JOURNAL OF MATERIALS SCIENCE 22 (1987) 109–114

Pressureless sintering of boron carbide with an addition of polycarbosilane

M. BOUGOIN, F. THEVENOT
Ecole Nationale Supérieure des Mines, 158 cours Fauriel, 42023 Saint-Etienne Cédex 2, et Centre de recherches Rhône Alpes des céramiques spéciales, CRRACS, France

Boron carbide B_xC ($x \geqslant 4$) is pressureless sintered with an addition of both polycarbosilane and a small amount of phenolic resin. After testing many green mixtures, it was found that it was necessary to have a minimal addition of carbon which could deoxydize the B_xC and also a second phase (SiC in this work) which could act in inhibiting grain coarsening. The resulting B_xC ceramics have high relative density ($\geqslant$92% theoretical density) and contain no free carbon and a small amount of SiC (about 5 wt%).

1. Introduction

Boron carbide, which has a high melting point, outstanding hardness, good mechanical properties, low specific weight, great resistance to chemical agents and a high neutron absorption cross-section ($^{10}B_xC$, $x \geqslant 4$) is currently used in high technology industries [1, 2].

A lot of methods have been tested for the pressureless sintering of boron carbide. Recent research has been most promising and consists of adding carbon to fine powders by pyrolysis of an organic precursor [3–9]. This method leads to sintered materials which contain small amounts of free carbon; this must be avoided in nuclear applications (control rods) because free carbon is thought to carburize the metallic cladding materials. Hence, in the present work, we sinter boron carbide with additions of both carbon and silicon carbide in an attempt to avoid free carbon.

2. Experimental method

The starting materials were a phenolic resin (alnovol PN320, Hoechst; PN) as the precursor of carbon, polycarbosilane (PC) as the precursor of SiC and a fine powder of boron carbide supplied by Electroschmelzwerk (West Germany), the main properties of which are listed in Table I.

The synthesis of polycarbosilane was described previously by Yajima [10–12]. The mechanism of PC transformation in silicon carbide has been studied by Hasegawa and Okamura [13]; β-SiC begins to crystallize at 1000° C and the size of the crystallites increases with temperature.

To begin with, the organic precursors are dissolved separately in their respective solvent: acetone for PN and *n*-hexane for PC. The B_xC powder is then added to a mixed solution of these resins and the slurry is dried while stirring, to obtain a paste. After further drying, the product is granulated and uniaxially pressed under 350 MPa into cylindrical pellets of 20 mm diameter. The pellets are sintered at 2175° C and held for 15 min under 1 atm of argon.

Polycarbosilane can be cured by heating in air at approximately 190° C [14]. The influence of such a treatment is being investigated.

Two types of mixtures were made. The corresponding green compositions are represented in a ternary diagram in Fig. 1. In the first type, the amount of organic additives (in the green mixture) was fixed at 10 wt% (PC + PN = 10%; B_xC = 90%). In the second type, the amount of phenolic resin was fixed at 2.5% (PN = 2.5%) while the amount of PC was varied between 0 and 17.5%.

3. Results

3.1. Addition of 10% phenolic resin and polycarbosilane (PC + PN = 10%)

Figs 2 to 5 illustrate the main properties of the achieved ceramics: the relative density before and after sintering; the open and closed porosity; the amount of free carbon; the grain size in the sintered material.

The relative green density was about 60% for each mixture. We can distinguish two groups in the achieved ceramics; when the mixture composition lay between "0% PC + 10% PN" and "7.5% PC + 2.5% PN" there was no open porosity and the relative

TABLE I Main properties of the boron carbide powder

Synthesis method:	arc melting
Grain size:	< 5 μm
Specific area:	10.5 m² g⁻¹
No BN or graphite detected by X-ray diffraction	
Total B:	77.8%
C:	20.0%
O:	2.1%
N:	0.04%
Mg:	< 0.01%
Si:	0.05%
Al:	< 0.01%
Fe:	0.01%
Ca:	0.02%
Ti:	0.29%*
Total B + Total C:	97.8%
Total B at %/Total C at %:	4.32

*TiB_2 detected by X-ray diffraction.

