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The fabrication of ceramic-coated carbon fibre duplex elements

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Attempts have been made to fabricate a bicomponent composite reinforcing element comprised of a central core of carbon fibre filaments surrounded by a cylindrical silicon carbide sheath. Such fibres are particularly attractive for composite reinforcement since they are potentially capable of exhibiting "duplex" type behaviour, thereby providing a possible means of minimizing anisotropy effects and increasing composite fracture toughness and ductility. Furthermore these elements should provide additional advantages such as eventually enabling multi-filament tows of high strength, low modulus carbon fibre to be formed into large compound fibres which combine high specific strength with a significantly improved overall Young's modulus arising from the stiffness of the ceramic sheath, which should also exhibit a high resistance to chemical attack. Methods of consolidating the multi-filament tow prior to coating have been investigated and suitable preliminary treatments evolved; tows have been coated with silicon carbide using a conventional vapour phase deposition technique to form elements basically conforming to "duplex" requirements. Initial tensile tests upon these elements are reasonably encouraging and reveal none of the side effects encountered previously with boron coatings; it is anticpated that much stronger silicon carbide tubes may be fabricated eventually by this technique using more closely controlled reaction conditions.

1. Introduction

1.1. Limitations of conventional composite materials

Composite materials ranging from carbon fibre reinforced resins to steel rods embedded in concrete suffer from two inherent disadvantages, namely their anisotropy and their failure to engender favourable "metallic" properties such as ductility, work hardening and high fracture toughness. In any orthodox composite material essentially consisting of cylindrical rods reinforcing a matrix the problem of anisotropy is basically attributable to the difference in mechanical characteristics of fibres and matrix but the position is aggravated still further by the conflicting requirements arising at the fibre matrix interface.

Thus while the high longitudinal shear strength and transverse tensile strength necessary to reduce anisotropy can only be achieved by means of a strong fibre matrix bond [1], the attainment of high fracture toughness [2] and good crack stopping ability [3] is dependent conversely upon this same interfacial bond being relatively weak. Fibre matrix bond strength must, therefore, be optimized to meet these conflicting demands and an orthodox composite must inevitably be something of a compromise which fails to realize fully the potential advantages of the constituent materials. The situation is summarized in Fig. 1.

The further problem of low composite extension to failure in the fibre direction arises from the dependence of this parameter on the failing strain of the fibres themselves and is, therefore, of particular relevance in the case of carbon fibre and other similar ceramic reinforcing fibres which exhibit a relatively low failing strain (normally of the order of 1 %); thus the attractive properties of high specific strength and specific stiffness offered by carbon-fibre reinforcement, for example, are nullified to some extent within a conventional composite structure.

1.2. Potential advantages of a duplex reinforcing element

In order to avoid such limitations it is necessary to provide an additional degree of freedom by

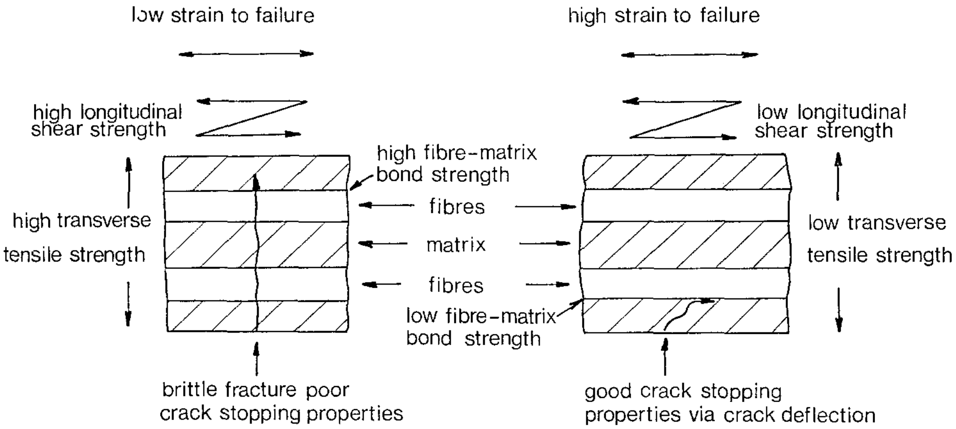


Figure 1 Influence of bond strength on composite properties.

modifying the geometrical form of the composite; further advantages can be incorporated provided the characteristics of the fibre-matrix interface are carefully controlled.

The first of these objectives can be achieved in principle by the use of a composite system containing two types of reinforcing element within a common matrix, thus providing a double interface [4-7]. It is convenient to arrange these concentrically to form a duplex reinforcing element comprised of a cylindrical outer sheath surrounding an inner core element (Fig. 2a). It is then the strongly bonded interface between the outer element and matrix which should be primarily active in resisting transverse tensile and longitudinal shear stresses whilst the much more weakly bonded internal core-sheath interface should improve fracture toughness and reduce sensitivity to transverse crack propagation. Initially it is essential that the inner core element should be adequately bonded to the outer tube element in order that both components of the compound fibre can effectively combine to act as a homogeneous reinforcing fibre in resisting longitudinally applied stresses up to a comparatively high stress level. In the case of continuous fibres this may be achieved with relatively small values of core-sheath interfacial shear strength. Provided, therefore, that the element is much longer than the stress transfer length, then the initial stress-strain curve of the composite is determined by the elastic moduli of the two components factored according to the rule of mixtures. Following failure of the outer sheath the integrity of the composite structure is maintained by the bridging core fibre up to relatively large extensions and the composite exhibits pseudo-ductility.

The nature of the core-sheath interface also requires careful consideration. In a conventional situation the shear strength of the fibre matrix interface is essentially constant and to a first approximation the tensile stress carried by the fibre can be regarded as increasing uniformly from the free end at a rate governed by this bond strength. Hence, the tensile stress σ_c carried by a cylindrical reinforcing fibre at any point along its length is given by

$$\sigma_l = \frac{2\tau l}{r} \tag{1}$$

where r is the fibre radius, l the distance from the free end and τ the effective shear strength of the interface; failure will occur if σ_l exceeds the fibre U.T.S. (σ_{ult}). Rearranging gives:

$$l = \frac{\sigma_l r}{2\tau}\,. \tag{2}$$

It is obvious from Equation 2 that the ratio r/τ controls the length of fibre over which stress can be transferred during tensile failure and hence the volume of composite involved in energy absorbing processes. In general, therefore, the composite work of fracture can be increased by increasing fibre diameter and decreasing the fibre matrix interfacial shear strength [2, 8].

