Porous Silicon Carbide

Silicon carbide sintered bodies comprising controlled porosity in the range of about 3 to 25 vol% are prepared from raw batches containing a multimodal distribution of silicon carbide particles. The silicon carbide particles are comprised of at least a first set of particles having one average grain size and a second set of particles having another average grain size larger than the first set of particles. The resulting pores in the sintered bodies are 3 to 5 microns in the largest dimension, with an aspect ratio between 1/1 and 3/1. The sintered porous bodies, when used in the form of mechanical seal members, exhibit good tribological properties.
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POROUS SILICON CARBIDE

This invention is in the field of ceramic materials and processes. More specifically, this invention is directed to a sintered silicon carbide body which includes a controlled porous phase, as well as to the raw batch from which the ceramic body is produced, the process by which the raw batch is converted to the finished ceramic body, and a mechanical seal member made from the sintered silicon carbide.

A number of the applications for silicon carbide depend upon the friction and wear (tribological) characteristics of the material, in addition to its outstanding thermal, chemical and mechanical properties. These applications include, for example, mechanical seal faces, valve lifters and nozzles. Mechanical seal applications are especially demanding in that the seal members are subjected to both a large compressive force (P) normal to the surface of the face and a sliding velocity (V) across the surface of the face. In evaluating the performance of mechanical seal members, the product (PV) under which the seal can operate is an important parameter.

Certain materials, such as boron nitride, graphite, fluorocarbons and silicones, are self-lubricating, but silicon carbide itself is not one of these. Consequently, mechanical seals which employ silicon carbide as one or both of the seal members may exhibit a squeaking sound when the faces are engaged, or excessive force may be required to initiate separation of the faces and opening of the seal. These behaviors are not desirable, and attempts have been made to introduce lubrication at the seal face surfaces to
eliminate these problems. The very liquid upon which the seal operates can be called upon to perform this lubricant role.

The use of various forms of silicon carbide in mechanical seal applications has been described by Lashway in Lubrication Engineering, 40, 356 (1984). Among the forms of silicon carbide tested by Lashway was a sintered silicon carbide containing "controlled porosity"; the manner in which it was produced was not disclosed. The pores in this silicon carbide, comprising 8 to 10 volume percent ("vol%" hereinafter) of the body, were said to be closed and 20 microns in size. For purposes of this application, vol% porosity = 100 - 100 x [observed density/theoretical density]. Lashway attributed the superior mechanical seal face performance of his porous silicon carbide to its ability to retain a hydrodynamic film of the sealed liquid on the seal face.

Silicon carbide of theoretical density (3.21 g/cm³) is seldom seen in commercial applications, and the silicon carbide of lesser density which is used generally contains a second, pore phase. These pores may be void or filled with silicon or some other material, depending upon the processing route and desired properties. Porosity of a few vol% is not a factor in many silicon carbide applications and is generally ignored. U.S. Patents 4,179,299 and 4,312,954 describe silicon carbide of less than theoretical density, and the silicon carbide disclosed therein can be found in many commercial mechanical seal applications. A more recent patent, U.S. 4,525,461. discloses a sintered silicon carbide which also contains graphite. This graphitized silicon carbide, which is said to be self-lubricating and useful in mechanical seal applications, also contains pores. Thus, silicon carbide sintered bodies which contain pores are not per se new.
The presence of pores in silicon carbide can be detrimental to its
performance to the extent physical properties of the sintered body affect its
performance. In this regard, Seshadri, et al., Ceramic Trans., 2, 215
(1987), reported preparing sintered silicon carbide bodies with a series of
porosities in the range 1 to 7.5 vol% by altering the sintering parameters
and carbon additions. The flexural strength of the resultant sintered
silicon carbide bodies was reported to be insensitive to the porosity up to a
porosity of 7 vol%, but the elastic constants and fracture toughness were
affected significantly.

Introducing porosity into a sintered silicon carbide body by variations
in the sintering time/temperature profile has not been reproducible enough to
enable this technique to be used for making commercial porous material.
Hence, such materials do not exhibit "controlled porosity". The term
"controlled porosity" as used herein is meant to include pores which can be
reproducibly introduced and uniformly distributed throughout the ceramic
body. Another method that can produce a porous sintered silicon carbide,
involves reduction in the amount of sintering aids used to make the silicon
carbide material. This method decreases densification and produces a porous
body with lower density. Lack of control over this process is the major
deterrent to its use. Precise control of the raw materials is also necessary
to make this method dependable. This is not possible with today's materials
at reasonable cost, thus making the processing window for this method very
small, and hard to predict.

