Impurity Effects in Carbon Fibres

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Outgassing experiments have been performed on a variety of polyacrylonitrile- and rayon-based carbon yarns. Major residual impurities, as well as those introduced from surface treatments, have been identified. Sulphur has been shown to be a major impurity of rayon-based carbon fibres, with concentrations up to 3110 ppm by weight having been determined by neutron-activation analyses. Removal of this contaminant as a volatile material commences at approximately 1300 °C. Interrelationships between sulphur removal and mechanical and crystallographic properties have been considered for one rayon-based carbon yarn. Decreases in both interlayer spacing and tensile strength are associated with sulphur evolution, whereas apparent crystallite size and Young's modulus are unaffected by the outgassing.

1. Introduction
Carbon/carbon composite materials are currently receiving considerable attention for high-temperature applications [1, 2]. For some applications, such as heat shields on re-entry vehicles, the composites may be subjected to temperatures exceeding those at which the component carbon fibres are manufactured. The chemical and physical behaviour of the fibres at temperatures above those employed in processing are of concern for two reasons. First, outgassing of the fibres could generate sufficient gas pressure to damage the composites mechanically [3]. Second, the physical properties of the fibres themselves could be affected by the additional heat-treatment.

In the present investigation a variety of polyacrylonitrile (PAN)- and rayon-based carbon fibres have been outgassed to temperatures between those employed in carbonisation and graphitisation processes, and the major volatile impurities have been identified. As anticipated, the outgassing behaviour and impurity contents of carbonised and graphitised fibres* are generally different. Impurities which would vaporise above graphitisation temperatures have not been studied.

An attempt has also been made to determine the effects of the removal of one contaminant, sulphur, on the physical properties of rayon-based carbon fibres. The paper is organised in

such a way that the outgassing experiments and identification of sulphur as a contaminant of rayon-based carbon fibres are established prior to considerations of impurity effects on fibre properties.

2. Experimental Method
The ten different carbon yarns outgassed are described in table I. Each carbon yarn was attached to a high-current AC source and heated resistively in a Consolidated Vacuum Corporation CVE-15 vacuum system. The temperature was changed in increments by means of a variable transformer. The apparatus was designed so that fibre temperature, gas pressure, and mass spectra could be obtained as functions of time. The gases evolved from the fibres were detected by a residual gas analyser which was located in a direct line-of-sight with the yarn. Because the system was continuously evacuated, the mean free path of the evolved gas molecules was long compared to the distance between the analyser and the yarn.

Temperature readings were obtained via a calibrated Leeds and Northrup Model No. 8634-C optical pyrometer; window corrections were applied in all cases. Representative temperature readings were difficult to obtain, because fibres on the outside of a bundle were often not part of the conduction path and were, consequently, at lower temperatures. For this reason,

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*For the purpose of this paper the terms "carbonised" and "graphitised" refer only to the maximum heat-treatment temperatures and do not necessarily imply differences in structure.

TABLE I Carbon yarns outgassed.

Material*	Precursor	Maximum temperature† during processing (°C)	Surface treatment	Maximum outgassing temperature (°C)
A1RC	Rayon	C	None	1823
A2RC	Rayon	C	None	1711
A3RG	Rayon	G	None	1625
B1RC	Rayon	C	None	1485
C1RG	Rayon	G	PVA‡ (coating)	2007
C2RG	Rayon	G	None	1508
D1PG	PAN	G	None	2034
E1PG	PAN	G	Proprietary treatment	2192
F1PG	PAN	G	Proprietary treatment	2270
G1PC§	PAN	C	None	2007

*Materials are designated such that the first letter refers to the commercial manufacturer, the following numbers refer to different yarns, and the last two letters identify the precursor (rayon or PAN) and heat-treatment (carbonised or graphitised).
†Exact processing conditions are generally proprietary, but are known to vary widely. The symbols C and G designate carbonisation and graphitisation temperatures, typically $\leq 1500\,^\circ C$ and $\geq 2500\,^\circ C$, respectively. The time at maximum processing temperature is typically of the order of seconds or minutes.
‡Polyvinyl alcohol.
§Not analysed for sulphur.

measurements were made of the highest observable temperatures. Pyrometer measurements were made at temperatures above 760°C; approximate values of lower temperatures were obtained by extrapolating curves of the variable transformer setting versus temperature measured at high temperatures.

