JOURNAL OF MATERIALS SCIENCE **24** (1989) 271–275

Evidence for a silicon oxycarbide phase in the Nicalon silicon carbide fibre

L. PORTE
Institut de Physique Nucléaire (et IN2P3), Université Claude Bernard Lyon I, 43 Bd du 11 Novembre 1918, 69622 Villeurbanne Cedex, France

A. SARTRE
Science et Surface S.A., La Combe de Charbonnières, 78 Route de Paris, 69260 Charbonnieres, France

The Nicalon silicon carbide fibre has been studied by X-ray photoelectron spectroscopy. Elements entering the fibre are carbon, silicon and oxygen. In addition to previously reported chemical entities (silicon carbide, silica and graphitic carbon) evidence is found of the presence of a new supplementary phase which is attributed to an intermediate silicon oxycarbide phase. As this phase is found to participate in very appreciable proportions to the composition of the fibre, some influence on the properties of this fibre can be anticipated.

1. Introduction

Fibre-reinforced composite materials have become important in various applications. After glass fibres, carbon and boron fibres, silicon carbide fibres have been developed. These have excited considerable interest because they are promising candidates for the reinforcement of composite materials in high-temperature applications. Thus SiC fibre, for which Nicalon is the trade mark given by the manufacturer (Nippon Carbon) was first developed by Yajima *et al.* [1–3]. Nicalon fibre consists primarily of SiC but the presence of other phases certainly influences its behaviour. In particular, significant amounts of oxygen are found in these fibres and it is important to know how oxygen atoms are incorporated into the network and thus, how they may influence the behaviour of the fibre. X-ray photoelectron spectroscopy (XPS) is a suitable technique to obtain such information. This paper reports some results obtained by XPS analysis of SiC Nicalon fibres. The main goal was to determine the precise role of oxygen atoms. These results demonstrate the existence of a ternary silicon oxycarbide phase which enters into the composition of the Nicalon fibre.

2. Experimental details

Fibre samples were selected at random from a spool of Nicalon fibre. The fibres are supplied coated with an acetate size which was partly removed by etching in concentrated sulphuric acid for 15 h at room temperature.

Just before performing the XPS analysis, the desized fibres were washed in an ultrasonic bath of acetone for 10 min. Two kinds of experiment were done: in the first, a bundle of fibres was analysed using the monochromatized Al*Kα* radiation ($h\nu = 1486.6$ eV) of a 5950 Hewlett-Packard photoelectron spectrometer with an overall resolution of 0.8 eV. The bundle of fibres was positioned on an indium foil and secured by sandwiching it between a sample holder and a golden window. The base pressure in the spectrometer was in the 10^{-9} mbar range. In order to determine bulk composition, fibres were etched by Ar^+ bombardment with an ion gun (2 keV incident energy). Because of the poor conductivity of the fibres, charging effects could arise. They were compensated by spraying the sample with a very low energy electron flow ($E = 1$ eV, $I = 0.1$ mA). In the second experiment, a single fibre (15 μm diameter) was analysed using the monochromatized microspot (150 μm diameter) of a Surface Science Laboratory 100-06 spectrometer. The single fibre was suspended on a special sample holder in order to avoid any contribution from the sample holder to the recorded spectra.

The binding energies (BE) were reported by reference to the C1s peak from graphitic carbon at 284.1 eV BE. A single crystal of α-SiC was also used as standard reference. Results obtained by the two experiments were very consistent and reproducible (cf. Table I).

3. Results

3.1. Quantitative analysis

An XPS survey spectrum recorded from a bundle of fibres revealed carbon, silicon and oxygen as the sole main components of the fibres (Fig. 1). After correcting the intensities of the C_{1s}, O_{1s} and Si_{2p} photopeaks for their respective photoionization cross-sections [4] the composition of the fibres could be evaluated. Such elemental compositions are reported in Table I for analyses performed first on the rough surface of the fibres and second after removing about 100 nm by Ar^+ bombardment. There is no significant change in the carbon content between surface and bulk analyses, but the surface layer exhibits a net oxygen enrichment and a silicon deficiency. These results are fairly