Porous sintered materials can also be produced by adding other materials
that thermally degrade and/or shrink, such as cellulose, plant products of
many types and shapes/sizes, and inorganic materials such as glass or low
temperature ceramics. These materials, however, present difficulties in
mixing with the fine silicon carbide powder and, further, may interfere with the sintering mechanism.

Consistent with Lashway's 1983 report, it was disclosed in German Offen. DE 3927300, laid open February 2, 1990, that sintered silicon carbide bodies having between 4 vol% and 13 vol% porosity, where the pores averaged between 10 microns and 40 microns in diameter, provided superior mechanical seals. Such porous bodies were prepared by introducing spherical organic polymeric beads into the raw batch from which the green bodies were produced and then heating the green bodies to remove the organic and densify the body. It was observed that, at pore volumes less than 4 vol%, the porosity was insufficient to effect the improvement, while at pore volumes greater than 13 vol%, the strength of the body was adversely affected, and the pores intercommunicated, causing leakage of the seal. Further, if the average pore diameter was less than 10 microns, the lubricating liquid in the pores was not sufficiently available, while at pore diameters greater than 40 microns, carbon seal face wear was accelerated and seal leakage occurred. It was said that the pores must be rounded in order to avoid stress concentration in the sintered body.

Whereas the introduction of porosity into a sintered silicon carbide body can be effected by introducing organic polymer beads into the raw batch, that technique is not without disadvantages. For example, the polymer must be homogeneously dispersed in the green ceramic body and then be removed from the ceramic body if pores are to be created. Presumably this occurs by thermal decomposition of the polymer beads in the sintering step. However, it is difficult for the resultant products of decomposition to leave the pores if they are truly independent; the interior pores probably communicate with other pores closer to the surface of the body. To the extent the decomposition products remain in the sintered body they constitute
contaminants which can affect the physical properties of the ceramic body. Furthermore, the somewhat elastic polymer beads can be compressed under the pressure utilized in forming the green ceramic body; release of the pressure with recovery of the beads can introduce microcracks in the surrounding silicon carbide matrix. In addition, the use of polymer beads can add additional manipulative steps and materials expense which may be reflected in the price of the product.

Thus, there is needed an alternative method for introducing a controlled amount of porosity into a sintered silicon carbide body, without the added expense and other problems that introduction of organic polymer beads causes.

Consequently, this invention provides, in one aspect, a silicon carbide sintered body comprising a porous structure having porosity in the range of 3 to 25 vol%, the pores therein being uniformly distributed throughout the body and of generally irregular shape, 3 to 5 microns in the longest dimension, and with an aspect ratio between 1/1 and 3/1. According to the invention, the silicon carbide grains exhibit a multimodal, such as, for example, a bimodal particle size distribution, and are comprised of at least a first set of particles having one average grain size, i.e. diameter, and a second set of particles having another average grain size which is larger than the first set of particles, the weight ratio of the first set to the second set lying in the range of 25/75 to 75/25.

In another aspect, this invention provides a raw batch for preparing the aforesaid silicon carbide sintered body, said raw batch comprising 75 wt% to 99 wt% silicon carbide having a multimodal particle size distribution as described above; 0.15 wt% to 5 wt% boron source; 0.38 wt% to 20 wt% carbon source; and 0.5 wt% to 15 wt% binder.
In another aspect, the invention concerns a process for producing the above-described silicon carbide sintered body, the process comprising:

(a) preparing a raw batch including (1) 75 wt.% to 99 wt.% silicon carbide particles exhibiting a multimodal grain size distribution as described above; (2) 0.15 wt.% to 5 wt.% boron source; (3) 0.38 wt.% to 20 wt.% carbon source; and (4) 0.5 wt.% to 15 wt.% binder by blending the silicon carbide particles, the boron source, the carbon source, and the binder;

(b) adding a solvent for said carbon source to the raw batch thereby forming a slurry;

(c) stirring said slurry;

(d) drying said slurry to yield a flowable powder;

(e) compacting said powder at 4,000 to 100,000 psi into a green body compact of desired shape; and

(f) sintering said green body compact at a temperature between 2060°C and 2200°C under an inert atmosphere.

