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# Sintering of silicon carbide
# I. Effect of carbon

Ludoslaw Stobierski*, Agnieszka Gubernat

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

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**Abstract**

The role of carbon in activating the process of SiC sintering is not fully understood. In the present work we examined the weight and microstructure changes of samples sintered with different additions of carbon (up to 16 wt.%). The measurements were carried out in the temperature range 1000–2200 °C. In comparative studies we examined the variations of oxygen content with the sintering temperature. The obtained results indicate that carbon blocks the mass transport processes which are ineffective in densification and enables maintaining proper dispersion of SiC grains up to the temperatures where, due to boron, pore elimination begins. On the basis of microstructural observations of SiC sintered with different amounts of carbon it has been stated also that this additive prevents grain growth of SiC on sintering.

*Keywords:* A. Sintering; D. Carbon; D. SiC; Sintering activators

## 1. Introduction

In the manufacturing of dense single-phase sintered bodies of silicon carbide, carbon and boron are necessary additives that activate sintering of SiC micropowders. The mechanism, which operates in this process, has not been explained so far. The hypothesis that carbon helps eliminating oxide impurities on grain boundaries [1–3] finds no confirmation in thermodynamic calculations [4–7] or experimental results [8–11]. As a consequence the assumption saying that carbon modifies surface energy of SiC grains is not supported experimentally. However, as proved by numerous investigations, an addition of a few percent of carbon is necessary to activate the sintering process of SiC. In order to find the reason of carbon effect a series of experiments has been planned involving sintering and hot pressing of SiC powders with different amounts of carbon. Microstructural observations were thought to provide information on the effect of this activator on sintering. In addition, comparative weight change and porosity measurements were conducted as a function of composition at temperatures of 1200–2200 °C.

## 2. Experimental

Materials used for the experiments were the following: α-SiC powder (Starck—UF-15), amorphous boron (Fluka Cat. No. 15580) and phenol-formaldehyde resin Novolak (Organika—Sarzyna), as a source of carbon. After thermal decomposition of the resin 50% of its mass was left as amorphous carbon. The specimens were prepared by homogenization of powder suspension in an alcoholic solution of the resin in the amount sufficient for the desired carbon concentration in the final product. In all experiments aimed at microstructural observation the addition of boron was kept at the same level, i.e. 0.5 wt.%, whereas the addition of carbon varied in a wide range: 0.00, 1.00, 1.50, 2.00, 2.50, 3.00, 4.00, 5.00, 6.00, 8.00, 10.00, 12.00 and 16.00 wt.%. After evaporation of the solvent and granulation the materials were pressed into pellets, of 20 mm diameter and thickness of 8 mm. The compaction was carried out in two stages, first in a steel die under the pressure of 150 MPa and then isostatically under 300 MPa. Additionally the samples of pure SiC were prepared in the analogous way as well as samples with a sole addition of carbon in the amount of 3.00 wt.% and samples with the sole addition of boron at the level of 0.50 wt.%.

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* Corresponding author. Tel.: +48-12-617-24-64; fax: +48-12-633-46-30.

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Samples—pure SiC (without activators), SiC containing 0.50 wt.% of boron and 3.00 wt.% of carbon as well as SiC containing the sole addition of carbon (3.00 wt.%) or boron (0.50 wt.%)—were used for the comparative measurements of oxygen content and for the measurements of weight change and porosity upon sintering. All the samples had a monomodal pore-size distribution and the average pore diameter was in the range 130–140 nm.

Sintering of materials prepared for oxygen content measurements and of samples for the weight-change and porosity measurements was carried out by heating them in an argon atmosphere with rate of 15 °C/min and annealing at the final temperature for 15 min. The samples were sintered at temperature range of 1000–2200 °C, keeping 100 °C increments in case of samples for weight-change measurements and 200 °C-intervals in case of samples for oxygen content measurements.

The materials prepared for microstructural observation were first heated with rate of 15 °C/min in vacuum ($10^{-2}$ mbar) to 1200 °C and then 10 °C/min to 2150 °C. At this temperature they were kept for 60 min. Under the hot pressing conditions the heating regime was exactly the same as earlier but the annealing time was shorter—30 min. The hot pressing was carried out in graphite moulds under pressure of 25 MPa.

