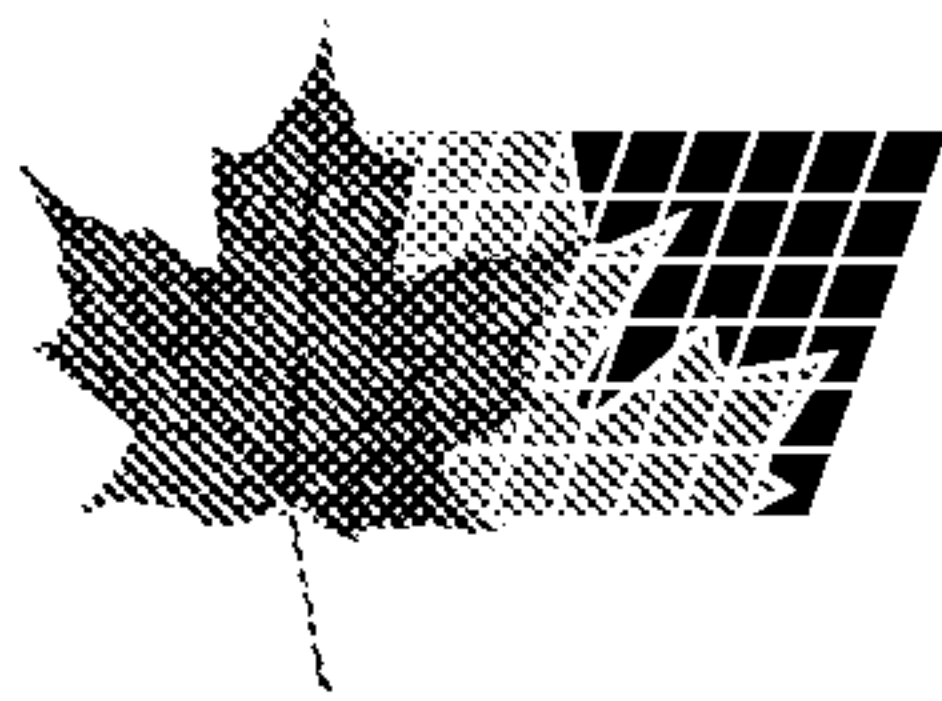




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(54) **BILLE DE ROULEMENT EN NITRURE DE SILICIUM**

POSSEDANT UNE RESISTANCE ELEVEE A LA FATIGUE

(54) **SILICON NITRIDE BEARING BALL HAVING HIGH FATIGUE
LIFE**

(57) Bille de roulement constituée essentiellement par:
(a) au moins 94% en poids d'une phase cristalline de
nitrure de silicium, (b) une phase unique de limite de
grain constituée essentiellement par Mg, Al, Si et O.

(57) A bearing ball consisting essentially of: (a) at least
about 94 w/o of a crystalline phase of silicon nitride, and
(b) a single grain boundary phase consisting essentially
of Mg, Al, Si and O.





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(21) International Application Number: PCT/US95/03187 (22) International Filing Date: 17 March 1995 (17.03.95) (30) Priority Data: 08/215,834 22 March 1994 (22.03.94) US (71) Applicant: SAINT-GOBAIN/NORTON INDUSTRIAL CERAMICS CORPORATION [US/US]; 1 New Bond Street, P.O. Box 15138, Worcester, MA 01615-0138 (US). (72) Inventor: YECKLEY, Russell, L.; 579 Barre Road, Oakham, MA 01068 (US). (74) Agents: DIMAURO, Thomas, M. et al.; Saint-Gobain/Norton Industrial Ceramics Corporation, 1 New Bond Street, P.O. Box 15138, Worcester, MA 01615-0138 (US).		(81) Designated States: AT, CA, CN, FI, HU, JP, KR, MX, NO, RU, SE, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>With amended claims.</i> 2185131
(54) Title: SILICON NITRIDE BEARING BALL HAVING HIGH FATIGUE LIFE (57) Abstract A bearing ball consisting essentially of: (a) at least about 94 w/o of a crystalline phase of silicon nitride, and (b) a single grain boundary phase consisting essentially of Mg, Al, Si and O.		

