were carried out to improve the specific surface area of the powder. A shorter synthesis time could increase the specific surface area up to 1 m^2/g by suppressing the recrystallisation of SiC grains. Before the synthesis the dopants were introduced to the mixture to allow electrically active integration into the SiC lattice. Boron was used to compensate unavoidable nitrogen impurities and VSi_2 to produce a semi-insulating SiC powder. The resulting electronic active levels are not discussed in this work. This is described in[11] where the thermally stimulated luminescence experiments were used to characterise the electronic levels in SiC powder and SiC single crystals.

3. Experimental procedure

The doped powder had to be milled in an attrition mill for 20 h to increase the sintering activity. High purity isopropanol and SiC milling balls were used. By this measure the specific surface area could be increased to about 10 m^2/g with an average particle size of 1.0 μm. A typical grain morphology is shown in Fig. 4. As a second starting powder a commercial Acheson α-SiC powder (Grade UF-25, H. C. Starck, Glosar, Germany) with a specific surface area of 25 m^2/g and d_{50} value of 0.5 μm was used. For LPS SiC starting powders and 10 vol.% of the sinter additives Al_2O_3 (Al_2O_3 reinst, Riedel-de Haen Seelze, Germany) and Y_2O_3 (Stanford, San Mateo, USA) in the molar ratio of 3:5 were mixed in an attrition mill for 4 h. The mixture was dried in air and sieved through a screen of 0.75 mm. Green bodies were produced by cold uni-axially pressing at a pressure of 125 MPa. The pressed pellets were placed inside a loose SiC powder bed in a closed graphite crucible. Different SiC packing powders were used, at first a powder bed consisting of pure SiC powder (UF-25 Starck) and secondly a mixture of 99 wt.% SiC (UF-25) and 1 wt.% VSi_2 (MaTecK, Jülich, Germany). In the crucible the SiC packing powder was bedded at the bottom and at the top with Al_2O_3 powder. Sintering was carried out in a graphite resistance furnace (FCT, Type FSW) in a flowing argon atmosphere at a heating and cooling rate of 10°C/min. The sintering temperature was between 1800 and 1950°C with a holding time of 30 min.

The sintered density was determined by the Archimedes method. According to the rule of mixtures the theoretical density of the $SiC/Al_2O_3–Y_2O_3$ mixture was calculated. The SiC ceramics were polished by ceramographic techniques to create a flat surface for electrical conductivity and thermal conductivity measurements. The microstructures of fracture surfaces were observed by scanning electron microscopy (SEM).

Electrical conductivity was determined in a three-point geometry in accordance to DIN 53482/VDE 0303 at room temperature. The applied voltage was in the range of 0–80 V. The resulting current through the specimens was measured with a highly sensitive electrometer. The specific resistance was calculated from the current based on the geometry of the specimens.

A flash method [12] was used to measure the thermal conductivity in accordance to DIN EN 821/2 of SiC ceramics at room temperature. A short-duration light pulse is absorbed at the upside of the ceramic. At the rear surface, a high resolution pyrometer determined the raise of temperature in dependence of time. The thermal diffusivity is calculated by the half of the maximum temperature rise in accordance to Parker[12] and the thermal conductivity by the product of thermal diffusivity, heat capacity and density.

4. Results and discussion

Sintering and densification of SiC starts with the formation of a liquid-phase of the sintering additives Al_2O_3 and Y_2O_3. The temperature of this eutectic decreases with the presence of SiO_2 located on the surface of the SiC grains. A solution-precipitation process of the SiC grains in the liquid phase is responsible for the densification. However, the specific surface area of the starting powder has also an important influence on the densification. Fig. 1 presents the sintered densities of the LPS SiC specimen from the two starting powders. LPS samples of both powders reach densities up to the theoretical density at temperatures of 1900°C. At a temperature of 1950°C only a little further densification takes place. In the temperature range of 1800–1850°C the two powders show a different densification behaviour. The ceramics of the commercial powder reach a density of 80% of the

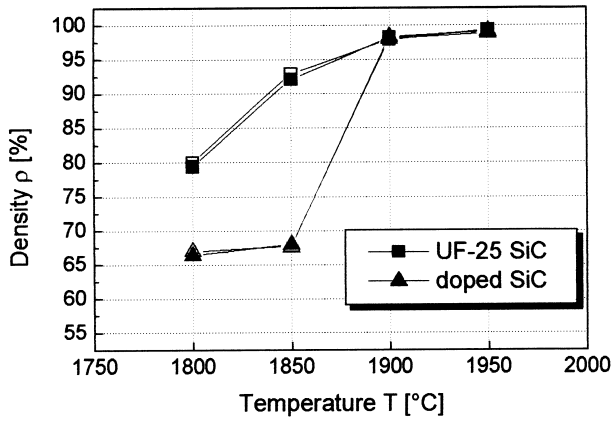

Fig. 1. Density of sintered SiC specimens in different packing powders as a function of sintering temperature. Filled out dots represent specimen sintered with VSi_2 and the others without VSi_2 in the SiC packing powder.

