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Origin of the carbon rich sliding interface in alkali containing matrix-SiC Nicalon fibre composites

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The interfacial Nicalon SiC/Nasicon matrix reaction and its influence on the micro- and macroscopic mechanical properties have been studied by chemical analysis, EDX, SEM, microindentation, fibre tensile and composite flexural strength. Reaction mechanisms and relationships with mechanical properties are discussed. An explanation of the origin of the "C" sliding interphase is proposed.

INTRODUCTION

To develop new engines in the fields of aeronautics and space requires materials with specific characteristics : lightness, high temperature, mechanical reliability and ability to withstand use in severe environments. Ceramic matrix composites with long woven fibres exhibit greater toughness owing to a specific micromechanism : a sliding fibre-matrix interface. If the fibre-matrix interface is too strong, a brittle fracture occurs through the fibres. If the fibre-matrix interface is weak, fibre-matrix decohesion takes place. A medium interface leads to optimal properties. This is obtained for example by C or BN film deposit before the matrix condensation in the CVI process. Previous electron microscopy analyses have demonstrated that the chemical reaction between Nicalon SiC fibres and molten alkali silicate matrix during the elaboration was large enough to provide a C film (1,2) But, the chemically changed volume is small $\sim 100\text{nm}$ which makes the analysis and understanding difficult. We have developed a new process (3,4) which allows the manufacture of multilevel composites without melting of the matrix. Refractory matrix composites can be obtained by low temperature sintering but the sintering time is lengthened (20-40 min, typically). Consequently, a thicker region (a few microns) results from the fibre-matrix reaction. Thus many techniques may be used to understand the fiber-matrix reaction. Our attention has been focused on Nicalon NLM 202 SiC fibre-sodium silicozirconophosphate NASICON matrix composite using SEM, X micro-analysis and Vickers microindentation.

EXPERIMENTAL

The fabrication of 2D SiC Nicalon NLM 202 woven fabrics reinforced composites was previously reported (4,5). The process is based on the hydrolysis-polycondensation of alkoxides. This method allows the tailoring of both interface and matrix microstructures. The preparation takes place in three stages : i) impregnation of SiC fibre yarns of fabrics by an interface gel precursor (a liquid which becomes a gel, *in situ*), ii) deposition of a fine amorphous and reactive powder (a matrix precursor), iii) hot pressing of the doubly impregnated fabrics in a carbon mold.

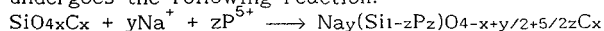
For the elaboration of NASICON composites the oxide compositions of matrix and interface precursors are $\text{Na}_{2.9}\text{Zr}_{2.5}\text{Si}_{11.9}\text{P}_{11}\text{O}_{42}$ and $\text{ZrO}_2\text{-2SiO}_2\text{-1.5P}_2\text{O}_5\text{-1.5B}_2\text{O}_3$, respectively. Boron oxide leads to the formation of liquid traces which promotes the densification, the Boron being then lost by evaporation during the hot-pressing dwell. Fibres are extracted from composites by HF dissolution of the matrix.

RESULTS AND DISCUSSION

SiC fibre-matrix interfacial reaction. The fibrous fracture observed in composites is usually explained by the presence of a graphitic carbon film at the SiC fibre-matrix interface (1,2,6). However, the deposit of such a film by CVD at the SiC interface leads to a dissipative fracture (7). A 50-500nm carbon film have also been evidenced at the interface between Nicalon fiber and alkali (or earth-alkali) containing matrix (Pyrex, LAS, CAS, ...) (1,2). The continuity of this film is however not demonstrated. On the other hand, the absence of such a "large" carbon film was pointed out for SiC Nicalon/Mullite matrix composites (8).

Previous microanalysis investigations (4,9) have shown that Na diffusion occurs within the fibre core in Nasicon matrix composites. Chemical analysis of extracted fibres and *in situ* EDX analysis give the same Na/Si atomic ratio (~2%). A higher Na concentration (~3%) is measured for the fibres located at the woven fabrics limit, in contact during the elaboration cycle with the sodium- and boron-rich liquid sintering aid. This liquid results from the reaction between the B-rich interface precursor and the Na-rich Nasicon matrix. As shown in Fig. 1a, we observe a black contour around the fibre (retrodiffused electron mode). Microanalysis shows that the P element replaces the Si one and simultaneously the oxygen content is increased to satisfy the electric balance : a true scorce of carbon-rich sodium phosphosilicate is formed (4,9).

