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Reactivity and molecular structure of silicon carbide fibres derived from polycarbosilanes

Part II *XPS analysis*

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X-ray photoelectron spectroscopy (XPS) characterization of Nicalon NML 202 was carried out on the desized initial fibre (fibre A), fibre A after treatment with hydrofluoric acid (fibre B) and fibre B oxidized in air at 970 K (fibre C). Non-etched and Ar^+-etched fibre bundles were studied. XPS analysis quantitatively fits the chemical analysis of the fibre: the Nicalon fibre is a continuous SiC and SiO_xC_y tetrahedron network with an excess of carbon and exhibits a silica sheath.

1. Introduction

The so-called SiC fibre (Nicalon NML 202) contains an excess of oxygen and carbon elements with respect to SiC composition. In Part I [1] the thermal behaviour of the fibre in the absence and in the presence of oxygen led us to describe the fibre as a mixture of SiC, SiO_xC_y, an excess of carbon and an external layer of SiO_2. These results are cross-checked here by X-ray photoelectron spectroscopy (XPS).

Porte and Sartre [2] evinced the presence of a silicon oxycarbide phase in the Nicalon silicon carbide fibre. Using extended X-ray absorption fine structure (EXAFS), X-ray diffractometry, electron spectroscopy for chemical analysis (ESCA) and nuclear magnetic resonance (NMR) Laffon *et al.* [3] concluded that SiC is embedded in a continuum of tetrahedral SiC_xO_y. It will be seen that by combining chemical treatments of the fibres and XPS it is possible to make more precise the description of the fibre.

2. Experimental procedure

The XPS analyses were made with a VG Scientific SSX 100.06 spectrometer, using the monochromatic radiation Al*K* ($h\nu = 1486.6$ eV). The pressure in the spectrometer was in the 10^{-9} Pa range.

Bundles of fibres positioned on an indium foil were outgassed at room temperature before introduction in the spectrometer. Charging effects, due to low conductivity of the fibres, were compensated with a very low-energy electron flow ($E = 1$ eV, $I = 0.1$ mA). The intensities of the Cls and Si2p photopeaks were corrected for their photoionization cross-sections [4]. The binding energies were obtained with respect to the Cls peak of graphitic carbon at 284.1 eV. The full width at half maximum peak height of the deconvoluted peaks was less than 2 eV.

The bulk compositions of the fibres were determined after etching by Ar^+ bombardment with an ion gun (2 keV incident energy). For 0.5 h etching the maximum abrasion was estimated as 1 to 2 μm. For such a long etching period the analysed zone might not correspond to the etched zone. Actually using a monofilament, it was confirmed that there was no mismatch between etched and analysed zones.

Three samples were studied: the desized initial NML 202 fibre, this fibre after treatment with hydrofluoric acid (HF) and the last one oxidized in air at 970 K until the oxygen fixed by the Si network had reached a pseudo-plateau (Fig. 6b of Part I [1]). We shall refer to these as fibres A, B and C, respectively.

3. Results

3.1. Surface analysis

3.1.1. Elemental analysis

An XPS survey spectrum of fibre A points out the presence of carbon, oxygen and silicon. Table I (first line) shows a large excess of carbon, as for all materials which are not thermally outgassed prior to analysis [5]. The Cls core-level spectra for the three samples studied exhibit the contribution of several functional groups: $-CH_2$,–C–O,–C=O,–COO (pollution).

3.1.2. Chemical analysis

From the above results it is clear that Cls cannot be properly used to describe the surface of the fibre. Fig. 1 shows the Si2p core-level spectra of the three samples.

