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Preparation, microstructure and mechanical properties of SiC–SiC and B_4C–B_4C laminates

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Abstract

Silicon carbide and boron carbide are high hardness materials with a low density but, like most ceramics, with a low toughness, that limits their use in various applications. One approach to reinforce ceramic materials consists in using crack deflection by weakening the interfaces in laminar materials. In our study, ceramic layers of different compositions were prepared by tape casting and stacked in predefined sequences. Different weak layers were tested: porous layers made with different pore forming agents for SiC; porous layers made with pore forming agent or by varying the quantity of sintering aid and weak interfaces made with graphite spray for B_4C. After debinding, SiC (Al_2O_3, Y_2O_3 additions) and B_4C (C addition) were pressureless sintered. For evaluation of the sintered parts, firstly the macrostructure and microstructure were characterized. Then, mechanical properties of multi-layered materials, obtained by stacking dense and porous layers that should contain enough porosity to initiate crack deflection, according to the models, were evaluated.

Keywords: Boron carbide; Silicon carbide; Laminar materials; Tape casting; Rupture; Crack deflection

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1. Introduction

A way to reinforce ceramics, often characterized by their low toughness that induces catastrophic rupture of the materials, is to use laminar materials. Thus, functionally graded materials were chosen to improve fracture toughness in non-oxide ceramics. The use of weak interfaces or interlayers allows to improve mechanical properties of ceramic materials. The weak interface can be made by the incorporation of graphite [1], boron nitride [2] or oxide ceramics ($LaPO_4$ or YPO_4) [3]. Another way to reinforce ceramic materials is to introduce porous ceramic interlayers. Thus, alternate dense–porous alumina [4] and alternate dense–porous SiC (solid phase sintering) were made [5]. In these materials, crack deflection occurred at the interface between porous and dense layers and the fracture energy was increased.

Clegg et al. [4,5] proposed an energetic criterion to explain crack deflection mechanism in alternate dense–porous ceramic materials. It is well-known that the interface crack deflection is influenced by the fracture energy and by Young's modulus of materials constituting each side of the interface [6,7]. These two properties are dependent on the porosity.

He and Hutchinson [8] established, in the case of a weak graphite interface in SiC material, that the ratio between fracture energies of the weak interface G_i and of the strong layer G_s must fulfil the following criterion to allow the crack to deflect at this interface:

$$G_i/G_s \leqslant 0.57. \tag{1}$$

For dense–porous laminates, Clegg et al. [4,5] expressed this criterion considering that the interface energy G_i is replaced by the ligament energy G_{lig} (ligament of ceramic material between pores in which the crack propagates):

$$G_{lig}/G_s \leqslant 0.57. \tag{2}$$

Therefore, Eq. (2) can be expressed in relation with porosity p:

$$G_p/(G_d(1-p)) \leqslant 0.57, \tag{3}$$

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where G_p is the fracture energy of the porous layer, G_d that of the dense layer.

According to Eq. (3), a minimum of porosity is required to initiate crack deflection at the interface between porous and dense layers, this porosity is 37 vol% and it was confirmed experimentally in SiC [4] and alumina [5] specimens.

To verify these energetic criteria, we have undertaken the study of different multi-layered materials fabricated by tape-casting:

- SiC (alternate dense–porous) densified by liquid phase sintering, this mode of sintering has not been used for this type of laminar composite up to now.
- B_4C (alternate dense–porous) densified by solid phase sintering, that also is a new laminar system.
- B_4C with weak graphite interfaces has been produced too.

2. Experimental

Different types of materials were prepared:

- Monolithic and alternate dense–porous specimens for SiC (the elaboration process is fully described in Ref. [9]).
- Monolithic and alternate dense–porous specimens for B_4C.

Tape casting and thermocompression processing was chosen to prepare multi-layered materials. This technique allows to obtain thick and uniform layers. First, the different constituents of the tape casting slurry will be presented. Then, the preparation of the samples will be explained. Finally, techniques of characterization will be given.