In a further aspect, the invention provides a mechanical seal member comprising the sintered silicon carbide body previously described.

This invention, including the manner and means by which it can be carried out, is clarified by reference to the drawings which accompany this specification and to the detailed description which follows.

Fig. 1 is a photomicrograph at 500X of an unetched, sectioned silicon carbide sintered body produced in accordance with Example 1 hereinafter.

Fig. 2 is a photomicrograph at 500X of the same sample shown in Fig. 1, except that the silicon carbide has been etched.

Fig. 3 is a photomicrograph at 500X of an unetched, sectioned silicon carbide sintered body produced in accordance with Example 2 hereinafter.
Fig. 4 is a photomicrograph at 500X of an unetched, sectioned silicon carbide sintered body produced in accordance with Example 3 hereinafter.

Fig. 5 is a view in perspective showing a mechanical seal member within the scope of this invention.

Fig. 6 is an elevational view, partially in section, showing a mechanical seal member of this invention as it may be used in a mechanical seal application.

The practice of this invention does not depend upon the specific nature of the silicon carbide starting material. According to the invention, porous, sintered ceramic bodies having densities in excess of 2.4 g/cm³, corresponding to at least 75% of the theoretical density for silicon carbide, (a silicon carbide with no more than 25 vol% pores) are readily produced and generally required to avoid seriously affecting the mechanical properties of the sintered body. Although by no means necessary, it is preferred that the silicon carbide be the alpha, non-cubic crystalline form, since the alpha form is relatively less expensive and more readily obtained than the beta, cubic crystalline form. However, the beta form, or mixtures of alpha and beta crystalline material, can be employed, as can amorphous, non-crystalline silicon carbide powder, provided the average grain size meets the requirements hereinafter specified. The process used to make the sintered bodies of this invention does not cause any substantial amount of phase transformation, so the crystalline habit of the silicon carbide starting material will be substantially retained in the finished sintered ceramic body.

The silicon carbide starting material can be obtained from any of a variety of sources. Vapor phase reacted material is produced in fine particle size and can be used if desired. Larger material can be ball milled or otherwise reduced in size until sufficient amounts of fine silicon carbide
particles are obtained, and the proper size of silicon carbide particles can be selected from the resulting ball-milled product by conventional means, such as water sedimentation and screening. Mechanically reducing the size of larger material is a preferred way to prepare silicon carbide useful in this invention. In any event, it is preferred that the silicon carbide material shall have been treated with acid (such as hydrofluoric and/or nitric acids, particularly mixtures of hydrofluoric and nitric acids) to remove extraneous materials which may interfere with the sintering operation.

As noted, the minimum density for sintered ceramic bodies according to the invention is 2.4 g/cm³ (corresponding to a porosity of 25 vol%), but a sintered density of at least 2.8 g/cm³, corresponding to no more than 13 vol% pores, is preferred. The minimum porosity required in order to substantially affect the tribological properties of the sintered body appears to be 3 vol%, preferably 10 vol% to 12 vol%. Such bodies can be used "as is" for applications such as mechanical seal faces, or they can be machined to the desired size and shape at a lower density and later subjected to further firing to produce additional densification.

The sintered ceramic body in accordance with the present invention contains from 91 wt% to 99 wt% silicon carbide, the silicon carbide being a blend of at least two silicon carbides of different average grain size, the number of individual grains of a given average size exhibiting a bell-shaped distribution about the average. The sintered body further includes from 0.5 wt% to 5.0 wt% carbon, from 0.15 wt% to 3.0 wt% boron, and up to 1.0 wt% additional carbon which is chemically associated with the boron, such as boron carbide. All weight percentages (wt%) herein are specified with respect to the total weight of the body or batch, unless otherwise specified. Within this broad composition, it is preferred that the sintered ceramic body contain from 0.5 wt% to 4 wt% carbon derived from carbonized organic
material, from 0.2 wt% to 0.4 wt% boron as boron carbide, and 0.05 wt% to
0.11 wt% additional carbon which is associated chemically with the boron,
with the balance of the composition being silicon carbide. Most preferably,
the sintered ceramic body contains 98 to 99 wt% silicon carbide, 1 to 1.5 wt%
carbonized organic material, 0.25 to 0.36 wt% boron as boron carbide and 0.07
wt% to 0.10 wt% additional carbon which is chemically associated with the
boron.

