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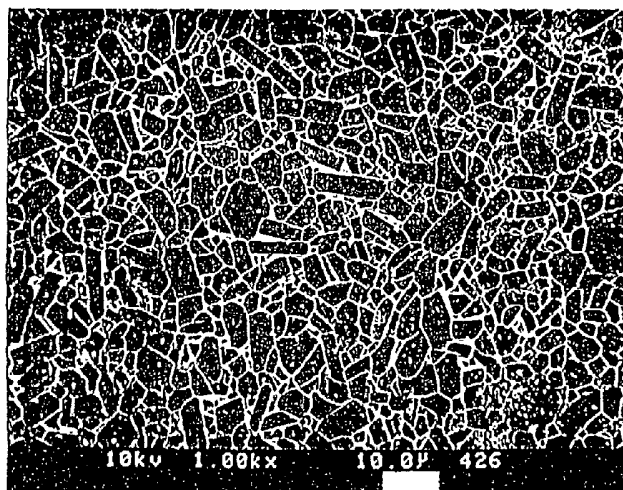
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[Continued on next page]

(54) Title: SILICON CARBIDE CERAMIC COMPOSITION AND METHOD OF MAKING



(57) Abstract: The present application is directed to ceramic compositions and, more specifically, to a silicon carbide composition and method of making it through liquid phase sintering. In one embodiment, the present invention is directed to an unsintered ceramic body including at least one liquid phase sintering aid. The unsintered ceramic body further includes a boron containing compound, a free carbon containing compound, and silicon carbide. In another embodiment, the present invention is directed to a method of making a sintered ceramic body. The method includes combining at least one liquid phase sintering aid, a boron containing compound, a free carbon containing compound, and silicon carbide to form a green ceramic, shaping the green ceramic into a ceramic body, and sintering the ceramic body.



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SILICON CARBIDE CERAMIC COMPOSITION AND METHOD OF MAKING

This application is a continuation-in-part of and claims priority to U.S. Patent Application No. 09/933,463, filed August 20, 2001.

5 The present invention is directed to ceramic compositions and, more specifically, to a silicon carbide ceramic composition and method of making it through liquid phase sintering.

10 Silicon carbide ceramic materials are used in a variety of applications requiring good heat resistance, strength and tribological properties. For example, silicon carbide is often used in automotive and industrial applications, such as in fluid seals. However, the limited toughness of silicon carbide has limited its utility in applications requiring this property.

15 Traditionally, silicon carbide is sintered by solid state sintering. Typically, solid state sintering employs boron and carbon as sintering aids. Solid state sintering is traditionally performed at about 2150 °C and yields a relatively high sintered density of about 96-98% of the theoretical density (of solid silicon carbide). The crystalline structure produced by solid state sintering, however, is undesirable for some applications. Specifically, solid state sintering results in an equiaxed crystalline microstructure with relatively low fracture toughness (approximately 2.5 MPa m^{1/2} as measured by the indentation crack length method, ASTM Test No. C1421).

20 It has also been discovered that silicon carbide can be processed by liquid phase sintering in a manner similar to silicon nitride. Liquid phase sintering is traditionally performed at about 1750-2000 °C. In liquid phase sintering, a rare earth metal oxide and alumina are typically used as sintering aids. The rare earth metal oxide and alumina form a liquid glass as the temperature is elevated during sintering. The liquid phase pulls silicon carbide particles together through capillary action. Smaller silicon carbide particles are dissolved into the glass phase and precipitate onto larger particles, densifying the material. Liquid phase sintering results in silicon carbide having elongated (acicular) crystalline microstructure. The acicular microstructure improves the fracture toughness of silicon carbide produced by liquid phase sintering over silicon carbide produced by solid state sintering by as much as two to three times (up to approximately 6 MPa m^{1/2} as measured by the indentation crack length method).

Liquid phase sintering is generally performed with β -phase silicon carbide powder, which is typically more expensive than the α -phase powder that may be used in the solid state sintering process. During the liquid phase sintering process, the β -phase transforms into elongated α -phase grains, improving toughness. The α -phase silicon carbide powder may be used in the liquid phase sintering process, but density and toughness are compromised. Where α -phase silicon carbide is used in a liquid phase sintering process, higher sintering temperatures (up to about 2050 °C) and hot pressing may overcome the density and toughness problems. However, hot pressing leads to increased cost and sintering temperature that leads to a thicker reaction layer, which often must be machined off, further increasing the cost.

In one embodiment, the present invention is directed to an unsintered ceramic body including at least one liquid phase sintering aid. The unsintered ceramic body further includes a boron containing compound, a free carbon containing compound, and silicon carbide.

In another embodiment, the present invention is directed to a method of making a sintered ceramic body. The method includes combining at least one liquid phase sintering aid, a boron containing compound, a free carbon containing compound, and silicon carbide to form a green ceramic, shaping the green ceramic into a ceramic body, and sintering the ceramic body.

FIG. 1 is a photocopy of a photomicrograph of a cross-section of a prior art silicon carbide ceramic;

FIG. 2 is a photocopy of a photomicrograph of a cross-section of a prior art silicon carbide ceramic;

FIG. 3 is a photocopy of a photomicrograph of a cross-section of a prior art silicon carbide ceramic;

FIG. 4 is a photocopy of a photomicrograph of a cross-section of a prior art silicon carbide ceramic;

FIG. 5 is a photocopy of a photomicrograph of a cross-section of a silicon carbide ceramic according to one embodiment of the present invention;

FIG. 6 is a photocopy of a photomicrograph of a cross-section of a silicon carbide ceramic according to the embodiment of FIG. 5;

FIG. 7 is a photocopy of a photomicrograph of a cross-section of a silicon carbide ceramic according to the embodiment of FIG. 5;

FIG. 8 is a photocopy of a photomicrograph of a cross-section of a silicon carbide ceramic according to the embodiment of FIG. 5;

FIG. 9 is a graph of cumulative % versus mean grain length;

FIG. 10 is a graph of toughness and density versus mean grain length;

5 FIG. 11 is a photocopy of a photomicrograph of a cross-section of a silicon carbide ceramic according to one embodiment of the present invention;

FIG. 12 is a photocopy of a photomicrograph of a cross-section of a silicon carbide ceramic according to one embodiment of the present invention;

FIG. 13 is a graph of toughness versus formulation;

10 FIG. 14 is a graph of density versus formulation; and

FIG. 15 is a graph of weight loss versus formulation.

The present application is directed to a sintered ceramic body and a method of making a sintered ceramic body. In one embodiment, the method includes combining a rare earth metal oxide, one of a glass phase metal oxide and a glass phase metal nitride, a boron containing compound, a free carbon containing compound, and silicon carbide to form a green ceramic. The method further includes shaping the green ceramic into a ceramic body and sintering the ceramic body at about 1800-2050 °C for about 1-5 hours.

By rare earth metal it is meant any of the following elements: Lu, Yb, Tm, Er, Ho, Y, Dy, Tb, Gd, Eu, Sm, Nd, Pr, Ce, La and Ti. By rare earth metal oxide, it is meant of oxides of any of the rare earth metals, as used herein. Any rare earth metal oxide may be used in the method of the invention. For example, oxides of yttrium, neodymium and titanium, such as yttrium oxide, neodymium oxide and titanium oxide, have been shown to usable in some embodiments. The particular rare earth metal oxide selected in a particular application may vary with the parameters of the application. The melting temperatures of rare earth metal oxides vary. Higher melting temperature materials are generally more expensive to produce, as will be described in more detail below, but also generally produce ceramics having better resistance to high temperature conditions. For example yttrium oxide generally produces sintered ceramic bodies having superior physical properties to those produced with neodymium oxide, but is also more expensive. Accordingly, yttrium oxide is preferred over neodymium oxide where quality is the driving factor, while neodymium oxide is preferred over yttrium oxide where price is the driving factor.

In order to decrease the melting temperature of the rare earth metal oxide, a glass phase metal oxide or glass phase metal nitride is typically also employed. By glass phase metal, it is meant any element that, as an oxide or nitride, produces a glass phase with a rare earth metal oxide at temperatures acceptable for sintering silicon carbide, such as Al, Ca and Mg. By glass phase metal oxide, it is meant oxides of glass phase metals, as used herein. Any glass phase metal oxide may be used in the method of the invention. For example, oxides of aluminum, such as aluminum oxide have been shown to usable in some embodiments. The particular metal oxide selected in a particular application may vary with the parameters of the application. As with rare earth metal oxides, glass phase metal oxides and glass phase metal nitrides have varying melting temperature. For example, Mg has a lower melting temperature than Al. Accordingly, selection of a glass phase metal oxide is also an engineering decision based upon the properties needed.

By glass phase metal nitride, it is meant nitrides of any element that produces a glass phase with a rare earth metal oxide at temperatures acceptable for sintering silicon carbide, such as Al, Ca or Mg. Any glass phase metal nitride may be used in the method of the invention. For example, nitrides of aluminum, such as aluminum nitride have been shown to usable in some embodiments. The particular metal nitride selected in a particular application may vary with the parameters of the application for the same reasons as described above with respect to glass phase metal oxides.

During sintering, the rare earth metal oxide and glass phase metal oxide or glass phase metal nitride (collectively referred to as "liquid phase sintering aids") form a liquid glass phase, as described in the Background. Any amount of liquid phase sintering aids may be used that will produce a sintered ceramic body having the desired properties. If too little liquid phase sintering aids are used, there may not be enough wetting of the silicon carbide by the glass phase for effective sintering. If too much liquid phase sintering aids are used, then there may be excessive weight loss during sintering and the sintered ceramic may have reduced corrosion and creep resistance. For example, depending on the embodiment, about 5-20 weight (wt.) %, 6-16 wt. %, 8-12 wt. %, 9-11 wt. %, 11-13 wt. % or 10 wt. % of the ceramic body may be liquid phase sintering aids prior to sintering.

Any amount of each of the rare earth metal oxide and glass phase metal oxide or glass phase metal nitride may be used that produces a sintered ceramic body having the desired properties. For example, depending on the embodiment, the amount of rare earth

metal oxide may be about 3-8%, 4-6% or 4% of the weight of the ceramic body prior to sintering. Similarly, depending on the embodiment, the amount of metal oxide or metal nitride may be, for example, about 3-8%, 6-8% or 6% of the weight of the ceramic body prior to sintering. In embodiments where both glass phase metal oxides and glass phase metal nitrides are used, the total glass phase metal may fall within these guidelines.