Pressure was recorded continuously via an ionisation gauge. Generally, pressure increases associated with temperature increases were recorded in the 10^{-6} torr range. In most cases, the pressure peaked within 0.2 min after the variable transformer was turned to a higher setting and thereafter decreased approximately in an exponential manner.

Mass spectra were obtained by means of an EAI QUAD 150A residual gas analyser equipped with a Tektronix Type 547 oscilloscope and a Hewlett-Packard Model 196A oscilloscope camera. Since the spectral scans were performed in 0.1 sec, it was possible to obtain a spectrum at each outgassing pressure peak by simply snapping a photograph of one scan when the pressure versus time curve peaked. A spectrum was also obtained of background vapours remaining after each outgassing increment; consequently it was possible to distinguish between residual gases and those evolved during each outgassing increment.

Structural aspects of the fibres were examined by means of X-ray diffraction analyses. Data for powdered samples were generated by means of a G.E. XRD-6 diffractometer with nickel-filtered $K\alpha$ copper radiation, and used to determine values of apparent crystallite size perpendicular

to the layer planes, L_c, and interlayer spacing, d_{002}. The former values were obtained from line broadening measurements and the latter values were corrected for Lorentz-polarisation and atomic scattering.

Mechanical properties of individual fibres were measured with a "Tecam" micro-tensile testing machine. Both Young's modulus, E, and ultimate tensile strength, σ, were obtained. Cross-sectional areas of representative fibres, embedded and polished in an epoxy matrix, were measured from optical micrographs.

Sulphur analyses were obtained by means of neutron-activation techniques and a chemical analysis was obtained via emission spectroscopy.

3. Results and Discussion
3.1. Outgassing Data
The data obtained during a typical outgassing run are illustrated in figs. 1-3. Detailed mass spectra for most of the materials have been presented elsewhere [4] and selected spectra are given in figs. 3-6. In all cases the period of time at each temperature is long compared to that required for gas removal. During the initial stages of outgassing, organic compounds on the fibres are volatilised. Decomposition of the polyvinyl alcohol coating on C1RG, for example, occurs at temperatures below 760°C. Fibres that have not been intentionally coated also yield organic vapours, because residual organic contaminants are removed from the fibre surfaces. Water vapour, CO, and CO_2 are generally evolved and largely removed by $\sim 1000\,^\circ C$. The ratio of CO to CO_2 is low at the
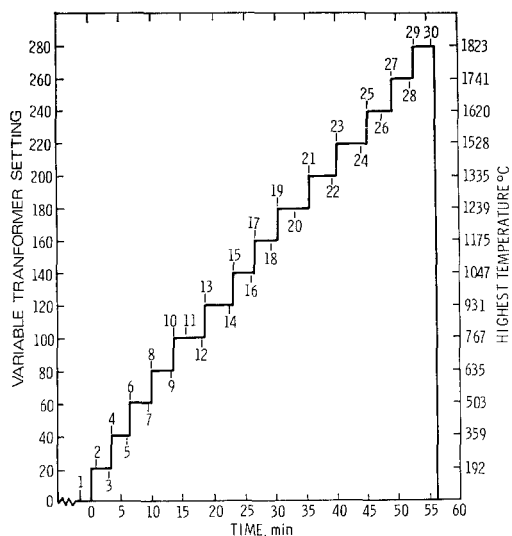
Figure 1 Variable transformer setting and temperature versus time for the outgassing of A1RC yarn. The numbers shown on the figure indicate when the various mass spectra were obtained.

ing the fibres to 1400 to 1600°C. Watt has recently reported that about 40% of the nitrogen in the precursor is evolved as gaseous nitrogen during carbonisation in the range 700 to 1300°C [5]. In contrast with the outgassing behaviour of the carbonised PAN-based material the mass spectra obtained during the outgassing of the three graphitised PAN-based materials yielded no evidence of nitrogen evolution.

Mass spectra obtained from E1PG and F1PG are shown in figs. 5 and 6, respectively. These two PAN-based products have been surface-treated following graphitisation in order to increase shear strength in organic matrices. Spectra obtained from the former show the presence of SO_2^+ and SO^+ in the approximate temperature range 900 to 1100°C, while those obtained from the latter exhibit CS_2^+, as well as SO_2^+ and SO^+, in the range 1000 to 1300°C. (The SO^+ peak is presumably an ion source fragmentation product.) The appearance and removal of these species over the small temperature ranges mentioned, and the fact that they were not observed during the outgassing of the two untreated PAN-based materials, suggests that they are a consequence of the surface treatments employed by the manufacturers.