0022-2461/89 $03.00 + .12 © *1989 Chapman and Hall Ltd.*

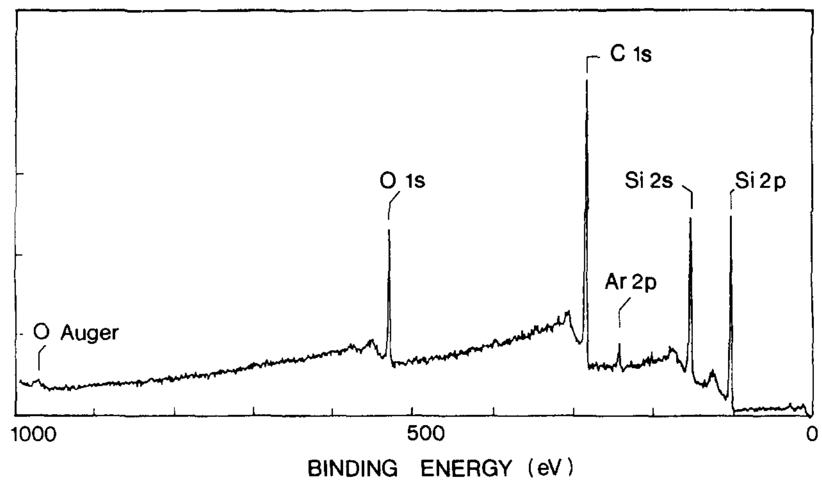


Figure 1 XPS wide scan from a bundle of Nicalon fibres. The small Ar2p signal originates from argon atoms embedded in the fibre during the bombardment by Ar^+ ions.

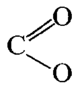
consistent with those obtained from XPS/Auger analysis by Macey *et al.* [5]. Bulk values are also in agreement with chemical analysis results [6] (Table I). It should be noticed that several factors can be responsible for differences in the analysis. First, the reproducibility in the composition of the fibres is questionable. Differences from fibre to fibre have been proved [5], as have differences between various batches of Nicalon fibres [7]. Second, analytical methods can also introduce discrepancies. When etching the material by Ar^+ bombardment, preferential elemental sputtering could cause perturbations. However, no such effects were noticed when sputtering SiC crystal [8].

When analysing fibres by surface sensitive techniques such as XPS, edge effects can be responsible for modifications in the ratio of surface to bulk signals. As such effects are difficult to evaluate in the case of bundles of fibres the reported compositions should be considered as indicative of mean values.

The main interest in these XPS measurements concerns the identification of the chemical entities entering the fibres. In order to minimize the problems mentioned above, measurements were also performed on a single fibre using the microspot XPS apparatus. However, it is noticeable that results obtained from a single fibre are basically in perfect agreement with results obtained from a bundle of fibres. In particular, the same chemical entities were identified in both cases. Only the XPS surface analysis reveals some differences between analyses from a bundle of fibres and from a single fibre (Table I). Because the experimental resolution is slightly better when recording results from a single fibre, only this last analysis is presented below.

3.2. Chemical entities

Fig. 2 shows the C1s core level spectra obtained from a single Nicalon silicon carbide fibre (a) before etching and (b) after etching about 150 nm. Several components appear clearly on these spectra. On the high binding energy (BE) side of the C1s photopeak, three shoulders, B, C and D, are visible in spectrum a and disappear after etching in spectrum b.

These components have too high BE to correspond to carbon species bound in the solid state. Their BEs are rather typical of carbon species in molecular state and could be attributed to molecular groups such as C–O, C=O,  $C\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix}$ [9], respectively, originating from a layer of the acetate size coating not being completely removed by the sulphuric acid treatment. Infrared spectroscopy reveals that this desizing treatment is not fully efficient [10].

