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Properties of reinforced boron carbide laminar composites

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Abstract

The reinforcement by crack deflection in boron carbide laminar composites is obtained by both controlling macrostructure and microstructure. This structure had never been studied before in boron carbide materials.

Composites were prepared using tape-casting technique. Different composites with either porous interlayers obtained by pore forming agent, or weak interlayers obtained without adding sintering aid, or weak interlayers obtained by a mixture of boron carbide and boron nitride, or weak graphite or boron nitride interfaces have been elaborated and characterized. Reinforcement by crack deflection was observed in most of these composites. In comparison to the work of rupture of the dense material, i.e. 23.09 kJ m^{-3}, the following values were obtained for the laminar composites: 38 kJ m^{-3} for composites with interlayers with corn starch (55 vol.%), 40 kJ m^{-3} for composites with B_4C-BN interlayers, 30 kJ m^{-3} for composites with weak interlayers in BN and 39 kJ m^{-3} for composites with weak interlayers in graphite.

Keywords: Tape casting; Composites, Porosity; Mechanical properties; B_4C; BN

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. The use of weak interfaces or interlayers in functionally graded materials could be efficient to improve toughness in non-oxide ceramics. The weak interface could be obtained by the incorporation of graphite,[1] boron nitride[2] or oxide ceramics ($LaPO_4$ or YPO_4).[3] Another way to reinforce ceramic materials was to introduce porous ceramic interlayers. Thus, alternate dense-porous alumina[4] and alternate dense-porous SiC (solid phase sintering)[5] have been studied. In these materials, crack deflection occurred at the interface between porous and dense layers leading to an increase of the fracture energy.

Clegg and coworkers[4,5] analyzed crack deflection mechanism in alternate dense-porous ceramic materials using an energetic criterion. It is well known that the interface crack deflection is influenced by the fracture energy and by the Young's modulus of materials constituting each side of the interface. These two properties are dependent on the porosity. In the case of a weak graphite interface in SiC material, He and Hutchinson[6] established 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:

$$\frac{G_i}{G_s} \leq 0.57 \qquad (1)$$

For dense-porous laminates, Clegg and coworkers[4,5] expressed this energetic criterion (Eq. (1)) considering that the interface energy G_i could be replaced by the ligament energy G_{lig} (ligament of ceramic material between pores in which the crack propagates):

$$\frac{G_{lig}}{G_s} \leq 0.57 \qquad (2)$$

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

$$\frac{G_\mathrm{p}}{G_\mathrm{d}(1-p)} \leq 0.57 \tag{3}$$

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

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

In this context, we have studied boron carbide laminar composites for their potential applications in armor and in nuclear energy fields.[7] Different boron carbide composites with various weak interlayers or weak interfaces were elaborated to study their reinforcement properties by crack deflection.[8] The energetic criterion and the level of porosity reported by Clegg and coworkers[4,5] to achieve crack deflection in the case of porous weak interlayers have been verified for boron carbide laminar composites.

2. Experimental procedure

2.1. Preparation

The different composites have been elaborated using the tape-casting technique. The complete description of the process has already been described.[9,10] Composites were composed of alternate dense boron carbide layers (94% of theoretical density) and weak layers or weak interfaces. Starting from boron carbide powder (Tetrabor 3000F, Wacker Ceramics, mean diameter 0.75 μm), solid state sintering of boron carbide was performed by pressureless sintering (2150 °C/1 h under argon) using phenolic resin as sintering aid.[8,10] Composites with different types of interlayers and interfaces have been elaborated (Table 1). Porous interlayers were obtained using corn starch as pore forming agent, under-sintered interlayers using no sintering aid and weak interlayers using a mixture of boron carbide and boron nitride (55/45 in volume). Weak interfaces were obtained using different sprays (graphite or boron nitride) which have been pulverized on dense layers before thermocompression.

Table 1
Denomination of the various composites elaborated.

Composites denomination	Composite with
NSA	Interlayers with no sintering aid
B_4C-BN	Interlayers with mixing B_4C-BN (55/45 in voume)
CS45	Interlayers prepared with 45 vol.% of corn starch
CS50	Interlayers prepared with 50 vol.% of corn starch
CS55	Interlayers prepared with 55 vol.% of corn starch
I-BN	Interfaces with boron nitride
I-G	Interfaces with graphite

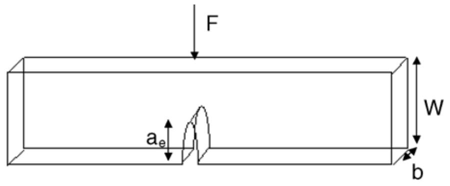


Fig. 1. Schematic representation of notched specimen tested in 3 point-bending fracture test. Span $L = 20$ mm; W: thickness; b: width; a_e: notch depth. F indicates the direction of the applied load. The layers are perpendicular to this direction.

2.2. Technical characterizations

Density of materials was calculated from the measured weight and the geometrically determined volume. Image analysis was used for characterization of grain and pore size using micrographs obtained by optical microscopy (for porosity) and SEM (for grain size).

