

Pyrolytic surface treatment of graphite fibres

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Thornel 50 was continuously coated with pyrolytic carbon from an atmosphere of acetylene. Using resistance heating to raise the temperature of the graphite fibre yarn to 1100 to 1200°C, as much as 60% increase in weight of pyrolytic carbon could be uniformly applied to the surfaces of the individual filaments. The treated fibres gave improved interlaminar shear strengths up to 60 MN m⁻² and improved flexural strengths up to 900 MN m⁻² in epoxy resin composites. Visual examination of the fractured surfaces indicated that while the adhesion of the resin to the pyrolytic carbon was satisfactory, the adhesion of the pyrolytic carbon to the Thornel 50 fibre surface may have been less satisfactory and led to premature failure. Such continuous one stage treatments of graphite fibres offer advantages in terms of improved handling characteristics, greater oxidation and corrosion resistance, improved wettability, and slightly better impact toughness than other commercially available treated fibres. The resultant increase in the weight of the treated yarn may improve the economic aspects for applications which do not require highly flexible yarns.

1. Introduction

Although the problem of achieving a high interlaminar shear strength in graphite fibre composites appears to have been adequately resolved by a number of investigators, there still remains considerable mystery and speculation about the nature of the interfacial bond and the exact locus of failure in such composites. It is well known that untreated high modulus graphite fibres exhibit poor adhesion to most thermosetting resins and, consequently, the cured composites tend to fail at relatively low shear stresses, often less than 30 MN m⁻². Various chemical post-treatments have been developed to increase interlaminar shear strengths to over 70 MN m⁻² without adversely affecting either the moduli or tensile strength of the graphite fibres. These investigations have been recently summarized by McKee and Mimeault [1, 2] and Larsen *et al* [3].

Surface treatments have involved chemical oxidation with reagents such as nitric acid [4-6] and sodium chlorate [7]. Shaver reported the catalytic growth of silicon carbide whiskers onto carbon fibres to form an interlocking mat

[8, 9]. Vapour deposited coatings of pyrolytic carbon, metals, carbides, and silica have also been reported with varying degrees of success [1, 4, 5, 10].

In the following study, untreated Thornel 50 yarns were coated by the pyrolytic deposition of carbon from a hydrocarbon gas. The yarn was heated by electrical resistance as it passed through a glass tube containing an atmosphere of the hydrocarbon. In the first experiments, mixtures of carbon monoxide and hydrogen were catalytically decomposed under conditions similar to those described by Walker [11] and Graydon [12].

However, none of these treated yarns showed any noticeable improvements in the interlaminar shear strength. Attempts to use natural gas were unsuccessful since the high pyrolysis temperatures resulted in local overheating and frequent fibre breakage. Acetylene required a lower pyrolysis temperature and the extent of carbon deposition could be easily controlled without causing yarn breakage. Moderately high interlaminar shear strengths (60 MN m⁻²) were obtained with this treatment which were

intermediate between the values reported by McKee and Mimeault [1, 2] for polyacrylonitrile based fibres (Modmor I and II). The vapour phase treatment offers a simple one-stage operation which is attractive from a commercial point of view. This paper describes an attempt to develop a satisfactory treatment which would not adversely affect the tensile properties of the original yarn.

2. Experimental

Untreated Thornel 50 (Union Carbide trademark), a rayon based two-strand graphite fibre yarn, was used throughout these experiments. The physical properties of this particular graphite fibre yarn are listed in Table I.

over the range 0 to 120 V to a maximum of 5 A. Fibre temperatures above 760°C were measured with a Leeds and Northrup Model 8622 optical pyrometer. The reaction gases were metered into the glass reaction tube (7 cm i.d. by 60 cm long) by means of calibrated flow meters, the reaction gases being allowed to escape freely at the fibre inlet and exit orifices (which were restricted but not sealed). The yarn was fed continuously from the supply creel through the reaction zone and rewound onto a takeup reel. The fibre was maintained under slight tension during treatment. The fibre speed could be varied up to a maximum of 8 cm sec⁻¹ (15 ft min⁻¹). Care was taken to minimize contact of the graphite fibre yarn with any surface before treatment owing to