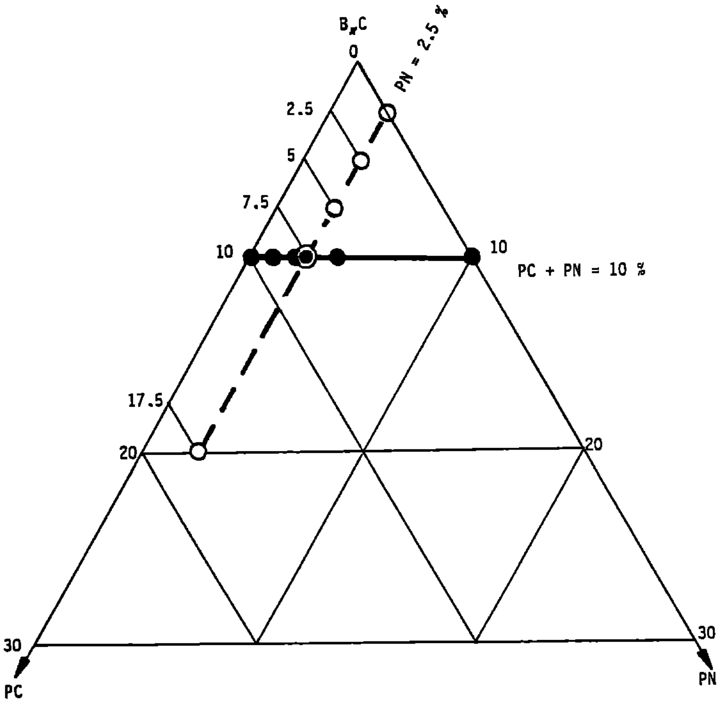

Figure 1 Studied green compositions presented in a ternary diagram: PN = phenolic resin (alnovol PN 320 Hoechst); PC = polycarbosilane.

