JOURNAL OF MATERIALS SCIENCE 29 (1994) 3759–3766

SIMS, EDX, EELS, AES, XPS study of interphases in nicalon fibre–LAS glass matrix composites

Part I *Composition of the interphases*

M. LANCIN
Physique Cristalline, IMN, 44072 Nantes-cedex 03, France
C. PONTHIEU*, C. MARHIC, M. MILOCHE
Physique des Matériaux, CNRS, 92 195 Meudon-cedex, France

Secondary ion mass spectrometry (SIMS) and energy dispersive X-ray spectroscopy (EDX) were used to analyse interphases which develop at the fibre–matrix interface during fabrication of SiC nicalon fibre–LAS (Li_2O, Al_2O_3, SiO_2) or LAS + Nb_2O_5 glass matrix composites. SIMS was performed on fibres extracted from composites by dissolution of the matrix in hydrofluoric acid (HF). The composition of the interphases which remain on the fibre periphery was studied using sputter-depth profiling. EDX analysis of the interphases was performed on nicalon–LAS + Nb_2O_5 composite cross-sections. These investigations show that in both composites the reaction products at the fibre–matrix interface consist of a carbon layer and a silicate phase, rich in oxygen, located between the carbon layer and the fibre core. The analyses also demonstrate the efficiency of SIMS for analysing compositional changes in the near surface of fibres of small diameter.

1. Introduction

Composites fabricated from SiC nicalon fibres and glass matrices are being developed for thermomechanical applications. Previous studies performed by Brennan [1], Marshall [2], Cooper and Chyung [3], Grande *et al.* [4] and Meier and Gratwhol [5] showed that the mechanical behaviour of these materials strongly depends on the characteristics of the fibre–matrix interphase and, in particular, on the formation of a carbon layer around the fibres during fabrication of the composites. The formation mechanisms of this carbon layer are still not completely understood. It is well established, however, that formation of such a carbon layer depends on the composition of the matrix. When the matrix is a LAS glass (Li_2O, Al_2O_3, SiO_2), formation of the carbon layer occurs and, besides, is enhanced by the addition of Nb_2O_5. In order to improve understanding of the formation mechanism of this carbon layer, and its effect on the mechanical behaviour of the composite, the interfacial region of two SiC nicalon fibres–LAS glass matrix composites, fabricated with model matrices which only differ by the addition of Nb_2O_5, have been studied.

This paper deals with the composition and chemistry of the interfacial region formed by the fibre–matrix reaction. Ponthieu *et al.* [6] showed in a previous study performed by high resolution transmission electron microscopy (HRTEM) that the interfacial layer, formed in both composites by fibre–matrix reaction, is divided into two sub-layers: an outermost sub-layer which probably corresponds to the carbon layer previously identified in similar composites, and a transition region located between the carbon layer and the fibre core. Special attention has been paid to the newly identified transition region while analysing the interfacial region. No particular attention was paid to the well-characterized NbC interphase formed by fibre–matrix reaction in the nicalon–LAS + Nb_2O_5 composite, and which consists of small discrete grains at the edge of the interface.

The composition and the chemistry of the interfacial layer were characterized using complementary techniques. The first part of this paper deals with the composition, the second one with the chemistry.

The composition of the interfacial region was investigated by secondary ion mass spectrometry (SIMS) on fibres extracted from both composites. In the nicalon–LAS + Nb_2O_5 composite, energy dispersive X-ray spectroscopy (EDX) was also performed. SIMS has extremely good sensitivity for oxygen (10^{-4} at %), but has poor lateral resolution (≈ 2 mm). As for the depth resolution, it could reach 0.5 nm, but may be limited by ion beam mixing, preferential

---

*Permanent address: Saint Gobain Recherche, 28 Quai Lucien Lefranc, BP 135, 93 303 Aubervilliers-cedex, France.

0022–2461

sputtering and curvature effects. Samples necessary for SIMS analysis are easily obtained and, except for their surface, their compositions are affected neither by the extraction method nor by oxidation at room temperature. EDX has poorer sensitivity than SIMS (0.1 at % at best), but has far better lateral resolution (e.g. ≈ 4 nm). However, suitable thin samples are difficult to obtain and their composition may be affected by oxidation.

Part I of this paper has a two-fold aim. Firstly, it analyses the composition of the interphases formed by fibre–matrix reaction, and in particular the composition of the transition region. Secondly, it demonstrates the efficiency of SIMS in revealing compositional changes at the periphery of fibres of small diameter (≈ 15 mm).

2. Samples

Composites were manufactured with 202 nicalon fibres of atomic composition $C/Si = 1.3 \pm 0.7$ and $O/Si = 0.45 \pm 0.15$ as obtained by SIMS by Lancin *et al.* [7]. According to Porte and Sartre [8], these fibres are made of SiC (≈ 45 mol %), SiO_xC_y (≈ 20 mol %), free carbon (≈ 30 mol %) and a few mol % SiO_2. In the fibres used, Ponthieu *et al.* [6] showed that the only crystalline phase is the β-SiC. The SiC grains are roughly 2 nm in diameter. The LAS matrix contains LiO_2, Al_2O_3, SiO_2 in a ratio of 1:1:4. The composition of the LAS + Nb_2O_5 matrix is similar to LAS, except for Nb_2O_5. The composites were fabricated by hot-pressing for 10 min at 1300 °C.