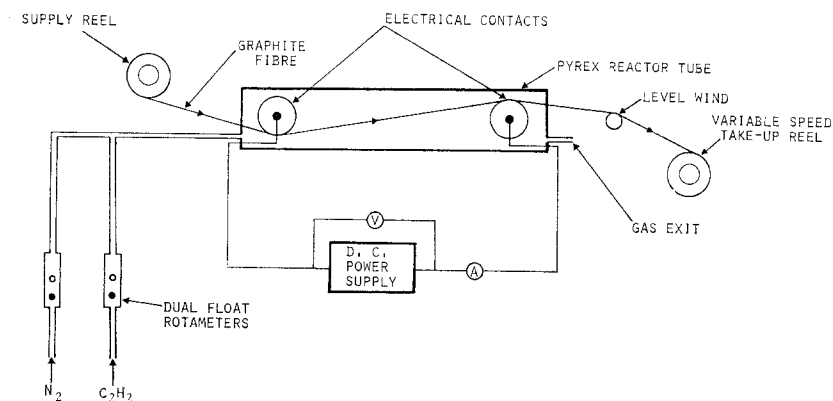


Figure 1 A schematic drawing of the apparatus used for vapour coating Thornel 50 graphite fibre yarn from an atmosphere of acetylene mixed with nitrogen. The yarn was admitted through a small capillary tube which also acted as the exhaust ports for the gases.

TABLE I Physical properties of Thornel[®] 50 graphite fibre yarn (two strand, 720 filaments per strand)

Tensile strength (MN m ⁻²)	2270
Tensile modulus (GN m ⁻²)	400
Density (g cm ⁻³)	1.63
Filament diameter (μm)	6-8
Axial electrical resistivity (Ω cm)	0.00097

The apparatus shown in Fig. 1 was used to deposit a coating of pyrolytic carbon onto the surfaces of the individual filaments in the yarn. The yarn was resistance heated by means of a pair of highly polished brass contacts. By changing the positions of the electrical contacts the length of the yarn which was being heated could be varied up to 47 cm. The variable voltage direct current was supplied by a power supply

the extremely delicate nature of the untreated yarn. Even the slight pressure exerted by the moving fibre on the highly polished brass electrical contact caused some fraying. After a coating of pyrolytic carbon had been applied, the fibres were far less sensitive to such damage.

In order to vary the partial pressure of the acetylene gas, nitrogen was admixed with the acetylene using calibrated flow meters. By adjustment of the voltage and current the temperature of the fibre in the reaction zone could be controlled. The residence time could also be adjusted by the winding speed and the length of the heated segment. The coated yarn was cut into short lengths and placed in an open ended mould [11] with an appropriate quantity of an epoxy resin mixture containing 100 parts of Epon 828 (Shell Chemical Co), 90 parts of

nadic methylanhydride and 2.5 parts of benzyl dimethylamine. The thickness of the moulded bar was adjusted with stops and cured for 2.25 h at 105°C and 20 h at 160°C. The moulded specimens (14 × 1 × 0.2 cm³) were tested in flexure using a three point loading at a span to depth ratio of 50. Interlaminar shear strengths were measured by the short beam shear test using a 5:1 span to depth ratio [13, 14]. The fractured surfaces were subsequently examined by scanning electron microscopy to assess the mode of failure.

3. Results and discussion

Using nitrogen and acetylene mixtures it was found that fast rates of carbon deposition could be achieved at temperatures as low as 900°C. Typical treatment conditions using this system are summarized in Table II.

TABLE II Experimental conditions for the pyrolytic vapour treatment of Thornel 50 with acetylene

Fibre temperature (°C)	1130 ± 40
Treatment duration (sec)	10.25 ± 0.25
Lineal speed of graphite yarn (m min ⁻¹)	3.0
Acetylene flow rate (cm ³ sec ⁻¹)	1.0
Nitrogen flow rate (cm ³ sec ⁻¹)	4.0
Percentage weight increase of treated fibre (%)	7.37
Power supplied to fibre (W cm ⁻¹)	5.24

The rate of carbon deposition was dependent upon the total residence time and the yarn temperature as shown in Fig. 2. The fibre temperature was proportional to the power supplied to the fibre so that constant conditions could be easily maintained through control of the voltage and amperage. The pyrolysis temperatures were sufficient to remove the polyvinyl alcohol sizing on the fibres.

