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# Mechanical properties of SiC/SiC composites with a treatment of the fiber/matrix interfaces by metal-organic chemical vapor co-deposition of C and $Si_xC_{1-x}$

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**Résumé** - Des films de carbone pyrolytique et de carbure de silicium ont été déposés sous pression réduite par décomposition thermique respectivement de cumène et de SiEt4. La pyrolyse simultanée de ces précurseurs conduit à des films $Si_xC_{1-x}$ riches en C dont la composition peut être ajustée à partir de la phase gazeuse. Différentes interphases ont été déposées sur fibres Nicalon avant la densification par la matrice SiC. Le degré de déchaussement des fibres augmente avec la teneur en C de l'interphase et a été trouvé comparable pour une interphase de C pyrolytique et une couche à gradient dont la composition varie continuellement du C (interface avec la fibre) à SiC (interface avec la matrice). Les propriétés mécaniques mesurées après un traitement thermique à l'air à 1300 °C ont révélé toutefois la supériorité du traitement des fibres avec une couche à gradient de composition.

**Abstract** - Thin films of pyrolytic carbon and silicon carbide have been prepared under low pressure by thermal decomposition of cumene and SiEt4, respectively. The simultaneous pyrolysis of these precursors leads to C-rich $Si_xC_{1-x}$ films in which the carbon content can be controlled by monitoring the gas phase composition. Representative interphases have been deposited on Nicalon fibers prior to infiltration by the SiC matrix. The degree of fiber pull-out increases with the C content of the interphase and has been found comparable for the pyrolytic carbon and a compositional gradient layer (CGL) in which the composition changes continuously from C (fiber interface) to SiC (matrix interface). The mechanical behavior after heat treatment at 1300 °C in air have revealed the superiority of the fiber treatment with the CGL layer.

## 1- Introduction

Composite ceramic/ceramic materials find increasing applications because of their remarkable mechanical properties and their oxidation resistance to high temperature. Isothermal chemical vapor infiltration (CVI) is the most widely used technique for their preparation, although recently the thermal gradient-forced flow technique has demonstrated promising capabilities [1].

The fracture toughness of these ceramic composites can be significantly improved by a suitable treatment of the fiber/matrix interface [2]. This precoating of the fibers, the interphase, weakens the fiber/matrix bond and protects the fibers against microcracks and chemical attacks [3]. Different materials have been used as interphases including Si [4], $Si_xC_{1-x}$ [5], pyrocarbon [6] and BN [7].

Carrying out a research programme on the synthesis at moderate temperature of $Si_xC_{1-x}$ films by metal-organic chemical vapor deposition (MOCVD), we have recently proposed a CVI process for the deposition of non-stoichiometric $Si_xC_{1-x}$ films [8]. The microstructure of these films has been analyzed [9] and their composition can be adjusted between $x = 0$ and $x \approx 0.5$ by monitoring the gas phase composition [10]. This paper deals with an application of this process for the surface treatment of Nicalon SiC fibers and the preparation of SiC/SiC composites. The mechanical behavior of representative samples is presented and discussed as a function of the interphase composition. The beneficial role of C and Si to improve the fracture toughness and the oxidation resistance, respectively, is emphasized.

## 2- Experimental

### *2.1- Growth of the interphase*

The tetraethylsilane $SiEt_4$ is a suitable organometallic precursor for the deposition of $Si_xC_{1-x}$ between 700 and 900 °C [11]. In this temperature domain, a wide range of composition is possible using addition in the gas phase of either $SiH_4$ or cumene $iPrC_6H_5$ for Si [12] or C [9] enrichment, respectively. For this study, C-rich $Si_xC_{1-x}$ interlayers have been deposited on the SiC fibers by the simultaneous pyrolysis of $SiEt_4$ and cumene. The C content is controlled directly from the initial gas phase composition. Except a few quantity of oxygen in the deposits (c.a. 2 at.%), the C content is given by the difference with Si for which the concentration is reported on figure 1.