The microstructural characteristics of the interphases were previously determined by Ponthieu *et al.* [6] by transmission electron microscopy (TEM) and HRTEM. The thickness of the carbon layer, CL, measured on cross-sections is equal to 120 ± 30 nm in the nicalon–LAS + Nb_2O_5 composite, and to 35 ± 5 nm in the nicalon–LAS composite. Its microstructure is either amorphous, or characteristic of highly misorientated turbostatic carbon. During TEM analysis, it was assumed that this outermost layer was made of carbon, whatever its structure was. The SIMS and EDX results presented here confirm this hypothesis. The microstructure of the transition region, TR, is neither that of the carbon layer nor that of the fibre core. Like the fibre, the TR is composed of small β-SiC grains surrounded by a mostly amorphous phase. Unlike the fibre core, however, the number of SiC grains decreases gradually throughout the TR, from the fibre core to the CL. Interfaces were located where microstructural changes were detected by HRTEM. The interface between the amorphous CL and the TR was located where the first SiC grains were detected, and it was found to be abrupt. The TR–fibre interface was located where the density of the SiC grains was estimated to be the same as in the fibre core. The structural change being progressive, the TR–fibre core interface was difficult to localize. The TR width, thus imprecisely known, was estimated to extend over roughly 100 nm in the nicalon–LAS + Nb_2O_5, and 40 nm in the nicalon–LAS.

EDX analyses were performed on thin cross-sections made by mechanical grinding and ion thinning of samples cut perpendicularly to the fibre axis from the nicalon–LAS + Nb_2O_5 composite.

SIMS analyses were performed on fibres extracted from the two composites by dissolution of the matrix in a hydrofluoric acid bath diluted at 48%. The analysis shows that HF removes the glassy matrix as well as the NbC grains present in the nicalon–LAS + Nb_2O_5. The possible influence of the etchant on the interphase composition was checked. SIMS analyses were performed by Ponthieu [9] on fibres removed from the nicalon–LAS + Nb_2O_5 by pull-out during flexural tests. They led to results similar to those obtained with fibres extracted from the matrix by HF attack. It was thus demonstrated that the etchant does not change the composition of the interfacial layer which lies over about 200 nm, although it is likely that it does modify the composition of the very surface of the CL and may change the thickness of the CL. Since the matrix and NbC are removed during HF etching, it is shown that the extracted fibre is composed successively of a carbon layer, a transition layer and a fibre core (Fig. 1).

Pure α-SiC, pure SiO_2 and the core of a nicalon fibre were also characterized by SIMS and EDX for calibration of the data.

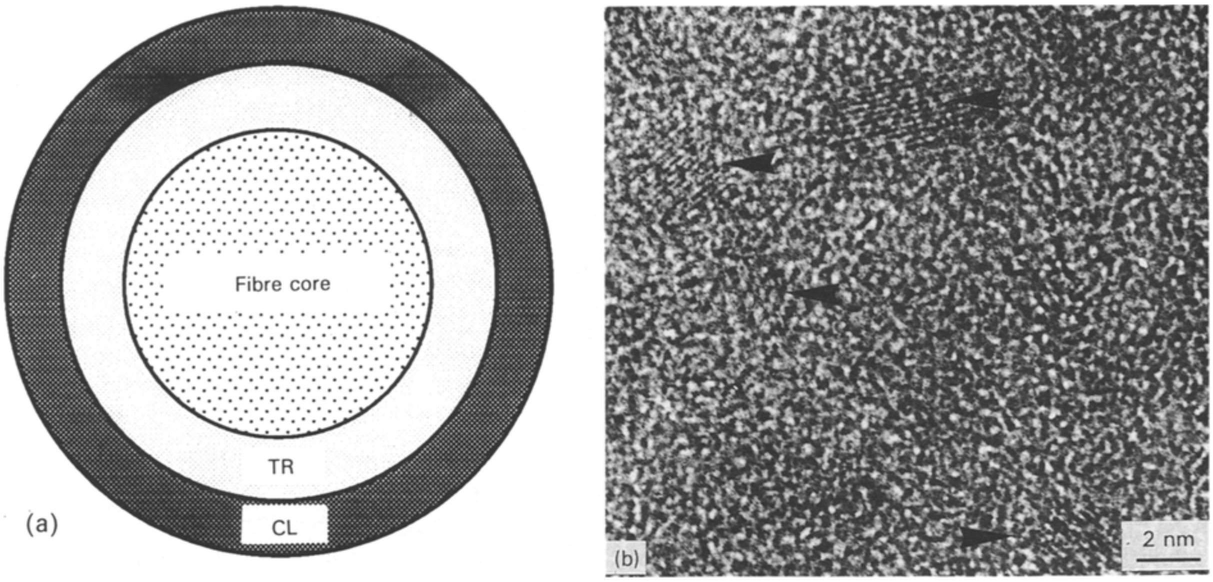
3. SIMS analyses

3.1. Experimental procedure

The analyses were carried out in a CAMECA IMS4F ion microscope; 10 keV Cs^+ ions were used for the analysing beam, and negative secondary ions were collected in order to measure the oxygen content and to obtain the best sensitivity in the detection of carbon and silicon signals.

The analyses were performed in the microscope mode, with experimental conditions selected to analyse the fibre near the surface. The field aperture and the contrast aperture were selected in order to obtain an analysed area of 1.4 ± 0.5 mm in diameter. The probe diameter (40 mm) and the crater width (250 mm) were selected because they give the most reproducible profiles. The Cs^+ ion current intensity (≈ 70 nA) was chosen to obtain a sputtering rate low enough to detect the thin CL and TR.

