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Review

Element-containing carbon fibres: recent USSR/Eastern European research in fibre technology

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This review is a survey of carbon fibre research work undertaken in the Soviet Union and Eastern European countries as reported in the literature up to the end of 1987. Matrix-modified fibres, ordered/crystalline structures, adsorption from gaseous and solution phases, catalytic properties, and the development of ion-exchange fibres and protective heat-resistant coatings are discussed in the context of comparable Western research.

1. Introduction

This survey provides a review of the chemistry, technology and application of carbon fibres as developed in the Soviet Union and Eastern European countries, and recorded in *Chemical Abstracts* (up to and including Vol. 107 (December 1987)) and the primary chemical literature where this was available. Most of the work reviewed relates to the use of additives (particularly metallic salts) in the production of carbon fibres and associated materials, and in the improvement of the final properties achieved. Because this has some similarity to research undertaken in this field in the West, reference is also made to Japanese, American and British work, for example, particularly where this both amplifies and extends USSR/Eastern European experiment and theory.

2. General preparative methods

Various methods have been employed for the production of element-containing carbon fibres. These can be subdivided into two groups, depending on whether the required elements are introduced into the composition of the initial organic raw material before, or during, the carbonization process, or whether such introduction is effected by modifying the already formed carbon fibres.

The first group includes the incorporation of elements by: (a) impregnation of cellulose hydrate fibre with solutions of suitable compounds (for example, aqueous solutions of metal halides [1]) or inclusion of particles containing the requisite elements in the pulp employed in the process leading to fibre formation;* (b) chemical modification of cellulose hydrate (hence, the introduction of phosphorus or boron by esterification of cellulose hydrate with phosphoric or boric acids) or adsorption of metal cations into the cellulose via an ion-exchange process [1, 3]; or (c) introduction of a modifying reagent into the flow gases employed for carbonizing the fibre, as with halides, acids, ammonia and volatile metal compounds (for example, $TiCl_4$) [4].

These methods are all distinguished by the fact that the element introduced is distributed throughout the volume of the final carbon fibre generated. However, the structure and properties of the resulting fibre are very dependent on the exact conditions of synthesis, and particularly on the final temperatures employed during carbonization. Not only do these depend on the total amount of the particular non-carbon element introduced, but also on the nature of that element (or of its chemical compound) and its spatial distribution throughout the fibre. Elements introduced into a carbon fibre may be distributed homogeneously as solid solutions in a carbon matrix, or may exist as a separate phase involving a simple substance or compound, e.g. as the free metal or a carbide. Phases of this type may occur as disperse inclusions in the fibre volume (inclusions of oxide or free metal particles) or as coating layers (carbon fibre "cores" covered by continuous or discontinuous metal "jackets"). The properties of carbon fibres wherein the element introduced is distributed widely throughout the carbon matrix (matrix-modified carbon fibres) are discussed in detail in Section 3 below.

Preferential distribution of the incorporated elements in the surface layers of the resulting carbon fibres is generally accomplished through the modification of already formed carbon fibres. Methods involving such procedures include: (a) chemical or electrochemical precipitation of the elements on to the fibre surface [5, 6]; (b) treatment of fibres subjected to preliminary activation with suitable solutions of compounds containing the required elements [7]; (c) application of such compounds to the carbon fibre surface followed by subsequent thermal annealing [8]; (d) use of high-temperature conversion processes involving reaction

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*Dispersions of heat-resistant metals, oxides, etc. have been introduced into cellulose hydrate in this way, prior to subjecting the resulting fibre to pyrolysis [2]. This method was favoured by earlier workers, despite the obvious experimental difficulties and the comparatively low physico-mechanical characteristics of the carbon fibres obtained.

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of the carbon fibre surface with suitable compounds in the liquid or gaseous form [9, 10]; or (e) chemical modification of fibres through their treatment with reagents containing ionic groups as occurs in phosphorylation [11, 12], sulphuration [13], amination [4] and oxidation [14, 15]. The properties of surface-modified carbon fibres are discussed in Section 4 below.

3. Matrix-modified carbon fibres

3.1. Development of ordered/crystalline structures

If elements or their compounds are introduced into a preformed, amorphous carbon matrix [16, 17] or into a carbon-containing polymeric material prior to the carbonization stage [7, 18–21], it is possible to catalyse those processes which lead to crystallization of the amorphous carbon fibres when the latter are annealed at high temperatures in the absence of oxidizing gases (i.e. carbon dioxide, air or steam). Indeed, examples are known where resins which cannot be graphitized under normal thermolysis conditions can be so induced by the prior addition of compounds such as copper fluoride or oxide [21]. This behaviour probably arises from the formation of intermediate compounds between copper cations and the products of the carbonization process. Under these circumstances, the metal atoms cause the cleavage of C–C bonds which are formed irregularly during condensation of the aromatic fragments, thus promoting the formation of ordered structures [21].

Most additives accelerate the formation of ordered carbon when fibres are subjected to heat treatment above 600° C, or of graphitic layers when the temperature is increased to 1400 to 1800° C. Data exist in the literature on the catalytic action of compounds containing cobalt [16], nickel [17–19, 22], iron [7, 19, 20, 23, 24], chromium [18, 23, 25], manganese [25], copper [21], bromine [26, 27], barium [28] and boron [27, 29, 30] on the formation of ordered structures and graphitic layers during the thermal treatment of cellulosic materials.

The temperature at which a given element catalyses an ordered structure often depends on the method used to introduce that element into the starting cellulosic material. In particular, if iron cations are introduced via an ion-exchange process into a cellulose modified by oxidation, the reduced iron phase will germinate an ordered structure at a lower temperature than when iron ions are introduced into the material by impregnation with an aqueous ferrous chloride solution [31, 32].

When cellulose fibres containing iron are exposed to low thermal treatment temperatures (400 to 600° C), the iron exists as various oxides; a reduced metal phase is formed, however, when the temperature is raised to 700 to 800° C. A further rise in temperature to 1000° C or above causes separation of iron from the iron–carbon fibre composition. Raising the heat-treatment temperature from 400 to 1600° C leads to a reduction in the iron content of the fibre from 15.1% to zero [19, 22]. Iron-containing carbon fibres have been studied by X-ray structural and electron microscopic methods [7]. Even when the carbonization temperatures are quite low ($\sim 600°$ C), the formation of bright platelets associated with the presence of carbon with an ordered crystalline structure is observed.

Iron-containing carbon fibres are pyrophoric and exhibit low ignition temperatures. A typical preparation involves the vacuum pyrolysis of iron salts of monocarboxycellulose or graft acrylic acid–rayon at 500 to 750° C [32]. Such pyrophoric properties have been related to the presence of highly dispersed iron in the composition of these fibres. However, many other metals (for example, cobalt, nickel, copper and cerium) are also reduced to the free metal when carbon fibres containing these elements are prepared. Because the reduced metal is in a finely dispersed state initially, these element-containing fibres are also pyrophoric. For iron–carbon fibres, pyrophoricity appears over the temperature range 500 to 700° C; for cobalt–, nickel– and chromium–carbon fibres, the range is 400 to 500° C; and for cerium–carbon fibres, 500 to 600° C.