The sintered ceramic body desirably contains from 0.15 wt% to 3.0 wt%
boron, preferably 0.2 wt% to 0.4 wt%, and most preferably 0.25 wt% to 0.36
wt%. In so specifying the boron content, it is not intended to limit the
form in which the boron may be present. The boron may be present as
elemental boron or chemically combined in boron compounds such as boron
carbide. Indeed, in most cases the boron will be present as a compound of
boron, such as boron carbide, in the finished sintered ceramic body. The
"additional carbon," i.e., the carbon chemically associated with the boron
and broadly specified as being present in an amount up to 1.0 wt%, is thus an
optional component of the finished sintered ceramic body, as the amount of
such additional carbon (carbon not associated with the silicon carbide or
present as carbonized organic material) will depend on the carbon associated
with the boron present in the raw batch mixture from which the sintered
ceramic body was made.

The amount of carbon present as carbonized organic material depends on
the amount of such organic material present in the raw batch and the char
yield (carbon content) of the organic material.

The raw batch for producing the sintered ceramic body in accordance with
the invention comprises 75 wt% to 99 wt%, preferably 94 wt% to 96 wt%
silicon carbide composed of at least two different silicon carbides which
differ in average particle size. In addition, it is preferred that none of
the silicon carbides have an average grain size larger than 15 microns, and
it is especially desirable if one of the silicon carbides has an average
grain size less than 1 micron. Increasing the relative amount of the larger
sized silicon carbide particle, at the expense of the smaller sized silicon
carbide particle, leads to a lower density in the sintered ceramic body and a
corresponding increase in its porosity. Although the weight ratio of the
larger sized silicon carbide particle to the smaller sized silicon carbide
particle may vary widely and still yield a suitable product, it is preferred
that the weight ratio lie in the range between 25/75 and 75/25, with a ratio
of 50/50 being especially attractive.

One important feature of the raw batch is the carbonizable organic
material or carbon source. The organic material can be soluble in organic
solvents, but is preferred that it be soluble in water for safety and
environmental reasons. In any case, it is important that it be easily
dispersed to coat the silicon carbide particles, thereby increasing the
availability of the carbonized organic material upon firing the shaped green
body produced from the raw batch. It has been found desirable that the
sintered ceramic body contain from 0.5 wt% to 5.0 wt% of carbonized organic
material, with the result that, if the carbonizable organic material has a
char yield of from 25 wt% to 75 wt%, as is preferred, there should be present
from 0.38 wt% to 20 wt% carbonizable organic material in the raw batch.
Within the range of from 25 wt% to 75 wt% char yield, it is preferred that
the organic material have from 33 wt% to 50 wt%, more particularly from 40
wt% to 45 wt%, char yield. If the char yield is between 33 wt% and 50 wt%,
the amount of carbonizable organic material in the raw batch should range
between 1.5 wt% and 10 wt% to produce the preferred 0.5 wt% to 5.0 wt% carbon
in the finished sintered ceramic body. The most preferred amount of
carbonized organic material in the sintered ceramic body is believed to be 1
wt% to 1.5 wt%, so that the optimum raw batch should contain 2 wt% to 4 wt% of carbonizable organic material, preferably soluble in water and having a char yield between 40 wt% and 45 wt%.

Carbonizable organic materials are represented by phenolic resins and coal tar pitch, which have char yields of 40 wt% to 42 wt% and on the order of 60 wt%, respectively. As between phenolic resins and coal tar pitch, phenolic resins are preferred, and B-stage phenolic resole resins, such as Resin No. 8121 available from Varcol Chemical Co., are particularly useful in this invention. Of greater utility, however, are phenol-formaldehyde resins, which in some instances are water soluble. An example is the "Plyophen 43290 Liquid One Step Phenolic Resin" available from Occidental Chemical Co.

The boron source can be added to the raw batch as elemental boron or as a boron-containing compound such as boron carbide. Boron carbide is essentially a non-stoichiometric material, and various boron carbides having a molar ratio of boron to carbon between 8:1 and 2:1 have been reported. It is, in general, preferred to use boron carbide as the boron source and, in particular, boron carbide which is so called "solid state reacted boron carbide," with a molar ratio of boron to carbon between 3.5/1 and 4.1/1. Such boron carbide can be produced in accordance with the process of U.S. Pat. No. 3,379,647. Boron carbides having higher ratios of boron to carbon are more chemically reactive than the material having a ratio of 3.5/1 to 4.1/1, but are less available, more expensive, and therefore not preferred.