Where high strength brittle reinforcing materials are concerned the final stages of composite failure are governed by the amount of energy absorbed irreversibly during pull out of broken fibres from the matrix. For an interface of constant shear strength, this pull out occurs at a constantly diminishing stress level so that the

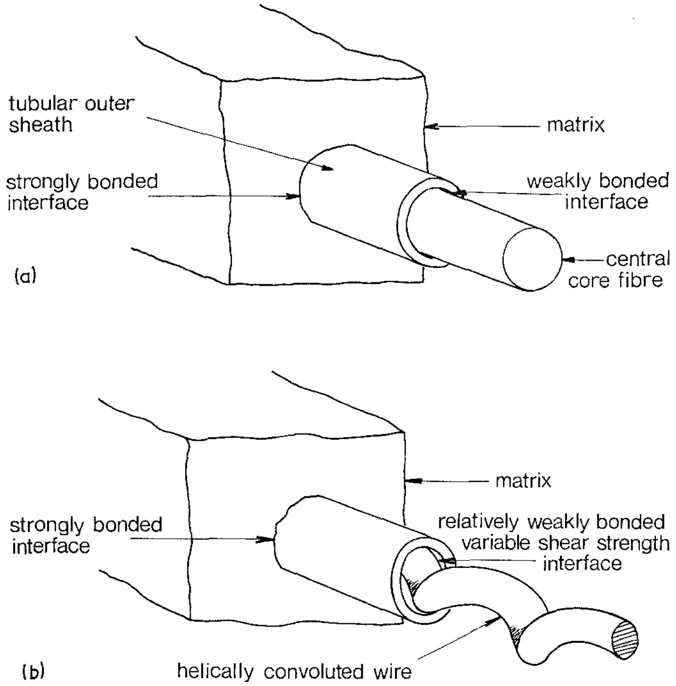


Figure 2 (a) Basic duplex fibre structure. (b) Steel wire–hypodermic tube duplex element.

fracture process ultimately becomes localized and exhibits a "work-softening" characteristic [7]. Ideally, for maximum energy absorption, the shear strength of the interface between the load bearing core and the failed sheath of a two component duplex element should not, therefore, be constant, but should diminish with increasing core fibre tensile stress. In such a system the maximum tensile stress which can be developed in the central fibre by stress transfer across the core-tube interface is limited to the stress at which the local shear strength of the interface falls to zero. If this stress ($\sigma_{\max}$) is arranged to be slightly less than the ultimate strength of the unflawed core fibre (σ_{ult}) then it is impossible to break this fibre whatever its length; where such fibres bridge a crack, fibre pull-out takes place when the fibre stress rises to $\sigma_{\max}$ and the core fibre will slide through the sheath against residual frictional forces generated at the interface. If the interfacial shear strength, τ, is a linear function of the fibre tensile stress σ such that $\tau = \tau_0$ when $\sigma = 0$ then:

$$\tau = \tau_0 - Q\sigma \tag{3}$$

where Q is a constant, and since $\tau = 0$ when $\sigma = \sigma_{\max}$:

$$Q = \frac{\tau_0}{\sigma_{\max}} \cdot \tag{4}$$

Hence it is readily shown that the stress distribution along the core fibre during pull-out takes the simple exponential form:

$$\sigma_l = \sigma_{\max}\,(1 - \mathrm{e}^{-2Ql/r}) \tag{5}$$

where σ_l is the stress on the fibre at a distance l from the free end. The fibre tensile stress therefore approaches $\sigma_{\max}$ asymptotically and for an inner fibre of high aspect ratio the work of fracture will be maximized since the fibre pull-out can occur at a high and sensibly constant stress level approaching $\sigma_{\max}$ until almost the entire element has been withdrawn. It is possible for composites reinforced with this type of duplex element to exhibit behaviour similar to that of work hardening in metals [9] during the initial elastic extension of the core prior to the onset of pull-out, and therefore a stress diffusing mechanism is initiated within the composite.

This type of tensile deformation mechanism thus produces macroscopic effects in fibrous composites broadly analogous to the plastic deformation shown by metals. The effectiveness of this type of variable shear strength interface has been demonstrated successfully both in composite structures [10, 11] and in linear energy absorbing devices [12] by means of simple reinforcing elements consisting of crimped or helically wound high strength steel wires within hypodermic steel tubes (Fig. 2b). The application of a tensile strain to such a core element causes it to decrease in diameter and contract away from the surrounding tube, thus reducing frictional interaction and hence the interfacial shear strength. Composite systems based on these materials thus offer the possibility of absorbing much larger amounts of mechanical energy under tensile deformation than the best available metal alloys whilst operating at a very high stress level.

It is theoretically possible to achieve even greater values of specific strength and toughness by employing high strength ceramic materials as mentioned previously. This possibly attractive long term application of the duplex fibre principle is considered in the present paper which is concerned with an assessment of the feasibility of fabricating duplex elements consisting of a central carbon fibre core within a suitable strong ceramic sheath. Provided the nature of the bonding of the core-sheath interface can be defined fairly closely then it becomes possible to consider incorporating similar advantages to those of the variable shear strength frictional interface in the all metal system outlined previously; mechanistically these latter effects might be produced by utilizing either the difference in Poisson's ratio between the carbon fibre core and ceramic tube or, failing this, by the geometrical effects arising from the inclusion of a slight twist in the fibrous core.

1.3. Additional advantages of bicomponent ceramic fibres

This latter type of two component fibre offers a number of advantages in addition to those associated with the duplex structure. These may be summarized as follows.

(a) This system affords a means of producing strong, stiff, lightweight ceramic fibres of controlled size. The direct dependence of composite fracture toughness on fibre diameter [2] has been mentioned previously and the production of large "compound" fibres formed by the aggregation of bundles of much smaller individual fibres is, therefore, of potential value even if they behave essentially as a solid homogeneous cylindrical element without any duplex characteristics as such. The dimensions of these large fibres can be controlled conveniently by a suitable choice of the number of carbon fibres within the core elements (nominally one thousand fibres in the work described here). Kelly has summarized the relative advantages and disadvantages of composite reinforcing fibres of various diameters [13] and has proposed the existence of an optimum range of fibre diameter.

(b) Ceramic-coated fibres of this type offer certain advantages over conventional fibres for potential use with a metal matrix when high temperatures are employed either in fabrication or use. The ceramic sheath which may itself possess highly attractive mechanical properties is obviously also more highly resistant to oxidation or nitridation [14] at elevated temperatures and, therefore, affords some degree of protection for the central fibre bundle whilst itself constituting only a relatively small volume fraction of the compound fibre. This may be directly contrasted with the case of individually coated fibres where the thickness of the ceramic coating must be minimal to maintain as high as possible a volume fraction of carbon fibre in the compound fibre.

(c) Manufacturing costs of these fibres may well be less than those for more conventional boron and silicon carbide fibres or high elastic modulus carbon fibres. For instance, by combining a stiff ceramic material (e.g. silicon carbide of elastic modulus approximately 410 GN m^{-2}) with type II carbon fibres of comparatively low Young's modulus ($\sim$ 280 GN m^{-2}), pyrolisation temperature 1500°C), it should prove possible to produce a large compound fibre of relatively high overall modulus, thus avoiding the necessity of employing the very high and costly graphitizing temperatures normally utilized in the manufacture of homogeneous high modulus carbon fibres (i.e. those normally designated as type I) [15]. In addition the geometry of the present system lends itself far more readily and, therefore, more economically, to the vapour phase deposition situation than does that of the thin tungsten wire substrate method of producing conventional boron or silicon carbide filaments by the "single end" manufacturing process [16, 17].