2.2.1. Description of the technique of observation of crack propagation

Crack propagation in multi-layered materials was evaluated using 3 point-bending fracture tests on notched specimens (Fig. 1). A mechanical testing machine was used (INSTRON 8562) with a cross-head speed of 0.025 mm/min. The displacement was measured by an LVDT sensor.

2.2.2. Measure of the work of rupture and of the crack deviation

The work of rupture was evaluated using load–displacement curves and the crack deviation was measured on fractographies of composites.

The work of rupture W_R was calculated using Eq. (4) where $C(x)$ corresponds to the hatched area below the curve (Fig. 2) until the load reached a plateau for a load C.

$$W_\mathrm{R} = \frac{1}{Lb(W-a_\mathrm{e})}\int C(x)\,\mathrm{d}x \tag{4}$$

An apparent friction stress can be calculated using Eq. (5).

$$F_\mathrm{f} = \frac{C}{b(W-a_\mathrm{e})} \tag{5}$$

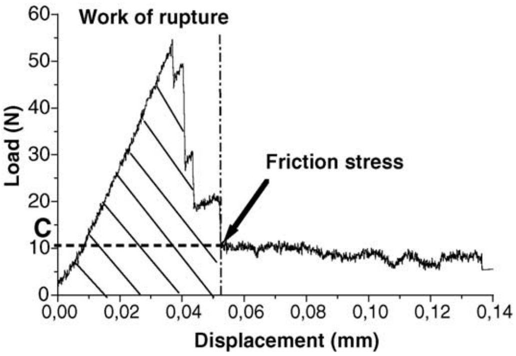


Fig. 2. Load–displacement curve obtained on lamellar composites.

An apparent fracture toughness has been calculated using the maximum load withstand by the composite. The fracture toughness was measured using SENB method[11] by Eq. (6) and correlated with the real fracture toughness by Eq. (7).[11] Indeed, the value measured with SENB method overestimates the value of the fracture toughness when the notch root radius increases. A correction of the SENB value has to be done.

$$K_{\mathrm{IC}}^{\mathrm{SENB}} = \sigma_{\mathrm{r}}\sqrt{a_{\mathrm{e}}}\sum_{i=0}^{4} A_i \left(\frac{a_{\mathrm{e}}}{W}\right)^{i} \tag{6}$$

where

$$A_0 = 1.9 + 0.075\frac{L}{W},$$

$$A_1 = -3.39 + 0.08\frac{L}{W},$$

$$A_2 = 15.4 - 0.2175\frac{L}{W},$$

$$A_3 = -26.24 + 0.2825\frac{L}{W},$$

$$A_4 = 26.38 - 0.145\frac{L}{W}.$$

$$K_{\mathrm{IC}} = K_{\mathrm{IC}}^{\mathrm{SENB}} \tanh\left(2Y\sqrt{\frac{a_{\mathrm{c}}}{\rho_{\mathrm{e}}}}\right) \tag{7}$$

where ρ_{e} is the notch root radius, a_{c} the size of critical defect and Y a geometrical factor equal to 1.12 for a sharp crack.

Lengths of crack deviation were measured on fractographies using the method developed by Kovar et al.[12] This method consists in obtaining the delamination distances measuring the distance between through-thickness crack in adjacent dense layers. An example of the method used is given Fig. 3. The length of deviation at each interface or interlayer was measured. For each specimen, the maximum deviation and the mean deviation for each interface or interlayer were given.

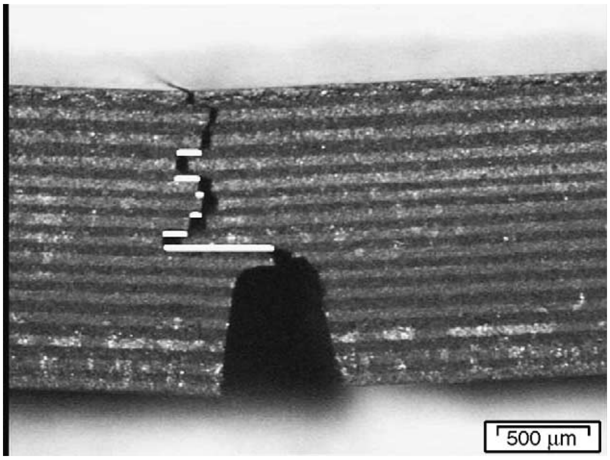


Fig. 3. Fractography of a lamellar composite (CS55), the white lines correspond to different crack deviations that have been measured.

3. Description of each type of composite: macrostructure and mechanical properties

Different types of interlayers or interfaces were elaborated. The denomination of each composite is indicated in Table 1. Whatever the material, the layers had uniform thickness and were parallel each other. The dense layers are similar in the different composites. The toughness of a material made of dense layers is equal to 2.9 MPa m$^{-1/2}$ and a work of rupture equal to 23 kJ m^{-3}.

