

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
13 August 2009 (13.08.2009)

PCT

(10) International Publication Number
WO 2009/098657 A1

(51) International Patent Classification:

C04B 35/573 (2006.01) **F27D 1/16** (2006.01)
C04B 35/66 (2006.01) **C04B 35/63** (2006.01)
C04B 35/64 (2006.01)

(21) International Application Number:

PCT/IB2009/050480

(22) International Filing Date:

5 February 2009 (05.02.2009)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

12/028,202 8 February 2008 (08.02.2008) US

(71) Applicant (for all designated States except US): **SAINT-GOBAIN CENTRE DE RECHERCHES ET D'ETUDES EUROPEEN** [FR/FR]; 18 avenue d'Alsace Les Miroirs, F-92400 Courbevoie (FR).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **JORGE, Eric** [FR/FR]; 1003 chemin de la Palestine, F-84210 Les Valayans (FR). **MARGUIN, Olivier** [FR/FR]; 4 Chemin des Bergers, F-84510 Caumont Sur Durance (FR). **MOITRIER, Olivier** [FR/FR]; Chemin de St Côme 1, lotissement les Lavandes, F-13370 Mallemort (FR). **CITTI, Olivier** [FR/US]; 1 Avon rd, Wellesley, Massachusetts 02482 (US).

(74) Agent: **SARTORIUS, Jérôme**; Nony & Partners, 3 rue de Penthièvre, F-75008 Paris (FR).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

(54) Title: A SINTERED REFRACTORY MATERIAL BASED ON SILICON CARBIDE WITH A SILICON NITRIDE BINDER

(57) Abstract: A sintered material based on silicon carbide (SiC) reactively sintered between 1,1000C and 1,7000C to form a silicon nitride binder (Si₃N₄), intended in particular for fabricating an aluminum electrolysis cell, including 0.05% to 1.5% of boron, the Si₃N₄/SiC weight ratio being in the range 0.05 to 0.45. Application, in particular, to an electrolysis cell.



WO 2009/098657 A1

A SINTERED REFRACTORY MATERIAL BASED ON SILICON CARBIDE
WITH A SILICON NITRIDE BINDER

This patent application is continuation in part of the
5 patent application filed in USA on November 25, 2005 under
No. 11/791 653 (PCT/FR2005/002936) in the name of SAINT GOBAIN
CENTRE DE RECHERCHES ET D'ETUDES EUROPEEN.

The invention relates to novel sintered refractory blocks,
especially for the construction of aluminum electrolysis
10 cells, to a method of manufacturing them, and to a cell
comprising said blocks.

As can be seen in Figure 1, aluminum metal 2 may be
produced on an industrial scale by electrolyzing alumina in
solution in a bath 10 based on molten cryolite. The
15 electrolyte bath 10 is conventionally contained in an
electrolysis cell 12. The cell 12 comprises a side wall 14 and
a bottom 16. The bottom 16 is composed of refractory bottom
blocks 17 and cathode blocks 24 and insulating blocks in the
lower portion. The side wall 14 is formed from refractory side
20 blocks 18 surrounded by a metal casing 20.

The dimensions of a refractory side block 18 can vary.
They are conventionally more than $30 \times 100 \times 100$ mm
[millimeter] and may attain $120 \times 300 \times 300$ mm.

The composition of the blocks 18 may be based on carbon
25 (graphite and/or anthracite). Typically, the mortar for the
blocks 18 is a refractory cement 21 disposed between them and
against the metal envelope 20. The cell 12 comprises at least
one anode 22 and at least one cathode 24. The anodes 22 and
cathodes 24 are disposed so as to be in contact with the
30 molten metal bath, the cathode 24 conventionally being
disposed close to the bottom 16.

When the electrodes 22 and 24 are placed under voltage, an
electrolysis reaction occurs in the bath 10, resulting in the
formation of a bath of aluminum in the cell, which bath is
35 deposited on the cathode.

Passing high electric current through the bath 10 also
causes heat to be released under the Joule effect. Evacuating
that heat through the wall 14 of the cell 12 causes a layer 26

of solidified cryolite to be deposited on the inner surface 27 of the blocks 18. That layer is termed a "self-lining" layer.

The blocks 18 must protect the metal envelope 20 and allow sufficient heat to be evacuated to ensure temperature stabilization of the molten bath 10. In particular, it is vital to avoid reaching temperatures beyond which the self-lining layer 26 of solidified cryolite liquefies again and could contribute to very rapid corrosion of the sides of the cell. Further, the blocks 18 are often exposed to corrosive environments (very hot liquid metal, molten cryolite in the lower portion, corrosive gas in the upper portion), and they are subjected to high temperatures and large thermal and mechanical stresses.