2. Experimental

2.1. Preparation of carbon fibre filaments

Attempts to produce suitable carbon fibre core elements from pre-impregnated carbon fibre sheet ("Hyfil pre-preg"; Rolls Royce Ltd) proved largely unsuccessful and it was decided, therefore, to concentrate on using one thousand filament type II carbon fibre tow which was readily available and was also of suitable initial dimensions to produce carbon substrate elements of the required nominal diameter (~ 0.5 mm).

In order that filaments produced by coating carbon fibre tows with a suitable ceramic sheath should exhibit duplex properties, it is important to control closely the nature of the inner core carbon element. Ideally, this should be of regular cross-section with a smooth outer surface to facilitate the sliding of the core element through the outer sheath after debonding occurs without the complications caused by uneven mechanical keying etc. It is also desirable to have a high packing density of individual fibres within the core to increase the volume fraction of fibre in the end product and it is, of course, essential that the fibre bundle be chemically stable under the deposition conditions employed.

Elevated temperatures in excess of 1000° C are normally necessary for the efficient pyrolysis of compounds such as those employed as initial reactants in the present work and it is important, therefore, that any material incorporated into the tow to act as a bonding agent between the individual fibres should be stable and inert at such temperatures. Carbon itself obviously fulfils these conditions and may be readily produced *in situ* by the pyrolysis of an organic polymer.

A fairly simple method of impregnating a fibre bundle with a reasonably uniform layer of polymeric material was developed. This consisted of threading the dry one thousand filament carbon fibre tow through a small glass capillary funnel with a suitable constriction ($\leqslant$ 0.5 mm). This funnel was then filled with liquid resin and lengths of tow pulled through at a constant, slow rate which ensured that any loose fibres were re-aligned and drawn together into a compact form under the influence of surface tension effects.

Since the role of the funnel in the process was to remove any excess resin from the tow and to flatten down or tear out any badly misaligned fibres, a gradual build up of broken fibres occurred above the mouth of the funnel and this eventually blocked up the neck of the funnel and prevented further tow from being pulled through without breaking. However, it was frequently possible to draw through several metres of tow before this took place. Suitable lengths of impregnated material were then cut off and cured overnight in an oven at an appropriate temperature (~ 100° C).

Although the consolidated tows produced in this manner varied somewhat in quality (e.g. the diameter often fluctuated noticeably over relatively short lengths, probably because of slight differences in individual fibre length and local misalignment and twisting of the tow during pull through), this method did provide reasonably satisfactory lengths of impregnated tow. These were subsequently divided up into lengths of approximately 150 mm each and either prepyrolysed at 800 to 900° C in a tube furnace under an argon atmosphere or used directly as filaments in the deposition chamber, pyrolysis in this latter instance being carried out *in situ* immediately prior to deposition of the silicon carbide. In either instance all volatile constituents of the resin were driven off during pyrolysis, the residue being almost pure carbon.

In order to select a convenient resin for the purpose in hand a variety of tows was prepared using both epoxy resins (e.g. Araldite MY750 plus 951 hardener) and phenolic resins (Bakelite resin and varnish); in addition some tows were also coated with polyacrylonitrile (P.A.N.) by treatment with various solutions of P.A.N. in propylene carbonate. The effects of the various pretreatments are discussed later.

2.2. Preparation of ceramic coatings

2.2.1. Method

Methods of preparing boron-coated metal filaments (e.g. tungsten, molybdenum) have become fairly well established in recent years [16, 18, 19] and it therefore seemed logical to employ boron as the coating material in the initial attempts to produce a carbon fibre duplex element. A simple pyrolytic technique (i.e. the decomposition on a hot substrate of material present in the vapour phase and the subsequent deposition of solid products to form the desired coating) appeared most attractive since the relative ease of purification of both reactants and deposition substrate enabled a high purity coating to be produced.

An apparatus which was essentially similar to that described later for the silicon carbide work was constructed and employed to produce samples of boron-coated carbon fibre filaments by the pyrolytic decomposition of boron trichloride over an electrically heated carbon fibre tow prepared as previously described.

Subsequent tensile testing of these coated tows revealed that some type of degradation of the carbon fibres had occurred and this resulted in a drastic reduction in the mechanical strength of the composite element. The deleterious effect of these coatings would appear to arise from the deposition conditions employed rather than from the existence of any basic incompatibility between boron and carbon; further consideration is given to both this and other aspects of the boron work in Section 3.2.

In view of these difficulties silicon carbide was adopted as the coating material. A vapour phase deposition process was again employed since, in addition to the advantages outlined earlier, such a technique is particularly attractive in the case of materials such as silicon carbide which exhibit high temperature stability and tend to dissociate at normal pressures before melting occurs, thus virtually precluding the use of alternative methods of coating such as flame or plasma spraying of molten reactants or evaporation onto a cold substrate. The basic method has been employed previously with varying degrees of success to produce coatings of silicon carbide etc., on rods and sheets of both metals (e.g. tungsten and molybdenum) and ordinary graphite [20-25].

2.2.2. Silicon carbide deposition apparatus

The apparatus employed is shown in Fig. 3 and is essentially based on a modified version of that used by Cartwright and Popper [22]. Except where stated, it was constructed from Pyrex glass and consisted of four main sections; the gas purification and storage system, the reactant evaporator unit, the reaction vessel and the exhaust system. Leakproof "O" ring type high vacuum stopcocks were employed throughout the glass system except where indicated in Fig. 3.

The flow rate of the carrier gas (argon or hydrogen) was controlled by means of a needle valve and measured using G.A.P. flow meters. The gas was initially purified by passage through a de-oxygenating unit and calcium chloride trap before entering an expansion bulb which eliminated any small pressure surges; it then passed into the main system comprised of the evaporator unit and actual reaction chamber.

The evaporator unit contained the methyltrichlorosilane (M.T.S.) used as a source of silicon carbide in this work. On bubbling the carrier gas through the reservoir containing this liquid a stream of gas saturated with methyltrichlorosilane at the temperature of the thermostatted condenser system was obtained. Any excess droplets of M.T.S. were removed from the vapour stream at high flow rates by the upper condenser. Although originally colourless

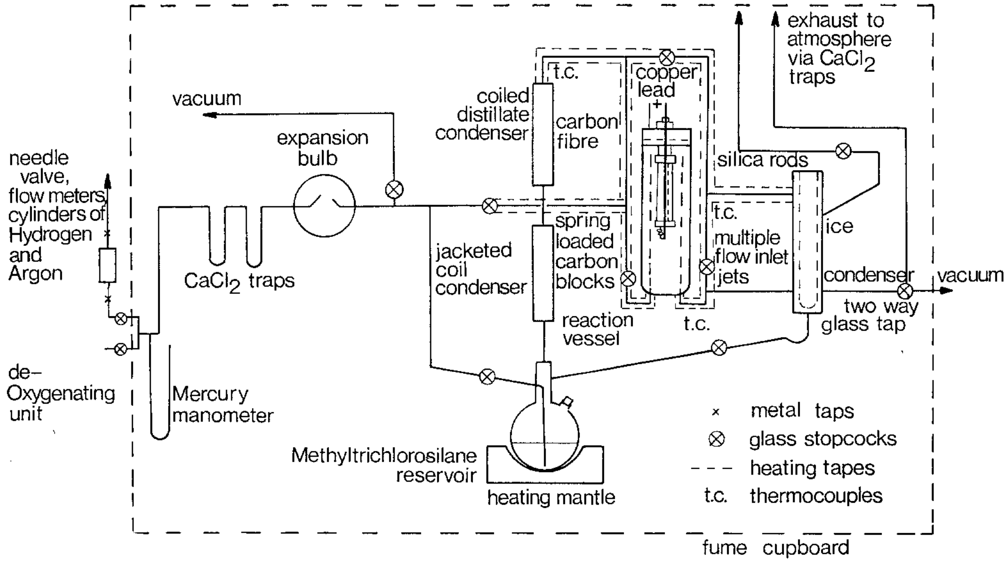


Figure 3 Silicon carbide deposition apparatus.

