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(54) POROUS SILICON OXYNITRIDE REFRactory BODIES

(71) We, NORTON COMPANY of 1 New Bond Street, Worcester 6, Massachusetts, United States of America, a corporation organized under the laws of the State of 5 Massachusetts, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following 10 statement:

This invention relates to a permeable refractory body comprising refractory grains. Porous plates, tubes and other shapes have been needed by the aluminum industry to 15 introduce gases into molten baths and metal without being attached by the molten materials. One specific need is a porous medium that will withstand chlorine or chlorinated gases at elevated temperatures to be used in an 20 aluminum electrolysis system of the type described in Jacobs U.S. Patent 3,785,594 assigned to Aluminum Company of America. The porous medium must also resist attack by molten chloride salts and molten aluminum. 25 Silicon oxynitride, in a low permeability form, has been demonstrated to withstand attack by the environment found in the above "ALCOA" process. "ALCOA" is a registered 30 trade mark. It has been found however, that simply reducing the density to increase the porosity does not provide adequate permeability and results in a body with fine discrete particles that are loosely bonded rather than as a dense matrix. What is needed is a dense matrix with 35 interconnecting pores or channels that are free to pass gas. Attempts, in the past, to produce a continuous pore network using a burnout material, upon nitridation, have resulted in either carbon filled pores or pores that are 40 filled with a fibrous deposit of alpha silicon nitride. Permeabilities of these bodies were greatly reduced. Similarly, early attempts to produce a continuous pore network by pressing size grains of green compacted silicon oxynitride 45 raw mix have also resulted in pores filled with

silicon nitride fibers after nitridation with subsequent reduced permeability.

Although there is considerable prior art on the formation of silicon oxynitride (i.e. Si_2ON_2) (e.g. Washburn U.S. Patents 3,356,513; 50 3,639,101 and 3,679,444 as well as U.S. Patent 3,193,399 for forming a Si_2ON_2 bond for silicon carbide grain), there is no known prior art showing the formation of a satisfactory Si_2ON_2 body. There are other porous refractory bodies such as those shown in U.S. Patents 2,806,772; 2,691,598 and 3,175,918 but none of these show a product having the porosity and corrosion resistance of a permeable refractory body according to the present invention (see later below). 55

In U.K. Patent Application 45738/77, which is an application for a patent of addition to be granted on the U.K. Patent to be granted on the present application, there is described and claimed a permeable refractory body, comprising refractory grains, said grains comprising refractory material other than silicon oxynitride, but said grains can optionally comprise silicon oxynitride present with said other material, 60 said grains being bonded together and substantially coated with bond material, said bond material comprising silicon oxynitride, said body having interconnecting pores so as to be permeable, said pores being free from silicon oxynitride whiskers. Reference should also be made to our U.K. Patents 1,442,009; 1,352,357; 70 1,349,664 and 1,064,923.

According to one aspect of the present invention, there is provided a permeable refractory body, comprising refractory grains, said grains comprising silicon oxynitride, said grains being bonded together by bond material comprising silicon oxynitride, said body having interconnecting pores so as to be permeable, said pores being free from silicon oxynitride whiskers. 80

According to a second aspect of the present invention, there is provided a method of withstanding attack by an environment, comprising using a said body according to said first aspect 85

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of the present invention so as to provide resistance against said attack.

A said body according to said first aspect of the present invention can be an open structure, and not have a carbonaceous residue or deposits of alpha silicon nitride fibers, and be essentially all silicon oxynitride. A said body according to said first aspect of the present invention can exhibit high permeability to gases with low pressure drops, have a dense oxynitride matrix, and an open pore network. Permeabilities can be adjusted to a desired level by adjusting the size and shape of said grains.

In preparing a said body according to said first aspect of the present invention, said grains can be grains that have been obtained from crushed silicon oxynitride plates. Said grains can be sized grains, the sizing thereof being chosen to enable the formation of a corresponding continuous pore network in said body. Examples of sized grains are grains having an average grain size of substantially 6848 microns or less, or grains having an average grain size of substantially 216 microns or more. One example of convenient sized grains is when said grains have an average grain size in the range 3460 to 1035 microns. Sized grains have been made by crushing rejected low permeability silicon oxynitride refractory scraps and screening out the desired sizes. The pore size of the low permeability silicon oxynitride made in accordance with U.S. Patent 3,679,444, for example is typically about 1 or 2 microns, ranging in size from 0.2 micron to 20.0 microns. The density of such material typically ranges from 2.0 to 2.2 g/cc. These grains can also be made by compacting an oxynitride raw batch and crushing and screening the green compacts to the desired mesh size and then nitriding the grains. The green grains made in this way may also be used directly to form a porous shape, provided a treatment is used to ensure that they do not break down during mixing with a suitable wet mix for bonding the grains together. Such a treatment could be for example, a heat treatment in air to a temperature of 500°C.

