CHAPTER 1

INTRODUCTION AND SCOPE OF THE PRESENT WORK
1.11 THE ELEMENT CARBON:

The word carbon is derived from the Latin “carbo”, which to the Romans meant charcoal (or ember). In the modern world, carbon is, of course, much more than charcoal. From carbon come highest strength fibers, one of the best lubricants (graphite), the strongest crystal and hardest material (diamond), an essentially non-crystalline product (vitreous carbon), one of the best absorbers (activated charcoal), and one of the best helium gas barriers (vitreous carbon). A great deal is yet to be learned and new forms of carbon are still being discovered such as the fullerene molecules and the hexagonal polytypes of diamond.

These very diverse materials, with such large differences in properties, all have the same building block - the element carbon.

The carbon element is the basic constituent of all organic matter and the key element of the compounds that form the huge and very complex discipline of organic chemistry.

The element carbon is widely distributed in nature [1]. It is found in the earth’s crust in the ratio of 180 PPM, most of it in the form of compounds [2]. Many of these natural compounds are essential to the production of synthetic carbon materials and include various coals (bituminous and anthracite), hydrocarbons complexes (petroleum, tar and asphalt) and the gaseous hydrocarbons (methane and others).

Only two polymorphous of carbon are found on the earth as minerals: natural graphite and diamond.
1.12 ALLOTROPIC FORMS OF CARBON:

Carbon based on its crystalline structure can be broadly categorised into colourless diamond and black carbon (graphite) which are the two well known allotropic forms of carbon. Recently a new allotrope of carbon has been investigated, which is called fullerene (buckminster). Fig. 1.1 shows the structures of these forms of carbon.

Diamonds are crystals with cubic systems which are extremely hard and which have a regular tetrahedron structure with carbon atoms at each of the four corners and in the centre. Graphite is a crystal with lubricating properties and extreme softness. It belongs to the hexagonal system (rarely rhombohedral system) in which hexagonal planar networks are stacked in a layered form.

Carbon is the sixth element (atomic number 6) and is on the upper most line of period IVb in the periodic table. Its electronic configuration in the normal state of carbon is \(1s^22s^22p^2\). There are two valence electrons in 2s and 2p. One 2s electron is excited and enters into the 2P orbital when carbon atoms are bonded, and the electronic configuration becomes \(1s^22s^22p^3\). The fact that carbon can assume a valence of four electrons, these four valence electrons can form equivalent orbitals by blending of the three 2p orbital electrons and one 2s orbital electron, specifically by formation of hybridised orbital. Moreover, the directionality of the bond can be given. Such hybridisation is termed an \(sp^3\) hybrid. This forms the regular tetrahedron diamond crystals. Specifically, four orbitals directed uniformly at the four apexes with equal angles from the centre of the regular tetrahedron are formed and those can form the basic cubic system structure of diamond by bonding through covalent bonds with adjacent carbon atoms.

If one 2s electron is hybridised with two of the three 2p electrons and when three hybrid orbitals, specifically \(sp^3\) hybrid orbitals are formed, these are oriented with 120° angle on a plane. A hexagonal reticular plane is formed through covalent bonding with adjacent carbon atoms. This is the graphite crystal. The remaining one 2p electron is oriented perpendicularly to the plane. This is termed as the \(\pi\) electron. The
Fig. 1.1 Structure of different types of carbons: (a) Graphite (b) Diamond (c) Polymeric carbon (d) Fullerene
three electrons participating in the formation of the plane are termed $\sigma$ electrons. The $\pi$ electrons mutually overlap above and below the plane, form a weak Van der Waals bond among the reticular planes and provide the characteristic properties of graphite. Various characteristics of diamond, graphite and carbon are shown in Table 1.1.

<table>
<thead>
<tr>
<th>Name of allotrope</th>
<th>Diamond</th>
<th>Graphite</th>
<th>Carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hybrid electron orbital</td>
<td>sp$^3$</td>
<td>sp$^2$</td>
<td>sp</td>
</tr>
<tr>
<td>Mode of bond</td>
<td>Single bond</td>
<td>Double bond</td>
<td>Triple bond</td>
</tr>
<tr>
<td>Structure</td>
<td>Cubic (regular tetrahedron)</td>
<td>Planar (hexagonal recticular plane)</td>
<td>Linear</td>
</tr>
<tr>
<td>Covalent bond distance of atoms ($\text{Å}$)</td>
<td>1.54 (C=C:1.54)</td>
<td>1.42 (C=C:1.33)</td>
<td>- (C=C:1.20)</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>3.52</td>
<td>2.26</td>
<td>1.9~2.0</td>
</tr>
<tr>
<td>Mohs hardness</td>
<td>10</td>
<td>2</td>
<td>Intermediate between diamond and graphite</td>
</tr>
<tr>
<td>Electrical conductivity</td>
<td>Insulator</td>
<td>Conductor</td>
<td>Semiconductor</td>
</tr>
<tr>
<td>Specific heat ($\text{kJ/Kg.k}$)</td>
<td>0.12</td>
<td>0.17</td>
<td>Greater than graphite</td>
</tr>
<tr>
<td>Heat of combustion</td>
<td>$\sim 7873$</td>
<td>$\sim 7850$</td>
<td>$\sim 7100$</td>
</tr>
<tr>
<td>Colour</td>
<td>Colourless-transparent</td>
<td>Black</td>
<td>Black</td>
</tr>
</tbody>
</table>

Table 1.1: Allotropic forms of carbon and their characteristics.
CRYSTAL STRUCTURE OF GRAPHITE:

Usually, carbon materials belong to the graphite system due to the crystal structure, but they are usually categorised conventionally carbon and graphite for convenience. Because of the lower crystallinity carbon can be referred as amorphous carbon and graphite as one of the allotrope of carbon. There is no distinct transition point between carbon and graphite.

Graphite is composed of series of stacked parallel planes shown schematically in fig. 1.2, with the trigonal $sp^2$ bonding.

In the fig. 1.2, the circles showing the position of the carbon atoms do not represent the actual size of the atom. Each atom, in fact, contacts its neighbours. Within each layer planes, the carbon atom is bonded to three others, forming a series of continuous hexagons in what can be considered as an essentially infinite two-dimensional molecule. The bond is covalent (sigma) and has short length (0.141 nm) and high strength (524 KJ/mole). The hybridised fourth valence electron is paired with another delocalized electron of the adjacent plane by much weaker Van der Waals bond (a secondary bond) of only 7 KJ/mole (pi bond). Carbon is the only element to have this particular layered hexagonal structure. The spacing between the layer planes is relatively large (0.335 nm) or more than twice the spacing between atoms within the basal plane.

The stacking of layer planes occurs in two slightly different ways: hexagonal and rhombohedral.

The most common stacking sequence of the graphite crystal is hexagonal with a - ABABAB - stacking order, in other words, where the carbon atoms in every other layer are superimposed over each other as shown Fig. 1.2[a(i)]. A view of the stacking sequence perpendicular to the basal plane is given in figure 1.2[a(ii)].