Above about 1300°C, peaks attributable to CS^+ and the fragmentation product S^+ are evident for the first four rayon-based yarns listed in table I. With removal of the volatile sulphur compounds, these peaks decrease in intensity, as shown for one yarn in fig. 3. A small peak due to CS_2^+ is sometimes detected, although the CS^+ peak is always the predominant one. These spectra have been compared with one generated from carbon disulphide and interpreted to mean that carbon monosulphide is the main gaseous sulphur compound produced during the outgassing of the four carbon yarns mentioned [6]. The increased gas evolution due to sulphur
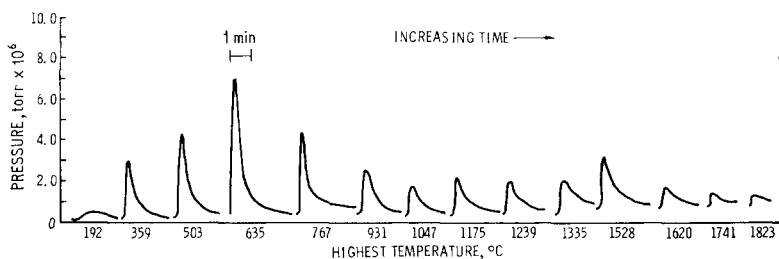
commencement of outgassing, but increases with increasing temperature, as determined from the mass spectra.

Differences in the outgassing characteristics of different materials become evident above approximately 1000°C. The mass spectra obtained during the outgassing of G1PC, a carbonised PAN-based material, are given in fig. 4 and show large peaks due to N_2^+ and N^+ in the temperature range 1000 to 1500°C. The presence of N^+ is due to ion-source fragmentation, rather than ionisation of gaseous monatomic nitrogen. Observation of the nitrogen peaks implies that this PAN-based material retains a significant quantity of residual nitrogen through the carbonisation processing cycle. The spectra indicate that most of the volatile nitrogen can be removed by heat-

Figure 2 Gas pressure versus time as a function of temperature for the outgassing of A1RC yarn. Note the increasing background pressure associated with out-gassing of the vacuum system as the temperature increases.
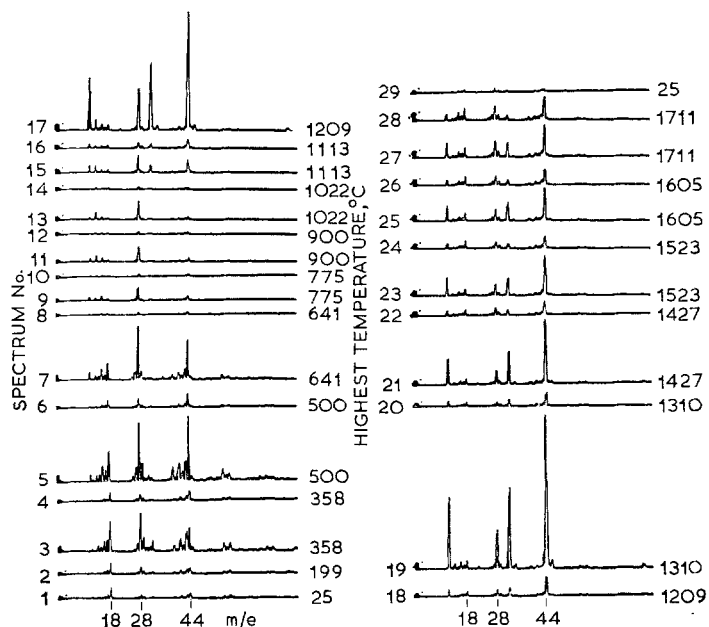
Figure 3 Mass spectra obtained during the outgassing of A1RC. The second spectrum at each temperature represents the background. Above $\sim 1300°C$, $m/e = 44$ corresponds to CS^+ and fragmentation products at $m/e = 12$ and 32 correspond to C^+ and S^+, respectively. Note that above $\sim 1300°C$ the intensity ratios of these three peaks are virtually constant.

removal can be seen in the pressure versus temperature curves, i.e. note the increased pressure maximum at the temperature of 1528°C in fig. 2. Positive identification of the sulphur-containing ions is not based solely on the mass spectra. The results of neutron-activation analyses, discussed later, confirm the presence of significant quantities of sulphur in the carbon fibres.

