ELSEVIER

Ceramics International 29 (2003) 961–965

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Dihedral angles in silicon carbide

Agnieszka Gubernat*, Ludosław Stobierski

Department of Advanced Ceramics, Faculty of Materials Engineering and Ceramics, University of Mining and Metallurgy, al. Mickiewicza 30, 30-059 Cracow, Poland

Received 11 February 2003; received in revised form 3 March 2003; accepted 10 March 2003

Abstract

The commonly accepted hypothesis says that the role of sintering activators such as carbon and boron consists in modifying the relation between the energy of surface and that of grain boundaries in SiC. This means that dihedral angles in samples containing one of the activators, both of them or none should be different. To verify this hypothesis we measured dihedral angles in all the mentioned cases. The observed values of dihedral angles were always much bigger than the limiting one of 60°. Moreover, they did not differ significantly and, according to the statistical analysis could be treated as constant. As a consequence our results contradict the opinion saying that the activators modify the energy of surface and grain boundaries.

Keywords: A. Sintering; D. Carbon; D. SiC; Dihedral angle

1. Introduction

The earliest and the commonly accepted hypothesis concerning the role of activators in SiC sintering is that formulated by Prochazka [1]. According to Prochazka the free energy changes of the sintered material are too small to bring about densification of pure silicon carbide grains. Therefore it is necessary to modify the surface energy and the energy of grain boundaries. Boron and carbon, in the S. Prochazka opinion, operate in this way. Carbon is believed to reduce silica on the surface of SiC grains due to which the surface energy of grains increases while boron segregating at grain boundaries is believed to decrease the grain-boundary energy. According to Young's equation the dihedral angle is:

$$\cos\frac{\phi}{2} = \gamma_{SS}/2\gamma_{SG} \quad (1)$$

where: ϕ—dihedral angle; λ_{SS}—grain-boundary energy; and λ_{SG}—energy of free surfaces.

The fundamental assumption of the earlier hypothesis is equivalent to the statement that the dihedral angle formed by a pore with the neighbouring grains is too small for the pore elimination by sintering. The ability of spontaneous pore elimination depends on the value of this angle. A pore surrounded by three grains can be eliminated when the dihedral angle is 60° while that surrounded by four grains—when dihedral angle is greater than 90° [2–4]. In a number of papers it is reported that the dihedral angles in the SiC materials free of boron and carbon exceed these limit values [5–7]. The doubts raised by those observations can be dispelled by systematic measurements of dihedral angles in pure materials and in materials doped with the activators.

2. Experimental

Investigations on the effect of activators on the value of dihedral angles were carried out with the following sintered materials:

- pure α-SiC;
- α-SiC + 0.5 wt.% of boron + 3.0 wt.% of carbon (SiC + 0.5%B + 3%C);
- α-SiC + 0.5 wt% of boron (SiC + 0.5%B); and
- α-SiC + 3.0 wt% of carbon (SiC + 3%C).

The sintered bodies were prepared using Starck Uf-15 α-SiC, Fluka (cat. no. 15580) amorphous boron, and

* Corresponding author. Tel.: +48-12-617-25-74; fax: +48-12-633-46-30.

E-mail address: gubernat@uci.agh.edu.pl (A. Gubernat).

0272-8842/03/$30.00
doi:10.1016/S0272-8842(03)00053-1

phenol-formaldehyde resin, Novolak (Organika-Sarzyna-Poland). The thermogravimetrically determined carbon residue after pyrolysis of the resin was 50%. The raw materials blended in adequate proportions were homogenized in ethyl alcohol or in an alcoholic solution of the resin for 12 h in a ball mill with tetrafluoroethylene balls. After the homogenizing treatment and evaporation of alcohol the powder mixture was granulated and pressed into cylindrical pellets, 20 mm in diameter and 8 mm thick. The uniaxial compaction performed at a pressure of 150 MPa in a steel die was followed by isostatic pressing at 300 MPa. All the samples were annealed at 2150 °C. First the materials were heated to 1200 °C in vacuum ($\sim 10^{-2}$ mbar) at a rate of 15 °C/min and then to 2150 °C—in flowing argon (20 ml/min) at a rate of 10 °C. Finally they were kept at this temperature for 60 min.

The cross-sections of the polished samples were etched in fused potassium salts (75%KOH + 25%KNO_3) at 480 °C to reveal grain boundaries. Then SEM micrographs were taken. They were used in dihedral angles measurements.