The hexagonal graphite is the thermodynamically stable form of graphite and is found in all synthetic materials.
Fig. 1.2 Stacking of layer planes in the graphite crystal.
The other graphite structure is rhombohedral with the stacking order - ABCABCABC -. The carbon atoms in every third layer are superimposed. A view of the stacking sequence perpendicular to the basal plane is also given in figure 1.2 [b (i and ii)].

Rhombohedral graphite is thermodynamically unstable and can be considered as an extended stacking fault of hexagonal graphite. It is never found in pure form but always in combination with hexagonal graphite, at times upto 40 % in some natural and synthetic materials. It is obvious in both the structures that no basal plane lies directly over another one.

1.14 POLYCRYSTALLINE GRAPHITE:

Carbon material produced industrially is called polycrystalline graphite. This is an irregular aggregation of large numbers of graphite crystals disordered in greater or lesser amounts in the structure of unit crystals themselves. Pyrolytic graphite, carbon fiber-carbon matrix composites (Carbon-Carbon), vitreous carbon, carbon black and many others, are actually aggregates of graphite crystallites or they are called as polycrystalline graphites [2]. The properties of the polycrystalline graphite result from a combination of various factors, including the type of bonding and aggregation, the size of the crystals which constitute the carbon material, as well as the disorder of the crystalline structure. A wide variation in properties are thus possible in polycrystalline graphite. For instance, the apparent crystallite size perpendicular to the layer planes (Lc) of some vitreous carbons may be as small as 1.2 nm which is the length of a few atoms, or upto 100 nm found in highly ordered pyrolytic graphites. The layer planes may or may not be perfectly parallel to each other, depending whether the material is graphitic or non-graphitic carbon. Some soot, are extremely small and contain only a few small crystallites. In such cases, the properties are mostly related to the surface area. Other aggregates may be relatively large and free of defects and essentially parallel to
each other, in which case the structure and its properties closely match those of the ideal graphite crystal. Such large aggregates are often found in pyrolytic graphite.

In other aggregates, the crystallites have an essentially random orientation. This occurs in turbostratic or amorphous carbon shown in figure 1.1c. In such cases the bulk properties are essentially isotropic.

The material differences in the various carbon materials were originally ascribed to the presence of an "amorphous" component. (as in lampblack for instance), presently, a more realistic approach is to relate these differences to the size and orientation of the graphite crystallites [2].

1.2 PROPERTIES OF GRAPHITE:

A wide range of materials come under the heading of carbon or graphite and these materials often have properties that are much different from those of the ideal graphite crystal (i.e. material that most closely corresponds to an infinitely large crystals). Obviously it is necessary to define the material accurately when speaking of the properties of "Carbon" or "graphite".

Anisotropy of the graphite crystal:

The peculiar crystal structure of graphite results in a considerable anisotropy, that is the properties of the material may vary considerably when measured along the ab directions (within the plane) or the c-direction (perpendicular to the planes). Such anisotropy, especially in electrical and thermal properties, can often be put to good use.

(a) Thermal Properties:

The physical properties are essentially unaffected by the size and orientation of the crystallites in the aggregate (with the exception of density). As a result, they can be considered valid for all forms of graphite. This is no longer true for some of the properties like electrical and thermal properties and these properties may vary
considerably depending on crystallite size and orientation and other factors related to the processing conditions.

The molar heat capacity (specific heat) of graphite is reported as 8.033 to 8.635 J/mol.K at 25°C [3,4]. The specific heat increases with temperature, up to 1500 K [5,6]. It is believed to be relatively insensitive to the differences between the various grades of synthetic graphite and the spread of values found may be attributed to experimental variations.

(i) Thermal conductivity:

The thermal properties of conductivity and expansion are strongly influenced by the anisotropy of the graphite crystal. The thermal conductivity (K) is the time rate of transfer of heat by conduction. In graphite, it occurs essentially by lattice vibration [7].

Thermal conductivity of a graphite crystal has been reported as high as 4180 W/mK in the ab directions for highly crystalline, stress annealed pyrolytic graphite [8]. Graphite, in the ab directions, can be considered a good thermal conductor comparable to high-conductivity metals and ceramics. Graphite fibers from pitch precursor have high thermal conductivity, nearly three times that of copper. The thermal conductivity in the c-direction is approximately 2.0 W/mK and graphite is a good thermal insulator comparable to phenolic plastic. The thermal conductivity of graphite decreases with temperature. This is due to the increase in vibration amplitude of the thermally excited carbon atoms [9].

(ii) Thermal expansion:

The thermal expansion has a marked anisotropy. It is low in the ab direction but an order of magnitude higher in the c direction. As seen from the fig.1.3., the coefficient of thermal expansion of graphite increases with temperature. At 1500°C, it is approximately twice the room temperature value [10].

The thermal expansion of graphite is an important property since many applications involve high temperature and expansion values must be known accurately [10].
Fig. 1.3 Average coefficient of thermal expansion (CTE) of Graphite as a function of temperature [10].
Thermal shock: The low modulus, high thermal conductivity and low thermal expansion combine to give graphite excellent thermal shock resistance. It is difficult to rupture the material by thermal shock alone.

(b) Electrical resistivity:
Electrically, graphite can be considered as a semi-metal, that is a conductor in the basal plane and an insulator normal to the basal plane. Its atomic structure is such that the highest filled valance band overlaps the lowest empty conduction band and delocalized fourth-valance electrons form a partially-filled conduction band between the basal planes where they can move readily in a wave pattern as they respond to electric fields [11]. Consequently, the electrical resistivity of graphite parallel to the basal plane (ab) directions is low and the material is a relatively good conductor of electricity.

In the c direction, the spacing between the planes is comparatively large and there is no mechanism for the electrons to move from one plane to another i.e. normal to the basal plane. As a result electrical resistivity in that direction is high and material is considered an electrical insulator. It may be 10,000 times higher than in the ab directions [11]. The electrical resistivity of the graphite crystal in the ab directions increases with temperature (Fig. 1.4). This increase is the result of the decrease in the electron mean free path. The electrical resistivity in the c direction, however, decreases slightly with increasing temperature, possibly because electrons can jump or tunnel from one plane to another due to increased thermal activation [9].

(c) Mechanical Properties of graphite

As mentioned the bond between atoms within the basal plane of a graphite crystal is considerably stronger than the bond between two planes with an anisotropy ratio of approximately 75. This means that, while the strength in the ab direction is considerable, that in the c direction (interlaminar strength) is low and graphite shears easily between basal planes [13].
Fig. 1.4 Electrical resistivity of Graphite as a function of Temperature[11]
The Young's modulus of elasticity of the crystal varies up to two orders of magnitude with the direction. It is plotted in fig. 5 as a function of the angle between the c direction and the direction of measurement [2]. The mechanical properties of "real" material, such as the molded graphite materials and pyrolytic graphite, are considerably different since they are controlled by the dominant crystallite orientation, porosity, structural defects, and other factors. This results in large variation depending on the type of graphite and process.