For the microscopic observations the cross-sections were etched in fused potassium salts (75% KOH + 25% $KNO_3$) at 480 °C. Thin foils for transmission electron microscopy were prepared from the hot-pressed materials with a carbon addition of 1.00, 4.00 and 8.00 wt.%. The Visilog 4 [12] software was applied in order to analyse microstructure of the samples. On the basis of this software mean grains section area E(A), mean equivalent circle grains section diameter E($d_2$) and mean grains section shape factor E(F) were calculated. The following formulas were used:

mean equivalent circle grain sections diameter

$$d_2 = [A/4\pi]^{0,5}\ [\mu\text{m}] \tag{1}$$

where:

*A*—mean grain sections area (which it was calculated by the software); mean grains sections shape factor

$$F = L^2/4\pi A \tag{2}$$

where:

*L*—length of grain sections perimeter.

Phase composition was determined by means of X-ray diffraction methods. Oxygen content was determined using of infrared absorption analysis (TC-336 LECO). Pore size distribution and average pore radius was measured using of mercury porosimetry methods.

## 3. Results

### 3.1. Oxygen content

The results of measurements of oxygen content in pure SiC and SiC with a 3 wt.% addition of carbon are given in Fig. 1. As can be seen, carbon reduces concentration of oxygen at temperatures lower than 1400 °C while at higher temperatures it does not substantially affect its concentration in the sintered materials in comparison to pure SiC. This experiment proves that silicon carbide itself can eliminate oxide impurities, and that other mechanisms by which carbon facilitates the sintering process should be operative. The variations of oxygen content are observed at temperatures much lower than the initial temperature of sintering.

### 3.2. Changes of porosity and weight

The results of porosity measurements as a function of temperature for the following materials: pure SiC (without activators), SiC containing 0.5 wt.% of boron and 3 wt.% of carbon as well as SiC containing the sole addition of carbon (3 wt.%) or boron (0.5 wt.%) are shown in Fig. 2. Pores are eliminated exclusively in samples with both additives present and the process starts at 1600 °C. In other samples the pores only change dimensions but total porosity remains constant. The evolution of average pore diameter is given in Fig. 3.

The weight changes within the studied temperature range are presented in Fig. 4. These results indicate that carbon addition lowers weight loses on sintering. It suggests that carbon prevents evolution of gaseous products of chemical reactions or thermal decomposition of SiC. When we compare the temperature range, where the highest weight losses of carbon-free samples are observed, with the data in Fig. 1 it becomes clear that

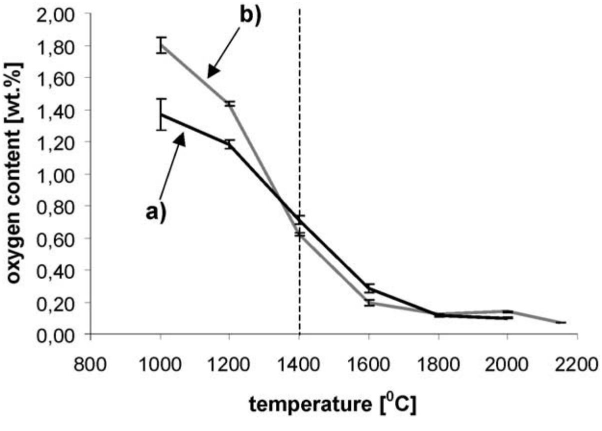

Fig. 1. Changes of oxygen content for the following systems: a—SiC containing 3 wt.% of carbon, b—pure SiC.

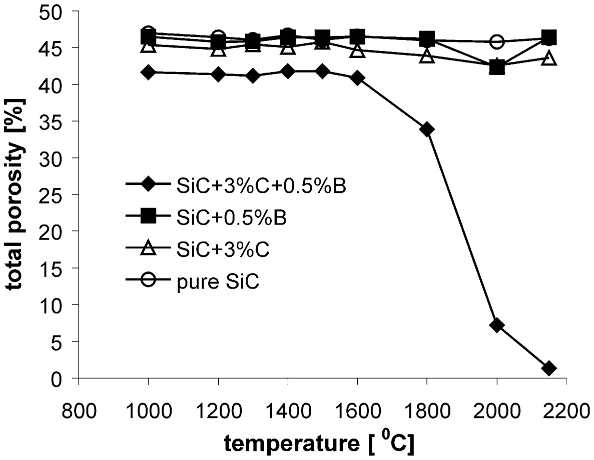

Fig. 2. Total porosity of SiC sintered body vs. temperature and initial composition.