2.1. Ceramic powders and organic additives

Slurries for tape-casting usually contain a mix of different organic compounds. As organic solvent, the MEK-Ethanol azeotrope (60 vol% butanone-2/40 vol% ethanol) was used. As dispersant, Beycostat C213 (CECA-France) was used to disperse the ceramic powder. An acrylic binder and a phthalate plasticizer ensured the cohesion and the flexibility of the tape, respectively. Polyamide powders (mean diameter: 4.7, 10.5 and 20.7 μm, PA12, Orgasol, Atofina, France) together with corn starch (mean diameter: 14 μm, Roquette, France) were used as pore forming agents (PFA). For SiC, a powder of graphite platelets (mean size: $8 \times 8 \times 3\,\mu m^3$, Union Carbide) was used. For B_4C, a graphite spray (Graphène, Orapi) was utilized to make weak interlayers.

Silicon carbide (SiC powder: Sika Tech FCP13, Norton-Norway, mean diameter 1 μm) samples were liquid phase sintered [10] (sintering aid: YAG/alumina eutectic 5 wt%).

Boron carbide (B_4C powder: Tetrabor 3000F, Wacker Ceramics, mean diameter 0.75 μm) samples were solid phase sintered [11–14] (sintering aid: phenolic resin 9 wt% (Novolac PN320, Solutia France).

2.2. Sample processing

Proportions of different components used for the fabrication of B_4C tapes are given in Table 1, the volume percentage of the main constituents in green tapes in Fig. 1, respectively.

Notably, there is a high amount of organic additives, especially in tapes containing PFA, which further induces burn-out difficulties, requiring to perform burn-out with very slow heating rate.

Preparation of SiC and B_4C slurries was very similar. The used processing steps are shown in the flow chart (Fig. 2).

The different constituents were milled and mixed at different rotation speeds. After de-airing at a very slow rotation speed and verifying the viscosity, slurries were tape cast. The tapes were cut, stacked in a predefined sequence and thermo-compacted under a pressure of 60 MPa at a temperature of 70°C. Then, the samples were debindered and pyrolyzed (in air for SiC and in argon atmosphere for B_4C) at very slow heating rate and finally they were sintered in VAS (Vide Appareillage System) graphite furnace under argon atmosphere (at 1950°C for 1 h for SiC and at 2150°C for 1 h for B_4C).

Table 1
Composition of green tapes for B_4C in wt%

	Dense layer	Porous layer (PFA)	Porous layer (under-sintered)
Ceramic	63	28.8	72
Dispersant	2.3	1	2.6
Sintering agent	12.5	5.7	0
PFA	0	50	0
Binder	9.5	6.2	12.7
Plasticizer	12.7	8.3	12.7

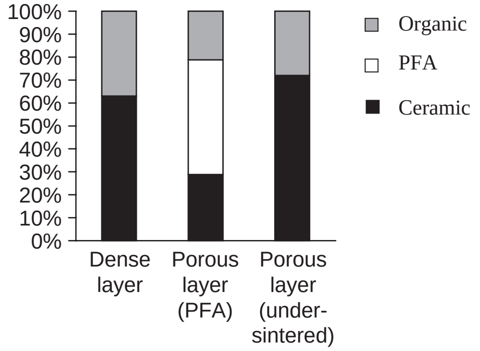


Fig. 1. Volume percentage of main constituents in green tapes for B_4C.

