Mechanical seals: some developments in face materials

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Carbon has been used as a face material in mechanical seals for well over fifty years. The first grades of carbon used were developed from carbon electrical brush materials, but the continuous increase in the severity of mechanical seal operating conditions has necessitated ever improving grades of carbon. This paper details some of the means available to the carbon technologist to achieve these improvements and gives examples of some special applications.

Keywords: carbon, face materials, mechanical seals,

Carbon

Elemental carbon exists naturally in many parts of the world in the forms of graphite and diamond. When mined, graphite is not particularly useful as an engineering material, because of its softness, high impurity level and limited size. The manufacture of carbon and graphite has developed for over three-quarters of the century with the properties of the resulting products being considerably improved over those of the natural material. Carbon has been long established as a prime material for one of the rubbing pairs in a mechanical seal, and the continuous manufacturing developments have kept pace with the increasingly severe requirements of the application.

By judicious selection of raw materials, and by using a variety of manufacturing processes, carbon and graphite can be modified to give a range of properties suitable for different seal applications. The raw materials are selected from naturally occurring graphites, from which some or all of the inorganic impurities have been removed. The original materials include coke derived from coal sources, residues taken from oil distillation (petroleum cokes), and carbon blacks which are obtained from the burning of oils and gases in limited supplies of air.

The raw materials are powdered and bonded together with a pitch or tar, and then moulded under pressure to form a convenient size and shape. The resulting product is fired in a protective atmosphere, to approximately 1000°C. During this process, the tar and pitch are converted to a coke, thereby cementing the particles of the other raw materials together to form a cohesive mass. Such a product is known as carbon-graphite.

Some grades of carbon are further heat-treated to temperatures of up to 2500°C, at which level the amorphous carbon is transformed into a crystalline electro-graphite. This material has greater purity, improved thermal conductivity, better oxidation resistance, but lower strength. Carbon and graphite materials that are produced by this means are porous. The properties, however, can be modified by impregnation with synthetic resins or metals. The impregnants confer increased strength, lower permeability and improved wear resistance characteristics to the basic carbons. Impregnation with oxidation inhibitors will improve the oxidation resistance and with some base materials both reduce and stabilize friction.

Carbon development is a continuous process to meet the needs of the seal and other industries. Tables 1–4 indicate the effects of various changes in the manufacturing process. The various possible process changes outlined are used in the development of special grades to meet specific applications. Some examples of this are given later.

Silicon carbide

In the constant quest for improvements in mechanical seal performance, new face materials are regularly tested. One of these materials which has shown superior qualities as a face material is silicon carbide. Silicon carbide's uniform hardness and density make it an extremely abrasion resistant material. Silicon carbide has excellent thermal shock resistance because of its high thermal conductivity combined with high tensile strength and low thermal expansion. These properties, together with its excellent corrosion resistance and low coefficient of friction, make silicon carbide an excellent seal face material. Four types of silicon carbide are in general use. These are:

- reaction-bonded
- pressureless sintered
- surface converted carbon and graphite
- silicon carbide/graphite composites

These various silicon carbide materials are discussed later in the paper.

Carbon grade developments

The alkylation process

In the petroleum industry, a process known as alkylation is carried out. This involves the chemical combination of isoparaffin with any one or a combination of olefines to form a mixture of highly-branched paraffins that have a high anti-knock rating and good stability. This process is expanding as lead-free petrol is demanded for environmental reasons.
Alkylation reactions involve the use of either sulphuric acid or, more commonly, anhydrous hydrofluoric acids as catalysts. The reactions are carried out at temperatures and pressures sufficiently high to keep the feed and reaction mixtures in a liquid phase. The concentration of hydrogen fluoride is usually 3 or 6%, but under breakdown conditions can rise to 90%.

The plant in which the reactions take place incorporates pumps fitted with mechanical seals having carbon sealing rings. Considerable problems were encountered with these pumps because of an almost catastrophic failure of the carbon sealing rings when brought into contact with the hydrofluoric acid and isoparaffin. The failed carbons usually showed a delamination structure as illustrated in Fig 1.

Analysis of the deposits found on failed rings suggested that the disruption of the carbon ring was caused by the attack of hydrofluoric acid on the inorganic constituents, such as silicon or aluminium, of the raw materials used in the manufacture of the carbon. A number of grades from different sources behaved in the same manner. Tests were carried out and these showed that a phenolic resin-impregnated hard carbon grade, with minimum inorganic impurities, withstood the chemical conditions of the alkylation process. Under dry conditions this hard carbon causes high wear of the counterface. In these circumstances, a softer, resin impregnated electrographite carbon grade can be used, though at the expense of a reduced wear life.