Above these temperatures, recrystallization of the metals takes place to yield coarser crystals which are not pyrophoric. Thus the introduction of nickel or cobalt into cellulose fibres leads to the formation of structured carbon at 800° C, where the distance between the carbon layer networks lies within the range 0.345 to 0.347 nm [18]. X-ray structural data and an analysis of the catalytic activity of such metallo-carbon fibres [33] have confirmed that both nickel and cobalt are reduced to the free metal under these circumstances. Subsequent thermal treatment of these fibres *in vacuo* at temperatures up to 1500° C results in the loss of some of the free metal through evaporation. Both types of metallo–carbon fibre disintegrate under these circumstances.

In contrast to the behaviour of nickel and cobalt, the introduction of chromium and vanadium into cellulose fibres does not yield a structured component in the resulting metal–carbon fibre if the latter is subjected to relatively low heat-treatment temperatures. It has been suggested that these metals hinder the formation of hexagonal carbon networks during the condensation of the intermediate products of the pyrolysis. However, thermal treatment of such fibres at 1500° C leads to the formation of the corresponding metal carbides, and these induce an ordered carbon structure with an interlayer distance of 0.343 to 0.345 nm. X-ray diffraction data for chromium-containing carbon fibres indicate the formation of a Cr_3C_2 phase under these conditions, in good agreement with results for bulk charcoals [34], which suggest that graphitization is induced in carbon fibres by the presence of certain carbide impurities. The high-temperature treatment of cellulose fibres containing such carbide-forming elements generates the formation of the carbide phase. This, in turn, induces the breakage of intercrystalline and transverse bonds involving carbon in the structure, so that the propensity of the latter to graphitize is increased.

Thermal treatment of platinum-containing cellulose fibres at 500 to 800° C leads apparently to the development of finely divided crystalline platinum within the composition of the fibre [35]. However, growth and improvement of the structure of these crystals was only observed when the sample temperature was increased above 800° C. Such temperatures are also necessary to achieve an increase in the proportion of condensed carbon structures present in the system [36]. In contrast, cellulose fibres containing 1 to 0.7 wt % boron, obtained by the esterification of monocarboxylcellulose in the presence of boric acid [37], required thermal treatment up to 3000° C before changes were observed in their structural parameters [38].

Although the behaviour of platinum and boron in catalysing graphitization in carbon fibres may be interpreted in terms of carbide formation, not all carbide-forming elements act in this way. Whereas the high-temperature treatment of carbon fibres containing vanadium, for example, leads to the formation of a vanadium carbide phase, this does not promote the generation of an ordered structure in the carbon fibre. This result agrees with other data [39] which support the view that graphitization is hindered rather than accelerated by the presence of vanadium in a cellulose fibre subjected to high-temperature annealing.

In a similar manner, the incorporation of aluminium into the composition of a carbon fibre has no marked effect on the structure when the fibre is subjected to high-temperature treatment. Thus, the X-ray diffraction patterns of aluminium–carbon fibre and carbon fibre samples have been shown to be similar to each other, with lines corresponding to crystalline aluminium or its compounds being absent from the diffraction patterns of the aluminium-containing material [7]. The only effect that increasing the thermal treatment temperature induces is to increase the carbon content of the fibre at the expense of hydrogen and oxygen.

X-ray studies of the effect of thermal treatment on copper–cellulose fibres have demonstrated that over the temperature range 260 to 600° C the copper is present as cuprous oxide and the free metal [40, 41]. Above 600° C complete reduction to the free metal occurs, but this has no marked catalytic effect on the formation of ordered carbon at these temperatures. In a similar manner, ruthenium has no catalytic effect on the formation of an ordered carbon structure at temperatures up to 930° C [42].

The structural characteristics and properties of carbon fibres may be changed appreciably by introducing phosphorus, and phosphorus in conjunction with metals, into their composition. Esterification of cellulose hydrate with phosphoric acid as a preliminary to the generation of phosphorus–carbon fibres, and the use of ion-exchange methods in the development of phosphorus–metal–carbon fibres, has been described [43–47].

The influence of phosphorus on structural ordering in carbon fibres has been studied by X-ray diffraction methods, which have shown that the thermal treatment of cellulose phosphate at temperatures up to 800° C induces only a limited degree of order [43]. From spectral data [44], it has been deduced that the presence of phosphate groups in cellulose fibres subjected to heat treatment favours the rapid accumulation of structures containing C=C groups, and that this leads to the restructuring of the charcoal residue with the participation of stable P–O–C bonds [44, 48]. Further restructuring occurs when the temperature is raised to 1500° C, accompanied by removal of the phosphorus from the structure of the fibre either as phosphorus pentoxide [49] or as elementary phosphorus with subsequent vaporization [43, 44, 48]. Where the element-containing carbon fibre contains several alloying elements, as in the case of a metal–cellulose phosphate, both metal carbides and phosphates can form during heat treatment. Formation of a given phase depends upon its stability under the heat-treatment conditions employed. For example, heating nickel–phosphate–carbon fibres to 800° C leads to the development of non-ordered carbon structures, together with the simultaneous formation of the nickel phosphide, Ni_2P. Continued heat treatment up to 1500° C generates hexagonal carbon layers in the final product, together with a nickel phosphide of formula Ni_7P_3 [43].

In contrast, heat treatment of the chromium and vanadium salts of cellulose phosphate at temperatures up to 800° C yields carbon fibres exhibiting a purely amorphous structure. Continued heating of these fibres up to 1500° C generates Cr_3C_2 and VC, respectively, rather than the corresponding phosphides. Formation of a structured carbon with an interlayer spacing of 0.340 to 0.342 nm was only observed with the chromium-containing material.

Noda has suggested [21] that the participation of inorganic elements or their compounds in the formation of graphite layers occurs because of the simultaneous occurrence of one or more of the following processes: (a) dissolution of carbon in the metals (or in their compounds, e.g. in carbides) followed by the subsequent crystallization of graphite from these solutions; (b) decompostion of carbides formed at earlier stages of the heat-treatment process; (c) structural changes in the carbon matrix formed during carbonization, arising from chemical reactions involving the inorganic additives; and/or (d) formation of solid solutions in which the added elements substitute for carbon.

In support of these suggestions, Noda has pointed out that the formation of ordered carbon can take place through the catalytic graphitization of gaseous, carbon-containing thermolysis products. For example, the growth of graphite layers in the presence of metallic catalysts occurs from transformations involving CO, CH_4, C_3H_8 and other hydrocarbons during heating [50–52], as well as to carbon vaporized from the surface of eutectic melts formed during heat treatment of carboniferous materials in the presence of metallic compounds [53].

Because of their ability to form different compounds with carbon and the effect of such compounds on the production of ordered structures, the introduction of other elements into carbon fibres has a considerable influence on the chemical stability of the latter. Thus the introduction of nickel and chromium, which leads to a high degree of ordering of the structure at high thermal treatment temperatures, increases the thermal stabilities of the resulting fibres by 100 to 240° C relative to fibres generated directly from monocarboxycellulose or from VO–monocarboxycellulose. Indeed the thermal stability of carbon fibres obtained from VO–monocarboxycellulose fibres is lower by some 130° C than that of fibres obtained directly from monocarboxycellulose, and this probably linked to the participation of vanadium in oxidation–reduction transformations during the thermal treatment in air of fibres containing this element.