The acetylene cracked smoothly onto each individual filament in the yarn producing a uniformly thick sheath as is readily observed in Figs. 3 and 4. This can be contrasted with the characteristic appearance of untreated rayon based graphite fibres shown in Fig. 5. Fig. 3 shows a fibre with a coating amounting to a 35% weight increase which still clearly shows the striations characteristic of the original filament. The yarn is considerably stiffened by this treatment, largely owing to the fusing together of many of the individual filaments in the yarn. This

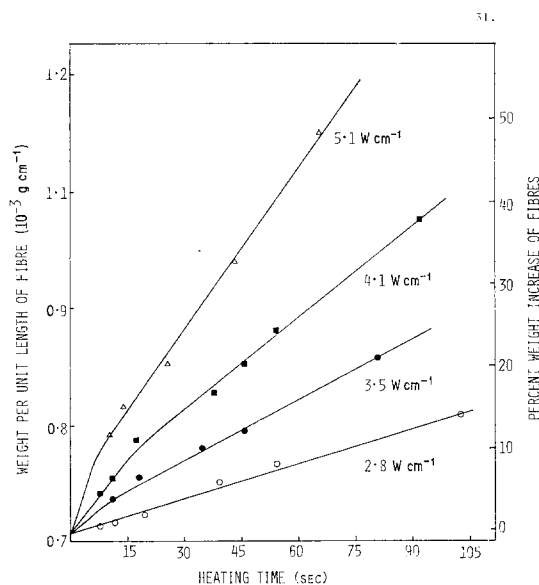


Figure 2 The rate of carbon deposition is dependent on the fibre temperature and the acetylene concentration. These results were obtained at 20 vol% acetylene for four different temperatures, 930, 1010, 1050 and 1120°C in order of increasing wattage. Much faster rates are possible at higher acetylene concentrations.

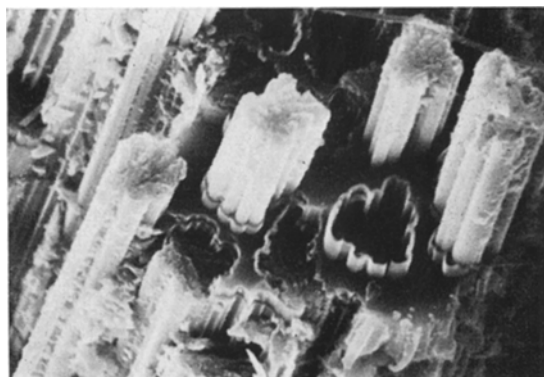


Figure 3 This photograph shows the appearance of the tensile fracture surface for a fibre with a 14.7% coating of pyrolytic carbon. The coating apparently shows good adhesion to the epoxy resin matrix but not to the fibre core as evidenced by longer pull-out lengths (× 3800).

is evident in Fig. 4. X-ray diffraction with a Siemens Goniometer Diffractometer using CuK α radiation with a nickel filter indicated that the surface coating consisted of small disordered graphitic crystallites.

In order to determine the relationship between the thickness of the deposited coating and the

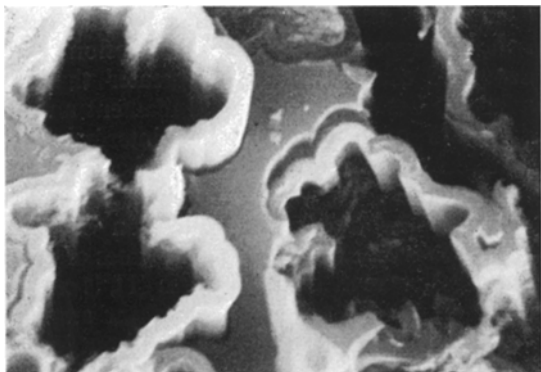


Figure 4 A close-up of a fractured surface shows some of the filaments fused together by the deposited carbon coating. Considerable variations in the thickness of the coatings were also noticed ($\times 10000$).

