CHAPTER IV

MICROSTRUCTURES
AND
PROPERTIES OF INDUSTRIAL CARBON
AND GRAPHITE
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MICROSTRUCTURES AND PROPERTIES OF INDUSTRIAL CARBON AND GRAPHITE

Introduction

Carbon and graphite materials possess unique combination of mechanical, thermal and electrical properties not exhibited by any other single material. Therefore, these materials are preferred for various mechanical and electrical applications especially at high temperature under non-oxidizing atmosphere. Monolithic carbon is extremely brittle in nature, and hence cannot be used for critical applications [1]. Graphite is an allotropic form of the element carbon consisting of layers of hexagonally arranged carbon atoms in a planer condenses ring system. The layers are stacked parallel to each other. The chemical bonds within the layers are covalent with sp² hybridization. The layers are then bonded as Van der Walls type.

Graphitic carbons are all varieties of carbons consisting of the element carbon in the allotropic form of graphite irrespective of the presence of structural defects. Graphitization is a solid state transformation of thermodynamically unstable non-graphitic carbon into graphite by thermal activation. The degree of graphitization depends on the temperature of the heat treatment and the time allowed annealing structure. Most graphitizable carbons pass through a semi fluid stage during carbonization [2]. This allows large aromatic molecules to align with each other so forming the meso phase precursor of the graphitic structure, which is essential to the development of the coke.

Artificial graphite produced by heating carbon in an electrical furnace is called graphitized carbon or electrographite [3]. For many applications, graphitic properties
are required which are obtained through the process of graphitization, a second heat treatment at temperatures up to 3000°C (5430°F).

In order to have insight of the microstructure and properties of carbon and graphite materials, studies were made on different types of commercially available carbon, graphite materials made by known companies in Gujarat.

Following carbon samples have been studied for microstructure and properties during present research work:

4.1 Commercial graphite

Different six commercial graphite samples have been characterized for their various properties. These samples were obtained from the carbon material suppliers and have been designated as CGA, CGB, CGC, CGD, CGE and CGF. In the samples, longitudinal direction was the direction of extrusion of carbon and perpendicular direction was across the direction of extrusion.

4.1.1 Physical properties

4.1.1.1 Densities of different grades of commercial carbon graphite samples
Apparent density is expressed as mass (m) per unit volume (v) of the amount of matter in an object compared to its volume. In common case density is expressed as:

\[ \rho = \frac{m}{v} \text{ (gm / cm}^3\text{)} \]

Apparent density of the commercial graphite samples were measured by physical measurements according to the ASTM C-838 t-91 [4]. Density of the samples was also experimentally measured by the Archimedes technique in distilled water, named as Bulk density. Each reading of the density was the average of five readings which were taken at different places on each sample. Bulk density is basic property of particulate materials. It is the mass-water density of graphite samples and was measured using Mettler Toledo AG204 densitometer.

Fig. 4.1 shows the densities of all six samples as measured by physical measurements (mass & volume) and also by Archimedes Principle (densitometer).

![Graph showing densities of commercial and graphite samples](image)

Fig. 4.1: Bulk and apparent densities of commercial and graphite samples.
Fig. 4.1 shows that apparent density by volume measurement and bulk density by densitometer are very close to each other. Bulk density is 2.3% higher than apparent density. This is due to exclusion of large pores which get penetrated by the water in densitometer and hence the actual bulk volume gets reduced.

4.1.1.2 Porosity of various grades of graphite specimens

Porosity is another important characteristic of bulk materials which decides various properties of the materials such as structural properties (strength etc.), hardness, thermal and electrical properties. Therefore porosity of the carbon samples under study was measured. Though there are various methods to measure porosities like open porosity (macro porosity) by kerosene method, nano porosity by mercury porosimetry and helium method to closed porosity by X-ray method, kerosene porosity is the most common method used for industrial applications [5]. Therefore, the carbon graphite samples under study were investigated for kerosene porosity using Mettler Densitometer. The results are shown in Fig. 4.2 (a) and (b). These results are tabulated in Table 4.1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Porosity</th>
<th>Apparent density (gm/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CGA</td>
<td>18.74%</td>
<td>1.662</td>
</tr>
<tr>
<td>CGB</td>
<td>19.41%</td>
<td>1.693</td>
</tr>
<tr>
<td>CGC</td>
<td>14.05%</td>
<td>1.726</td>
</tr>
<tr>
<td>CGD</td>
<td>10.08%</td>
<td>1.761</td>
</tr>
<tr>
<td>CGE</td>
<td>17.66%</td>
<td>1.653</td>
</tr>
<tr>
<td>CGF</td>
<td>25.76%</td>
<td>1.643</td>
</tr>
</tbody>
</table>