The most reasonable assumption is that the oxycarbide second phase of SiC Nicalon fiber undergoes the following reaction.



This reaction needs to be oxygen balanced. Assumption can be made that oxygen results from partial dissociation of the oxycarbide phase, as follows. e.g. : $\text{SiO}_3\text{C} \longrightarrow \text{SiO}_2 + \text{C} + \text{O}$

These reactions explain the observation of glassy phase with carbon precipitates. The high dc conductivity measured on fibres extracted from Nasicon ($\sigma_{dc} \sim 10 \text{ S m}^{-1}$) composite indicates that the C precipitates are roughly connected (4). Oxygen can also be provided by the matrix.

Relationship between interfacial reaction and mechanical properties. Micro-Vickers indentation confirms that the scorce is a glass ($\text{Hv} \sim 5\text{-}6 \text{ GPa}$) whereas the SiC core retains the mechanical properties ($\text{Hv} \sim 25 \text{ GPa}$) of unreacted fibre (9). Thus, in the composite the fibres can be classified in three types : a-fibres exhibiting no visible scorce at our resolution ($\sim 0,2 \mu\text{m}$), b-fibres exhibiting a visible but small black contour ($\sim 1,5 \mu\text{m}$), c-fibres exhibiting a large scorce such as shown in Fig. 1b. Micro-Vickers indentation gave also evidence that the formation of a visible scorce lowers both the interfacial shear stress and the sliding load threshold (9). The Fig. 2 shows the evolution of the three points flexural mechanical strength versus the duration and the temperature of the hot-pressing dwell. Highest values are obtained for composites sintered between 1035 and 1070°C. The lowest open porosity ranges between 4 and 7 %. The minimum is however not correlated to the highest flexural strength. The dwell duration leading to the highest value is reduced when the dwell temperature increases. Determination of the relative proportions of the a-, b- and c- fibre types has been made by visual examination of composite polished sections. Results are given in Fig. 2c. We observe that the highest value corresponds to the highest proportion of b-fibres. This is confirmed by the measure of the tensile strength of extracted fibres. Two kinds of Weibull distributions are evidenced, corresponding to a-, b- and c-fibres, respectively (Table I). a- and b-fibres keep roughly the tensile strength of SiC Nicalon fibres heated at the same temperature in N₂ (2400-2100MPa). The a+b/c relative proportion is consistent with the visual determination.

Table I : Evolution of the tensile strength (σ) of extracted fibres (gauge length = 10mm)

| Dwell | Mean diameter | Fiber type | Number | σ MPa |
|---------------|--------------------|------------|--------|----------------|
| 1035°C-45min | 15.9 μm | a,b | 18 | 2500 \pm 170 |
| | | c | 12 | 1300 \pm 150 |
| 1070°C-20min | 15 μm | a,b | 19 | 2200 \pm 180 |
| | | c | 13 | 1500 \pm 150 |
| 1100°C-180min | 13.5 μm | a,b | 8 | 2000 \pm 130 |
| | | c | 19 | 1300 \pm 115 |