3. Measuring method

The measurements of the median value of dihedral angles were carried out according to the procedure developed by Riegger and Van Vlack [8]. For each composition 50 observed values of dihedral angles were measured on the microphotographs. Then the results of measurements were presented in the form of cumulative curves. The median value of dihedral angle was found graphically from the curves.

4. Results

Fig. 1 shows scanning microphotographs of the investigated samples. The cumulative curves for the following composition: SiC + 0.5%B; SiC + 3%C and pure SiC are presented in Fig. 2 but Fig. 3 demonstrates the cumulative curve for the composition containing both activators. Table 1 presents the median values of dihedral angles determined from curves in Fig. 2 and the values of the $\gamma_{SS}/2\gamma_{SG}$ ratio calculated from the median values of dihedral angles at using the Young's equation

Table 1
The median value of dihedral angle and $\gamma_{SS}/2\gamma_{SG}$ ratio (on the ground of the median dihedral angle value was calculated) for the following systems

	pure SiC	SiC + 0.5%B	SiC + 3%C
dihedral angle ϕ [deg.]	120.5° ± 5°	110° ± 5°	111° ± 4°
$\gamma_{SS}/2\gamma_{SG}$	0.50	0.57	0.57

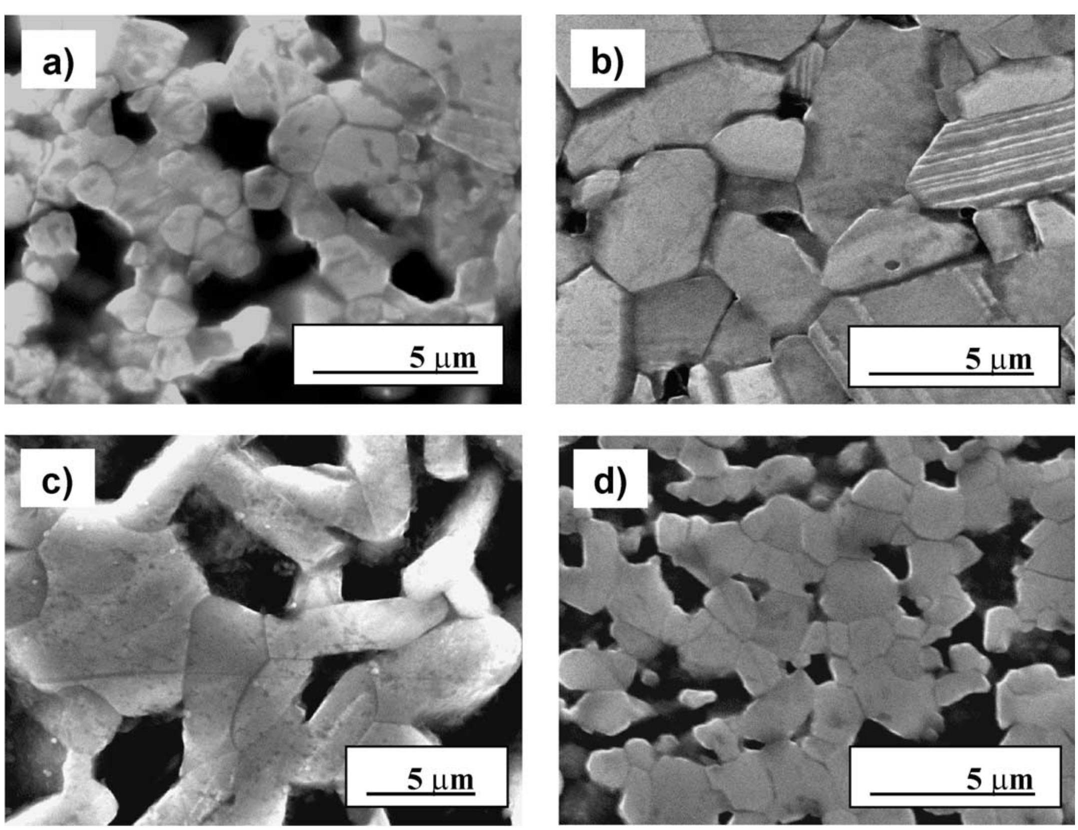

Fig. 1. SEM micrographs of samples which were used to dihedral angle measurements: (a) pure SiC; (b) SiC + 3%C + 0.5%B; (c) SiC + 0.5%B; (d) SiC + 3%C.

