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HAL Id: jpa-00226197
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Submitted on 1 Jan 1986

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STRUCTURAL EXAFS STUDY OF COMPOSITE MATERIALS OF THE SiC TYPE

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RESUME
L'environnement du silicium dans les fibres composites type SiC a été étudié par EXAFS et comparé à celui trouvé dans la silice, et dans le carbure de silicium cristallin. Notre étude conclut à l'existence dans ces fibres de microcristaux de SiC noyés dans une matrice d'oxyde.

ABSTRACT
The Silicon environment in composite SiC fibres has been investigated by EXAFS and compared to the SiO₂ glass and quartz, crystalline SiC and pure Si. We concluded that these fibres are a microcrystalline structure of SiC embedded in an oxide matrix.

INTRODUCTION
Recently, there has been much interest in heat resistant silicon carbide composites in fibrous form since they can be used to reinforce metals or plastics. We present here a structural study of fibres of the SiC type which have been previously developed by Yajima et al (1,2) and have a high tensile strength, a high Young's modulus and a good oxidation resistance. These continuous fibres which are produced by heating melt spun polycarbosilane, are now manufactured under the trademark name of "Nicalon" by Nippon Carbon Company Ltd. They are already used for metal or plastic strengthening and are planned to be employed for reinforcing ceramic materials or glasses to improve their toughness making them promising materials for motors due to their excellent thermal behaviour. These fibres are not quite characterized either from a mechanical point of view, or on a structural one. We have undertaken EXAFS experiments on the Si K edge in order to understand, in such complex systems, the environment of silicon atoms and the role of oxygen.

I-EXPERIMENTAL PROCEDURE
Silicon absorption spectra above the K edge have been measured on two SiC fibres of the "Nicalon" type named NLP101 (plastic strengthening) and NLM202 (metal strengthening). Measurements over the same energy range have been undertaken on model compounds such as pure crystalline silicon c-Si, crystalline silicon carbide SiC and amorphous and crystalline SiO₂. All samples were ground to produce particle sizes less than a few microns and deposited on a Millipore polycarbonate membrane.
Amorphous SiO$_2$ was also prepared as very thin blown bubble in order to check any spurious effect arising from possible inhomogeneities in the powdered sample.

Absorption experiments have been carried out on the two-crystal monochromator at ACO, using InSb crystals, and an ion chamber filled with a low pressure of air as a detector. The experimental X-Ray absorption for a typical scan for NLM202 and c-SiC are compared in figure 1. Glitches on the InSb monochromator appear at about 2100eV and a spurious absorption appears around 2140eV which we have determined to be due to a small amount of phosphorus in the Millipore sheet. Therefore most of the data have been collected up to a highest energy value of 2100eV, i.e. 260eV above the silicon edge (1836eV).

![Absorption spectra on Si K edge](image)

**Fig. 1** - Absorption spectra on Si K edge

**2. DATA ANALYSIS AND RESULTS**

For all samples, data analysis has been carried out using the same procedure. We isolate the oscillatory part of the X-Ray absorption by a classical analysis. The origin of the photoelectron wavenumber $E_0$ is chosen at the inflexion point of the edge. Two types of modelling of the background "atomic" absorption have been attempted: one using a fourth order polynomial expression, the other a 3-region cubic spline, both spanning over the whole post edge region. The final conclusions were the same for both cases.

![Comparison of the F.T. of $k^2X(k)$ for a-SiO$_2$ (scale 1/2), c-SiC and composites fibres (Hanning window:12,260eV)](image)

Data are then Fourier transformed using different $k$ weightings and Hanning windows starting more or less far from the edge. Figure 2 (a and b) shows the magnitude of the $k^2$ weighted Fourier transform of the signal for each of the two fibres, compared to the standards SiO$_2$ and SiC. The main peak for a-SiO$_2$ is due to the four oxygens surrounding a Si atom at an average distance of 1.62Å; beyond this the quartz structure become disordered and further peaks are damped. On the other hand silicon carbide, SiC, has the ZnS structure for which we have previously shown (3) that the data can be understood in term of single backscattering of the photoelectron by the neighbours with all peaks identified with a crystalline distance.
A qualitative interpretation can be directly obtained by observing the Fourier transforms: the structure of NLM202 is composed of microcrystals of SiC since not only the first (Si-C \( d=1.89\AA \)) and second (Si-Si \( d=3.07\AA \)) peaks are in coincidence with those of the standard SiC, but also are the outer shells up to more than 6\( \AA \) (6th). The structure of the NLP101 fibre seems to be less organised since the peaks at distances greater than 4\( \AA \) are no longer present.

a-Analysis of the first shell

A numerical fit is performed on the filtered signal obtained by backtransforming the data using an R space window centered around the first peak. Using the standard EXAFS expression (4) in the plane wave approximation we have extracted amplitudes and phases shifts for the pairs Si-Si, Si-O and Si-C from the results on the model compounds.