(d) Chemical Properties:

Pure graphite is one of the most chemically inert materials. It is resistant to most acids, alkalies, and corrosive gases. However, impurities are almost always present to some degree in both natural and artificial graphites and often have an important catalytic effect with resulting increase in the chemically reactivity.

The anisotropy of the graphite crystal is reflected in its chemical behaviour. Reaction with gases or vapours occurs preferentially at "active sites", i.e. the end of the basal planes of the crystal which are zigzag face and the arm chair face and at defect sites, such as dislocations, vacancies, and steps. Reaction with the basal plane surfaces is far slower. The reason is that the graphite crystal exhibits large differences in surface energy in the different crystallographic directions. These differences account for the different rate of reaction [14]. Consequently, graphite materials with large crystals and few defects have the best chemical resistance.

The chemical reactivity is also appreciably affected by the degree of porosity, since high porosity leads to large increase in surface area with resulting increase in reactivity. Differences in reactivity between one form of graphite or another can be considerable. Obviously, high surface area materials such as activated carbon are far more reactive than dense, pore free or closed-pore materials such as glassy carbon.

Reactivity also generally increases with increasing temperature and at high temperatures, graphite becomes far more reactive. For instance, above 450°C, it...
Fig. 1.5 Young's modulus of elasticity as a function of the angle between the c-direction and the direction of measurement [2]
oxidizes readily with water, oxygen, some oxides and other substances. This low temperature oxidation is in contrast with the behaviour of other refractory materials, carbides do not oxidize and many carbides form a protective oxide film on their surface that delays oxidation. In contrast the oxides formed by the oxidation of graphite are gaseous (CO and CO₂) and offer no protection to the surface. The controlled oxidation of graphite, known as activation, results in open structures with extremely high surface area [15,16,17].

Graphite reacts readily with the alkali metals Potassium, calcium, strontium and barium. The atoms of some of these metals, notably potassium, can readily penetrate between the basal planes of the graphite crystal to form intercalated (or lamellar compounds) with useful properties.

Graphite reacts with metals that form carbides readily such as the metal of groups IV, V and VI [17] [18]. These carbides are the so called hard carbides, which include the carbides of tungsten, molybdenum, titanium, vanadium as well as the non-metal carbides of silicon and boron.

Oxidizing acids attack graphite to varying degree depending on the nature and surface area of the material [19].

Concentrated Nitric acid and boiling sulfuric acid attacks graphite, but hydrofluoric acid (HF) and the alkali hydroxides generally do not react with graphite.

1.3 PROCESS AND PRODUCT CLASSIFICATION:

The minerals diamond and natural graphite are formed in nature. All other carbon products are man-made and derive from carbonaceous precursors. These synthetic products are manufactured by a number of processes summarised in table 1.2.
<table>
<thead>
<tr>
<th>Process</th>
<th>Carbon Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molding / Carbonization</td>
<td>Molded graphite</td>
</tr>
<tr>
<td></td>
<td>Vitreous carbon</td>
</tr>
<tr>
<td>Pyrolysis / combustion</td>
<td>Lampblack</td>
</tr>
<tr>
<td></td>
<td>Carbon black</td>
</tr>
<tr>
<td>Extrusion / Carbonization</td>
<td>Carbon fibre</td>
</tr>
<tr>
<td>High-Pressure / shock Processing</td>
<td>Diamond</td>
</tr>
<tr>
<td>Chemical Vapour Deposition</td>
<td>Polycrystalline diamond</td>
</tr>
<tr>
<td></td>
<td>Pyrolytic graphite</td>
</tr>
<tr>
<td>Sputtering / plasma</td>
<td>Diamond-like carbon (DLC)</td>
</tr>
</tbody>
</table>

Table 1.2. Major processes for the production of carbon materials

The industrial applications of carbon materials are also classified by product functions such as chemical, structural, electrical and optical. [20]. Fig 1.6 shows some of the industrially important carbon forms and their properties.

Conventional carbon and graphite products are manufactured like ceramic materials. The heterogeneous structure consists of granular particles and binder bridges with an unavoidable volume fraction of pores. The granular particles of carbon can be obtained through either of the first two pyrolysis (liquid phase, solid phase and gaseous phase) routes. The structure properties and applications of synthetic carbon, depend on the processing techniques. Carbon obtained through decomposition of hydrocarbons such as pyrolytic graphite or liquid state pyrolysis such as needle coke or pitch based carbon fibers are highly ordered materials and hence are highly anisotropic with very high Young’s modulus and thermal conductivity along the graphitic planes.

At the same time disordered solid carbons are obtained through solid state pyrolysis of thermosetting resins. These are termed as glassy carbons.
<table>
<thead>
<tr>
<th>Products</th>
<th>Fine dispersed carbons</th>
<th>Granular carbons</th>
<th>Monolithic carbons</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Carbon black</td>
<td>Coarse</td>
<td>Pyrolytic carbons</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fine</td>
<td>Glassy carbon</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Moulded products</td>
<td>Carbon fibers</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Brushes)</td>
<td>Active carbons</td>
</tr>
</tbody>
</table>

| Utilized properties | Surface properties | Bulk properties | Surface properties |

**Fig. 1.6 Variety of Carbon and Graphite materials**
1.4 CONVENTIONAL TECHNIQUE FOR PRODUCTION OF CARBON:

Carbon can be produced from the organic precursors by a process called carbonization[19]. There are three major routes through which the carbonization can be carried out.

Carbonization is a reaction in which only carbon, the principal constituent materials remains; in which hydrogen and other elements are driven out by pyrolysis (The principal mechanism is dehydrogenation); in which the residual carbon atoms undergo polycondensation and in which the formation of hexagonal planer network proceed [21].

During carbonization, the precursor is heated slowly in a reducing or inert environment, over a range of temperature that varies with the nature of the particular precursor and may extend to 1300°C. The organic material is decomposed into a carbon residue and volatile compounds diffuse out to the atmosphere. The process is complex and several reactions may take place at the same time such as dehydrogenation, condensation and isomerization.

The carbon content of the residue is a function of the nature of the precursor and the pyrolysis temperature. The diffusion of the volatile compound to the atmosphere is a critical step and must occur slowly to avoid disruption and rupture of the carbon network. So carbonization is a slow process. It duration may vary depending on composition of the end product, the type of precursor, the thickness of the material and other factors[22].

The carbonized material is often called “amorphous” or baked carbon. It is without long range crystalline order and the deviation of the interatomic distances of the carbon atoms (from the perfect graphite crystal) in both the basal plane and between planes.

The typical modes of carbonization is divided into liquid phase, solid phase and gas phase. The properties of carbon thus produced differ greatly. Liquid phase
carbonization is the most common of these and the majority of commercial carbon materials are produced by this method.