For fibre A, the entire spectrum corresponds to SiO_2 bond. This confirms the presence of a silica layer formed during the manufacture of the fibre. For fibre B, the Si2p spectrum is strongly asymmetrical which corresponds to the contribution of different

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TABLE I Elemental analysis of fibre A versus etching time (XPS analysis)

	Composition (at %)		
Etching time	Si	C	O
Before etching	5.8	66.8	27.4
30 s	11.4	63.2	25.4
13 min 30 s	33.4	52.1	14.5
33 min 30 s	37.8	49.8	12.4

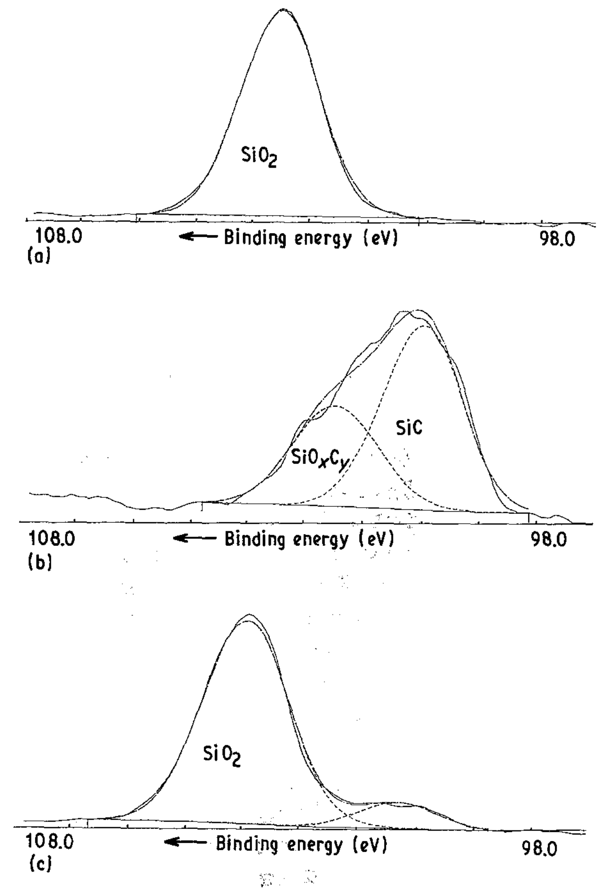

Figure 1 Si2p core-level spectra: (a) fibre A, (b) fibre B and (c) fibre C.

chemical components. No contribution of SiO_2 (103.5 eV) was observed. The fitting of the spectrum can be obtained by adding the contributions of the SiC bond (101 eV) and a bond at 102.5 eV, intermediate between SiC and SiO_2. The fitting was achieved by addition of Gaussian–Lorentzian components, for SiC and for the component corresponding to 102.5 eV. According to several authors [2, 3] this component is a silicon oxycarbide SiO_xC_y. In the spectrum corresponding to fibre C, the major contribution is SiO_2. An SiC contribution is also observed.

3.2. Bulk analysis of the fibres

3.2.1. *Elemental analysis*

From the XPS survey spectrum recorded for different times of abrasion, the composition of the different fibres has been evaluated. The atomic elemental composition are indicated in Table I for three times of abrasion: 30 s, 13 min 30 s and 33 min 30 s.

3.2.2. *Chemical analysis*

The Si2p and Cls core-level spectra of the etched fibre A are represented in Figs 2 and 3, respectively. In Fig. 2 (Si2p spectra), for increasing binding energies, the deconvoluted peaks correspond to SiC, SiO_xC_y and SiO_2. The contribution of SiO_2 decreased with abrasion time and had totally disappeared for 0.5 h abrasion. The contributions of SiC and SiO_xC_y increased with abrasion time.

In Fig. 3, the Cls spectra exhibit a large pollution which decreases with etching time. For 11 min 30 s and 33 min 30 s, beside the SiC contribution, a component corresponds to carbon either as free carbon or involved in an SiO_xC_y bond.

4. Discussion

From the surface elemental and chemical analysis, it is clear that fibre A (desized NML 202 fibre) is covered with an SiO_2 layer formed during fibre preparation in agreement with Part I [1]. The pollution of the fibres by carbon from organic impurities makes it difficult to know more about the initial fibre.

In fibre B, SiO_2 is not observed in contradiction with the composition initially proposed by Yajima *et al.* [6]. They proposed, indeed, the molecular composition $SiC{:}C{:}SiO_2 = 1{:}0.55{:}0.31$.