**Development of an anti-blistering carbon**

Carbon blistering has been a recognized phenomenon for over fifteen years. Sealing failures due to this phenomenon appeared to increase at a prodigious rate since this mode of seal face degradation was first reported. Whilst this failure mode is recognized as being one of the major causes of seal failure encountered in the petro-chemical industry, it must be emphasized that many other failure modes have been wrongly attributed to blistering.

It is significant that blistering is experienced only in association with the sealing of light hydrocarbons and organic refrigerants. Many theories have been advanced as to the cause of blistering. The common theme to all the theories is...
Table 4 Physical properties of typical grades

<table>
<thead>
<tr>
<th>Grade reference</th>
<th>Description</th>
<th>Transverse bend strength (kgf/cm²)</th>
<th>Bulk density (kg/m³ x 10³)</th>
<th>Hardness scleroscope</th>
<th>Dynamic elastic modulus (kgf/cm² x 10³)</th>
<th>Thermal conductivity (Wm K)</th>
<th>Coefficient of thermal expansion (°C⁻¹ x 10⁻⁶)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Carbon-graphite 40% carbon/60% graphite (large particle size)</td>
<td>315</td>
<td>1.70</td>
<td>60</td>
<td>180</td>
<td>12.0</td>
<td>3.4</td>
</tr>
<tr>
<td>2</td>
<td>Carbon-graphite 60% carbon/40% graphite (large particle size)</td>
<td>460</td>
<td>1.60</td>
<td>67</td>
<td>180</td>
<td>12.0</td>
<td>3.6</td>
</tr>
<tr>
<td>3</td>
<td>100% carbon</td>
<td>422</td>
<td>1.60</td>
<td>90</td>
<td>150</td>
<td>9.0</td>
<td>4.2</td>
</tr>
<tr>
<td>4</td>
<td>Electro-graphite (heat treated grade 3)</td>
<td>300</td>
<td>1.72</td>
<td>50</td>
<td>84</td>
<td>63.0</td>
<td>4.1</td>
</tr>
<tr>
<td>5</td>
<td>Grade 1 plus wax impregnation</td>
<td>315</td>
<td>1.70</td>
<td>60</td>
<td>180</td>
<td>12.0</td>
<td>3.4</td>
</tr>
<tr>
<td>6</td>
<td>Grade 1 plus phenolic resin impregnation</td>
<td>560</td>
<td>1.84</td>
<td>80</td>
<td>240</td>
<td>12.0</td>
<td>4.5</td>
</tr>
<tr>
<td>7</td>
<td>Grade 2 plus phenolic resin impregnation</td>
<td>650</td>
<td>1.80</td>
<td>83</td>
<td>230</td>
<td>12.0</td>
<td>4.0</td>
</tr>
<tr>
<td>8</td>
<td>Carbon-graphite plus phenolic resin impregnation (small particle size)</td>
<td>665</td>
<td>1.80</td>
<td>84</td>
<td>215</td>
<td>13.8</td>
<td>4.8</td>
</tr>
<tr>
<td>9</td>
<td>Grade 1 plus copper-lead impregnation</td>
<td>685</td>
<td>2.60</td>
<td>70</td>
<td>300</td>
<td>25.0</td>
<td>5.4</td>
</tr>
<tr>
<td>10</td>
<td>Grade 2 plus antimony impregnation</td>
<td>910</td>
<td>2.50</td>
<td>80</td>
<td>340</td>
<td>13.0</td>
<td>4.7</td>
</tr>
</tbody>
</table>

the generation of frictional heat in isolated hot spots. The mechanism for the formation of the blister is, however, a point of great debate.

The approach based on frictional heat generation led to the experimental concepts of thermal cycling the system. This approach enabled a quantitative assessment of blister resistance and severity of blistering to be made by visually analysing the blistering surface.

**Aims of experimental work**

1. The major aim of this work was to establish a system in the laboratory that would consistently reproduce the blistering phenomena, using a material known to consistently blister in the field.
2. To evaluate a range of carbon grades and post impregnation treatments with respect to blistering.
3. To relate, if possible, the available reported data from seal manufacturers to the results achieved in the laboratory.

