

High performance carbon–carbon composites

LALIT M MANOCHA

Department of Materials Science, Sardar Patel University, Vallabh Vidyanagar
388 120, India

Abstract. Carbon–carbon composites rank first among ceramic composite materials with a spectrum of properties and applications in various sectors. These composites are made of fibres in various directions and carbonaceous polymers and hydrocarbons as matrix precursors. Their density and properties depend on the type and volume fraction of reinforcement, matrix precursor used and end heat treatment temperature. Composites made with thermosetting resins as matrix precursors possess low densities ($1.55\text{--}1.75\text{ g/cm}^3$) and well-distributed microporosity whereas those made with pitch as the matrix precursor, after densification exhibit densities of $1.8\text{--}2.0\text{ g/cm}^3$ with some mesopores, and those made by the CVD technique with hydrocarbon gases, possess intermediate densities and matrices with close porosities. The former (resin-based) composites exhibit high flexural strength, low toughness and low thermal conductivity, whereas the latter (pitch- and CVD-based) can be made with very high thermal conductivity ($400\text{--}700\text{ W/MK}$) in the fibre direction. Carbon–carbon composites are used in a variety of sectors requiring high mechanical properties at elevated temperatures, good frictional properties for brake pads in high speed vehicles or high thermal conductivity for thermal management applications. However, for extended life applications, these composites need to be protected against oxidation either through matrix modification with Si, Zr, Hf etc. or by multilayer oxidation protection coatings consisting of SiC, silica, zircon etc.

Keywords. Carbon fibres; carbon–carbon composites; high temperature materials; mechanical/thermal properties.

1. Carbon–carbon concept

Carbon is a truly remarkable element existing as four allotropes, viz. diamond, graphite, carbynes and fullerenes, each having significant scientific and technological importance. Its most abundant allotrope, graphite, can take many forms with respect to microstructure, amorphous to highly crystalline structure, highly dense with density 2.2 g/cm^3 to highly porous with density 0.5 g/cm^3 and different shapes. These types of graphites are called synthetic carbons and in technical terms, engineered carbons. Examples are cokes, graphite electrodes, mechanical carbons, glassy carbons, carbon black, porous carbons, activated carbons, carbon fibres and composites etc.. Solid carbons are preferred for structural applications under extreme environmental conditions of temperature or corrosion (liquid as well as gaseous) etc. This is mainly because, theoretically, carbon materials with covalently bonded atoms possess very high specific strengths ($40\text{--}50\text{ GPa}$) and retain this strength at high temperatures

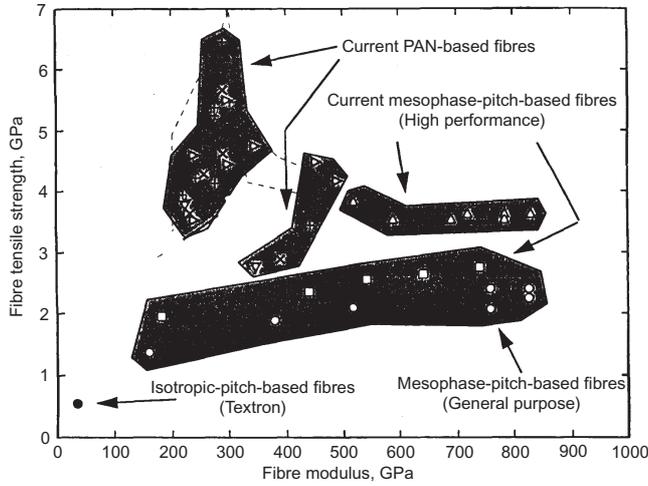


Figure 1. Mechanical properties of commercial PAN-based and mesophase pitch-based carbon fibres.

in the temperature range over 1500°C (Pierson 1993; Burchell 1999). However, the normal bulk synthetic graphite exhibits less than 2% of the theoretical strength. Therefore, for long there has been a quest by scientists to explore and achieve the maximum possible strength in carbon materials. This, coupled with the requirement of high performance reinforcing fibres for composite materials, had led to the development of carbon fibres (Fitzer 1989).