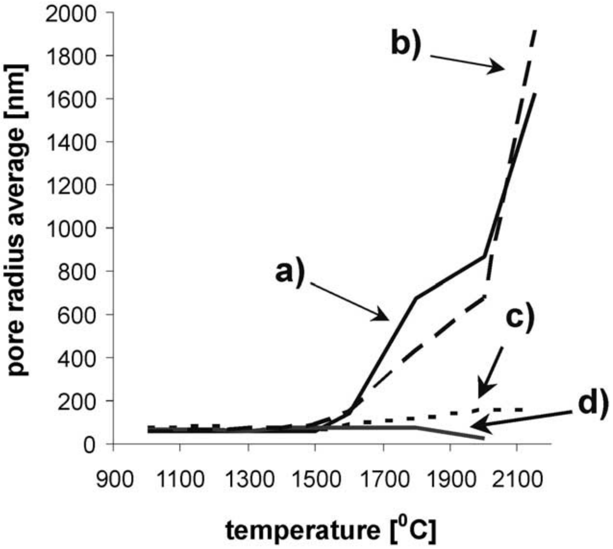

Fig. 3. Average pore radius vs. sintering temperature and composition: a—pure SiC, b—SiC containing 0.5 wt.% of boron, c—SiC containing 3 wt.% of carbon as well as d—SiC containing 3 wt.% of carbon and 0.5 wt.% of boron.

the weight variations take place at temperatures higher than those of favourable oxide impurity reduction.

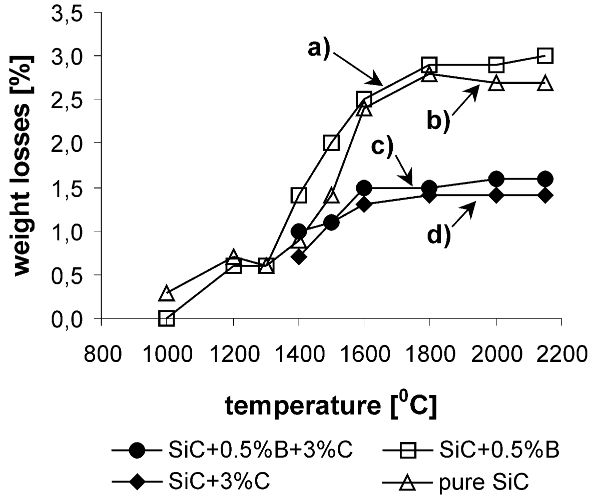

Fig. 4. Weight losses for the following systems: a— pure SiC, b—SiC containing 0.5 wt.% of boron, c— SiC containing 3 wt.% of carbon, d— SiC containing 3 wt.% of carbon and 0.5 wt.% of boron.

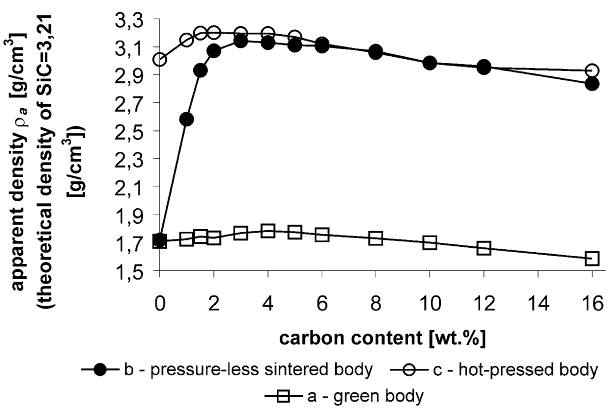

Fig. 5. Apparent density for the following materials: a—green body, b—pressure-less sintered body, c—hot-pressed body.

