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BN interphase processed by LP-CVD from tris(dimethylamino)borane and characterized using SiC/SiC minicomposites

S. Jacques, B. Bonnetot, M.-P. Berthet and H. Vincent

Laboratoire des Multimatériaux et Interfaces
UMR 5615 University of Lyon 1 / CNRS
43, boulevard du 11 Novembre 1918
F – 69622 Villeurbanne Cedex, France

ABSTRACT

SiC/BN/SiC 1D minicomposites were produced by infiltration of a Hi-Nicalon (from Nippon Carbon, Japan) fiber tow in a Low Pressure Chemical Vapor Deposition reactor. Tris(dimethylamino)borane was used as a halogenide-free precursor for the BN interphase processing. This precursor prevents fiber and CVD apparatus from chemical damage. FT-IR and XPS analyses have confirmed the boron nitride nature of the films. Minicomposite tensile tests with unload-reload cycles have shown that the minicomposite mechanical properties are good with a high interfacial shear stress. Transmission electron microscopy observation of the interphase reveals that it is made of an anisotropic turbostratic material. Furthermore, the fiber/matrix debonding, which occurs during mechanical loading, is located within the BN interphase itself.

INTRODUCTION

In SiC/SiC type ceramic matrix composites, a good toughness can be achieved by adding between the fiber and the brittle matrix a thin film of a compliant material called "interphase"¹. Anisotropic pyrolytic boron nitride obtained from BF₃/NH₃/H₂ mixture can play such a role. But its processing by LP-CVD (Low Pressure Chemical Vapor Deposition) from BF₃ requires protecting the fiber from gaseous chemical attack^{2,3}. Furthermore, the CVD apparatus is quickly deteriorated by the aggressive halogenated gases and expensive maintenance is needed. On the other hand, some authors have reported the use of a halogenide-free precursor: B[N(CH₃)₂]₃ (tris(dimethylamino)borane, TDMAB) for CVD semiconductor *h*-BN film processing⁴.

The aim of the present contribution was to prepare within one dimensional minicomposites a BN interphase from TDMAB and to characterize this interphase and the properties of these SiC/BN/SiC minicomposites.

EXPERIMENTAL

SiC/BN/SiC minicomposites were produced by infiltration of the BN interphase within a Hi-Nicalon (from Nippon Carbon, Japan) fiber tow by LP-CVD in a horizontal hot-wall reactor (inner diameter: 24 mm) at a temperature close to 1100°C during 90 seconds. TDMAB vapor was carried by hydrogen through a bubbler at 30°C (TDMAB is liquid at this temperature and the vapor pressure is 780 Pa). The H₂ gas flow rate was 15 sccm. NH₃ was

added to the gaseous source with a flow rate of 100 sccm in order to enhance nitrogen source and favor amine group stripping from the precursor and carbon suppression in the coating. A BN film was also deposited with the same conditions on a Si wafer for Fourier transform infrared (FT-IR) spectroscopy (Nicolet spectrometer, Model MAGNA 550, USA) and X-ray photoelectron spectroscopy (XPS) analyses (SSI model 301 spectrometer). The SiC matrix was classically infiltrated in the fiber tow from $\text{CH}_3\text{SiCl}_3/\text{H}_2$ precursor gases at 950°C in a second LP-CVD reactor. In both cases, the total gas pressure in the reactors was as low as 2 kPa in order to favor infiltration homogeneity within the fiber tows.

The interphase thickness was about 150 nm and the fiber volume fraction was about 40 % (measured by weighing). The minicomposites were tensile tested at room temperature with unload-reload cycles using a machine (MTS Systems, Synergie 400, USA) equipped with a 2 kN load cell. The minicomposite ends were glued with an epoxy resin (Lam Plan, ref 607, France) in metallic tubes separated by 40 mm that were then gripped into the testing machine jaws. The crosshead speed was 0.05 mm/min. The strain was measured with an extensometer (MTS, model 634.11F54, USA) directly gripped on the minicomposite itself. The extensometer gauge length was 25 mm. The total number of matrix cracks was verified by optical microscopy on polished longitudinal sections of the failed minicomposites after chemical etching (Murakami reactant) in order to reveal the matrix microcracks which were closed during unloading. The interfacial shear stress τ was then estimated from the last hysteresis loop recorded before failure by following the method described in reference⁵.