From Fig. 4.2 and Table 4.1 it can be seen that the porosity of all samples lies in the range of 10% to 20%. Porosity is lower in the case of samples CGC and CGD.
and so the density is higher. So, one can conclude that the sample CGD contains small pores than other samples, and same was derived from the optical micrographs of the specimens. From the optical analysis it can be observed that the sample CGD has minimum porous structure. Well dispersed fillers gives good packing density with minimum voids / porosity. It is due to the, good packing of fillers having higher density (1.76 gm/cm³) packed within definite volume of sample and because of the well dispersion of fillers in matrix.

![Graph showing density and porosity of different graphite samples](image)

**Fig.4.2**: (a) Density and (b) % Porosity of different grade of graphite samples.

Both the plots show reciprocal nature of density and porosity. Plots in **Fig.4.2** show that sample D have maximum density and least porosity among all samples. This is also justified by its optical micrographs (**Fig.4.3**).
4.1.2 Optical microscopy of commercial carbon graphite material

Specimens were prepared by mounting the samples in a resin block and polishing the surface to optical flatness using alumina paste of size 1μ to 0.03μ. The polished surfaces were examined using reflected light microscopy with polarized light. The Figs. 4.3 to Fig.4.5 show optical micrographs of the polished surfaces of the samples. These micrographs show bulk features like distribution of constituents, macro pores and other essential features of the samples.

All these Figs. 4.3 to 4.5 show that these materials are multiphase materials consisting of filler and binders. All these phases are well distributed.

Fig. 4.3 shows that sample CGA and CGB are fine grained materials with lot of voids and macropores. These pores are of bigger size in sample CGA than CGB. Moreover, these are well distributed. Fig. 4.4 shows that CGC and CGD samples are well compacted. Here again sample CGC has more pores than sample CGD. This agrees well with the densities of these samples. Further, sample CGC and CGD exhibit coarse grains oriented in particular direction. These are the characteristic features of pitch cokes which give graphitic structure to the carbon graphite materials [6]. These oriented structures (graphitic cokes) are more in samples CGE and CGF (Fig.4.5). Since graphite has higher density than carbon, one would have expected higher density in samples CGE and CGF than for CGC and CGD. But at the same time samples CGE and CGF contain more voids and pores as seen from Fig. 4.5. Therefore even though samples CGE and CGF are graphitic samples, the density is lower than for CGC and CGD and accordingly is the porosity. Therefore presence of graphitic carbons as well as compaction of fillers and binders is essential for dense carbon and graphite materials.
Fig. 4.3: Optical micrographs of samples CGA and CGB.
Fig. 4.4: Optical micrographs of samples CGC and CGD.
Fig. 4.5: Optical micrographs of samples CGE and CGF.
4.1.3 Conductivity of commercial carbon graphite materials

Electrical conductivity or specific conductivity is a measure of material’s ability to conduct an electric current [7]. Electrical conductivity is one of the important properties of carbon graphite materials. In the inorganic materials category, carbon-graphite are the best electrically conducting material and therefore, these materials are used in many electrical and electronic appliances. The conductivity of carbon and graphite depends on their heat treatment, temperature and microstructure [8]. The conductivity $\sigma$ is defined as the ratio of the current density to the electric field strength. Conductivity is the reciprocal of electrical resistivity and has unit as mho.cm$^{-1}$. Therefore electrical conductivity of different commercial carbon and graphite samples was measured by four-probe method. It was measured in longitudinal as well as in cross sectional direction [9].

For measurement of DC electrical volume (bulk) conductivity, three complete runs were taken to check repeatability of measurement for each specimen and mean of three readings was taken. Three identical samples having physical dimensions of (130x40x3) mm$^3$ with perfect flat surfaces were utilized for this and measurement was carried out using Keithley 2400 source meter. Samples were sandwiched between four copper electrodes and mass where all electrodes edges are coated with silver paint to make proper electrical contact. Measurements were taken at room temperature (27$^\circ$C to 28$^\circ$C) and carried out through bulk of material.