Subjecting a carbon fibre containing phosphorus, and a similar fibre incorporating both phosphorus and chromium, to heat treatment at 1500° C increases the resistance to thermo-oxidative reactions in air by 100 and 190° C, respectively, relative to carbon fibres obtained directly from cellulose [43]. The increased thermal stability of such carbon fibres may be connected to the high degree of ordering induced in their structures by the introduction of phosphorus and chromium.

3.2. Adsorption characteristics

3.2.1. Development of porosity

As a result of the exposure of carbonized fibres and/or cloths to an oxidizing atmosphere at high temperatures, it is possible to burn out any disorganized carbonaceous residue present and generate a highly porous material. This process is called activation and, as demonstrated by work undertaken in this Department and elsewhere, the porosity of the activated carbon fibres and/or cloths so produced may be readily controlled by varying the heat treatment employed during carbonization, and by altering the length and temperature of the activation process. The incorporation of non-carbon elements into fibres, particularly when those elements influence the decomposition processes occurring during carbonization, also has a considerable influence on the development of porosity. The generation of both micropores (pore width $\langle$ 2 nm) and mesopores (pore width 2 to 50 nm) has been reported on activation of element-containing carbon fibres carbonized initially within the temperature range 600 to 900° C, with apparently only micropores being formed if higher heat-treatment temperatures are employed [54].

The introduction of appropriate additives is of fundamental importance in controlling the porous structure. Thus the presence of additives, even in the form of ash impurities, accelerates the activation process substantially [55–57], while the use of halide admixtures leads similarly to a reduction in the activation temperature [1]. Indeed, the introduction of additives into the fibre composition, followed by a suitable vapour/gaseous activation process, apparently generates activated carbon fibres with improved physicomechanical properties [58–62]. Hence the introduction of nitrogen and phosphorus into the initial cellulosic precursor facilitates the formation of elastic fibres with strengths of $\sim$40 MPa, in comparison with a strength of 10 MPa or less for activated fibres based on pure carbon [60].

The influence of additives on the strength of the final activated carbon fibre is governed by the nature of their reaction with the basic carbonaceous material produced. If thermolysis of an element-containing cellulosic fibre causes the precipitation of metallic agglomerates (as occurs during heat treatment of a cellulose pretreated with a metal halide), the nature of the metal generated has a considerable influence on the reaction of the carbon with the activating gas. Thus the incorporation of $CuCl_2$ into a cellulosic precursor leads to the precipitation of copper crystals during subsequent thermolysis [59], and the presence of such crystals causes preferential burning of carbon in those zones which adjoin the precipitated metal. This result in a loss of connectivity between the individual carbon fragments, so that the activated fibres obtained subsequently have a relatively low strength. In contrast, thermolysis of a cellulose fibre incorporating $ZnCl_2$ does not lead to the formation of a metallic phase capable of catalysing the gasification of carbon at the metal–carbon interface, with the result that the final activated carbon fibres generated possess considerable mechanical strength [59].

The sorption capacities and selectivities of activated carbon fibres are also increased in the presence of mineral additives [63–66]. Thus, the introduction of phosphorus into the initial composition of the cellulosic precursor not only simplifies and accelerates the processes of pyrolysis and activation, but also generates activated carbon fibres with molecular sieve properties [67]. The regulating effect of additives is even more pronounced in chromium–, aluminium–, iron–, zinc–, cobalt– and calcium–carbon fibres; activation of chromium–carbon fibres, for example, yields an ultramicroporous structure from which mesopores are completely absent [68].

The porous structure of a carbon fibre is not only regulated by the nature of the metallic additive, but also by the method employed to introduce metal cations into the composition of the initial cellulosic precursor. Thus activated carbon fibres obtained via the pyrolysis of the aluminium, lanthanum and zinc salts of methylcarboxycellulose exhibit molecular sieve properties, whereas both micropores and mesopores arise from the pyrolysis and activation cellulose impregnated with solutions of the corresponding chlorides [1].

The use of aluminium salts to generate microporous materials has been studied extensively, because such metal-containing fibres generate an optimum micropore size on activation [1]. For this reason, carbon adsorbents containing aluminium have been prepared both in fibre and cloth forms. If aluminium chloride is introduced into the initial composition of the precursor, finer and more homogeneous pore structures are generated during its subsequent carbonization and activation [69].

The structural properties of carbon adsorbents prepared by the pyrolysis of NH_4Cl-containing rayon have also been investigated. In this case, high strength rayon was treated with aqueous 0.75 M NH_4Cl, dried in air, pyrolysed in a neutral medium at 900° C and activated with steam at 800° C. The parameters of the resulting microstructure, which contained numerous small size micropores, were examined using a simplified form of the Dubinin–Astakhov equation [70]. Although initial treatment of cellulose fibres with aqueous KCl solution also resulted in the formation of activated adsorbents with a uniform microporosity, treatment with LiCl or NaCl solutions led to the development of both micropores and mesopores in the resulting material [71].

Argon adsorption measurements have shown that impregnation of viscose rayon fibres with 10% aqueous ammonium hydrogen phosphate, followed by carbonization at temperatures within the range 773 to 1073 K and activation with steam in the absence of air at 873 to 1173 K, generates a microporous/mesoporous structure. The final structure depended mainly on the temperatures employed for carbonization and activation, with the maximum mesoporosity being observed for samples carbonized at 973 K [72].

3.2.2. Sorption of ammonia

Activated carbon fibres have been used widely, both in industry and elsewhere, as sorbents for the removal of gases. Typically, they have been used for the removal of ammonia, the high sorption rate exhibited by fibres subjected to 22 to 57% burn-off resulting in ~ 90% ammonia being adsorbed during the first 10 min exposure [73]. However, increasing burn-off also leads to a decrease in the extent of ammonia adsorbed, an observation attributed to an increase in the dimensions of the micropores produced in the fibres.

An increase in the capacity and selectivity of sorbents towards ammonia is observed if activated carbon fibres are used as chemisorbent carriers. This has been achieved, for example, by spraying with an aqueous copper sulphate solution, drying the product and then spraying with an aqueous K_2CO_3 solution [74]. Alternatively, activated fibres generated from poly(furfuryl alcohol) have been modified by treatment with concentrated nitric acid and impregnated with solutions containing transition metal salts. In this case, the uptake of ammonia by the materials produced depended very much on the extent of the acidic treatment employed [75]. In another method involving impregnation with salts capable of forming complex compounds, fibres subjected to high burn-off were found to be most suitable.

Studies of the kinetics of ammonia adsorption by activated carbon fibres containing $CoCl_2$ have shown that, under the same sorption and burn-off conditions, impregnated samples exhibit an almost two-fold increase in sorption capacity compared to non-impregnated samples, with the total weight of ammonia sorbed being 160 mg g^{-1} [73]. The adsorption isotherms may be described by the equation $\log a = \log k + n \log p$, where a (mg g^{-1}) = sorption capacity, p (torr) = pressure of ammonia, and k and n = constants. A similar increase in the degree of sorption of ammonia is also observed when activated carbon fibres are impregnated with $CuCl_2$. For example, when the content of the latter in the fibre is 45% by mass, the degree of sorption is increased ~ 4.5 times in comparison to the non-impregnated fibre, with the total weight of ammonia sorbed being 300 mg g^{-1} in this case [76].