The extracted fibres were analysed using sputter-depth profiling. The depth resolution was about 0.5 nm, excluding ion beam effects and sputter profiling artifacts due to the curvature of the sample. Depth profiling was carried out as follows, to obtain reliable information. The sputtering rate varied all around the fibre surface due to its curvature, and it was experimentally observed that the results were reproducible only if the analyses were performed where the mean sputtering yield was at its maximum. Therefore, the analyses were performed at the area where the mean sputtering yield of the analysis were found to be maximum. This region was determined by studying changes in the Al ion image intensity during sputtering. Al, which has diffused from the matrix into the fibre during composite fabrication, can be detected



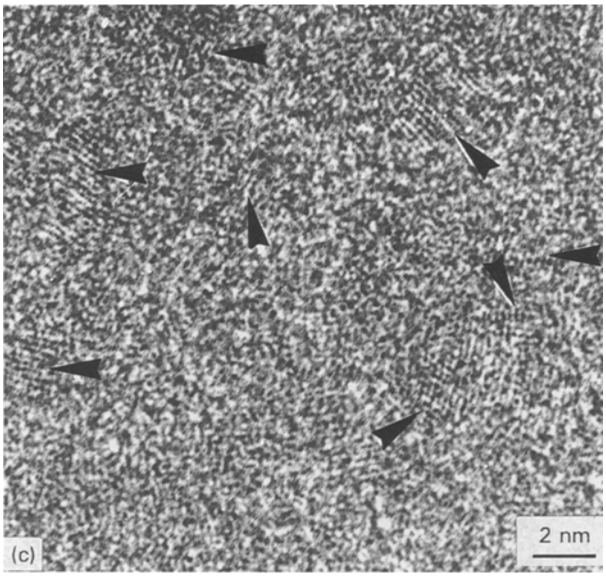


Figure 1 Near surface of fibres extracted from nicalon–LAS or nicalon–LAS + Nb_2O_5 composites. (a) schematic showing the carbon layer, CL, and the transition region, TR, which are surrounding the fibre core as revealed by HRTEM [6], HRTEM images of (b) the TR and (c) of the fibre core.

only in the outermost part of the fibre, and its concentration decreases with depth. Thus, the intensity of the Al ion image reaches zero at first in the area where the mean sputtering yield is maximum. This region is located on one side of the fibre axis, as shown by the surface topography of a fibre after sputter-depth profiling (Fig. 2). In order to avoid sample sputtering before the analysis, the fibre surface was coated with roughly 5 nm of gold, and the fibres were translated over a few hundreds millimetres after setting. The location of the analysed area was always checked after the analysis, because the area where the mean sputtering yield was maximum may have been lost during fibre translation.

3.2. Calibration

In order to calibrate the data, a pure α-SiC single crystal and segments of the nicalon fibres used for the fabrication of the composite were analysed under the experimental conditions mentioned above.

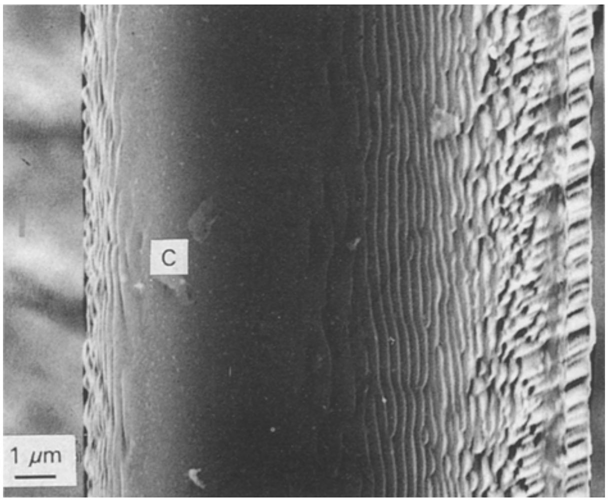


Figure 2 Surface of a fibre extracted from nicalon–LAS + Nb_2O_5 composite, imaged by SEM after a SIMS analysis. The fibre surface eroded by the primary ions is labelled c.

For a flat SiC single crystal, the sputtering rate was reproducible within 2% and equal to 16 ± 2 nm min^{-1}. The sputtering yield of the nicalon, 15 nm min^{-1}, derived from previous measurements, was of the same order of magnitude [10]. Attempts to measure crater depth on fibres being unsuccessful, the sputtering yields of the CL and of the TR, which may be different from one another, were assumed to be reproducible. As stated in Reference 11, the sputtering yield was reproducible for a SiC coating deposited on a carbon fibre 6 mm in diameter. Moreover, the reproducibility of profiles obtained on the same fibre segment also justifies this assumption.

For quantitative analysis, the ratios of the ionic intensities have to be considered. The reference element must be a major component of the material. In the SiC standard and in the nicalon fibre, carbon was chosen as the reference element.

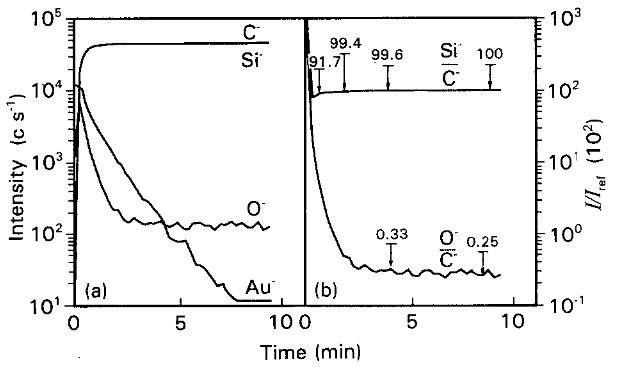


Figure 3 SIMS depth profile of the α-SiC standard. The surface was coated with a gold layer about 5 nm thick. The sputtering rate was equal to 16 ± 2 nm min^{-1}.

The profiles obtained on the SiC standard (Fig. 3) provide several points of interest for fibre analysis. Firstly, some gold still remains on the surface after setting. Secondly, the gold–fibre interface is very sharp, as shown by the simultaneous and rapid increase of the C^-, Si^- and O^- ionic intensities, which occur when the Au^- ionic intensity starts to decrease. The variation of the ionic intensities at the interface occurs in a few tens of seconds. Non-congruent sputtering of the elements, which occurs at the beginning of sample sputtering, is thus limited. Thirdly, no influence of gold recoil implantation on the possible recoil implantation of carbon, silicium and oxygen, and on their sputtering yields, was detected. In fact, C^-, Si^- and O^- ionic intensities reach constant values after 1–3 min, whereas gold recoil implantation is detected after about 8 min. Variation of the ionic intensities, which occurs after the gold–SiC interface, is likely due to some oxidation of the SiC surface rather than to sputtering artifacts.