To meet those challenges, blocks are known that are based on silicon carbide granulates which have generally satisfactory resistance to attack. Conventionally, silicon carbide granulates are sintered at a temperature in the range 1600°C to about 2000°C. Sintering fine grained silicon carbide granulates at very high temperatures (2150°C) is also known, enabling boron and carbon to be added. However, silicon carbide is very difficult to sinter and/or its cost is prohibitive. Further, the format of the sintered silicon carbide blocks is limited, especially due to a great deal of shrinkage on firing.

Blocks based on dense sintered silicon carbide granulates are also known, with less than 1% of B₄C and C, for example Hexolloy SiC®. However, they are currently extremely expensive.

Finally, blocks based on silicon carbide (SiC) are known, bound by a matrix of silicon nitride (Si₃N₄). The materials for such blocks were developed at the end of the 1970s and are described, for example, in United States Patent No. US-A-2 752 258. They improve the compromise between oxidation resistance, mechanical strength (erosion), and thermal conductivity compared with carbon blocks. The improvement in abrasion resistance is particularly advantageous at the bottom of the cell where the bath, which moves under the effect of magnetic fields, may cause a great deal of abrasion.

Said blocks are obtained by reactive sintering of a mixture of silicon carbide and silicon, with nitrogen deriving from firing in a nitrogen atmosphere.

By "reactively sintered product" is meant a ceramic product having a nitrogenous matrix, whether crystallized or not, obtained during the thermal treatment (known also as sintering) from precursors introduced within the starting charge. These precursors are preferably in the form of powders having a median diameter of less than 200 microns, and preferably contain silicon. By definition, a matrix ensures an essentially continuous structure between the silicon carbide grains.

To gain useful volume and facilitate heat evacuation, research has been concentrated on reducing the thickness of such blocks. However, the thickness cannot be reduced without affecting the service life of the cells. Thus, it must be accompanied by an improvement in the oxidation resistance and resistance to attack by the cryolite bath. That need is greater if the stresses on the refractory blocks are higher. In particular, electrolysis cells are now used with a current of more than 200,000 amps and from which, as a result, a great deal of heat must be evacuated, large quantities of oxidizing gas are generated, and the self-lining layer may become unstable.

Thus, there is a need for a novel refractory block based on silicon carbide (SiC) with a nitride binder (Si_3N_4) that can effectively and durably resist the thermal and/or chemical stresses that may be produced in an aluminum electrolysis cell, in particular in the side wall thereof.

The invention aims to answer this need.

According to the invention, this aim is achieved by means of a sintered refractory block based on silicon carbide (SiC) with a silicon nitride (Si_3N_4) binder, in particular intended for fabricating an aluminum electrolysis cell, which block is remarkable in that it includes, as a percentage by weight, a total calcium and boron content in the range 0.05% to 1.5%, preferably 1.2%. Preferably, it includes at least 0.05%,

preferably at least 0.3%, and more preferably at least 0.5% of boron, and/or in the range 0.05% to 1.2% of calcium.

Surprisingly, the inventors have discovered that the presence of boron and/or calcium provides a substantial improvement in properties as regards aluminum electrolysis cell applications, in particular resistance to oxidation and to attack by the cryolite bath, and dimensional stability under oxidation conditions.

The refractory block of the invention also exhibits one or more of the following preferred characteristics:

- the refractory block includes less than 3% of boron, as a percentage by weight;

- silicon nitride (Si_3N_4) in the beta form represents, as a percentage by weight, at least 40%, preferably at least 60%, and more preferably at least 80%, of all of the silicon nitride (Si_3N_4) in the beta form and in the alpha form;

- the Si_2ON_2 content, as a percentage by weight, is less than 5%, preferably less than 2%;

- the porosity of the sintered block is preferably 10% or more; and

- the boron is not in the TiB_2 form, as that form of titanium is not stable in contact with molten cryolite, in an oxidizing atmosphere. Further, TiB_2 is also unstable towards aluminum.

Preferably again, the $\text{Si}_3\text{N}_4/\text{SiC}$ weight ratio is in the range 5% to 45%, preferably in the range 10% to 20%, i.e. in the range 0.05 to 0.45, preferably in the range 0.1 to 0.2.

Preferably, the $\text{Si}_3\text{N}_4/\text{SiC}$ ratio is less than 0.3 and/or more than 0.05. Further, the Si_3N_4 content is preferably 11% or more, as a percentage by weight.

The invention also provides an electrolysis cell including a side wall comprising a plurality of refractory blocks, at least one of said blocks being in accordance with the invention. Preferably, all of the blocks forming the side wall of the cell of the invention are in accordance with the invention.

In particular for this application, a block in accordance with the invention does not, preferably, contain any alumina.

In the other applications of the invention, and in particular for kiln furniture and particularly supports to sinter porcelain pieces, a block, and more generally a refractory product in accordance with the invention, may contain at least 0.8%, at least 1% of alumina. It may also contain more than 0.1%, or more than 0.2% of Fe_2O_3 .