theoretical density at a temperature of 1800°C and the density increases to 92% at a temperature of 1850°C. Densification of the specimens from the doped powder exhibit much lower densities around 67% of the theoretical density in the same temperature range. This different densification behaviour can be explained by the different specific surface areas of the powders. The commercial powder with a specific surface area of 25 m^2/g has a much higher sinter activity as the doped powder with 10 m^2/g. Therefore, a lower temperature is sufficient to start the densification process. To densify a specimen of the doped powder, temperatures of 1900°C are necessary.

Fig. 2 displays the specific resistivity of the SiC specimen sintered at different temperatures using different powder beds. For both powders a reduction of the specific resistivity with increasing sinter temperature independent of the used powder bed is observed. In the sintering temperature range of 1850–1950°C the resistivity of the specimen changes slightly and has values of approximately 1×10^4 Ωcm. At a sinter temperature of 1800°C sintering in a pure SiC powder bed increases the resistivity nearly two orders of magnitude. In addition the powder bed has a significant influence on the resulting resistivity. All specimens sintered in a powder bed mixture of SiC and VSi_2 exhibit higher values of resistivity. Especially at a sinter temperature of 1800°C the resistance of the SiC ceramics increases about 4 orders of magnitude and the value is close to the value for an insulator.

In Fig. 3 the specimen from the doped SiC powder shows a similar trend of the resistivity in dependence of the sintering temperature. At a sintering temperature of 1800°C the resistivity is significantly higher as in the range of 1850–1950°C. In this range there is only a small change in resistivity even if the density increases about 30%. The type of packing powder has no influence on the resulting resistivity of the specimen with the doped powder, which is in contrast to the commercial starting powder.

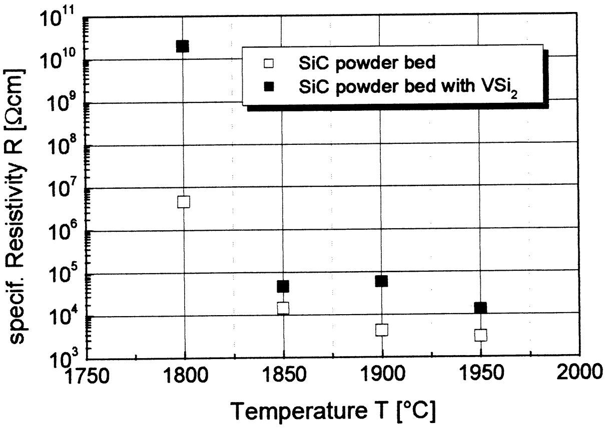

Fig. 2. Specific resistivity as a function of sintering temperatures for UF-25 as starting powder sintered in different packing powders.

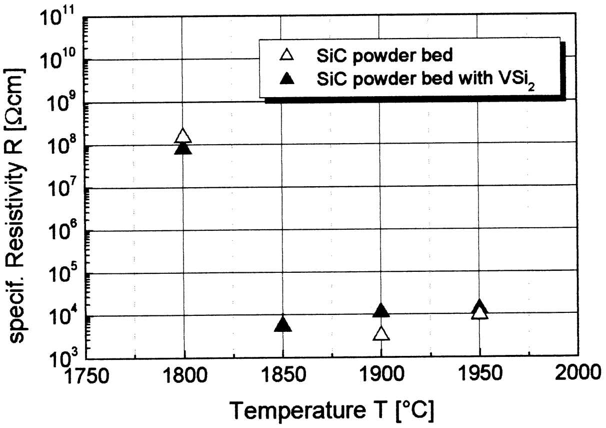

Fig. 3. Specific resistivity as a function of sintering temperatures for doped SiC powder sintered in different packing powders.