Over the past three decades, carbon fibres have proved to be the main reinforcement for advanced composites for a wide range of applications. The majority of products still belong to high technology space and aeronautics (Manocha 2001). Carbon fibres are a few micron thick, light weight, very strong and stiff black synthetic fibres with long aromatic molecular chains comprising mainly carbon. These fibres are capable of maintaining their structure and properties under extreme conditions of temperature and pressure, fluids etc. and therefore can be used with all types of matrices, polymer, ceramic and metal, employing different composite processing techniques. Interest in carbon fibres as reinforcement for composites for structural applications started with the demand from the aeronautical sector for light weight strong and stiff material. Subsequently its application extended to civilian sector, especially in sports goods and biomedical sectors (Edie 1998). Though major consumption of carbon fibres is for polymer matrix composites, these are the only choice materials for special application high temperature composites with specific high thermal and thermo-mechanical properties. This kept alive the interest in carbon and carbon fibre research. Presently a large variety of carbon fibres derived from PAN (polyacrylonitrile polymers) and pitch precursors with varying properties are available, some in the open market and some for restricted sale. Figure 1 shows present status of these fibres. However, the properties are getting continuously upgraded.

Carbon fibre reinforced carbon matrix composites or the so called carbon-carbon (C/C) composites have densities in the range $1.6\text{--}2.0\text{ gm/cm}^3$, much lower than those of metals and ceramics and hence make lower component weight an important consideration for aero-vehicles (Buckley 1988; Fitzer & Manocha 1998). Some of the most important and useful properties of carbon-carbon composites are light weight, high strength at high temperature (3000°C) in non-oxidising atmospheres, low coefficient of thermal expansion, high thermal conductivity (higher than that of copper and silver), high thermal shock resistance and low recession in high pressure ablation environments. The mechanical strength of C/C increases with temperature, in contrast to the strength of metal and ceramics, which decrease with

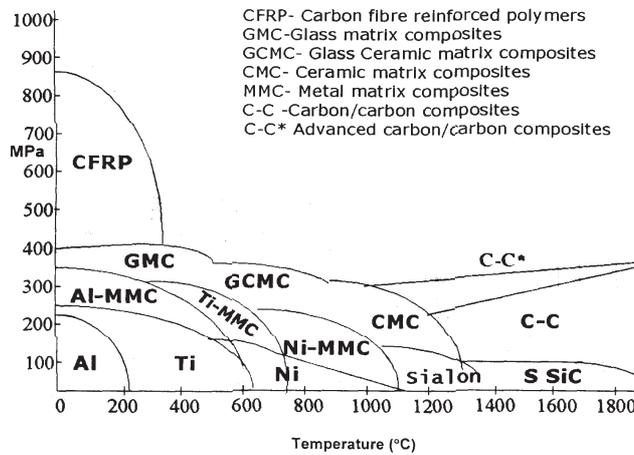


Figure 2. Variation of strength of some engineering materials with temperature.

increasing temperature (see figure 2). These extraordinary properties of carbon/carbon composites have made these materials extremely useful right for aerospace and defence applications such as brake discs, rocket nozzles, leading edges of re-entry vehicles, furnace heating, thermal management components in space vehicles etc. to those for common man as biomedical implants, glass and high temperature glass and ceramic industry etc. (Fitzer & Manocha 1998). A well-known example for the practical application of C/C composites is in the American Space shuttle, wherein the fuselage nose and the leading edge of the wings are manufactured from C/C composites and have withstood a total of 100 missions under the extreme re-entry condition (Kochendorfer 2001). A national programme has been launched in India for indigenous development of carbon/carbon composite and related technologies. These composites have been successfully developed and used as nose-tip for the Agni missile and as brake pads for LCA.

2. Processing of carbon/carbon composites

Like carbon, carbon-carbon composites can also be manufactured by using different techniques such as all solid pyrolysis using thermosetting resins, or pitch route using liquid infiltration carbonization route or CVD route. Fabrication method of C/C composites involves fabrication of a 3D (three directionally reinforced) or MD porous carbon fibre preforms having the desired shape or a porous carbon-carbon skeleton (UD, 2D or 3D) with carbon fibres and a carbonaceous matrix followed by their densification (see figure 3). The densification can be achieved through vapour phase infiltration (CVI) wherein the hydrocarbon gases such as methane, propane etc. infiltrate into porous fibrous structure heated to a temperature of 1000–1400°C and are made to crack therein. Commercially, isothermally heated stack of components are impregnated simultaneously in a large-size furnace. Principally, the gases should infiltrate into the pores and interfilamentary spaces and then crack. But these gases have a tendency to crack at the outer surface itself which blocks the passages and causes closed pores. In order to have dense composites, the surfaces are ground and the components are reinfiltreated. CVD is a very slow process and it takes months together to get dense carbon-carbon composites. Porous structures can also be impregnated with liquid phase pitch/phenolic resin followed by carbonisation and high temperature heat treatment (1000–2700°C). Pyrolysis of the pitch/resin matrix can be done under normal pressure or under high pressure (HIP).