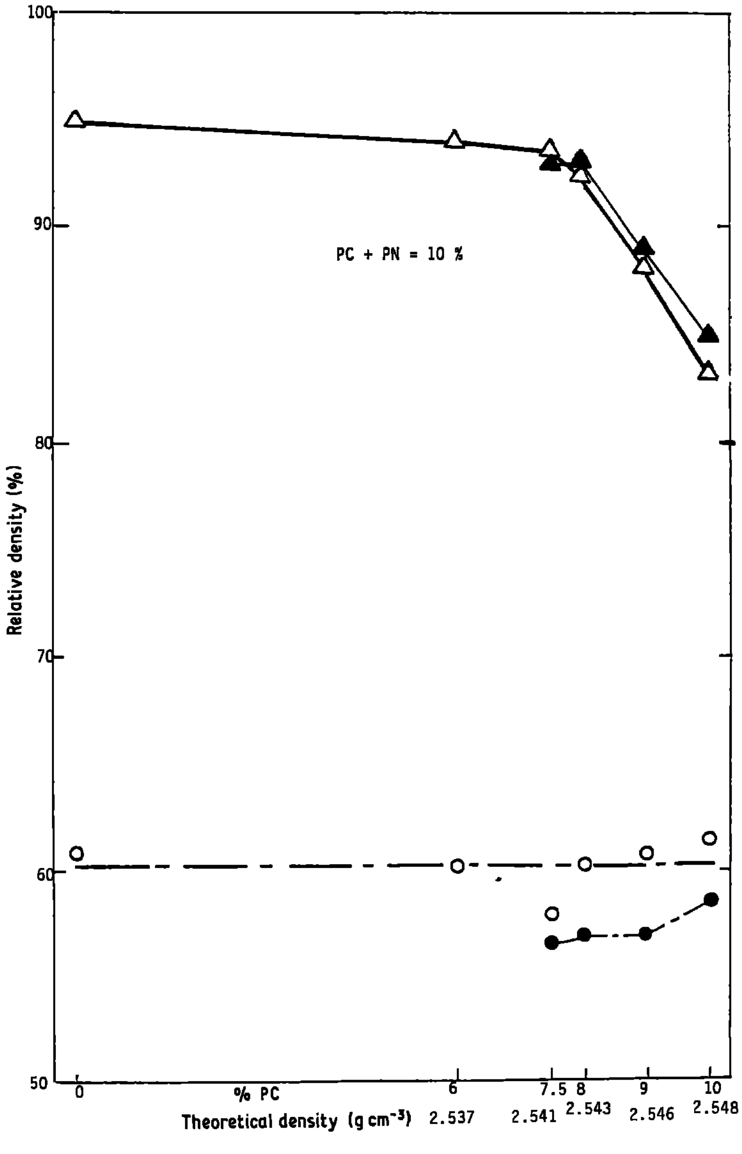

Figure 2 Influence of the addition of both polycarbosilane (PC) and phenolic resin (PN) on density when PC + PN = 10%. After sintering: (△) without curing polycarbosilane; (▲) after curing polycarbosilane at 200° C. Before sintering: (○) without curing polycarbosilane; (●) after curing polycarbosilane at 200° C.

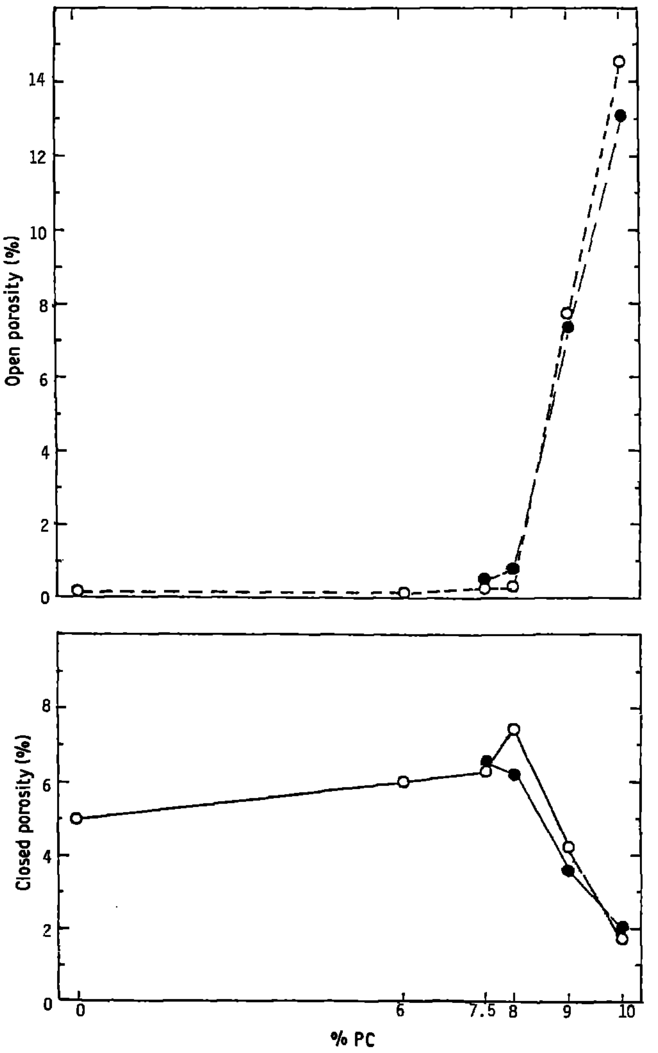

Figure 3 Influence of the addition of both polycarbosilane (PC) and phenolic resin (PN) on closed and open porosities when PC + PN = 10%. (●) After curing polycarbosilane at 200° C, (○) without curing polycarbosilane.

density was about 95%. These materials contain free carbon which decreases with the amount of phenolic resin in the green mixture (Fig. 4). "7.5% PC + 2.5% PN" is a limit mixture. Above 7.5% PC sintering decreased (Fig. 3) and no more free carbon was obtained (Fig. 4).