The amount of boron source added to the raw batch depends on the boron content of the boron source and the amount of boron desired in the final sintered ceramic body. The sintered ceramic body desirably contains from 0.15 wt% to 3.0 wt% boron, and in particular from 0.2 wt% to 0.4 wt% boron is present in the preferred ceramic bodies of the present invention. The most
preferred boron content of the sintered ceramic body is 0.25 wt% to 0.36 wt%.
The amount of boron source added to the raw batch should be chosen accordingly. Thus, if the boron source is elemental boron, it should most preferably be present in the raw batch in an amount sufficient to yield a sintered ceramic body having from 0.25 wt% to 0.36 wt% boron. For the preferred solid state reacted boron carbide, with a molar ratio of boron to carbon between 3.5:1 and about 4.1:1, the boron carbide should be present in the raw batch in an amount from 0.2 wt% to 4 wt% to produce such an amount of boron in the finished sintered ceramic body.

The boron source can be crystalline, or amorphous, and preferably is powder of an average grain size less than 30 microns. Within this limitation, it is preferred that the particle size be in the range from 0.1 micron to 10 microns.

The temporary binder can be selected from a wide range of organic resins and other materials well known to those skilled in the art, such as polyvinyl alcohol, acrylic resins, coal tar pitch, long chain fatty material (for example "CARBOWAX"), metallic stearates, such as aluminum stearates and zinc stearates, sugars, starches, alginates, and polystyrene. Many of these materials are, of course, capable of functioning as a carbonizable organic material which is added to yield at least some of the carbon in the sintered body. Thus, a single material can serve two functions in the raw batch. The temporary binder should comprise between 0.5 wt% and 15 wt% of the raw batch, depending upon the char yield, for example.

The binder preferably includes polyvinyl alcohol having associated therewith from about 5 to about 15 parts by weight water per part of polyvinyl alcohol, as a temporary binder vehicle. In particular, it is preferred to use 10 parts by weight polyvinyl alcohol plus 90 parts by weight...
water as a temporary binder vehicle. In addition, the aqueous polyvinyl alcohol may have associated therewith an acrylic resin, such as "RHOPLEX® HA-8 Emulsion," available from Rohm & Haas Company. The raw batch preferably contains from 1 wt% to 2 wt% each of aqueous polyvinyl alcohol and aqueous acrylic resin, the binder preferably comprising between 2 wt% and 3 wt% of the raw batch.

The process for producing the sintered ceramic body according to another aspect of the invention begins by mixing together the components of the raw batch to contain from 75 wt% to 99 wt% silicon carbide; between 0.38 wt% and 20 wt% of the carbonizable organic material; from 0.15 wt% to 5 wt% of the boron source; and from 0.5 wt% to 15 wt% temporary binder. If the temporary binder includes aqueous polyvinyl alcohol, the first mixing step preferably includes stirring the powdered components, silicon carbide, carbonizable organic material and boron source, together with the temporary binder, prior to optionally adding a solvent in which the carbonizable material is soluble. In any event, after the solvent is added, the raw batch should be stirred for 5 to 15 minutes to coat the carbonizable organic material onto the silicon carbide particles of the raw batch. After the raw batch has been sufficiently stirred, the stirred mixture is dried by one of the techniques known in the art, such as passing a quantity of dry gas over the stirred mixture or by spray-drying the mixture, thereby yielding a flowable powder.

Following this drying step, the dried mixture can be formed to produce a shaped green body, preferably having a density of at least 1.60 g/cm³. For example, the mixture can be formed into mechanical ring seal faces if desired. This can be accomplished by any of a variety of techniques which are known to those skilled in the art. For example, the mixture can be shaped by extrusion, injection molding, transfer molding, casting, cold pressing, isostatic pressing, or by compression. If compression is used.
preferred pressures are between 4,000 and 100,000 psi, with between about 16,000 and 20,000 psi, such as 17,000 psi at room temperature, being more preferred.

If the temporary binder requires curing, e.g., if the binder contains polyvinyl alcohol, the next step, curing the temporary binder, can be accomplished by heating the shaped body at a temperature of 90°C to 100°C for 1 to 2 hours. Other curing conditions known to those skilled in the art may be required for other binders.