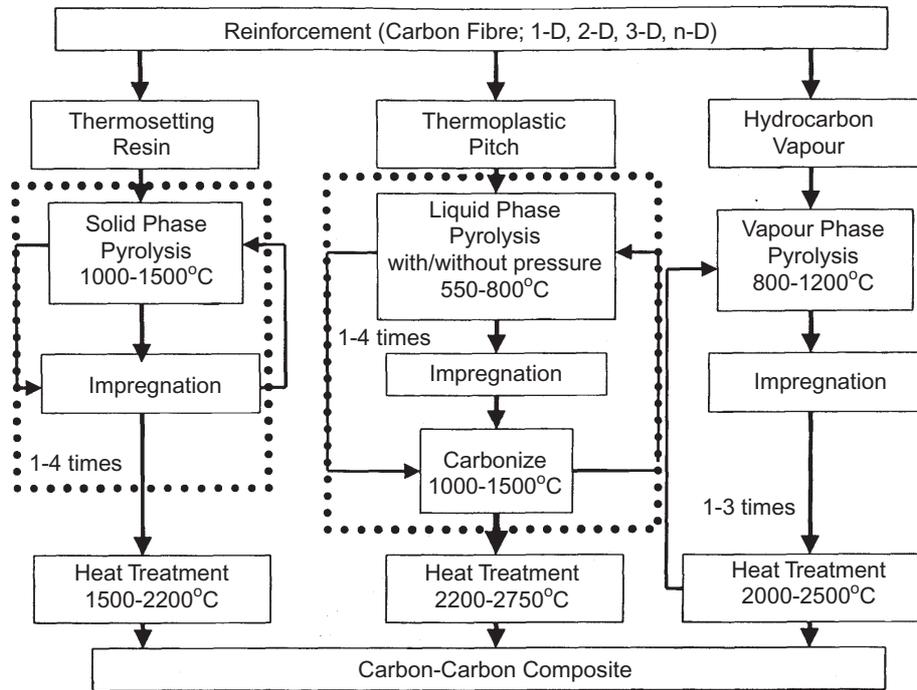


Figure 3. Processing of carbon/carbon composites.

Depending on the densification approach, two or more densification cycles are required to get the desired density, the number of impregnation cycles being fewer when HIP processes is used. A new approach of intermediate graphitisation has been evolved in which the composites after certain impregnation/normal pressure carbonisation cycles are heat-treated to high temperature and then reimpregnated. This intermediate high temperature heat treatment opens up the pores for further infiltration. Figure 4 shows generic comparison of densification processes. Often a combination of processing routes is used. These comprise fabrication of host composites using a pitch or resin route followed by densification and pore sealing by CVD.

3. Structural aspects of carbon–carbon composites

Prime factors of importance in achieving tough and high thermal conductive carbon/carbon composites are proper choice of reinforcing carbon fibres, carbon matrix microstructure, density and macrostructure of the composites. Processing routes and the choice of carbon precursor greatly influence the density, macrostructure (type, size and quantities of defects i.e., defects, pores, cracks etc.) and matrix microstructure (orientation of graphitic planes). Some of these striking structural features of carbon/carbon composites are listed in table 1 and are shown in the SEM micrograph of the composites (see figure 5). The voids and macrocracks are normally fewer in pitch-derived C/C composites processed through HIP route than in those made by CVD route or phenolic resin derived carbon route. The latter exhibit low densities. These features also control the thermal transport mechanism in carbon–carbon composites. In order to have desired fibre/matrix bonding and to reduce cracking at the fibre/matrix interface, pyrolytic carbon coatings are also used at the surface of the fibres.