It is clearly shown in Fig. 2 that a mixture of SiC and VSi_2 in the powder bed increases the resistivity of a specimen of commercial SiC powder. The doped SiC powder does not show the same behaviour. It is suggested, that VSi_2 introduced in a packing powder changes the sintering atmosphere by producing a vapour pressure of evaporated VSi_2 in the crucible. The microstructure of such sintered SiC is not changed in comparison to SiC sintered in a powder bed without VSi_2 (Fig. 4). On the one hand the evaporated VSi_2 can modify grain boundaries of the SiC grains, on the other hand a diffusion of vanadium into the lattice of the SiC grains is imaginable. Vanadium has been found to occupy silicon substitutional sites. The huge atom diameter permits only a slight solubility (3×10^{17} cm^{-3}) of vanadium in SiC.[11] The modification of grain boundaries without a change in microstructure is possible, e. g. thin amorphous intergranular films could be formed. But this effect should be observed in sintered SiC of both starting powders and should result in both cases in an increase of resistivity. A possible mechanism is the diffusion of vanadium into SiC grains in spite of the well known low diffusion coefficient and low solubility. In the SiC grains vanadium acts as an amphoteric dopant providing two midgap levels and due to the compensation mechanism this results in a higher resistivity.

Diffusion of vanadium should not be possible in the doped SiC powder, because the maximum solubility was already reached during the powder synthesis. But the specimen from the doped starting powder exhibit a lower resistivity than the SiC ceramics from the commercial powder. It is possible that the long milling in the attrition mill contaminates the SiC powder by wear loss of the grinding media.

All specimens sintered at a temperature of 1800°C show a much higher resistance independent of the starting powder and packing powder. As shown in Fig. 4 at 1800°C a solution-precipitation process with a

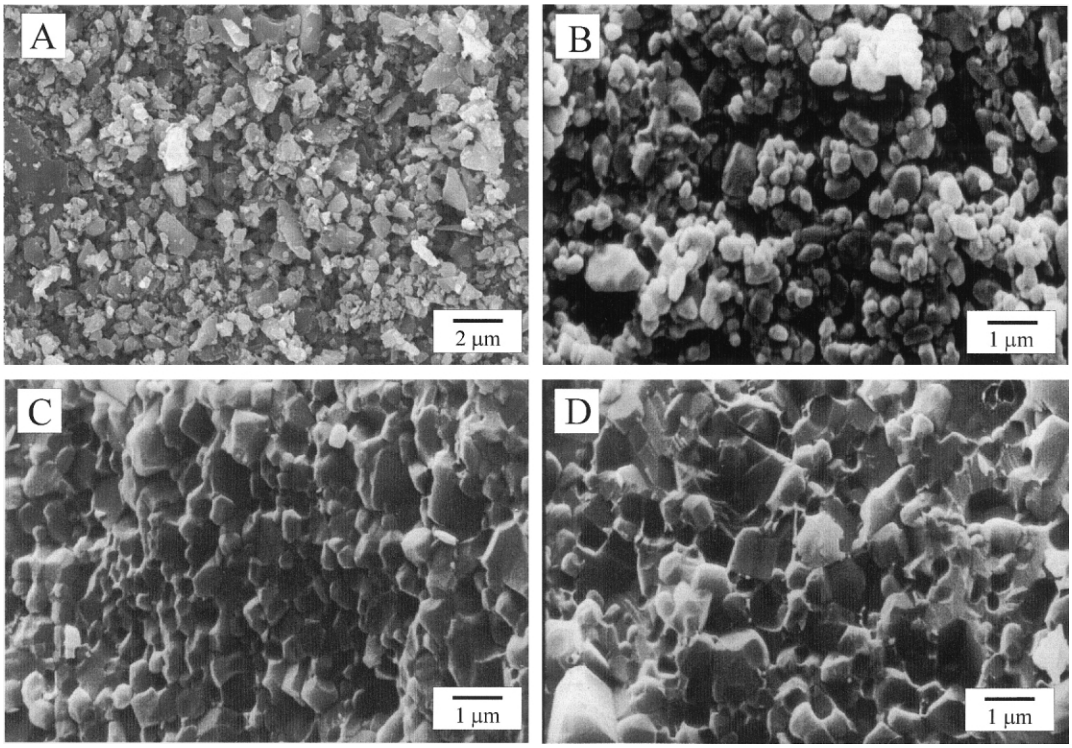

Fig. 4. SEM pictures of the synthesised SiC powder (A) after milling and fracture surfaces of SiC ceramics from UF-25 powder sintered at different temperatures in a mixture of SiC and VSi_2 powder bed. (B) 1800°C, (C) 1900°C, (D) 1950°C.