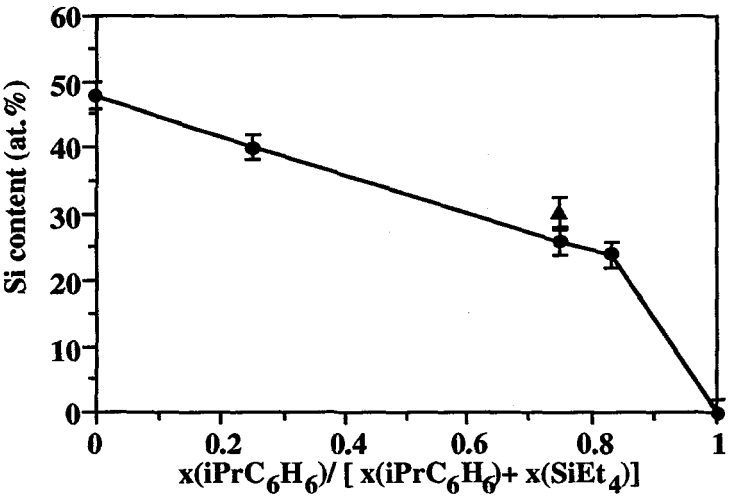



Fig. 1: Variation of the Si content of the films as a function of the gas phase composition. The films were deposited on flat alumina substrates at 845 °C under 3 Torr using He (●) or $H_2$ (▼) as carrier gas.

According to the optimization of the processing conditions for the infiltration of porous fiber preforms [8], the interphases have been deposited at 770 °C under a reduced pressure of 6 Torr and a total $H_2$ flow rate of 725 sccm. The good conformal coverage and uniformity of the thin films are shown on the SEM micrograph of a fracture surface (Fig. 2).

The CVD apparatus is equipped with a computer system for real-time control of the process parameters such as temperature (reactor and precursors), flow rates, reactant mole fractions and

reactor pressure. Multilayers or compositional gradient layers (CGL) coatings are easily deposited with this process by discrete or continuous changes of the gas phase composition, respectively. Fig. 3 illustrates such a multilayer coating whereas a typical CGL layer has been reported elsewhere [10].

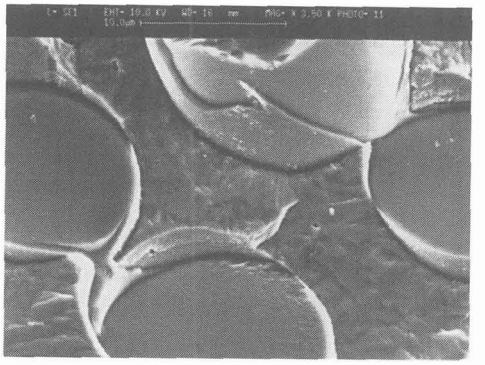


Fig. 2: Fracture surface of a SiC/SiC composite showing a uniform thin interphase $Si_{0.25}C_{0.75}$ on the Nicalon SiC fibers.

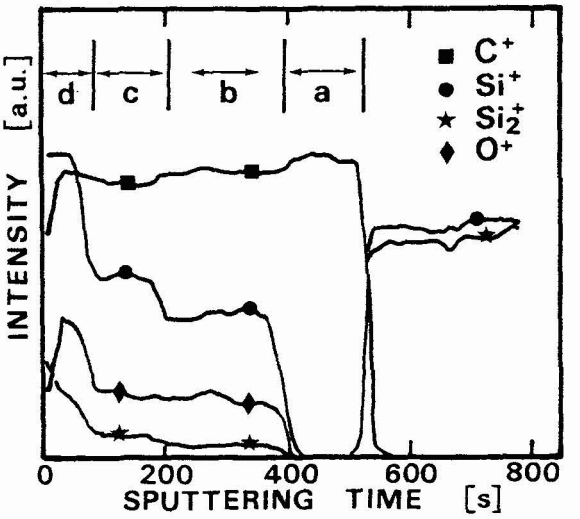



Fig. 3: Typical SIMS depth profiles ($Ar^+$ sputtering) showing four successive layers with different C content adjusted from the gas phase ratio $x(iPrC_6H_5)/[x(iPrC_6H_5)+x(SiEt_4)]$ fixed at 1 (a); 0.85 (b); 0.5 (c) and 0 (d). Films were deposited at 845 °C on a Si(100) wafer.