Such impregnated fibres still retain a high sorption velocity despite the addition of salts, although the absolute magnitude of this velocity depends very much on the salt introduced into the fibre. Studies of $CuCl_2$, $CoCl_2$ and $NiCl_2$ as impregnants have shown that the sorption velocity of the resulting fibres towards ammonia decreases in the order ACF–$NiCl_2$ > ACF–$CuCl_2$ > ACF–$CoCl_2$, where ACF denotes the activated carbon fibre. In contrast, varying the cation present in the salt has little effect on the capacity of an impregnated carbon fibre, provided that the same quantity of salt is added in each case.

The presence of moisture significantly increases the sorption capacity of fibrous carbonaceous $CuCl_2$-containing materials with respect to ammonia in air [77], with the sorption capacity increasing with increasing concentrations of water vapour [78]. Under these circumstances, the general adsorption process appears to consist of physical adsorption followed by heterogeneous complexation of $CuCl_2$ with ammonia. The sorbents can be readily regenerated and re-used many times.

Salt-impregnated activated carbon fibres exhibit substantial advantages over similarly treated granulated carbons. Comparative studies of the sorptional capacities of a granulated and fibrous activated carbon impregnated with a nickel salt towards ammonia have shown that the maximum capacity of the granulated material (160 mg g^{-1}) is only about one-half that exhibited by the activated fibres [79]. Despite impregnation, such fibres may be regenerated by thermal treatment and are, therefore, capable of being used as sorbents repeatedly. However, materials obtained by the oxidation of carbon fibres with melts of the crystal hydrates of aluminium and cobalt(II) nitrates exhibited a reduced capacity of ~ 30% during the first three to five sorption cycles, although this value remained fairly constant thereafter [80].

When polyacrylonitrile-derived activated carbon fibres (PAN–ACF) subjected to sulphuric acid oxidation have been employed, increased reduction of ammonia has been observed in the presence of nitric oxide [81]. ESCA and TPD studies have shown, in this case, that oxygen-containing groups provide the active sites for ammonia and nitric oxide sorption.

3.2.3. Sorption from solution

The adsorption behaviour of porous carbon fibres is not limited to the vapour/gaseous phase. Some studies have also been made of their sorptive capacities towards solutes dissolved in aqueous media. It has been shown that highly porous metal-containing fibres are compatible with blood, and since they exhibit good sorption properties towards toxic materials they are useful clinically [82]. In a study of the adsorption by activated carbon fibres of fibrinogens, γ-globulins and blood albumins from a 0.067 M phosphate buffer (at pH 7.4) and from blood plasma at room temperature, it was shown that the adsorption behaviour is very dependent both on the nature of the proteins and on their concentration. The greatest adsorption was exhibited by γ-globulins, their concentration being decreased from 75.4 to 9.7 mg g^{-1} after exposure for

60 min to the activated carbon fibre. Under the same conditions, 76.2 mg g^{-1} albumins were adsorbed whereas the concentration of fibrogens decreased from 112 to 54.3 mg g^{-1}. The limited adsorption of fibrogens have been attributed to their ability to form binary mixtures with γ-globulin or albumin [83].

3.3. Catalytic properties

Activated carbons are used widely in heterogeneous catalysis, both as catalysts and as carriers of an active phase [84–97]. In this respect they are similar to zeolites, various metal oxides, asbestos, pumice and quartz which have been used as catalyst supports when prepared with a prescribed surface area and structure.

The value of element-containing carbon fibres as catalysts or supports in heterogeneous catalysis may be related both to the fibrous form of the materials and to the distribution of the elements within the fibre. Thus, depending on the conditions chosen for the production of the fibres, the metal may be present in the free state and hence fixed rigidly within the carbon matrix. In other circumstances the metal or its compound may be confined to the surface layers of the carbon fibre, with the consequence that the active phase of the catalyst will be readily accessible to the reactant molecules. Furthermore, a fibrous catalyst may be distinguished from a catalyst in a powder or granulated form, albeit with the same particle diameter, by the lower hydraulic resistance of its packed layers. This leads to a shorter diffusional path allowing a greater output of product at lower reaction temperatures. Equally, because the mechanisms of many heterogeneous processes involve sorptional interactions, porous fibrous catalysts with a high surface area have additional substantial advantages over granular materials. These are especially significant when high flow rates are employed, as occurs widely in modern technological processes.

The optimum characteristics of a catalyst depend not only on the nature of the process, its kinetics and its mechansim, but also on the properties of the active component and on its support. Indeed the selection of the carrier is most important, because it determines a whole series of catalyst properties, i.e. the extent of the specific surface, the distribution of the active component throughout the body of the catalyst, its mechanical strength, sintering protection at high temperatures, removal of the heat evolved during the reaction, etc. As a consequence, the carrier can affect the activity and selectivity of the catalyst quite substantially.

For these reasons, a catalyst on a carrier is often regarded as an interconnected system. This distinction also applies to element-containing carbon fibres when these are used as catalysts. In these circumstances such fibres may be regarded as the catalyst *in toto,* or alternatively the carbon fibres may be regarded as the carrier while the structural elements contained in the fibre (including any added metallic components) may be regarded as the catalyst which directly influences the interaction of the reactants. The nature of the structural elements is determined to a large extent by the method employed to introduce them into the composition of the carbon fibre, and for this reason the catalytic activity of heteroelement fibres obtained by impregnating preformed activated carbonaceous materials with a solution of a metal compound, followed by subsequent reduction, often differs from that obtained by carbonization/activation of polymeric fibrous precursors to which compounds of the same metal have been added prior to thermal treatment.

Catalysts containing nickel, cobalt, chromium and manganese, which are useful in the dehydrogenation of cyclohexanol, have been obtained by the heat treatment at temperatures within the range 600 to 800° C of salts of methylcarboxycellulose with these metals [33]. X-ray structural studies have shown that nickel is present in the free state in the composition of such carbon fibres from 600° C, while the free metal is apparent in a cobalt-containing fibre at 800° C. As a consequence, both nickel- and cobalt-containing carbon fibres exhibit high catalytic activities.

Copper–carbon fibres, prepared by treating oxidized cellulose with 0.05 M $CuCl_2$, washing with water, drying in air, and pyrolysing in an inert gas, demonstrate a similar high activity in the dehydrogenation of cyclohexanol and isopropanol [40]. In this case, however, the catalytic behaviour may be related not only to the presence of free copper in the structure of the carbon fibre (at thermal treatment temperatures of 500° C and above), but also to the state of dispersion of the metal. In such fibres, the metal is present in the form of highly disperse inclusions, and this leads to quite a high surface contact despite the relatively modest copper content of the samples studied (5.2 to 7.6 wt %). Data on the catalytic activity of copper–carbon catalysts in the dehydrogenation of secondary alcohols [40] indicate that a change in the volume velocity from 0.8 to 1.2 h^{-1} at the thermal treatment temperature employed in the preparation of the catalysts had virtually no effect on the yield of ketone, whereas an increase in the reaction temperature to a value some 280 to 350° C above the thermal treatment led to a significant increase in the product yield. In these cases yields of $>90\%$ were obtained, with the selectivities of the processes being close to 100%.