The Si2p spectrum of fibre C points out that the silicon oxycarbide SiO_xC_y is converted into SiO_2. We have seen in Part I that the thickness of SiO_2 at the pseudo-plateau of oxidation at 970 K is ca. 10 nm. This value is much higher than the extraction depth of photoelectrons (ca. 4 nm). Therefore the SiC contribution does not correspond to SiC structure beneath the external SiO_2 layer but to SiC remaining in the layer oxidized at 970 K.

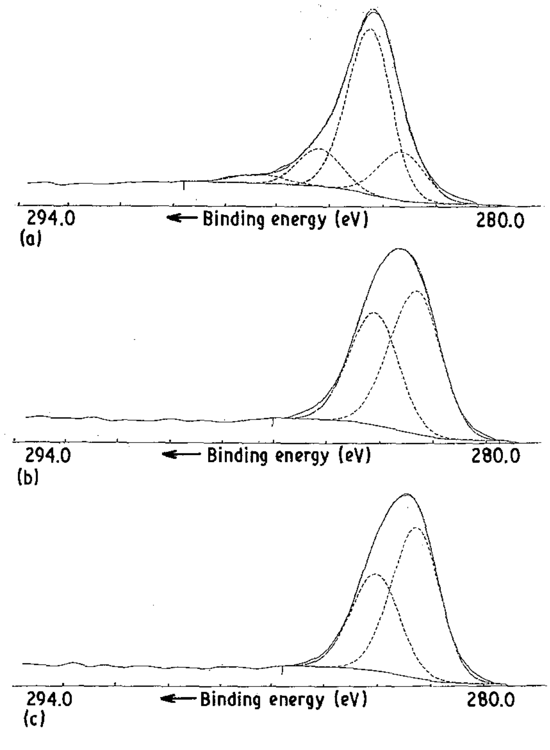

Figure 2 Si2p core-level spectra of fibre A versus etching time *t*: (a) 30 s, (b) 11 min 30 s, (c) 33 min 30 s.

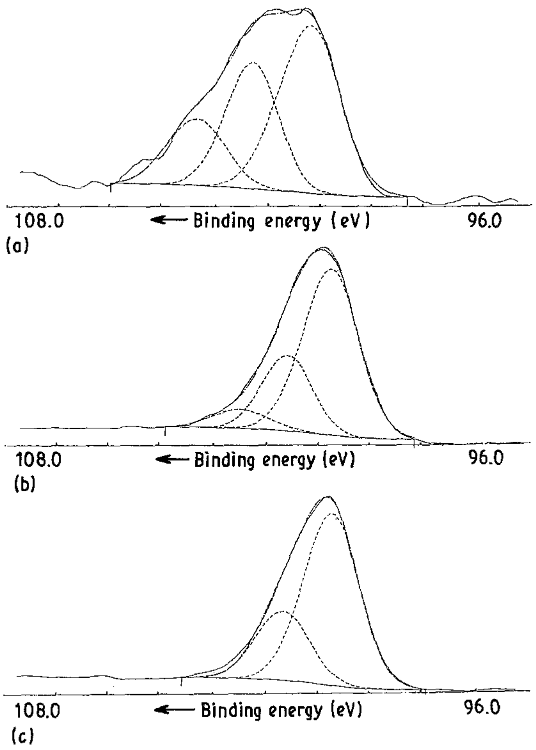

Figure 3 Cls core-level spectra of fibre A versus etching time *t*: (a) 30 s, (b) 11 min 30 s, (c) 33 min 30 s.

From the spectra of etched fibres, it appears (Table I) that the atomic elemental composition in the bulk of the fibre is fairly close to the values obtained by classical elemental analysis, namely Si 35 %, C 52 %, O 13 %. In the bulk of the fibre the SiO_2 signal is insignificant while an SiO_xC_y contribution is indeed necessary to fit experimental and calculated spectra.

Porte and Sartre [2] from XPS spectra had given for Nicalon NML 202 the composition $SiC:SiO_xC_y:C:SiO_2 = 1:0.5:0.75 \pm 0.25:0.08$. Of course, because of the low reproductibility of the industrial fibre itself and of the difficulty of quantifying XPS results, these ratios must be considered as approximate average values.