Fig. 4 shows an example of a sputter-depth profile in as-received nicalon fibres. The variation of C^-, Si^- and O^- ionic intensities confirm that the gold coating results in efficient protection of the surface during setting. The gold–fibre interface is reached after 1 min sputtering, which is after the sharp increase in C^-, Si^- and O^- ionic intensities and the beginning of the decrease in Au^- ionic intensity. Beyond the gold–fibre interface, following about 2–4 min sputtering (over 30–60 nm), the O^- ionic intensities are significantly higher than in the fibre core. Non-congruent sputtering of the elements, or oxidation of the fibre surface, may account for the signal variations. The last hypothesis is the most likely, because oxidation of the nicalon fibre surface was previously reported [8, 12]. The composition still varies after about 5 min sputtering, but only within a few per cent.

The O^-/C^- and the Si^-/C^- ratios vary quite a lot from one fibre to the other (≈ 30–50%), whereas Si^-/C^- is reproducible within 7% in an SiC single crystal while using the same experimental settings. As a consequence, the most accurate standard which can be used to discuss the possible compositional changes of the fibre periphery is provided by the fibre core itself. Single crystal analyses were thus performed only to check the reproducibility of the settings or to compare the Si/C ratios observed in different fibres.

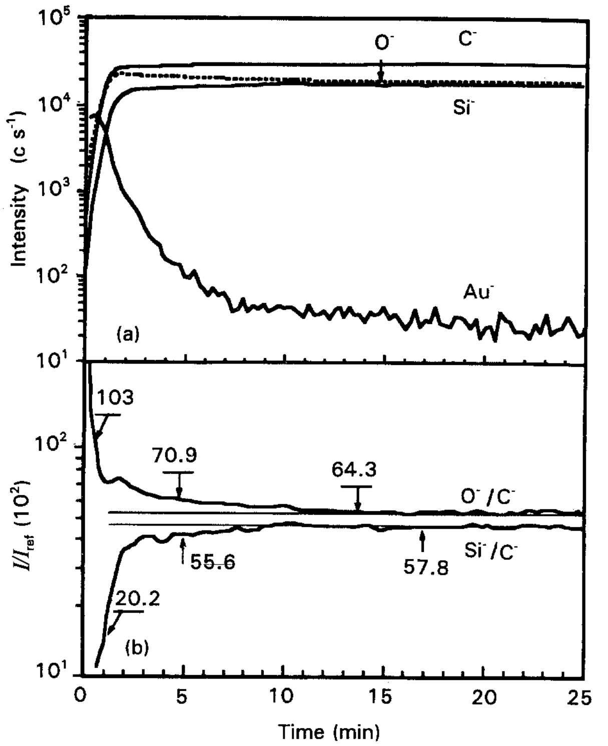


Figure 4 SIMS depth profile of an as-received nicalon fibre. The surface was coated with a gold layer about 5 nm thick. The sputtering rate was about 15 nm min^{-1}.

3.3. SIMS analysis of the near surface of the extracted fibres

3.3.1. Results

The depth profiles obtained on fibres extracted from the LAS + Nb_2O_5 or LAS matrix composites exhibit similar features (Figs 5a and 6a). Carbon was chosen as the most reliable reference to study the compositional variation of the fibre periphery (Figs 5b and 6b). Three different regions, Z_1 to Z_3 can be distinguished on the profiles from the variation of the Si^-, C^- and O^- signals and of the Si^-/C^- and the O^-/C^- ratios.

When the sputtering time, t, is higher than t_2, the ionic intensities remain constant within a few per cent and their relative values are characteristic of the nicalon fibre. The Z_3 zone thus corresponds to the fibre core, which was not involved in the fibre–matrix reaction during composite fabrication.

When the sputtering time is less than t_1, the C^- ionic intensity stays constant, then decreases slowly; whereas Si^- and O^- increase versus the depth. The Z_1 zone, the outer-most part of the extracted fibre, is composed mainly of carbon.

Let us first discuss the variation of ionic intensities between t_1 and t_2 in the nicalon–LAS + Nb_2O_5 composite. Near the beginning of Z_2, a peak in the O^- intensity and depletion in the C^- and Si^- intensities, compared to Z_3, are simultaneously observed (Fig. 5a). These variations correspond to a peak in the O^-/C^- ratio and a depletion in the Si^-/C^- ratio (Fig. 5b). Then, the O^-/C^- ratio decreases slowly towards the Z_3 value. The Si^-/C^- ratio often shows a more complex variation than the O^-/C^- ratio, as shown on Fig. 5b. It increases slightly, and then decreases towards the Z_3 value. These variations of