The shaped green body is then fired to carbonize the organic material and accomplish the densification necessary to produce the porous sintered ceramic body of the invention. Firing requires heating the formed body for 20 to 60 minutes at temperatures between 1900°C and 2500°C. The use of lower temperatures is generally to be avoided, since at lower temperatures densification of the body may not be reproducible, and controlled porosity may not be achieved. At higher temperatures sublimation of the silicon carbide can occur.

The firing step can be carried out in a conventional batch or continuous furnace, wherein the shaped body is passed through the hot zone of the furnace at a rate to provide a prescribed residence time at the desired temperature and for the desired time. Details of such furnaces are known in the art and are described, for example, in U.S. Patent 3,689,220. The firing step accomplishes a "pressureless sintering," referred to herein for simplicity merely as "sintering." By "sintering" or "pressureless sintering," it is meant that no mechanical pressure is applied to the object being fired or sintered to promote densification. Instead, the object being sintered, usually in an inert container such as a graphite crucible, is maintained under an atmosphere of inert gas, a reducing gas, a vacuum, or
nitrogen. Reducing gases include hydrogen, carbon dioxide and carbon monoxide; while inert gases include argon, helium, and neon. The gases in which the sintering operation can be carried out thus include argon, carbon dioxide, carbon monoxide, helium, hydrogen, neon, nitrogen, and mixtures thereof. Although nitrogen, under sintering conditions, enters into reaction to some degree with the silicon carbide, it does so in sufficiently minor degree that the composition of the sintered ceramic body is not noticeably changed thereby. The use of nitrogen does, however, raise the sintering temperature, so that if nitrogen is the surrounding atmosphere, the preferred sintering temperature is between 2260° and 2300°C. Under the other gases, particularly inert gases such as argon, helium or neon, the preferred sintering temperature is between 2060° and 2200°C. The firing can also be carried out under vacuum. By "vacuum" is meant a practical vacuum of 1.0 torr or less.

The following specific Examples illustrate the practice of the several aspects of this invention.

**EXAMPLE 1**

A silicon carbide powder (47.525 g of alpha powder having an average grain size of 0.5 micron) was blended with another silicon carbide powder (47.525 g, alpha powder having an average grain size of 3.0 microns) and with 0.35 g boron carbide (solid state reacted), 2.4 g carbon source (PLYOPHEN 43290 resin from the Occidental Chemical Company having a char yield of 42.5%) and a binder consisting of 1.2 g of 18 wt% polyvinyl alcohol in water and 1.0 wt% acrylic resin (RHOPLEX® HA-8 emulsion from Rohm & Haas Company). The char yield of the binder was zero under the sintering conditions employed. Water was added to form a slurry, which was then spray dried to form a free flowing powder. The resultant powder was formed into a compact
at a pressure of 17.0 Ksi and sintered at 2150°C under an argon atmosphere.

The sintered silicon carbide body produced thereby had a density of 2.95 g/cm³, [2.95/3.21] x 100 = 92% of the theoretical density for silicon carbide, implying a pore volume of 8%. Microscopic analysis of the surface from the sectioned, sintered body indicated 12.6% of the surface area comprised pores, the average pore being 3.6 microns long and 2.3 microns wide, with an average pore area of 8.1 micron². Representative photomicrographs of the sectioned sintered body appear as Figures 1 and 2, the unetched body (Fig. 1) showing most clearly the generally irregular shape of the pores, the etched body (Fig. 2) showing the silicon carbide grain. The following physical properties of the sintered body were determined:

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<td>Fracture toughness</td>
<td>4.3 KSI/in 1/2</td>
</tr>
<tr>
<td>Modulus of elasticity</td>
<td>56.2 Mpsi</td>
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<tr>
<td>Knoop hardness</td>
<td>3272 Kg/mm²</td>
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**EXAMPLE 2**

A silicon carbide powder (61.126 g of alpha powder having an average grain size of 0.5 micron) was blended with 32.914 g of alpha silicon carbide powder having an average grain size of 3.0 microns and with 0.46 g boron carbide (solid state reacted), 2.7 g carbon source comprising the same phenolic resin described in Example 1, and a binder consisting of 1.5 g of the solution and 1.3 g of the acrylic resin as described in Example 1. Water was then added to form a slurry which was spray dried to produce a free flowing powder. A green body compact was formed from the powder under 17.0 KSI pressure, and then sintered as in Example 1, yielding a sintered silicon
carbide body having a density of 3.05 g/cm$^3$, 95% of theoretical density for silicon carbide, with a calculated pore volume of 5%. Microscopic analysis of the sectioned, sintered body yielded 9.4 area% pores, the average pore being 2.8 microns long, 1.8 microns wide and having a total area of 5.0 micron$^2$. A representative photomicrograph of the sectioned sintered body appears in Fig. 3.