In some embodiments, the amounts of the rare earth metal oxide and glass phase metal oxide or glass phase metal nitride may be selected (for example with the aid of a phase diagram) to produce a desired ratio of rare earth metal oxide to glass phase metal oxide or glass phase metal nitride. For example, this ratio may be selected based on the melting temperature of the liquid phase sintering aids for a given ratio of rare earth metal oxide to glass phase metal oxide or glass phase metal nitride. Due to the loss of liquid phase sintering aids at higher temperatures, in some embodiments, the ratio of the liquid phase sintering aids may be selected such that the liquid phase sintering aids melt and form a glass phase at a lower temperature. For example, in some embodiments, the ratio may be selected based upon the eutectic for the particular combination of liquid phase sintering aids. It is to be appreciated that the ratio corresponding to the eutectic will vary with different combinations of liquid phase sintering aids. In an embodiment where the rare earth metal oxide is yttrium oxide and the transition metal oxide is aluminum oxide, a ratio of about 2:3 yttrium oxide:aluminum oxide has been found to be acceptable. It is also to be appreciated that combinations of more than one rare earth metal oxide and/or glass phase metal oxide or glass phase metal nitride are possible and there need not be only one of each species in the liquid phase sintering aids.

While the use of boron and carbon as sintering aids is associated in the art with solid state sintering techniques, it has been discovered that boron and carbon may also be beneficially used in liquid phase sintering. Liquid phase sintering of silicon carbide evolved from liquid phase sintering of silicon nitride, which does not use boron or carbon as sintering aids. Without wishing to be bound by any particular theory, it is believed that boron and carbon improve the characteristics of silicon carbide produced according to the method of the invention because they favor the formation of particular polytypes of silicon carbide grains. In particular, it is believed that boron and carbon increase the number of acicular 6H polytype grains, which are believed to improve the toughness of sintered silicon carbide according to the present invention. Further, carbon aids in densification. Liquid phase sintered ceramic with carbon is denser than that without.

Any amounts of boron and carbon may be used in the preset method that produce a sintered silicon carbide body having the desired properties. For example, in particular embodiments, about 0.05-4%, 0.1-1%, 0.25-2%, 0.5-1%, 0.05-0.15%, or 0.75% of the weight of the ceramic body prior to sintering may be boron and about 0.25-5%, 0.5-4%,
5 2-3%, 0.25-1%, or 2.5 % of the weight of the ceramic body prior to sintering may be free carbon, as defined below.

Boron added according to the method of the application may be in any form that allows the boron to improve any property of the sintered ceramic body. For example, the boron may be in a form that is chemically active as a sintering aid at sintering
10 temperatures. Boron that is chemically active at sintering temperatures is referred to herein as free boron. Examples of a suitable boron compounds include boron carbide, boron nitride and various hexaborides, such as yttrium hexaboride and cerium hexaboride. Similarly, carbon added according to the method of the application may be in any form that allows the carbon to improve any property of the sintered ceramic body.
15 For example, the carbon may be in a form that is chemically active as a sintering aid at sintering temperatures. Carbon that is chemically active as a sintering aid at sintering temperatures is referred to herein as free carbon. The carbon in certain carbides, such as silicon carbide and boron carbide, is not believed to be chemically active as a sintering aid at sintering temperatures and is specifically excluded from this definition. Examples
20 of suitable carbon sources include carbon black, other carbides that are chemically active as a sintering aid at sintering temperatures, including titanium carbide, and any of a variety of carbon-based binders used to hold the unsintered ceramic green body together. Such binders may include phenolic resin, polyvinyl alcohol and polyethyl glycol. Free carbon content can be measured using LECO combustion techniques.

Where boron or carbon is not added in elemental form, the percent by weight of the unsintered ceramic body comprised of the material added may be selected to provide the desired amount of boron of carbon. For example, on a weight basis, more boron carbide must be added than elemental boron to provide the same amount of boron in the unsintered ceramic body. As another example, in one embodiment, about 1-6 weight %
30 of the a free carbon containing material may be added.

The method of the present application may be performed with any type of ceramic base material that produces a sintered ceramic having the desired properties, such as silicon carbide, silicon nitride, alumina, zirconia and boron carbide. For

example, α -phase or β -phase silicon carbide may be used. The ability to use α -phase silicon carbide in a liquid phase sintering process without requiring subsequent hot pressing or generating an excessive reaction layer that must be machined off represents a significant advance in the art. Any size particles of silicon carbide may be used as a starting material, though larger particles will typically require milling to achieve a desired fineness for sintering. For example, in one embodiment, coarse (approximately 10 micron) α -phase silicon carbide powder is used as a starting material, such as that available from Saint-Gobain (Lillesand, Norway) and Stark (Newton, MA).

Coarse silicon carbide powder may be milled to a desired fineness prior to combination with other components. As a general rule, finer powders produce better properties in the sintered silicon carbide body, but cost more to produce, leading to an engineering decision as to the particle size used in a particular application. However, it has also been noted that, in some embodiments, very fine particles performed less well than particles in a more traditional size range. A fineness of about 12-13m²/g (as measured by the BET method, ASTM Test No. C1274-00), representing a range of particles from about 0.1-2.0 microns in diameter having an average diameter of about 0.6-0.8 microns has been found to be acceptable in some embodiments. A fineness of about 15m²/g (as measured by the BET method, ASTM Test No. C1274-00) has also been found to be acceptable. Milling may be performed using any apparatus capable of producing silicon carbide particles having the desired fineness. For example, milling may be performed in a conventional milling machine containing grinding media, such as balls or chunks averaging about 1-10 millimeters in diameter of silicon carbide, silicon nitride, or the like.

In some embodiments, the ceramic body may include a material or materials intended to improve packing density and/or grain microstructure. For example, the ceramic body may include a lubricant. Examples of a suitable lubricants include stearic acid, aluminum stearate, magnesium stearate and ammonium stearate.

The silicon carbide, boron, carbon and liquid phase sintering aids and any other additives may be combined in any manner that produces a green ceramic body having the desired components and that may be sintered to produce a ceramic body having the desired properties. Individual components may be mixed with one another and then mixed with other pre-mixed components or individual components. Whatever the order of mixing, the mixing may be performed such that components being mixed are well

distributed within one another. Mixing may occur as each component is added or after all the components are combined. For example, in one embodiment, silicon carbide powder of a desired fineness is used as a base material and other materials are added thereto. In this embodiment, boron and carbon (in some cases in the form of a binder) may be added to the silicon carbide powder followed by thorough mixing. The liquid phase sintering aids may then be added, again followed by thorough mixing.

Any mixing performed may take any amount of time required to obtain a desired level of mixing. For example, where thorough mixing is desired, mixing may take hours to days. Mixing may be performed with any equipment that produces the desired level of mixing in an acceptable amount of time. For example, a high shear mixer such as an attrition mill, high power blender or paint shaker may be used where thorough mixing is desired. The mixer may also mill the particles, lowering the particle size, particularly where the mixer is an attrition mill.

Once mixed, the silicon carbide and other materials may be formed into a ceramic green body. In some embodiments, prior to being formed into a green body, the mixture may be slurried and spray-dried into granules, for example averaging about 80-150 microns in diameter, which may then be formed into a green body. The green body may be formed in any manner that allows it to generate a sintered ceramic body of a desired shape, size and physical properties. For example, the mixture of silicon carbide and other materials may be pressed into a desired shape. This pressing may produce a green body having about 60% theoretical density. Where the sintered ceramic body is to have a complex shape, the green body may be machined to a desired shape.

Unlike conventional liquid phase sintering, the method of the application does not require that binder, if used, be burnt out before sintering. On the contrary, as the binder may serve as a source of carbon during sintering, the binder may be left in the green body, where it may char during sintering, becoming a source of free carbon.

Sintering of the ceramic body may be performed in any manner that produces a sintered body having the desired properties. For example, sintering may occur at a temperature that is not so high as to promote excessive weight loss, nor so low as to inhibit sintering. In some embodiments, sintering temperatures between about 1700-2100°C, 1800-2050°C or 1900-2000°C have been found to be acceptable, while in others a sintering temperature of about 1950°C is preferred. In some embodiments, a material that reduces the sintering temperature, such as a flux, may be used to reduce the sintering

temperature. It should be appreciated that higher sintering temperatures may be desired where larger, or more, ceramic bodies are sintered to facilitate enough of each ceramic body seeing the desired sintering temperature.

The sintering temperature may be reached in any manner that produces a sintered body having the desired properties. For example, the temperature may be raised such the unsintered ceramic body is not thermally shocked and sintering is even. In one embodiment, the temperature may be gradually raised until the sintering temperature is achieved. One acceptable range of heating rates is about 7-15°C per minute, however, it should be appreciated that this heating rate may vary with the particular materials being sintered, the size and shape of the body being sintered, and the like.

Sintering may be performed for any amount of time short enough to inhibit excessive weight loss and long enough to promote sintering. The sintering time may be selected based upon the sintering temperature. For example, higher sintering temperatures may work better with lower sintering times and lower temperatures may work better with longer sintering times. As it is believed that growth of longer grains occurs later in the sintering process, the sintering time may also be long enough to promote growth of longer grains and improved toughness. Improved toughness may be balanced against increased weight loss due to longer sintering to select an appropriate sintering time for a given application. By way of illustration, it has been found that, for some embodiments, a sintering time of about 2-3 hours provides adequate grain growth (as demonstrated by adequate toughness) without excessive weight loss at sintering temperature of 1900-1950°C and a sintering temperature of 1920-1935°C is preferred.

The manner in which the temperature is reduced after sintering may also affect the properties of the sintered ceramic. For example, whether the ceramic is step cooled may affect its properties. As used herein, "step cooling" refers to holding the temperature at a certain level or in a certain range for a period during the cooling process. It is believed that step cooling allows crystallization of the grain boundary phase, improving toughness. Step cooling for about 30-90 minutes at about 1550-1650°C may improve the toughness of silicon carbide ceramics according the present invention. In some embodiments, the step cooling may take place in more than one step, such as, about 15 minutes at 1650°C followed by about 15 minutes at 1550°C.