In a said body according to said first aspect of the present invention, said bond material can surround said grains and extend between said grains. At least one said grain can have a coat of said bond material which coat can have any suitable thickness. Preferably, such a thickness is in the range 20 to 100 microns. said bond material can be denser than at least one said grain.

Said bond material can be synthesized in situ by a nitriding process. Preferably, in said nitriding process, said bond material is synthesized from silicon, a source of silica, and a source of nitrogen. Examples of said source of silica are at least one of ortho ammonium silicate, silicon dioxide, and ethyl silicate. Preferably, a said source of silica comprises ortho ammonium silicate, which can result in a sticky adherent bonding mix that coats said grains, and bonds them together under relatively low pressure. A said source of silica can be in colloidal form, e.g. an aqueous suspension of colloidal silica, for instance "Ludox" 130M (made by DuPont). "LUDOX" is a registered trade mark.

Said nitriding process can be carried out in the presence of at least one additive for aiding that process. Said at least one additive can comprise at least one of a compound of calcium and a compound of magnesium. Preferably said at least one additive comprises at least one of oxide of calcium and oxide of magnesium. Preferably, said at least one additive comprises at least one of fluoride of calcium and fluoride of magnesium. An example of the total amount of said at least one additive in said process is when said at least one additive is present in a total amount that is in the range 2 to 5% by weight of the bonding ingredients.

In preparation for synthesis of said bond material in situ by a nitriding process, said grains can be mixed with a mixture of bonding ingredients. One example of a bond mix is a mixture containing 32 weight percent of silicon particles having a nominal average particle size of 2 microns; 65 weight percent ortho ammonium silicate containing substantially 34 weight percent silica in aqueous solution; and 3 weight percent of magnesium fluoride powder. Such a bond mix can be mixed with said grains so as to obtain a wet and sticky mixture, which can be rammed, tamped, or pressed into a desired shape. Hand tamping with a wooden block has been found an adequate forming technique. Wax paper has been found to provide a suitable release medium for the resultant shaped material. After air drying, or oven drying in air, wax paper can be peeled from surface of the shaped material. The resultant green item has good strength after drying and can be handled with ease. The green item can then be nitrided in a typical silicon oxynitride firing cycle such as described in said U.S. Patents 3,356,513 and 3,639,101.

Said bond material can have pores. For example, said bond material can have pores of pore size substantially less than 10 microns, for instance said bond material can have pores of pore sizes substantially 2.0 microns.

In a said body according to said first aspect of the present invention, at least one said interconnecting pore can have a pore size in the range $\frac{1}{4}$ to $\frac{1}{10}$ of the grain size of at least one said grain. At least one said interconnecting pore can have a pore size in the range 20 to 1000 microns, or a pore size in the range 200 to 2000 microns. Said interconnecting pores can exhibit at least some re-entrant angles. At least 14.0% by volume of the volume of said body can consist of said interconnecting pores. Preferably, said interconnecting pores comprise interconnecting channels. A said body can have pores in the matrix thereof and pores in the bond provided by said bond material, these

matrix pores and bond pores being smaller in pore size than the pore size of said interconnecting pores. Said matrix pores and said bond pores can be substantially less than 10 microns, for 5 example said matrix pores and said bond pores can have an average size substantially 2 microns or less.

A said body of said first aspect of the present invention can have a porosity represented 10 by the ratio of flow rate "F" to pressure drop "P" greater than 6.0/1.0, wherein F is a ratio "cubic feet/hour", and P is a ratio "inch of water/inch of thickness of said body" or "inches of water/inch of thickness of said body", P 15 being measured at substantially 0.1 inch water pressure.

A said body of said first aspect of the present invention can have a bulk density of substantially 1.8 g/cc or less.

It will be appreciated that a said body of said first aspect of the present invention can be 70 a shaped body. For example, a said shaped body can be platelike or tubelike.

The present invention is illustrated by the following Examples I to VII. It should be noted that these Examples are followed by a discussion 75 of materials used in said Examples, e.g. a discussion of ortho ammonium silicate (OAS).

EXAMPLES I to V

Five different formulations were mixed in a stainless steel bowl by hand, and hand tamped 80 with a wooden block in 6 in. x 6 in. waxed paper boxes.