Since the liquid phase carbonization occurs through multi stage process, various types of cokes can be produced, depending on the conditions of carbonization and on the composition of raw materials. Therefore, both of these factors must be controlled in order to achieve the desired final product.

a) Liquid phase carbonization: Generally leads to a soft carbon, since growth and orientation occur in a state in which the condensed polycyclic aromatic macromolecules have considerable mobility during thermal reaction. Specifically, coke with the best graphitizing properties and outstanding orientation (needle coke) is produced when pitch is in the state in which the flat molecules are mobile and can be oriented immediately before completion of solidification due to pyrolysis and carbonization [23].

b) Solid carbon: Hard carbon is generally produced when pyrolysis and carbonization occur in the solid phase without an intermediate liquid phase. The contribution of the heat treatment conditions or other secondary factors is very slight. Typical examples in which solid state carbonization takes place include thermosetting synthetic resins, such as phenol formaldehyde resin, polyfurfural alcohol resin, as well as cellulose. Natural materials include charcoal, anthracite, lignite and brown coal [24].

The organic substances mentioned above are already highly crosslinked before the start of pyrolysis. As a result, the mobility and orientation of the molecules are suppressed during heat treatment and structure is highly crosslinked. In this state, reorientation of the crystal is difficult [25]. Consequently, the size of the crystallites is extremely small and the inclusion of large amounts of oriented structures (three dimensional bonding) is observed.

Since softening and melting do not occur during heat treatment in solid phase carbonization, conversion to carbon occurs virtually in the original shape without appreciable deformation. Consequently, when phenolic resins are used as a binder,
carbonization can be carried out with the original formed shape maintained and dense, homogeneous material can be produced[26].

c) Gaseous Phase transformation (CVD) : Pyrolytic graphite is the example of CVD technique. It is a vapour phase process which relies on the chemical reaction of a vapour near or on a heated surface to form a solid deposit and gaseous by-products. This CVD of pyrolytic graphite is theoretically simple and is based on the thermal decomposition (pyrolysis) of a hydrocarbon gas. Its main use is in the form of coating, deposited on substrate such as molded graphite, carbon fibers or porous carbon-carbon structures. As such, it is part of a composite structure and is not as readily identifiable as other forms of carbon. It is the only graphitic material that can be produced effectively as a coating. The coating can be sufficiently thick that, after removing the substrate, a free standing object remains.

CVD is now well-established process that has reached major production status in areas such as semiconductor and cutting tools.

1.41 RAW MATERIALS (PRECURSORS) FOR INDUSTRIAL CARBONS:

The selection of the appropriate raw materials is the first and critical step in the manufacturing process of any material or product. It determines to a great degree, the properties and the cost of the final product.

Raw materials for carbon products can be divided into four generic categories: Fillers, Binders, Impregnates, and Additives[26,27].

i) Fillers: The filler is usually selected from carbon materials that graphitize readily. Such materials are generally cokes, also known in industry as “soft fillers”. They graphitize rapidly above 2700°C. Other major fillers are synthetic graphite from recycled electrodes, natural graphite and carbon black.

Petroleum coke is the filler of choice in most applications. It is a porous by-product of the petroleum industry and almost pure solid carbon at room temperature. It is obtained by high temperature pyrolysis of petroleum residues[28].
In coking, raw material oil is heated to 400°C to 500°C and introduced into thermally insulated coke drum under pressure of 4 to 5 kg/cm². Coking is then completed in 24 hrs. under pressure. Needle coke with very good graphitizability in which good crystallization is achieved is produced by controlling the operating conditions (temperature, pressure, residue time) and by selecting the raw material oil (high aromatic content, low insoluble fraction, low sulfur) [28].

The coke produced in this fashion has a very low coefficient of thermal expansion. It is an indispensable raw material for graphite electrodes for ultra high-power operation in electrically steel. An abnormal expansion phenomenon called puffing occurs in the course of graphitization of coke. It leads to cracks in the material. The magnitude of expansion varies greatly with the type of coke. This phenomenon is believed to be due primarily to rapid evaporation of sulfur. In coke with large sulfur content, the addition of several percent of ferric oxide (Fe₂O₃) during blending of the filler is generally employed as an inhibitor. Ferric oxide combines with sulfur in the coke forming FeS. The purpose is to moderate the composition and evaporation of sulfur in course of graphitization[29].

By varying the source of oil and the process parameters, it is possible to obtain various grades of petroleum-coke filler with different properties.

Needle coke, a premium grade with distinctive needle shape particles, produced by delayed coking from selected feedstocks with low concentration of insolubles. It exhibits a glossy appearance with a stripped like fibrous structure. The particles have great anisotropy. It is used in applications requiring high thermal shock resistance and low electrical resistivity. Anode coke is for less demanding applications. Isotropic coke is used as filler in applications where isotropic properties and a fine-grained structure are required.

ii) Binders: The most common binder is coal tar pitch which is a hard, brittle and glassy material. It is a by product of metallurgical-coke production and is obtained
by the distillation or heat treatment of coal tar.

- It has high specific gravity
- high benzene insoluble (BI)
- quinoline insolubes are not too high (so called free carbon-prevents crystalline growth in the course of carbonization);
- high C/H ratio (high aromatic content) and
- high coking value.

Petroleum pitch has outstanding graphitization properties but due to its inferior binding power it has not been used extensively. However, it is being used extensively as a result of improvements in reforming technology. Furthermore, synthetic resins, such as phenolics and furans, are also used in special applications, such as in molded materials and high density materials. However, since synthetic resins generally produce hard carbons, their uses are limited[30]. Fig.1.7. summarises the types of carbon products, principle functions and suitable fillers for some typical carbon products.
<table>
<thead>
<tr>
<th>Type of product</th>
<th>Main functions</th>
<th>Suitable fillers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Artificial graphite electrodes (for electrically produced steel)</td>
<td>Electrical conductivity, thermal shock resistance</td>
<td>Petroleum coke (especially needle like coke) (needle like pitch-coke)</td>
</tr>
<tr>
<td>Graphite anodes for electrolysis</td>
<td>Electrical conductivity, corrosion resistance (oxidation resistance) (purity, especially low V)</td>
<td>Pitch coke (petroleum coke)</td>
</tr>
<tr>
<td>Carbon blocks (for lining blast furnaces)</td>
<td>Thermal strength, thermal volumetric stability, corrosion resistance (especially alkaline resistance)</td>
<td>Anthracite (artificial graphite)</td>
</tr>
<tr>
<td>Mechanical carbon</td>
<td>Mechanical strength, wear resistance, lubrication properties</td>
<td>Pitch coke (natural graphite)</td>
</tr>
<tr>
<td>Carbon brushes (for electrical motors)</td>
<td>Electrical conductivity, lubrication properties, wear resistance, rectification capability</td>
<td>Carbon black, pitch coke, natural graphite</td>
</tr>
<tr>
<td>Electrodes for electrical discharge machining</td>
<td>Isotropy, precision machinability, electrical conductivity</td>
<td>Pitch coke, petroleum coke (especially Isotropic coke)</td>
</tr>
<tr>
<td>Nuclear graphite</td>
<td>Neutron moderator function, reflection function, (purity, especially low B), high density, radiation damage stability</td>
<td>Petroleum coke (low B content, Isotropy) gilsonite coke (carbon black).</td>
</tr>
</tbody>
</table>

Fig. 1.7. Principal functions and suitable fillers for typical carbon products.