Sintering may be performed under any atmospheric conditions that produce a sintered body having the desired properties. For example, sintering may be performed in

an atmosphere that reduces weight loss. In one embodiment, sintering is carried out at ambient pressure in the presence of an inert gas, such as a noble gas, like argon. In another embodiment, sintering is carried out in the presence of nitrogen.

In some embodiments, weight loss may be inhibited by introducing into the sintering chamber silicon carbide that has previously been present in a sintering chamber where similar sintering aids were used. Such previously sintered silicon carbide may inhibit the reactions responsible for weight loss by increasing the concentration of the weight loss reaction products in the sintering atmosphere, shifting the equilibrium away from weight loss. The silicon carbide used to inhibit weight loss may be present in the sintering chamber in any manner that makes it available to the sintering atmosphere. Preferably, such silicon carbide is in powder form to improve its surface area. Powdered silicon carbide may be provided in the form a bed at the base of the sintering chamber or it may be provided within a receptacle within the sintering chamber. These two arrangement are commonly referred to as powder beds and powder boats, respectively. It should be appreciated that other powder beds that produce an atmosphere that reduces weight loss are also usable. For example, alumina and carbon (e.g., in graphite form) may be used as a powder bed and may form AlO at elevated temperatures, reducing weight loss. Alumina and carbon powder beds are also typically cheaper than other alternatives. While the presence of a powder bed or boat may reduce weight loss and improve hardness, it is also believed that it inhibits the action of boron and carbon sintering aids, reducing the toughness of the sintered body. Accordingly, the decision whether to use a powder bed or boat may be made based upon the desired properties of the sintered body, i.e. whether toughness or hardness is a greater concern.

The composition of the sintered ceramic body of the present invention may vary depending, for example, on the materials used to form the green body, the method in which these materials are prepared and constructed into the green body, and the sintering conditions. It is generally believed that sintered ceramic compositions according to the present invention will have greater amounts of elemental oxygen, free carbon, rare earth metal, and glass phase metal and lesser amounts of silicon carbide than traditional liquid phase sintered silicon carbide. Furthermore, the sintered ceramic may contain boron, which is not present, except at trace levels, in traditional liquid phase sintered silicon carbide. Depending on the embodiment, elemental oxygen may be greater than about 1 %, 1.2 %, 1.4% or 1.6 % by weight of the sintered ceramic body and in some embodiments may be about 1.6 % by weight. Depending on the embodiment, free

carbon may be greater than about 0.12 %, 0.14 %, 0.16 % or 0.18 % by weight of the sintered ceramic body and in some embodiments may be about 0.18 % by weight.

Depending on the embodiment, glass phase metal may be greater than about 2.4 %, 2.6 %, 2.8 % or 3.0 % by weight, or even as high as 5% by weight, or higher, of the sintered

5 ceramic body and in some embodiments may be about 3.0 % by weight. Depending on the embodiment, rare earth metal may be greater than about 0.6 %, 0.8 %, 1.0 % or 1.2 % by weight, or even as high as 4% by weight, or higher, of the sintered ceramic body and in some embodiments may be about 1.2 % by weight. Depending on the embodiment, boron may be greater than about 0.05 %, 0.1 %, 0.2 %, 0.3 % or 0.35 % by weight of the
10 sintered ceramic body and in some embodiments may be about 0.35 % by weight.

Depending on the embodiment, silicon carbide may be less than about 94 %, 92 %, 90 % or 89 % by weight, or even as low as 85% by weight, or lower, of the sintered ceramic body and in some embodiments may be about 89 % by weight.

The sintered ceramic of the present invention may be used in any application
15 where silicon carbide ceramic is traditionally used. For example, the sintered ceramic of the present invention may be constructed into products for the automotive industry, mechanical seals, armor, faucet washers, heat exchangers, bearings, blast and atomization nozzles, semiconductor hardware, valves and valve trim, paper industry products, and thermal components for high temperature applications. The sintered
20 ceramic of the present invention may also be useful for DC magnetron sputtering where the ceramic is conductive, such as where it contains graphitic carbon. In addition to traditional silicon carbide applications, the sintered ceramic of the present invention may also be used in applications requiring higher toughness. For example, silicon carbide sintered according to the present invention may be used in applications where a higher
25 toughness ceramic, such as silicon nitride, has traditionally been used, such as ball bearings. Another example of an application for the improved toughness sintered ceramic of the present invention is cutting tools. By "cutting tool" it is meant any device or tool having a relatively sharp edge. By way of example, cutting tools constructed of the sintered ceramic of the present invention be used in the paper industry as knives in
30 pulp processing.

The sintered ceramic of the present invention may benefit from post sintering treatment. For example, it may be possible to further increase the density and strength of the sintered ceramic. In one embodiment, the strength and density of the sintered ceramic may be improved through hot isostatic pressing (HIPping). HIPping may be

particularly effective where the ceramic has closed porosity, typical in sintered ceramics of the invention having a density greater than about 95% of theoretical density. Sintered ceramics having improved strength and density may be used in applications where such properties are desirable. For example, gas seals subject to high rotational speeds may be constructed of HIPped sintered ceramic.

Example 1

Experiments were conducted in order to determine whether boron and carbon sintering aids improved the properties of liquid phase sintered silicon carbide ceramics. Fourteen batches of silicon carbide were prepared with a variety of sintering aids. The composition of each batch is shown in Table 1.

Table 1

Batch	SiC wt.%	B ₄ C wt.%	FC wt.%	Al ₂ O ₃ wt.%	AlN wt.%	Y ₂ O ₃ wt.%	Nd ₂ O ₃ wt.%	TiO ₂ wt.%
1	96.5	0.5	3	-	-	-	-	-
2	86.5	0.5	3	6	-	4	-	-
3	86.5	0.5	3	6		4		
4	90	-	0	6	-	4	-	-
5	90	-	0	6	-	4	-	-
6	86.5	0.5	3	6	-	2	2	-
7	86.5	0.5	3	3	3	2	2	-
8	92.5	0.5	3	-	-	3	1	-
9	90	-	0	-	6	4	-	-
10	86.5	0.5	3	5.5	-	-	4.5	-
11	86.5	0.5	3	7	-	-	-	3
12	83.5	0.5	3	-	5	8	-	-
13	83.5	0.5	3	-	5	-	8	-
14	83.5	0.5	3	-	5	-	-	8

For each batch, coarse silicon carbide was obtained from Saint Gobain Corporation of Worcester, MA. The silicon carbide used in batches containing boron and carbon was HEXOLOY® SA silicon carbide and had boron carbide and free carbon containing material (denoted FC in Table 1) pre-added. The silicon carbide used in the remaining batches was SIKA® FCP-15 silicon carbide. The appropriate weight percent

of sintering aids and silicon carbide were combined to produce batches of 1200 grams. To this were added 794 grams of de-ionized water having a pH adjusted to 9.5 with ammonium hydroxide and 6 grams of DARVAN® 821A surfactant from R.T. Vanderbilt of Norwalk, CT to bring the total weight of each batch to 2000 grams.

5 Each batch was then milled for four hours by the attritor union process (a vertical attrition mill) with silicon nitride (Si_3N_4) media. This milling resulted in silicon carbide particles having an average diameter of about one micron. Batch 3 was milled until it had an average particle diameter of about 0.5 micron. After milling, each batch was filtered through a 20 micron Pall filter. Each batch was then spray and/or freeze dried
10 and screened with a 175 micron screen. The screened batches were pressed by cold isostatic pressing at 20 ksi pressure into one or more tiles.

Each tile was sintered under one of the following sintering conditions:

- A: 1950 °C for 3 hours in the presence of a powder bed;
- B: 1950 °C for 3 hours without a powder bed;
- 15 C: 1900 °C for 2 hours in the presence of a powder bed;
- D: 1900 °C for 2 hours without a powder bed;
- E: 1950 °C for 2 hours in the presence of a powder bed; and
- F: 1950 °C for 2 hours without a powder bed.

Where used, the powder beds included silicon carbide and alumina.

20 The density, hardness and toughness of each of the sintered tiles was tested. The results of these tests are reported in Tables 2, 3 and 4, respectively, wherein S.C. stands for the various sintering conditions described above. Density is reported in % of theoretical density. Hardness is reported in GPa and was tested with a 10kg load. Toughness is reported in $\text{MPa m}^{1/2}$ as measured by the indentation crack length method.
25 Batches were not tested at all sintering conditions.

Table 2

S. C.	Batch									
	2	3	4	5	9	10	11	12	13	14
A	98.77	-	97.94	98.40	97.87	-	-	-	-	-
B	99.08	-	98.06	98.71	97.00	-	-	-	-	-
C	97.37	99.15	98.83	99.27	94.38	93.19	98.48	96.13	97.36	96.64
D	99.34	99.26	98.96	99.16	95.29	93.62	96.13	97.01	97.16	96.10
E	95.76	-	-	-	-	89.38	100.19	100.09	88.28	90.95
F	98.45	-	-	-	-	93.85	98.36	99.22	95.46	96.99

Table 3

S. C.	Batch									
	2	3	4	5	9	10	11	12	13	14
A	19.31	-	-	-	-	-	-	-	-	-
B	17.81	-	18.26	18.05	16.78	-	-	-	-	-
C	18.55	-	20.58	20.83	-	3.36	20.06	14.86	7.87	3.47
D	20.63	-	21.19	20.58	-	4.02	18.69	16.83	7.79	2.56
E	15.96	-	-	-	-	-	18.62	17.96	-	-
F	18.38	-	-	-	-	-	18.26	18.08	8.98	9.94

Table 4

S. C.	Batch									
	2	3	4	5	9	10	11	12	13	14
A	5.09	-	-	-	-	-	-	-	-	-
B	5.78	-	5.13	4.96	4.65	-	-	-	-	-
C	3.39	-	3.68	3.63	-	-	3.68	4.04	-	3.71
D	3.53	-	3.32	4.06	-	-	4.13	3.92	-	-
E	5.32	-	-	-	-	-	2.99	3.63	-	-
F	3.42	-	-	-	-	-	3.56	3.32	-	-

5 To compare the composition of the invention to traditional solid phase sintered compositions, the toughness and hardness of batches 1 and 2 were measured after sintering at 1950°C for 3 hours. Batch 2 was tested both with and without the use of a powder bed during sintering. As toughness and hardness are sometimes measured using varying loads, loads of 5 kg, 10 kg and 20 kg were used to test hardness and loads of 10
10 kg and 20 kg were used to test toughness. The results of these tests are reported in Table 5. As above, hardness is reported in GPa and toughness is reported in MPa m^{1/2} as measured by the indentation crack length method. The results shown in Table 5 demonstrate that embodiments of the composition of the present invention have a toughness roughly double that of traditional solid state sintered silicon carbide with only
15 a modest loss of hardness. The results further emphasize that a powder bed may improve hardness, but also compromises toughness to some degree.