The maximum catalytic activity corresponded to a catalyst prepared by thermal treatment at a temperature of 600° C. Higher temperatures (800° C) led to recrystallization of the metal, with enlargement of the copper particles and a resulting reduction in the catalytic activity. This was confirmed by studying the catalytic activity of a charcoal fibre possessing a deposited surface layer of copper obtained by successive dipping into an aqueous solution of a copper salt and a reducing agent. By this method it was possible to vary the metal content of the fibre between 5 and 95 wt %. Such fibres exhibited activities during the dehydrogenation of cyclohexanol which were 2.5-times lower than those for copper–carbon fibres in which the metal was present in a finely dispersed state and enclosed within the carbon matrix. This has been attributed to the difficulty of particle enlargement on the fibre surface both during the preparation of the catalyst and in its subsequent use.

Catalysts prepared by the incorporation of metals derived from Group VIII of the Periodic Table within the composition of various non-fibrous carriers have been used widely in conversions involving hydrocarbons. Because of the high activity of carbon fibres as carriers, such conversions have also been studied using platinum-containing fibres [98]. In this case the catalyst was prepared by impregnating hydrated cellulose fibres in a solution of chloroplatinic acid, followed by subsequent carbonization at temperatures within the range 600 to 1000° C. The metal in the carbon fibre thus obtained was present in a reduced form, and in order to increase its activity it was subjected to further activation by air at 350° C [99].

The activity of the resultant catalyst, which contained up to 3 wt % platinum, was evaluated for the following series of standard reactions: dehydrogenation of cyclohexane, benzene hydrogenation, configurational isomerization in dialkylcyclanes and hydrogenolysis of cyclopentanes [35]. It was found that the catalyst properties depended not only on its platinum content but also on the form of the latter. Thus a high catalytic activity was observed in the above reactions when platinum–carbon fibres subjected to thermal treatment at 500 to 700° C were employed after activation by air at 300 to 350° C. For example, the degree of conversion from the *cis* to the *trans* isomer observed in the configurational isomerization of *cis*-1,2-dimethylcyclopentane was 0.2 to 0.9% on the non-activated platino–carbon fibre and 37 to 75% on the activated fibre. This increase in catalytic activity after fibre activation is attributed to oxidation accompanied by the formation of surface carbonate–carboxylate groups which react with platinum particles increasing their catalytic activity.

The formation of specific oxygen-containing complexes exhibiting catalytic activity at the boundary between the metal and the carrier has also been confirmed by an EPR study of the interaction of platino–carbon fibres with oxygen [36]. Such studies have shown that these complexes act as special activating ligands in the conversion of hydrocarbons. Platinum promotes the virtual complete removal of chemisorbed oxygen from carbon fibres during their thermal treatment, leading to a reduction in the spin–lattice relaxation time and to a broadening of the EPR signal. Apparently, the subsequent increase in activity following treatment in air is related to interaction of oxygen with the platino–carbon fibre.

4. Surface-modified carbon fibres

4.1. Ion-exchange fibres

Pyrolysed cellulosic fibres, polymeric organic fibres containing functional groups capable of participating in ion-exchange processes, namely cellulose phosphate, carboxymethylcellulose or oxidized cellulose fibres, and even chemically modified coals, are all unsuitable as ion-exchange fibres, either because they show no ion-exchange properties (pyrolysed cellulosic fibres), exhibit inadequate chemical and thermal resistance (cation-exchange organic fibres) or cannot be used in conditions which require fibrous materials such as cloth filters (chemically modified coals) [11]. Cation-exchange carbon fibres may be prepared, however, by subjecting organic fibres to pyrolysis, followed by oxidation, sulphonation or phosphorylation of the resulting carbon fibre. The ionogenic groups thus introduced are located chiefly on the surface of the fibre, their variety enabling exchange capacities of up to 7 mg eq. g^{-1} to be produced.

However, the exchange capacity is governed by factors other than the method of oxidation employed. Thus, the number of ionogenic groups capable of being introduced decreases as the carbonization temperature employed in the initial pyrolysis is increased. For example, when a fibre subjected to carbonization at 500° C was oxidized by treatment with 70% nitric acid solution for 1 h at 90 to 95° C, a cation-exchange fibre with a capacity of 2.2 mg eq. g^{-1} was obtained. Increasing the carbonization temperature to 810° C followed by the same oxidation treatment led to a decrease in the exchange capacity to 1.1 mg eq. g^{-1} [100]. Equally, if a carbon fibre carbonized at 600° C is oxidized by means of a similar treatment with nitric acid, such treatment must be continued for 30 to 60 min to reach an exchange capacity of 3 to 4 mg eq. g^{-1}. If the final carbonization temperature is raised to 900° C, oxidation must be allowed to proceed for 120 to 180 min to achieve the same exchange capacity.

This decrease in exchange capacity with increasing carbonization temperature has been attributed to a decrease in the number of reactive –CH– groups in the carbon fibre composition. These groups undergo subsequent oxidation, so that their decrease will diminish the final exchange capacity generated. In addition, an increase in the carbonization temperature leads to greater structural ordering, making it more difficult for the oxidizing reagent to penetrate the fibre.

Because of the different carbon matrix produced on carbonization, carbon fibres based on polyacrylonitrile fibres carbonized at 900° C are readily oxidized in comparison to those based on cellulose subjected to the same thermal treatment [101]. The introduction of aluminium cations into the composition of the carbon fibre leads to a decrease in the exchange capacity subsequent to sulphonation or nitric acid oxidation, but the strength of the ion-exchange fibres generated is much higher than for corresponding fibres which do not contain aluminium [11, 13, 102]. In this case the fibre is first oxidized using N_2O_4(g) at room temperature to increase the content of COOH groups to 12%, and then esterified by means of a 0.1 M solution of $Al_2(SO_4)_3$. Prior to pyrolysis, the impregnated fibre was washed with distilled water until the washings contained no aluminium ions.

If the specific surface areas of carbon fibres are increased by preliminary activation employing water vapour or carbon dioxide, the ion-exchange fibres produced exhibit a considerable increase in exchange capacity although their resulting strengths decrease [102–104]. Thus carbon fibres with a high cation-exchange capacity have been manufactured from cellulosic fibres by impregnating the latter with $AlCl_3$ solutions, followed by pyrolysis and activation with water vapour or CO_2 at 700 to 900° C and subsequent oxidation [105]. Even if the modifying groups are introduced prior to fibre carbonization, subsequent activation will increase the exchange capacity. An example is the introduction of amino groups into halogenated fibres as a preliminary to the formation of anion-exchange fibres [106].

Similarly, if carbon fibres are subjected to a preliminary activation prior to sulphonation, it is possible to obtain ion-exchange fibres with enhanced capacity, capable selective sorption of polar substances from the vapour or gaseous phase, or of polyvalent cations, pigments and polar organic substances from aqueous solutions even under very dilute conditions [84].

The same functional groups may be introduced by various methods. Thus the nature of the modifying reagent, the temperature and the time taken for surface modification influences the way in which the functional groups are distributed on the surface and the type of bonding to the latter. Furthermore, such modification has an impact on the content of secondary functional groups introduced. The nature of these groups has been established by infrared spectroscopic studies [107]. On treatment with nitric acid, the process of oxidation is accompanied by the formation of carboxyl, hydroxy and nitroether groups [107–112]. Thus intense bands in the infrared spectrum at $1730\,\mathrm{cm}^{-1}$ (arising from the valence vibrations of the $>C{=}O$ groups in COOH) and $1260\,\mathrm{cm}^{-1}$ (valence vibrations of C–O groups) point to the presence of carboxyl groups in the carbon structure. If the hydrogens of the carboxyl groups are replaced by sodium ions, a reduction occurs in the intensity of the band in the $1730\,\mathrm{cm}^{-1}$ region of the spectrum, and new bands appear at 1390 and $1600\,\mathrm{cm}^{-1}$ associated with the symmetric and antisymmetric vibrations of the carboxyl groups.