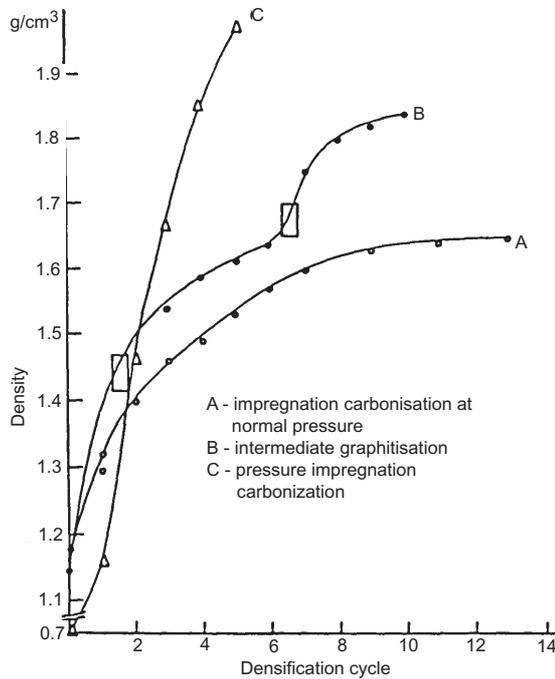


Figure 4. Increase in density of carbon/carbon composites with densification.

The matrix microstructure (degree of graphitisation) is also an important aspect governing the properties of carbon-carbon composites. From the strength point of view, a semicrystalline or randomly oriented carbon matrix is desired which can arrest crack propagation whereas for thermal and electrical properties, highly graphitic matrix is a prerequisite. The development of crystalline carbon matrix originates from CVD route or pitch route. Thermosetting polymer route result in amorphous carbon matrix. However, in composites made with high strength carbon fibres or surface treated carbon fibres, due to strong fibre/matrix bonding at polymer stage and differential pyrolysis shrinkage in fibres and matrix, thermal stresses are generated

Table 1. Micro/macrostructural features of carbon/carbon composites and their effect on composites properties.

Nature	Scale	Position	Effect
Micromechanical cracking	Fibre dia scale	Cracking in matrix Fibre/matrix interface	Load transfer among fibres Transverse properties of fibre bundles
Minimechanical cracking	Cloth layer thickness scale	Fibre bundle Interface between fibre bundles Interyarn pocket of unreinforced matrix Interface between fibre bundle and matrix pocket Matrix-matrix interface	Porosity Load transfer among fibre bundles and laminaes Major influence on mechanical & thermal properties

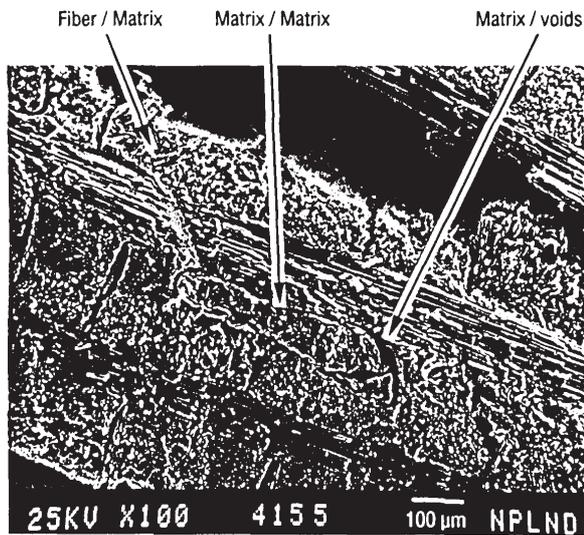


Figure 5. SEM micrograph of a 2D carbon/carbon composite.

in the matrix which on heat treatment to 2000°C and above cause stress graphitisation of the matrix (Rand 1993; Manocha 1994; Fitzer & Manocha 1998). This subject has been of great scientific interest, especially correlating fibre/matrix bonding and resulting orientation of graphite basic structural units in the matrix. The technological importance of this phenomenon has been to control the fibre/matrix bonding so that low priced carbon fibres can be used for making carbon/carbon composites for mechanical and general purpose application.