Outgassing of two graphitised rayon-based materials, C1RG and C2RG, yielded no evidence of the evolution of volatile sulphur compounds or contaminants other than hydrogen and oxygen.

3.2. Sulphur Considerations

From the outgassing data it is apparent that sulphur is an important volatile contaminant of the rayon-based carbon fibres. Whereas free sulphur readily vaporises at 100 to 200°C, sulphur remains in the solid fibres at temperatures in excess of 1000°C. The literature [7, 8] indicates that sulphur is readily incorporated into carbon and that the complexes so formed are not easily removed. Puri and Hazra [9] have reported, for example, that heating carbon in vacuum at

1200°C is not sufficient to remove all of the sulphur introduced into the carbon at lower temperatures.

Because carbon disulphide is used in the preparation of viscose rayon [10], it seems likely that use of this reagent results in some residual sulphur which remains in the carbonised fibres. Such a hypothesis suggests that a sulphur contaminant can be expected in all rayon-based fibres, in an amount partially determined by heat-treatment during processing. It also suggests that sulphur contamination should not be as significant in non-rayon based carbon fibres. To test this hypothesis, quantitative sulphur analyses were obtained via neutron-activation techniques for a variety of as-received carbon fibres. The results, given in table II, are consistent with the hypothesis. For rayon-based fibres the sulphur contents of the graphitised fibres are all lower than those of the carbonised materials. Of the A yarns, for example, the material A3RG heated to a graphitisation temperature has a sulphur content of 390 ppm by weight, whereas the materials A2RC and A1RC heated to lower maximum temperatures have sulphur contents of 1400 and 1050 ppm, respectively. Note the relatively high
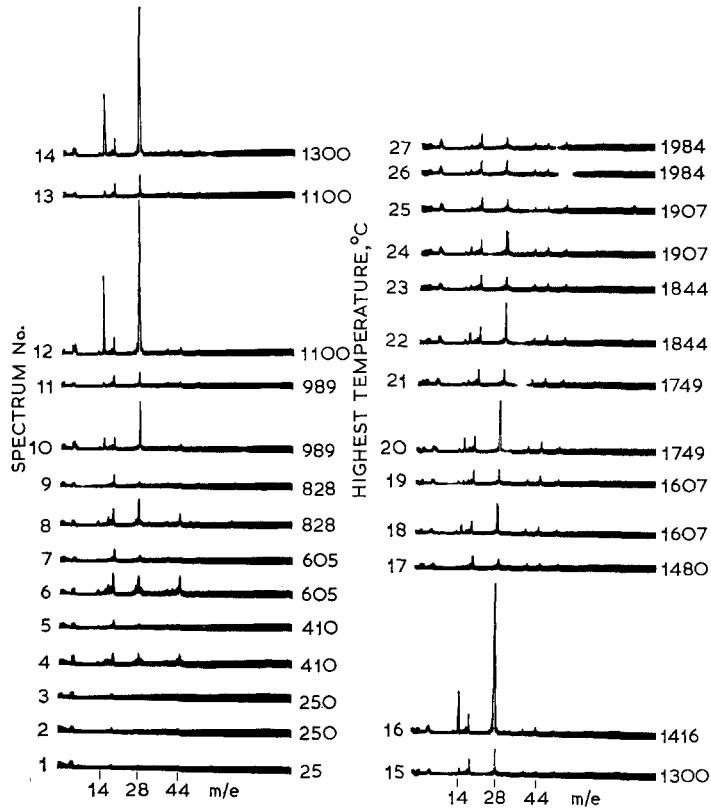
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Figure 4 Mass spectra obtained during the outgassing of G1PC. Above ~1000°C, $m/e = 28$ and 14 correspond to N_2^+ and the fragmentation product N^+, respectively. Note that in this temperature range, the intensity ratio of the two peaks is virtually constant.

TABLE II Sulphur contents of various carbon fibres.