These surface entities are not characteristic of the Nicalon fibre and will not be further discussed. Here we focus upon the main C1s and Si2p photopeaks. Fig. 3 compares these photopeaks recorded from (a) the non-etched and (b) the etched fibre. The BE values from C1s and Si2p levels in α-SiC crystal and SiO_2 are also indicated. Dissymmetries and linewidths of the main C1s and Si2p peaks show that these signals do not correspond to unique chemical form. In order to resolve the different chemical components in the fibre, a computerized procedure was undertaken. Theoretical C1s and Si2p spectra were constructed by addition of Gaussian–Lorentzian components, each component being representative of a chemical entity. The width of each component was maintained in a range compatible with the experimental width obtained from

TABLE I Elemental atomic compositions for Nicalon fibres. Values obtained from a bundle of fibres, except those in parentheses which were obtained from a single fibre using XPS microspot analysis

	Surface analysis		Bulk analysis		
Element	This work (XPS)*	Macey *et al.* [5] (XPS)†	This work (XPS)‡	Macey *et al.* [5] (AES)§	Yajima *et al.* [6] (chemical)
C	54 (67)	47.5	56 (53)	53	45
Si	10 (8)	13.4	31 (35)	33	37.5
O	36 (25)	39.1	13 (13)	14	17.5

*Sulphuric acid desized fibres.
†Flame desized fibres.
‡After etching about 100 nm.
§After etching about 45 nm.

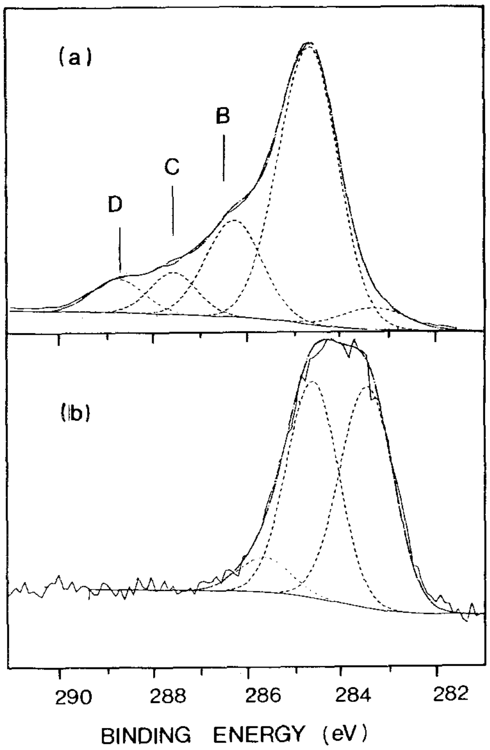


Figure 2 Carbon 1s core level spectra from a single Nicalon fibre: (a) as-received; (b) after Ar^+ etching.

SiC and SiO_2. Modification of the intensity of the components was allowed until the best fitting between experimental and calculated spectra was obtained. Table II gives the BEs and relative intensities of the different components deduced from this resolution procedure. As shown in Fig. 3a and b the presence of three chemcial components (I, II, III) for both C1s and Si2p photopeaks, is evident, thus indicating the chemically complex nature of the fibres.

4. Discussion

From the BE deduced by the resolution procedure in Fig. 3 the attribution of components I and III and Si2p photopeak is unambiguous: component I corresponds to silicon from SiC and component III corresponds to silicon from SiO_2. Moreover, the decrease of component III in Si2p after etching indicates that the main part of SiO_2 is located on the surface of the fibre, and then originates from oxidation of the surface. Component I in the C1s photopeak clearly corresponds to carbon from SiC.

The identification of the chemical entities responsible for component II in Si2p and for components II and III in C1s, is not so straightforward. The BE of component II in Si2p indicates an oxidation state for silicon intermediate between the oxidation state of silicon in SiO_2 and that of silicon in SiC. As elemental analysis shows that only silicon, oxygen and carbon are present in the fibre, such an oxidation state for silicon can only originate from a silicon suboxide of general formula SiO_x, or from a silicon oxycarbide of general formula SiO_xC_y.

The occurrence of silicon suboxide is highly improbable. According to thermodynamic considerations, silicon monooxide should be unstable in the solid state. In fact, the existence of solid SiO has never been demonstrated experimentally. Evidence of lower oxidation states for silicon in the oxygen–silicon system was only given by an XPS study of the