4. Properties of carbon–carbon composites

Carbon/carbon composites in the true sense, cover a large range of materials with the targeted properties. The properties of interest are strength and stiffness, fracture toughness, frictional properties, thermal conductivity and resistance to oxidation at high temperatures. The operating mechanisms for these properties are quite different, especially in such multiphase composite materials. The mechanical properties of the constituents and their volume fraction, bonding, and crack propagation mechanism control the mechanical properties of the composites, whereas thermal properties are governed by thermal transport phenomena. Moreover, the constituents, both reinforcement and matrix, are likely to undergo a change in properties during processing as influenced by heat treatment temperature, differential dimensional changes, thermal stresses etc. All these factors influence the ultimate properties of the composites. It is difficult to cover completely all these aspects in this article. However, a general trend of the most fascinating properties of carbon/carbon composites are given below.

4.1 Mechanical properties of carbon–carbon composites

The strength and fracture of carbon/carbon composites are governed by the Cook–Gorden theory for strengthening of brittle solids (Cook & Gorden 1964), which states that if the ratio of the adhesive strength of the interface to the cohesive strength of the solid is in the right range, a large increase in strength and toughness of otherwise brittle material is achieved. Extensive work has been done in achieving highest possible translation of fibre properties in carbon/carbon composites. Composites with strong fibre/matrix bonding fail

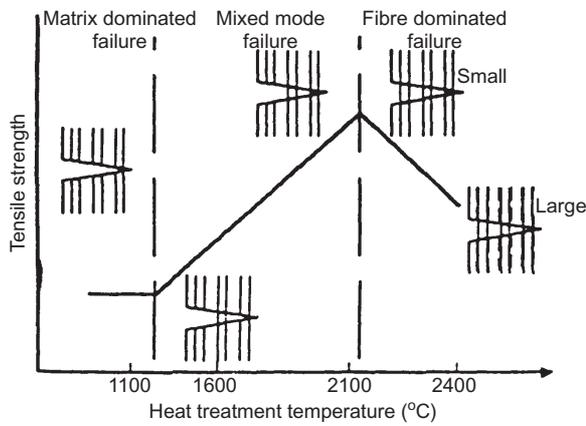


Figure 6. Effect of heat treatment temperature on strength and fracture mode of carbon/carbon composites – a general view.

catastrophically without fibre pull-out while those with controlled interface fail in mixed tensile cum shear mode exhibiting high strength (Manocha 1988, 1994). A generalised view of the effect of processing temperature, on fracture modes and strengths of different types of carbon/carbon composites is given in figure 6. Numerical values of the mechanical properties of the composites are dependent on the fibre architecture and the direction of measurement of the properties w.r.t. fibre orientation etc. as shown in figure 7. Other architectures and fibre lay-ups (angle-plyed, sandwiched) have similar effects and the values lie in-between (Fitzer & Manocha 1998). Similarly, these composites exhibit a range of high fracture toughness (20–100 Nm m^{3/2}) and good creep and fatigue resistance. When subjected to high temperature testing, carbon/carbon composites have been found to exhibit about 10–20% increase in mechanical properties at 2000°C under inert atmosphere. However, in air, the properties drop down to 10–20% depending on the temperature and time i.e. the weight loss. Carbon is a stable and highly sought after material for nuclear applications. So are carbon/carbon composites. Under neutron irradiation at low fluence levels of 10²¹n/cm², these composites exhibit an increase in strength and fracture toughness by 20–30% and Young’s modulus by about 30%.

4.2 Thermal properties of the composites

Carbon/carbon composites being of heterogeneous structure consisting of fibres, matrix and pores, with the first two having a variety of microstructures, estimation of their thermal trans-

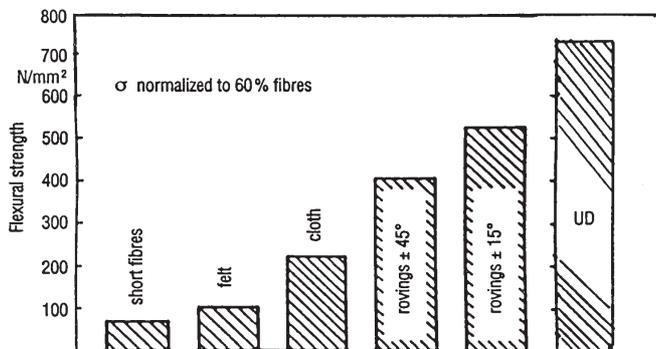


Figure 7. Strength of carbon-carbon composites with fibre orientation.