The electrical conductivity (in longitudinal as well as perpendicular direction) is plotted in Fig. 4.6 (c). These plots show that electrical conductivity of carbon samples is dependent on the macrostructure i.e. porosity as well as on the microstructure, i.e., presence of graphitic constituents. Fig.4.6 (b) shows that for
CGA sample the bulk DC conductivity is 482 mho.cm\(^{-1}\) and that for CGD sample it is 687 mho.cm\(^{-1}\), which shows the maximum conductivity among all samples. Sample CGF has minimum conductivity of 273 mho.cm\(^{-1}\). As seen from Fig. 4.6 all the samples have same order of electrical conductivity though absolute values are different. It means that all samples are graphitic, heat treated to 7250°C. Samples (CGC and CGD) having high density and lower porosity have higher conductivity. Sample CGE has though lower density as compared to samples CGA and CGB but the conductivity of former sample is higher than that of latter samples. This is because of the presence of more graphitic fillers in samples CGE as seen by optical microscopy.

**Fig.4.6:** (a) % Porosity (b) Bulk conductivity (c) Longitudinal and transverse conductivity of different grades of commercial graphite samples.
Chapter IV

The conjugated π bonding of the layered structure results in the electrons being delocalized throughout the structure providing a means of conducting electricity similar to metallic conduction bands [10]. Across the layers, however, there is no electron movement so conduction in this direction is a minimum. This is an excellent example of the anisotropy exhibited by graphite. The Fig.4.6 (c) also shows that the electrical conductivity is higher in the longitudinal direction but lower electrical conductivity across the length means in the cross sectional direction.

From these results it can be concluded that electro graphite materials generally possess excellent sliding properties and offers low electrical resistance in the longitudinal direction. They are used for applications where enhanced sliding properties and temperature cycling as well as a high purity are required as an individual characteristic or as a combination of properties [11].

4.1.4 Mechanical property

The mechanical properties of solid materials generally depend on the compactness of the material especially when it consists of two phases, filler and binder. For graphite, it also depends on reinforcing materials, i.e. graphitic content, shape, porosity/cracks, interfacial bonding between filler and binders etc. Though tensile strength and compressive properties are of prime importance for any material but in graphite, hardness is more important since it is used for sliding applications [12].

4.1.4.1 Rockwell hardness of industrial carbon graphite materials

Bulk (Rockwell) hardness of commercial carbon graphite materials was measured as per ASTM D 785 on Rockwell hardness testing machine for 60 Kg load on HRR scale. The results obtained from the mechanical testing are discussed below.
Randomly cut samples were utilized for this test/evaluation. Three identical samples were used for this purpose. Mean of measurements was taken as a final value to enhance the accuracy.

The Fig.4.7 shows bulk hardness for all six samples. Though all samples show value in the same domain, but effect of porosity is clearly seen. More compacted samples CGC and CGD exhibit higher hardness than samples CGA and CGB. Moreover all samples are graphitic; the values are in same range.

![Graph showing bulk hardness for different samples](image)

**Fig.4.7:** Variation of bulk hardness in different commercial graphite samples.

Even though the values of bulk hardness of all samples are in same domain there is a variation in bulk hardness of all samples. Sample CGD possesses maximum hardness of 99 HRR while sample CGA having minimum hardness of 82 HRR.

### 4.2 Carbons processed to different conditions (Schutz Carbons)

Three samples were obtained from Schutz carbons. These carbons were processed to different stages. These samples were:

- **Baked carbon (BC):** Carbon which are heat treated to a maximum temperature of 1200° C called "Baked Carbon".
• **2PI Baked Carbon (PIBC):** Baked Carbon impregnated with pitches and rebaked are called “Pitch Impregnated Baked Carbon”. These are also heat treated to 1200°C.

• **Graphite Carbon (GC):** Second heat treatment given to baked carbon is about 2500°C to 3000°C. These are called “Graphite Carbon”.

4.2.1 Physical properties

4.2.1.1 Densities and % porosity of different grades of Schutz carbon

Apparent as well as bulk densities of these samples were measured in the same way as for commercial carbons described in 4.1.1.1.

\[
\rho = \frac{m}{v} \text{ (gm/cm}^3\text{)}
\]

![Graph of densities of Schutz carbon samples](image)

**Fig.4.8:** Densities of Schutz carbon samples.

The graphical representation of apparent and bulk densities of Schutz carbon samples is given in **Fig.4.8**. As seen from the figure, the density of carbon increases with impregnation cycle as well as with heat treatment temperature. With
impregnation, the pores get filled up and hence result in increase in density. On higher
temperature heat treatment, the filler / binder get compacted due to graphitization
resulting in increase in density and decrease in porosity as seen in Fig. 4.9.