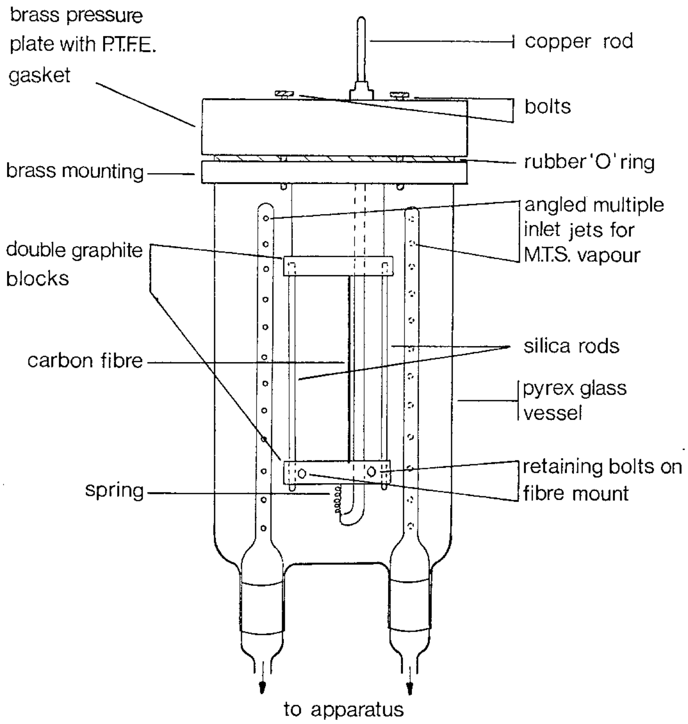


Figure 4 Reaction chamber.

the M.T.S. was very pale yellow in colour after use probably because of the presence of some hydrochloric acid produced as a by-product of the decomposition.

The M.T.S. reservoir was kept simmering when necessary by means of a heating mantle and unwanted condensation in the lines leading to the reaction vessel was prevented by warming these slightly above the condenser temperature by means of heating tapes controlled by a variac. The temperature at various parts of the system was monitored by thermocouples attached to a thermocouple potentiometer control unit.

The actual reaction chamber (Fig. 4) consisted of a cylindrical Pyrex glass vessel about 26 cm long by 8 cm in diameter fitted with multiple flow inlet jets through which reactant vapours could be both introduced to and removed from the system. In order to allow for any expansion or contraction which occurred on heating, the carbon filament prepared as previously described was mounted between spring loaded graphite blocks which were in turn supported by silica rods along which they could slide freely. By suitable adjustment of the retaining spring attached to one of the graphite blocks, it could be arranged that any slack produced in the fibre by thermal expansion etc., was compensated for by the excess tension in the spring such that the filament was kept permanently under a slight tension. The whole of this assembly complete with suitable electrical contacts was attached to a brass pressure plate which served to seal the reaction vessel when bolted to it by means of a specially devised arrangement incorporating both rubber "O" ring and gasket type seals. With this type of mounting the tow could be maintained at reasonably constant high temperatures for considerable lengths of time.

A voltage stabilizer was used to resistance heat the specimen thus avoiding mains voltage fluctuations which might have affected the temperature stability of the filament. Temperature measurements were made by means of a disappearing filament optical pyrometer. When using this instrument due allowance (approximately 10 to 20° C) was made for the absorption of the Pyrex glass walls of the apparatus; the image of the heated one thousand fibre tow appeared about the same size as the pyrometer filament when correctly focused in the instrument and this enabled a fair comparison of brightness to be made. Attempts were also made to improve the accuracy of the pyrometry by correcting readings by use of the appropriate spectral emissivity factors (i.e. temperature correction factors formulated to allow for the radiation emitter not being a perfect black body, these being 0.75 for silicon carbide [26] and 0.80 to 0.93, depending on temperature for carbon [27]).

Despite these precautions the accuracy of the temperature measurements made with the optical pyrometer was open to considerable doubt and must have involved an error of several tens of degrees; the position was further complicated in some of the experiments by the formation of hydrogen chloride fumes together with an obscuring film of silica on the reaction vessel walls during the reaction and this made temperature measurements somewhat difficult during the final stages of these particular experiments. An attempt was made to establish the degree of reliability of the instrument by cross-checking with a second, independent pyrometer in conjunction with a temperature calibrated nickel wire; this served to illustrate that the method was only reliable to within ± 30°C.

The effluent from the reaction vessel containing excess reactants and unwanted reaction products was exhausted to the atmosphere, any unreacted M.T.S. being removed when desirable (e.g. during preliminary flushing of the apparatus) for subsequent re-circulation by means of a cold-finger condenser containing ice. Calcium chloride traps were incorporated in the outlet exhaust pipes to prevent diffusion of atmospheric moisture into the system. The M.T.S. reservoir and condenser system was normally isolated from the rest of the apparatus and kept under an argon atmosphere apart from when actually in use during the course of an experiment; the complete apparatus was contained in a fume cupboard because of the unpleasant and corrosive nature of the materials employed.

2.2.3. *Experimental technique*

Runs were carried out using the following procedure. The apparatus (with the exception of the M.T.S. reservoir and condenser system) was initially evacuated over a period of several hours to an ultimate pressure of approximately 0.05 Torr using a rotary pump attached to either of the inlets indicated in Fig. 3.

During the latter part of the evacuation the carbon filament was usually heated to the particular temperature employed in the subsequent deposition experiment and then allowed to degas for about 30 min. The apparatus and gas supply lines were then thoroughly flushed with argon; it was essential to carry out this operation extremely rigorously before each experiment in order to ensure that any isolated airpockets were completely removed from the apparatus. It was necessary to take this precaution since M.T.S. reacted with any residual moisture in the system to produce silica and various other decomposition products which tended to interfere with the smooth operation of taps etc. This procedure also served to minimize any explosion hazard when employing hydrogen as the carrier gas in subsequent experiments.