**Experimental work**

A number of test rigs and conditions were tried before carbon blistering was experienced. Eventually a set of test conditions was determined using a proprietary seal under which blistering could be consistently reproduced with a range of carbon materials. These were:

- Rotational speed: 2890 r/min = 1530 ft/min
- Oil pressure: 200 lb/in²
- Nose pressure (spring pressure 47 lbf, face area 1.45 in)

**Conclusions**

1. There is no simple alternative treatment which can be applied to standard impregnated carbon grades to make them totally blister-resistant.
2. All carbon grades will blister when run against highly polished hard counterfaces, e.g. tungsten carbide.
3. Blistering is caused by local hot spots, the heat being generated very rapidly by dry running.
4. The carbon blister is due to differential expansion of the materials used in impregnation and the carbon matrix itself.
5. The oil becomes absorbed into the surface, filling the gaps left by the impregnant when it shrinks either by cooling as for a metalized grade, or due to cross linking in a resin impregnated grade.
6. The differential expansion (4–10 times as great for impregnants over carbon) generates a pressure on the oil now filling the air gaps left after impregnation that normally allow for expansion of the impregnant on heating. This increased pressure is sudden, and if all the oil cannot escape, the pressure can cause sub-surface cracks that lead to blistering.
Aircraft turbine seals

The modern gas turbine employed for propulsion of commercial and military aircraft is a complex and high technology piece of machinery. It has three basic component sections, namely compressor, combustion and turbine. The turbine presents a number of difficult sealing problems, and special grades of carbon have been developed for use in these applications.

The turbine section is divided into a high and low pressure turbines which are mechanically linked to respective high and low pressure compressors. The turbine blades extract kinetic energy from the expanding air and burning gases being received from the combustion section, converting it to shaft horsepower which is used to drive the compressor and all of its accessories. The remaining energy, represented by the ratio of the remaining pressure relative to ambient pressure, and the remaining temperature to ambient, generates thrust. The main shaft in a turbine engine rotates at speeds approaching 10000 r/min and operates in an environment of changing high temperature conditions. The shaft is supported by a series of bearing components associated with an extensive lubrication system. Main shaft bearing compartment seals are used to protect the rotor support bearings from the hot gases flowing through the engine and to prevent the loss of the lubricant being fed to the bearings.

Main shaft seals are designed as labyrinth, ring and face types. The labyrinth seals are giving way to ring and face designs due to decreases in weight and space and an increase in engine efficiency afforded by the latter types. There is also a trend toward face seals having an aluminum oxide coating on the inside diameter of the seal to provide additional wear resistance at the contact point with metal piston ring-type secondary seals.

The carbon materials used today for these seals are the result of many years of development. The carbon must have high strength, good oxidation resistance, low friction and long wear life. These properties have been achieved by the selection of optimum raw materials and manufacturing processes and the addition of antioxidation impregnants.

Two special carbon grades have been developed for aircraft turbine main shaft sealing applications. The first of these is a high strength, fine-grain carbon-graphite containing a special high temperature resistant impregnant that is suitable up to 450°C (850°F) in oxidizing environments and in excess of 650°C (1200°F) in neutral or reducing atmospheres. This grade is used for both rings and seals; it has over 30 years and millions of flying hours to its credit.

The second grade has been developed to meet the higher temperature and rotational speeds of newer engine designs. It has a special non-exuding impregnant that gives greater oxidation resistance and lower running friction. Its greater thermal conductivity derives from the use of a fine grained electrographite base stock.

Pressed-to-shape components for mechanical seals

At the other end of the spectrum to the application of carbon in aircraft turbine seals is its use in low duty mechanical seals as found in the automotive and domestic appliance industries. However, performance and life is of equal importance whatever the application. These industries also require high volume, low cost products and special carbon grades and manufacturing processes have been developed to meet this dual requirement of performance and cost.

Process capability

Size, shape and tolerance limits are the main features which need to be considered when describing the capability of the PTS process. The following guidelines relate to typical plant and processes, the specific details may vary from manufacturer to manufacturer.

Size

Size is limited by press capacity and size of the special kiln:

(1) The component shape should be contained within a circle of 79 mm (3.11 in) diameter (plan view).
(2) The dimension of the component in the direction of pressing should not exceed 36 mm (1.4 in).

Tolerances

Dimensional control in the PTS process is achieved by careful selection and blending of powders to achieve a consistent contraction figure. This and careful control of kiln temperature and speed influence the size of the post-kiln component. Detailed below are the tolerance capabilities of the process. When considering multi-featured components, it is important that the tightest tolerances are only applied to critical dimensions.

Total tolerance expressed as a percentage of the dimensions

(1) Dimensions at right angles to the direction of pressing:

- 0.5%
- 0.1%
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<table>
<thead>
<tr>
<th>Impregnant</th>
<th>General tolerance (0.004 in)</th>
<th>Tightest tolerance (0.006 in)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon-graphite</td>
<td>1.25%</td>
<td>0.80%</td>
</tr>
<tr>
<td>Metal impregnated carbon-graphite</td>
<td>2.50%</td>
<td>1.60%</td>
</tr>
</tbody>
</table>

(2) Dimensions in the direction of pressing:
As (1), but with a minimum general tolerance of 0.3 mm (0.012 in) and a minimum tightest tolerance of 0.2 mm (0.008 in) for all grades.