Table 5

Batch	1	2	2
Powder Bed	NA	Yes	No
Density	3.16 g/cc	3.208 g/cc	3.218 g/cc
Hardness			
⇒ 5 kg.	24.53	18.64	16.81
⇒ 10 kg.	24.32	19.31	17.81
⇒ 20 kg.	25.15	19.66	17.25
Toughness			
⇒ 10 kg.	2.61	5.09	5.78
⇒ 20 kg.	2.60	5.07	5.54

5 Referring to the figures, FIGS. 1-4 show the microstructure of a ceramic produced by sintering material from Batch 4, which does not include boron or carbon, for 3 hours at 1950°C with a powder bed. FIGS. 5-8 show the microstructure of a ceramic produced by sintering material from Batch 2, which is identical to Batch 4 save for the addition of boron and carbon, and which was sintered under the same conditions.

10 Comparing FIGS. 1-4 to FIGS. 5-8, the greater number of acicular grains in FIGS. 5-8 is seen. This demonstrates that the boron and carbon promote the formation of acicular grains, which are believed increase toughness of the sintered material.

The results qualitatively observed from the figures were also objectively measured. As reported in Table 6, the number of 6H grains, which are acicular grains, is

15 much higher in ceramics produced from Batches 2 and 3 versus Batch 4, which contained no boron or carbon.

Table 6

Sample	Polytype (in wt.%)			
	3C	4H	6H	15R
2	1.0	6.5	87.6	4.9
3	2.1	11.4	75.6	10.9
4	0.6	50.0	41.4	8.0

In order to determine the chemical composition of an embodiment of the sintered ceramic of the invention, and to compare this composition to the composition of traditional liquid phase sintered silicon carbide, an elemental analysis of batches 2 and 4 was performed using an inductively coupled plasma technique. The results of the elemental analysis are reported in Table 7. The results illustrate that the composition of this embodiment of the invention differs from that of traditional liquid phase sintered silicon carbide, having more elemental oxygen, more free carbon, more rare earth metal, and more glass phase metal. This composition also contains boron, while traditional liquid phase sintered silicon carbide is expected not to have more than trace amounts of boron (batch 4 was not tested for boron content).

Table 7

BATCH	Elemental Analysis (in weight percent)				
	O	Free C	Al	Y	B
2	1.61	0.18	3.06	1.24	0.37
4	0.98	0.11	2.36	0.60	---

Example 2

Experiments were performed in order to study the effect of increased sintering aid and decreased boron and carbon (compared to Example 1) on the hardness, toughness and other properties of liquid phase sintered silicon carbide. The compositions tested are shown in Table 8. Batches 15 and 17 have the same composition, except batch 15 used HEXOLOY® SA silicon carbide while batch 17 used SIKA® FCP-15 silicon carbide. Similarly, batches 16 and 18 have the same composition, except batch 16 used

HEXOLOY® SA silicon carbide while batch 18 used SIKA® FCP-15 silicon carbide. The HEXOLOY® SA silicon carbide was milled until it had a BET surface area of 15 m²/g, matching the surface area of the SIKA® FCP-15 silicon carbide.

The process to prepare each batch was similar to that described in Example 1.

- 5 The materials to make the batches were added in the following order: de-ionized water, boron carbide, yttrium oxide, aluminum oxide, and silicon carbide.

Table 8

Batch	SiC wt. %	B ₄ C wt. %	FC wt. %	Al ₂ O ₃ wt. %	Y ₂ O ₃ wt. %
15	87.4	0.1	1.5	6.6	4.4
16	86.5	0.15	1.5	7.8	5.2
17	87.4	0.1	1.5	6.6	4.4
18	86.5	0.15	1.5	7.8	5.2

- 10 Batches 15-18 were sintered under a variety of conditions in order to determine better sintering conditions.

G: 1925 °C for 2 hours in the presence of a powder bed;

H: 1925 °C for 1.5 hours in the presence of a powder bed; and

I: 1995 °C for 3 hours in the presence of a powder bed.

- 15 The density, hardness and toughness of each of the sintered ceramic bodies was tested. The results of these tests are reported in Table 9, where S.C. stands for the various sintering conditions described above. Density is reported in percent of theoretical density. Hardness is reported in GPa and was tested with a 10kg load. Toughness is reported in MPa m^{1/2} as measured by the indentation crack length method.

- 20 Batches were not tested for all sintering conditions.

Table 9

Batch	S.C.	Density	Hardness	Toughness
15	G	95.09	15.87	3.65
16	G	96.48	16.13	3.59
17	G	97.79	17.72	3.87
	H	97.42	18.17	3.90
18	G	97.88	17.2	3.84
	H	97.09	16.68	4.25
	I	94.73	14.34	4.11

The data in Table 9 illustrates that the SIKA® FCP-15 silicon carbide created generally superior properties in the sintered ceramic compared to HEXOLOY® SA silicon carbide. Without wishing to be bound by a specific theory, it is believed that the SIKA® FCP-15 silicon carbide has more fine particles and that this results in the improved properties. It is also of note that the sintered ceramic with 11 wt. % sintering aids and 0.1 wt. % boron carbide was overall harder, but less tough, than the sintered ceramic with 13 wt. % sintering aids and 0.15 wt. % boron carbide. This further demonstrates the tradeoff between strength and toughness and how increasing the boron shifts the balance toward toughness. Finally, it is noted that longer sintering times and higher sintering temperatures may be adverse to the properties of the sintered ceramic, as shown by batch 18, sintered under sintering condition I.

The results of the tests on the properties of the sintered ceramic in this example demonstrate that increasing the amount of sintering aid and decreasing the amount of carbon and boron produce a sintered ceramic having desired strength, toughness and density.

Example 3

In order to demonstrate the effect of boron on grain length, density and toughness in liquid phase sintered silicon carbide, silicon carbide having a variety of boron carbide compositions was sintered and its mean grain length measured. Specifically, silicon carbide compositions having 10 wt. % sintering aid, including 6 wt. % yttrium oxide and 4 wt. % aluminum oxide, and 0, 0.10, and 0.50 wt. % boron carbide were sintered. Further, two samples having no boron carbide were tested, each having different sintering aids. The mean grain length of each of the sintered ceramics was measured.

The mean grain lengths of the samples without boron carbide were 3.16 and 2.61 micrometers. At 0.10 wt. % boron carbide, the mean grain length rose to 4.8 micrometers, and, at 0.50 wt. %, it was 9.69 micrometers. The percent of grains in each sample having a particular grain length was also measured and the cumulative % plotted versus the mean grain length in FIG. 9. The increase in grain lengths with the increasing amounts of boron is clearly illustrated by FIG. 9. Accordingly, the effect of boron on grain length in a liquid phase sintered silicon carbide has been demonstrated. This data correlates with the observation that higher boron compositions generally lead to higher toughness and supports the proposition that longer grain lengths lead to greater toughness.

The toughness and density of each of the sintered ceramics was also measured. This data is plotted against mean grain length in FIG. 10. FIG. 10 demonstrates the inverse relationship between toughness and density with respect to mean grain length. At low mean grain length, toughness is low, but density is high, while at high mean grain length toughness is high while density is low. This further demonstrates that the toughness and strength/density of the ceramic may be optimized for a particular application by adjusting the mean grain length with the boron composition.

Example 4

In order to demonstrate the effect of boron on liquid phase sintered silicon carbide, batches of silicon carbide with and without boron carbide were sintered and their microstructure examined. Both batches included SIKA® FCP-15 silicon carbide and 10 wt. % sintering aid. One batch also included 0.10 wt. % boron carbide. Photocopies of photomicrographs of the batches without and with boron carbide are shown in FIGS 11 and 12, respectively. Comparing these figures, it is readily apparent that the silicon carbide having boron carbide contains many more acicular grains, which, as described previously, are associated with increased toughness.

Example 5

In order to demonstrate the effect of step cooling on toughness of liquid phase sintered silicon carbide, the toughness of samples prepared by free cooling was compared to the toughness of samples prepared by step cooling. The same four silicon carbide compositions used in Example 3 were sintered with and without step cooling. Step cooling was performed at 1600°C for 30 minutes. The toughness of the sintered ceramics was then measured. The results are shown in FIG. 13. For each formulation, step cooling resulted in higher toughness. The improvement in toughness was most dramatic for the composition containing 0.1 wt % boron carbide and least dramatic for the composition containing 0.5 wt. % boron carbide. The data demonstrates that step cooling improves the toughness of liquid phase sintered silicon carbide.

Example 6

In order to demonstrate the effect of a powder bed on density and weight loss of liquid phase sintered silicon carbide, the density and weight loss of samples sintered with a powder bed was compared to the density and weight loss of samples prepared without such a bed. The same four silicon carbide compositions used in Example 3 were sintered with and without a powder bed. The powder bed contained carbon and alumina, with the bed weighing 2-6 % of the total weight of ceramic to be sintered. The density and weight loss of the sintered ceramics were measured. The results are shown in FIGS. 14 and 15. For each formulation, the presence of the powder bed resulted in higher density and lower weight loss. The data demonstrates that the use a powder bed improves the density and weight loss of silicon carbide ceramics with and without boron.

It will be understood that each of the elements described above or two or more together may also find utility in other applications different from those described above. While the application has been illustrated and described as using particular sintering aids, it is not intended to be limited to the details shown, since various modifications and substitutions may be made without departing in any way from the spirit of the present invention. Such modifications and substitutions may include using solid state sintering aids in sintering ceramics other than silicon carbide and using other solid state sintering aids with silicon carbide. Further modifications and equivalents of the invention herein disclosed will occur to persons skilled in the art using no more than routine experimentation, and all such modifications and equivalents are believed to be within the spirit and scope of the invention as defined by the following claims.