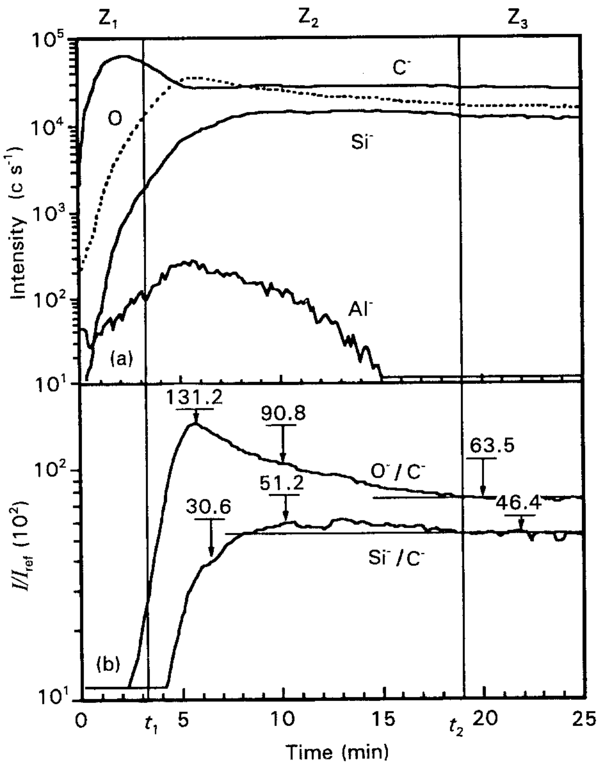


Figure 5 SIMS depth profiles of a fibre extracted from the nicalon–LAS + Nb_2O_5 composite. The surface was coated with a gold layer about 5 nm thick. Three zones of distinct composition can be distinguished. The location of their boundaries, t_1, and t_2, is discussed in the text.

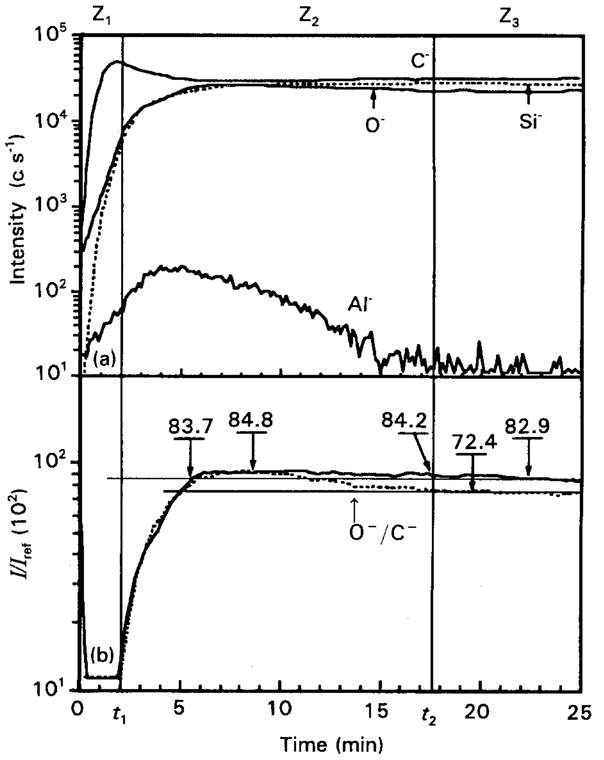


Figure 6 SIMS depth profiles of a fibre extracted from the nicalon–LAS composite. The surface was coated with a gold layer about 5 nm thick.

ionic intensity, and of O^-/C^- and Si^-/C^- ratios, are quite different to those observed in the nicalon fibre (Fig. 4). For similar sputtering times in the nicalon fibre, an oxygen concentration as high as in Z_2 was never observed. The Al content is the last characteristic of Z_2. In Z_2, Al is detected and the Al^-/C^- variation is observed over about the same depth as the O^-/C^- variation.

In nicalon–LAS, variation of ionic concentration is much less pronounced than in nicalon–LAS + Nb_2O_5; however, they exhibit the same trends. In both composites, Z_2, located between the CL and the fibre core, should correspond to the TR sub-layer identified by HRTEM.

3.3.2. Possible influence of artifacts

Artifacts due to sputtering, and to the geometry of the sample, may have a detectable influence on the variation of the ionic intensities versus the sputtering time, and particularly on the features of Z_2.

Non-congruent sputtering, limited to about 1 min in SiC and nicalon fibres, should be of the same order of magnitude in the extracted fibre. As a consequence, Z_2 features are not likely to be influenced by this phenomenon.

The variation of composition versus depth, derived from the profiles, may be modified both by ion beam mixing during sputter profiling and by convolution of signals coming from regions located at different depths which were sputtered simultaneously because of the curvature of the surface. However, these artifacts alone cannot account for the variation of the signals, such as the high level of the O^- ionic intensity in Z_2 shown in Fig. 5. Therefore, Z_1 and Z_2 regions are not artifacts of the analysis. Nevertheless, these phenomenon smooth the compositional variations at the interfaces, and explain why the sharp CL–TR interface revealed by HRTEM does not correspond to an abrupt variation of the ionic intensities. On the other hand, these artifacts do not entirely justify the more extended transition between Z_2 and Z_3. As expected, the progressive microstructural change throughout the TR revealed by HRTEM corresponds to a progressive compositional variation throughout Z_2.

As already mentioned, the compositional characteristics of the TR in nicalon–LAS are less pronounced than those identified in nicalon–LAS + Nb_2O_5. It is assumed that these differences are related not only to differences in composition, but also result from the smaller thickness of the sub-layers in nicalon–LAS than in nicalon–LAS + Nb_2O_5, as established by TEM. Artifacts which reduce the depth resolution are less prevalent in thicker layers, such as in nicalon–LAS + Nb_2O_5, allowing better resolution for the oxygen signal. Therefore, SIMS analyses, demonstrate that, in both composites, the TR contains an increasing amount of an oxygen-rich phase from the fibre core to the CL.

4. EDX analyses

4.1. Experimental procedure

Analyses were performed with a Jeol 2000 FX, equipped with a Link Si–Li UTW detector. The take-off angle being equal to 72°, the sample was maintained perpendicular to the electron beam. These experimental conditions minimize spurious X-rays and the thickness of the analysed area.