3.1. *Weak interlayers*

3.1.1. *Macrostructures and fractographies of the composites containing weak interlayers*

Different weak interlayers were studied, some had porosity obtained with corn starch (CS), others were obtained using no sintering aid (NSA), others mixing boron carbide and nitride (B_4C-BN). The grain size in the porous layers was similar to that of the dense ones (0.8 μm). The porosity in the layers with corn starch was interconnected and had a mean size of 10 μm. In the porous layer without sintering aid, the material is under-sintered and the porosity was finer (around the micrometer). The weak layers obtained by a mixture of boron carbide and boron nitride have a skeleton of boron carbide containing boron nitride grains. Macrostructures of the different composites elaborated were represented in Fig. 4.

Considering the characterization of the reinforcement taking place in these composites, the typical results of 3 point-bending tests were represented for each type of composite in Figs. 5–7. Reinforcement by crack deflection was observed in the case of interlayers with corn starch for a porosity larger than 0.51 (CS55) (Fig. 5) and for the interlayers made with a mixing of B_4C-BN (Fig. 7). In addition, as can be observed on the load–displacement curves, in these two cases, there was a friction stress due to the succession of crack deflections that induced a load resistance. In opposition, no crack deflection was observed in the composite (NSA) where interlayers are under-sintered. The rupture was brittle (Fig. 6).

3.1.2. *Weak porous interlayers in composites CS*

The influence of the porosity in the porous layers and the relative thickness between the dense and the porous layers on the work of rupture and on the lengths of crack deflection was studied in the composites (CS) with weak interlayers with corn starch.

3.1.2.1. Influence of the porosity on crack deflection in CS. First, let us see the results concerning the influence of the level of porosity on the crack deflection properties. When the

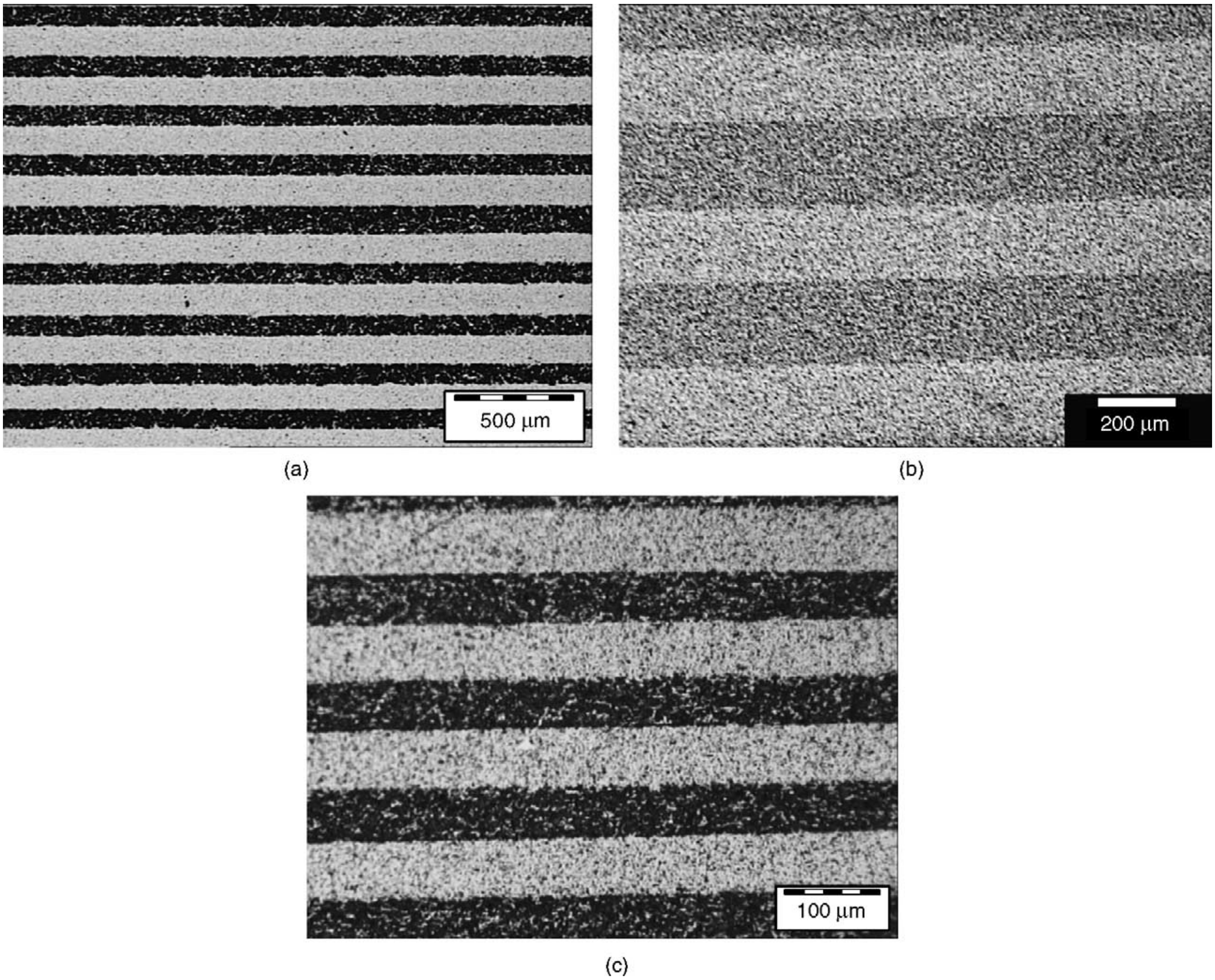


Fig. 4. (a–c) Macrostructures of the different composites: (a) interlayers with corn starch (CS50); (b) interlayers under-sintered (NSA); (c) interlayers of B_4C-BN. Black layers: porous; grey layers: dense.