The grain size in the sintered boron carbide was generally large and was probably caused by too high a sintering temperature (Fig. 5). However, it was decreased by increasing the amount of polycarbosilane in the green mixture. Curing polycarbosilane did not seem to influence the sintering.

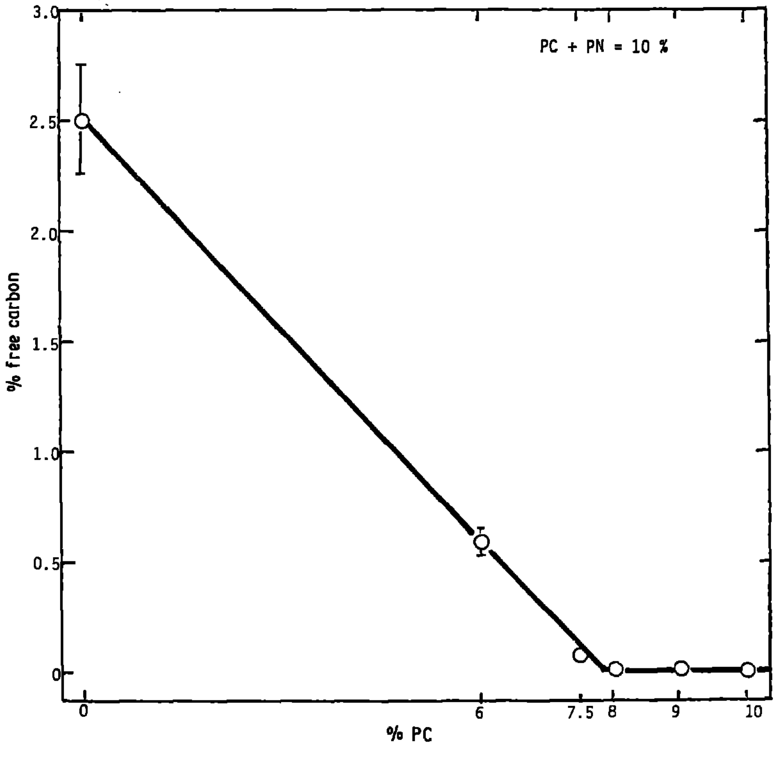

Figure 4 Influence of the addition of both polycarbosilane (PC) and phenolic resin (PN) on the amount of free carbon in the sintered ceramics, when PC + PN = 10%.

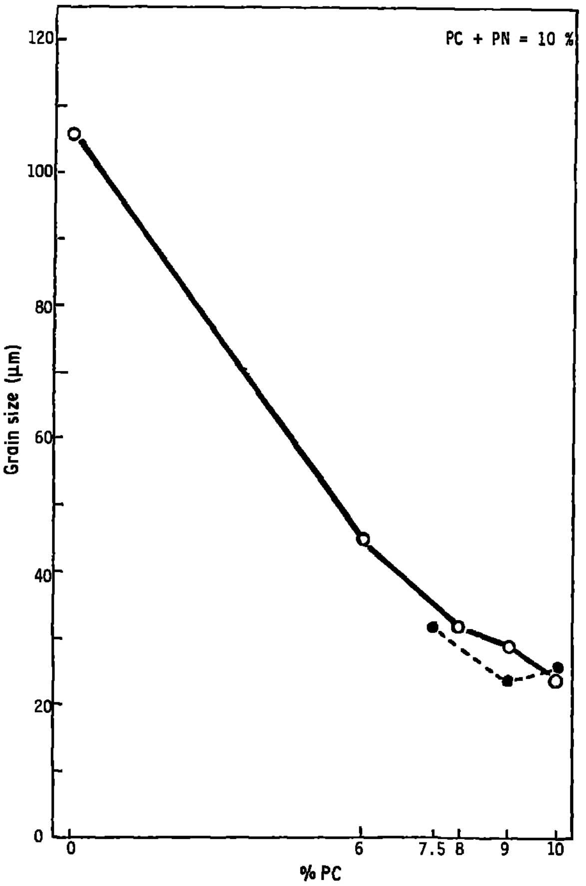

Figure 5 Influence of the addition of both polycarbosilane (PC) and phenolic resin (PN) on the microstructure of the ceramics, when PC + PN = 10%.