The simulation of the EXAFS is obtained by a least square fitting procedure using a two-shell model. For this computation we did not allow the mean free path and the Debye-Waller factor to vary, while \( E_0 \) the origin of the photoelectron has been permitted to shift slightly. Calculated results are summarized in table 1.

<table>
<thead>
<tr>
<th></th>
<th>Si-O</th>
<th>Si-C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( d (\AA) )</td>
<td>( N )</td>
</tr>
<tr>
<td>NLM202</td>
<td>1.62</td>
<td>.1</td>
</tr>
<tr>
<td>NLP101</td>
<td>1.62</td>
<td>.7</td>
</tr>
</tbody>
</table>

b-Interpretation of the 2nd peak of the F.T.

The second peak of the Fourier transform is attributed for both SiC and c-SiO\(_2\) to a Si-Si distance between the vertex of the tetrahedra (d=3.07\( \AA \)). A corresponding peak exists for the two fibres but is less intense for NLP101. We have fitted this peak using Si-Si amplitude and phase shift from crystalline silicon. The results are reported in table 2.

<table>
<thead>
<tr>
<th></th>
<th>Si-Si</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( d (\AA) )</td>
</tr>
<tr>
<td>NLM202</td>
<td>3.05</td>
</tr>
<tr>
<td>NLP101</td>
<td>3.09</td>
</tr>
</tbody>
</table>

3-DISCUSSION

The apparent average coordination number of the atoms of a cluster is smaller than that observed in the bulk crystal because of the higher proportion of surface atoms. This effect depends on the size and the shape of the crystallite. This effect has been quantitatively studied for supported metal clusters and catalysts \((5,6,7)\). It has been shown that average coordination numbers, as determined by EXAFS for the first to the fourth shell, can be used to estimate the size and shape of the crystallites.
These calculations have been done for f.c.c. metals, so that they can be used in our case if we only consider the silicon sublattice, in which the 2.5Å peak in the Fourier transform corresponds to the first shell, up to the peak at about 6Å in the F.T. which corresponds to the fourth one.

For a three dimensional f.c.c. crystallite, an average coordination number of 7.3 (first shell) implies a diameter of 13Å. Starting from a central silicon atom, this cluster extends therefore up to the fifth shell, which is 6.8Å from the origin. In view of the very small amplitude of the Si-Si contribution (compared to the first shell) in amorphous silica (see figure 2) due to the large disorder of this shell, we can neglect in our calculation silicon-silicon bonds coming from Si-O-Si units.

Therefore this cluster contains about 80 atoms, and assuming that 20 atoms on the periphery have replaced one of the carbon by oxygen atoms, the average carbon coordination lowers down to 3.5 while the average oxygen coordination becomes 0.5, values in good agreement with the measured ones renormalised to 4. (table I). In this model, the carbon atoms of the border of the cluster are linked to silicon atoms belonging only to the cluster, and share other bonds with possibly other carbon or oxygen atoms.

In this case, the silicon-silicon average coordination becomes about 5, which corresponds to a very small cluster made up by one central silicon atom and its twelve neighbors. Within the same model of one carbon being replaced, at the twelve outer silicon, by an oxygen, we obtain a mean carbon coordination (4+12*3)/13=3.07, and a mean oxygen coordination 12/13=0.9, which compares favourably with the results of table I, within the expected accuracy of a coordination measurement by EXAFS also renormalised to 4.

Comparing the high R side of the second peak for the NLP sample to the SiC and the amorphous silica results, we definitely see a feature (at about 3Å) reminiscent of outer shells in a-SiO2. This may be the signature of an Si-O-Si unit which would bond SiC microcrystals together, but this feature has not yet been analysed.

The first EXAFS study of these composite samples has therefore given quite a precise insight of the middle-range structure around the silicon atoms: microcrystals of SiC are present in the material. However, we still have only a little information about the way such clusters are linked together. More experiments on the carbon and the oxygen edges may be helpful to answer these questions.

We want to thank P. Olry of the S.E.P. and R. Hagège from the J.T.F. for providing us with the samples, and the persons in charge of ACO for operation of the ring.

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