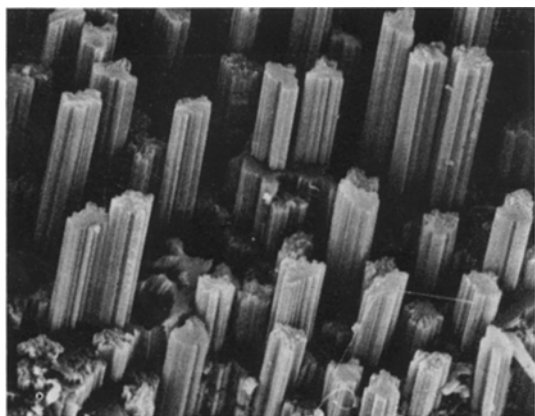


Figure 5 This fracture surface is typical for untreated Thornel 50 fibres. Note the smooth surfaces of the fibres and the long pull-out lengths. Evidence of debonding of the fibre from the resin can be observed at the resin fracture surface ($\times 1700$).

mechanical properties of the resulting epoxy resin composite, a series of treated yarns were prepared at relatively constant temperatures (1130 to 1200°C) and constant acetylene concentrations (20%) while the residence time of the yarn was varied. This produced a series of treated yarns with deposited carbon coatings up to 30% by weight. The moulded composites were prepared such that the volume fraction of the original untreated Thornel 50 was kept constant at 0.5 and the epoxy resin plus the carbon coating combined to give a volume fraction of 0.5 also. The interlaminar shear strength values for this series is plotted in Fig. 6. The shear strength increases from about 35 MN m⁻² (5000 psi) to a maximum of 60 MN m⁻² (9000 psi) at a coating

level of near 25 wt%. The decrease in shear strength at higher coating levels is believed to be in part due to low resin content in these composites. Samples prepared with higher levels of coating but with the resin content held constant at 0.5 volume fraction showed a continued increase in shear strength at coating levels beyond 30 wt%. The coated yarns are far less sensitive to fraying and can be handled manually without noticeable damage (unlike the untreated yarns).

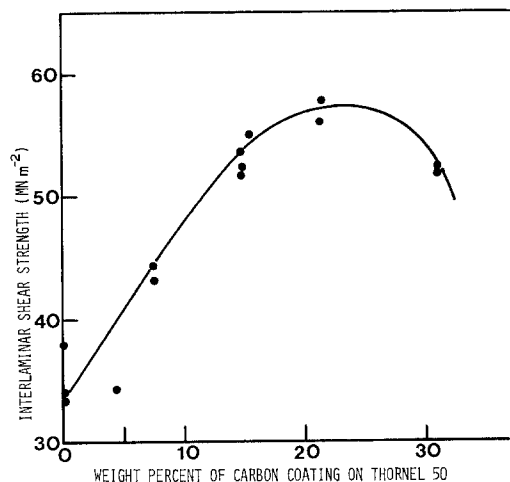


Figure 6 The interlaminar shear strength shows a maximum around 20 to 25% wt % of deposited carbon. These results were obtained in 20 vol % acetylene. Slightly higher shear strengths were obtained with 80 vol % acetylene. No runs were conducted in pure acetylene nor with other types of fibres. The volume fraction of the Thornel 50 yarn was held constant at 0.5.

The flexural strengths also show a corresponding increase reaching 900 MN m⁻² (130000 psi) at a coating level of 25% by weight. These results are plotted in Fig. 7. These improved flexural strengths were attributed to the increased breaking load of the treated Thornel fibres as well as the increased bonding which prevents compressive failure in the upper face as was found in composites prepared from untreated fibres. The average breaking load of six samples of the dry yarn for a 1 in. gauge length increased from 4.45 \pm 0.05 kg for untreated Thornel 50 to 5.50 \pm 0.05 for yarns having a 14.7% carbon coating. The breaking load of dry fibres accurately reflects the tensile strength but the tensile strength calculated from the dry test is normally much lower than tensile strengths determined under humid conditions or with untwisted filaments or tows [15].

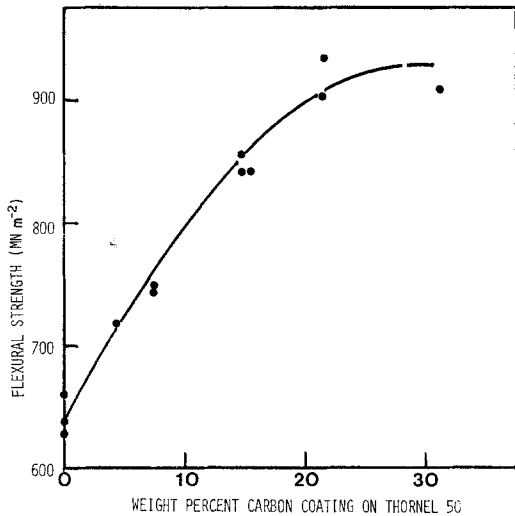


Figure 7 The flexural strength also increased as the weight of the carbon coating increased, reaching a maximum at 30% by weight. The volume fraction of the Thornel 50 yarn (minus the coating) was held constant at 0.5.