SILICON NITRIDE BEARING BALL HAVING HIGH FATIGUE LIFE

Advanced structural ceramic materials have gained the attention of industry by virtue of their superior performance qualities. These qualities, such as superior high temperature strength, high toughness, and resistance to thermal shock and oxidation, provide the bases for their potential use in a variety of applications.

U.S. Patent No. 4,935,388 (Lucek) suggests that the reliability of a ceramic material can be correlated with its spatial homogeneity, and that such homogeneity can be characterized by the extent to which the material exhibits optical anomalies. In particular, Lucek teaches that the reliability of silicon nitride greatly improves when the material is spatially homogeneous, e.g., has no optical anomalies greater than about 70 microns. Lucek suggests that the above optical anomalies signify a number of inhomogeneous phenomena, including, but not limited to, regions of porosity, regions of contamination from materials such as iron, and regions having microcracks. The silicon nitride ceramics disclosed by Lucek, which contained about 1 w/o MgO as a sintering aid, have a rolling contact fatigue life ("RCF life") defined by an L10 value of at least four million stress cycles in ASTM test STP 771 under 6.9 GPa applied contact stress. Although this RCF life is one of the highest known, commercial desire for silicon nitride materials having improved RCF life continues.

Accordingly, it is the object of the present invention to provide a silicon nitride material having a superior RCF life.

SUMMARY OF THE PRESENT INVENTION:

In accordance with the present invention, there is provided a bearing ball consisting essentially of:

- a) at least about 94 w/o of a crystalline phase of silicon nitride, and
- b) a single grain boundary phase consisting essentially of Mg, Al, Si and O.

In preferred embodiments, the grain boundary phase consists essentially of between 1 and 2 w/o Mg, as magnesia; between 0.2 and 1.0 w/o Al, as alumina; between 2 and 4 w/o Si, as silica; and oxygen. More preferably, the Mg component of the grain boundary phase is between 1.0 and 1.6 w/o, as magnesia, the Al component of the grain boundary phase is between 0.3 and 0.6 w/o, as alumina, and the Si component of the grain boundary phase is between 2.0 and 3.0 w/o, as silica, of the bearing. In especially preferred embodiments, the bearing has an L10 value of between 50 and 80 million stress cycles in ASTM test 771 under 6.9 GPa applied contact stress.

DETAILED DESCRIPTION OF THE PRESENT INVENTION:

It has been unexpectedly found that adding between about 0.20 w/o and about 1.0 w/o alumina to a green body consisting essentially of silicon nitride and about 1 w/o MgO results in a ceramic having an unexpectedly high RCF life.

Without wishing to be tied to a theory, it is believed that, during the sintering of the conventional silicon nitride ceramics of Lucek, the MgO sintering aid and the 3 w/o silica (present in silicon nitride power as an impurity) formed at least two immiscible liquid phases at equilibrium, resulting in at least two grain boundary phases in the sintered body. This non-uniform grain boundary phase probably degraded the strength, toughness and RCF life of the ceramic. The alumina addition of the present invention is believed to provide a single MgO-SiO₂-Al₂O₃ phase at equilibrium, resulting in a single grain boundary phase according to a phase diagram. Hence, more uniform and higher properties result.

The silicon nitride ceramic of the present invention can be made from typical materials and conventional processing steps. In preferred embodiments, the ceramic is made from a silicon nitride powder or a precursor thereof. If the ceramic is made from a silicon nitride powder, any typical silicon nitride powder can be used. Typically, silicon nitride comprises at least about 94 w/o of the

ceramic of the present invention, preferably between about 97 and about 98.5 w/o.

In preferred embodiments of the present invention, magnesia and alumina are used as sintering aids. Magnesia is added in amounts of from about 1.0 w/o to about 2.0 w/o, preferably between about 1.0 and about 1.6 w/o of the sintered ceramic. Most preferably, about 1 w/o of MgO, having a purity of more than 99% and an average particle size of less than 1 micron, is added. Similarly, alumina may be added in amounts of from about 0.20 w/o to about 1.0 w/o, more preferably between about 0.4 and about 0.6 w/o of the sintered ceramic. Most preferably, about 0.47 w/o of Al_2O_3 , having a purity of more than 99% and an average particle size of less than 1 micron, is added.