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1.42 INDUSTRIAL TECHNIQUES FOR THE PRODUCTION OF CARBON:

Fig 1.8. illustrates the general steps in the production of industrial carbon materials. The solid lines in the flow sheet represent the most basic production steps. The majority of carbon materials which are used in the greatest quantities at present are primarily produced by these steps[26,29].

The individual operations included in these steps are often very similar to those in the production of ceramics from the viewpoint of handling of the powdered raw materials. However, since the binder in the heat treatment step passes through a liquid stage, measures to suppress oxidation and to prevent deformation are required at that time. Bonding of the filler particles by carbonization of the binder is also essentially different from the sintering of the powdered raw material used in ceramic processing.

The production of industrial carbons comprises following steps:

a) Milling and sizing:

Filler and binder are grounded or milled to the particle size requirement which may vary from 1μm to 1.25cm. Various types of pulverizers may be used alone or in combinations to conform to the desired particle size and the original size of the raw material. The principal pulverizing devices are the jaw crusher, gyratory crusher, roll crusher, hammer crusher, tube mill, roller muller, impact type pulverizer and oscillating ball mill, but caution is required since coke and anthracite are exceedingly abrasive materials [12].

Individual particles of pulverized coke are often irregular in shape and long and narrow. The degree of orientation differs considerably, depending on the type of precursor coke since coke itself already contains the orientation of graphite crystals and the layer planes are arranged virtually in the length-wise direction of the particles.

In general, longer particles are produced with coke which undergoes graphitization more readily. Also the shape of the particles is an important factor which affects the anisotropy of the properties of the final product. Larger particles are used
Fig. 1.8 General steps for production of Industrial Carbon.
with materials of larger dimensions. A batch usually consists of more than one size. This allows better control of the packing characteristics and optimizes the density of final product. Control of the particle size distribution is required in the case of fine particles[31].

b) Mixing:

Filler and binder are weighed in proper proportion and blended with large mixers into a homogeneous mix where each filler particle is coated with the binder. Blending is usually carried out at 160-170 °C, but a temperature range must be selected so that the marked changes in composition of the pitch does not occur and sufficient fluidity is maintained for thorough wetting of the filler. When mixing at lower temperature (below the melting point of the binder), volatile solvents such as acetone or alcohol are often added to promote binder dispersion. The amount of binder added would vary considerably with the type of filler and with the particle size distribution. The final properties of the moulded product are controlled to a great degree by characteristics of the filler-binder paste such as: (a) the temperature dependence of the viscosity, (b) the general rheological behaviour and (c) the hydrodynamic interaction between filler particles [32]. The amount of the binder would be from 25 to 50 parts per 100 parts of filler. Deformation occurs in the later steps and porous, inhomogeneous material develops when the amount of binder is excessive, while forming becomes difficult and strain as well as cracks readily occurs when the amount is insufficient.

c) Forming Techniques:

Three major techniques are used to form the carbon products (graphite mix) extrusion, compression (uniaxial loading) and isostatic pressing. They are shown graphically in fig.1.9.

1) Extrusion: Extrusion is a major technique which is favoured for the production of parts having a constant cross section, such as electrodes. The mix is
cooled to just above the softening point, then extruded through steel dies, cut to length and rapidly cooled to solidify the pitch before distortion occurs. The resulting shape is known in the industry as a “green shape”.

Extrusion pressures are of the order of 7 MPa (100 psi). Some alignment of the coke filler particles takes place which imparts anisotropy to the properties of the finished product. This anisotropy can be controlled to some extent by changing the mix formulation and the extrusion geometry [27]. The center of the extruded material is usually of lower quality than the material near the outside edge and defects such as flow lines and laminations are difficult to avoid. On the plus side, it is the lowest cost technique which is satisfactory for most large parts, such as furnace electrodes.

ii) Compression (uniaxial molding) : The mix in compression molding is usually a fine powder as opposed to the coarser material used in extrusion. Tungsten carbide dies are frequently used with pressures of the order of 28 to 280 MPa (4000 to 40,000 psi). Complex shapes can be produced by this process [29]. However, die-wall friction and die edge effect may cause non-uniformity in the density and other properties of the finished products.

iii) Isostatic molding : In isostatic molding, pressure is applied from all directions through a rubber membrane in a liquid-filled chamber, resulting in a material with great uniformity, isotropic properties and generally with few defects. However, the molding process is expensive and cost is higher than extrusion or compression molding [31].
Fig. 1.9 Forming techniques for moulded graphites.
The selection of the given technique has a great influence on the final properties of the moulded product as shown in table 1.3.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extrusion</td>
<td>Anisotropic properties</td>
</tr>
<tr>
<td></td>
<td>Non-uniformity of cross section</td>
</tr>
<tr>
<td></td>
<td>Presence of flow lines and laminations</td>
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<tr>
<td></td>
<td>Limited to parts of constant cross section</td>
</tr>
<tr>
<td></td>
<td>Production of large parts possible</td>
</tr>
<tr>
<td></td>
<td>Low cost</td>
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<tr>
<td>Compression</td>
<td>Non uniformity</td>
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<td></td>
<td>Edge effect</td>
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<tr>
<td></td>
<td>Presence of flow lines and laminations</td>
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<tr>
<td></td>
<td>Medium cost</td>
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<tr>
<td>Isostatic</td>
<td>Isotropic properties</td>
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<tr>
<td></td>
<td>Uniformity</td>
</tr>
<tr>
<td></td>
<td>No flow lines or laminations</td>
</tr>
<tr>
<td></td>
<td>High cost</td>
</tr>
</tbody>
</table>

*Table 1.3: Characteristics of forming techniques.*

d) Carbonization, Graphitization and Machining:

Carbonization (also known as baking) the green shape is the next step. Carbonization takes place in a furnace in an inert or reducing atmosphere. Variation exist in the baking step, depending on the type of furnace and the size of the formed product.

The temperature is raised slowly to 600°C, at which stage the binder softens, volatiles are released and the material begins to shrink and harden. The parts must be supported by a packing material to prevent sagging. The temperature is then raised to 760 to 980°C (or upto 1200°C in special cases). This can be done faster than the first temperature step, since most of the volatiles have by now been removed, the material is already hard and sagging is no longer a problem. Ten to twenty days are usually required for heating while five to ten days are required for cooling.
Impregnation: Approximately thirty to forty percent of the binder evaporates during the baking step and the material has high degree of porosity. To further densify it, it is necessary to impregnate it with coal tar pitch or a polymer such as phenolic. Molten pitch fills these pores and the open pores already present in the filler coke particles. The impregnation is usually carried out at high pressure in autoclaves and the carbonization process is repeated. In special, limited use applications, non-carbon impregnating materials such as silver and lithium fluoride impart specific characteristics, particularly increased electrical conductivity [33].