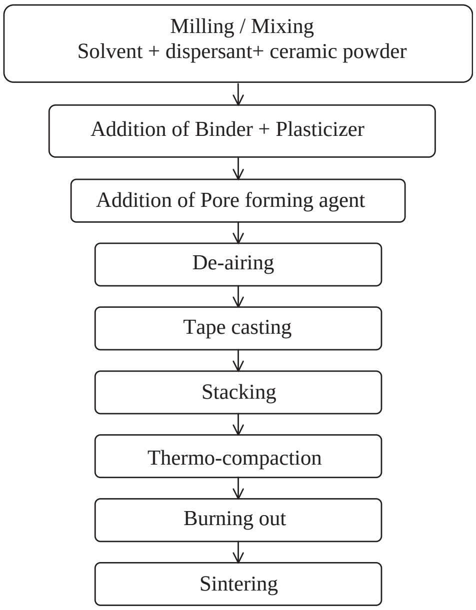


Fig. 2. Steps for preparation of ceramic–ceramic laminates.

Specimens were diamond polished using different stages to obtain a mirror finish. To reveal the microstructure, materials were etched. For B_4C, polished surfaces were electrolytically etched with KOH solution. For SiC, polished surfaces were plasma etched (in CF_4/8 vol% O_2 atmosphere).

2.3. Sample characterization

Density of materials was calculated from measured weight and the geometrically determined volume. The porosity was determined by helium pycnometry for closed porosity; however, the size distribution and proportion of open porosity were determined by mercury porosimetry.

Image analysis was used for characterization of grain and pore size using micrographs obtained by optical microscopy (for porosity) and SEM (for grain size).

Crack propagation in multi-layered materials was evaluated using 3 point-bending fracture tests on notched specimens (20 mm span, INSTRON 8562, displacement measured by LVDT sensor, cross-head speed 0.025 mm/min).

3. Results and discussion

3.1. Macrostructural and microstructural characterization

3.1.1. SiC

Different polyamide powders and corn starch were tested as pore forming agents [9].

Polyamide powders allowed to obtain different pore sizes (from 4 to 20 μm), corn starch led to spherical pores of approximately 10 μm. Corn starch led to the highest level of porosity (47 vol% for 55 vol% of corn starch). In addition, the pyrolyzation was easier with starch.

In the multi-layered materials, the thickness was 70 μm for dense layers and 80 μm for porous layers. The microstructure of dense layers and of ligaments in porous layers were similar (grain size 1.2 μm, aspect ratio 1.6) [9].

3.1.2. B_4C

Different types of multi-layered materials were prepared (Fig. 3, Table 2):

Alternate dense–porous materials with porous layer made with pore forming agent or with porous layer made in the absence of sintering aid: Whatever the material, the layers had uniform thickness and were parallel each other. The grain size in the porous layers was similar to that of the dense ones. The mean grain size was 0.8 μm.

The porosity in the layer made with corn starch was interconnected and had a mean size of 10 μm. In the porous layer made in the absence of sintering aid, the porosity was finer.

Weak interfaces made with graphite spray: These specimens were produced by graphite coating via spraying and drying on each layer of B_4C before thermocompaction. However, this method led to problems of uniformity and reproducibility of the weak interfaces.

Dense layers had a thickness of 100 μm (Fig. 4) and a relative density of 0.94.

3.2. Fracture behavior

3.2.1. SiC

Mechanical properties of monolithic materials have been measured: Young modulus, toughness, fracture energy [15]. Clegg's criterion Eq. (3) predicted crack deflection for the SiC alternate multi-layered materials with porous layers containing a porosity larger than 37 vol%, but no significant crack deflection was observed in our case (Fig. 5).

Two issues must be considered in a discussion of the results. First, if we consider the second phase, at grain boundaries, formed by the sintering additives, the chemical composition of this phase, determined from local chemical analysis, continuously changes from dense to porous layers and there are no abrupt changes in fracture energy. As a consequence of this difference in the chemistry between the dense layers and the ligament in the porous layers, Eq. (3) is no longer valid.