Silica may be present in the starting silicon nitride powder as an impurity. As a result, silicon may be present in the grain boundary phase of the sintered ceramic in an amount of between about 2 and 4 w/o, preferably 2 and 3 w/o of the ceramic, as silica.

The silicon nitride and sintering aid powders may be mixed by any known mixing process including, but not limited to, ball milling and attrition milling. In preferred embodiments of the present invention, vibratory milling is preferred.

If a green body is formed, green body formation may be performed by any typical process used in art. These processes include slip casting, injection molding, freeze casting and cold isostatic pressing. In preferred embodiments of the present invention, the powders of the present invention are cold isostatic pressed.

The sintering cycle of the present invention may include any conventional sintering process, including pressureless sintering, gas pressure sintering, hot pressing and hot isostatic pressing using glass ("glass encapsulated hiping"). In preferred, embodiments of the present invention, the glass encapsulation hiping processes as described in U.S. Patent Nos. 4,446,100, and 4,339,271 are used. It is further preferred that

embodiments utilizing U.S. Patent Nos. 4,446,110 and 4,339,271 be practiced at very high packing efficiency, i.e., with parts touching each other.

EXAMPLE I

5 Silicon nitride powder with the following characteristics was used as the powder in this example: more than about 90 w/o alpha Si_3N_4 , less than about 2.0 w/o total oxygen, less than 0.1 w/o calcium, about 0.03 w/o iron, about 0.05 w/o aluminum, and a surface area of about
10 5 - 9 m^2/g .

About 98 parts by weight of this powder was combined with about 1.33 parts by weight of reagent grade magnesium carbonate and about 0.47 parts by weight alumina and isopropyl alcohol to form a slurry having 45% solids. The
15 slurry was simultaneously blended and milled in a vibratory mill with Si_3N_4 milling media. The final surface area was about 10 - 14 m^2/g . The resultant slurry was passed through a 20 micron screen and a magnetic separator. The slurry was concentrated to 65% solids by cross-flow filtration.
20 Next, PVP (polyvinylpyrrolidone) was added to the slurry in an amount of about 1.25 w/o of the powder. The slurry was then dried in an explosion-proof spray dryer. The dried powder was then passed through a 30 mesh nalgene screen. All of the above operations were performed in a class 1000
25 clean room dedicated to silicon nitride processing. The dried agglomerated powder was cold isostatically pressed at 30 ksi into cylinders and ground into rods having a diameter of about 0.52 inches and a length of about 3.8 inches. The powder compacts were air fired at 600°C to
30 remove the PVP. Samples were encapsulated in glass media and hot isostatically pressed at 30,000 psi (20.7 MPa) pressure for about 1 hour at about 1790°C.

EXAMPLES II and III

35 The above process was repeated essentially identically, except that $\frac{1}{4}$ inch balls and 3 x 4 x 50 mm flexure rods were produced.

The resulting ceramics were measured for hardness. Vickers diamond pyramid hardness indentations from 10 kg

loads were created. The mean hardness was found to be about 15.2 GPa. In comparison, NBD-200, a 1 w/o MgO silicon nitride bearing material manufactured by the Norton Company of Worcester, MA, has a hardness of about 15 - 15.6 GPa.

Fracture toughness was determined by the fracture of 4 point bend specimens of 3 x 4 x 50 mm containing a Vickers indentation (10 kg load) on the tensile surfaces within the inner span, at a crosshead speed of about 0.5 mm/min, according to procedures described by P. Chantikul et al., in "A Critical Evaluation of Indentation Techniques for Measuring Fracture Toughness II: Strength Methods", J. Am. Ceram. Soc. 64(9), pp. 539-544 (1981). The average toughness of the ceramics of the present invention was about 5.6 MPa m^{1/2}. In comparison, NBD-200 has a fracture toughness of about 5 - 5.8 MPa m^{1/2}.