Graphitization: When carbon which has been backed, it is subjected to heat treatment at a temperature of approximately 3000°C, fine graphite crystals arranged irregularly grow sufficiently and the orientation become regular. This change varies greatly depending on the type of raw material, but the properties of the carbon material also change markedly due to the development of crystals resulting from such graphitization, specifically due to the transition from carbon to graphite. Coke particles are packed into the furnace as packing material and the baked stock is subjected to resistance heating by direct electric charging in the longitudinal direction of the furnace.

In graphitization step, two to four days are required for electric heating and one to two weeks are required for cooling. This means that the temperature cycle is shorter than the carbonization cycle.

Graphitization increases the resistance of the material to thermal shock and chemical attack. It also increases its thermal and electrical conductivities [31].

Puffing: Puffing is an irreversible expansion of molded graphite which occurs during graphitization when volatile species, such as sulfur from the coke, are released. Puffing is determinental as it causes cracks and other structural defects. It can be eliminated (or at least considerably reduced) by proper isothermal heating and by the addition of metals or metal compounds with a high affinity for sulfur [34].

Purification: For those applications that require high purity such as semiconductor compounds and some nuclear graphite, the material is heat-treated in a
halogen atmosphere. This treatment can remove impurities such as aluminium, boron, calcium, iron, silicon, vanadium and titanium to less than 0.5 ppm [35]. The halogen reacts with the metal to form a volatile halide which diffuses out of the graphite.

Machining: The graphitized material can now be machined to the final shape. Since it is essentially all graphite, machining is relatively easy and is best performed dry to avoid water contamination. Common cutting tool materials are tungsten carbide, ceramic and diamond. A good ventilation system is necessary to control and collect powdery dust[36].
1.43 PROCESSING OF CARBON FROM SELF SINTERABLE ROUTE:

As described in section 1.42, conventional carbon and graphite materials are normally made using a calcined filler coke and binder, such as coal tar or petroleum pitch, through carbonization and graphitization processes. In this complex commercial process, the carbon products contain large voids which weaken the strength and the ability to withstand stress. Therefore, in order to make a high density carbon, various modified techniques have been used in their fabrication, such as repeated impregnation with pitch and heat treatment in autoclave. Use of high char yield pitch or the filling up of pores with a deposition of pyrolytic carbon[37]. Therefore, it is known to be difficult to fabricate a dense and strong carbon and graphite body for structural applications.

Carbon can also be prepared by high temperature (2000°C) high pressure (200 Kg/cm²) sintering. This process is costly and requires sophisticated high temperature press. It is also difficult to fabricate large size or complex shapes. And since pitch or pitch based materials are used, problems of harmful pollution result from the use of the process on a commercial scale[38].

If a new sintering method could be established, the processing period could be shortened and dense, strong carbon materials could easily be manufactured with no need to use pitch binder phase in the process[39,40,41].

With this in view, recently new techniques have been evolved by making carbon itself self sinterable from polyaromatic mesophase for fabrication of solid carbon and graphite bodies with extraordinary mechanical properties [42,43] without any use of binder materials.

Such binderless or sintered carbon have strengths upto about 150 MPa, especially when the grain size is small. Various applications such as electro discharge machining, containment vessels for semiconductors manufacture, valve seals, pistons and piston rings can be envisaged. The fabrication route comprises (Fig.1.10) the compaction of a fine mesophase powder, which is than carbonized and graphitized. Heat treatment of the compacted powder causes considerable densification due to a
volumetric shrinkage of the order of 30 - 40%. In common with the ceramic process, the powder characteristics and processing details are critical in determining the final structure and properties[43].

![Flow chart for the production of carbon from mesophase](image)

**Mesophase microbeads:**

Coking coke is transformed from coal to coke by way of liquid crystal development due to pyrolysis. The development of the anisotropic mosaic structure in coke is attributed to mesophase (liquid crystal) development. This phenomenon is easiest to demonstrate when certain petroleum refinery feed stocks, and/or coal tar pitches are carbonized. During heating of the parent material, spherical anisotropic liquid crystals (nematic) form and grow and coalesce to form large domains that, with time form a solid with a mosaic anisotropic pattern. Marsh [46] (1986), give a detailed mechanism for the formation of coke structures. Many of the properties of carbons such as electrical resistivity, hardness and strength can be related to the microstructure. The microstructure can be controlled by the selection of feed stock and control of the carbonization process. Spherulitic mesophase has been found to be a more useful raw
material than bulk mesophase [44,45]. Therefore, it has been attempted to produce a mesophase pitch with as much as possible high content of spherulitic mesophase. 

Sintering of mesophase spherules give the solid carbon or graphite with good strength. Carbon materials do not sinter in the conventional sense and the densification and shrinkage arise from the substantial change in solid structure from polyaromatic molecular solid to carbon and ultimately to graphite, with the associated increase in true solid density. Carbon of high bulk density only result when the individual grains are strongly bonded to each other such that the bulk shrinkage of the body matches that of the grain. The porosity should remain constant in this ideal case, but with reduced pore size. The only possibility for pore elimination by convention sintering is if the mesophase particles show sufficient fluidity to allow a measure of viscous sintering prior to solidification as carbon, as has been discussed by Huttinger et. al. [44,45]. This would reduce the porosity from the green value. In the absence of this mechanism the carbon porosity can not be less than that in the green state. However, the carbon porosity can increase during carbonization as a result of the opening of cracks to eliminate stressed developed during the shrinkage processes or due to differential thermal contraction on cooling (Mrozowski cracks). This can be a significant source of voids in the material. Another mechanism whereby porosity can be generated is by bloating, when the precursor is fluid enough to create closed pores which expand when filled with pyrolysis gases.

The other raw material for fabrication of self sintered carbon and graphite is a well ordered semicoke. It is mechanically treated to make self sinterable carbon powder. It results in a fine grained carbon product with short range order. These products isotropic in character, possess very high density, mechanical and thermal properties. In fact they exhibit a combination of polymeric carbon and graphitic characteristics, or to say combination of ordered-disordered carbon material “Sintered” carbon from mesophase powder.
In this case the particle size distribution is significant. If viscous sintering is adopted then small particles will provide greater driving force and enhanced sinterability. Another important role of particle size is its effect on the development of shrinkage cracks during the heating and cooling stages[47]. Differential shrinkage leads to greater stresses at the boundaries of large particles and cracks develop at the interface. If the particles comprise large anisotropic units then cracks may develop across the particle themselves. These cracks and their connectivity determines the critical flaws that control the tensile strength. Large anisotropic units can be also develop if the particle fuse and attain high enough fluidity to allow reorganization of the lamellar structure. This is undesirable for high strength products.

The heating rate has several effects on the properties that are related to the changes in physical state that occur during carbonization. Increasing the heating rate decreases the transient viscosity that can exist in the low temperature region. This can be used to control bonding or allow some true sintering, too. High a heating rate allows a low viscosity and facilitates bloating. It can also facilitates the reorganisation to coarse flow texture[48]. Increases in the heating rate also tend to reduce the amount of volatile matter released which can result in higher bulk densities but not higher true density. Latter is controlled by the structural perfection of the carbon. Low molecular weight species have been reported to cross link larger aromatic units, restricting molecular growth and orientation [49].