Thin longitudinal sections of minicomposites were studied by transmission electron microscopy (TEM: Topcon 002B, Japan) after tensile test using bright-field (BF), high resolution (HR) and selected area electron diffraction (SAED) techniques. The samples were embedded in a ceramic cement (CERAMABOND 503, Aremco Products Inc., USA) and mechanically thinned. The thin sheets ($\sim 60\ \mu\text{m}$ in thickness) were then ion-milled (GATAN PIPS, USA) to electron transparency.

RESULTS AND DISCUSSION

Only two absorption bands are seen on the transmittance FT-IR spectra at $810\ \text{cm}^{-1}$ and $1380\ \text{cm}^{-1}$ typical of *h*-BN; OH bonds are not detected (Fig. 1).

At the film surface, the B/N atomic concentration ratio determined by XPS is close to one. After ionic etching, the carbon content due to surface pollution decreases drastically; the nitrogen deficit is due to a preferential etching (Fig. 2). Both analyses confirm the BN nature of the films.

Figure 3 displays a typical force-strain curve for SiC/BN/SiC minicomposites. 588 matrix cracks were detected after failure along the 25 mm gauge length. The composites exhibit a non-brittle behavior: a non-linear domain evidencing matrix microcracking and fibre/matrix debonding follows the initial linear elastic region up to a high force at failure (170 N). Therefore, (i) the BN interphase acts as a mechanical fuse and (ii) the Hi-Nicalon fibers were not damaged during the interphase BN processing from TDMAB. Furthermore, the calculated τ is 230 MPa. This value corresponds to a good load transfer between the matrix and the fibers and is as high as the best values obtained with BN interphases processed from classical halogenated gases^{3,6}.

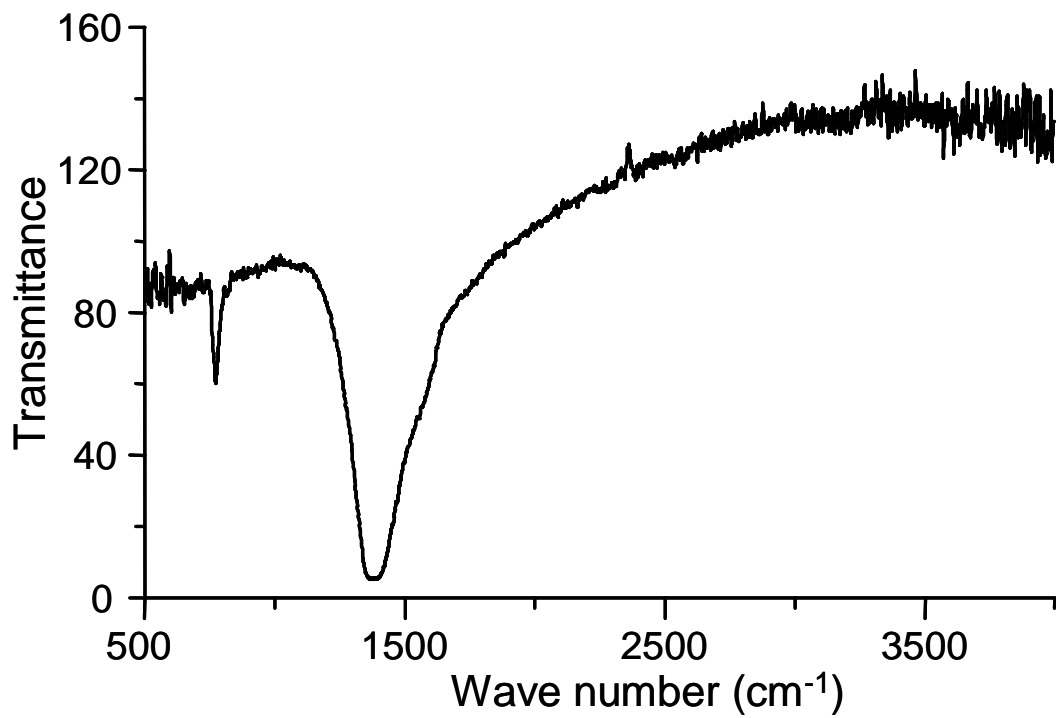


Figure 1: Transmittance FT-IR spectra of the BN film.