What is claimed is:

Claims

1. An unsintered ceramic body, comprising:
at least one liquid phase sintering aid;
a boron containing compound;
5 a free carbon containing compound; and
silicon carbide.
2. The unsintered ceramic body of claim 1, comprising about 5-20 weight % of the
at least one liquid phase sintering aid.
3. The unsintered ceramic body of claim 2, comprising about 9-13 weight % of the
10 at least one liquid phase sintering aid.
4. The unsintered ceramic body of claim 3, comprising about 11-13 weight % of the
at least one liquid phase sintering aid.
5. The unsintered ceramic body of claim 1, comprising about 0.05 to 1 weight % of
boron.
- 15 6. The unsintered ceramic body of claim 5, comprising about 0.05 to 0.15 weight %
of boron.
7. The unsintered ceramic body of claim 1, wherein the boron is in the form of
about 0.06-1.3 weight % of boron carbide.
8. The unsintered ceramic body of claim 7, wherein the boron is in the form of
20 about 0.06-0.20 weight % of boron carbide.
9. The unsintered ceramic body of claim 1, comprising about 1-6 weight % of the
free carbon containing compound.
10. The unsintered ceramic body of claim 9, comprising less than about 3 weight %
of the free carbon containing compound.
- 25 11. A method of making a sintered ceramic body, comprising:
combining at least one liquid phase sintering aid, a boron containing compound, a
free carbon containing compound, and silicon carbide to form a green ceramic;
shaping the green ceramic into a ceramic body; and
sintering the ceramic body.
- 30 12. The method of making a sintered ceramic body of claim 11, wherein combining
further comprises combining no less than about 5 weight % and no more than about 20
weight % of the at least one liquid phase sintering aid.

13. The method of making a sintered ceramic body of claim 12, wherein combining further comprises combining no less than about 9 weight % and no more than about 13 weight % of the at least one liquid phase sintering aid.
14. The method of making a sintered ceramic body of claim 13, wherein combining
5 further comprises combining no less than about 11 weight % and no more than about 13 weight % of the at least one liquid phase sintering aid.
15. The method of making a sintered ceramic body of claim 11, wherein combining further comprises combining no less than about 0.05 weight % and no more than about 1 weight % of boron.
- 10 16. The method of making a sintered ceramic body of claim 15, wherein combining further comprises combining no less than about 0.05 weight % and no more than about 0.15 weight % of boron.
17. The method of making a sintered ceramic body of claim 11, wherein combining further comprises combining no less than about 0.06 weight % and no more than about
15 1.3 weight % of boron carbide.
18. The method of making a sintered ceramic body of claim 17, wherein combining further comprises combining no less than about 0.06 weight % and no more than about 0.20 weight % of boron carbide.
19. The method of making a sintered ceramic body of claim 11, wherein combining
20 further comprises combining no less than about 1 weight % and no more than about 6 weight % of the free carbon containing compound.
20. The method of making a sintered ceramic body of claim 19, wherein combining further comprises combining no more than about 3 weight % of the free carbon containing compound.
- 25 21. The method of making a sintered ceramic body of claim 11, further comprising hot isostatic pressing the ceramic body after sintering.
22. The method of making a sintered ceramic body of claim 11, further comprising:
cooling the ceramic body to between about 1550 °C and about 1650 °C; and
maintaining the ceramic body between about 1550 °C and about 1650 °C for
30 between about 30 minutes and about 90 minutes.
23. The method of making a sintered ceramic body of claim 22, wherein maintaining comprises maintaining the ceramic body at a substantially constant temperature for between about 30 minutes and about 90 minutes.

24. The method of making a sintered ceramic body of claim 22, wherein maintaining comprises maintaining the ceramic body at about 1600 °C for about 30 minutes.

1/11

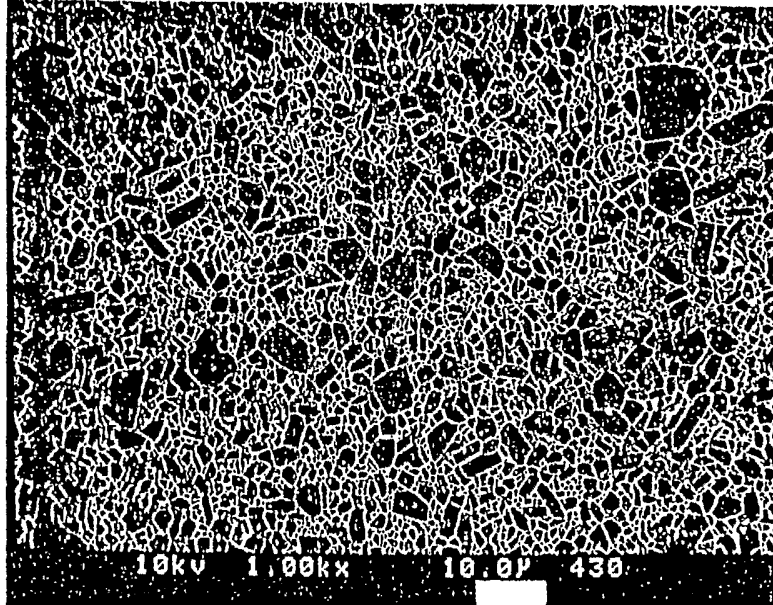


Fig. 1
(PRIOR ART)

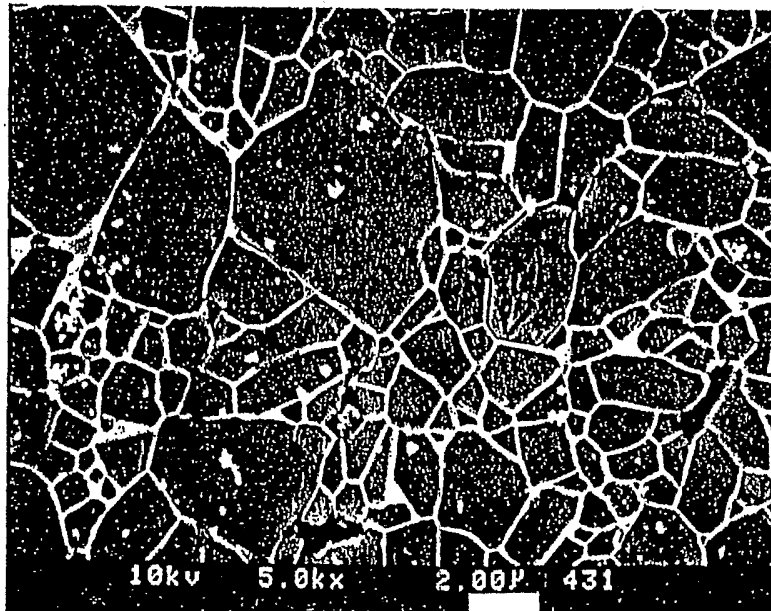


Fig. 2
(PRIOR ART)

2/11

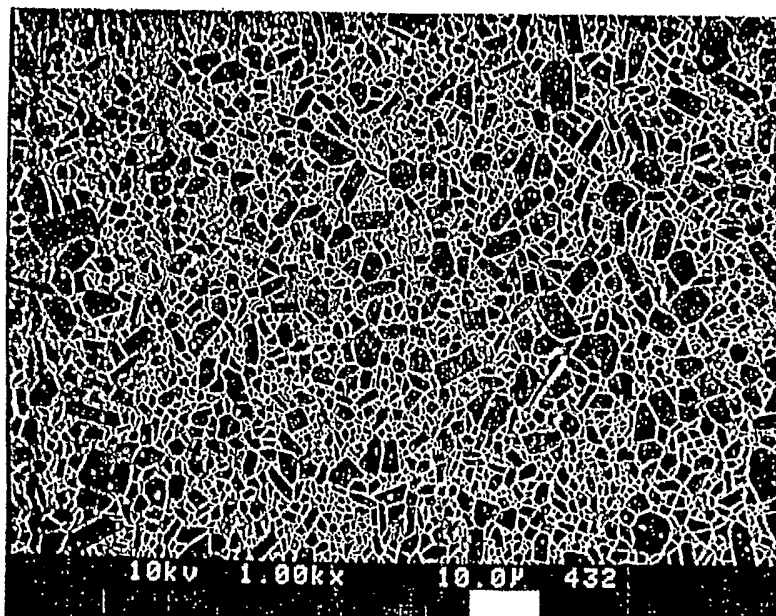


Fig. 3
(PRIOR ART)

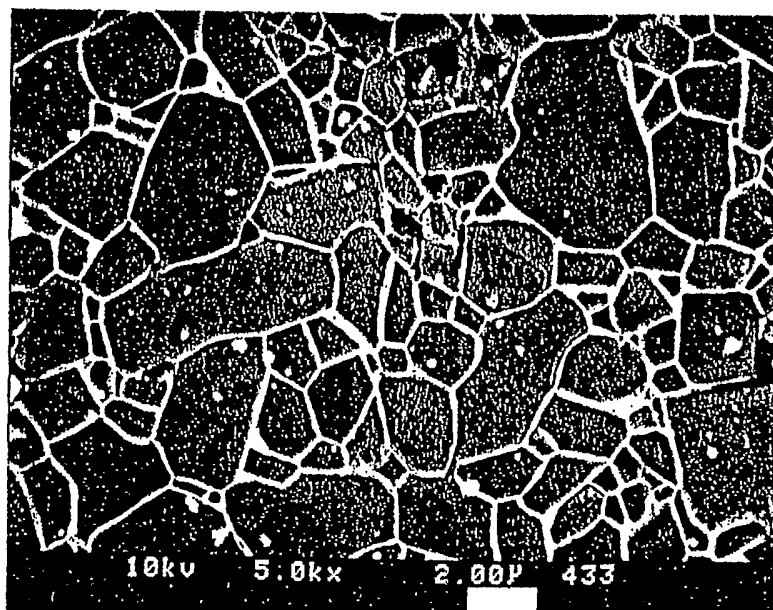


Fig. 4
(PRIOR ART)