After these preliminary operations the flow rate of the carrier gas (argon or hydrogen) was adjusted by means of the needle valve to some suitable value (usually approximately 500 $\text{cm}^3\ \text{min}^{-1}$) to give an excess pressure of several Torr (normally 2 to 10 Torr measured by means of a simple mercury manometer) in the apparatus. The gas was then passed through the main system (i.e. by-passing the M.T.S. reservoir) for several minutes during which time the carbon filament was resistance heated to the required reaction temperature and again allowed to outgas for some 15 min or so; the various taps were adjusted to give optimum conditions and the flow was diverted through the evaporator unit so that this was flushed out immediately prior to commencing the experiment; the reaction vessel itself was isolated from the rest of the system during the short period of flushing the reservoir.

Finally, the stream of M.T.S. vapour was directed into the reaction chamber containing the heated filament and the temperature of the reservoir was adjusted by means of the heating mantle to give a suitable overall vapour flux (i.e. velocity × concentration) of M.T.S. The deposition was allowed to proceed until a satisfactory thickness of coating had been formed on the carbon filament.

The coated filament was slowly cooled to room temperature over a period of some minutes and the apparatus thoroughly reflushed with the carrier gas after isolating the M.T.S. reservoir. Finally, the sample was removed from the apparatus after evacuating the system for about 30 min.

3. Results and discussion

3.1. The effects of tow pre-treatment

Carbonized filaments produced by coating fibre tows with either epoxy or phenolic resins showed little significant variation as regards their behaviour during subsequent silicon carbide deposition. There seemed to be some reason to favour the phenolic precursor as filaments treated with this resin appeared less prone to premature burning out during the deposition process. The phenolic treated specimens were reasonably smooth and of fairly uniform surface appearance. The epoxy impregnated filaments were similar in appearance to the phenolic samples, but were somewhat stiffer. The P.A.N. coated specimens were less well consolidated and there seemed to have been little penetration of resin into the bulk tow.

Pyrolysis of the tows in the tube furnace appeared to have no effect on the mechanical properties of the carbon fibre bundle. The pyrolysed P.A.N. samples were relatively loosely packed with very little filling in of surface irregularities. Pyrolysis of the phenolic coated tows produced a much stiffer consolidated fibre bundle with a smoother overall surface appearance. Although the volume reduction which occurred during pyrolysis of phenolic resins was relatively small it was sufficient to give rise to numerous fine surface shrinkage cracks. These were eliminated to some extent by repeating the impregnation and pyrolysis treatment. Pyrolysis of the epoxy resin samples produced an effect somewhat intermediate between that of the P.A.N. and phenolic resins.

Preliminary attempts to heat electrically the P.A.N.-coated samples in the reaction chamber proved largely unsuccessful. In almost every case the tow either hotspotted or splayed out and broke when heated under slight tension in the deposition apparatus. In comparison the epoxy and phenolic coated samples proved far more reliable and the P.A.N. method of pretreatment was therefore abandoned.

The normal observation in the case of the epoxy or phenolic resin treated samples was that the pre-pyrolysed tows appeared to exhibit a much lower tendency to form hot spots and consequently burn out prematurely than did those which had been outgassed under vacuum and subsequently pyrolysed in a stream of argon in the apparatus immediately prior to the commencement of the deposition process. The explanation for this is most probably to be found in the different modes of heating used in the respective carbonization processes. In the pre-pyrolysation process the fibre tow was gradually carbonized by means of an external heating source (i.e. the tube furnace) and was then allowed to cool slowly. In contrast, when the tow was pyrolysed *in situ* by electrical resistance heating it was subjected to a relatively sudden burst of heat from an "internal" source. This resulted in a rapid evolution of gaseous carbonization products from the interior of the tow which could have led to a splaying out of the fibres with some consequent disruption of their initial relatively ordered and compact state. In addition fibres pyrolysed *in situ* were continuously constrained during carbonization by virtue of the method of mounting employed and this also may have affected the quality of the filaments produced in this manner.

The breaking loads of the pre-treated fibres were determined by means of an Instron Tensile Test machine. The fibres were mounted on standard test cards which provided support whilst fixing into the grips; these cards were cut immediately prior to testing to leave a nominal free fibre gauge length of approximately 23 mm. Typical breaking loads for epoxy resin coated filaments produced from similar initial fibre tows are shown in Table I. Carbonization was carried out in the tube furnace where appropriate.

TABLE I

Filament pretreatment	Diameter of capillary funnel (mm)	Mean breaking load (N)
Uncarbonized epoxy	0.4	103
Carbonized epoxy	0.4	79
Uncarbonized epoxy	0.5	120
Carbonized epoxy	0.5	61
Uncarbonized double coated epoxy	0.4	119
Carbonized double coated epoxy	0.4	91
Untreated tow	—	60

It is interesting to compare the breaking load of the completely impregnated specimens with that of filaments prepared by simply "painting" resin onto the tow. The breaking load of these latter samples in the unpyrolysed condition is of the order of 70 N on average. Thus, thorough impregnation of the tow leads to a higher mean breaking load as might be anticipated, since essentially, in this condition, the filament is equivalent to a miniature composite with the cured resin matrix acting as a stress transfer agent in the usual manner, thus reducing the effects of flaws in the individual fibres.

Double coating of the tow appeared to lead to some improvement in the tensile properties of the filament. Although the same effect was achieved by depositing a thicker layer of resin on the tow using a wider bore capillary funnel, this latter method also produced a less compact filament which led to some difficulties, as described later, when these were used in deposition experiments. The double coating technique also reduced filament surface roughness to a considerable extent and was additionally advantageous when treating a particularly "hairy" tow since most of the loose fibres which remained following the initial resin impregnation were burnt off during carbonization and any remaining gross surface imperfections were removed to a large extent during the second treatment.

Thus, in addition to consolidating the loose tow into a reasonably uniform electrically conducting filament, the production of a thin uniform anisotropic surface layer of carbon on the fibre bundle tends to minimize the incidence of surface abnormalities which might subsequently serve to initiate stress concentrating flaws in the silicon carbide layer deposited over the carbon fibres, thus reducing the mechanical strength of outer sheath. It is likely that this carbon layer will also serve as a lubricating agent to promote sliding of the core element within the sheath during fibre pull-out, thus providing a possible method for varying the interfacial bonding. Furthermore, by effectively sealing the surface of the filament the carbon would be expected to reduce the possibility of penetration of silicon carbide into the bulk of the tow during the deposition process.