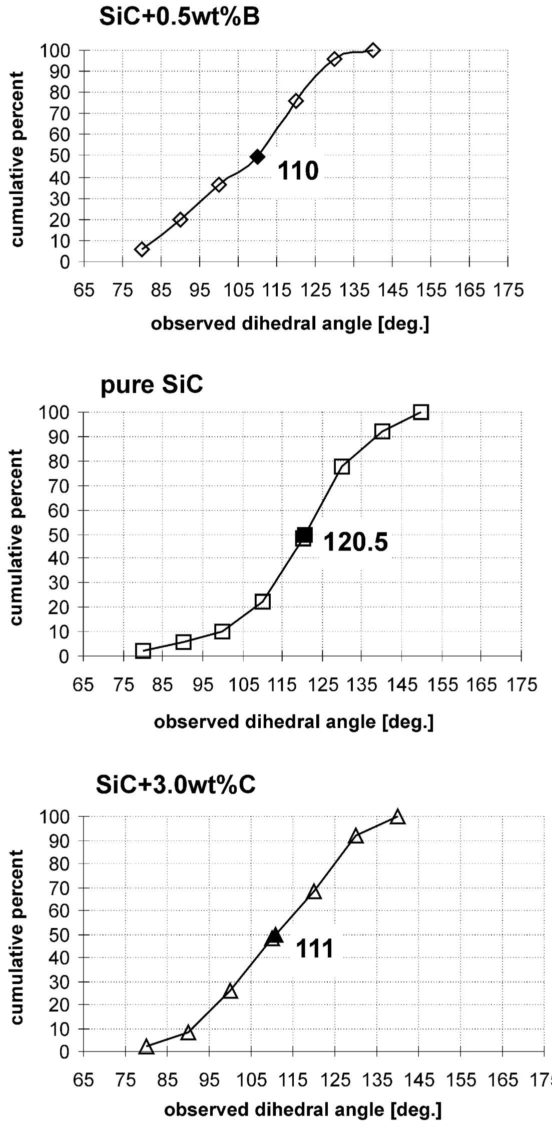

Fig. 2. Cumulative distributions of the observed dihedral angles for the following compositions: SiC containing 0.5 wt.% of boron; SiC containing 3 wt.% of carbon and pure SiC (the median values of dihedral angles are indicated in black).

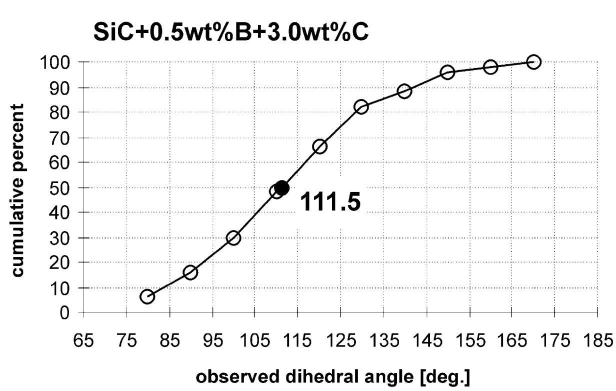

Fig. 3. Cumulative distributions of the observed dihedral angles for the SiC samples containing 0.5 wt.% of boron and 3.0 wt.% of carbon (the median value of dihedral angle are indicated in black).

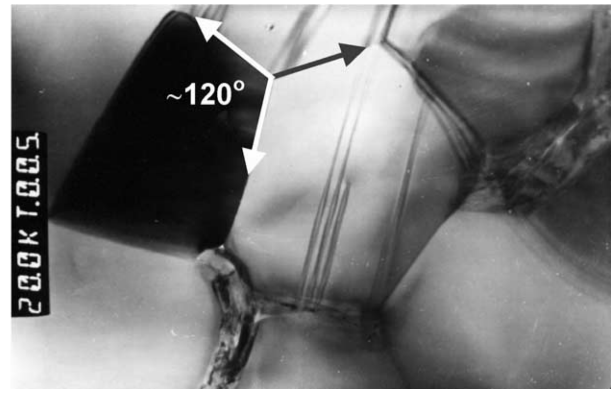

Fig. 4. TEM micrograph of sintered body containing 0.5 wt.% of boron and 4 wt.% of carbon (magnification 20,000×).