Material	PPM sulphur by weight*		Precursor	Maximum temperature† during processing (°C)
A1RC‡	1050	± 50.0, 2570 ± 130	Rayon	C
A2RC	1400	± 100	Rayon	C
A3RG	390	± 20.0	Rayon	G
B1RC	769	± 50.0	Rayon	C
C1RG	101	± 5.0	Rayon	G
C2RG	234	± 12.0	Rayon	G
H1RG§	255	± 13.0	Rayon	G
D1PG	42.8 ±	2.0	PAN	G
E1PG	48.8 ±	2.5	PAN	G
F1PG	98.4 ±	5.0	PAN	G
I1RC§ (felt)	3110	± 150.0	Rayon	C
Sandia Laboratories (Albuquerque)				
Felt Run No. 15§	1030	± 50.0	Rayon	1100

*Estimated uncertainties are for the chemical analyses. Variations due to material inhomogeneities are appreciably greater, as shown by the values of the two samples of A1RC.
†Exact processing conditions are generally proprietary, but are known to vary widely. The symbols C and G designate carbonisation and graphitisation temperatures, typically $\leqslant 1500°C$ and $\geqslant 2500°C$, respectively. The time at maximum processing temperature is typically on the order of seconds or minutes.
‡Duplicate samples from the same spool of yarn.
§Not outgassed.

sulphur contents of the rayon-based carbon felts, 1030 and 3110 ppm; these materials have relatively low processing temperatures, i.e. 1100°C.

The sulphur contents of the three PAN-based materials are all below 100 ppm and are below the lowest sulphur content obtained for all of the rayon-based fibres. Two of these PAN-based materials have received surface treatments which presumably result in residual sulphur being deposited on the surfaces of the fibres. Even with this addition of sulphur, the PAN-based fibres have lower sulphur contents than the rayon-based ones. Consequently, it appears that the sulphur contents of untreated PAN-based graphitised fibres are significantly lower than those of rayon-based fibres. This also implies that sulphur contamination is not significant in the preparation of the polyacrylonitrile precursor.

The neutron-activation analyses show that sulphur is very likely the most extensive impurity (excluding oxygen and hydrogen) in rayon-based carbon fibres. For B1RC fibres, for example, the sulphur content is equal to the total impurity content of the twenty-two elements determined via emission spectroscopy. The latter analysis indicates each metallic impurity present in the concentration range ≤ 20 ppm by weight. The fact that sulphur is not detected by routine emission spectrographic analyses is undoubtedly the reason why it has not been previously reported as a major impurity of carbon fibres.

3.3. Consideration of Relationships between Sulphur Evolution and Fibre Properties

Because of the relatively high sulphur contents of the rayon-based carbon fibres, an attempt was made to evaluate the effects of sulphur removal, via outgassing, on the crystallographic and mechanical properties of the fibres. Only A1RC, which is presumably a representative relatively high sulphur content yarn, was examined. The possibility of adding the impurity to a low sulphur content yarn was rejected because of uncertainties regarding whether or not the added impurity would be bonded and located identically to the residual sulphur [7].

Different samples of yarn were outgassed to different maximum temperatures in the range 1031 to 1823°C. Values of the properties subsequently determined are given in table III.

The X-ray diffraction data show that the interlayer spacing, d_{002}, decreases only 0.016Å, and the apparent crystallite size, L_c, remains constant with increasing outgassing temperature through 1230°C. Over this temperature range virtually no sulphur is removed from the fibres (on the basis of the mass spectra shown in fig. 3). When the outgassing temperature is increased above 1300°C, however, sulphur is evolved (see fig. 3) and the d_{002} value decreases markedly, from 3.484 to 3.435Å, with increasing outgassing temperature, from 1230 to 1627°C. Additional outgassing to 1823°C does not reduce the d_{002} value further.

The virtual constancy of L_c with increasing outgassing temperature shows that no appreciable growth of crystallites has taken place. This means that the observed changes in the d_{002} values are not associated with a graphitisation process. The conditions employed in the outgassing are such that graphitisation would not be expected, since the temperatures are below those at which graphitisation generally occurs (i.e. 2500°C), and the time at maximum temperature is no more than several minutes. As a result, diffusion of carbon atoms in the solid fibres is considered to be insignificant. The possibility of

TABLE III Properties of outgassed A1RC carbon fibres.