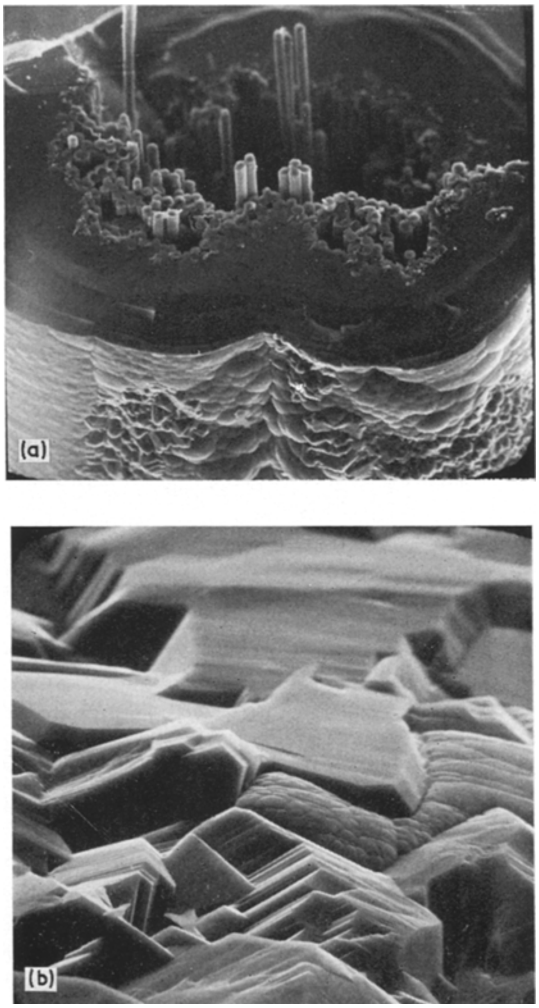


Figure 5 (a) Boron-coated fibres showing the typical "corn-cob" appearance of the vapour deposited layer and a glassy fracture surface (× 170). (b) Detailed appearance of boron surface showing both crystalline and amorphous regions (× 570).

3.2. Boron-coated carbon fibres

3.2.1. Deposition experiments

During the initial stages of the present work numerous attempts were made to deposit boron on carbon fibre filaments by the pyrolytic decomposition of boron trichloride in a hydrogen atmosphere. These usually resulted in the formation of a solid boron layer with the familiar "corn cob" appearance (Fig. 5a and b) frequently associated with vapour deposited materials; in most cases this layer exhibited a glassy, amorphous fracture surface when broken during tensile testing (Figs. 5a and 7b). Unfortunately, the boron appeared to possess negligible strength in this particular form and in addition the process invariably reduced the strength of the carbon fibres to a minimal value. Often the treated filament was so weak as to make it impossible to even mount on specimen cards for tensile testing. No significant improvement in the measured strength of either the deposited boron or the coated carbon fibre substrate was achieved by varying the deposition conditions (i.e. temperature, flow rate, vapour pressure, etc).

3.2.2. Compatibility experiments

Attempts were made to isolate the cause of this degradation of fibre strength by simple compatibility tests. These were carried out by heating short lengths of pre-pyrolysed tow to about 1200°C in a dry hydrogen atmosphere. The fibres were then placed in a small alumina boat, covered with pure boron powder and heated to various temperatures under an argon atmosphere in an alumina tube.

The specimens were allowed to cool to room temperature and then mounted and tested under tension in the normal manner. The results thus obtained were compared with those of identical tensile tests carried out on analogous "blank" specimens which had been cut from the same length of tow but not heated in contact with boron. It was impossible to detect any variation in strength between the different specimens and it was therefore concluded that the properties of the carbon fibres were unaffected by heating in boron at 1200°C. This view is substantiated by the work of Allen *et al.* [28] who observed that boron doping had no effect on the tensile strength of P.A.N.-based carbon fibres.

It thus appears that the degradation of the fibre substrate which occurred during the boron deposition in the present work must have been attributable to the presence of some type of impurity. The boron trichloride employed was nominally 99% pure but trace analysis revealed the presence of iron, silicon and chlorine in small but detectable quantities. Therefore, it seems highly likely that these impurities could have combined to form, for instance, ferric chloride, which is well known for its ability to combine with graphite to produce intercalatial compounds; under certain conditions these lamellar compounds undergo swelling thus causing a disruption of the ordered layer structure of the carbon and presumably leading to a weakening of the carbon fibres themselves [29].

3.3. Silicon carbide-coated carbon fibres

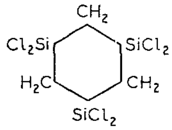
3.3.1. Decomposition of methyltrichlorosilane

Although several combinations of vapour phase reactants have been used in silicon carbide deposition work (see, for example, [22, 24]), methyltrichlorosilane (CH_3SiCl_3) was employed exclusively in this instance because of its suitable boiling point (65.7°C) [30] and also, originally, because of its 1:1 ratio of silicon to carbon content; less importance is now attached to this latter property [22].

The relevant reaction mechanism has been discussed elsewhere [22, 24, 31] and further detailed consideration would seem unnecessary here; it will suffice for present purposes to represent the basic decomposition of M.T.S. at elevated temperatures as:

$$CH_3SiCl_3 \xrightarrow[>1000^\circ C]{H_2} SiC + 3HCl\,.$$

It is also perhaps worth noting that the decomposition is thought to proceed [31] via ring compounds of the type:



This sort of mechanism would help to explain the botryoidal type of surface appearance often observed in silicon carbide deposits (although the compound itself is isotropic). Such a structure was sometimes observed in this work using a scanning electron microscope (Stereoscan Mk II, Cambridge Scientific Instruments). A typical example is shown in Fig. 6. It has also been suggested [22] that such a structure may be associated with the presence of pyrocarbon layers within the deposit. When observed under the optical microscope the silicon carbide coatings deposited in the lower temperature range (< 1300°C) were normally black and shiny in appearance; on some occasions small patches of a brownish nature were also observed [cf. 22] in these low temperature specimens. High temperature deposits were normally very dark grey in colour with a distinct greenish hue); this presumably reflected a decrease in the amount of pyrocarbon present.

3.3.2. Effects of deposition temperature, flow rate, etc. on the silicon carbide deposits

The majority of the silicon carbide coatings initially produced were deposited at comparatively low reaction temperatures (~ 1300°C) using argon as carrier gas at low flow rates (< 500 cm^3 min^{-1}). These conditions led to a substantial penetration of silicon carbide into the bulk tow and coating of individual fibres occurred. Although some hydrogen is formed as a reaction byproduct during disproportionation of methyl radicals produced by cleavage of the Si–C bond in M.T.S., insufficient is available by this means to completely reduce the silicon

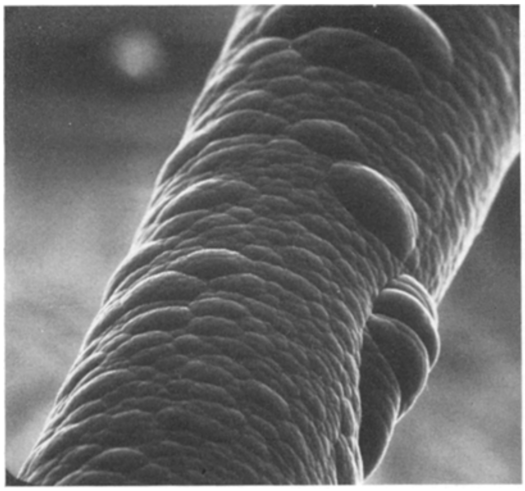


Figure 6 Silicon carbide-coated carbon fibres showing the botryoidal nature of the surface layer (× 70).

dichloride evolved to free silicon [22]. This, in turn, leads to an excess of free carbon which remains unreacted in the deposits; the silicon carbide is relatively weak, therefore, when any significant proportion of these pyrocarbon inclusions are present. The amount of free carbon is reduced to negligible proportions by the provision of excess hydrogen in the form of the carrier gas. A typical example of silicon carbide deposited throughout the bulk tow is shown in Fig. 7a.