		I	II	III	IV	V	
20	Si ₂ ON ₂ grain having an average grain size in the range 3460 to 1035 microns	360 g	85				
25	2 micron Si	40	40	40	40	40	90
	CaF ₂ powder	0	4	0	2	0	
30	MgF ₂ powder	0	0	4	0	2	95
	OAS solution	80	80	80	80	80	

The plates were air dried and then removed 35 from the boxes. They were set flat on alumina setting batts in a nitriding chamber and fired in a series of sequential steps with exothermic control to a temperature of 1420°C. The resulting plates were hard and well bonded and exhibited a "ring" when struck.

Pressure drop was measured at various flows of nitrogen at room temperature using a 4 in. round gasketed chamber connected to a calibrated flow meter and gas pressure sensor. The following pressure drops were found across the $\frac{5}{8}$ in. thicknesses.

		I	II	III	IV	V	
40	Flow (CFH) (i.e. cu. ft per hour)	0	0	0	0	0	105
45	Pressure (in. H ₂ O)	0.007	0.007	0.008	0.008	0.008	110
	Flow (CFH per in. ²)	0	0	0	0	0	
50	Pressure * (in. H ₂ O per inch thick)	0	0	0	0	0	115
	Flow (CFH)	3.0	6.2	6.0	2.5	11.5	
55	Pressure (in. H ₂ O)	0.028	0.015	0.02	0.015	0.05	120
	F, Flow (CFH per in. ²)	0.24	0.49	0.48	0.2	0.91	
60	P, Pressure * (in. H ₂ O per inch thick)	0.03	0.01	0.018	0.01	0.06	125
	F/P	8.0	49.0	26.6	20.0	15.2	

65 *Pressure drop after subtracting base pressure out. 130

		I	II	III	IV	V	
5	Flow (CFH)	25.6	27.0	27.0	26.2	28.0	70
	Pressure (in. H ₂ O)	0.159	0.048	0.071	0.091	0.09	
	F, Flow (CFH per in. ²)	2.03	2.14	2.14	2.08	2.22	
10	P, Pressure * (in. H ₂ O per inch thick)	0.225	0.059	0.094	0.124	0.117	75
	F/P	9.0	36.3	22.8	16.8	19.0	

15 *Pressure drop after subtracting base pressure out.

These data show that pressure drops across the plates are reduced when either CaF₂ or MgF₂ are added to the bonding ingredients. The plates with 4 parts of either fluoride show lower pressures than those with 2 parts and both additions result in significantly lower pressures than the plate without such additions. This indicates that the interconnecting channels are more open when the fluorides are added.

25 EXAMPLE VI

A plate measuring 12 in. x 11 in. x 3/4 in. was hand tamped from the following mixture: Si₂ON₂ grain having an average grain size in the range 3460 to 1035 microns 74.4
2 microns (nominal average) silicon 8.3
35 MgF₂ 0.8
OAS (34 weight % SiO₂) 16.5
100.0 parts by weight

40 The plate was dried and fired as in the previous examples. The plate was hard and well bonded with an open structure and no alpha silicon nitride fibers in the pores. Modulus of rupture of a 9 x 2-1/8 in. bar cut from the plate was 1560 p.s.i. and the density of the bar was 1.56 g/cc.

45 EXAMPLE VII

A plate measuring 12 x 11 x 3/4 in. was pressed from the following mixture:

50 Si₂ON₂ grain having an average grain size in the range 3460 to 1035 microns (2 microns nominal average) silicon 4.46 lbs.
55 MgF₂ 0.5 lbs.
OAS 0.05 lbs.
1.0 lbs.

60 The plate was air dried overnight then dried in an oven at 80°C. It was fired as in the previous Examples and then examined.

65 The permeability of the plate, measured by a standard porous plate test (for one inch thick plates) using 2 inches of water back pressure, was scfm/ft² (standard cubic feet per minute per square foot).

An X-ray diffraction pattern of a sample of the plate showed essentially all Si₂ON₂ with no peaks showing for alpha Si₃N₄, beta Si₃N₄, cristobalite, or silicon. A small peak for SiC was found with an estimated quantity of 2 to 5 weight percent. Spectrographic analysis of the metal phases showed essentially all Si with 1.2 weight % Al, 0.2 weight % Ca, 0.3 weight % Fe, and 0.3 weight % Mg.