Maximum observable outgassing temp. (°C)	d_{002} (Å) $\pm$ 0.005*	L_c (Å)†	Tensile strength,‡ $\sigma \times 10^{-3}$ (psi)§	Young's Modulus,‡ $E \times 10^{-6}$ (psi)§
As-received	3.500	16	143 $\pm$ 20	5.6 $\pm$ 0.5
1031	3.491	16	—	—
1230	3.484	15	151 $\pm$ 30	5.5 $\pm$ 0.6
1409	3.459	18	123 $\pm$ 28	5.1 $\pm$ 0.6
1627	3.435	21	99 $\pm$ 23	6.1 $\pm$ 0.5
1823	3.435	22	103 $\pm$ 16	5.4 $\pm$ 0.6

*Estimated uncertainties.
†These values are near the lower limit of crystallite size measurements obtainable from line broadening; consequently, the uncertainties are not known.
‡Average values of 8 to 10 fibres. Gauge lengths ranged from 6.16 to 12.09 mm. An average cross-sectional area of 0.947×10^{-7} in² was used in the calculations. Uncertainties are standard deviations.
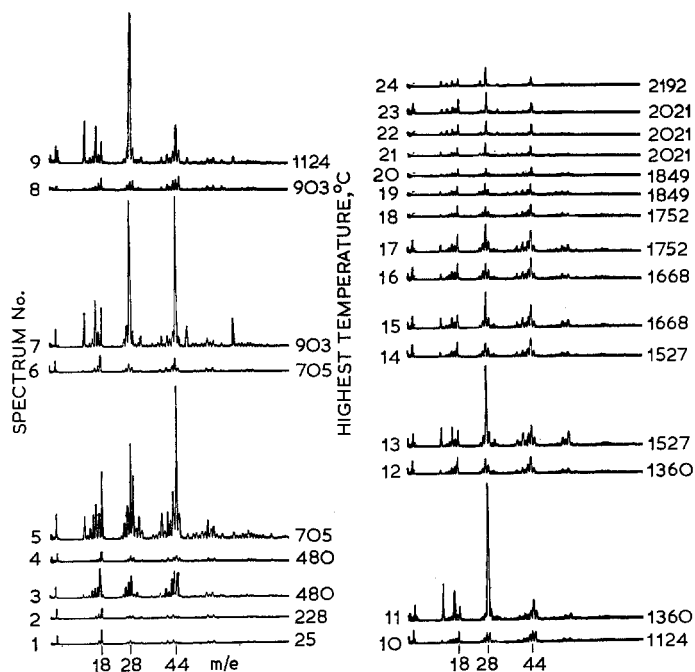§10^3 psi $= 0.703$ kg.mm^{-2}.

Figure 5 Mass spectra obtained during the outgassing of E1PG. The peaks at $m/e = 64$ and 48 correspond to SO_2^+ and SO^+, respectively.

catalytic graphitisation occurring due to the sulphur appears unlikely because of the relatively small concentration of sulphur present in the fibres and the evidence in favour of its acting as a graphitisation inhibitor when present in larger quantities, i.e. 2.5 to 10.0% [11].

Because no significant variation in fibre cross-sectional area resulted from the outgassing, the mechanical properties given in table III are based on the average area obtained from unheated fibres, as well as those heated to 1230, 1627, and 1823°C. (Measurements were not made on the material heated to 1409°C because insufficient material remained.) The average value, 0.947×10^{-7} in^2., and standard deviation, 0.206×10^{-7} in^2., resulted from measurements of eighty-one fibres, approximately twenty in each group.*

The Young's modulus is apparently unchanged by the outgassing treatments, whereas the tensile strength decreases markedly through the 1627°C treatment and then remains approximately constant. The statistical significance of the observed trends in average tensile strength have been considered by means of the Student's t-test [12]. The analyses show that at the 90%

confidence level there is no statistical difference between the as-received sample and that outgassed at 1230°C or between the samples outgassed at 1627 and 1823°C, but statistical differences do exist between all other pairs of samples. Even at the 99.9% confidence level there is a statistical difference between the as-received sample and that outgassed at 1627°C (or 1823°C).

Questions regarding causes and effects cannot be definitely answered from the data presented because the properties measured do not vary independently. In addition, the significant variation in residual sulphur content from sample to sample of the same spool of yarn (see A1RC in table II) completely masks composition changes due to the outgassing; i.e. all outgassed samples had sulphur contents within the range observed for the as-received material. Consequently, empirical correlations between sulphur evolution and properties are not possible. The only conclusive statement that can be made is that outgassing above approximately 1300°C results in decreases in sulphur content, interlayer spacing, and tensile strength.