3/11

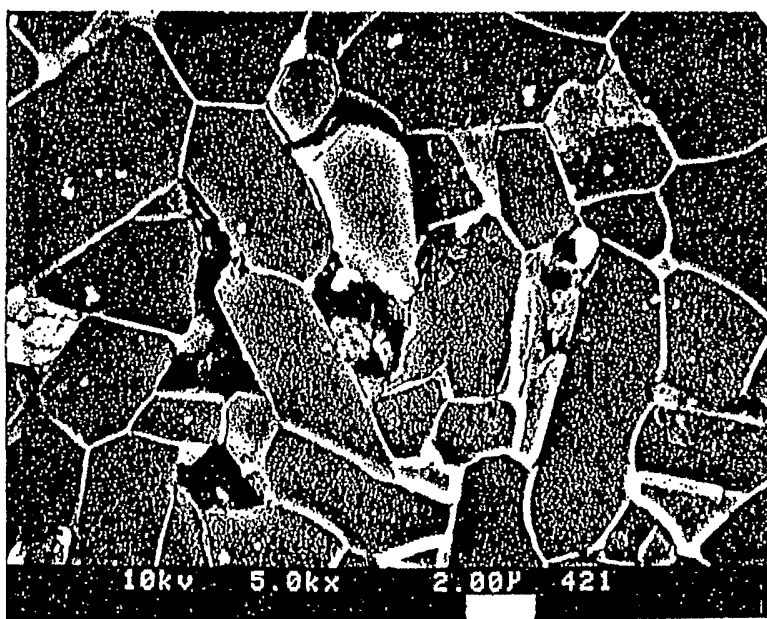


Fig. 5

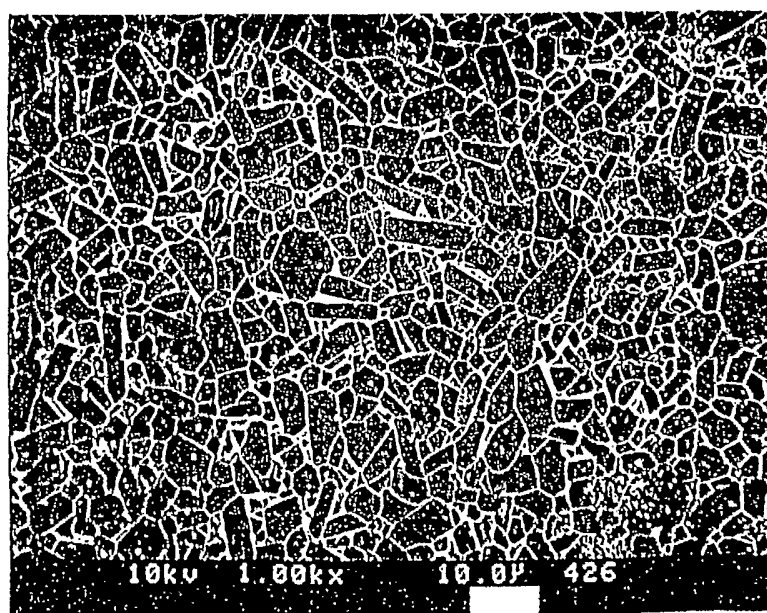


Fig. 6

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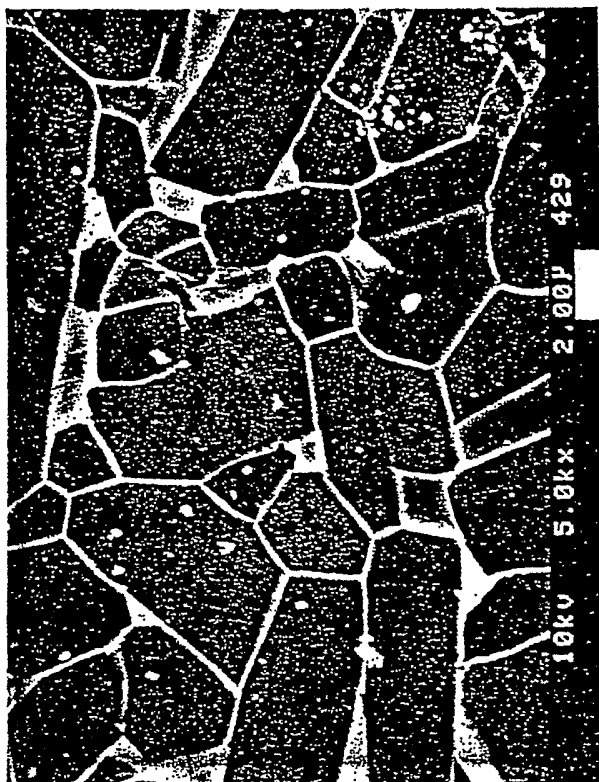


Fig. 7

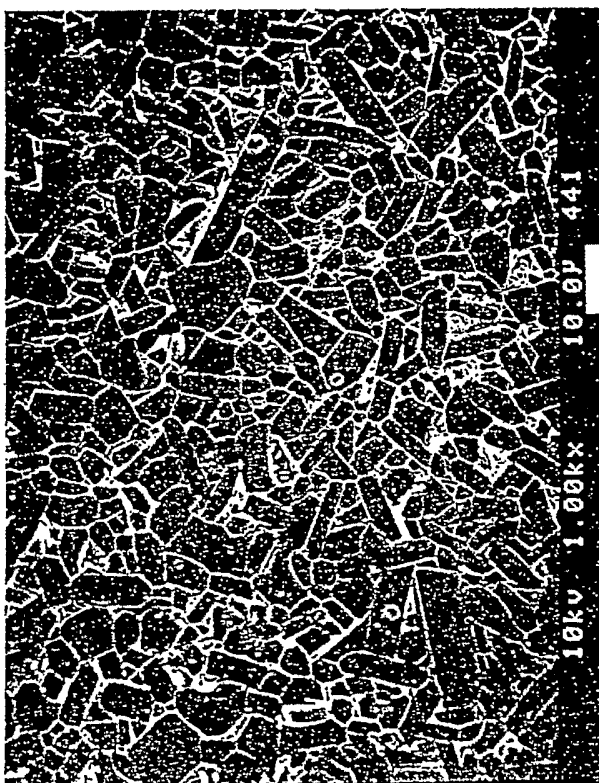


Fig. 8

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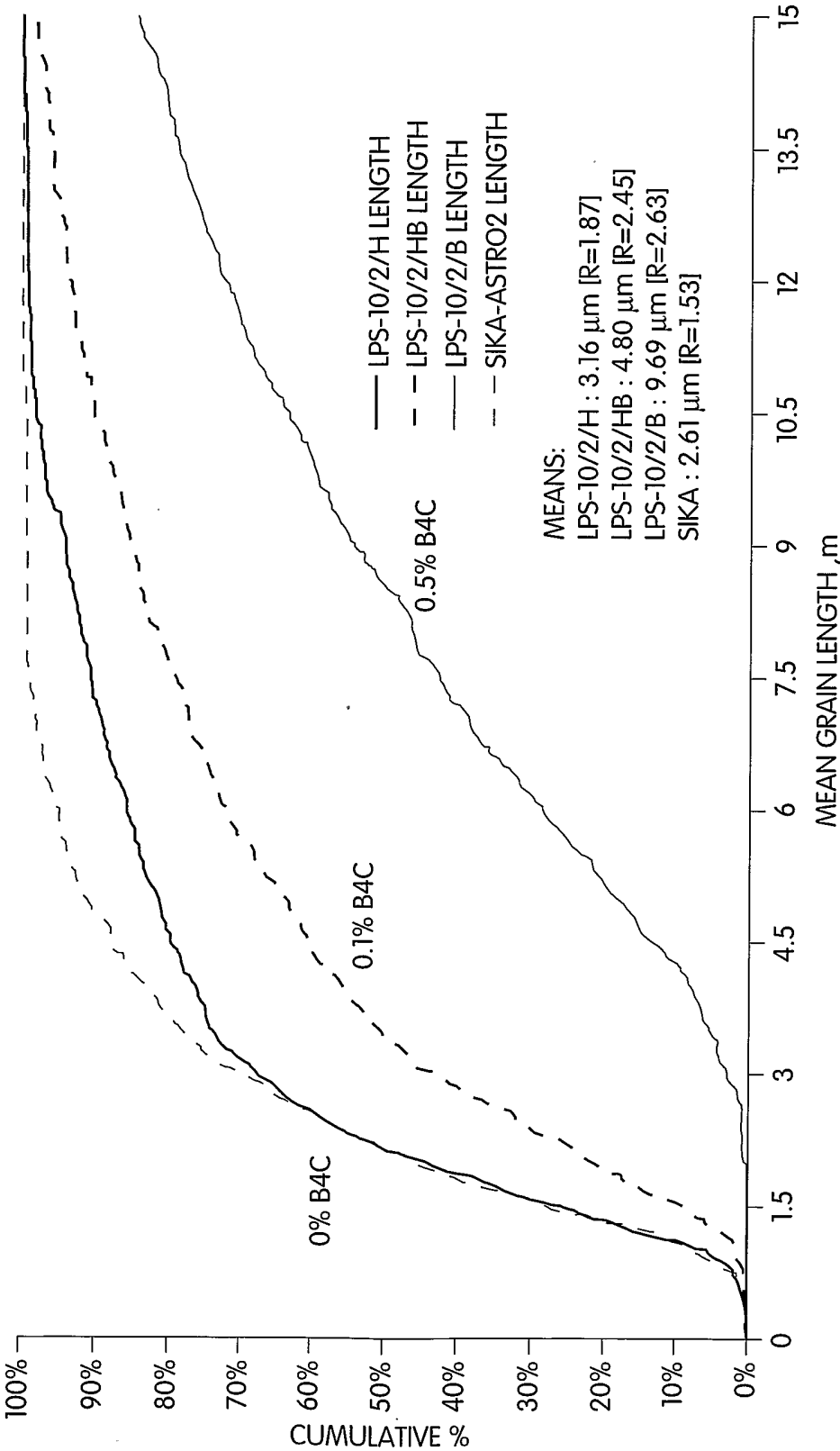