The SEM micrographs (Fig. 6) show a clear intergranular silicon carbide phase; a few small grains (< 3 μm) are in an intragranular position.

The finest porosity found inside the grains (< 5 μm) is evidence of a secondary recrystallization. X-ray diffraction showed that β-SiC obtained from polycarbosilane was partially transforme into the α-phase during sintering.

3.2. Addition of 2.5% phenolic resin (PN = 2.5%)

Figs 7 and 8 give the relative density and the open and closed porosity for the ceramics. The relative density of the sintered samples was improved when the amount of polycarbosilane increased from 0 to 7.5%. The ceramics which are sintered with an addition of PC, comprised between 7.5 and 17.5% had a relative density of about 94% and no open porosity.

When the polycarbosilane addition was great (17.5%), the coarsest SiC grains were acicular and they could reach 50 μm in length (Fig. 9); this phenomenon is evidence of the β to α phase transformation of SiC.

4. Discussion

The preceeding experimental results make it possible draw the following conclusions:

1. the addition of only SiC (10% PC ~ 5 wt % SiC) is not sufficient to obtain a good relative density (> 90% theoretical density) of boron carbide;
2. a good sinterability of boron carbide can be obtained with partial substitution of an organic precursor of SiC with the organic precursor of carbon. But a minimal amount of carbon must be added because it can act in the deoxidation of boron carbide or combine with the B_xC phase (when $x > 4$);
3. this minimum carbon addition (2.5% phenolic resin ~ 1.2% C) is not enough to ensure a good shrinkage. It is necessary to associate it with additional carbon or with silicon carbide which gives segregation at grain boundaries, and hence could limit grain coarsening or help diffusion in grain boundaries.

When an insufficient amount of organic carbon precursor was used, an abnormal grain growth in sintered boron carbode was sometimes observed [7, 8, 15].

The green mixture composed of 90% B_xC, 7.5% PC and 2.5% PN is of great interest because it is then