The 4-point flexure strength of the ceramics of the present invention were also determined. 3 x 4 x 50 mm type B specimens on a 40 mm outer span and a 20 mm inner span test jig (ASTM C1161-90) were selected. The mean flexure strength was determined to be about 950 MPa. In comparison, NBD-200 has a flexural strength of about 700 - 850 MPa.

Tensile strength was also analyzed by the ASCERA Tensile Test Procedure. This procedure is set out in Brit. Ceram. Trans J., 89, 21-23, 1990. The tensile strength of the present invention was found to be about 475 MPa. In comparison, NBD-200 has a tensile strength of about 400 MPa.

The rods made in Example II were subjected to rolling contact fatigue (RCF) tests, specifically the accelerated bearing test procedure described in ASTM-STP 771. This test procedure applies contact pressure higher than that normally encountered in service in order to accelerate the fatigue failure of the test material. The test uses statistical analysis of data from numerous test specimens, and the results are normally reported in terms of a variable L_x, which denotes the number of stress cycles

which cause failure in X percent of the specimens tested at a given stress level. In carrying out the RCF test for the present invention, three slave balls made of AISI 52100 steel were loaded against a rod consisting of the silicon nitride of the present invention at an average contact stress of about 6.9 GPa. The rod was rotated at about 3600 rpm with an electric motor. Both the slave balls and the rod were lubricated with lubricating oil supplied by a drip feeder at a rate of about 8 drops per minute. The test produced circumferential fatigue tracks in the rod which were about 0.1 inches in width. The silicon nitride of the present invention displayed normal failure modes and uniform wear. Of the 24 rods of the present invention which were subjected to RCF testing, the first rod to fail did so at about 54 million cycles. If a Weibull slope of about 0.74 is assumed (i.e., it is assumed the present invention has the same failure mechanism as NBD-200), an L10 of about 80 million cycles is realized for the present invention. In comparison, NBD-200 has an L10 RCF life of 4 million cycles.

The mechanical characteristics of the present invention as exemplified by Examples I - III are summarized in Table 1, along with comparative silicon nitride ceramic NBD-200.

TABLE 1		
PROPERTY	EXAMPLES I - III	NBD-200
L10 RCF Life (cycles)	80,000,000	4,000,000
Tensile Strength (MPa)	475	400
Flexural strength (MPa)	950	<850
Fracture Toughness (MPa m ^{1/2})	5.6	< 5.8
Hardness (GPa)	15.2	<15.6

The silicon nitride of the present invention may be

used in a number of conventional ceramic applications, including but not limited to, ball bearings, roller bearings, plain sliding bearings and other structural or wear applications.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A sintered silicon nitride ball bearing consisting of:

5 a) at least about 94 w/o of the ball bearing being a crystalline phase of silicon nitride, and

b) a single grain boundary phase consisting essentially of Mg, Al, Si and O,

10 wherein the grain boundary phase consists essentially of between 1 and 2 w/o of the ball bearing being Mg, as magnesia; between 0.2 and 1.0 w/o of the ball bearing being Al, as alumina; between 2 and 4 w/o of the ball bearing being Si, as silica; and oxygen, characterized by an L10 value of at least 50 million stress cycles in ASTM test 771 under 6.9 GPa applied contact stress.

15 2. The sintered silicon nitride ball bearing of claim 1 wherein the Al component of the grain boundary phase is between 0.3 and 0.6 w/o, as alumina, of the ball bearing.

3. The sintered silicon nitride ball bearing of claim 1 wherein the Si component of the grain boundary phase is between 2.0 and 3.0 w/o, as silica, of the ball bearing.

20 4. The sintered silicon nitride ball bearing of claim 1 having an L10 value of at least 60 million cycles.

5. The sintered silicon nitride ball bearing of any one of the preceding claims 1-3 having an L10 value of at least 70 million cycles.

6. The sintered silicon nitride ball bearing of claim 1 having a flexural strength of at least 950 MPa.