(3) Concentricity and ovality:
0.15 mm (0.006 in) TIR up to 30 mm (1.18 in).
0.20 mm (0.008 in) TIR over 30 mm (1.18 in).

(4) Parallelism:
0.10 mm (0.004 in) TIR up to 30 mm (1.18 in) across.
0.15 mm (0.006 in) TIR over 30 mm (1.18 in) across.

Shape
This is the most difficult feature of the PTS process to prescribe in detail, but there are basic rules to be considered.

(1) PTS is a vertical forming process, pressure needs to be applied across the whole piece and it must be possible to eject the piece from the die.
(2) Tools with a radial wall thickness of less than 1 mm (0.04 in) are to be avoided.
(3) Steps or recesses more than 30% of overall length are to be avoided if produced in fixed tool features.
(4) The maximum ratio of axial thickness to radial thickness is 4:1.
(5) Grooves and undercuts cannot be produced in diameters during the pressing process.

PTS grades
The physical properties of two grades that have been specially developed for PTS components are given here. These contain either a phenolic resin or antimony impregnant in the same base carbon-graphite, the latter also manufactured with a final resin impregnation when enhanced pressure tightness is required. The physical properties of these two grades are:

<table>
<thead>
<tr>
<th>Impregnant</th>
<th>Grade A</th>
<th>Grade B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenolic resin</td>
<td>600</td>
<td>630</td>
</tr>
<tr>
<td>Antimony</td>
<td>1.80</td>
<td>2.30</td>
</tr>
<tr>
<td>Hardness (scleroscope)</td>
<td>75</td>
<td>75</td>
</tr>
<tr>
<td>Dynamic elastic modulus (kgf/cm² × 10³)</td>
<td>225</td>
<td>280</td>
</tr>
<tr>
<td>Thermal conductivity (Wm⁻¹ K⁻¹)</td>
<td>13</td>
<td>17</td>
</tr>
<tr>
<td>Coefficient of thermal expansion (°C⁻¹ × 10⁻⁴)</td>
<td>4.2</td>
<td>4.9</td>
</tr>
<tr>
<td>Porosity (apparent) (%)</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

Applications
The main markets for PTS carbon components lie in the automotive and domestic appliance industries, although there are increasing requirements from industrial seal and submersible pump manufacturers.

(1) Automotive applications:
The major current demand in Europe is for carbon faces in automotive coolant water pump seals, and a number of large constructors are changing to carbon from resin-bonded materials. There are also applications for seal faces in air conditioning units.

(2) Domestic appliance applications:
Sealing ring applications are found in domestic dishwashers, waste disposal units and domestic water pumps.

(3) Industrial applications
To justify the cost of tooling the PTS process is normally only used for quantities of 20000 and above for simple rings and 100000 and above for complicated components. Most demands from the industrial sector do not reach these levels, but, in some areas, demand for mechanical seals for general application has increased to a level where the PTS process can be used.

Silicon carbides
A range of silicon carbide materials is available to the mechanical seal design engineer, and their use, both as the counterface and seal face, is growing. Each of these materials offers certain common advantages as a seal material and these include:

- low specific gravity
- excellent abrasion resistance
- good thermal shock resistance
- extremely high hardness
- high elastic modulus
- high thermal conductivity
- low thermal expansion
- low friction
- good chemical resistance
- ability to withstand high temperatures

All available silicon carbide materials combine these properties to a lesser or greater extent and a number of factors become of prime importance when selecting the correct grade of silicon carbide for a specific application. These include:

- cost
- availability in the size and shape required
- corrosion resistance
- technical performance

Details of the various types of silicon carbide are given in the following sub-sections and general physical properties for these materials are listed in Table 5, together with some other hard face materials included for comparison.

Reaction-bonded silicon carbide
This type of material was the first silicon carbide introduced to the mechanical seal market. It is made by subjecting a compact of alpha silicon carbide and carbon to liquid silicon at high temperature. The liquid silicon penetrates the compact and reacts with the carbon to form beta silicon carbide which bonds the original alpha silicon carbide grains together. Some residual silicon remains, which will vary from 10—20% depending on the manufacturer, and this fills up the remaining porosity. The resultant material is impermeable.