### 3.3. Microstructure

Apparent densities of pressure-less sintered and hot-pressed samples and apparent densities of materials prior to sintering vs. carbon content are collected in Fig. 5. In each case boron content amounted to 0.5 wt.%. The qualitative changes of apparent density of the sintered and hot-pressed materials, caused by different carbon additions, have similar character. Initially, density increases with carbon content. Exceeding its certain critical level, different for the two discussed processing methods, apparent density decreases. It is noteworthy that high relative density (0.93) in case of hot pressing can be achieved even without any addition of carbon. In the case of hot pressing, the changes of apparent density are smaller and the nearly theoretical density is obtained at carbon concentration of 1.5 wt.%. Whereas on pressure-less sintering, the changes of apparent density are larger and the highest densification degree is attained at carbon concentration level of 3 wt.%. The fact that apparent density increases with increasing concentration of carbon is connected with pore elimination whereas decreasing apparent density above 4 wt.% of carbon additive results from the appearance of carbon phase in the materials (Figs. 6c and 7c). X-ray analysis of a sintered body with 8 wt.% carbon additive revealed that the lattice constant of the carbon phase, $d_{(002)} = 0.3358$ nm, was very close to that of graphite $d_{(002)} = 0.3354$ nm [13,14]. It can plausibility be assumed that the observed precipitates are built of

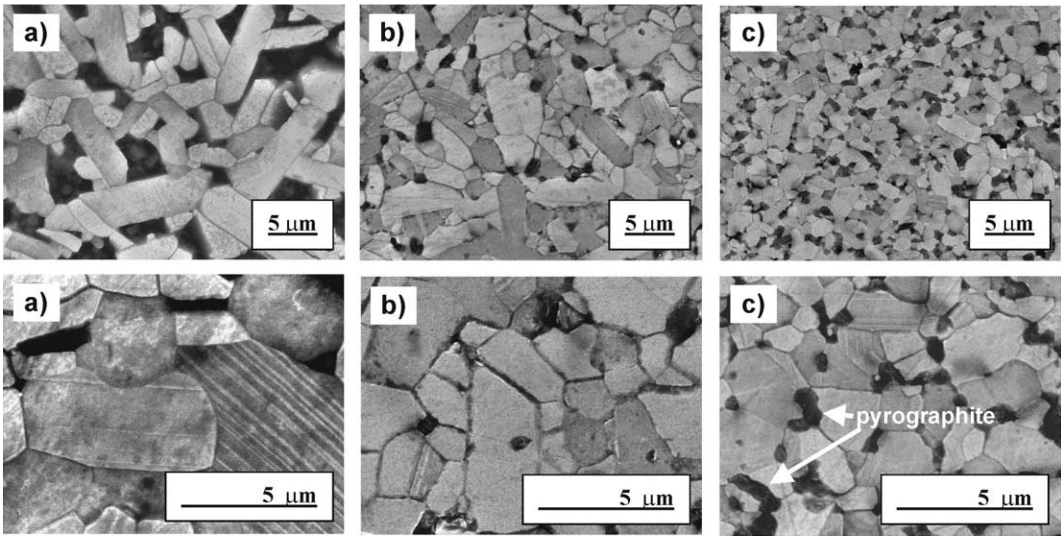

Fig. 6. SEM micrographs SiC sintered bodies containing 0.5 wt.% of boron and different amounts of carbon: (a) 1.00 wt.%, (b) 4.00 wt.%, (c) 16.00 wt.%.

pyrographite which density is close to that of graphite. The microscopic examinations reveal that sparsely distributed graphite precipitates occur in samples sintered with carbon additive as low as 3 wt.%. They also show that porosity of sintered samples, which contain the pyrographite precipitates, does not undergo any significant changes. Total porosity of all sintered bodies with a carbon content exceeding 2.5 wt.% is lower than 3 wt.%. Fig. 6 shows the microscopic pictures of sintered bodies containing 1, 4 and 16 wt.% carbon. The most important differences in microstructure, brought about by varying carbon concentration, are those of SiC grain size and shape. The most visible effect of increasing carbon concentration is decreasing of grain growth. In Table 1, the data on mean grain sections area E(A), mean equivalent circle grain sections diameter E($d_2$) and mean grains sections shape factor E(F) are listed. As follows from the latter the grain shape changes evolve from the elongated to the uniaxial one. There are also changes of the grain boundaries shape. When carbon concentration is less than 2 wt.% the boundaries are curved and some symptoms of discontinuous grain growth are observed while in other sintered bodies the grain boundaries are predominantly flat. These features are also observed in the materials obtained by hot pressing, which were examined by transmission electron microscopy, Fig. 7. The microphotographs of sintered bodies containing 4 and 8 wt.% carbon reveal also the pyrographite grains localized on flat SiC grains boundaries. The results of these investigations prove that carbon, over the whole range of concentrations used in this work, significantly limits the growth of SiC grains.