*2.2- Preparation of the representative composite samples*

Preforms were fabricated by stacking 10 layers of SiC Nicalon plain-weave fabrics in a graphite holder. Four typical interphases have been deposited on Nicalon SiC fibers prior to infiltration by the SiC matrix. Two intermediate coatings with the uniform composition $Si_{0.5}C_{0.5}$ and $Si_{0.25}C_{0.75}$ were synthezised using a mole fraction ratio of reactants

$SiEt_4$:$iPrC_6H_5$ of $5x10^{-2}$ : 0 and $5x10^{-2}$ : $1.5x10^{-1}$, respectively. Their thickness estimated from weight gain measurements is 115 nm and 170 nm, respectively. The Nicalon fibers of the third sample have been precoated with a pyrolytic C thin film (thickness ≈ 95 nm) by thermal decomposition of cumene. The behavior of this C precoating deposited at moderate temperature could be compared with other pyrocarbon treatments which are widely used for industrial applications [13]. The fourth interfacial coating is a compositional gradient layer (CGL) of about 100 nm in which the composition changes continuously from C (fiber interface) to SiC (matrix interface). The densification of these treated specimens was achieved by the conventional methyltrichlorosilane/$H_2$ CVI process above 1000 °C.

Bars 3 mm thick for tensile and flexure mechanical tests were cut parallel to the long axis of the samples. Three different tensile strength measurements have been done for each interfacial treatment except for the $Si_{0.5}C_{0.5}$ film for which only two measurements are reported because of the high brittleness of these specimens. Flexural strengths were measured at room temperature using a four-point bending method, with a support span of 15 mm, a loading span of 5 mm and a crosshead speed of 0.05 cm/min. The typical dimensions of the bend bars were 3x5x20 $mm^3$. They were loaded perpendicular to the layers of cloth.

## 3- Results and discussion

### *3.1- Tensile tests*

As expected, there is no improvement of the ductility of the composite specimens containing fibers precoated with $Si_{0.5}C_{0.5}$ film. They exhibit a linear elastic behavior and features of a brittle material similarly to a sample with uncoated fibers (Fig. 4a). This interphase has the same composition as the matrix and it is considered as a reference state for this series of interfacial treatments. The increase of the C content of the interphase improves significantly the strength and the fracture behavior. The elastic range is independent of the interfacial treatment and a Young's modulus of ~ 270 GPa is estimated. Above this range, a typical non-linear behavior appears (Fig.4). The strength to failure of composites reinforced with fibers precoated with $Si_{0.5}C_{0.5}$, $Si_{0.25}C_{0.75}$ and C increases (98, 150 and 200 MPa, respectively) as well as their mean strain to failure which reaches 0.23 % for C interphase. The results for the C interphase is in agreement with previous works [14].

The strength to failure of the specimen treated with the CGL layer (210 MPa) is comparable to that with the pyrocarbon interphase (200 MPa) and, in spite of a low reproducibility, presumably due to inhomogeneities of the treatment, the average strain to failure is slightly higher (0.27 %).

Intermediate coatings are applied to weaken the fiber/matrix bond and produce crack deflection and fiber pull-out. The degree of fiber pull-out is estimated by observation of fracture surfaces. The difference between a typical brittle failure obtained with an $Si_{0.5}C_{0.5}$ interphase and a more ductile fracture obtained with the CGL precoating is shown on Fig. 5. Plots of the relative number of fibers as a function of their length (measurements of 150 to 200 fibers) indicate that the degree of fiber pull-out increases with the C content of the fiber precoating (Fig. 6). Most of the fibers have a length in the range 0 - 5 μm for an $Si_{0.5}C_{0.5}$ interphase, 15 - 20 μm for an $Si_{0.25}C_{0.75}$ interphase and 20 - 25 μm for pyrolytic C intermediate layer. Furthermore, satisfactory fiber slip is found for the CGL layer. Its degree of fiber pull-out is comparable to that of the C precoating although the plot is less symmetrical, probably because of inhomogeneities of composition and/or thickness of the CGL layer.