porosity increased in the interlayers, an important increase of the work of rupture (Fig. 8) and of the length of crack deflection (Fig. 9) was observed for a porosity of 0.51. Moreover the presence of a friction stress indicated some reinforcement in the case of a porosity equal to 0.46 and 0.51 (Table 2). The apparent fracture toughness was also increased with porosity (Table 2). More the interlayers were porous, so brittle, better was the reinforcement of the composite. Then, the porosity in the porous interlayers is an important criteria for crack deflection in composites. In the introduction, a porosity of 0.37 was required by Clegg and coworkers[4,5] to observe crack deflection in such type of materials. In boron carbide composites, deflection appeared from a porosity of 0.51. There is a great difference between our observations and those predicted by the theory of Clegg. This difference can be explain by studying the energetic criterion,[8] that is fully developed in a further article.[13]

Table 2
Values of apparent toughness and friction stress in function of the porosity in the interlayers in composites (CS) with interlayers with corn starch

Composites	Porosity in porous interlayers	K_{IC} (MPa m$^{1/2}$)	F_f (MPa)
CS45	0.42	1.54 ± 0.16	0
CS50	0.46	1.95 ± 0.34	1.26 ± 0.78
CS55	0.51	3.44 ± 0.95	1.81 ± 0.59

3.1.2.2. Influence of the relative thickness of the layers in CS55. The influence of the relative thickness of the dense and of the porous layers e_d/e_p was studied in composites containing a porosity of 0.51 in the porous layers (CS55). This parameter was varied between 0.27 and 2.57. Macrostructures of these types of composites were represented in Fig. 10.

As we can observe for work of rupture (Fig. 11), lengths of crack deflection (Fig. 12) and also for the apparent friction stress[8] and the apparent fracture toughness[8], there was a great dispersion of the values in function of e_d/e_p. This criterion seemed to have no significant influence on reinforcement by crack deflection. All the composites tested (CS55) presented reinforcement.

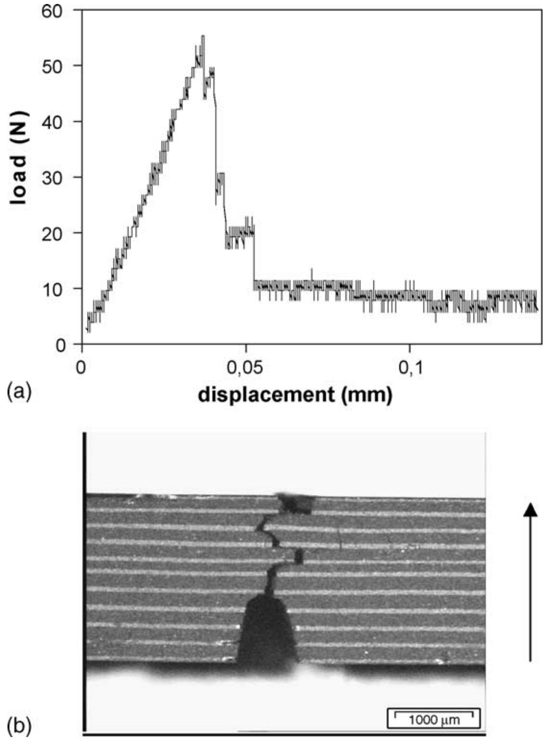


Fig. 5. (a) Load–displacement curve of a composite (CS55) with interlayers with corn starch and with a porosity of 0.51. (b) Fractography of a composite (CS55) with interlayers with corn starch and with a porosity of 0.51. The arrow next to the fractography indicates the direction of the crack propagation.

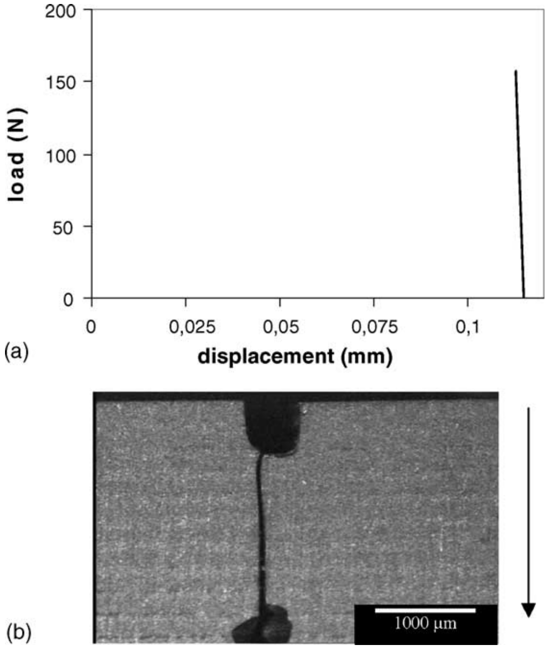


Fig. 6. (a) Load–displacement curve of a composite (NSA) with interlayers under-sintered. (b) Fractography of a composite (NSA) with interlayers under-sintered. The arrow next to the fractography indicates the direction of the crack propagation.