**EXAMPLE 3**

Example 1 was repeated, except that the weight ratio of the silicon carbide with average grain size of 0.5 micron to the silicon carbide of 3.0 microns average grain size was 35/65. This composition yielded a sintered silicon carbide body with a density of 2.80 g/cm$^3$, 87% of the theoretical density of silicon carbide, and a calculated pore volume of 13%. Microscopic examination of the sectioned sintered body showed 18.0 area% pores with the average pore dimension being 4 to 5 microns. A representative photomicrograph of the sectioned sintered body appears in Fig. 4.

**EXAMPLE 4**

Utilizing the raw batch described in Example 1, adding solvent to dissolve the phenolic resin, stirring, and then drying the stirred mixture, a mechanical seal member green body was formed in a mold under 17 Ksi compression, with dimensional allowances for shrinkage, and the green body was heated to 100°C for 1.5 hours to cure the binder. The green body was then sintered under argon at 2100°C for 40 minutes. The finished mechanical seal member is illustrated in Fig. 5, and its use is shown in Fig. 6. Referring to Fig. 6, which shows a valve with a portion thereof broken away, liquid enters the valve at 12, passes into housing 15, and exits at 11. The
mechanical seal members 13 and 14, which are shown disengaged, permitting the liquid to flow, are engaged face to face by rotating screw handle 16, bringing seal member 13 down upon seal member 14 to close off the liquid flow. Either or both of seal members 13 and 14 will be porous silicon carbide within the scope of this invention. Evaluation of the seal members in sealing applications demonstrates that seal members within the scope of this invention are useful in such applications.

It will be evident that this invention can be carried out in ways other than the ways illustrated in the aforesaid specific Examples. Accordingly, the scope of this invention is not to be limited to those specific Examples, but is to be accorded the full scope represented in the following claims.
1. A silicon carbide sintered body comprising a porous structure having porosity in the range of about 3 to 25 vol%, the pores therein being uniformly distributed throughout the body and of generally irregular shape, 3 to 5 microns in the largest dimension, and with an aspect ratio between 1/1 and 3/1, the silicon carbide grains exhibiting a multimodal particle size distribution and comprised of at least a first set of particles having one average grain size and a second set of particles having another average grain size larger than the first set of particles, the weight ratio of the first set to the second set lying in the range of 25/75 to 75/25.

2. The sintered body of claim 1 wherein said first set of particles has an average grain size of 0.5 micron, and said second set of particles has an average grain size of 3 microns.

3. The sintered body of claim 1 further comprising 91 wt% to 99 wt% silicon carbide, 0.5 wt% to 5.0 wt% carbon, 0.15 wt% to 3.0 wt% boron, and up to 1.0 wt% additional carbon chemically associated with the boron.

4. The sintered body of claim 3 further comprising 0.5 wt% to 4 wt% carbon, 0.2 wt% to 0.4 wt% boron as boron carbide, and 0.05 wt% to 0.11 wt% additional carbon chemically associated with the boron carbide.

5. The sintered body of claim 3 further comprising 98 wt% to 99 wt% silicon carbide, 1 wt% to 1.5 wt% carbon, 0.25 wt% to 0.36 wt% boron as boron carbide, and 0.07 wt% to 0.10 wt% additional carbon chemically associated with the boron carbide.
6. The sintered body of claim 1 wherein said silicon carbide is alpha silicon carbide substantially free of beta silicon carbide.

7. The sintered body of claim 1 having a porosity between 5 vol% and 13 vol%.

8. The sintered body of claim 1 wherein the weight ratio of said first set of silicon carbide particles to said second set of silicon carbide particles is 50/50.

9. A mechanical seal member comprising a sintered silicon carbide body according to any of one of Claims 1 to 8.

10. A raw batch for preparing the silicon carbide sintered body of claim 1 comprising:

   (a) 75 wt% to 99 wt% silicon carbide particles exhibiting a multimodal grain size distribution and comprised of at least a first set of particles having one average grain size and a second set of particles having another average grain size larger than the first set of particles, the weight ratio of the first set to the second set lying in a range of 25/75 to 75/25;

   (b) 0.15 wt% to 5 wt% boron source;

   (c) 0.38 wt% to 20 wt% carbon source; and

   (d) 0.5 wt% to 15 wt% binder.