From the Cls and S2p core level spectra, corresponding to the internal structure of the fibre (Fig. 2 for 33 min 30 s etching) it is possible to compute the chemical composition of the fibre expressed in SiC, SiO_xC_y and excess carbon; it was assumed that carbon atoms give the same XPS intensity whatever their atomic environment (SiC or SiO_xC_y). The following values have been obtained: from the Si2p spectrum

$$SiC:SiO_xC_y = 1:0.43 \qquad (1)$$

and from the Cls spectrum

$$SiC:[C + y(SiO_xC_y)] = 1:0.75 \qquad (2)$$

The corresponding elementary composition (Table I) is Si 37.8%, C 49.8%, O 12.4%. To fulfil Equations 4 and 5, *x* can be equal either to 1.09 or 1.32 which gives for the fibre

$$SiC:SiO_xC_y:C = 1:0.43:0.45$$
$$x = 1.09 \quad y = 0.45$$

$$SiC:SiO_xC_y:C = 1:0.33:0.64$$
$$x = 1.32 \quad y = 0.34$$

The molecular composition of the fibre can be written

$$SiC:SiO_xC_y:C = 1:0.38 \pm 0.05:0.54 \pm 0.09$$
$$x = 1.20 \pm 0.11 \quad y = 0.39 \pm 0.06.$$

This composition is not very different from those proposed by Porte and Sartre [2], though we have not been able to determine any SiO_2 contribution.

At this stage of investigation, what appears important is not the values of *x* and *y* which in any case are average values with no meaning with respect to the structural organisation of the fibre, but the necessity to have an SiO_xC_y structure and an excess of carbon to interpret the XPS characterization which agrees with the oxidation behaviour of the fibre [1]. One can wonder whether the SiO_xC_y is a kind of memory of the organic precursor of the SiC fibre and therefore can be eliminated by an appropriate thermal treatment. This question can be differently formulated: considering the elemental compositions of the fibres ex-polycarbosilane, is it possible to have a molecular structure including only SiO_2, SiC and C at the exclusion of SiO_xC_y? One method would be to model the possible ways to statistically distribute the silicon, carbon and oxygen elements in a three-dimensional network based on SiC and fulfilling the values and the proportion of the three elements. As an approximation, a two-dimensional network was built. A random distribution of silicon, carbon and oxygen was achieved in a 100 × 100 bidimensional matrix able to distribute 10^4 chemical elements. The possible molecular species were determined by combining the three elements, taking into account the elemental composition of the fibre and considering the possible bonds with close neighbours. The following conditions were considered: a silicon element surrounded with four carbons is counted as a silicon carbide unit. We made the following hypothesis:

(i) unsaturated silicon is forbidden as well as Si–Si, O–O, C–O–C bonds, and
(ii) –C=C bonds are possible.

Results of the simulation are plotted in Table II. It appears that silicon has a probability of 51% to be in an SiO_xC_y environment. The proportion of SiO_2 is very low. About half of the carbon is necessarily bonded to at least another carbon atom and the ratio of unsaturation is very high.

From this bidimensional modelling, the proportion of the SiC is slightly smaller than that of SiO_xC_y for an oxygen content of 16%. The reverse situation is observed for an oxygen content of 13%. The simulated values are quite different from those resulting from XPS, which is not surprising when one considers the simple model which was used. What is noteworthy is that SiO_2 units are indeed statistically insignificant, while a large proportion of SiO_xC_y is obtained which decreases with the oxygen content of the fibre. The Nicalon NML 202 fibre can be described as a continuum of SiC and SiO_xC_y tetrahedrons containing an excess of carbon.

TABLE II Simulation of fibre A structure

Fibre	Composition (at %)			Silicon (%)			Carbon (%)[a]	
	Si	C	O	SiC	SiO_xC_y	SiO_2	C–C	Unsaturated C
Less mineralized Nicalon fibre	35	49	16	48	51	1	46	50
Fibre A	35	52	13	54	45	1	54	65

[a] With respect to total carbon non-bonded to Si.

5. Conclusion

XPS and thermal behaviour of Nicalon fibre in the presence and in the absence of oxygen led to the same description of the fibre structure. The core is made of a continuous SiC and SiO_xC_y tetrahedral network including an excess of carbon. An external layer of silica is formed during the industrial preparation of the fibre.

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