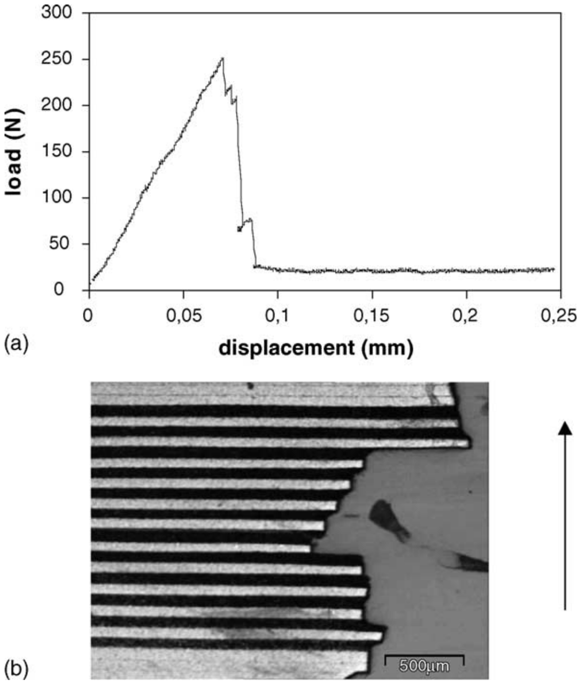


Fig. 7. (a) Load–displacement curve of a composite (B_4C-BN) with interlayers with a mixture of boron carbide and boron nitride. (b) Fractography of a composite (B_4C-BN) with interlayers with a mixture of boron carbide and boron nitride. The arrow next to the fractography indicates the direction of the crack propagation.

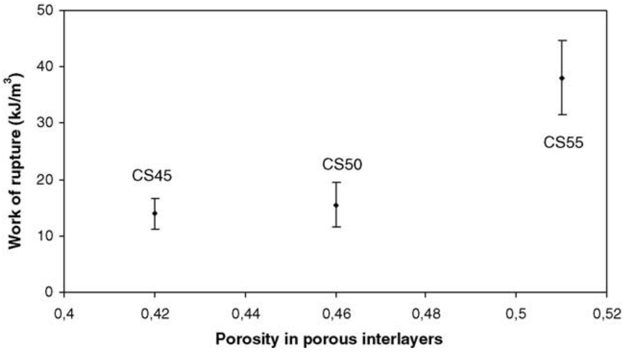


Fig. 8. Work of rupture in function of the porosity in porous interlayers in composites (CS) with interlayers made with corn starch.