Consequently, the conditions of testing should be stated when comparing values. Notice that the composite flexural modulus, as shown in Fig. 8, is relatively unaffected by the surface treatment.

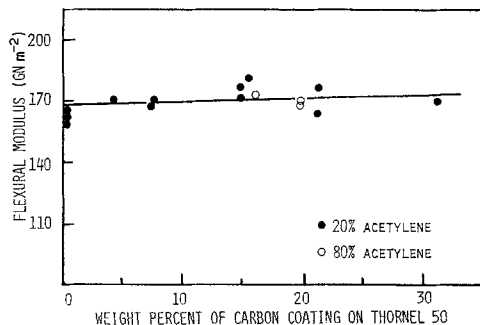


Figure 8 The flexural modulus remained constant and independent of the weight per cent of deposited carbon. The volume fraction of the Thornel 50 yarn (minus the coating) was kept constant at 0.5.

Scanning electron microscope photographs of the surfaces of the fractured test specimens reveal the nature of the failure mode. In general, the flexural specimens tend to fail in tension in the lower half of the cross section, and in compression in the upper half (three point loading). Referring to a tensile fracture surface as shown in Fig. 3 the individual filaments, their pyrolytic carbon sheaths, and the resin matrix are clearly distinguished. If it is assumed that short pull-out

lengths indicate good interfacial bonding, then it would appear that the resin adhesion to the deposited carbon coating is greater than the adhesion between the original filament and the deposited coating. The latter interface may, therefore, limit the interlaminar shear strength improvement. There is also evidence in the literature that the greater adhesion of epoxy resins to carbon fibres with low degrees of order, e.g. VYB untreated carbon fibres [1], is capable of imparting high interlaminar shear strengths of 80 MN m^{-2} (12000 psi). The pull-out lengths in Fig. 3 may be compared with the much longer pull-out lengths for untreated Thornel 50 fibres as shown in Fig. 5. Note also the resin separation at the base of the exposed filaments. It is, therefore, reasonable that attempts to correlate the interfacial shear strength of resin composites

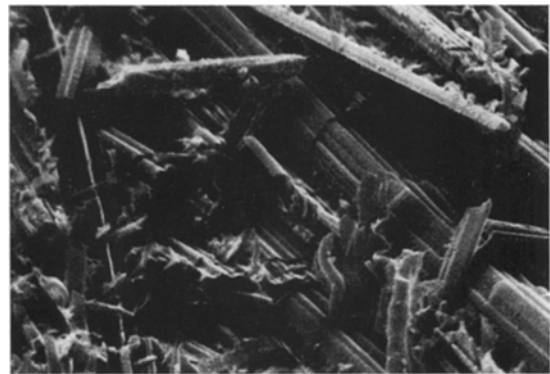


Figure 9 Samples which fractured in shear showed evidence of considerable matrix deformation and stripping away of the carbon coating. Shell Epon 828 cured with nadic methyl anhydride/benzyl dimethylamine was used throughout these experiments ($\times 2700$).

with the wetting characteristics of coated fibres would not be successful since the locus of failure is not at the exposed surface of the treated fibre but at the interface between the fibre and its coating. Further attempts to improve the interlaminar shear strength should, therefore, be directed at the latter interface. A typical photograph of a sheared section for a treated fibre (Fig. 9) exhibits considerable deformation of the epoxy resin matrix which is not apparent in the case of untreated fibres. Large sections of the coating have been stripped from the fibres in some areas.

It is usually found that the interlaminar shear strengths of PAN based fibres are consistently higher than those of rayon based

fibres. Composites prepared from surface oxidized, high modulus (400 GN m^{-2}) PAN based fibres exhibit shear strengths up to 90 MN m^{-2} (13000 psi) [1, 7, 17, 18].

The circular cross-section of PAN based filaments may be partly responsible for the superior shear strengths attainable with these fibres. Such smooth exteriors would lead to a more uniform stress distribution than in the case of rayon based filaments. Further differences may be attributable to variations in twist between relatively parallel filaments in tows and helically wound and twisted yarns, the latter being characteristic of the Thornel 50 yarns used in this study. Such variations owing to twist have been discussed by Claus [16].