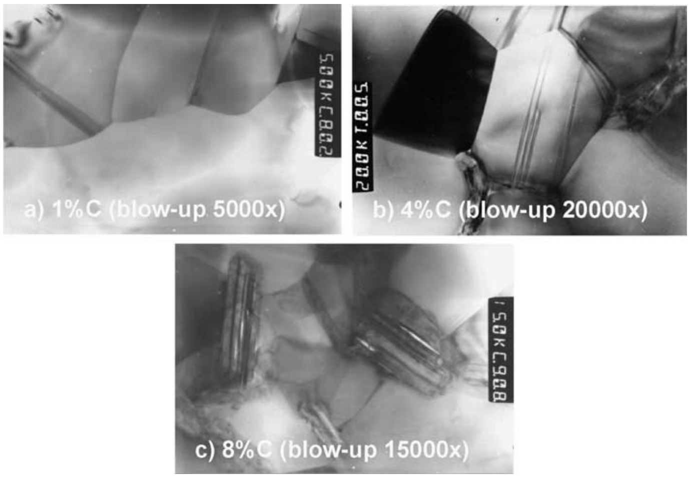

Fig. 7. TEM micrographs SiC hot-pressed materials containing 1, 4 and 8 wt.% of carbon (all materials containing 0.5 wt.% of boron). On micrograph (c) the darker grains are pyrographite.

Table 1
The mean grain sections area E(A), the mean equivalent circle grain sections diameter E($d_2$) and the mean grain sections shape factor E(F) vs. carbon content

| Carbon (wt.%) | Mean grain sections area E(A) [$\mu m^2$] (±standard deviation) | Mean equivalent circle grain sections diameter E($d_2$) [μm] (±standard deviation) | Mean grain sections shape factor E(F) (±standard deviation) |
|---|---|---|---|
| 1 | 5.77±0.06 | 2.307±0.009 | 1.436±0.002 |
| 1.5 | 5.54±0.05 | 2.214±0.008 | 1.481±0.002 |
| 2 | 6.83±0.06 | 2.265±0.010 | 1.445±0.002 |
| 3 | 2.79±0.01 | 1.642±0.003 | 1.395±0.001 |
| 4 | 3.14±0.01 | 1.739±0.004 | 1.382±0.001 |
| 5 | 2.53±0.01 | 1.556±0.003 | 1.360±0.001 |
| 5 | 2.19±0.01 | 1.428±0.003 | 1.363±0.001 |
| 8 | 2.08±0.01 | 1.415±0.002 | 1.385±0.001 |
| 10 | 1.79±0.01 | 1.324±0.002 | 1.406±0.001 |
| 12 | 1.82±0.01 | 1.327±0.002 | 1.399±0.001 |
| 16 | 1.35±0.01 | 1.136±0.002 | 1.391±0.001 |

## 4. Discussion

The results presented in the paper prove that carbon essentially influences the material microstructure in the whole range of experimental temperatures. The role of carbon is not limited to the reduction of the oxide impurities. According to the oxygen content measurements, carbon—as a reducing agent—enhances deoxidation at temperatures lower than 1400 °C. At higher temperatures carbon limits the weight losses of the materials. Therefore it can be concluded that carbon reduces gas transfer of the products of chemical reactions of silica layer reduction or of SiC thermal decomposition. The most pronounced differences in weight losses, between the samples with and without carbon addition occur the temperature range of 1400–1600 °C, i.e. before any thermal decomposition of SiC takes place. Within this temperature range differences in oxygen content are observed between the samples with carbon addition and pure SiC, although both of them still contain oxygen (Fig. 1). The observed differences in weight loss (Fig. 4) can result from the different course of reduction of $SiO_2$ which passives the SiC grains [2,4,5].