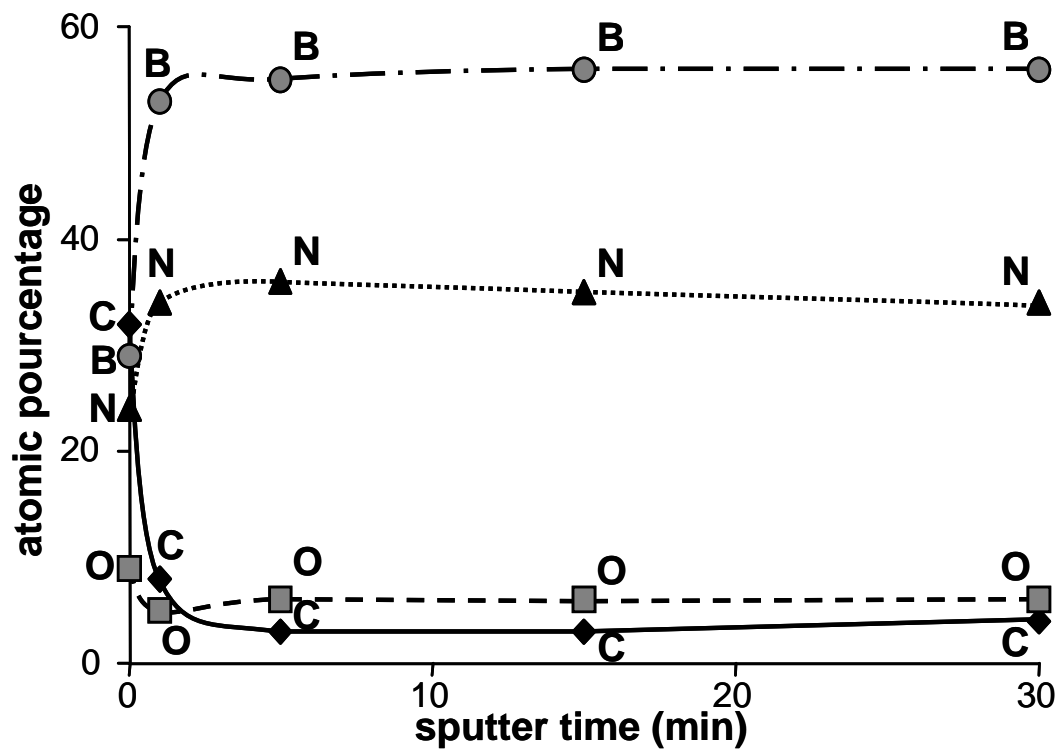


Figure 2: XPS depth atomic concentration profiles for the BN film (sputter rate: ~ 1 - 4 nm/min).