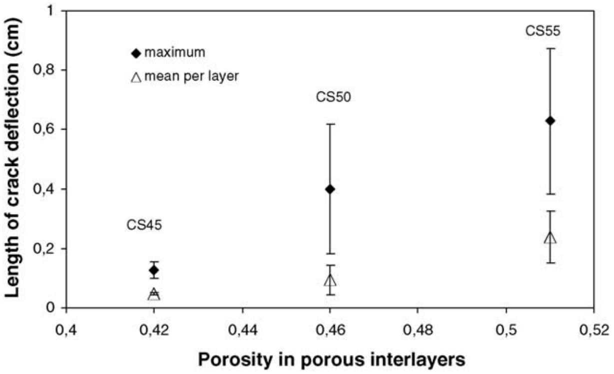
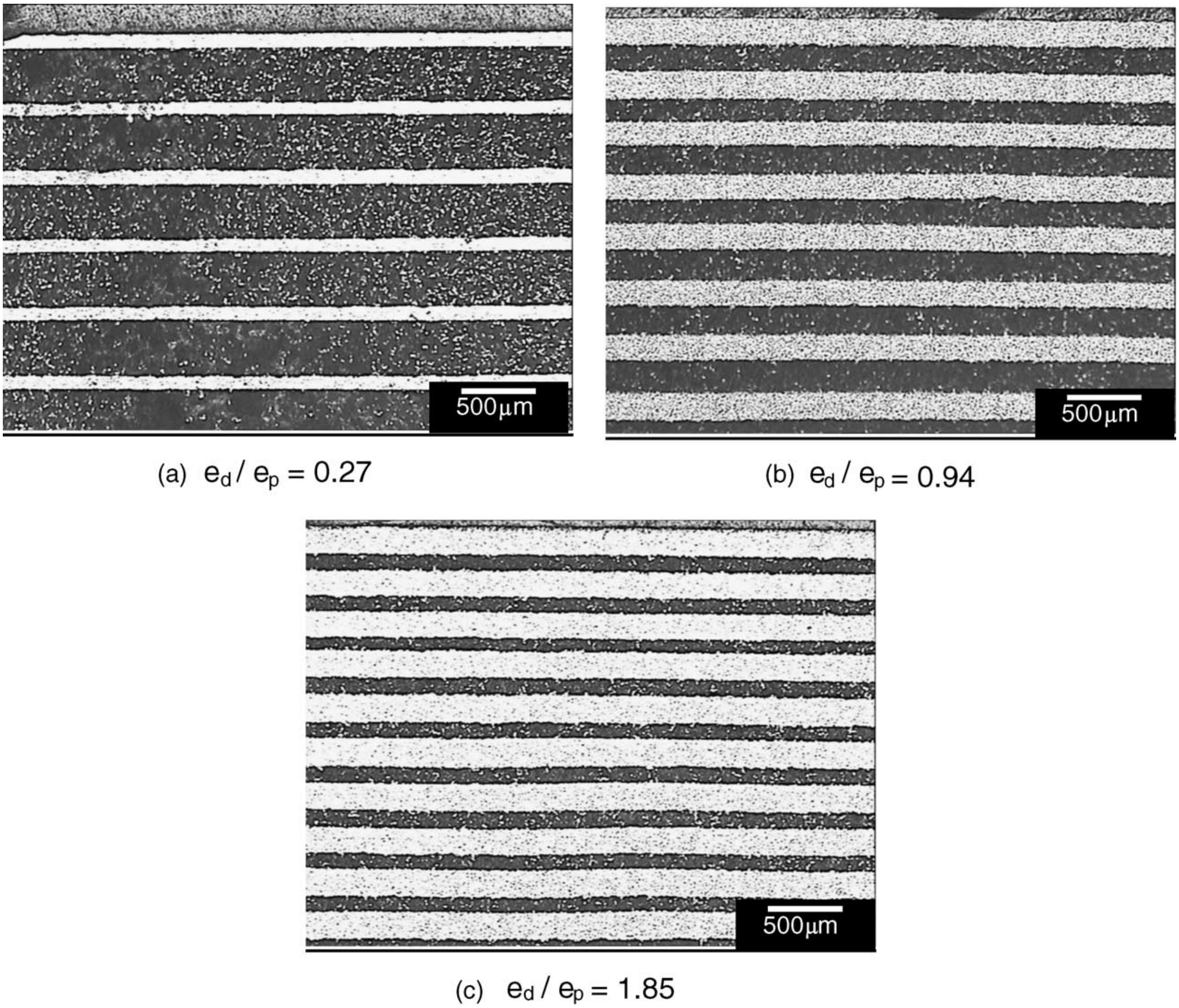


Fig. 9. Lengths of crack deflection in function of the porosity in porous interlayers in composites (CS) with interlayers made with corn starch.



(a) $e_d / e_p = 0.27$ (b) $e_d / e_p = 0.94$

(c) $e_d / e_p = 1.85$

Fig. 10. (a–c) Macrostructure of composites (CS55) with interlayers obtained by the use of corn starch ($p = 0.51$) with different relative thicknesses.

3.2. Weak interfaces

Two different weak interfaces were studied: some with graphite spray (I-G) and some with boron nitride spray (I-BN). Dense layers had a thickness of approximately 100 µm and were separated by thin interfaces of graphite or boron nitride (less than 5 µm). The vaporization of the spray did not lead to a constant thickness of interfaces (Fig. 13). Long crack deflections and sometimes layer delaminations were observed on these two types of composites (Figs. 14 and 15). An increase of the work of rupture was also observed.[8] A significant reinforcement by crack deflection was observed in composites with weak interfaces, either for weak interfaces in graphite (I-G) or in boron nitride (I-BN). The problem encountered in this type of composite is linked in the difficulties to reproduce the weak interfaces. This was related to the method used to pulverize the spray that could be improved.

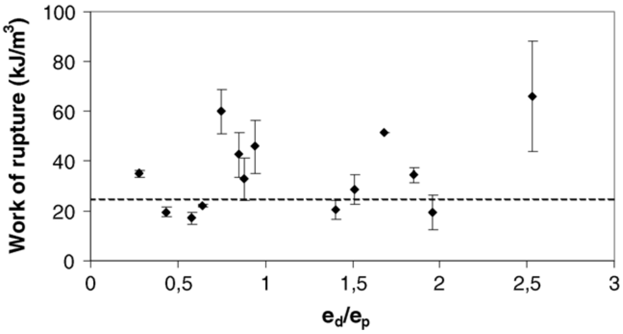


Fig. 11. Work of rupture in function of the relative thickness in composites (CS55) with interlayers with corn starch. The dote line correspond to the value of work of rupture for the dense boron carbide.