In the carbon-free samples the reaction proceeds in the following way:

$$SiO_2 + n\mathrm{SiC} = \mathrm{Si}\uparrow + \mathrm{SiO}\uparrow + \mathrm{CO}\uparrow + (n\text{-}1)\mathrm{SiC} \qquad (3)$$

Thus silicon, silicon monoxide and carbon monoxide evaporate from the system. On the other hand in the presence of carbon the volatile products, such as Si and SiO become chemically bonded and only carbon monoxide is transferred to the gaseous phase. The reaction can be written as follows:

$$SiO_2 + n\mathrm{SiC} + 3\mathrm{C} = (n+1)\mathrm{SiC} + \mathrm{CO}\uparrow \qquad (4)$$

In this case, the role of carbon is to bond chemically the gaseous products of silica reduction. The proposed explanation is valid, however, only at temperatures lower than that of the onset of sintering.

Sintering of silicon carbide activated with boron and carbon takes place at high temperatures. Shrinkage of the material and varying pore morphology (Figs. 2 and 3), begins at temperatures higher than 1600 °C, full densification is attained at temperatures exceeding 2000 °C. Within this temperature range carbon limits weight losses and arrests the grain growth process. This indicates that carbon modifies mechanisms of mass transport. Therefore the explanation involving chemical effect is not sufficient.

At sintering temperatures thermal decomposition of SiC should also be considered consideration. Investigations on dissociation pressures of SiC [6,7] carried out with SiC–Si and SiC–C systems, results given in Fig. 8, indicate that in the SiC–C system the dissociation pressures are by one order of magnitude lower than in the SiC–Si system. The main volatile component among the decomposition products is silicon. Partial pressures of other two- and three-atomic molecules are two to three orders of magnitude lower. The occurrence of silicon vapour inside sintered material can counteract densification because of activation of surface diffusion. This mass transport mechanism favours grain growth, but at the same time does not lead to pore elimination.

The analyses of chemical composition of SiC prove that the molar ratio Si/C is higher than 1 [15,16]. This fact shifts the chemical composition of sintered powders to the SiC–Si boundary. So far, there has not been any evidence to decide whether the earlier ratio is a real silicon excess or carbon deficit. With carbon addition the system approaches the SiC–C boundary and therefore lowering of dissociation pressure should be observed, i.e. limited transport through the gaseous phase. Che-

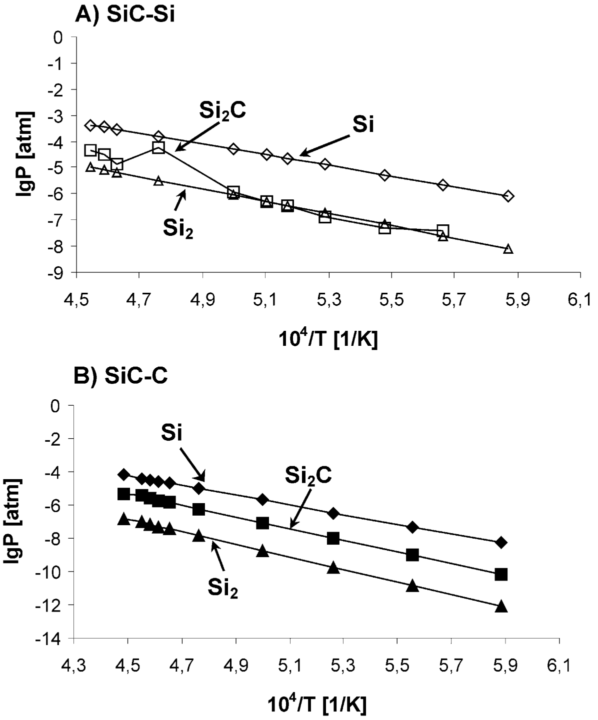

Fig. 8. Partial pressure of thermal decomposition products of SiC for the following systems: a—SiC–Si, b—SiC–C [6,7].

mical bonding of silicon by carbon, which dominates in the products of thermal decomposition of SiC, leads to the lower weight losses. Thereby lowering dissociation pressures limits transport through the gaseous phase which is an ineffective process from the point of view of shrinkage. Chemical immobilisation of silicon by carbon limits also the surface diffusion, which is considered as an ineffective processes in pore elimination [17–19]. The postulated above effect of carbon is corroborated by the weight loss measurements and the mean pore size changes with materials containing 3 wt.% of carbon or without carbon addition (Figs. 3 and 4). For example, average pore radius in material containing 3 wt.% of carbon is 13 times lower than in case of the one with 0.5 wt.% of boron content and the one without activators.