80 Examination of a polished section of a sample of the plate showed a network of interconnecting channels ranging in size from about 0.2 to 2.0 mm (i.e. 200 to 2000 microns with an average of about 1.0 mm. i.e. 1000 microns). Although the channels were irregular in shape, the walls were smooth and showed no evidence of fiber formation. At points of contact between grains, bond necks were well established with smooth rounded transitions from grain to grain. The channels exhibited many re-entrant angles thereby avoiding direct openings surface to surface. At a magnification of 56X the nature of the bond between the grains showed rounding of pores and the formation of a dense layer on the walls of the pores. Holes and defects in the structure of the grains themselves were sealed off by the coating which ranged in thickness from 20 to 100 microns. The pore size of the coating was typically about 2 microns. However, the density of the coating appears to be greater than that of the starting grains, that is the relative pore volume of the coating is less than that of the starting grains.

85 90 95 100 105 110 115 120 125 130
In these Examples, we have used only one size of silicon oxynitride grain and have made plates. For filtering or for flow control it is often desirable to have different pore sizes and other shapes e.g. tubes. The preferred characteristic of the interconnecting pores is that there should be channel passages rather than spherical isolated pores. A continuous pore network permits low pressure drop for a given flow rate. The use of sized particles gives such channels, providing the channels are not plugged by the bond either by whisker growth or by the use of large volumes of bond.

The pore structure of a said body of said first aspect of the present invention can be bimodal. There can be relatively large said

interconnecting pores and very small pores in the matrix and bond. Matrix and bond pores can be substantially less than 10 microns e.g. have an average pore size substantially 2.0 5 microns or less. Said interconnecting pores are those between said grains, and will be less than the grain diameter but continuous. The bodies made with abrasive grains having an average grain size in the range 3460 to 1035 microns 10 correspond to particle diameters of 1000 to 3500 microns. Pore sizes observed under the microscope in polished sections range from 200 to 2000 microns. The 2000 micron pore is probably a channel. The diameter of a said interconnecting pore can be $\frac{1}{4}$ to $\frac{1}{10}$ of the grain size of at least one said grain.

In Example VI, the bulk density of the product body was 1.56 g/cc. The matrix and bond have a density of substantially 2.1 g/cc.

20 56 volume percent of the body is silicon oxynitride. 18 volume percent of the body is fine pores in the matrix. 26 volume percent of the body is channel pores.

We can make a said body of said first aspect 25 of the present invention so that said body can have any of a range of grain sizes, pore sizes, and volume of said interconnecting pores. The principal limitations are (a) too low a strength for the highest porosity, or (b) too little bond, 30 or (c) too low a permeability for the finest grain sizes, or (d) too large a volume of bond. Experience with porous ceramic bodies in other materials indicates that silicon oxynitride grains having an average grain size of 6848 microns is 35 as large as desired, and silicon oxynitride grains having an average grain size of 216 microns can be the lower limit. The diameters of said interconnecting pores can be in the range 1000 to 20 microns. The densest packing, with appreciable permeability, can be a said body with a 40 bulk density of 1.8 g/cc, which can correspond to 64.3 volume percent solid, 21.4 volume percent pores in said grains, and 14.3 volume percent pores in the form of said interconnecting pores.

45 In the above Examples, said grains were obtained from crushed Si_2ON_2 plates which had been prepared as described in Washburn U.S. Patent 3,356,513. The silicon was obtained from 50 Union Carbide Corporation, under the designation of technical grade; it had a nominal analysis, percent weight, of 98.5 Si, 0.9 Fe, 0.5 Al, and 0.1 Ca. The MgF_2 was finely divided purified powder. The CaF_2 had an average 55 grain size of 74 microns, and contained finer "native" powder. The ortho ammonium silicate was obtained from Philadelphia Quartz Company, and had the designation "OAS #3", which contained 34 weight percent SiO_2 and a 60 mole ratio of $\text{SiO}_2/\text{Cation}$ of 4.5.

WHAT WE CLAIM IS:

1. A permeable refractory body, comprising refractory grains, said grains comprising silicon oxynitride, said grains being bonded together by bond material comprising silicon 65 oxynitride, said body having interconnecting pores so as to be permeable, said pores being free from silicon oxynitride whiskers.

2. A body as claimed in claim 1, wherein said grains are grains that have been obtained from crushed silicon oxynitride plates. 70

3. A body as claimed in claim 1 or 2, wherein said grains have an average grain size of substantially 6848 microns or less.

4. A body as claimed in claim 1 or 2, wherein said grains have an average grain size of substantially 216 microns or more. 75

5. A body as claimed in claim 1 or 2, wherein said grains have an average grain size in the range 3460 to 1035 microns. 80

6. A body as claimed in any one of claims 1 to 5, wherein said bond material surrounds said grains and extends between said grains. 85

7. A body as claimed in any one of claims 1 to 6, wherein at least one said grain has a coat of said bond material which coat has any thickness in the range 20 to 100 microns.

