Table 1. Results of N₂ adsorption tests for coated carbon membranes

<table>
<thead>
<tr>
<th>Characteristic property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micropore volume</td>
<td>0.054 cm³/g</td>
</tr>
<tr>
<td>Characteristic energy of adsorption</td>
<td>21.8 kJ/mol</td>
</tr>
<tr>
<td>Specific surface area</td>
<td>1120 m²/g</td>
</tr>
<tr>
<td>Half-width of micropores</td>
<td>0.60 nm</td>
</tr>
</tbody>
</table>

with radii up to 390 nm. No pores with the radii more than 45 nm (pore size determination limit of the technique used) were detected in the coated carbon membranes.

In conclusion, pyrolytic coating of carbon membranes with TiC and subsequent chlorine treatment resulted in the formation of a thin microporous carbon layer on the outer surface of the membranes. Mesopores of the outer skin of carbon membranes were blocked by the microporous layer to give an asymmetrical microporous carbon membrane. The separation properties of the coated carbon membranes are being studied.

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"Harmless" carbon tubes around "dangerous" asbestos fibres

(Received 6 December 1993; accepted 14 December 1993)

Key Words - nanotubes, asbestos

Carbon nanotubes were found first by Iijima in soot-like deposits on the cathode of a carbon-arc chamber [1]. Their formation is based on graphitic planes rolling up at high temperatures to form seamless cylinders [1,2,3]. Following the principles of capillary suction of the carbon tubes [4], a Pb-containing phase as well as yttrium carbide have been successfully introduced inside pre-existing carbon tubes [5,6]. We have, for the first time, demonstrated that the growth of carbon tubes can take place around asbestos fibres (Mg₃Si₂O₅(OH)₄).

The asbestos cylinders behave as substrates around which the nucleation and growth of carbon tubes take place.

A small amount of asbestos fibres, with a diameter between 20 and 40 nm, was mixed into the arc chamber during the preparation of the carbon tubes. A carbon soot bar deposited on the cathode was broken and soot pieces were scraped out from the broken section. By means of scanning electron microscopy, the asbestos needles were located. A number of carbon nano-tubes and needles were picked up, crushed and suspended on a holey carbon copper grid for examination in a 200kV transmission electron microscope.

Fig. 1a shows several individual cylindrical asbestos fibres encapsulated by carbon tubes. The cylindrical asbestos (black) inside the carbon tubes are found to be either hollow or solid, in agreement with the observation of Yada [7]. Selected-area electron diffraction (SAED) patterns demonstrate the well crystallized cylindrical asbestos structure which we will describe later. Most encapsulated asbestos fibres are straight, but sinusoidal and curved morphologies are also present (indicated by arrows A, B, C, and D), particularly in some relatively short carbon tubes. This sinusoidal morphology is particularly visible in fig. 1b. The tubes surrounding the asbestos fibres vary from 0.1 µm to more than 1 µm in length, while the diameters are between 20 nm and 50 nm. The majority of the tubes however have diameters around 30-40 nm, which is substantially larger than that for pure carbon nanotubes [8,9]. The thickness of the tube wall is about 3 nm. Tilting around the length axis of the tube does not alter its shape, confirming the cylindrical shape of the tube. Some of the tubes however have a prismatic shape, which is evidenced by tilting the tube around the cylinder axis. Most of the tubes however have diameters at both ends with dome caps (arrows A and B) though opened ends are not exceptional (arrows C and D). The opened ends however can be a consequence of crushing and breaking the sample during preparation for transmission electron.
Fig. 1. (a) Morphology of the carbon tubes surrounding asbestos fibres. Arrows A, B, C and D indicate tubes with sinusoidally shaped asbestos inside. Tubes indicated by arrows A and B are closed at both ends whereas those indicated by arrows C and D have open ends. (b) Part of tube C at a larger magnification. The sinusoidal shape of the encapsulated asbestos fibre is clearly visible. The asymmetrical projecting tube shape (double edge lines in the bottom and single in the top) suggests a prismatic shape of the tube.

Microscopy. The empty or amorphous regions between the asbestos fibre and encapsulating tube may be due to a chemical reaction of asbestos with the carbon tubes. This reaction could explain the rough surface of the asbestos fibres as presented in fig 1. Moreover, attempts to obtain lattice images of the carbon tubes or of the asbestos fibres failed because of the fast amorphous transition under the electron beam.

Energy dispersive X-ray spectroscopy (EDX) was performed to investigate the tube content. The regions used to obtain the spectra are carefully selected and marked in fig. 2 by A and B. Region A comprises a part of interior asbestos and the surrounding tube whereas region B comprises only part of the surrounding tube. The spectra recorded from regions A and B are depicted in fig. 3a and fig. 3b, respectively. Mg, Si, O and C peaks in fig. 3a are consistent with the MgSi2O3(OH)4 composition of the asbestos fibre. The fact that the Mg peak disappears while the Si and O peaks are strongly weakened in region B, confirms that the outer surrounding tubes are not asbestos-related; the surrounding tubes only consist of carbon. We have convinced ourselves that the tubes are not formed under the electron beam, and we have also verified that the tubes are not to be confused with specimen contamination.