Fig. 4.9: % Porosity and densities of different grades of Schutz carbon samples.

4.2.2 Optical microscopy of Schutz carbons

Aim of performing optical microscopy was to investigate the microstructure
and pores size distribution of each micro constituent of carbon samples. Specimens
were prepared for their optical microscopy and observed by optical microscope using
reflected light microscopy normally with polarized light as discussed in 4.1.2. Fig. 4.10 shows different optical micrographs of Schutz carbon samples at different stages.

Optical micrographs show that out of three specimens, backed carbon sample
contain more porous structure [Fig. 4.10(a) and (b)] than other two samples [Fig.
4.10(e) and (f)] and has minimum density. Because it has more porous structure the
interparticle distance between the particles is more. In PIBC sample, backed carbons
were impregnated with pitches and rebacked at higher temperature (1200°C). The open
pores get filled up with reduction in interparticle distance and porosity decreases
compare to backed carbon. Graphitized carbon is highly crystalline in nature because of its high temperature treatment and interparticle distance is much less and naturally has less porosity [13].

Anisotropic, oriented characteristic of pitch coke filler is well recognized in Fig. 4.10 (b, d, f).

Fig. 4.10: Optical micrographs of Schutz carbon samples processed at different stages.
4.2.3 Electrical conductivity of Schutz carbons

For these samples also the electrical conductivity was measured by four-probe technique. It was measured in longitudinal and cross sectional direction. The electrical conductivity of carbon depends greatly on the degree of preferred orientation of the carbon layers. This degree is enhanced by heat treatment, high graphitizability of the precursor materials and alignment of the carbon units (such as the carbon fibers in a composite material) during processing. This will be more evident from the measurements of Schutz carbon samples which have been processed and heat treated to different conditions.

DC electrical conductivity of these specimens was measured at room temperature using designed sample holder employing four probe methodology.

Fig.4.11 shows the electrical conductivity of different Schutz carbon samples. As seen from the figure sample BC has lowest conductivity. This is due to lower heat treatment temperature of the samples and higher porosity. As the porosity decreases, conductivity increases. This is evident from electrical conductivity of sample PIBC. Heat treatment at higher temperature i.e. 2500°C-3000°C increases the crystallinity of the sample. At higher temperature because of graphitization, crystallinity increases. Crystalline carbons have higher ordering and more free electrons responsible for conductivity in planer direction [14]. Also hopping and tunneling may be possible because of alignment of graphite particles that increasing electrical contact area and bridge the electrical network. It is because of these reasons that, sample GC which has been heat treated to 7250°C possess higher electrical conductivity [15].
Fig. 4.11: (a) % Porosity (b) Electrical conductivity of Schutz carbon samples.

4.2.4 Rockwell hardness of Schutz carbon

Fig. 4.12: Variation of bulk hardness in different Schutz carbon samples.

Fig. 4.12 shows hardness of different Schutz carbons. It is clearly seen from Fig. 4.12 that sample GC has least bulk hardness compared to other two samples. It is
well known that graphite particles are lubricative in nature due to weak bonding of Van der Waals forces between layers of these particles, so tends to slip from one another, means layers are little bit slippery in nature [16]. This characteristic makes them ductile in nature, when load is applied to bulk of these composites. As graphitic carbon is soft as compared to backed and impregnated carbon, its bulk hardness is lower than that for other two backed carbon samples.

4.3 Molded Industrial Carbons

Carbon graphite materials are produced either through extrusion or by molding. Section 4.1 described properties of extruded carbons. In order to see the effect of processing route; studies were made on molded carbons as well. For study, four different given industrial carbon samples were taken and characterized for their various properties like physical, optical, electrical and mechanical properties.

4.3.1 Physical property

4.3.1.1 Densities and % porosity of different grades of commercial graphite

![Graph showing densities and % porosity of different grades of commercial graphite](image)

Fig. 4.13: % Porosity and densities of different industrial carbon specimens.