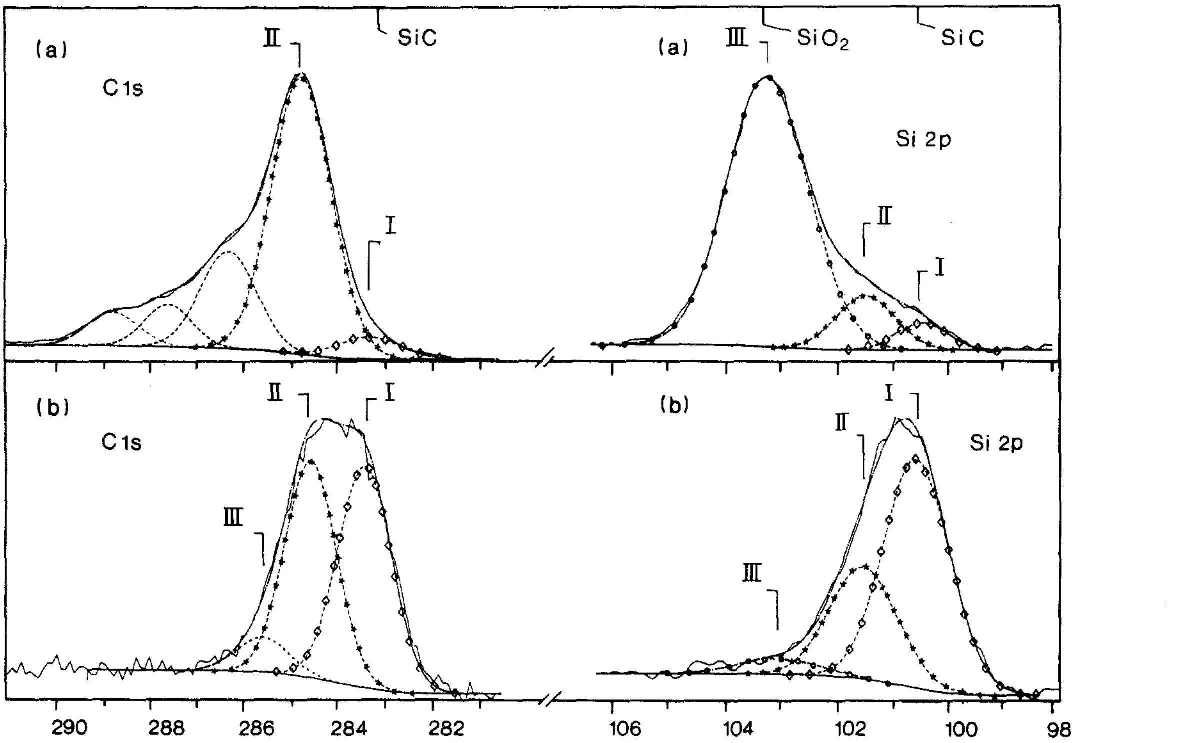


Figure 3 C1s and Si2p core level spectra recorded from (a) non-etched and (b) Ar^+-etched single Nicalon fibre. Ticks on the upper line of the frame indicate the C1s and Si2p binding energies from bulk silica and silicon carbide. (———) Experimental spectra and background substraction. (—·—) Calculated spectra. (– – –) Components obtained from the resolution procedure (see text). (○) SiO_2, (◇) SiC, (★) intermediary phase attributed to silicon oxycarbide (for attribution of the different components see text and Table II).

TABLE II Binding energies, relative intensities and attribution of the C1s and Si2p components obtained from the resolution of the spectra, Fig. 3

	Carbon 1s			Silicon 2p		
	III	II	I	III	II	I
Fibre as-received:						
Binding energy (eV)		284.9	283.3	103.2	101.5	100.5
Intensity*		15	1.2	16.2	2.35	1
Fibre after etching:						
Binding energy (eV)	285.6	284.6	283.4	103.1	101.5	100.5
Intensity	0.15	1.1	1.15	0.08	0.5	1
Attribution		SiO_xC_y + C	SiC	SiO_2	SiO_xC_y	SiC

*Intensities are relative to component I in Si2p.
BE reference values: for SiC (relative intensity) Si2p = 100.5 eV (1), C1s = 282.9 eV (1.1), from [8]; for SiO_2 Si2p = 103.4 eV, from [17].

interface occurring between a silicon substrate and a very thin SiO_2 layer [11]. However, these oxidation states intermediary between Si^{4+} and Si^0 were clearly localized in a path some tenths of nanometres wide at the Si–SiO_2 interface: only a very small number of silicon atoms were involved giving very weak signals on the Si2p photopeaks. Thus the high intensity found for the component II in Si2p is not consistent with the presence of some silicon sub-oxide in the fibre.