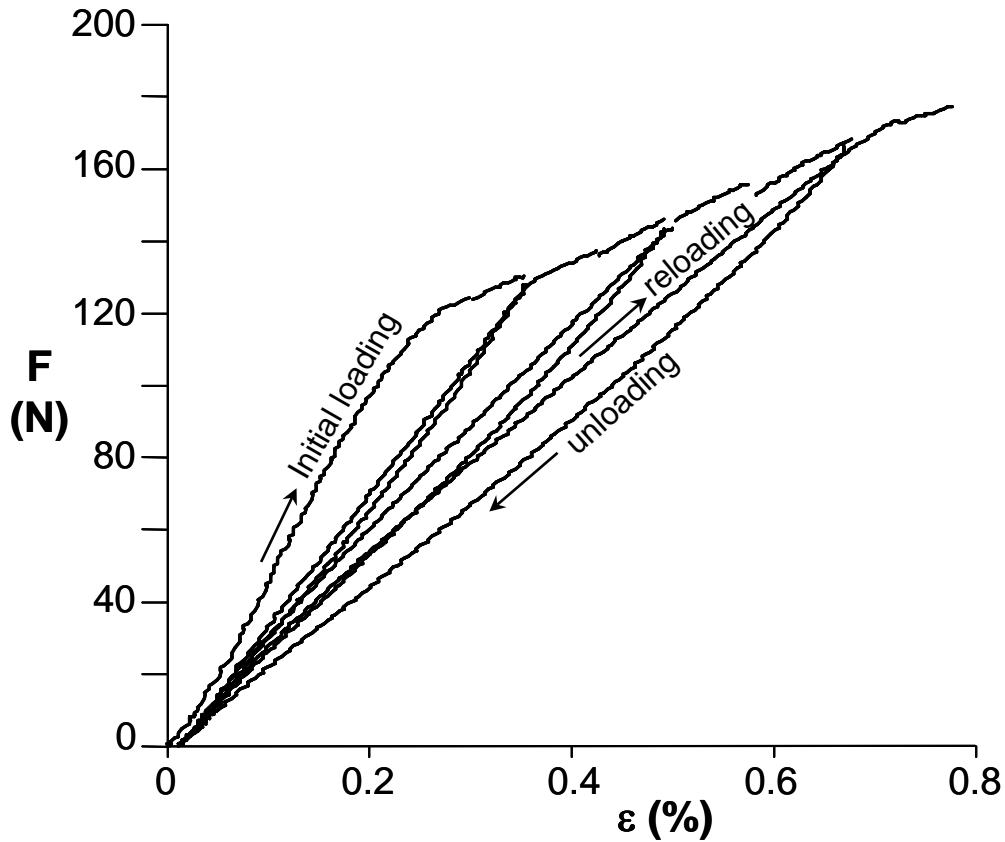


Figure 3: Tensile force-strain curve with unload-reload cycles for the minicomposites (for clarity only a few hysteresis loops are represented).

TEM observation of minicomposite pieces after failure (Fig. 4) shows that the matrix cracks deflections are preferentially localized within the BN interphase. Figure 4.a exhibits a thin matrix microcrack with a small opening displacement that is stopped within the interphase before reaching the fiber. In figure 4.b, a larger matrix crack which has been widened by the ion-milling is observed. In that case, some BN material remains bonded on both the fiber and the matrix. Thus, neither the interface with the fiber as in reference⁷ nor the interface with the matrix is a weak link. The role of mechanical fuse is played by the boron nitride interphase itself. This feature agrees with the good interfacial shear stress measured for these minicomposites and corresponds to a strong fiber bonding characterized by a high strength and a high toughness⁸.

In figure 4.c, a crack is observed within the interphase. A higher magnification in HR mode (Fig. 4.e) reveals that the orientation of the 002 BN planes seems to influence the crack path: the crack and the lattice fringes have the same curvature. Furthermore, the existence of two distinct BN 002 diffraction arcs in the SAED pattern (Fig. 4.d) is due to a preferential orientation parallel of the 002 planes to the fiber axis. This structural anisotropy promotes the mode II crack propagation observed in the interphase.