Fig. 9

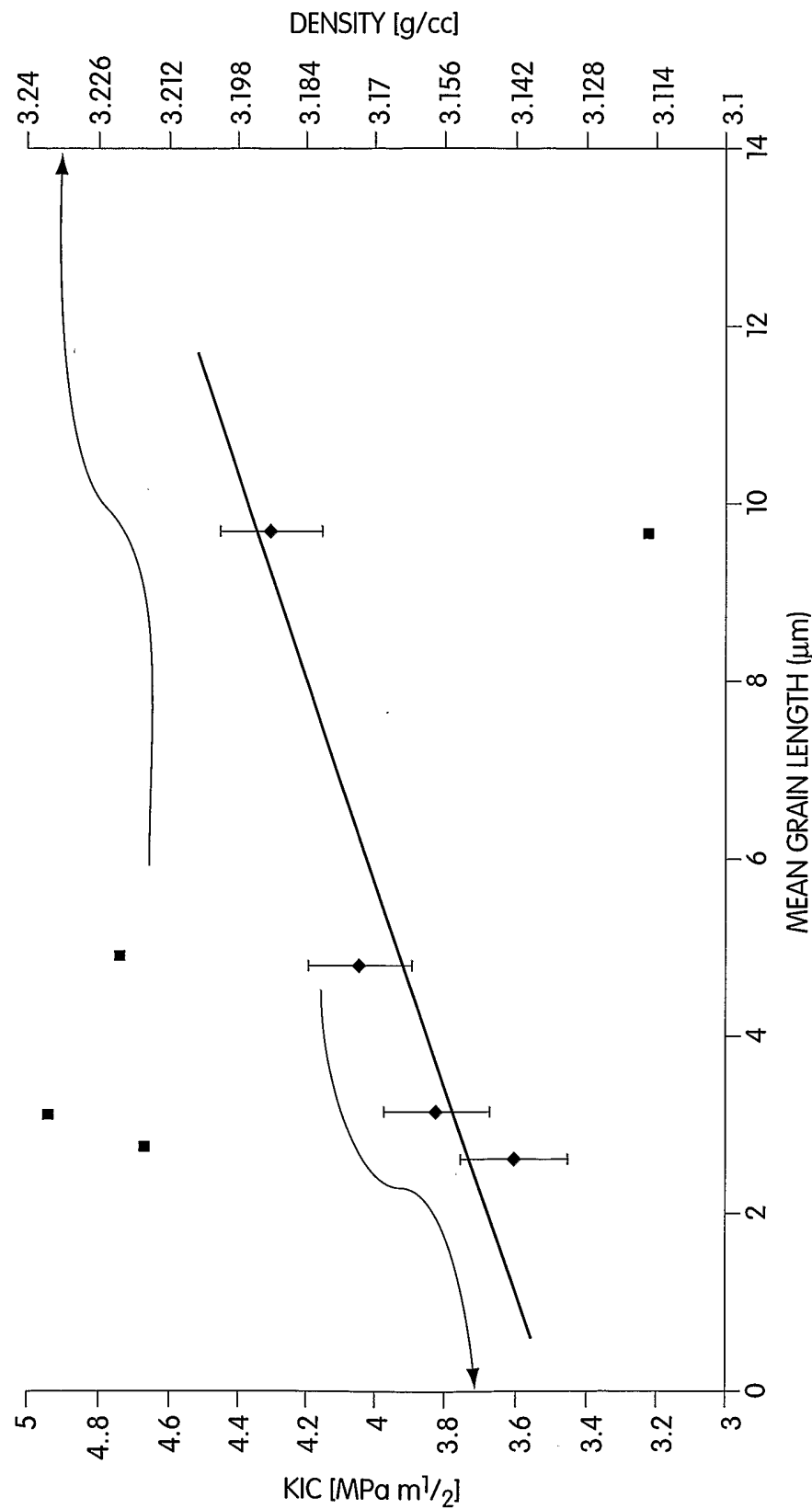


Fig. 10

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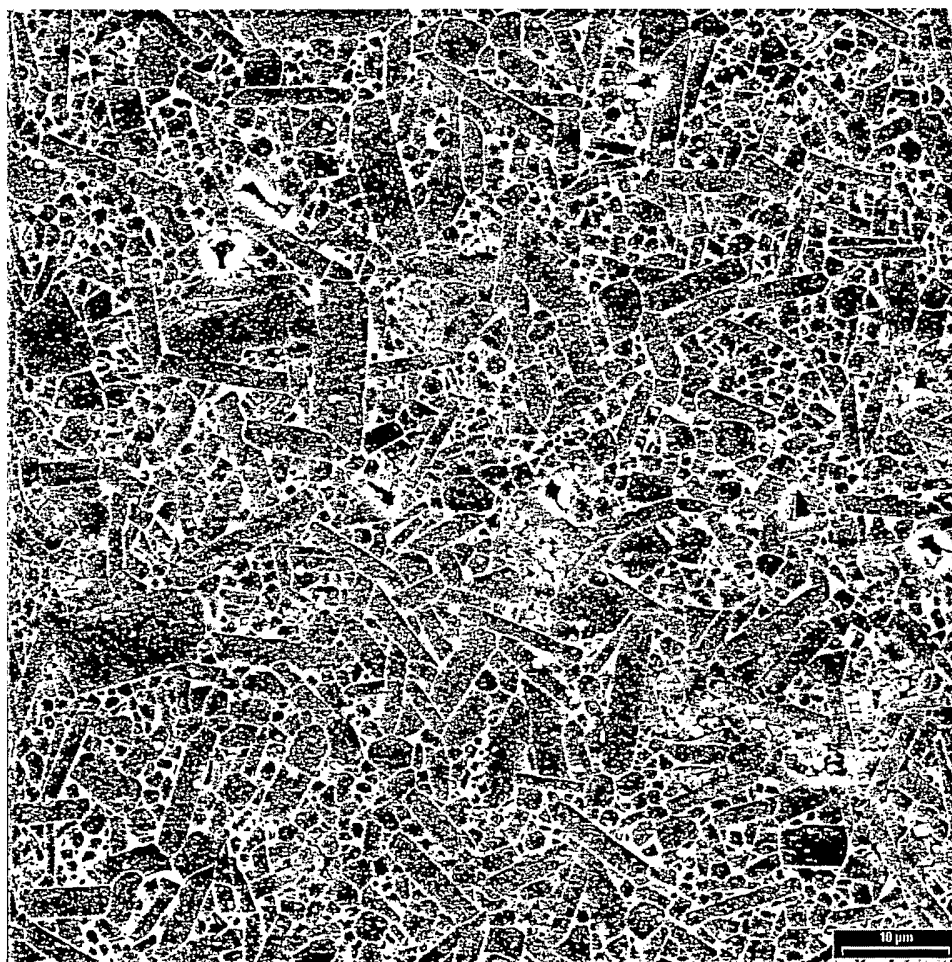