Consider now the hypothesis of SiO_xC_y compound. By comparison with SiC the incorporation of oxygen gives an electron charge transfer from silicon to oxygen, thus increasing the Si2p BE and resulting in component II in the Si2p photopeak. It should also produce an electron charge transfer from carbon to oxygen and thus induce a structure on the high BE side of the SiC component (i.e. component I) in the C1s photopeak. Two components, II and III, are found on the left of the SiC component. However, the nearly complete vanishing of component III in C1s after etching of the fibre (Fig. 3b) leads one to demonstrate that components II in C1s and Si2p are both correlated with the presence of a SiO_xC_y compound.

The formation of a silicon oxycarbide phase has been reported by Pampuch *et al.* [12] during the oxidation of SiC. In agreement with the present description, their XPS results show that the formation of the SiO_xC_y phase gives an Si2p component in between the SiC and SiO_2 components and a C1 component on the high BE side of the SiC component. However, inspection of the relative intensities of the different Si2p and C1s components given in Table II indicates that the situation here is still more complex. The ratio between component I from C1s and component I from Si2p is always around unity, which is consistent with the attribution of these components to silicon carbide SiC. Conversely, the ratio between component II from C1s and component II from Si2p is greater than unity, and still increases after etching. One can first notice that the BE of component II in C1s is close from the C1s BE in graphitic carbon (284.1 eV) and argue that graphitic carbon is also incorporated into the fibre. In support of this, Yajima *et al.* [13] have observed small graphite crystallites in the fibre, using high-resolution transmission electron microscopy. Moreover, Raman studies demonstrate the presence of graphitic carbon incorporated into the fibre [14]. Even though amounts of graphitic carbon should contribute to the intensity of the component II in the C1s peak, one cannot attribute the whole of this intensity to graphitic carbon. Indeed, this would signify that there is no SiO_xC_y phase and therefore component II from Si2p would be unexplained. Another explanation for the intensity change of components II could be found in the hypothesis of a non-stoichiometric silicon oxycarbide phase. Incorporation of variable amounts of carbon and oxygen could explain these variations of stoichiometry. It is worth noting that the quantity of oxygen found in the fibres can vary to a very large extent, according to different lots of fibres [5, 7].

In the preparation process of the fibres, a significant oxygen content is incorporated during the curing treatment [15, 16]. Polycarbosilane chains are cross-linked by oxygen. The conversion of the polymer chain to inorganic SiC occurs after subsequent heating. Because in the final product oxygen is not present in the unique form of silica, it is very tempting to connect the presence of the silicon oxycarbide phase with incomplete conversion of the polymer chains to SiC. Then this silicon oxycarbide phase could be supposed to have retained some memory of the polymer precursor. It transpires from this discussion that the way in which the fibres are prepared could determine the silicon oxycarbide phase characteristic and that an intimate mixing of SiC and SiO_xC_y phases could be an important parameter governing the properties of the fibres.

Component III from C1s has still to be explained. At the moment no strong argument allows an unambiguous chemical identification to be made. Because of its high BE, this component could be more properly attributed to carbon atoms bound in some molecular species. Following the idea of the above discussion, a quite logical hypothesis could be to correlate this component with the presence in the fibres or residual carbon species carrying hydrogen or methyl groups and originating from an incomplete decomposition of the precursor. This hypothesis would be supported by the results of chemical analysis of the fibres which revealed a residual content of 3 at % hydrogen [3].

Finally, because this work emphasizes the existence of some silicon oxycarbide phase in the Nicalon fibre (a phase not pointed out before), a brief discussion of the chemical composition is relevant. In previous works [6, 7] the chemical composition was obtained assuming that the oxygen atoms were only in the SiO_2 form. For example, Yajima *et al.* [6], deduced from a chemical analysis the molar ratio $SiC:C:SiO_2 = 1:0.55:0.31$. It is clear from our results that this procedure leads to an overestimate of the SiO_2 content. Table II gives for the etched fibre, i.e. for the values relevant to the bulk composition, the molar ratio $SiC:SiO_2 = 1:0.08$. From Fig. 3 and Table II the molar ratios can easily be deduced. The Si2p components give $SiC:SiO_xC_y:SiO_2 = 1:0.5:0.08$, and the C1s components give $SiC:(C + y\ [SiO_xC_y]) = 1.15:1.1$. Then, neglecting the small component III in C1s and assuming realistic values for y, an estimation of the molar ratio can be made. Extreme limiting values for y are 0 and 1. Then extreme values for carbon graphite are obtained, giving the molar ratio $SiC:SiO_xC_y:C:SiO_2 = 1:0.5:0.75 \pm 0.25:0.08$. Because of the important compositional variability of the fibres, these ratios should be regarded as mean indicative values. However, they show that the silicon oxycarbide phase is actually, with carbon and silicon carbide, one of the three main chemical entities which constitute the fibre.