In the light of the earlier discussion the main role of carbon is to preventing the occurrence of mass transport mechanisms that are ineffective in the densification process.

## 5. Summary

All described effects, i.e. changes in weight loss on sintering, changes in size and shape of pores, changes in size and shape of SiC grains, brought about by carbon additions indicate that this additive is active in sintering. It is reasonable to accept the hypothesis saying that carbon limits those mass transport mechanisms, which are ineffective in the sintering process. When these ineffective mass transport mechanisms are arrested, already at temperatures lower than the onset of sintering, small size of SiC grains is preserved up to the temperatures where boron activates the mass transport mechanisms leading to pore elimination.

## References

[1] S. Prochazka, The role of boron and carbon in the sintering of silicon carbide, in: P. Propper (Ed.), Special Ceramics, Vol. 6, British Ceramic Research Association, Stoke-on -Trent, England, 1975, pp. 171–182.

[2] W. Rijswijk, D. Shanefield, Effect of carbon as a sintering aid in silicon carbide, J. Am. Ceram. Soc. 73 (1) (1990) 148–149.

[3] W.J. Clegg, Role of carbon in the sintering of boron-doped silicon carbide, J. Am. Ceram. Soc. 83 (5) (2000) 1039–1043.

[4] P.D. Miller, J.G. Lee, I.B. Cutler, The reduction of silica with carbon and silicon carbide, J. Am. Ceram. Soc. 62 (3–4) (1979) 147–149.

[5] W.W. Pultz, W. Hertl, $SiO_2 + SiC$ reaction at elevated temperatures: I, Trans. Faraday Soc. 62 (9) (1966) 2499–2504.

[6] J. Drowart, G. De Maria, Thermodynamic study of the binary system carbon–silicon using a mass spectrometer, in: J.R. O'Connor, J. Smiltens (Eds.), Silicon Carbide a High Temperature Semiconductor, Pergamon Press, London, 1960, pp. 16–23.

[7] S.K. Lilov, Thermodynamic analysis of phase transformations at the dissociative evaporation of silicon carbide polytypes, Diam. Rel. Mater. 4 (1995) 1331–1334.

[8] C. Greskovich, J.H. Rosolowski, Sintering of covalent solids, J. Am. Ceram. Soc. 59 (7–8) (1976) 336–343.

[9] L. Stobierski, A. Gubernat, Sintering aids in silicon carbide densifications, Bulletin of the Polish Academy of Sciences, Technical Sciences 47 (4) (1999) 411–421.

[10] A. Gubernat, The Role of Boron and Carbon in Sintering of Silicon Carbide, PhD Thesis, University of Mining and Metallurgy, Cracow, 2001 (in Polish).

[11] 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.

[12] K.J. Kurzydlowski, B. Ralph, The quantitative description of the microstructure of materials, in: B. Ralph (Ed.), CRC Series Materials Science Technology, CRC Press, Boca Raton, New York, London, Tokyo, 1995, pp. 166–169, 256–264, 274–277.

[13] B.T. Kelly (Ed.), Physics of Graphite, Applied Science Publisher, London and New York, 1981, pp. 245–248.

[14] W.M. Kenan, Anual minerals reviev, Am. Ceram. Soc. Bull. 70 (5) (1991) 865–866.

[15] D.P. Birinie III, W.D. Kingery, The limit of non stoichiometry in silicon carbide, J. Mater. Sci. 25 (1990) 2827–2834.

[16] P.T.B. Schaffer, The SiC phase in the system $SiC–B_4C–C$, Mater Res. Bull. 4 (1969) 213–220.

[17] R.F. Walker, Mechanism of material transport during sintering, J. Am. Ceram. Soc. 38 (6) (1955) 187–197.

[18] J. Lis, R. Pampuch, Sintering, University of Mining and Metallurgy, Cracow, 2000 (in Polish).

[19] R.L. Coble, Diffusion sintering in the solid state, in: W.D. Kingery (Ed.), Kinetics of High-Temperature Processes, Copyright by the Massachusetts Institute of Technology, 1959, pp. 147–163.