Fig. 11

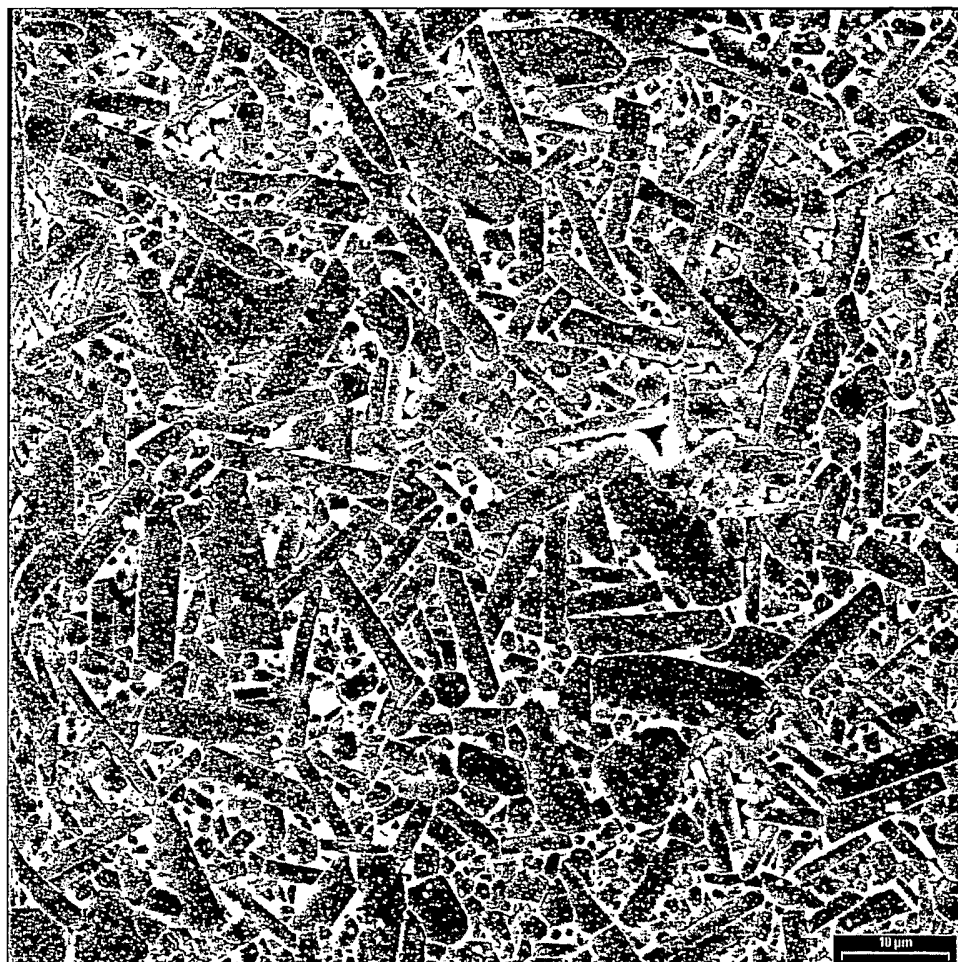


Fig. 12

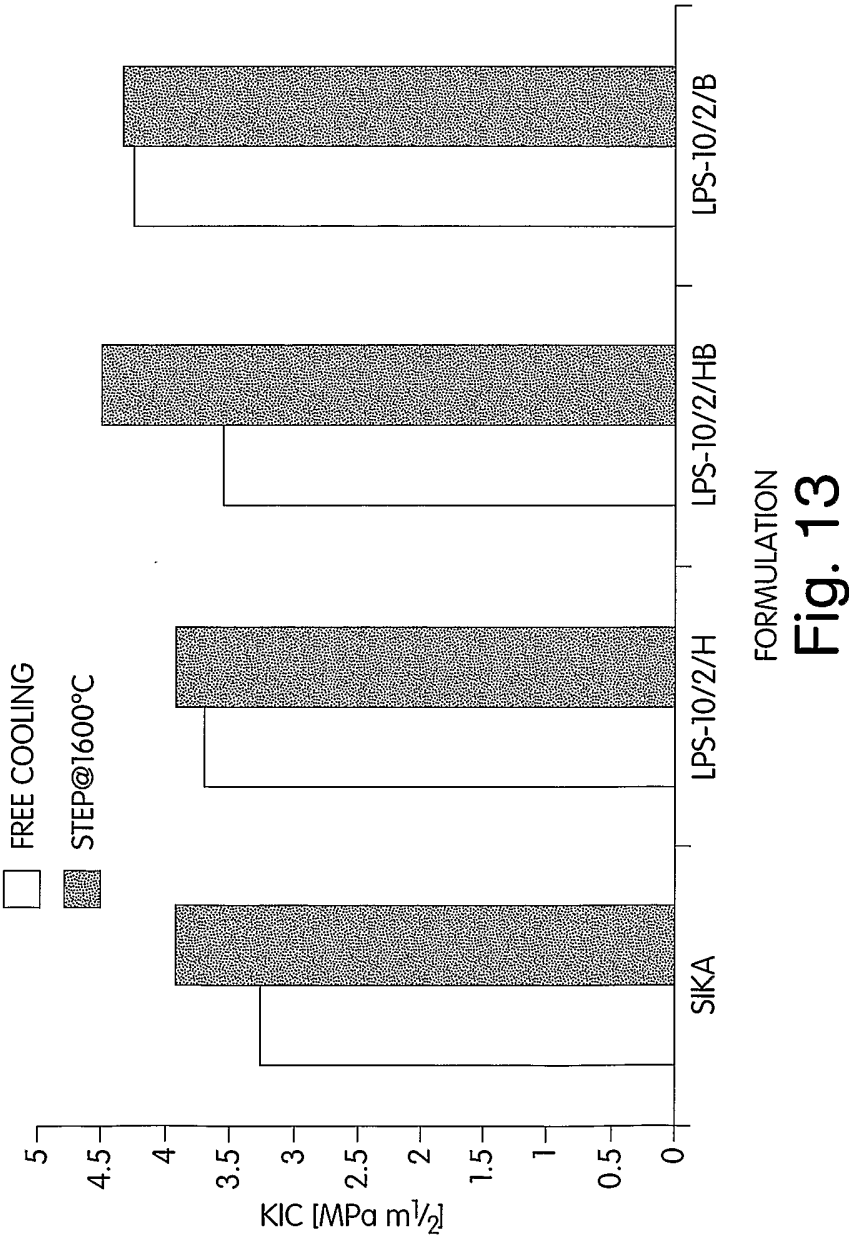


Fig. 13

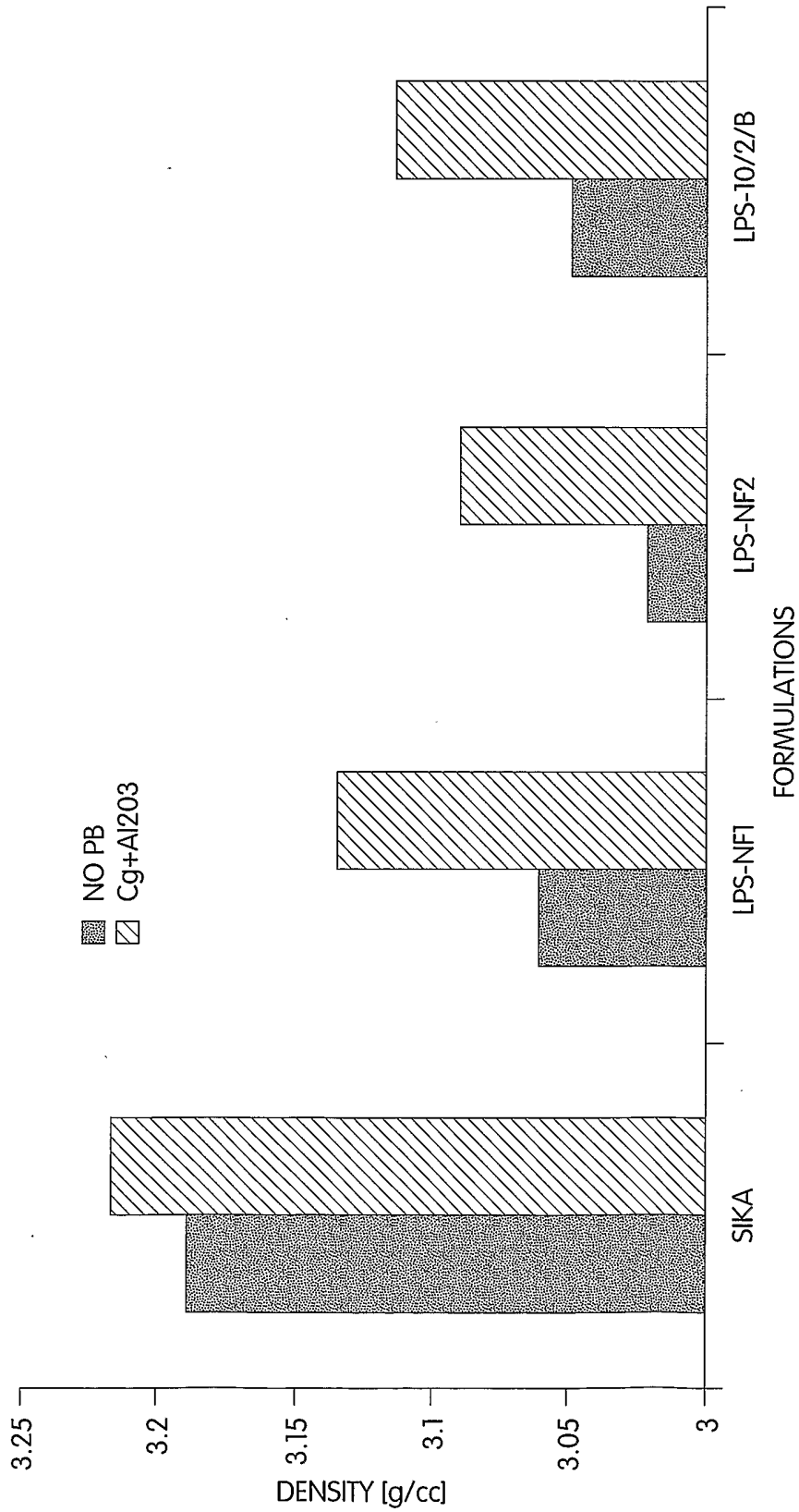


Fig. 14

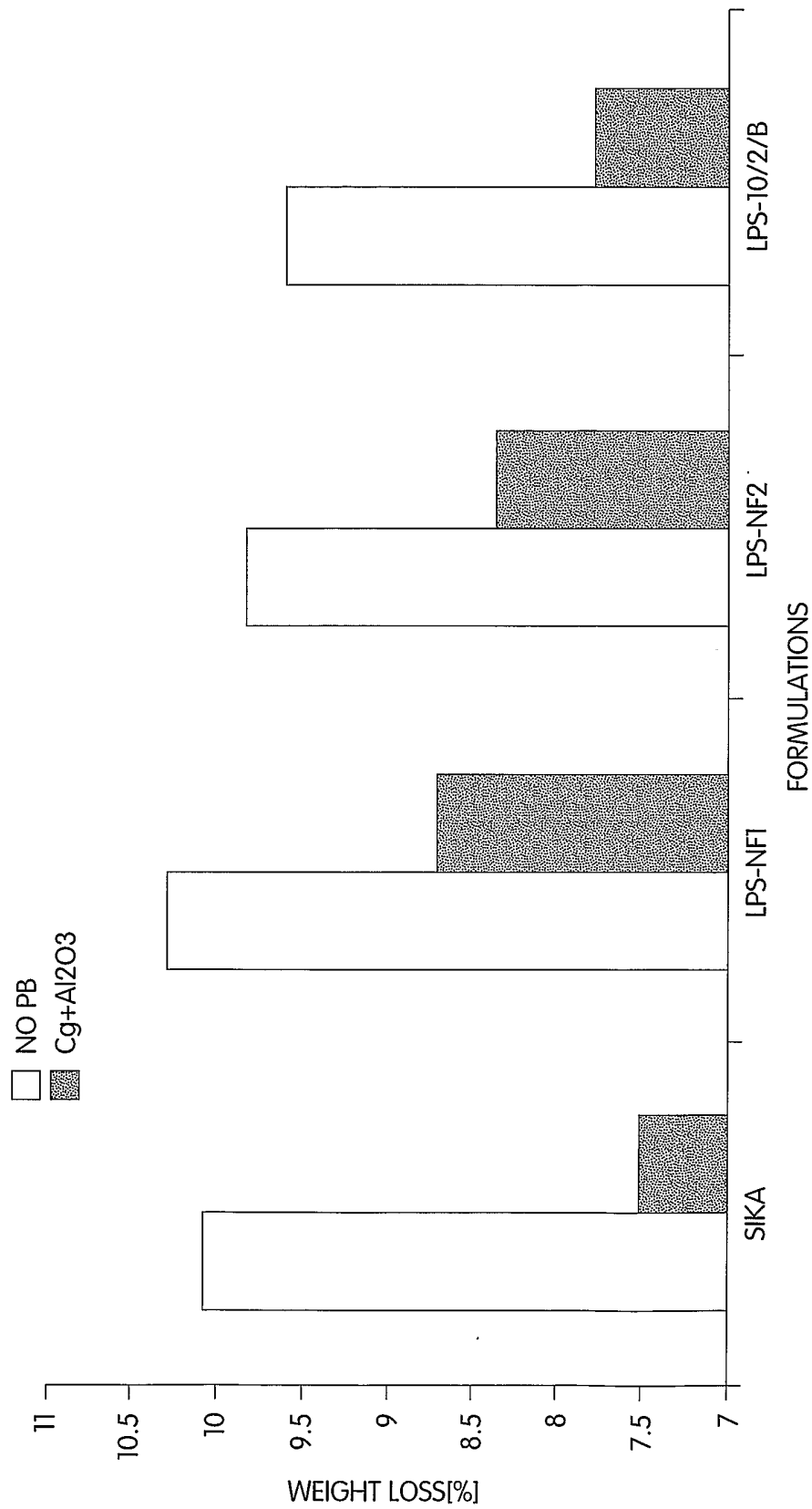


Fig. 15