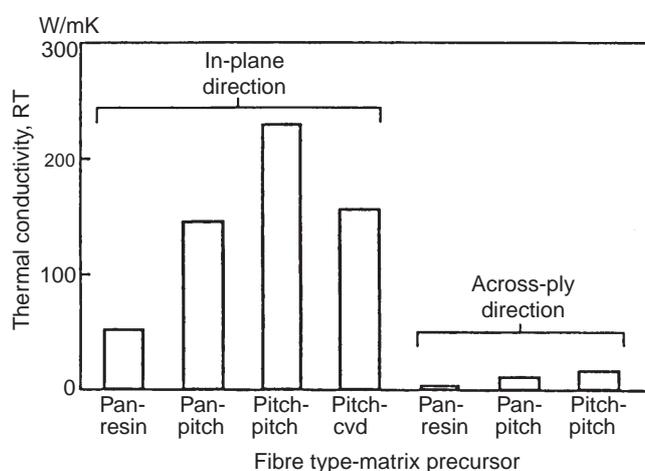


Figure 8. Thermal conductivity of carbon/carbon composites with different fibre/matrix combinations.

port properties becomes complex. However, carbon/carbon materials with tailored thermal conductivities can be fabricated by proper choice of constituents, their configuration, and processing conditions. A comparison of thermal conductivities of carbon/carbon composites with different fibre/matrix combinations is given in figure 8. Composites having highly oriented graphitic fibres or matrices or their combination, like vapour-grown carbon fibres and matrix or mesophase pitch-based carbon fibres and matrix, exhibit very high thermal conductivities of the order of 250–350 W/MK in the fibre direction. Though these composites exhibit highly anisotropic character and low conductivities in transverse directions, there is always scope of improvement by varying the fibre architecture and their addition in different forms and ways. Coefficient of thermal expansion of the composites is dictated largely by the fibre orientation. It is 0–1 ppm/°C in the fibre direction and 6–8 ppm/°C in a direction perpendicular to the fibres.

4.3 Frictional properties of the composites

Carbon–carbon composites have widened the scope of application of carbon-based materials in wear-related applications from bearing seals and electrical brushes to brake pads for heavy duty vehicles such as military, supersonic and civilian aircrafts to trucks and railways. This has been due to basic tribological properties of carbon with additional high strength and thermal conductivity contribution from the reinforcing fibres. Carbon/carbon composites exhibit low coefficient of friction μ in the fibre direction (0.3–0.5) and 0.5–0.8 in the perpendicular direction. Wear rates also follow similar trends (0.05–0.1 and 0.1–0.3 mm). The friction and wear mechanism of carbon/carbon composites on application of brakes is quite complex and various factors like peak temperature, formation of debris and films on sliding surfaces further effect the coefficient of friction etc. which is too vast to cover here. In general, for fabricating brake discs for different vehicles, different types of fibres (PAN and pitch-based high strength and high thermal conductivity) are used in a number of configurations, either alone or in combinations with carbon matrix derived from different type of precursor, pitch or CVD. In commercial carbon–carbon brake pads, carbon fibre fabric plies are used with fibre tows inserted in the third direction and pitch/CVD route for densification. However, choice of the constituents and processing parameters is at the discretion of the manufacturers.

5. Oxidation protection of carbon/carbon composites

Carbon is prone to reaction with oxygen at temperature of 450°C and above. For long time application of these composites at elevated temperature in a normal environment, it is essential that these composites be protected against oxidation. Therefore studies on oxidation protection of carbon/carbon composites are as important as the development of the composites themselves. Oxidation protection systems for carbon/carbon composites are based on (i) modification of matrix through addition of some oxidation inhibitors (like B, Si, Zr or their compounds) or/and (ii) deposition of ceramic coatings on the surface. These coatings are generally multilayer coatings of functionally gradient materials of carbides, nitrides and oxides of Si, Zr, Ta, Al etc. (Mckee 1981; Fitzer & Manocha 1998)

6. Applications of carbon/carbon composites

Carbon/carbon composites, developed about three decades ago to meet the needs of the space programme, are nowadays considered high performance engineering materials with potential application in high temperature industries. Accordingly, steady growth also prevails in the civil market segment. In terms of mass consumption, the main application of carbon/carbon composites are still in high performance braking systems. New innovations still owe to requirements from space industries. In general engineering sectors these are used in engine components, as refractory materials, as hot-pressed dies and heating elements, as high temperature fasteners, liners and protection tubes, as guides in glass industries etc. Some of the applications are shown in figure 9. Carbon/carbon composites have great potential in energy