Secondly, the use of graphite platelets appears more favorable to deflect cracks than equi-axed corn starch. Then, pore shape appears to be an important

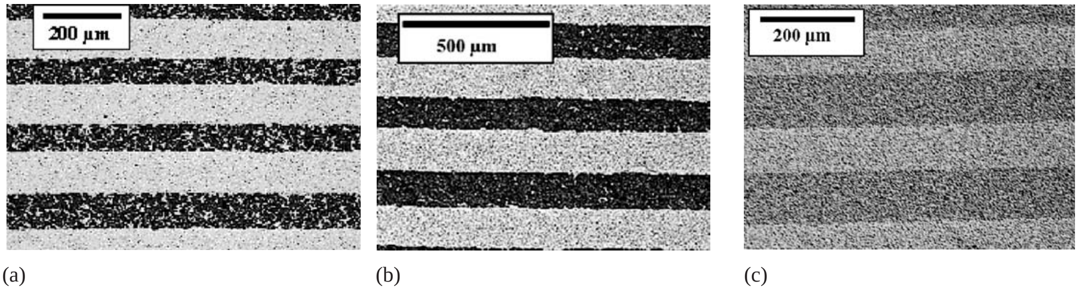


Fig. 3. Micrographs of multi-layered B_4C materials: (a) black porous layers made with 50 vol% of corn starch, (b) black porous layers made with 55 vol% of corn starch, (c) dark grey porous layers made in absence of sintering aid.

Table 2
Thickness and density of layers in different B_4C multi-layered materials

	Dense layer		Porous layer	
	Thickness (µm)	Relative density	Thickness (µm)	Relative density
a (50 vol% corn starch)	150	0.94	100	0.55
b (55 vol% corn starch)	150	0.94	100	0.50
c (without sintering aid)	100	0.94	150	0.65

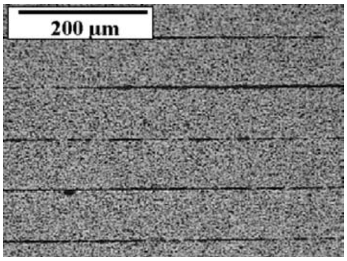
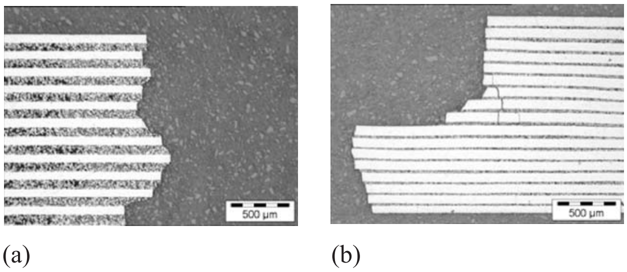
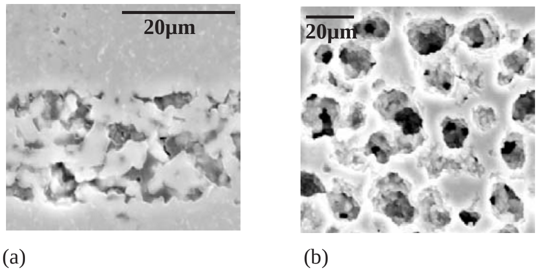


Fig. 4. Micrograph of multi-layered B_4C with weak interfaces formed by graphite coating.



(a) (b)

Fig. 5. Micrographs of SiC multi-layered materials: (a) porous layer made with corn starch $P = 46–47$ vol%, (b) porous layer made with graphite platelets $P = 40–41$ vol%.



(a) (b)

Fig. 6. Pore shape made by graphite platelets (a) or by polyamide powder (b) in SiC laminates.

characteristic. Lengthened pores aligned in the plane of the layers (Fig. 6a) seem to be more efficient that circular pores (Fig. 6b).

3.2.2. B_4C

The pictures and graphs (Fig. 7) show the crack propagation and the associated strain versus displacement curves in the different cases of laminar B_4C materials.