A band associated with the valence vibrations of hydroxy groups appears at $3600\,\mathrm{cm}^{-1}$, this being displaced to lower frequencies by vacuum treatment or heating at 200° C. According to Zawadski [110], the appearance of this band may be explained by hydrogen bond formation of the type common to sorbed water molecules with acidic proton groups indicating that they possess the properties of a weak acid. Finally, the ability of nitric acid to induce nitration as well as oxidation is demonstrated by the appearance of absorption bands at 1350 and $1540\,\mathrm{cm}^{-1}$, corresponding to the symmetric and antisymmetric vibration modes of the NO_2 groups.

Polyfunctional ion-exchange fibres are also generated when carbon fibres are sulphonated with sulphuric acid, since bands corresponding to both sulpho ($-HSO_3$) and carboxyl groups are apparent in the infrared spectra of such fibres. The sulpho groups may be identified by the appearance of a sharp absorption band in the spectrum at $1045\,\mathrm{cm}^{-1}$, attributed to the symmetric vibrations of the $-S({=}O){=}O$ groups. In a similar manner, the treatment of carbon fibres with phosphorylating agents leads to the generation not only of phosphate groupings, which may be identified by the appearance of a band at a frequency of 1200 to $1290\,\mathrm{cm}^{-1}$ corresponding to the vibration modes of the P=O groups, but also to the development of carboxyl groups as in nitric and sulphuric acid treatments [12].

These various groups have a considerable influence on the behaviour of ion-exchange fibres during potentiometric titration [13, 101, 109, 111]. Thus, the potentiometric curves arising from the fibres are characterized by several inflection points at different pH values. The characteristic sulpho group produced by the sulphonation of carbon fibres is strongly acidic, exhibiting a point of inflection at a pH value of 3. In contrast, the weakly acidic carboxyl group has an equivalence point in the region of pH 7 [13].

The potentiometric titration curves for phosphorylated carbon fibres, produced by treating the initial cellulose fibre with phosphoric acid and then carbonizing at 500° C, exhibit inflection points at pH values of 4.5, 7.0 and 10.0, respectively [111, 112]. Such inflections indicate the presence of pyro- and tri-polyphosphate structures in the composition of the ion-exchange fibre. If the initial carbonization temperature is increased, the degree of condensation of the phosphate groups is increased, and this is accompanied by a decrease in the exchange capacity of the fibre.

The character of the potentiometric curves depends further on the initial precursor employed in fibre preparation. This is particularly true for any carboxyl or phenolic groups contained within the fibre, because the dissociation constants of these groups appear to vary over quite wide ranges. This may be due to the development of a non-uniform energy state on the surface over which the functional groups are distributed. Thus, the ion-exchange groups introduced will possess differing chemical activities depending on whether they are located on the edges or faces of crystallites, whether they are linked with aromatic or aliphatic groupings, whether they are close together or far apart, and whether they are located in pores with different adsorption potentials.

Despite possessing a wide range of groups, ion-exchange carbon fibres possess considerable selectivity towards cations, with the following range of exchange capacities having been determined [108]: $NH_4^+ < Na^+ < Rb^+ < Cs^+ < Mg^{2+} < Cd^{2+}, Mn^{2+} < Sr^{2+} < Ca^{2+}, Zn^{2+}, Fe^{2+}, Co^{2+} < Ni^{2+}, Al^{3+} < Y^{3+} < La^{3+} < Cr^{3+} < Be^{2+} < Cu^{2+} < Fe^{3+}$.

When carbon fibres are oxidized using solutions containing nitric acid, the exchange capacity generated depends on the ratio of the components in the solution [113], with an increase in the HNO_3 concentration in the system leading to a considerable increase in the exchange capacity. This capacity also depends substantially on other oxidation parameters, such as the temperature at which oxidation is conducted and the duration of oxidation. Spectral data have shown [110] that the concentration of functional groups on which the ion-exchange properties depend increases with increasing temperature, thus explaining the increase in the exchange capacity under such conditions.

To obtain ion-exchange carbon fibres with an exchange capacity exceeding 2 mg eq. g^{-1}, it is necessary to increase the length of oxidation to more than

3 h or the temperature of the oxidizing solution. Increasing the length of oxidation is not advisible from the strength point of view. Significant structural changes occur in carbon fibres exposed to oxidizing conditions for prolonged periods, with such changes occurring not only on the surface of the fibres but also within their bulk. These are brought about by the movement of defects, linked with diffusional processes, which lead to the break-up of the carbon fibres into longitudinal bundles of microfibrils [114]. Equally, an increase in the temperature of the oxidizing solution is limited by the boiling point of the latter. Because of this, it is not possible to increase the temperature of the oxidizing agent above 122° C when nitric acid solutions are employed [115].

One method of overcoming this problem would be to oxidize carbon fibres with atmospheric oxygen. However, this type of treatment only leads to the introduction of a sufficient number of ionogenic groups at high temperatures, for example at 760° C [116]. In addition, the surface morphology is also changed: a drop in strength occurs and the specific surface area of the material increases. Because the use of gaseous oxidizing agents at high temperatures leads to an irregular change in the properties of the ion-exchange carbon fibres obtained, such methods have not enjoyed widespread application.

These disadvantages are less pronounced when melts of crystal hydrates of various nitrates are employed as oxidizing agents [14]. In a typical treatment [15], fibres which had been carbonized at various temperatures within the range 680 to 810° C were exposed to either $Al(NO_3)_3 \cdot 9H_2O$ or $Fe(NO_3)_3 \cdot 9H_2O$ melts at 140° C or 130° C, respectively, for various periods up to 120 min. Cation-exchange fibres with an increased exchange capacity were generated as a result, with the exchange capacity decreasing only marginally when the carbonization temperature was increased.

This improvement has been attributed to the higher oxidation efficiency of such melts in comparison to boiling HNO_3, allowing high exchange capacities to be achieved after shorter treatment times and enabling the fibre strength to be retained. An increase in the effectiveness of oxidation is possible not only because of the higher temperatures achieved, but also because oxidation involves the participation of the decomposition products of the nitrates which exhibit a high reaction capacity.

Because of these factors, the length of the oxidation period necessary with such melts is much shorter. Thus, in order to achieve an exchange capacity of 2 mg eq. g^{-1} it is only necessary to oxidize carbon fibres carbonized at 810° C for 45 min. If oxidation had been effected by means of a boiling solution of concentrated HNO_3, up to 360 min treatment would have been necessary to achieve the same capacity and this would have been accompanied by a decrease in strength amounting to a factor of 1.9. It is stated that carbon fibres oxidized by $Al(NO_3)_3 . 9H_2O$ melts possess not only narrower micropores but also a greater pore volume than fibres oxidized by HNO_3 [117].