11. The raw batch of claim 10 wherein said first set of particles has an average grain size less than 1 micron, and said second set of particles has an average grain size no larger than 15 microns.
12. The raw batch of claim 10 wherein said first set of particles has an average grain size of 0.5 micron, and said second set of particles has an average grain size of 3 microns.

13. The raw batch of claim 10 wherein said carbon source is selected from the group consisting of phenolic resins and coal tar pitch.

14. The raw batch of claim 10 wherein said boron source is boron carbide having a boron/carbon molar ratio of 3.5/1 to 4.1/1.

15. The raw batch of claim 14 wherein said boron carbide is powder having an average grain size less than 30 microns.

16. The raw batch of claim 10 wherein said silicon carbide is alpha silicon carbide substantially free of beta silicon carbide.

17. The raw batch of claim 10 wherein said binder is selected from one or more of the group consisting of aqueous polyvinyl alcohol, acrylic resins, coal tar pitch, long chain fatty material, metallic stearates, sugars, starches, alginates, and polystyrene.

18. A process for producing a silicon carbide sintered body which comprises (a) preparing a raw batch including (1) 75 wt% to 99 wt% silicon carbide particles exhibiting a multimodal grain size distribution and comprised of at least a first set of particles having one average grain size and a second set of particles having another average grain size larger than the first set of particles, the weight ratio of the first set to the second set lying in the range of 25/75 to 75/25; (2) 0.15 wt% to 5 wt% boron source; (3) 0.38 wt% to 20 wt% carbon source; and (4) 0.5 wt% to 15 wt% binder by
blending the silicon carbide, the boron source, the carbon source, and the binder;
(b) adding a solvent for said carbon source to the raw batch, thereby forming a slurry;
(c) stirring said slurry;
(d) drying said slurry to yield a flowable powder;
(e) compacting said powder at 4,000 to 100,000 psi into a green body compact of desired shape; and
(f) sintering said green body compact at a temperature between 2060°C and 2200°C under an inert atmosphere.

19. The process of claim 18 wherein said first set of particles has an average grain size less than 1 micron, and said second set of particles has an average grain size no larger than 15 microns.

20. The process of claim 18 wherein said first set of particles has an average grain size of 0.5 micron, and said second set of particles has an average grain size of 3 microns.

21. The process of claim 18 wherein said carbon source is selected from the group consisting of phenolic resins and coal tar pitch.

22. The process of claim 18 wherein said boron source is boron carbide having a boron/carbon molar ratio of 3.5/1 to 4.1/1.

23. The process of claim 18 wherein said silicon carbide is alpha silicon carbide substantially free of beta silicon carbide.

24. The process of claim 18 wherein said binder is selected from one or more of the group consisting of aqueous polyvinyl alcohol, acrylic resins, coal
tar pitch, long chain fatty material, metallic stearates, sugars, starches, alginates, and polystyrene.
Fig. 3.

Fig. 4.
2/3
SUBSTITUTE SHEET
A. CLASSIFICATION OF SUBJECT MATTER
   IPC(5) : C04B 35/56
   US CL : 428/446; 501/90; 428/698; 428/212; 428/704; 264/59
   According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
   U.S. : 428/446; 501/90; 428/698; 428/212; 428/704; 264/59

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<td>Y</td>
<td>JP, A, 61-65499 (IBIDEN CO LTD) 04 APRIL 1986, Abstract.</td>
<td>1-8</td>
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<td>Y</td>
<td>JP, A, 59-223273 (TOYOTA JIDOSHA KK) 15 DECEMBER 1984, Abstract.</td>
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[ ] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

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<th>Special categories of cited documents:</th>
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<tr>
<td>&quot;T&quot; late document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</td>
</tr>
<tr>
<td>&quot;X&quot; document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</td>
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<tr>
<td>&quot;Y&quot; document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</td>
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<td>&quot;A&quot; document member of the same patent family</td>
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Date of the actual completion of the international search: 01 JULY 1993
Date of mailing of the international search report: 01 SEP 1993

Name and mailing address of the ISA/US Commissioner of Patents and Trademarks
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