5. Conclusions

XPS analysis of SiC Nicalon fibres performed either on a bundle of fibres or on single fibre reveals that these fibres contain only carbon, oxygen and silicon atoms. The chemical nature of the compounds forming the fibre appears to be more complex than is generally admitted. The main chemical entity entering the fibre is SiC. It is seen that only one fraction of the oxygen atoms is incorporated into the fibre in the SiO_2 form. One important part of the oxygen atoms is present in the fibre in the form of a ternary phase intermediary between SiC and SiO_2: the origin of this phase has been ascribed to a silicon oxycarbide species. The fibre is found to contain about twice as much silicon carbide molar entities than silicon oxycarbide molar entities. Finally, the presence of the silicon oxycarbide phase, SiO_xC_y, poses the question as to how such a phase can influence on the thermomechanical properties of the Nicalon fibre.

Acknowledgement

We thank J. C. Viala, Laboratoire de Physico-Chimie Minérale, for numerous fruitful discussions.

References

1. S. YAJIMA, M. OMORI, J. HAYASHI, K. OKAMURA, T. MATSUZAWA and C. LIAW, *Chem. Lett.* (*Chem. Soc. Jpn*) (1976) 551.
2. S. YAJIMA, Y. HASEGAWA, J. HAYASHI and M. IIMURA, *J. Mater. Sci.* **13** (1978) 2569.
3. Y. HASEGAWA, M. IIMURA and S. YAJIMA, *ibid.* **15** (1980) 720
4. J. H. SCOFIELD, *J. Electron Spectrosc. Relat. Phenom.* **8** (1976) 129.
5. C. J. MACEY, R. L. LEHMAN and R. L. MOORE, "Scanning Electron Microscopy", Vol. IV (SEM Inc., AMF O'Hare, Chicago, 1984) p. 1643.
6. S. YAJIMA, J. TANAKA, K. OKAMURA, H. ICHIKAWA and T. HAYASE, *Rev. Chim. Min.* **18** (1981) 412.
7. G. SIMON and A. R. BUNSELL, *J. Mater, Sci.* **19** (1984) 3649.
8. L. PORTE, *J. Appl. Phys.* **60** (1986) 635.
9. D. T. CLARK, in "Handbook of X-ray and Ultraviolet Photoelectron Spectroscopy", edited by D. Briggs (Heyden, London, 1977) p. 359.
10. J. C. VIALA, personal communication (1987).
11. G. HOLLINGER and F. J. HIMPSEL, *Appl. Phys. Lett.* **44** (1984) 93.
12. R. PAMPUCH, W. PTAK, S. JONAS and J. STOCH, *Mater. Sci. Monographs* **6** (1980) 435.
13. S. YAJIMA, K. OKAMURA, T. MATSUZAWA, Y. HASEGAWA and T. SHISHIDO, *Nature* **279** (1979) 706.
14. Y. SASAKI, Y. NISHINA, M. SATO and K. OKAMURA, *J. Mater. Sci.* **22** (1987) 443.
15. H. ICHIKAWA, F. MACHINO, S. MITSUNO, T. ISHIKAWA, K. OKAMURA and Y. HASEGAWA, *ibid.* **21** (1986) 4352.
16. H. ICHIKAWA, H. TERANISHI and T. ISHIKAWA, *J. Mater. Sci. Lett.* **6** (1987) 420.
17. D. BRIGGS and M. P. SEAH, (eds), "Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy", (Wiley, Chichester, 1983).

Received 30 November 1987
and accepted 21 March 1988