On raising the deposition temperature and flow rate, penetration into the bulk tow was concomitantly reduced such that at about 1400 to 1500° C and 500 cm^3 min^{-1} it was possible to produce a reasonably well defined interface between the core element and deposited sheath. Further improvements were achieved by using double resin impregnated carbon fibre tow. An example of this type of filament is shown in Fig. 8a. The silicon carbide "tube" which remains after removal of the carbon fibre core is shown in Fig. 8b; although the bulk of the core has been removed by pull out of almost the entire central element during tensile testing, some fibres remain bonded to the silicon carbide. This type of filament conforms therefore to the basic duplex model and contains a distinct core-sheath interface. The only readily apparent explanation for the decrease in bulk penetration of the fibre tow by silicon carbide at higher reaction temperatures would seem to be that these conditions lead to the rapid formation of an initial surface layer on the bundle and that this layer serves to prevent further penetration into the interior.

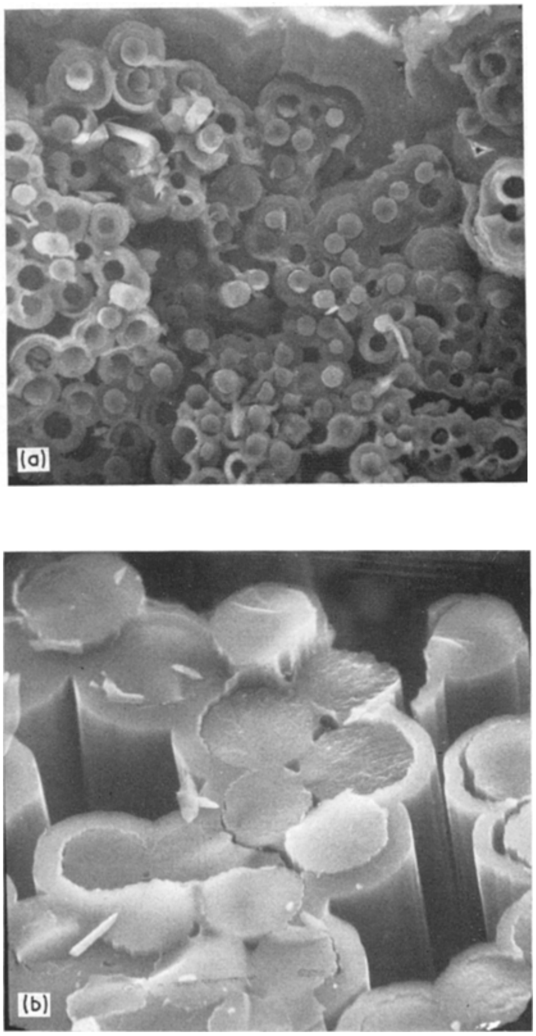


Figure 7 (a) Fracture surface of silicon carbide-coated fibres showing evidence of penetration into the bulk tow (× 420). (b) Similar fracture surface for boron-coated tow (× 1680).

The temperature range employed for deposition is doubly important since too low a temperature may lead to incomplete decomposition of the M.T.S. and hence contamination of the coating as shown in the earlier part of this work; too high a temperature on the other hand may result in an inhomogeneous deposit being obtained because of the occurrence of excessive gas phase reaction (e.g. at very high temperatures where dissociation of silicon carbide can occur the Si–C bond in CH_3SiCl_3 or its decomposition

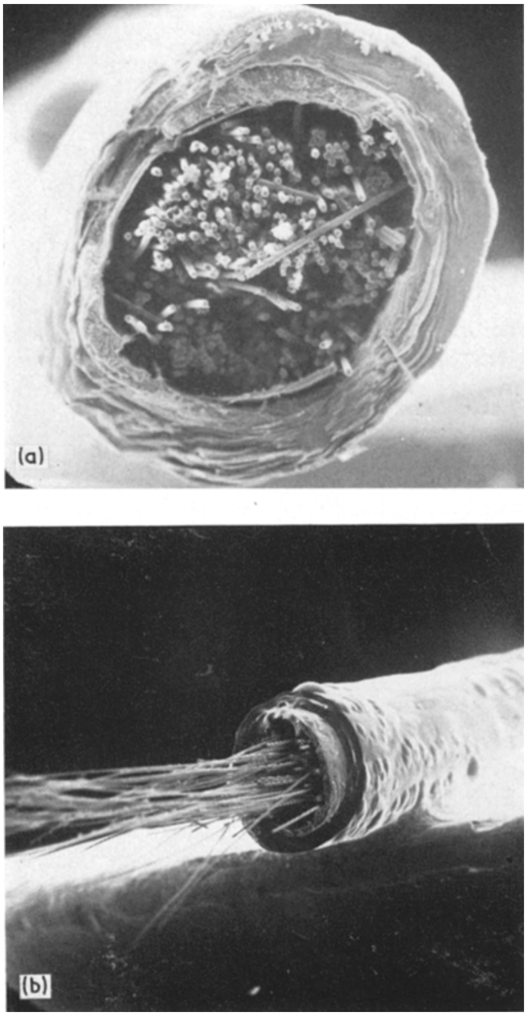


Figure 8 (a) Example of a well defined tube of silicon carbide around a carbon fibre bundle (× 100). (b) The tube-like silicon carbide sheath which remains after almost complete removal of the carbon fibre core element (× 40).

products may become unstable. The M.T.S., could, therefore, decompose to give silicon carbide vapour species enriched in free silicon and solid carbon; the resulting deposit would contain many inclusions of carbon and correct independent control of the vapour pressures would be necessary to produce pure silicon carbide which normally shows no deviation from stoichiometry) [22, 32].

It seems fairly well authenticated that high reaction temperatures (> 1500°C) yield deposits consisting entirely of the β modification of silicon carbide whereas lower temperatures (~ 1300°C) have been shown by X-ray analysis to favour mixed deposits of both α and β silicon carbide [23, 24]. High temperature decomposition of dichlorodimethylsilane over a tungsten wire substrate leads to the formation of deposits consisting entirely of the β modification. Such filaments are claimed to have a somewhat higher strength (but lower modulus) than those produced from M.T.S. [17]. Free carbon has also been detected in deposits grown from dichlorodimethylsilane at low temperatures [33]. It would seem, therefore, that the reactant temperature employed is more important than the choice of initial reactants in governing the form of silicon carbide deposit.

The type of tow pre-treatment (Section 2.1) does not appear to affect drastically the nature of the silicon carbide in any way. As might be anticipated it does appear that the looser the packing in the tow following resin impregnation and carbonization, then the greater is the possibility of penetration of silicon carbide into the bulk during subsequent deposition. Thus, for example, on attempting to put down a thick surface layer of resin on the filament in one step by pulling the tow through a comparatively wide bore capillary, it was found that the resulting loosely compacted fibres tended to splay out rather badly upon initial pyrolysis *in situ*. On depositing silicon carbide on this tow, individual fibres were coated and the resulting loosely bound filament was relatively weak.