The porosity of carbon product is controlled by the interparticle shrinkage (as the crystal structure develops) and bulk shrinkage, (determined by the mutual shrinkage of the grain assembly). Stresses developed between shrinking grains can open up voids during the carbonization process and also differential thermal contraction opens voids on cooling. The porosity variation as a function of heat treatment temperature can be dominated by these stress induced effects. Mechanical properties are controlled by the porosity and the change from molecular solid to disordered carbon. The later effect is particularly important in the region upto 1000°C.
It is clear from the above analysis that the composition, carbon yield and deformability are all important parameters and are interrelated. It is difficult to control the properties of the powders because they lie in the region of the pitch carbon transformation where glass transition temperatures are increasing rapidly with small changes in volatile content. Powder should have high carbon yield, high Tg, develop sufficient transient plasticity above Tg that they can be compacted to high density with strong interparticulate bonding[43].

1.5 CARBON-CARBON COMPOSITES:

With the advent of the fibers, a new class of materials called composite materials took birth some where around 1930s or so. Composite is made by the combination of two or more dissimilar materials in order to achieve properties that the constituent materials cannot provide by themselves. Carbon compounds central position in this new class of materials (composites) especially when composites have to be used at elevated temperature [50].

Carbon, which holds an important place in the periodic table, is one of the lightest elements and also the most refractory retaining its strength up to 2000°C and above. It is truly a unique solid that can be made to exhibit the broadest variety of structures as well as properties.

In carbon the various properties are achieved through changes in the carbon structure. However, monolithic carbons are extremely brittle in nature and hence can not be used for critical applications. This requirement or the gap was filled up by carbon fiber reinforced composites which are tailored materials exhibiting properties designed to fit the needs of the user. When matrix material is also carbon, we get what is called carbon-carbon composites. More precisely, a carbon-carbon composite or carbon fiber reinforced carbon matrix composite is a combination of carbon or graphite fibers in a carbon or graphite matrix [50].
Carbon-Carbon composites with strength properties exceeding those of pyrolytic graphite by a factor 2 or 3 is a highly desirable material for high temperature applications [51].

Some typical characteristics of Carbon-Carbon composites are:

1) Light weight and low density
2) High strength and stiffness
3) Low thermal expansion
4) High thermal conductivity
5) Hence, high thermal shock resistance
6) High fracture toughness
7) Pseudoplastic behaviour
8) Good fatigue and creep resistance

In no other single material, we can find combination of above properties.

Applications of Carbon-Carbon composites:

Carbon-carbon composites find applications mainly in aerospace, defence, nuclear and bio-medical fields due to their high-heat of ablation, high sublimation temperature, low coefficient of thermal expansion, high specific heat, low density and high strength at elevated temperature [52].

Aerospace and Defence applications:

Carbon-carbon composites are being used as heat shields and nose tips for reentry vehicles, leading edges as well as rocket nozzles for solid propellants due to its more erosion resistant increased dimensional stability and low recession in high pressure ablative. Carbon-carbon composites are also used to protect isotopes during its reentry into earth's atmosphere. These isotopes are used in aerospace applications to generate heat and electric power [53,54,55,56].

The other most important application of carbon-carbon composites is in use of brake-pads for military as well as civilian aircrafts due to its desired wear rate with
temperature, high coefficient of friction and high specific heat [57,58,59]. It provides smooth friction over the braking period. Their stopping power is four to five times that of metal brakes which increases the safety in landing. They also offer a saving in weight over those of steel brakes per pair of brakes.

Additionally, the ultimate temperature upto which carbon-carbon composites brakes can be used is around 2000 °C as compared to 700-900°C with conventional braking materials [60].

Bio-medical applications:

Carbon-carbon composites find applications as bio materials such as bone-plates [61,62], total hip prosthesis, tooth implant, heart valve etc. due to their excellent bio-compatibility along with superior mechanical properties. The properties of carbon-carbon composites can be tailored to match exactly that of bone. The specific weight of carbon-carbon composites matches with that of bone [63].

Nuclear applications:

Carbon-carbon composites are increasingly being used as first wall material in Tokamak reactors due to superior thermophysical and mechanical properties such as high thermal conductivity, high thermal shock resistance and fracture toughness [64 - 68].

Engineering applications:

Although cost of carbon-carbon composites is quite high due to its low volume of production but still they are replacing the conventional materials in certain engineering applications. They are being used as hot pressing dies, high performance heating elements, high temperature ducting system, electrical contacts, hot seals and bearing.

Limitations of carbon-carbon composites:

The limitation for use of carbon-carbon composites is its susceptibility to oxidation at high temperatures.
As stated above though carbon-carbon composites possess excellent properties, their applications are limited to few sectors only because of high cost of production and susceptibility to oxidation at high temperatures. The application scope of these materials can be widened up if above drawbacks could be overcome to some extent. Continuous efforts are being made to develop new techniques to fabricate low cost carbon-carbon composites and to make them resistant to oxidation by incorporating oxidation resistant additives either during fabrication or on the finished products.

Conventional Techniques for processing of Carbon-Carbon composites:

Carbon-Carbon composites consisting of fibrous carbon substrate in a carbonaceous matrix sound extremely simple since both the constituents are carbon. In reality, however, these materials are extremely complex, both from the point of view of processing as well as performance. The main reason for its complexity can be the fact that each constituent can vary (in structure) from carbon to graphite.

Fig. 1.11 depicts a general flow diagram for making carbon-carbon composites. Broadly speaking there are two main routes which are often followed

- Chemical vapour impregnation/deposition
- Liquid infiltration/carbonization techniques.

The first method involves depositing carbon into fibrous perform while the second method is based on thermal pyrolysis of thermosetting resins or thermoplastic pitches.

Chemical Vapour infiltration (CVI) techniques:

In the Chemical Vapour infiltration technique the carbon bearing hydrocarbon gas such as methane, propane etc. is diffused on hot surface of the substrate resulting in a pyrolytic carbon deposit. There are three types of chemical vapour infiltration techniques used for the fabrication of carbon-carbon composites.

- Isothermal technique
- Thermal gradient technique
- Differential pressure technique
Fig. 1.11 Schematic diagram of processing of carbon-carbon composites
In the isothermal process [69 - 72] substrate and gas are kept at the same temperature. The substrate is heated radiantly by induction furnace susceptor. The hydrocarbon and carrier gasses are introduced into the reactor at low pressure and are allowed to infiltrate into the preform or substrate. The hydrocarbon gas cracks at the substrate resulting in deposition of the carbon matrix.

In the thermal gradient technique [73 - 75] the part to be infiltrated is supported by a mandrel which is inductively heated. Therefore the hottest portion of the substrate is the inside surface which is in direct contact with the mandrel. Under proper condition of infiltration, carbon is first deposited on the inside surface and progresses radially through the substrate as the densified substrate itself becomes inductively heated.