The most widely used sulphonating agents for obtaining ion-exchange carbon fibres are concentrated, sulphuric acid [11, 13, 102, 118–121], oleum [119] and gaseous SO_3 [122]. Ion-exchange carbon fibres with exchange capacitities up to 7.4 mg eq. g^{-1} can be obtained, depending upon the sulphonating agent employed [13]. The optimum ratio between carbon fibre and sulphonating agent (H_2SO_4) is said to be 1 : 10 [118]. The temperature at which sulphuric acid sulphonation is undertaken is such as to achieve an adequate rate of reaction between the carbon fibre and the sulphonating agent, but to avoid thermal decomposition of the acid groups attached to the fibre. On this basis, a temperature range of 170 to 220° C appears to achieve the best results [13, 121].

One method of producing pyrolytic carbon fibres having cation-exchange properties by sulphonation is to subject polymeric organic fibres, such as polyacrylonitrile, cellulose or cellulose-derived fibres, to pyrolysis in a vacuum or in an inert atmosphere. The resulting carbon fibres are washed with water and then sulphonated by heating at 160 to 180° C for 3 h in concentrated sulphuric acid or oleum. In another method [13], carbon fibres prepared by the vacuum pyrolysis of carboxycellulose or aluminium carboxycellulose fibres at 500 to 600° C or 500 to 530° C, respectively, were sulphonated by heating with concentrated sulphuric acid at 170° C for 3 h. Pyrolysis above 500° C gave high ion-exchange capacity but reduced the resistance of the fibres to alkaline solutions.

Because the exchange capacity of the sulpho group does not normally exceed 1 mg eq. g^{-1} [13, 118], such high ion-exchange capacity is achieved mainly through the simultaneous introduction of carboxyl groups brought about by sulphuric acid oxidation of the carbon fibre [13, 120, 121]. As a result, sulphocarbons are polyfunctional ion-exchange materials characterized by two inflection points in their potentiometric curves.

Carbon fibres subjected to a final carbonization temperature of $\sim 1000°C$ do not generate ion-exchange fibres with a satisfactory exchange capacity on sulphonation. This arises from the low reaction capacity of the carbonaceous material, and for this reason SO_3 has been suggested as a more suitable sulphonating agent. Because the reaction of SO_3 with a carbon residue, i.e.

$$R\text{–}H + SO_3 \rightarrow R\text{–}SO_3H$$

takes place without the liberation of water capable of hydrolysing the sulpho groups generated, the exchange capacity of the fibres produced can amount to 4.7 mg eq. g^{-1}.

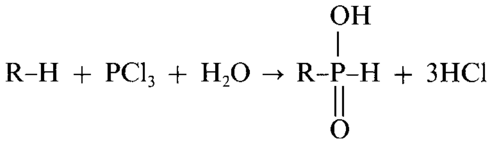
Ion-exchange carbon fibres containing phosphate groups can be obtained by carbonizing phosphorylated cellulose [48, 123, 124]. However, fibres with a sufficiently high exchange capacity are only produced by this method if low carbonization temperatures are employed, with the consequence that the strength of the resulting fibre is low. For this reason, studies have been made of the use of phosphoric acid [100, 119–121] and PCl_3 [12, 100, 125] to phosphorylate unmodified fibres carbonized at temperatures above 500° C.

Only a little phosphorus is introduced into the carbon fibre if phosphoric acid is used alone, so that the exchange capacity of the resulting fibre is not high. Such incorporation of phosphoric acid residues is effected by treating the carbon fibre with orthophosphoric acid at 200 to 220° C for 2 h. Under these conditions the major contribution to the total exchange capacity is from the carboxyl groups introduced as a result of the oxidizing effect of H_3PO_4 under elevated conditions [120, 121]. The resulting phosphorylated carbon fibres contain phosphoric acid residues in which the phosphorus atoms are linked to carbon atoms in the fibre matrix via C–O–P bonds, and are reported as having an exchange capacity of 2.2 mg eq. g^{-1}.

Phosphorus trichloride is much more effective. If carbon fibres are treated with this agent as a vapour [12], it is possible to obtain ion-exchange fibres with an exchange capacity of 1.5 to 4.5 mg eq. g^{-1}. The resulting fibres possess phosphorus atoms linked directly to the carbon atoms in the fibre matrix. Such fibres have a high chemical stability, because the C–P bond in the ionogenic groups is resistant to various agents.

It is also possible to generate ion-exchange fibres by heating carbon fibres in PCl_3 vapour at 200 to 600° C in the absence of oxygen [12]. These fibres contain P(O) OH, COCl and other reactive groups. The rate of phosphorylation depends not only on the temperature but also on the conditions of fibre preparation. Thus, fibres made by pyrolysing cotton in a vacuum at 500° C, after oxidizing them with N_2O_4 (g), were converted to ones containing up to 9.8% P. Phosphorylation with PCl_3 vapour does not change the physical structure of the carbon fibres, and because of the strength of the C–P bonds, the ion-exchange fibres produced exhibit excellent chemical stability and can be used in corrosive media.

The process involved in the phosphorylation of carbon fibres using PCl_3 vapour can be described by the following equation [12]



$$\mathrm{R{-}H + PCl_3 + H_2O \rightarrow R{-}\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle O}{\|}}{P}}{-}H + 3HCl}$$

where R is the carbon fibre residue. Other reactions can occur, however, in particular the formation of acid halides with the liberation of phosphoric acid.

Carbon cation exchangers can also be prepared by the carbonization of cellulosic fibres at 500° C, followed by treatment in a solution of PCl_3 at 75° C for 10 h and then in a 25% solution of nitric acid at 60° C for 8 h. The resulting fibres apparently had an exchange capacity of 4.5 mg eq. g^{-1} [100].

The generation of ion-exchange fibres with satisfactory exchange capacities and mechanical strengths via the phosphorylation of carbon fibres prepared at higher carbonization temperatures using both H_3PO_4 and PCl_3 has not proved to very effective because of the low reaction capacity of such fibres. For this reason, other methods have been sought to increase the strength of phosphate-based ion-exchange fibres derived from carbon fibres subjected to low carbonization temperatures. One such method which shows considerable promise is the treatment of phosphorylated carbon fibres with various resins such as epoxides [126] or styrene formaldehyde [111, 127].

4.2. Protective heat-resistant coatings

Reference has already been made to the increase in thermal resistance exhibited by carbon fibres containing added elements capable of inducing ordered carbon structures at elevated temperatures (see Section 3.1 above). A similar effect is observed if elements capable of reacting with carbon to form carbides at elevated temperatures are employed, because in many instances carbides exhibit higher thermal stabilities. Such an example is provided by zirconium and titanium. Exposure of a carbon fibre containing either of these elements to heat treatment at a temperature of 1250 to 1400° C leads to the formation of the corresponding oxides; however, further reduction to the free metal does not occur on heating to a temperature above 1400° C because under these conditions zirconium and titanium react with carbon to form carbides [2, 128]. Hence, the chemical transformations of additives introduced into cellulose prior to its processing to form element-containing carbon fibres can have a substantial influence on the thermal properties of the end product, not only because of their effect on the structural ordering of the carbon but also because of changes induced in the physical properties of the fibre arising from the formation of a new compound or phase.