Despite this obvious disadvantage of loosely compacted tows it would be desirable to have some small degree of lateral "give" in the core in order to enable simulated "necking down" of the tow to occur where necessary (e.g. in order to progressively decrease the shear strength of the core-tube interface during fibre pull-out). This should enhance the differential Poisson's ratio effect and thereby facilitate debonding by virtue of the relatively greater lateral contraction of the core under an applied tensile stress compared to that of the sheath. An alternative method of incorporating this facility into these particular duplex elements might be to use a twisted fibre bundle (i.e. of rope-like construction) as a core element.

A further attraction of this capacity for lateral contraction might be to minimize the possibility of any "spalling" [23, 24] of the ceramic coating which might occur on heating or cooling of the specimen because of the existence of thermal expansion incompatibility between the inner and outer elements of the fibre. The thermal expansion coefficient for β silicon carbide in the range 25 to 1200° C is 4.6×10^{-6} °C^{-1} [21]. The corresponding value for carbon fibres perpendicular to the fibre axis varies considerably according to type and temperature. Although no directly measured values are available for the fibres used in this work, similar fibres yield values in the range 4.3 to 17.5×10^{-6} °C^{-1} (900 to 1450° C) [34]. These latter fibres show virtually zero thermal expansion in the direction of the fibre axis. It has been pointed out [35] that this differential thermal expansion factor could be of some advantage under certain circumstances. For instance, should the sample be subjected to rapid heating then the existence of a decreasing temperature gradient across the silicon carbide–carbon interface might compensate to some extent for any thermal expansion mismatch.

The overall flow rate was maintained within the range 500 to 1000 cm^3 min^{-1} for all reactions studied. A few deposition experiments carried out on a standard substrate (0.1 mm tungsten wire) revealed that while the absolute deposition rate was approximately proportional to flow rate, there was some indication of an improvement in reaction efficiency by virtue of an increase in relative deposition rate as the flow rate was reduced; this is in agreement with the earlier work by Cartwright and Popper [22]. Results of tensile tests indicated a tendency to form stronger deposits at lower flow rates for a fixed temperature, possibly because there was less tendency to form voids and impurity inclusions under these latter conditions.

It has been emphasized [22] that whilst higher flow rates result in a greater rate of M.T.S. usage and correspondingly large growth rates, the overall reaction efficiency is reduced considerably. These factors are obviously of importance when studying the basic economics of the deposition process where it is necessary to consider the strength etc. of the deposit in relation to the optimum conditions of flow rate, temperature and overall efficiency. Whilst efficiency may not be very important in the case of relatively cheap reactants like M.T.S. (1 cm^3 of M.T.S. (1.27 g) produces 0.34 g of silicon carbide at 100% conversion), high growth rates naturally result in savings in power consumption and reaction time. Thus, for instance, although increasing the M.T.S. supply to the chamber would yield a higher growth rate at the expense of efficiency it might also result in imperfections occurring in the deposit which would lead to a consequent reduction in tensile strength.

3.3.3. *Tensile tests*

Results of typical tensile tests carried out on the resin treated carbon fibre filaments have been described previously in Section 3.1. A fairly typical average breaking load for a pyrolysed double resin impregnated filament was of the order of 80 to 90 N which would correspond to a U.T.S. of 1.6 to 1.8 GN m^{-2} based on a nominal fibre diameter of 8 μm. A direct estimate of the cross-sectional area of actual fibre in the core was difficult to obtain in view of the uncertainty associated with estimating the fibre volume fraction in the pyrolysed, impregnated tow; where necessary a nominal value of 60% was assumed. Fibrous filaments pulled out of a silicon carbide sheath showed no evidence of any significant decrease in tensile strength if due allowance was made for the small number of fibres which adhered to the sheath (e.g. as in Fig. 8b). Values normally fell within the typical ranges quoted for the pyrolysed precursor material in Table I.

In the preliminary experiments where silicon carbide containing inclusions of pyrocarbon was deposited within the bulk tow (Section 3.3.2) the U.T.S. of the silicon carbide was very low, a typical estimate being < 0.1 GN m^{-2} on simple volume fraction considerations. Although it was impossible to make a direct measurement in this case, the strength of the fibres themselves did not appear to have been affected to any great extent; relatively little fibre pull-out was obtained at the fracture surface as shown in Fig. 7a. Some reduction in fibre U.T.S. might be anticipated in view of earlier work carried out on individual carbon fibres coated with titanium carbide [36] In this latter instance fibre failure was thought to be facilitated by cracks propagating in the coating.

Where it was possible to determine the strength of short lengths of the silicon carbide "tube" after removal of the carbon fibre core the maximum U.T.S. obtained was of the order of 0.2 GN m^{-2}. It is obvious that further improvements in sheath strength are to be anticipated in view of the strength of the silicon carbide deposits produced on a much larger graphite substrate by similar experimental techniques [22, 24]; these ranged up to 0.23 GN m^{-2} and even so this value is far short of that ultimately obtainable in theory. Small diameter fibres (100 μm) consisting of silicon carbide deposited onto a thin tungsten wire substrate are commercially available with strengths of the order of 2.0 GN m^{-2}; on present evidence there seems little doubt that, given optimum reaction conditions, it should be feasible to deposit a tubular silicon carbide sheath of similar U.T.S. around a carbon fibre tow substrate.

4. Conclusions

The feasibility of producing a basic duplex bicomponent structure by coating pretreated one thousand filament carbon fibre tows with a well defined silicon carbide sheath has been established. The silicon carbide tubes were relatively weak but it seems reasonable to assume that with some slight modifications to reaction conditions, the method should be capable of yielding much stronger deposits of silicon carbide in the required form. A reasonably distinct core-sheath interface has been produced but has not been examined in any detail. The exact nature of this interface and its potential role in enabling advantageous variable shear strength characteristics to be incorporated into this particular form of duplex element requires further investigation. Despite the lack of success in attempting to produce similar boron coated carbon fibres it is probable that the use of more highly purified initial reactants, e.g. boron trichloride, etc. should enable a satisfactory sheathing material to be produced.

Scaling up of the process is of importance in the long term where the continuous production of ceramic coated fibres is to be considered. The basic method described here has been adapted with reasonable success by several previous workers to produce continuous ceramic coated tungsten filaments [16, 17]. Initial attempts to produce continuously coated graphite filaments by silicon carbide deposition have not proved altogether satisfactory however [24]. A preliminary continuous production apparatus essentially based upon those of Wawner [16] and Galasso *et al.* [17] has been constructed in this laboratory in order to identify the problems which are likely to be encountered in the continuous production of this type of duplex element.

The production of these ceramic bicomponent fibres represents one potential application of the duplex principle based on carbon fibre. Methods of producing textile fibres with a basic core-tube type structure from polymeric materials are well established [37]. Such fibres might provide an alternative source of exclusively carbonaceous duplex fibre material since by initially employing a suitable combination of polymers it should prove possible to produce a bicomponent filament containing a weak internal interface [38]; this could then be used as precursor material in the usual simple pyrolisation process for converting textile yarns into carbon fibres. Thus, for example, it might be feasible to manufacture "pre-preg" carbon fibre sheet with built in duplex characteristics.

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