as well as standard deviation. It should be emphasized that the measured observed values of dihedral angles as well as their the median values in the dense SiC sintered body (i.e. sintered in presence of both activators) reflect the equilibrium state in the polycrystalline material, unlike in the case of three remaining compositions (SiC + 3%C; SiC + 0.5%B and pure SiC), where the equilibrium is attained between gaseous and solid phases. Therefore from the value of dihedral angle $111.5^\circ \pm 6^\circ$ for the SiC + 3%C + 0.5%B sintered material can be drawn conclusions on the ratio of energy of two grain boundaries $\gamma_{SS_1}/2\gamma_{SS_2}$ or on the anisotropy of energy of these boundaries. In this case the value of $\gamma_{SS_1}/2\gamma_{SS_2}$ ratio is 0.56. Fig. 4 shows a typical picture of dense polycrystalline SiC, observed under the transmission electron microscope.

5. Statistical verification of hypotheses

The empirically found median values of dihedral angles measured through the gaseous phase and, calculated on this basis, ratios of grain boundaries energy to the surface energy are very similar in case of SiC with addition of boron, SiC with addition of carbon and pure SiC. This fact allows us to state that the activators have no influence on the free surface energy or the energy of grain boundaries. The hypothesis was subjected to statistical verification. First a zero hypothesis, H_o, was formulated that there were no differences between the median values of dihedral angles for materials with different compositions and an alternative hypothesis, and H_1, being the negation of the former one. In accordance with the rules of statistical verification of hypotheses, the positive results of F-Snedecor and Student tests allowed us to accept of the zero hypothesis as the correct one (Tables 2 and 3). Thus the differences between the median values of dihedral angles for the examined compositions are statistically insignificant and result from the measuring errors.

6. Determination of spontaneity of sintering process

When it is assumed that one grain-boundary unit is formed from two surface units, sintering can occur spontaneously when:

$$\Delta G = \gamma_{SS} - 2\gamma_{SG} < 0 \quad (2)$$

on combining the earlier equation with the value of free surface energy ($\gamma_{SS} = 2\gamma_{SG} \cdot \cos\frac{\phi}{2}$), one arrives at the following relation:

$$\Delta G = \gamma_{SG} \cdot \left(2\cos\frac{\phi}{2} - 2\right). \quad (3)$$

It can be stated that the bigger the dihedral angle, the smaller ΔG, otherwise saying—the greater the ability of the system to undergo spontaneous elimination of free surfaces to the advantage of grain boundaries. When this reasoning is referred to the measured values of dihedral angles for different materials: SiC containing 3% of carbon, SiC containing 0.5% of boron and pure SiC, it appears that ΔG is always negative and its absolute values are comparable with the energy of free surfaces.

The presented discussion makes it clear that in all the investigated materials, i.e. SiC modified with boron, SiC modified with carbon and in pure SiC, the free surfaces spontaneously transform into grain boundaries, which is accompanied by pore elimination. The negative ΔG value and the ratio $\gamma_{SS}/2\gamma_{SG}$, determined from the measurements of dihedral angles support this conclusion.

Table 2
The data for statistic verification of hypotheses

No. of experimental set of results	SiC containing:	Arithmetic weighted mean $\bar{x}$ [deg.]	Empirical weighted variance S [deg.]^2	Number of classes	Number of measurements
1	0.5 wt.% of boron	106	286	7	50
2	without activators	119	236	8	50
3	3 wt.% of carbon	111	217	7	50

7. Microstructure

Microstructure characteristic of dense materials is represented by sintered body with both activators. They are built of densely packed isometric grains (Figs. 1 and 4). The values of dihedral angles (111.5°±6°) (Fig. 3) formed by three neighbouring grains are close to the equilibrium ones of 120°. In accordance with the sintering theory this indicates the state with minimum free enthalpy and isotropy of energy of each grain boundary in a dense SiC sintered body [9,10].

The smallest grains with isometric shapes are observed in the sintered material with carbon addition only (Fig. 1). An analogous microstructure—with grains similar in shape—is found in the sintered pure SiC. The material with boron addition of 0.5% is built of big directionally oriented grains. The microstructures of porous materials, i.e. containing only one additive and pure SiC, are characterized by dense regions surrounded by numerous pores. Variations in shape and size of grains suggest the role of activators connected with the modification of mass transport mechanisms. Lange and Gupta [11] contrary to Prochazka's hypothesis suggest that either reaction sintering or liquid phase sintering is responsible for the densification of sample containing boron and carbon additives. Our other investigations [7,12,13] corroborate this suggestion.