The experiments were done at 200 kV. The diameter of the analysed area was estimated to be about 10 nm. Analyses were performed next to the edge to minimize the absorption effect. Interfaces perpendicular to the foil edge were thus selected. Analyses were also performed in the hole next to the foil to verify that no X-rays were detected. A Gatan sample holder, cooled with liquid nitrogen, was used to avoid contamination during the analysis. Owing to the small counting rate of light elements in thin areas, a 10 min counting time was selected to record the EDX spectrum. The counting was interrupted every minute to control the location of the probe. However, in thin samples of plain contrast an error of a few nanometers on the probe location is not excluded. This error results both in an increase of the analysed area and in an error in the width of the different analysed zones.

Quantitative analysis was performed using Cliff–Lorimer factors derived from analysis of the following standards: α-SiC single crystal similar to those used for SIMS and AES calibration, pure SiO_2 powder and an Al_2O_3 single crystal. The standard deviations for the $k_{C/Si}$ and $k_{O/Si}$ Cliff–Lorimer coefficients were equal to 12 and 5%, respectively. As stated above, analysis of the fibre core under the same conditions is the best reference for evaluating the compositional change of the fibre periphery. Fig. 7 shows the local variation of composition in the fibre core.

4.2. EDX analysis of the interphases in the composite

The analyses were performed throughout the reaction layers, from the matrix–carbon layer interface to the fibre core, where the composition was not modified by processing. Fig. 8 shows a concentration profile obtained in a zone without NbC grains. In Fig. 9 are given the EDX spectra obtained when the probe was located at positions on the profile shown in Fig. 8, and which were used to calculate the atomic concentrations.

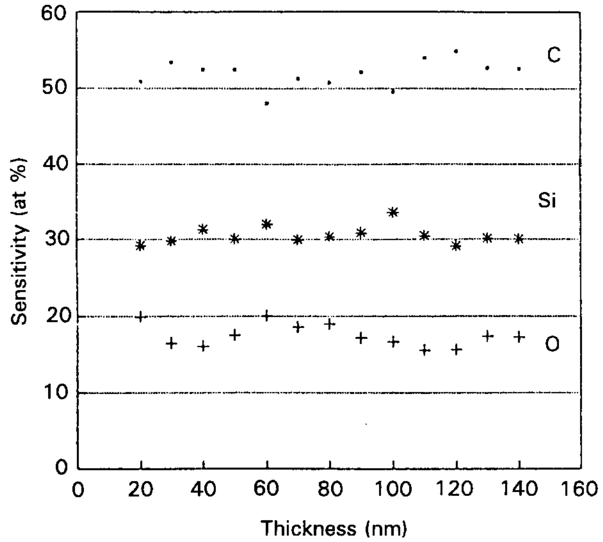


Figure 7 EDX analysis of the fibre core in a nicalon–LAS + Nb_2O_5 composite. The analyses were performed on a cross-section of the composite. The analyses were realized in thin areas located in the centre of the fibre.

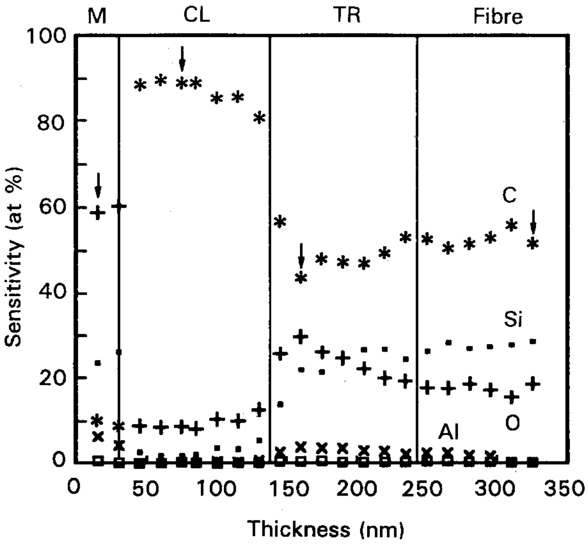


Figure 8 EDX analysis of the interphases in a nicalon fibre–LAS + Nb_2O_5 composite. Each point on the profile corresponds to an analysed area about 10 nm in diameter. The spectra used to calculate the concentrations of the CL, the TR and the fibre are given in Fig. 9.

As for the SIMS analyses, three zones of distinct composition can be distinguished on the profile: the carbon layer next to the matrix, a transition layer (whose composition is neither that of the CL nor that of the fibre) and the fibre (whose composition remained unchanged during composite fabrication).

The matrix–CL interface is always easily located, either by the NbC grains which are found along side it or by large and rapid compositional variations (Fig. 8). The CL–TR interface is also rather well localized by a rapid decrease of the carbon content and by an increase in the silicon and oxygen contents. Next to the matrix or the TR, the measured O and Si contents may be influenced by the surrounding phases. Despite these artifacts, a steep matrix–carbon interface is found. As a consequence, the variation of C, O and Si contents near the TR are characteristic of the CL. The TR–fibre interface is more difficult to determine, because of local variations in the fibre composition (Fig. 7), and because the silicon and the carbon contents reach values characteristic of the fibre core before the oxygen. The limit was put where the oxygen reached the characteristic content of the fibre core. The width of this as-defined zone is about 100–120 nm.

Despite the possible error in the TR limits, it is clear that the TR is richer in oxygen than the fibre core and that a peak in the oxygen content is observed next to the CL. Depletion of carbon and silicon next to the CL is ambiguous. Note that Al is detected beyond the chosen TR limit.