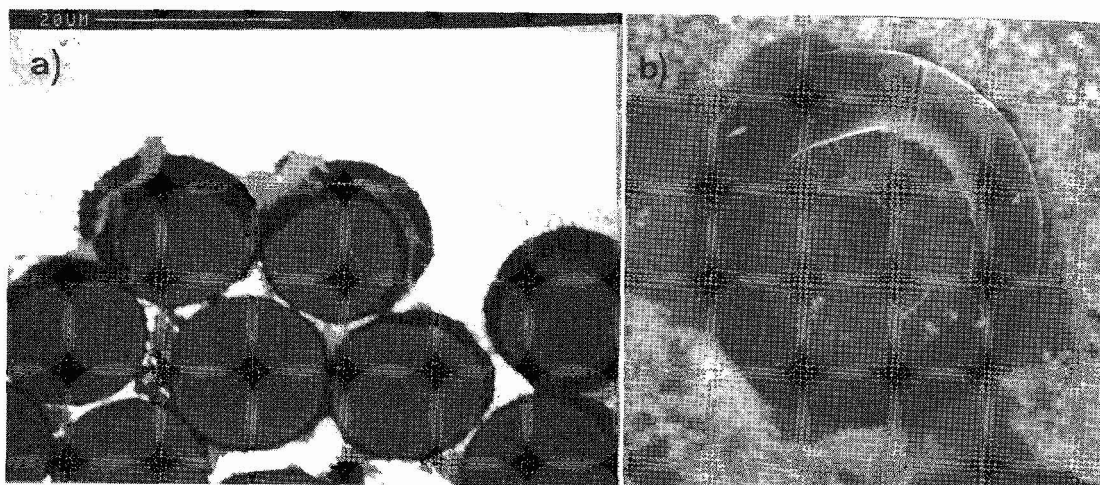


Fig. 1 : Photomicrographs of polished sections of a composite at the limit of the woven fabrics (a). The double decohesion observed after microindentation at the fibre core/score and score/matrix interfaces is shown in (b) (backscattered electron mode).

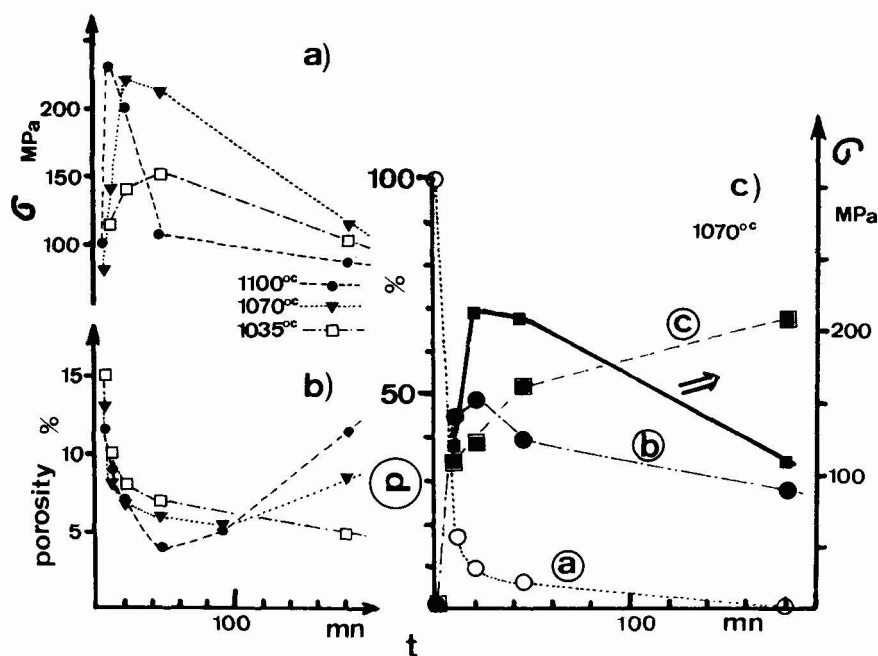


Fig. 2 : Relationship between densification and fibre score formation in Nasicon composites : 3 points flexural strength (σ , a), open porosity (b) and relative proportions (P) of the various fibres (c), as a function of the dwell duration (t in minutes) for various hot-pressing temperatures. The corresponding values of σ are given.

CONCLUSION

The "sliding" carbon interphase formed by reaction of SiC Nicalon fibre with alkali containing matrix is more complex than a simple C film. An origin of the carbon precipitation can be found in the attack of the Nicalon oxycarbide second phase by Na (and P) elements leading to a glassy scorce. A moderate attack is necessary to obtain optimal mechanical properties. Sliding interface occurs both at the fibre/scorce and scorce/matrix limit. The replacement of Si^(iv) by P^(v) element at the fiber periphery is associated to the trapping of oxygen atoms, and to the carbon precipitation at the interfaces. On the other hand, when Si is replaced by Al⁽ⁱⁱⁱ⁾ element after reaction with a pure aluminosilicate matrix (e.g. mullite), the local oxygen excess could favour the departure of carbon by volatilization, leading to a carbon free sliding interface (8).

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