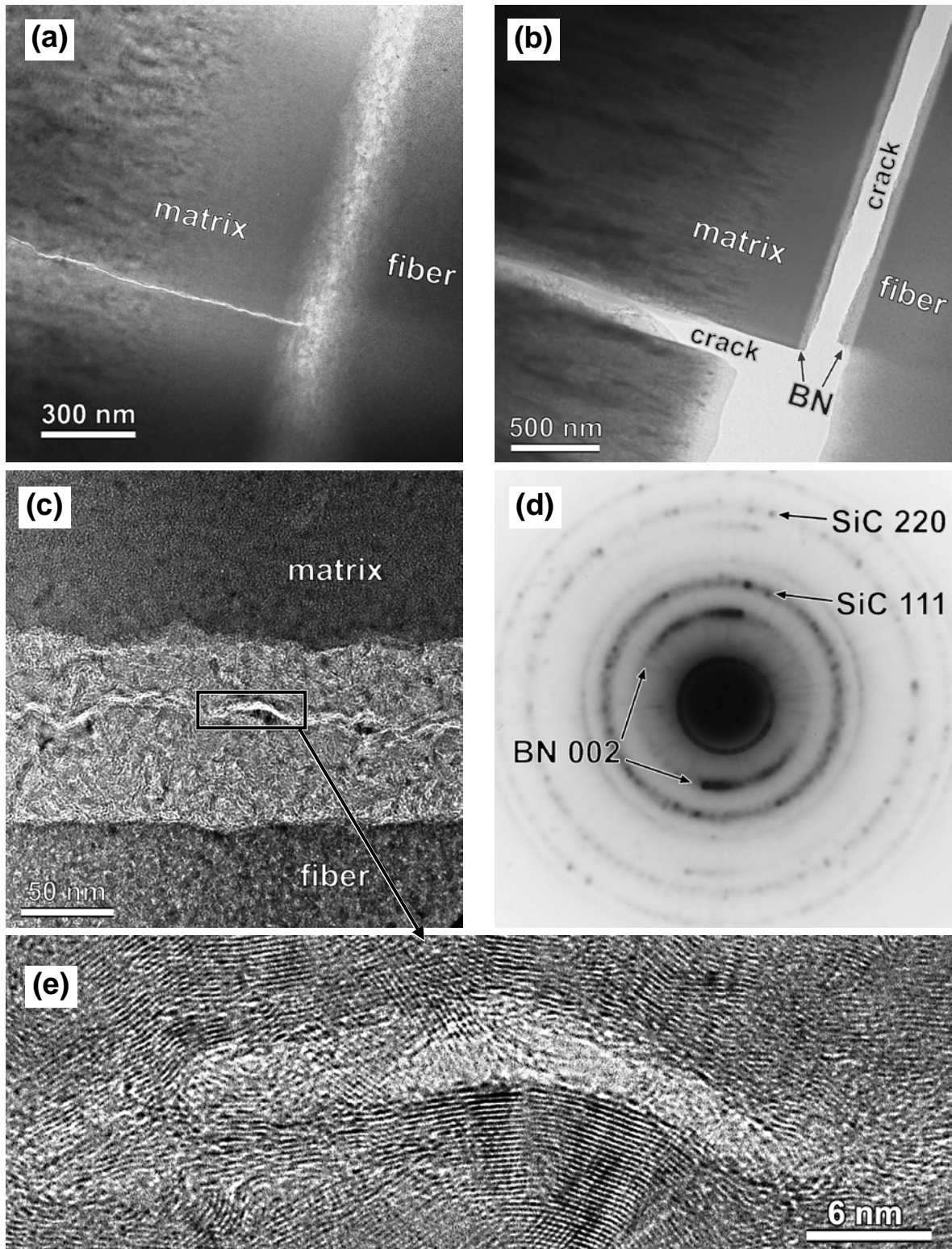


Figure 4: TEM observation of the SiC/BN/SiC minicomposite according to the BF mode (a), (b) and (c), the SAED technique (negative pattern of the Hi-Nicalon fiber and the interphase) (d) and the HR mode (e).

CONCLUSION

A BN interphase was processed by LP-CVD within SiC/SiC minicomposites from tris(dimethylamino)borane, a halogenide-free precursor. The structure of the BN material is anisotropic and allows deflecting the matrix cracks during mechanical damaging. This interphase is strongly bonded to the fiber and plays the role of a mechanical fuse. The good mechanical properties of the composites allow considering the TDMAB as a new alternative precursor to classical aggressive halogenated gases for LP-CVD boron nitride interphase processing.

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