5. Discussion

In this section, we will first discuss the composition of the interphases in nicalon–LAS + Nb_2O_5, where

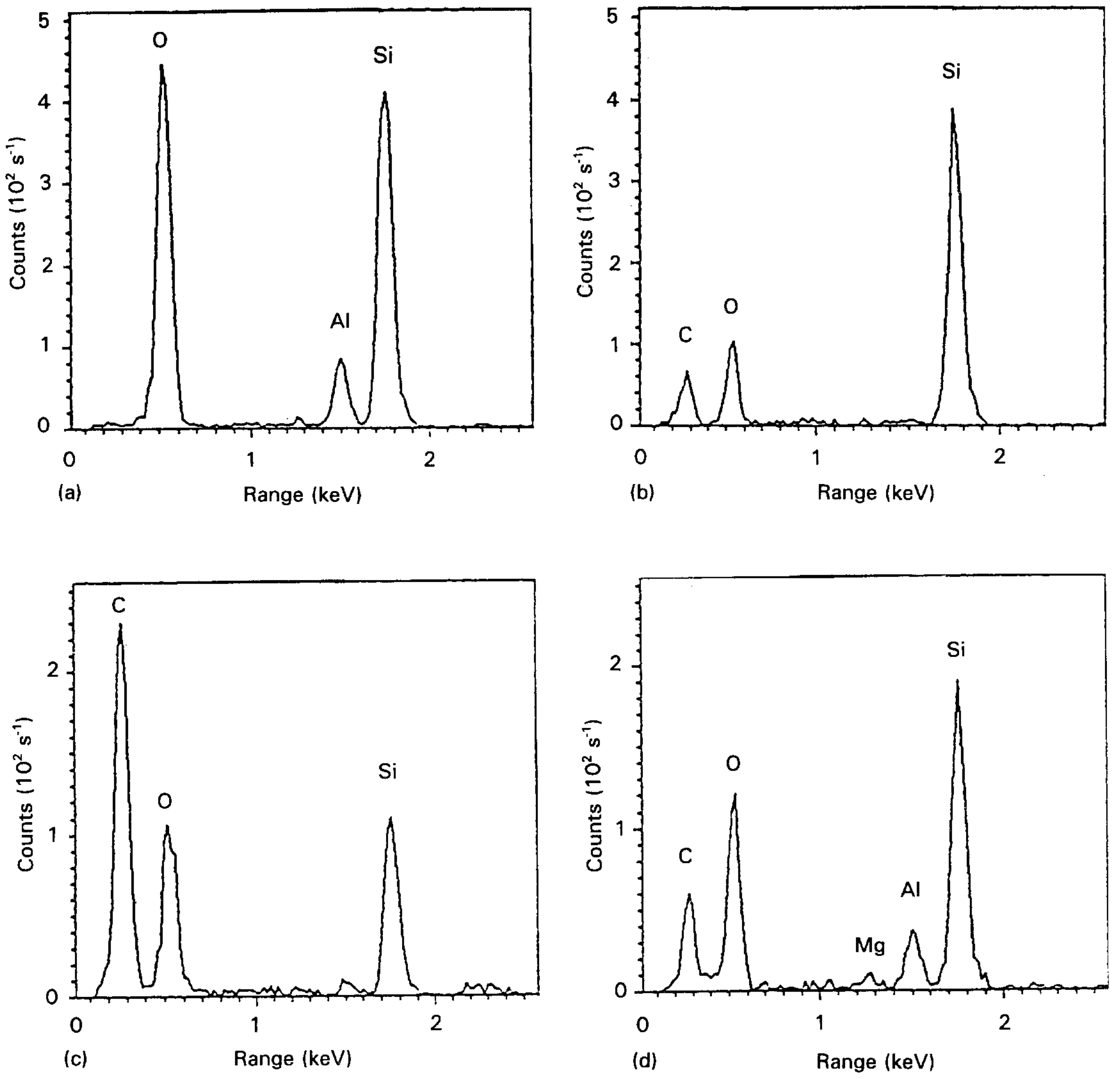


Figure 9 EDX spectra of (a) the matrix, (b) the fibre core, (c) the CL and (d) the TR. The depths where the analysis were performed are arrowed on the concentration profile given in Fig. 8.

both SIMS and EDX analyses have been performed. The main features of the interphases previously identified by HRTEM can be derived from comparison of the results of SIMS and EDX.

The analyses prove that the amorphous layer, observed by HRTEM, i.e. the CL, was effectively made up of carbon, as had been assumed earlier [6]. The CL, whatever its structure, is the carbon interphase previously identified in LAS + Nb_2O_5 composites. It contains some amount of oxygen and silicon, however. The EDX results confirm the SIMS analyses. They show that the concentration gradients in the CL, revealed by SIMS, are due not only to analysis artifacts, but are characteristics of the material. The amount of oxygen and silicon increases, whereas the carbon content decreases near the TR. However, the silicon content always remains low in the CL (less than a few per cent).

The TR is richer in oxygen than the fibre core. The EDX analysis may be influenced by oxidation of the thin foils during preparation. However, no such preferential oxidation occurs during preparation of samples for SIMS analysis. Next to the CL, the peak in the oxygen content is correlated to a depletion in carbon and silicon contents, which are less pronounced, however. Note that the depletion, compared to the level in Z_3 is more pronounced for silicon than for carbon. Such features of the oxygen, silicon and carbon contents next to the CL, although not discussed by the authors, are also observed on the profiles previously published by Brennan and obtained by Auger electron spectroscopy (AES) in nicalon fibres–glass matrix composites of similar composition [12]. These variations in the oxygen, silicon and carbon contents of the TR are thus typical of these composites.

Now, let us compare the difference in composition between the TR and the fibre core detected by SIMS and EDX. As shown on the SIMS profiles (Fig. 5a), O^-/C^- ratio in the TR is roughly twice the O^-/C^- in the fibre. It was shown that the calibration coefficient used to calculate O/C from O^-/C^- in SiC varies by less than 1% when the oxygen content varies from 2 to 15% [13]. It was also shown that this calibration coefficient is suitable for the nicalon fibre [7]. Assuming it is still valid in the TR, the O/C derived from SIMS analysis is twice as high in the TR compared to the fibre core. EDX analysis confirms this result. O/C is about 0.66 in the TR, and 0.35 in the fibre core.