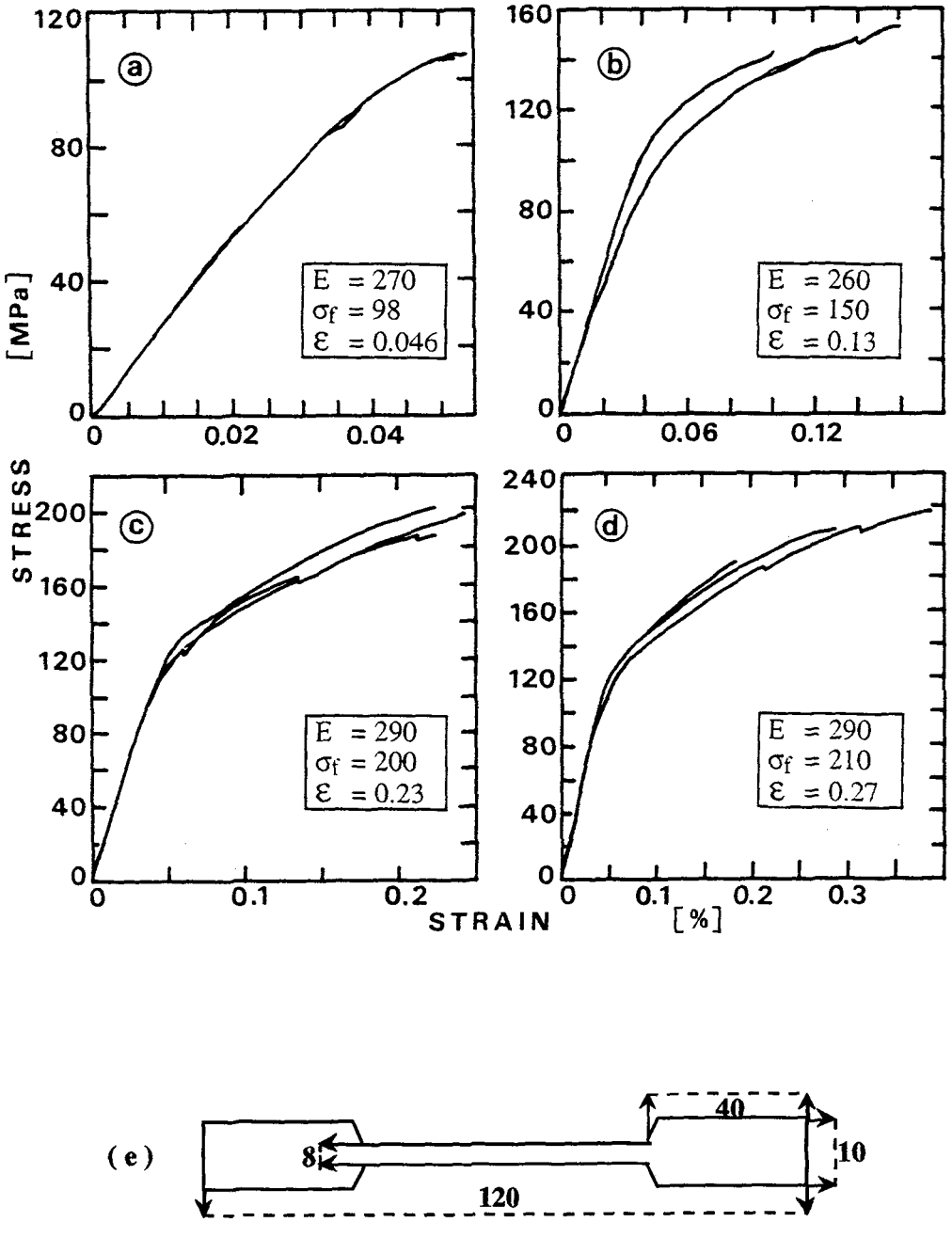
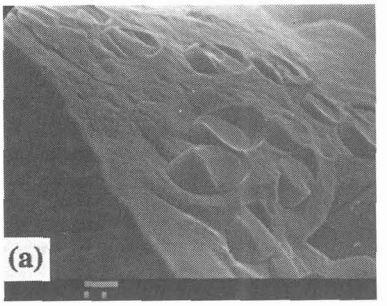
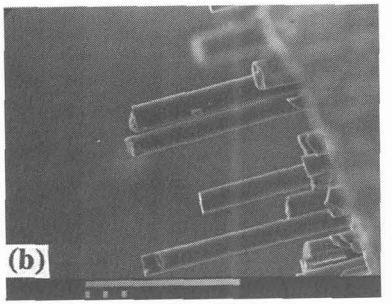