In general, the concentration of the acetylene in the reaction zone did not have a pronounced effect on the resultant physical properties. Rates of deposition were faster at the higher concentrations and gave slightly higher interlaminar shear strengths. However, fouling of the reaction chamber with tarry deposits accompanied the higher (80% by volume) acetylene concentrations.

A few samples were tested for their Izod Impact Strength (ASTM D747-63) using a modified notched sample, in which the depth of the specimen was only 0.394 in. instead of the ASTM recommended depth of 0.5 in. Consequently, the values reported here should not be compared with ASTM data. The results are summarized in Fig. 10. There is a decrease in the notched Izod from an average value of $7.28 \text{ ft lb in.}^{-1}$ of notch for the untreated fibres to $4.15 \text{ ft lb in.}^{-1}$ at a coating level of 22 to 23% by weight. This is consistent with an increased tendency towards shorter pull-out lengths and brittle fracture.

Morley [19, 20] has previously proposed a method for improving the fracture energy of a fibrous composite involving a well bonded outer sheath with an inner core to provide strength and stiffness. The assumption here is that the long pull-out length of the inner core would provide an energy absorbing failure mode. The results of this study show a slight improvement in the Izod values compared with surface oxidized fibres [21] lending some support for this theory. However, it appears more practical to employ a ductile matrix such as polycarbonate resin or polypropylene if additional toughness is required [22].

Similar experiments were conducted in atmos-

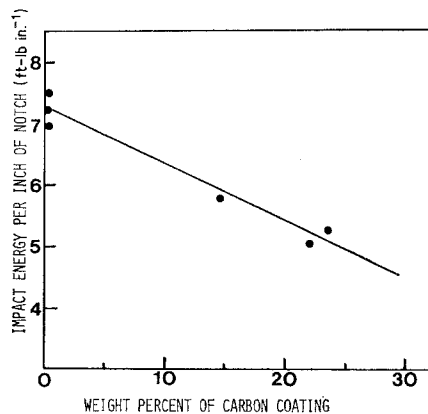


Figure 10 As is commonly observed, the fracture energy decreases as the interlaminar shear strength increases. The loss of impact strength in this case is not as pronounced as with other methods of treatment. The volume fraction of the Thornel 50 yarn (minus the coating) was 0.5.

pheres of carbon monoxide and hydrogen catalysed with iron pentacarbonyl. Since these experiments did not improve the interlaminar shear strength, they are not included in this discussion. However, a summary of the results may be found in the thesis of Pinchin [23].

The discovery of the laser has enabled Raman spectroscopy to become a valuable technique for the characterization of carbon and graphite materials. The work of Tuinstra and Koenig [24] and Larsen *et al* [3] are particularly noteworthy. These studies confirm that the crystallite size in untreated graphite fibres correlates rather well with the interlaminar shear strength but fails to predict the outcome when surface coatings are involved. The excellent results achieved when polymeric coatings were carbonized on the fibre surface may be attributed therefore to better adhesion of the resultant sheath to the fibre itself rather than to the matrix [26].

4. Conclusions

The post-treatment of graphite fibre yarns by the pyrolysis of acetylene onto the surfaces of the individual filaments has been shown to substantially increase the interlaminar shear strength and the flexural strength of epoxy resin composites. The treated yarns are less susceptible to damage when coated with pyrolytic carbon. Pyrolytic graphite is more resistant to oxidation and chemical attack and will retain its properties at temperatures beyond those of other

forms of graphite [25]. The total weight of the fibre was substantially increased by this treatment (up to 30%) and resin wetout was improved.

The locus of failure probably occurs first at the interface between the pyrolytic coating and the graphite fibre instead of at the resin interface. Adhesion of the resin to the pyrolytic graphite coating appears to be excellent based on observations of the short pull-out lengths of the outer sheaths. Consequently, investigations aimed at relating the surface characteristics of such treated fibres to the mechanical properties of the composite might be unrewarding for this reason.

Acknowledgements

The authors are indebted to R. E. Steele for his many helpful suggestions and to Professor Ursula Franklin for her assistance with the interpretation of the X-ray diffraction data. This research was supported by the Defense Research Board of Canada under Grant No. 7501-08.

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Received 21 May and accepted 1 August 1973.