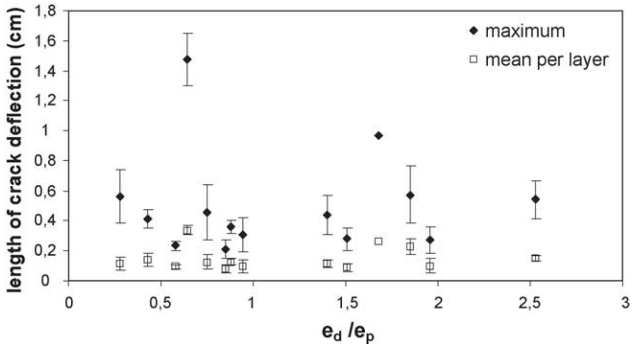


Fig. 12. Lengths of crack deflection in function of the relative thickness in composites (CS55) with interlayers with corn starch.

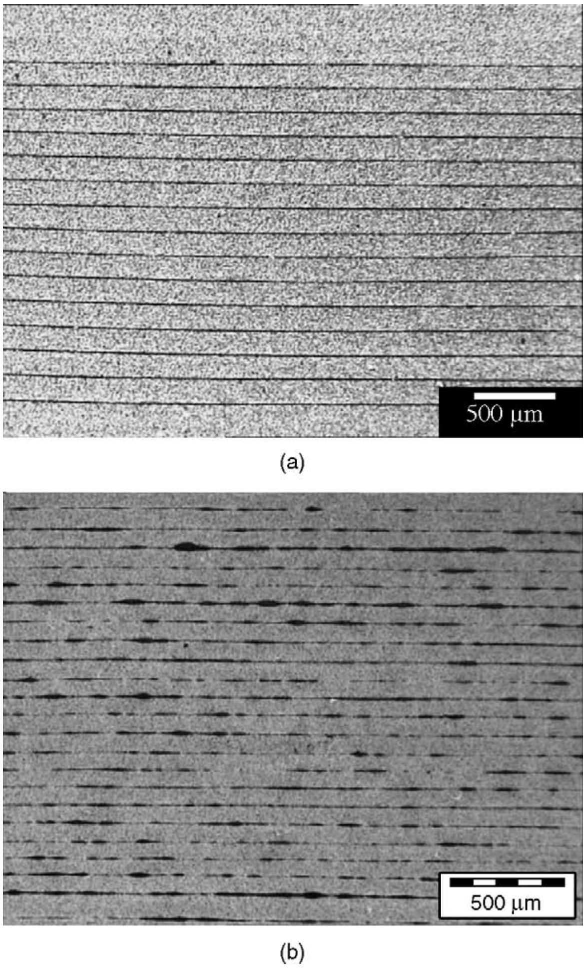


Fig. 13. (a) Macrostructure of a composite with interfaces of graphite (I-G). (b) Macrostructure of a composite with interfaces of boron nitride (I-BN).

4. Comparison of the reinforcement by crack deflection in the different composites tested

In order to compare the different composites, the different results of work of rupture (Fig. 16), length of crack deflection (Fig. 17), apparent fracture toughness[8] and apparent friction stress[8] were analyzed.

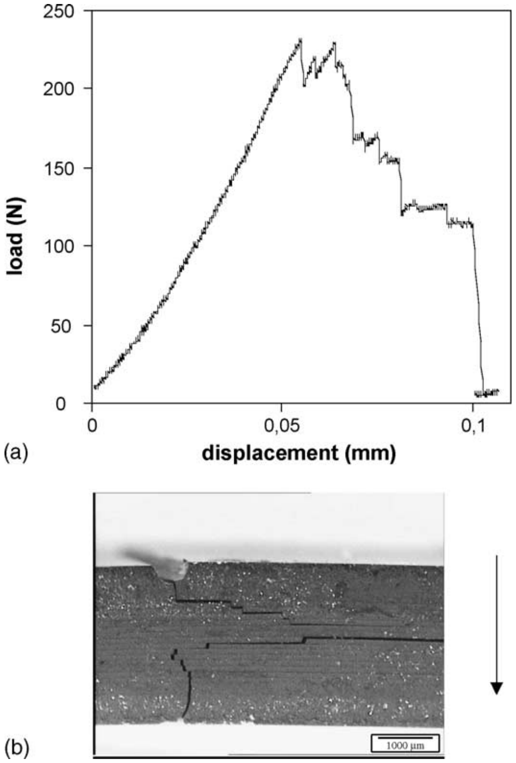


Fig. 14. Load–displacement curve and fractography of a composite (I-G) with interfaces of graphite. The arrow next to the fractography indicates the direction of the crack propagation.