Fig. 4: Stress-strain curves from tensile measurements of SiC/SiC composites with different fiber/matrix interface treatments: (a) $Si_{0.5}C_{0.5}$; (b) $Si_{0.25}C_{0.75}$; (c) pyrolytic C and (d) CGL interphase. The Young's modulus E (GPa), the failure strength $\sigma_f$ (MPa) and the mean strain to failure $\varepsilon$ (%) are given for each sample in the inset. The dimensions of the tensile bars given in (e) are in mm.



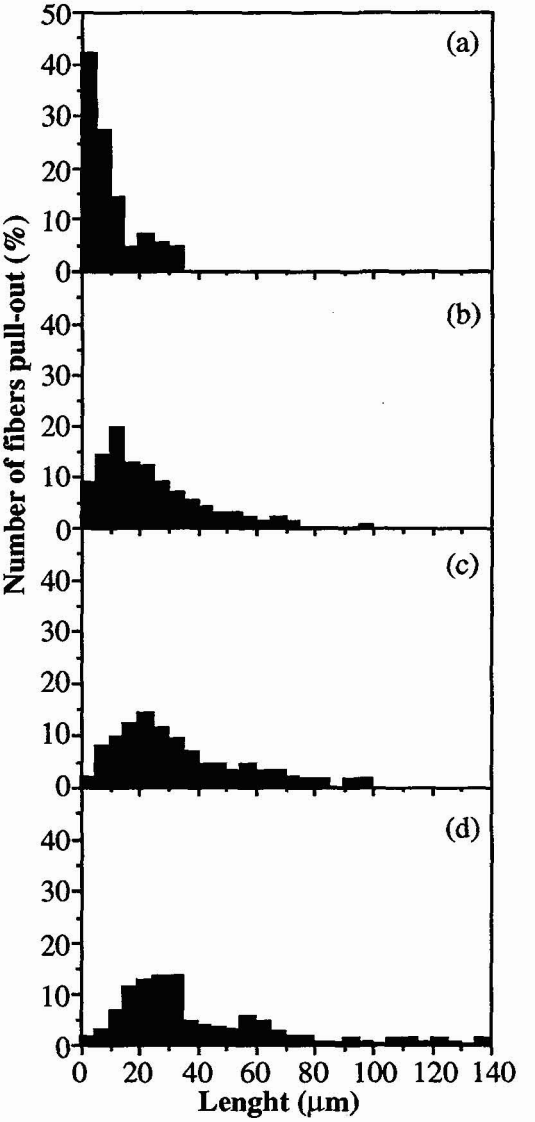




Fig. 5: Fracture surface of SiC/SiC composites showing (a) a brittle failure behavior ($Si_{0.5}C_{0.5}$ interphase) and (b) a strain tolerant behavior (CGL interphase). The scale of micrographs (a) and (b) is 10 and100 μm, respectively.

Fig. 6: Statistical number of fibers pull-out versus their length after the failure of the composite material in which the fibers were precoated with (a) $Si_{0.5}C_{0.5}$; (b) $Si_{0.25}C_{0.75}$; (c) pyrolytic C and (d) a CGL layer from C to SiC. Data were determined from SEM micrographs of the fracture surfaces.

*3.2- Mechanical behavior and oxidation resistance*

Flexure tests performed before and after heat treatment at 1300 °C in air for 20 h are reported in Fig. 7. The C interphase is very sensitive to oxidation at high temperature [3, 15]. As a result, the strength behavior of a composite reinforced with C precoated fibers dramatically decays (Fig. 7a). In agreement with previous work [5], addition of Si to the interphase clearly improves the oxidation resistance (Fig. 7b). This is due to the formation of silica seals to the pore entrances which stops the oxidation of the C-rich interphase.