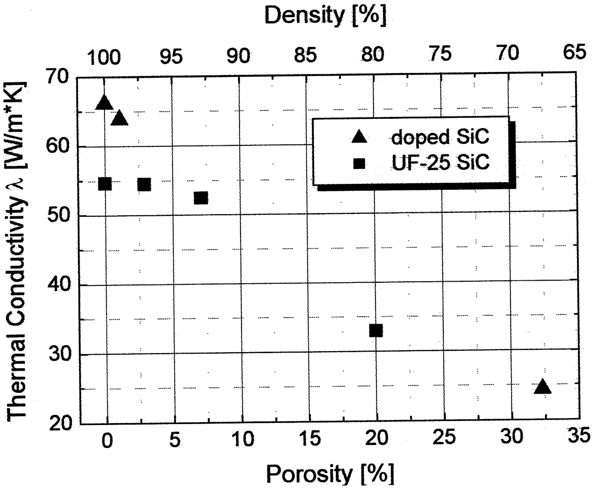

Fig. 5. Thermal conductivity as a function of porosity for SiC ceramics from different starting powders with VSi_2 in the powder bed.

pronounced grain growth does not take place. In this stage SiC is only consolidated by particle rearrangement, the reached densities verify this mechanism. A better rearrangement at 1800°C is possible for the starting powder with the higher specific surface area and smaller particle size, which causes a higher density. At higher temperatures densification accelerates by solution-precipitation of the whole microstructure. Consequently the high resistivity of the specimens at 1800°C is explained by the different sintering mechanism. At higher temperatures impurities are incorporated into the SiC lattice, which decreases the resistivity of the samples of both powders.

Fig. 5 shows the measured thermal conductivities of the sintered SiC ceramics. For both starting powders the thermal conductivity increases with lower porosity. Specimen from doped starting powder have a higher thermal conductivity at comparable porosities and reach a value of about 70 W/mK. SiC ceramics from commercial powder have thermal conductivity of 55 W/mK in case of a small porosity. The higher thermal conductivity of the SiC ceramics from the doped powder is due to the larger grain size in these ceramics. This allows phonon dispersion over a larger distance with less scattering. The different packing powders have no significant influence on the thermal conductivity.

5. Conclusion

The densification of a boron/vanadium doped and of a commercial SiC powder was possible by liquid phase sintering. Due to the lower sintering activity the doped powder demands higher sintering temperature. The sintered SiC ceramics have a thermal conductivity at neglectable porosity of 55–70 W/mK. It was shown, that VSi_2 in the packing powder increases the specific resistivity of SiC ceramics from the commercial powder to a value of 2×10^{10} Ωcm. Influences from volatilised

VSi_2 on grain boundaries and diffusion could not be explicitly explained. Further research is necessary to improve and explain the observed effects.

References

1. Prochazka, S., Sintering of silicon carbide. General Electrical Report 73 CRD 325, 1973.
2. Mulla, M. A. and Krstic, V. D., Low-temperature pressureless sintering of β-silicon carbide with aluminum oxide and yttrium oxide additions. *Ceram. Bull.*, 1991, **70**, 439–443.
3. Lee, S. K. and Kim, C. H., Effects of α-SiC versus β-SiC starting powders on microstructure and fracture toughness of SiC sintered with Al_2O_3–Y_2O_3 additives. *J. Am. Ceram. Soc.*, 1994, **77**, 1655–1658.
4. Kim, J.-Y., Kim, Y.-W., Mitomo, M., Zhan, G.-D. and Lee, J.-G., Microstructure and mechanical properties of α-silicon carbide sintered with yttrium-aluminium garnet and silica. *J. Am. Ceram. Soc.*, 1999, **82**, 441–444.
5. Sigl, L. S. and Kleebe, H.-J., Core/rim structure of liquid-phase-sintered silicon carbide. *J. Am. Ceram. Soc.*, 1993, **76**, 773–776.
6. Ye, H., Pujar, V. V. and Padture, N. P., Coarsening in liquid-phase-sintered α-SiC. *Acta Mater.*, 1999, **47**, 481–487.
7. Lee, J.-K., Tanaka, H. and Kim, H., Movement of liquid phase and the formation of surface reaction layer on the sintering of β-SiC with an additive of yttrium aluminium garnet. *J. Mater. Sci. Lett.*, 1996, **15**, 409–411.
8. Winn, E. J. and Clegg, W. J., Role of the powder bed in the densification of silicon carbide sintered with yttria and alumina additives. *J. Am. Ceram. Soc.*, 1999, **82**, 3466–3470.
9. Roosen, A., Ceramic substrates: trends in materials and application. *Ceram. Trans.*, 2000, **106**, 479–492.
10. Choyke, W. J. and Pensl, G., Physical properties of SiC. *MRS Bull.*, 1997, 25–29.
11. Hartung, W., Analysis of electronic levels in SiC: V, N, Al powders and crystals using thermally stimulated luminescence. *Mater. Sci. Eng.*, 1999, **B61-62**, 102–106.
12. Parker, W. J. et al., Flash method of determining thermal diffusivity, heat capacity, and thermal conductivity. *J. Appl. Phys.*, 1961, **32**, 1679–1684.