Fig. 2. A tube with asbestos used for EDX analysis. Two circular dark regions are caused by electron beam contamination during the spectra acquisition. Region A contains a part of interior asbestos as well as the surrounding carbon tube; region B only contains a part of the carbon tube.
Selected-area electron diffraction (SAED) patterns obtained from individual asbestos fibres inside the carbon tube are shown in fig. 4. The pattern of fig. 4a is symmetrical with respect to the vertical axis, which is typical for a cylindrical wrapping of the crystal structure and has also been observed for the pure carbon tubes [2,3]. The present pattern can be perfectly indexed according to the monoclinic structure of asbestos [10], taking into account the cylindrical symmetry of the fibre, which introduces apparent twin related patterns, as the ones indicated in fig. 4a by full and broken lines. The reciprocal angle $\beta' = 87^\circ$ corresponds to the monoclinic angle $\beta = 93^\circ$ in real space. The simultaneous appearance of (h00), (0k0) and (00l) reflection rows in one SAED pattern is a typical and well known feature for cylindrical structures [2,3]. The unique rolling direction as well as the non-helical feature of the asbestos cylinders can be concluded from the fact that no SAED patterns differing from the one in fig. 4a have been found. As pointed out by Pauling, the asymmetrical layered structure of asbestos is perfectly suited to form the cylindrical shape [11].

Fig. 3. EDX spectra from (a), region A and (b), region B in fig. 2.

Fig. 4. (a) SAED pattern from an asbestos and carbon tube entity. The reflections are indexed according to the monoclinic $\text{Mg}_5\text{Si}_2\text{O}_5(\text{OH})_4$. Two parallelograms which locate symmetrically with respect to the cylinder axis are outlined by full and broken lines. Reflections arising from two regions of the asbestos fibre are indicated by small arrowheads and arrows respectively. (b) SAED pattern showing the presence of the (0002) graphite reflection next to the (004) asbestos reflection.
In fresh samples and by careful selection, the representative (0002)-type reflections of the tubular graphite structure can be discerned in the SAED patterns (fig. 4b). These reflections, which correspond to a 3.45Å lattice spacing in real space, are lying very close to the asbestos (004) reflection but can still be distinguished as indicated by arrowheads in fig. 4b. Presumably, they imply a graphite structure for the tubes surrounding the asbestos fibres, though we have not yet obtained sufficient evidence for the graphite structure. Contrary to the empty tubes, or to pure graphite, the present surrounding carbon tubes are always straight, presumably because of the unstable behavior of asbestos under the electron beam [7].

A possible growth model for the carbon tubes around the asbestos fibres is based on the idea that the asbestos fibres behave as substrates for graphite growth. Carbon tubes probably nucleate randomly and grow independently along the asbestos fibre. These independently grown tubes finally coalesce to form the complete tubes as observed in fig. 1. The whole procedure is schematically illustrated in fig. 5. It is reasonable to assume, as shown in fig. 5a, that the nucleations prefer to start at both ends of the asbestos substrate although nucleations at other places are possible. These separate nucleations grow independently along the asbestos fibre by continuously adding carbon atoms (fig. 5b). When two tube pieces meet (fig. 5c), two situations may occur which are illustrated either in fig. 5d or in fig. 5e. For the former situation, the coalescence is perfect, and the length of the tube will be the same as the length of the encapsulated asbestos fibre, which keeps its original (straight) shape. However, in a number of situations the connections between adjacent tube pieces will not be perfect and strains will be generated at the interconnections. The strain along the cylinder axis can be relaxed by altering the tube length. In the case of a length reduction, the interior asbestos will be forced to bend within the diminished space as shown in fig. 5e. Both situations represented schematically in fig. 5d and fig. 5e are indeed observed in fig. 1a.

If we would on the contrary suppose that the carbon tubes nucleate and grow around an originally sinusoidal shaped asbestos fibre, sinusoidal carbon tubes should result. This however has never been observed; the surrounding carbon tubes are always straight, independent of whether the interior asbestos is straight or sinusoidal. In addition, no half or partially filled tubes have been observed. These facts are convincing evidence that carbon tubes nucleate and grow around the pre-existing asbestos fibres.

The present results illustrate for the first time the possibility of growing a "harmless" carbon protection around microscopic fibres, which could be toxic or chemically active. We are indeed convinced that asbestos fibres are not the only fibres which can be wrapped in a carbon protection; experiments on other fibre-like materials are under the way.

Acknowledgement - This paper presents research results of the Belgian programme on Inter University Poles of Attraction initiated by the Belgian State, Prime Ministers Office of Science Policy Programming (IUAP48). The scientific responsibility is assumed by the authors.

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REFERENCES