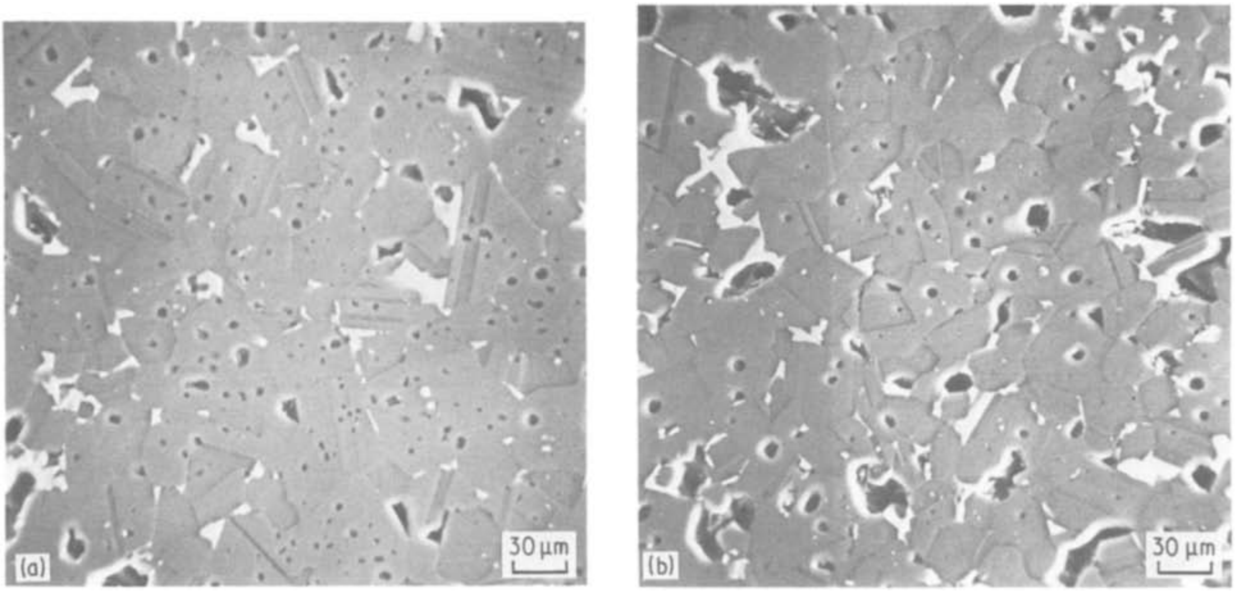

Figure 6 SEM micrographs of polished and electrolytically etched ceramics after sintering with an addition of polycarbosilane (PC) and phenolic resin (PN): (a) 7.5% PC + 2.5% PN; (b) 9% PC + 1% PN.

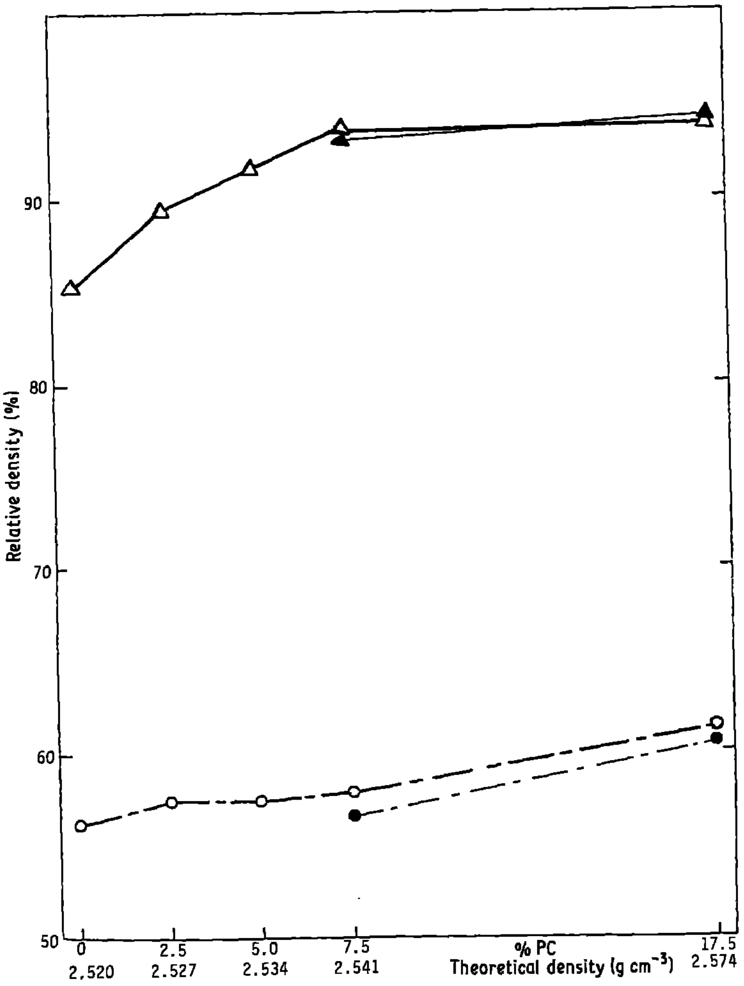

Figure 7 Influence of the addition of both polycarbosilane (PC) and phenolic resin (PN) on the density when PN = 2.5%. After sintering: (△) without curing polycarbosilane; (▲) after curing polycarbosilane at 200° C. Before sintering: (○) without curing polycarbosilane; (●) after curing polycarbosilane at 200° C.