8. Conclusions

The dihedral angles in the investigated sintered materials: SiC + 0.5%B, SiC + 3%C and pure SiC, have similar values, the differences being statistically insignificant. It can be stated that the ratios of grain-boundary energy to free-surface energy are almost the same. These results allow for rejecting the hypothesis formulated by Prochazka that boron and carbon activators

Table 3
Comparative statistic tests made during statistics verification of hypotheses

Comparison of exp. set of results	F-test	Results	Comparison of exp. set of results	Student test	Results
	$\alpha = 0.05$			$\alpha = 0.05$	
1 z 2	$F_{critical} = 3.87$		*1 z 2*	$t_{critical} = 2.16$	
$F_{calculated}$	1.24	$F_{calc.} < F_{crit.}$	$t_{calculated}$	1.45	$t_{calc.} < t_{crit.}$
2 z 3	$F_{critical} = 4.21$		*2 z 3*	$t_{critical} = 2.16$	
$F_{calculated}$	1.07	$F_{calc.} < F_{crit.}$	$t_{calculated}$	0.96	$t_{calc.} < t_{crit.}$
3 z 1	$F_{critical} = 4.28$		*3 z 1*	$t_{critical} = 2.179$	
$F_{calculated}$	0.76	$F_{calc.} < F_{crit.}$	$t_{calculated}$	0.55	$t_{calc.} < t_{crit.}$

modify the energy of free surfaces and grain boundaries. The values of dihedral angles for all investigated materials are much bigger than the critical ones, 60 or 90°, which, according to the sintering theory, enable pore elimination, i.e. densification of the material. The ΔG value calculated from the measured dihedral angles for all studied materials, i.e. SiC doped with carbon, SiC doped with boron and pure SiC, are negative and there are no thermodynamic obstacles for the densification process. The values of dihedral angles, both observed and the median ones, in dense sintered body containing both additives oscillate around the equilibrium value of 120°.

References

[1] S. Prochazka, The role of boron and carbon in the sintering of silicon carbide, in: P. Propper, F. Fiee (Eds.), Special Ceramics, British Ceramic Research Association, Stoke-on-Trent, 1975, pp. 171–182.
[2] B.J. Kellet, F.F. Lange, Thermodynamics of densification: I, sintering of simple particle arrays, equilibrium configurations, pore stability, and shrinkage, J. Am. Ceram. Soc. 72 (5) (1989) 725–734.
[3] W.D. Kingery, B. Francois, The sintering of crystaline oxides. Interaction between grain boundaries and pores, in: G.C. Kuczyñski (Ed.), Sintering and Related Phenomena, Gordon Research, New York, 1966, pp. 471–497.
[4] C.S. Smith, Grains, phases and interfaces, Trans. AIME 175 (15) (1948) 15–51.
[5] C. Greskovich, J.H. Rosolowski, Sintering of covalent solids, J. Am. Ceram. Soc. 59 (7-8) (1976) 336–343.
[6] H. Suzuki, T. Hase, Boron transport and charge of lattice parameter during sintering of β-SiC, J. Am. Ceram. Soc. 63 (5–6) (1980) 349–350.
[7] A. Gubernat, The Role of Boron and Carbon in Sintering of Silicon Carbide, PhD thesis, University of Mining and Metallurgy, Cracow, 2001 (in Polish).
[8] O.K. Riegger, L.H. Van Vlack, Dihedral angle measurement, Trans. AIME 218 (10) (1960) 933–935.
[9] W.D. Kingery, Introduction to Ceramics, J. Wiley and Sons, New York, 1960.
[10] R.L. Coble, Diffusion sintering in the solid state, in: W.D. Kingery (Ed.), Kinetics of High-temperature Processes, Massachusetts Institute of Technology, New York, 1959, pp. 147–163.
[11] F.F. Lange, T.K. Gupta, Sintering of SiC with boron compounds, J. Am. Ceram. Soc. 59 (11-12) (1976) 537–538.
[12] L. Stobierski, A. Gubernat, Sintering of silicon carbide I. Effect of carbon, Ceram. Int. 29 (2003) 287–292.
[13] L. Stobierski, A. Gubernat, Sintering of silicon carbide II. Effect of boron, Ceram. Int. 29 (2003) 355–361.