An advantage of this method of manufacture is that components can be shaped in the 'green' state before conversion. Negligible dimensional changes take place during conversion and if non-critical dimensions can be used as converted the
Table 5 Typical physical properties of silicon carbides

<table>
<thead>
<tr>
<th>Material</th>
<th>Thermal shock parameter (Cal/sm s⁻¹)</th>
<th>Density (kg/m³ × 10³)</th>
<th>Thermal conductivity at room temperature (W m⁻¹ k⁻¹)</th>
<th>Hardness knoop (kg/mm²)</th>
<th>Compressive strength (MPa)</th>
<th>Flexural strength (MPa)</th>
<th>Modulus elasticity (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction-bonded silicon carbide</td>
<td>59</td>
<td>2.9–3.10</td>
<td>120</td>
<td>2500–3500</td>
<td>3400</td>
<td>475</td>
<td>400</td>
</tr>
<tr>
<td>Sintered silicon carbide</td>
<td>60</td>
<td>2.95–3.12</td>
<td>115–125</td>
<td>2400–2800</td>
<td>3900</td>
<td>530</td>
<td>400</td>
</tr>
<tr>
<td>Surface converted carbon</td>
<td>&gt; 50</td>
<td>2.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silicon carbide/graphite composites</td>
<td>2.60–2.80</td>
<td>60–75</td>
<td>800–1000</td>
<td>160–230</td>
<td>140</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hot-pressed silicon nitride</td>
<td>29</td>
<td>3.2</td>
<td>17.5 (500°C)</td>
<td>2500–3500</td>
<td>690</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td>Tungsten carbide</td>
<td>48</td>
<td>14.8</td>
<td>86</td>
<td>1800</td>
<td>4500</td>
<td>1650</td>
<td>600</td>
</tr>
<tr>
<td>Carbon-graphite (resin-impregnated)</td>
<td>&gt; 50</td>
<td>1.8–1.9</td>
<td>10–18</td>
<td>200–250</td>
<td>65</td>
<td>23</td>
<td></td>
</tr>
</tbody>
</table>

The main disadvantage of reaction-bonded silicon carbide is the presence of the residual silicon, which makes it unsuitable for certain chemical conditions. The main chemicals to be avoided are caustic alkalis and nitric/hydrofluoric acid mixtures.

Carbon-graphite against reaction-bonded silicon carbide is an excellent combination of materials for mechanical seals. The reaction-bonded silicon carbide has been run against carbon-graphite for PV limits of up to 4200 bar m/s. This is approximately 50% higher than the PV limit used for tungsten carbide against carbon-graphite.

Pressureless sintered silicon carbide

This material, made by sintering, has the advantage that it does not contain any free silicon. This provides it with outstanding corrosion resistance. The resultant material does have some porosity, but the pores are isolated individual pores so the material is impermeable. Pressureless sintered material has good 'as pressed' surface finishes but is more brittle than reaction-bonded grades.

Surface converted carbon and graphite

In this process, the surface of a carbon or graphite component is converted to beta silicon carbide by a vapour phase reaction. Unlike conventional chemical vapour deposition, the surface carbon of the component reacts with the vapour to form silicon carbide in situ. A high degree of integrity in the silicon carbide/carbon interface derives from the process and, hence, there is no chance of the silicon carbide layer peeling off in service. An advantage of this process is that components can be pre-machined in carbon or graphite rather than extremely hard silicon carbide. This method of manufacture lends itself to large quantity production.

Material for surface conversion treatment must be selected from the wide range of unimpregnated carbons and graphites, pressed grades being the most suitable. To achieve a converted layer of silicon carbide with minimum stresses, the important parameters are the porosity of the base material and the extent of mismatch between the coefficients of expansion of the base material and converted layer of beta silicon carbide. In practice, the porosity of the base material is effectively reproduced in the converted silicon layer. Typical properties of this material vary according to the depth of silicon carbide conversion and the substrate used. The depth of conversion can be made to vary between 0.5 and 2.0 mm. Since the converted layer retains the porosity of the base material, it is necessary to resin impregnate to obtain imperviousness. The type of resin used will dictate the chemical resistance of the material.

Silicon carbide/graphite components

The latest, and possibly most exciting, development in the range of silicon carbide materials is a composite of silicon carbide and graphite. This material is made by infiltrating a specially structured graphite base with liquid silicon. This results in silicon carbide containing a substantial amount of graphite (30–50%) and a very low level of free silicon.

This material combines the high strength of silicon carbide with the lubricating properties of graphite. It has better dry running properties than solid silicon carbide but is not so resistant to abrasion. It will be chemically attacked by nitric/hydrofluoric acid mixtures.