Furthermore the superiority of the fiber treament by the CGL layer is shown in Fig. 7c. For this precoating, the Si enrichment near the matrix interface acts as a seal coat to protect both the underlayer C-rich interphase and the Nicalon fiber whereas the C enrichment near the fiber interface has an efficiency comparable to pyrocarbon to weaken the fiber-matrix bond and improve the toughness of the material. This ceramic composite reinforced with fibers protected by CGL layer preserves its mechanical properties after ageing in air at 1300 °C. Moreover the plastic behavior is significantly enhanced presumably because this heat treatment increases the degree of graphitization of the C-rich zone of the interphase which was deposited at moderate temperature (770 °C). However, structural changes of the Nicalon fibers are also possible under such heat treatment. Further microstructural characterizations are underway to check these assumptions.

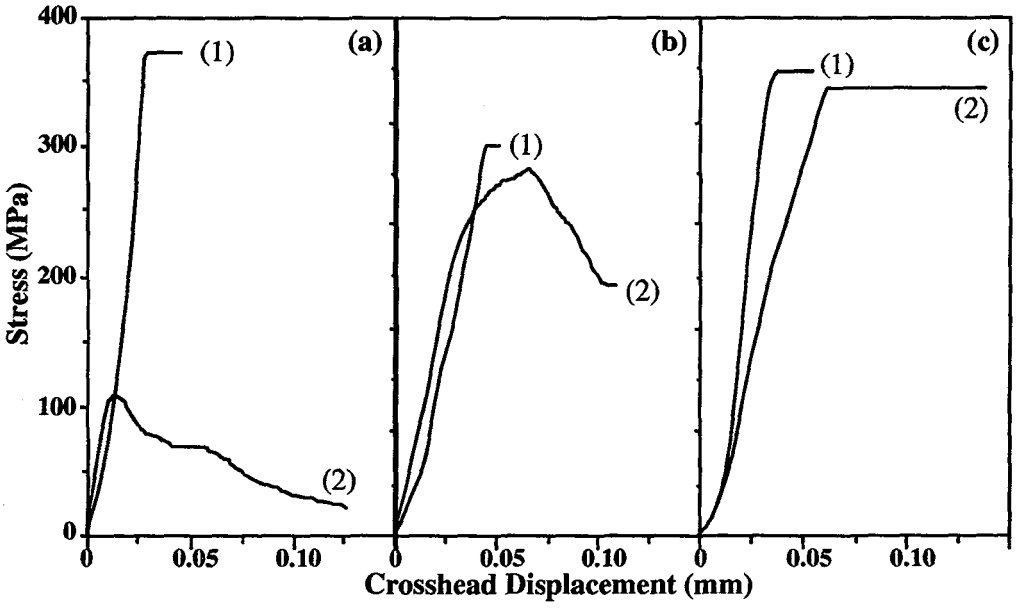



Fig. 7: Stress-displacement curves from four-point flexure testings at 25 °C before (1) and after (2) oxidation in air at 1300 °C during 20 h for different fibers/matrix interface treatments: (a) pyrolytic C, (b) $Si_{0.25}C_{0.75}$ (c) CGL layer from C to SiC.

## 4- Conclusion

A chlorineless CVI process has been used for the treatment at moderate temperature of fiber/matrix interfaces of SiC/SiC composites. Fibers were precoated by $Si_xC_{1-x}$ (x = 0 - 0.5) thin films prior to densification. Their mechanical behavior has shown that on one hand, the degree of weakening of the fiber/matrix bond increases with the C content of the interphase but on the

other hand, oxidation resistance at high temperature requires a Si addition to this interphase. Consequently, compositional gradient layer in which the composition changes continuously from C (fiber interface) to SiC (matrix interface) is the best compromise to improve the toughness of these ceramic/ceramic composite materials which are used at high temperature in atmosphere containing oxygen.

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