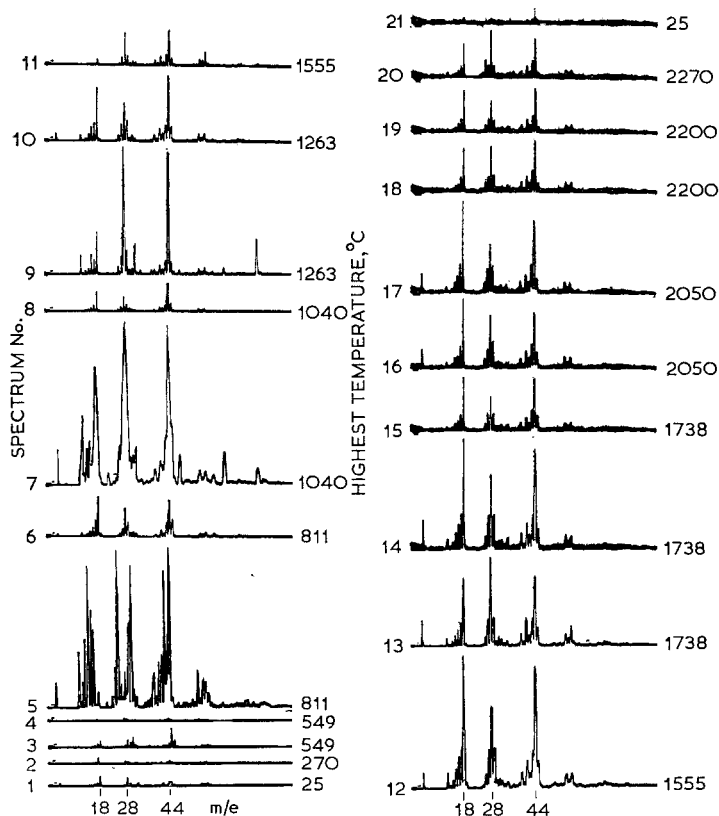One possible qualitative explanation for the data is based on the assumption that removal of

Figure 6 Mass spectra obtained during the outgassing of F1PG. The peaks at $m/e = 76, 64$, and 48 correspond to $CS_2{}^+$, $SO_2{}^+$, and SO^+, respectively.

sulphur occurs from between the graphitic basal planes. The decreases in d_{002} which occur when sulphur is eliminated suggest that much of it is effectively located there and the slight increases in L_c, if significant, imply that removal of sulphur results in a somewhat improved packing of the basal planes. The fact that both σ and d_{002} decrease markedly over the same temperature range and then both become constant, suggests that the variation in tensile strength is a consequence of the variation in structure (i.e. interlayer spacing). The decrease in tensile strength could also be associated with the formation of cavities during the outgassing; Sharp and Burnay [13] have shown that this is the case in carbonised acrylic fibres. Constancy of the Young's modulus is not unexpected, since this property is primarily determined by the orientation of the graphitic basal planes, which is established during the preparation of the carbon fibres [14, 15].

4. Summary

Mass spectra obtained during the outgassing of various carbon yarns have shown the presence of volatile impurities which are retained by the fibres through carbonisation. The carbonised PAN-based material contains nitrogen as a volatile contaminant. Three different graphitised PAN-based materials, however, yielded no evidence of nitrogen when outgassed at temperatures below maximum processing temperatures. Surface treatments of two PAN-based materials apparently result in the formation of sulphur-containing surface groups which can be volatilised at temperatures up to 1300°C.

Rayon-based carbon fibres contain sulphur as a major impurity. Neutron-activation analyses have revealed sulphur concentrations up to 3110 ppm (0.31 wt %). Removal of some of this impurity as a volatile material requires heat-treatment above 1300°C. Decreases in interlayer

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spacing and tensile strength are associated with the evolution of sulphur for at least the one commercial carbon yarn considered. The apparent crystallite size and Young's modulus, however, are virtually unaffected by the outgassing. The possible relationship between sulphur removal and fibre properties has been considered, although no definite mechanism has been established.

Acknowledgements

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