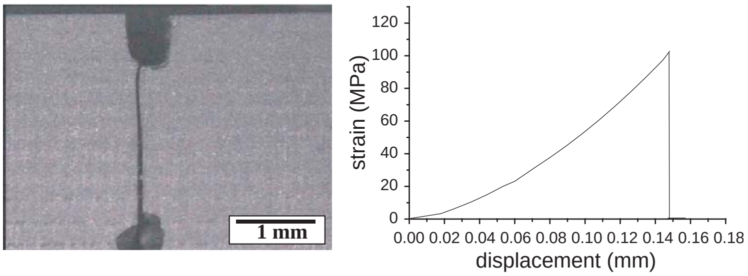
In cases (a) and (b), the rupture of the samples remains purely brittle. There is no reinforcement of materials.

However, in cases (c) and (d), crack deflection took place at the interfaces. The rupture is no more brittle and the work of fracture is improved.

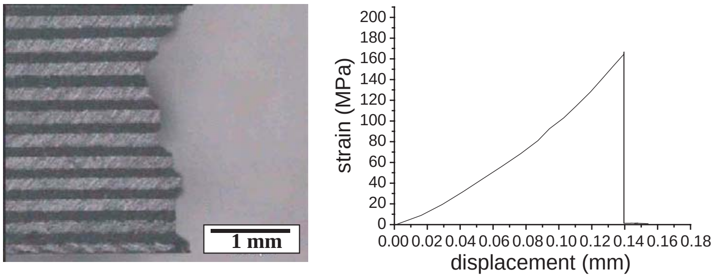
4. Conclusions

Different SiC and B_4C multi-layered materials were prepared by using tape casting and thermocompression. Characteristics of specimens were in agreement with those required to initiate crack deflection according to Clegg et al. [4,5]. Even though specimens had the required level of porosity, significant crack deflection did not occur in liquid phase sintered SiC specimens. The absence of crack deflection at the interfaces may be linked to the continuous variation of properties (rupture energy) from dense to porous layers due to the presence

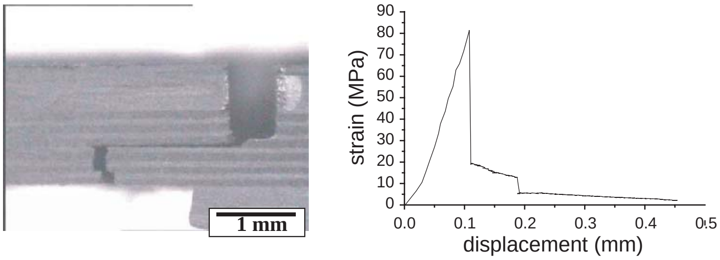
(a) Porous layers densified without sintering aid (35 vol% of porosity)



(b) Porous layers made with 50 vol%of corn starch (45 vol% of porosity)



(c) Porous layers made with 55 vol%of corn starch (50 vol% of porosity)



(d) Weak interlayers made with a graphite spray

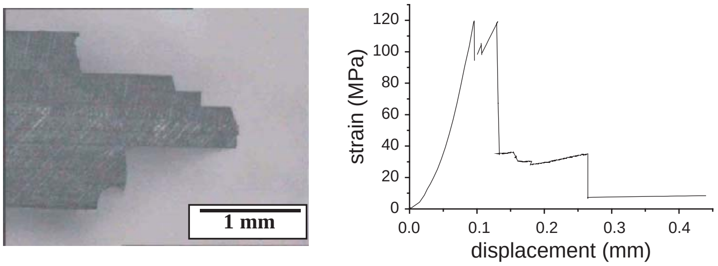


Fig. 7. Fractographies and strain versus displacement curves of different B_4C laminar materials.

of a second phase at the silicon carbide grain boundaries formed by sintering aids.

In the case of the solid phase sintered B_4C multi-layered materials, significant crack deflection was observed in few specimens.

The shape of pores seems to be a crucial parameter and elongated pores aligned with the plane of the layers seem to be more favorable to initiate crack deflection.

Studies on B_4C multi-layered materials containing weak interfaces like platelets of graphite or boron nitride are in progress to verify these conclusions.

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