8. A body as claimed in any one of claims 1 to 7, wherein said bond material is denser than at least one said grain. 90

9. A body as claimed in any one of claims 1 to 8, wherein said body material was synthesized in situ by a nitriding process.

10. A body as claimed in claim 9, wherein said bond material was synthesized from silicon, a source of silica, and a source of nitrogen. 95

11. A body as claimed in claim 10, wherein said source of silica comprised at least one of ortho ammonium silicate, silicon dioxide, and ethyl silicate. 100

12. A body as claimed in claim 10, wherein said source of silica comprised ortho ammonium silicate.

13. A body as claimed in any one of claims 10 to 12, wherein said source of silica was in colloidal form. 105

14. A body as claimed in any one of claims 9 to 13, wherein said nitriding process was carried out in the presence of at least one additive for aiding that process. 110

15. A body as claimed in claim 14, wherein in said process said at least one additive comprises at least one of a compound of calcium and a compound of magnesium. 115

16. A body as claimed in claim 15, wherein in said process said at least one additive comprises at least one of oxide of calcium and oxide of magnesium. 120

17. A body as claimed in claim 15 or 16, wherein in said process said at least one additive comprises at least one of fluoride of calcium and fluoride of magnesium.

18. A body as claimed in any one of claims 14 to 17, wherein in said process said at least one additive is present in a total amount that is in the range 2 to 5% by weight of the weight of the bonding ingredients. 125

19. A body as claimed in any one of claims 1 to 18, wherein said bond material has pores. 130

20. A body as claimed in claim 19, wherein said bond material has pores of pore size sub- stantially less than 10 microns.	“inch of water/inch of thickness of said body” or “inches of water/inch of thickness of said body” P being measured at substantially 0.1 inch water pressure.	
21. A body as claimed in claim 20, wherein 5 said bond has pore sizes substantially 2.0 microns.	32. A body as claimed in any one of claims 1 to 31, wherein said body has a bulk density of substantially 1.8 g/cc or less.	50
22. A body as claimed in any one of claims 1 to 21, wherein at least one said interconnect- ing pore has a pore size in the range $\frac{1}{4}$ to $\frac{1}{10}$ of 10 the grain size of at least one said grain.	33. A body as claimed in any one of claims 1 to 32, wherein said body is a shaped body.	
23. A body as claimed in any one of claims 1 to 21, wherein at least one said interconnect- ing pore has a pore size in the range 20 to 1000 microns.	34. A body as claimed in claim 33, wherein said shaped body is platelike.	55
24. A body as claimed in any one of claims 1 to 22, wherein at least one said interconnect- ing pore has a pore size in the range 200 to 2000 microns.	35. A body as claimed in claim 33, wherein said shaped body is tubelike.	
25. A body as claimed in any one of claims 1 to 24, wherein said interconnecting pores exhibit at least some reentrant angles.	36. A body as claimed in claim 1, sub- stantially as described with reference to Example I.	60
26. A body as claimed in any one of claims 1 to 24, wherein at least 14.0% by volume of the volume of said body consists of said inter- 25 connecting pores.	37. A body as claimed in claim 1, sub- stantially as described with reference to Example II.	
27. A body as claimed in any one of claims 1 to 26, wherein said interconnecting pores comprise interconnecting channels.	38. A body as claimed in claim 1, sub- stantially as described with reference to Example III.	65
28. A body as claimed in any one of claims 1 to 27, wherein said body has pores in the matrix thereof and pores in the bond provided by said bond material, these matrix pores and bond pores being smaller in pore size than the pore size of said interconnecting pores.	39. A body as claimed in claim 1, sub- stantially as described with reference to Example IV.	70
29. A body as claimed in claim 28, wherein said matrix pores and said bond pores are sub- stantially less than 10 microns.	40. A body as claimed in claim 1, sub- stantially as described with reference to Example V.	
30. A body as claimed in claim 29, wherein said matrix pores and said bond pores have an 40 average size substantially 2 microns or less.	41. A body as claimed in claim 1, sub- stantially as described with reference to Example VI.	75
31. A body as claimed in any one of claims 1 to 30, wherein said body has a porosity re- presented by the ratio of flow rate “F” to pressure drop “P” greater than 6.0/1.0, wherein 45 F is a ratio “cubic feet/hour”, and P is a ratio	42. A body as claimed in claim 1, sub- stantially as described with reference to Example VII.	
	43. A method of withstanding attack by an environment, comprising using a body as claimed in any one of claims 1 to 42 so as to provide resistance against said attack.	80
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