The differential pressure technique [76] is a variation of the isothermal technique. In this process the part of the substrate is isolated from the furnace chamber by sealing around the base. Gases are fed into the inner substrate at a positive pressure with respect to the furnace chamber. It creates a pressure differential across the wall of the preform facilitating gas to pass through the pores. The gas cracks while it passes through the pores of the substrate.

In CVI the microstructure of the carbon matrix may be varied widely by optimising the processing parameters. Nature of the substrate, carrier gas, temperature, composition of gases, pressure in the reaction chamber and its geometry are some of the factors that influence the microstructure of the CVI derived carbon matrix. Smooth laminar, rough laminar and isotropic are the three types of carbon microstructures commonly seen in CVI processing.

Liquid impregnation technique:

A large variety of carbon yielding liquid precursor could be used as impregnates. The following characteristics of the matrix precursors must considered while selecting to make high density carbon-carbon composite.

1) Viscosity 2) Coke yield 3) Coke microstructure and 4) coke crystal structure
The common carbon precursor used for making carbon-carbon composites are

a) thermosetting Resin : Poly Furfuryl Alcohol

b) thermoplastic : Coal Tar Pitch, Petroleum Pitches

Before doing densification the preform has to be rigidified. This can be done using thermosetting resins or thermoplastic pitches or CVI technique etc. Then after densification is carried out using either thermosetting or thermoplastic resins or CVI. These processes are simple but pose certain problems.

The char yield of most of the carbon precursors is between 55 % to 76 % [77]. So there will be certain amount of porosity left during first baking, which will have to be filled up by subsequent impregnation. In case of thermosetting resin the volume of mesopores are minimum compared to macro and micro pores. And mesopores is only useful for the densification. Because of this reason the density is lower than that of the composite made using thermoplastic resins. i.e. most of the porosity is made up of mesopores which are extremely important from the density point of view.

The another problem in the composites using thermosetting resin is, resin undergo volume shrinkage of the order of 45-50%. Since the resin is present in and around the carbon fiber bundles. The carbon fiber tend to inhibit the shrinkage, degree of inhibition depends on surface groups present on the surface of the carbon fibers and carbon fiber volume.

The bonding between the fiber and matrix is also equally important. In polymeric composites the fiber matrix bonding is strong in case of composites with treated carbon fiber as compared to that in untreated [78]. Because of that, during pyrolysis the gap is generated between the matrix layer and the carbon fiber surface, extent of which depends on the degree of surface treatment imparted to carbon fibers. Carbon fiber would tend to get damaged and in extreme cases, it can totally crumble down even because of a strong fiber-matrix bonding [79,80].

In case of thermoplastic resins any grade of pitch is much less energetic as compared to thermosetting resins in terms of bonding with carbon fibers. So chances of
carbon fiber damage during pyrolysis are remote. Coke yield here is 45-50 % only [81].
Pitch undergoes various changes like volatilization of low molecular weight compounds, polymerisation etc. at their softening point about 400°C. It has been discovered that at 400°C small spheres of around 0.1 μm diameter start appearing in the isotropic liquid pitch. These spheres which have been designated as mesophase exhibit highly oriented structure with characteristics similar to liquid crystals.

On prolonged heating, these spheres grow in size undergo coalescence and form large regions of extended order. This ultimately favours the formation of graphite structure on further heating to 2500°C and above.

Because of the low coke yielding [50%] [82] in this techniques impregnation step has to be repeated at least 5-7 times in order to fill up the pores. And the ultimate density will not be exceed from 1.6 to 1.65 gm/cc using this carbonization technique. So the new technique has been evolved to increase the density up to 1.8 to 2.0 gm/cc, using hot isostatic pressing. In this technique the pressure is applied at the time of carbonisation process [83 - 91].

HIP has the following advantages over the normal pressure carbonisation.

a) Char yield of the pitch goes about 95-97% due to forced thermal polymerisation of the pitch[85].
b) Due to high pressure (700 Mpa) the pitch prevtales much more effectively in fiber pores.
c) Percolation due to gasses/reaction products is reduced to minimum.

Due to this reason one can tend to get columner type microstructure rather than the usual type[92].

Intermediate graphitization, where in the composites are subjected to a heat treatment temperature of 2700°C after densification. On graphitization the entrance to the pores open up due to rearrangement of crystallites in the matrix. These opened
pores then become available to the pitch during the further impregnation. This leads, once again to an appreciable increase in density.

Two to three graphitization are carried out at the intermediate stages of fabrication, whenever a saturation in the increase in density of the composites is observed. By following this technology, carbon-carbon composites possessing a density of 1.84 gm/cc have been developed. Above mentioned techniques are being commercially used for fabrication of advanced carbon-carbon composite products. World wide research is being done to use less expensive oxidised PAN fibers and alternative techniques for deposition of carbon into the structure to evolve less expensive technology for fabrication of carbon-carbon composites.
1.6 SCOPE OF THE WORK:

Over the past few years, Japanese have developed a new technology to carbon products through pressureless sintering[38,93]. Carbon in the raw form is treated mechanichemically to make its surface highly reactive and sinterable. This reactive carbon is moulded to require shape at ordinary temperature and then sintered at high temperature of 2200 to 2700°C. Very little has been reported in the open literature about the pressureless sintering except the Japanese who have mastered this process.

The another requirement in developing carbon products for mechanical and structural applications is to improve mechanical properties of carbon specially hardness and bending strength. As well as the important thermostructural property that is the thermal stability under oxidizing atmosphere while maintaining electrical and thermal properties. Therefore, carbon in different forms is combined with some ceramic material mostly in carbide forms resulting in composite materials with improved properties, called carbon/ceramic composites[94]. The conventional technique to fabricate carbon/ceramic composites through CVD, carbothermal reactions or liquid impregnation routes are not only costly but also pose problems in controlling the process.

Low cost carbon-carbon composites can also be developed using chopped fibers alone or with SiC and boron compounds as reinforcement and self sinterable coke as matrix.

A noval technique of fabricating carbon/ceramic composites through solid-solid reaction could be developed through this self sinterable route and ceramic powder in which the sinterable coke act as a sintering aid.

Boron has been known to be only one element to be substitutionally doped into graphite structure[95]. So addition of boron carbide along with silicon carbide to this sinterable carbon powder has great attraction because of its accelerating effect on graphitization and also improvement of their properties, particularly mechanical, thermal
and electrical. The antioxidation property can also be improved because of formation of B$_2$O$_3$ protective film on the surface of the composite.

Therefore, the present studies were undertaken for the first time in India to develop process for making solid carbon products, carbon-ceramic particulate composites and carbon-carbon composites using self sinterable semicoke. Since there is not much open literature available on this technique, the basic mechanism of sintering and its effect on the final characteristics of the products is also not known. Therefore the present studies were aimed at investigating sintering mechanism in self sinterable carbon products and to evolve technology for fabricating a variety of products therefrom.