The Si^-/C^- ratio in the SIMS profiles, corresponding to the O^-/C^- peak, is significantly smaller in the

TR (0.3) than in the fibre core (0.46). However, the EDX analysis does not confirm such a big difference.

The question is now to correlate the compositional and the microstructural observations. EDX analysis does not permit a direct and precise correlation. The resolution of the microscope used for EDX analysis was not sufficient enough to image the structure of the TR and the fibre core.

The thickness of the CL measured by EDX is of the same order of magnitude as the thickness of the CL revealed by TEM. However, the compositional variation at the CL–TR interface is less steep than the microstructural variation revealed by HRTEM. The thickness of the CL cannot be derived from SIMS analysis of the extracted fibres for the two following reasons: the sputtering rate of the CL is not known, and the thickness of the CL may be modified when removing the matrix.

The microstructural and compositional variations in the TR are now considered. The mean TR thickness estimated by HRTEM is about 100 nm. On the EDX profiles, the variation of composition from the CL–TR interface towards the fibre core is detected over about 80–90 nm for the carbon and silicon contents, and over 100–120 nm for the oxygen content. Variation in composition is detected over much larger depths by SIMS. If it is supposed that the sputtering rate of the TR is roughly the same as in the nicalon fibre, then the Z_2 ranges between 220–250 nm. Z_2 is much larger than the TR revealed by EDX or HRTEM. This discrepancy could be due to an error in the TR sputtering rate. However, the TR sputtering rate is unlikely to be very different from the fibre sputtering rate, because the composition and microstructure of the TR are rather similar to the fibre for a great depth. In fact, this discrepancy between SIMS and EDX is due to the much better sensitivity of SIMS compared to EDX. Similarly, in a SCS6 fibre–Ti matrix composite, SIMS was able to reveal compositional variations beyond the reaction front, which were detected neither by AES nor by EDX or electron energy loss spectroscopy (EELS) [14]. Despite measurement errors, it is clear that the compositional changes detected by SIMS go far beyond the region where microstructural changes are detected by HRTEM, that is to say far beyond the reaction zone, TR. As a consequence, Z_2 includes both the reaction layer, TR, and the part of the fibre whose structure remains unchanged during composite fabrication, but whose composition is modified by fibre–matrix interdiffusion.

In the nicalon–LAS composite, the compositional characteristics of the TR are not sufficient to make undisputed conclusions. However, they confirm information provided by analysis of the nicalon–LAS + Nb_2O_5 composite. The increase in the oxygen content of the TR compare to the fibre is only about 10% in nicalon–LAS, instead of 100% in nicalon–LAS + Nb_2O_5; but it is still detected. As already discussed in Section 3.3, it is believed that the O/C peak is smoothed in nicalon–LAS due to the thinness of the interphase. The Z_2 width, about 200 nm, is larger than the TR width, about 40 nm, measured on HRTEM images. In both composites, the compositional changes are observed over larger depths than the microstructural changes.

6. Conclusions

The SIMS and EDX results can be interpreted as follows. In nicalon–LAS and in nicalon–LAS + Nb_2O_5 composites, fibre–matrix reaction results in two phases: a carbon phase and a silicate phase rich in oxygen. These phases are located in the two zones identified by HRTEM. The carbon phase is located next to the matrix, in what was previously identified as the CL. The silicate phase rich in oxygen is located between the carbon layer and the fibre core, in the TR. SIMS reveals that the compositional changes are detectable beyond the TR, in the fibre core. The composition changes extend over a larger area than the microstructural changes.

This comparative study by SIMS and EDX also demonstrates that SIMS is the most efficient method for analysing compositional changes in materials, even at the periphery of fibres of small diameter.

Acknowledgements

The authors thank Saint Gobain Recherche for the composites supplied and for the research grant for one of them. They also thank the DRET for financial support. They are grateful to M. Schuhmaher of CAMECA for stimulating discussions.

References

1. J. J. BRENNAN, *J. Phys. suppl.* **10 C5** (1988) 791.
2. D. B. MARSHALL, *ibid.* **10 C5** (1988) 25.
3. R. F. COOPER and K. CHYUNG, *J. Mater. Sci.* **22** (1987) 3148.
4. D. H. GRANDE, J. F. MANDELL and K. C. C. HONG, *J. Mater. Sci.* **22** (1988) 311.
5. B. MEIER and G. GRATWHOL, *Fresenius Z. Anal. Chem.* **333** (1989) 388.
6. C. PONTHIEU, M. LANCIN and J. THIBAULT-DESSEAUX, *Phil. Mag.* **62** (1990) 605.
7. M. LANCIN, F. ANXIONNAZ, M. SCHUHMACHER, O. DUGNE and P. TREBBIA, *Mater. Res. Soc. Symp. Proc.* **78** (1989) 231.
8. L. PORTE and A. SARTRE, *J. Mater. Sci.* **24** (1989) 271.
9. C. PONTHIEU, Thèse de l'Université Paris VI (1990).
10. F. ANXIONNAZ, Thèse de l'Université Paris XI (1987).
11. M. LANCIN, M. MILOCHE and C. PONTHIEU, to be published in Microscopy, Microanalysis, Microstructures, 1994.
12. J. J. BRENNAN, in Proceedings of the Conference on Tayloring Multiphase and Composite Ceramics, Pennsylvania State University, 1985, edited by G. L. Messing, C. G. Pastaso and R. E. Newnham (Plenum, 1986).
13. M. SCHUHMACHER, CAMECA, private communication.
14. M. LANCIN, J. S. BOUR, J. THIBAULT-DESSEAUX and N. VALIGNAT, in "Acta Scripta Met. Proc" Vol. 4, edited by M. Rhule, A. G. Evans, M. F. Ashby and J. P. Hirth, (Pergamon Press, New York, 1989) p. 121.

Received 24 May
and accepted 10 November 1993