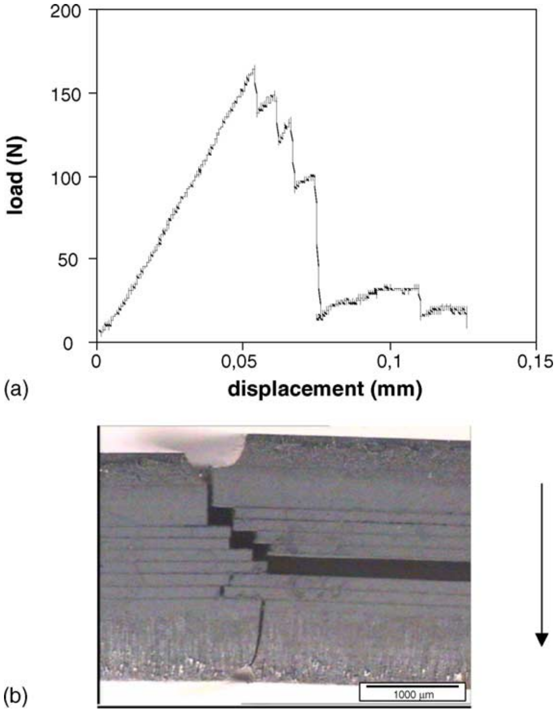


Fig. 15. Load–displacement curve and fractography of a composite (I-BN) with interfaces of boron nitride. The arrow next to the fractography indicates the direction of the crack propagation.

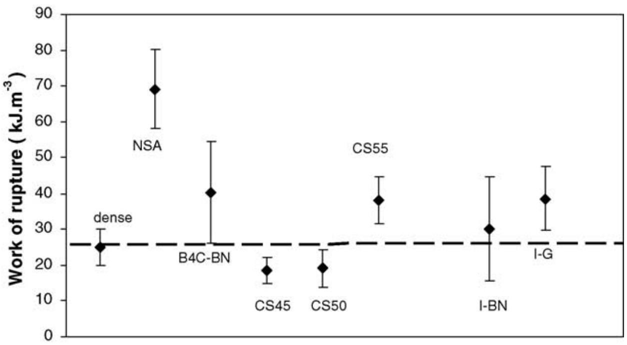


Fig. 16. Work of rupture in the different composites.

The composite NSA presented a gain of 175% for the work of rupture compared with dense material whereas no crack deflection was observed: in this case, there was no reinforcement by crack deflection. The composite with interlayers obtained by the lowest quantity of corn starch (CS45) presented no gain of work of rupture and small crack deflection: there is no reinforcement. In these two cases, no friction stress was observed.

All other composites presented reinforcement by crack deflection. Concerning composites with interlayers obtained by the use of corn starch (CS), the reinforcement was better for a large value of porosity in the interlayers: a gain of 50% for the work of rupture compared with dense material was observed and long crack deflection were measured for CS55 containing 51 vol.% of porosity. A slight gain of apparent fracture toughness (16%) was also noticed for the composite. The composite with interlayers made with a mixture of boron carbide and boron nitride presented a significant reinforcement by crack deflection: a gain of 60% in work of rupture and significant crack deflections. Both the composites with weak interfaces with graphite (I-G) and boron nitride (I-BN) presented a gain in work of rupture (54% and 20%, respectively) and a gain in apparent fracture toughness (13% and 105%, respectively).

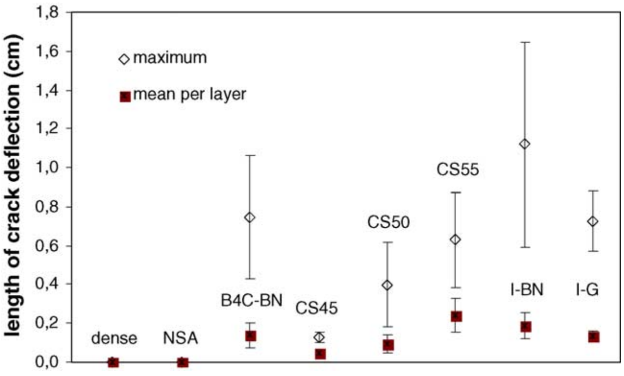


Fig. 17. Lengths of crack deflection in the different composites.

5. Conclusion

Different types of boron carbide composites have been elaborated by tape casting and lamination. These types of composites had never been studied before with boron carbide materials.[8] Different composites with either porous interlayers obtained by pore forming agent, or weak interlayers obtained without addition of sintering aid, or weak interlayers obtained by a mixture of boron carbide and boron nitride, or weak interfaces in graphite or boron nitride have been realized. Most of them presented reinforcement by crack deflection as we can see on the values of work of rupture: 38.07 kJ m^{-3} for composites with interlayers with corn starch (55 vol.%), 40.25 kJ m^{-3} for composites with B_4C-BN interlayers, 30.11 kJ m^{-3} for composites with weak interlayers in BN and 38.64 kJ m^{-3} for composites with weak interlayers in graphite. An increase is observed compare with the value for a dense boron carbide (25.09 kJ m^{-3}).

Concerning the most promising materials, further researches should be carried out concerning (i) the influence of relative thickness on weak interlayers obtained with lower contents of pore forming agent and (ii) mixtures of B_4C-BN, varying the content of BN. Concerning weak interfaces, the technique of deposition of the interlayers should be better mastered.

Acknowledgement

This work is a part of the thesis of S. Tariolle.

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