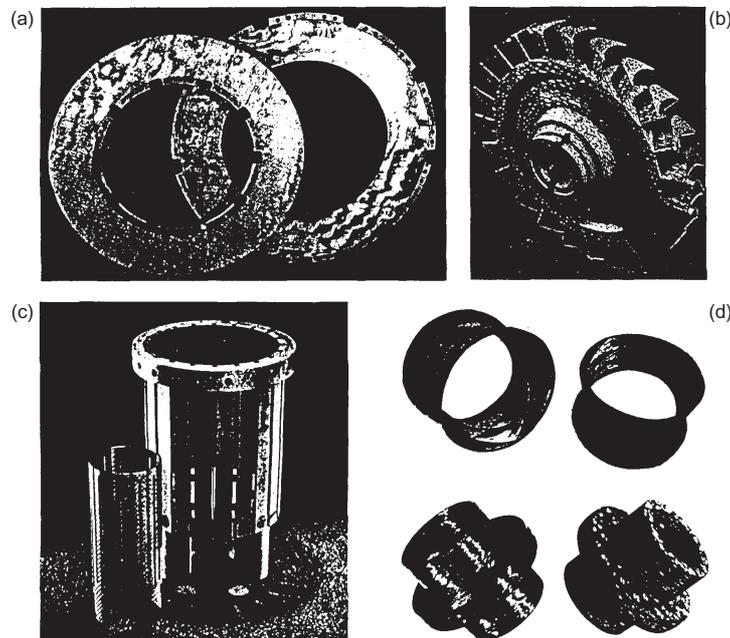


Figure 9. Carbon/carbon composite components. (a) carbon-carbon brake discs, (b) turbine rotor, (c) resistance-heating elements, (d) protection tubes and grids.

sectors as polar plates for fuel cells, in storage batteries etc. As the technology becomes more economical a viable, more and more applications get evolved.

7. Conclusions

With carbon fibre reinforcements in different forms and directions and thermosetting resins or thermoplastic pitches or hydrocarbon gases as matrix precursors, these composites can attain densities between 1.6–1.98 g/cm³. Reinforcing fibres are more anisotropic in structure and properties than the carbon matrix. Accordingly, the properties of carbon–carbon composites are dependent on fibre volume content and fibre orientation. Unlike polymer matrices, carbon matrices contribute significantly to the ultimate properties of the composites, especially in case of pitch and CVD-derived carbon matrices. Carbon–carbon composites are a family of materials with choice of variation in fibre and matrix architecture, structure, microstructure, mechanical, thermal and physical properties etc. Hence these provide high performance materials for application in a number of sectors.

References*

- Buckley J D 1988 *Ceram. Bull.* 67: 364
Burchell T D 1999 *Carbon materials for advanced technologies* (Pergamon)
Cook J, Gorden J E 1964 *Proc. R. Soc. London A2*: 508
Edie D D 1998 The effect of processing on the structure and properties of carbon fibres. *Carbon* 36: 345–362
Fitzer E 1989 *Carbon fibers – Present state and future applications in carbon fibers, filaments and composites* (eds) J L Figueiredo *et al* (Kluwer Academic) pp 3–41
Fitzer E, Manocha L M 1998 *Carbon reinforcements and carbon–carbon composites* (Berlin: Springer-Verlag)
Kochendorfer R 2001 *Ceramic matrix composites in ceramic engineering and science* (eds) M Singh, T Jessen (Am. Ceram. Soc.) vol. 22, pp 11–22
Pierson H O 1993 *Handbook of carbon, graphite, diamond and fullerenes* (Noyes)
Manocha L M 1988 *Carbon* 26: 333
Manocha L M 1994 *Carbon* 32: 213
Manocha L M 2001 Carbon fibres. In *encyclopaedia of materials science and technology* (eds) K J Jurgen Buschow *et al* (Elsevier) pp 906–916
McKee D W 1981 In *Chemistry and physics of carbon* (eds) P L Walker, P A Throver vol.1, p. 1
Rand B 1993 Matrix precursor for carbon–carbon composites. In *Essentials of carbon–carbon composites* (ed.) C R Thomas (London: R. Soc. Chem.)

*References in this list are not in journal format