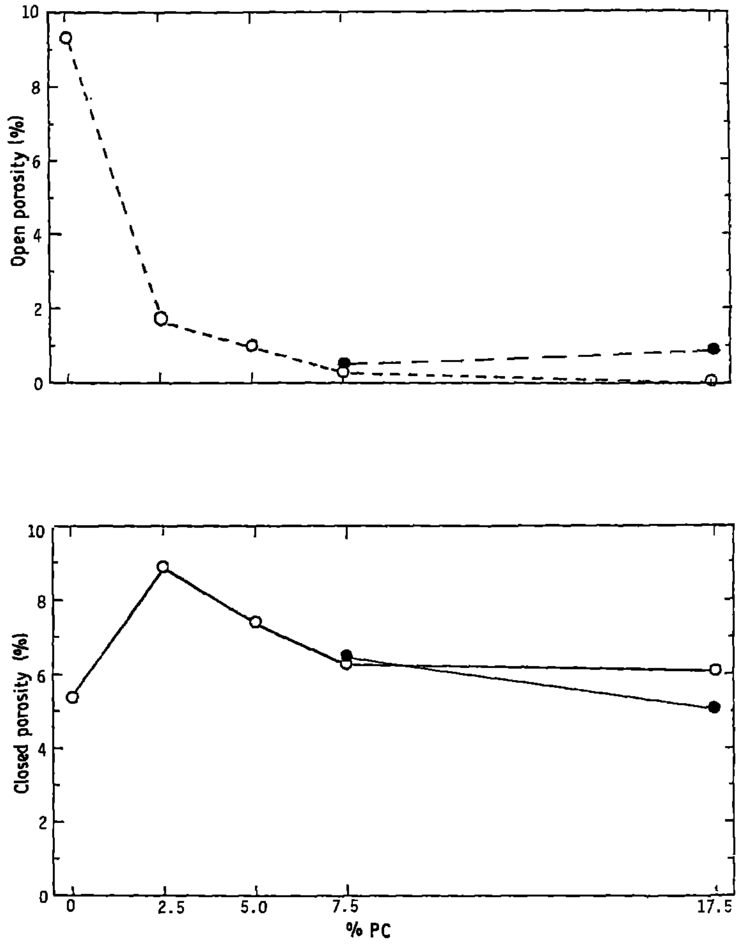

Figure 8 Influence of the addition of both polycarbosilane (PC) and phenolic resin (PN) on closed and open porosity when PN = 2.5%. (●) after curing polycarbosilane at 200° C, (○) without curing polycarbosilane.

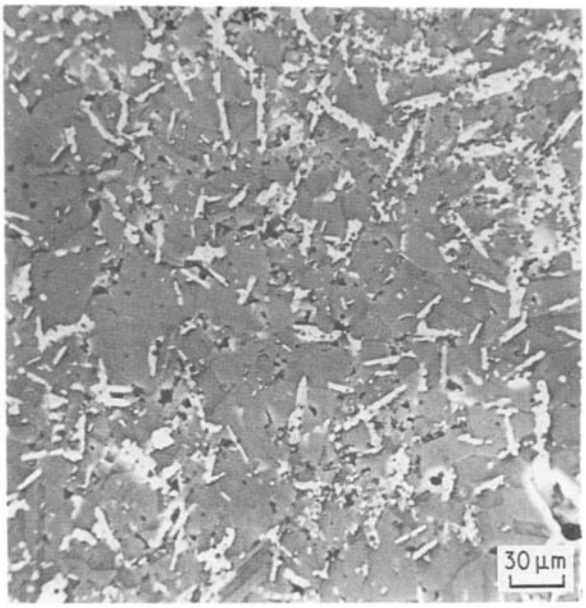

Figure 9 SEM micrograph of polished and electrolytically etched ceramics after sintering with an addition of 17.5% polycarbosilane and 2.5% phenolic resin (wt % in the green compact).

possible to obtain ceramics with high relative density and without free carbon.