The Fig. 4.13 shows densities and porosity of these four samples. It is seen that density and % porosity of these samples do not follow general rule as for
extruded samples. Sample B has higher density than sample A, but the total porosity of sample B is also higher than that of sample A. This means that there are factors as well. Which control the compactness of the samples made by molding techniques [17, 18]. These are particle size, particle size distribution, and process of molding. These were investigated using optical microscopy.

4.3.2 Optical microscopy of industrial molded graphite

The industrial molded graphite samples were prepared for their optical study as discussed before. Optical microscopy was performed to study the microstructure, pores size distribution and anisotropic behavior of each micro constituent of each sample. Fig. 4.14 (A) and (B) show optical micrographs of these samples under crossed polarized light.

These optical micrographs show that all samples consist of small grains equally distributed with porosity in between the grains. Sample-A (face1) exhibits the anisotropic nature of the sample [19]. Microstructures of sample B (face 1) and (face 2) shows highly porous structure among all four structures. Sample –C (face 1) and (face 2) contain less porous structure but grains are of different types of anisotropic materials. Sample-D contains large pores in both the faces with anisotropic grains, well distributed in the sample. These observations follow the density results, where sample C exhibits maximum density and lowest porosity.
Fig. 4.14 (A) and (B): Optical micrographs of industrial carbon samples.
4.3.3 Electrical conductivity

For measurement of an electrical conductivity, four probe set up technique was used with Keithley 2400 as source meter. Total three complete runs were taken to check repeatability of measurement for each specimen. Three identical samples having physical dimensions of (130x40x3) mm³ with perfect flat surfaces were utilized for this. Specimen were placed between current & potential electrodes and definite mass (for pressure to make perfect contact) of four probe assembly. Faces of electrodes were coated with silver paint to make proper electrical connectivity. Designed assembly is then connected with Keithley 2400 source meter. Measurements were taken at room temperature (27°C to 28°C).

![Fig.4.15](image)

**Fig.4.15:** DC electrical conductivity of industrial carbon samples.

The Fig. 4.15 shows electrical conductivity of these samples. From the plots of Fig.4.15 it can be seen that the electrical conductivity of sample C is the maximum. This is because sample C possesses least porosity and consist of maximum amount of anisotropic graphitic phases. There are number of factors that must be taken into
account regarding electrical properties and porosity. At first glance, electrical connectivity between particles will be influenced by the quality of particle boundaries and the area of contact throughout the bulk. This means that percolation can be analyzed [20], as it is related to porosity within the bulk. From the studies of these samples it can be concluded that the porosity and electrical conductivity can be modified by changing the processing parameters [21, 22]. In molded products it can be done through varying process pressure which also affects the pore size and distribution of pores. Comparing the electrical conductivities of samples in 4.1 and 4.3, it is noticed that molded graphite samples possess higher electrical conductivity than molded samples.

4.3.4 Rockwell hardness of molded graphites

The hardness of the given samples was evaluated using Rockwell hardness testing machine with 100 kg load and 0.5 mm diameter steel ball indenter. The indentation time for hardness measurement was 5 seconds.

Table 4.2: Rockwell hardness of industrial carbon samples.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Diff. Types Of Industrial Carbon</th>
<th>Rockwell Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A</td>
<td>38.5 HRR</td>
</tr>
<tr>
<td>2</td>
<td>B</td>
<td>23.2 HRR</td>
</tr>
<tr>
<td>3</td>
<td>C</td>
<td>48.8 HRR</td>
</tr>
<tr>
<td>4</td>
<td>D</td>
<td>29.9 HRR</td>
</tr>
</tbody>
</table>

Table 4.2 clearly shows that sample C is hardest among all four samples, and sample B is soft compare to all four samples. From above results it can be concluded that Sample C is more porous and Sample B is least porous. The bulk hardness of samples increases because of their graphitized nature [23]. Optical micrographs also justified this phenomenon/effect.
Fig. 4.16: % Porosity and bulk hardness of industrial carbon samples.

Nature of above plot concludes that increased porosity reduced the bulk hardness of the material that justified by the optical microscopy (Fig. 4.14) and characterization results.

4.4 Conclusion

From results of various samples characterized in this chapter, it is concluded that molded samples exhibit higher densities, lower porosity and higher electrical conductivity than extruded samples.

In molded samples as well, the properties may depend on processing parameters.

The properties of carbonized as well as graphitized materials are porosity dependent. The porosity decreases with impregnation and high temperature heat
treatment that also results in anisotropic graphitic structures and high electrical conductivity.

4.5 References


Chapter IV