In general, if additives are introduced into the cellulosic precursor before thermolysis, the elements involved are distributed throughout the bulk of the element-containing carbon fibres subsequently obtained. Even this type of distribution has a profound influence on the physical and chemical properties of the resulting fibre. Thus, carbon fibres into which molybdenum and vanadium have been incorporated exhibit a considerable increase in surface roughness after exposure to gaseous oxidizing agents arising from enhanced reaction with such agents [129]. Metallic inclusions of this kind often lead to selective corrosion of pits on the surface of the fibre, and this, in turn, induces an increase in the shear strength of epoxycarbon plastics into which such fibres have been introduced [130]. Oxidation of carbon fibres by atmospheric oxygen at high temperatures is similarly enchanced by the introduction of titanium oxide or vanadium pentoxide into their structures [131], or by the incorporation of copper, lead, cobalt or cadmium salts through the use of the corresponding formates, acetates and nitrates [132].

Whereas the additives mentioned above increase the susceptibility of the fibre to oxidation, it is also possible to increase the resistance of the latter to thermal oxidation by distributing heat-resistant components throughout the volume of the carbon material. For example, the heat resistance of carbon fibres can be substantially increased by the introduction of ~ 14% phosphorus into their composition by impregnation with PhP or $(PhO)_3PO$ compounds, followed by annealing at 1500 to 2000° C [133]. Impregnation with boric acid salts, glycerine borate and borobutyl acid, followed by annealing at 350 to 1000° C gives equally good results [134, 135]. An increase in the resistance of carbon fibres towards thermal oxidation can also be produced by introducing elements capable of forming heat-resistant compounds at high temperatures into the composition of the initial cellulose precursor prior to thermal pyrolysis [2, 136], or by chemical modification of the precursor as occurs, for example, during the introduction of boron [37].

In all these cases, the heat-resistant elements are distributed throughout the bulk of the fibre. For practical purposes, however, it is often more desirable to locate such additives (or their compounds) in the surface layer of the fibre. To achieve such a situation, the corresponding elements are not added to the starting cellulosic precursor, nor introduced into the finished fibres as described above, but added to the carbon surface by processing under suitable conditions. Because the chemical changes which now occur involve only the surface layer, such treatment is usually referred to as surface modification of the carbon fibres.

At present, the most widely used method for protecting the surface of a carbon fibre is to coat the latter with a layer of a metallic carbide. The methods by which such protective treatments are undertaken are determined both by the purposes to which the fibres are to be applied, and by the chemical and physical nature of the modifier. Such methods must guarantee a coating thickness sufficient to protect the carbon fibre from oxidative attack without undermining its mechanical strength. Numerous investigations have shown that the optimum thickness for a protective film which meets the above criteria is of the order of $10\,\mu$m, with fibre uniformity and absence of porosity being of decisive importance.

Various methods are available for generating carbide coatings. Thus, titanium and silicon coatings have been produced by heat treating samples of carbon fibres to which the metals have been applied by ionic deposition at 600 to 1500° C [5, 6]. A very widely used method is the precipitation of carbides from the gaseous phase, brought about by reduction of various halides with hydrogen and methane. Typical examples are provided by $SiCl_4$ [9, 10], methylchlorosilane [137] and volatile halides of refractory metals [138]. Depending on the choice of reagent, the optimum temperature for carbide formation varies between 1100 and 2200° C.

Carbide coatings of the required thickness are obtained by varying the length of exposure of the fibre to chemical treatment. Hence, a protective layer of adequate thickness has been formed by treating carbon fibres for 10 min in a mixture of hydrogen gas and the vapours of silicon compounds; when the treatment was extended to 30 min, fibres composed entirely of silicon carbide were obtained [139, 140]. Protective silicon carbide coatings have also been achieved by impregnating carbon fibres with a solution of an organosilicon polymer, followed by annealing at 600 to 1400° C [8].

Refractory oxides have not been used directly for the formation of protective surface layers. Extensive use has been made, however, of such oxides as an intermediate stage in the formation of carbide coatings. Thus, preformed carbon fibres have been impregnated with solutions of oxygen-containing compounds of various elements and subjected to heat treatment to provide protective coatings [141–144]. The temperatures employed depend on the elements introduced, being 700 to 1200° C for titanium [143], ~ 1400° C for zirconium [2, 128] and 1400 to 2500° C for tantalum, rhenium and tungsten [141]. However, the formation of carbides during thermal decomposition of salts deposited on carbon fibres can also take place without the intermediate formation of oxides, particularly in those cases where reducing agents are employed during the annealing process [145].

Nitride coatings are obtained following the high-temperature treatment of carbon fibre samples containing compounds of elements capable of forming nitrides in the presence of a nitride-containing gas or vapour [146]. Such coatings can also be produced by precipitation from the gaseous phase [147, 148]. Thus, nitride precipitation in the form of a thin film on to a carbon fibre has been achieved via the reaction of volatile boron compounds with a nitrogen/hydrogen mixture at high temperatures [147]. Carbon fibres may also be protected against oxidation by applying a glassy layer to their surfaces [149]. In a typical example, a phosphate glass, free from alkali metals but containing Al_2O_3, P_2O_5, SiO_2 and ZnO, has been applied at 1100 to 1300° C.

The use of plasma treatment for the surface modification of carbon and metal-containing carbon fibres (aluminium, iron, chromium, cerium) seems most promising [150–154], with both argon and hydrogen plasmas at relatively low temperatures (9000 to 12 000° C) being employed for such purposes. The particular features of plasma treatment which make it more attractive than traditional coating methods are (i) the possibility of very rapid warm-up and cooling, (ii) the presence of a high temperature gradient along the fibre radius, and (iii) the possibility of inducing sublimation processes on the surface of the fibre [153]. Thus, short-term treatment (0.6 to 21.1 sec) of carbon fibres containing ZrO_2 in an argon plasma at 10 000 to 12 000° C smoothed out the fibre surface, increased the stability of the fibre towards high-temperature oxidation and decreased its electrical resistance as a result of the formation of ZrC both on the surface and throughout the cross-section of the fibre [153]. If the contact time of the sample with the plasma is increased the carbide content is further enhanced, and this also increases the resistance of the fibre towards thermal oxidation. In addition, plasma treatment anneals cracks and other defects within the material without impairing the inner structure of the carbon fibre; this enhances the resistance of the material towards thermal oxidation [152, 154].

The use of plasma treatment has also been extended to activated carbon cloths [155]. When a hydrogen plasma was employed with such a cloth, its main effect was to induce a reduction in the fibre diameter with no apparent change in its surface morphology. Water sorption and heat of immersion measurements showed that the effect of the plasma did not extend to the narrower pores in the material, however. Although the action of a carbon dioxide plasma appeared to be similar to that of a hydrogen plasma, gross changes in fibre morphology were observed in this instance.

Surface modification of carbon fibres induces other changes in properties which greatly improve and extend the various fields of application of these materials. One example is provided by the formation of carbide coatings: because such coatings involve deposition in the cavities, cracks, etc. already existing on the fibre surface, they also have the ability to increase the mechanical strength of the resulting material [138, 156]. Indeed, it has been reported that the formation of a carbide coating produces carbon fibres with superconducting properties [157]. The formation of a metallic coating apparently increases the wettability of a carbon fibre surface as a result of the formation of various metallocarbon compositions [136]. It is also interesting that such a coating can act as a barrier layer, and thus block any undesirable back-diffusion of components out of carbon fibres at high temperatures. Finally, it has been shown that electrolytic treatment of the surface of a carbon fibre with the melt of a $KF(HF)_n$ complex leads to the development of water-repellent properties.

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