The use of polycarbosilane is a suitable method to obtain very homogeneous B_xC–SiC mixtures without a milling operation, which generally causes pollution. Furthermore, polycarbosilane acts as a temporary binder and plasticizer in the pressing of green compacts.

The main drawback of polycarbosilane is that it produces β-phase SiC which can transform into α-SiC coarse grains during sintering.

In an extension of this work, we studied the pressureless sintering of boron carbide with the addition of a carbon organic precursor and fine silicon carbide powder [8, 16].

5. Conclusion

Boron carbide can be pressureless sintered with the addition of both carbon and silicon carbide organic precursors. This method makes it possible to obtain B_xC ceramics with high relative density ($\geqslant 92\%$ theoretical density) and without free carbon, It is necessary to introduce a minimal amount of carbon which could act in deoxidizing the boron carbide and to create a second phase which inhibits grain coarsening.

The carbon-rich limit of the boron carbide phase is $B_{4.0}C$. The homogeneity range extends from $B_{10.4}C$ (8.8 at % C) on the boron-rich side to stoichiometric $B_{4.0}C$ (20.0 at %) on the carbon-rich side [17–19].

Acknowledgement

This work is part of the doctoral thesis of M. Bougoin [8].

References

1. F. THEVENOT and M. BOUCHACOURT, *Ind. Céram.* **732** (1979) 655.
2. M. BEAUVY and F. THEVENOT, *ibid.* **734** (1979) 811.
3. K. A. SCHWETZ and G. VOGT, European Patent 0002067 (1978).
4. K. A. SCHWETZ and W. GRELLNER, *J. Less Common Metals* **82** (1981) 37.
5. J. W. HENNEY and J. W. S. JONES, UK Patent Application 2014193 A (1978).
6. H. SUZUKI, T. HASE and T. MARUYAMA, *Yogyo-Kyokai-Shi* **87** (1979) 430.
7. M. BOUGOIN, F. THEVENOT, J. DUBOIS and G. FANTOZZI, *J. Less Common Metals* **114** (1985) 257.
8. M. BOUGOIN, Thèse Docteur Ingénieur, Saint-Etienne, France (1985).
9. F. THEVENOT and M. BOUGOIN, International Conference on the physics and chemistry of boron and higher borides, Albuquerque, USA, July (1985), AIP Conference Proceedings 140, "Boron-rich Solids", edited by E. Emin *et al.* (American Institute of Physics, New York, 1986) p. 51.
10. S. YAJIMA, *Ceram. Bull.* **62** (1983) 893.
11. *Idem, ibid.* **62** (1983) 903.
12. *Idem, ibid.* **62** (1983) 915.
13. Y. HASEGAWA and K. OKAMURA, *J. Mater. Sci.* **18** (1983) 3633.
14. K. OKAMURA, M. SATO and Y. HASEGAWA, *J. Mater. Sci. Lett.* **2** (1983) 769.
15. S. PROCHAZKA, S. L. DOLE, C. I. HEJNA, *J. Amer. Ceram. Soc.* **68** (1985) C235.
16. J. DUBOIS, G. FANTOZZI, M. BOUGOIN and F. THEVENOT, *Sci. Ceram.* **13** (1985); *J. Phys. Colloque C1 Suppl.* **47** (1986) C1-751.
17. M. BOUCHACOURT, F. THEVENOT and J. RUSTE, *J. Less Common Metals* **59** (1978) 139.
18. M. BOUCHACOURT and F. THEVENOT, *ibid.* **82** (1981) 219.
19. M. BOUCHACOURT, Doctoral Thesis, INPG Grenoble and Saint-Etienne, France (1982).

Received 3 February
and accepted 10 April 1986