Preferably, a powder of calcined alumina is added in the starting charge. Preferably, the mean size of added alumina powder ranges between 0.4 and 10 microns

Finally, the invention provides a method of fabricating a refractory block in accordance with the invention, comprising the following steps in succession:

a) preparing a charge comprising a particulate mixture comprising a silicon carbide granulate and at least one boron and/or calcium compound, a binder optionally being added to said particulate mixture;

b) forming said charge in a mold;

c) compacting said charge in the mold to form a preform;

d) unmolding said preform;

e) drying said preform, preferably in air or a moisture-controlled atmosphere; and

f) firing said preform in a reducing atmosphere of nitrogen at a temperature in the range 1100°C to 1700°C .

The inventors have discovered that adding boron and/or calcium to the formulations improves the properties of sintered silicon carbide (SiC) based refractory blocks with a silicon nitride binder (Si_3N_4) which are obtained. In particular, the resistance to corrosion by fluorine-containing products and molten cryolite is improved.

The method of the invention also has one or more of the following preferred characteristics:

- said boron and/or calcium compound contains boron;

- said boron and/or calcium compound is added in a predetermined quantity so that the refractory block obtained at the end of step f) is in accordance with the invention, in particular so that it comprises, as a percentage by weight, at

least 0.05%, preferably at least 0.3%, more preferably at least 0.5% of boron, and/or less than 3% of boron;

- said boron and/or calcium compound is free of oxygen, i.e. added in a "non-oxide form";

5 • said boron compound is selected from the group formed by oxides, carbides, nitrides, fluorides and metal alloys containing boron, in particular B_4C , CaB_6 , H_3BO_3 , and BN , preferably from the group formed by B_4C and CaB_6 . More preferably, said boron compound is CaB_6 ;

10 • said calcium compound is selected from the group formed by oxides, carbides, nitrides, fluorides and metal alloys containing calcium, preferably selected from CaB_6 , $CaSi$, $CaSiO_3$, and $CaCO_3$;

15 • said calcium compound is added in a predetermined quantity such that the calcium content of the refractory block obtained at the end of step f) is in the range 0.05% to 1.2%, as a percentage by weight.

Other characteristics and advantages of the present invention become apparent from the following description, made with reference to the accompanying drawings in which:

20 • Figure 1 is a diagrammatic representation of an electrolysis cell in cross section along a substantially medial plane;

25 • Figure 2 represents in the form of graphs, the percentage variation in the increase in volume due to oxidation as a function of time for different blocks tested in accordance with American Standard ASTM C863 at 900°C;

- Figure 3 represents schematically the device used for the test 8.

30 Unless otherwise indicated, all of the percentages in the present description are percentages by weight.

When a granulate is said to be "based on" a constituent, this means that said granulate comprises more than 50% by weight of that constituent.

35 Known methods of fabricating refractory blocks may be employed to fabricate a block in accordance with the invention, provided that at least one oxygen-free boron compound is added to the starting charge.

Preferably, the method employed comprises the following steps:

a) preparing a charge comprising a particulate mixture comprising a silicon carbide granulate and at least one boron and/or calcium compound, a binder being added to said particulate mixture;

b) forming said charge in a mold;

c) compacting said charge in the mold to form a preform;

d) unmolding said preform;

e) drying said preform, preferably in air or a moisture-controlled atmosphere, using conventional preform fabrication procedures; and

f) firing said preform in a reducing atmosphere of nitrogen at a temperature of 1100°C to 1700°C, and drying.

In step a), the particulate mixture preferably comprises, as a percentage by weight, 30% to 90% of refractory grains wherein at least 90% have a size in the range 50 µm [micrometer] to 5 mm [millimeter], and 10% to 60% of at least one refractory powder wherein at least 90% of the particles have a diameter of less than 200 µm. Advantageously, said granulometric distribution can endow the fabricated block with optimum cohesion.

The boron may be supplied in a particulate form or in any other form provided that the maximum moisture content of the mixture remains below 7%, preferably below 5%.

The function of the binder is to form with the particulate mixture a mass that is sufficiently rigid to preserve its shape until step e). The choice of binder depends on the desired shape. Because of the binder, the mass may advantageously take the form of a layer of varying thickness, which can follow the wall of the mold, to form blocks.

Any known binder or mixture of known binders may be used. The binders are preferably "temporary", i.e. they are completely or partially eliminated during the block drying and firing steps. More preferably, at least one of the temporary binders is a solution of modified starch derivatives, an aqueous solution of dextrin or of lignone derivatives, a solution of a processing agent such as polyvinyl alcohol, a

phenol resin or another epoxy type resin, a furfuryl alcohol, or a mixture thereof. More preferably, the quantity of temporary binder is in the range 0.5% to 7% by weight relative to the particulate mixture of the charge.

5 Pressing additives as are conventionally used in fabricating sintered blocks may be added to the particulate mixture and the binder. Said additives comprise plasticizers, for example modified starches or polyethylene glycols and lubricants, for example soluble oils or stearate derivatives.
10 The quantities of such additives are those conventionally used when fabricating sintered silicon carbide (SiC) based refractory blocks with a silicon nitride binder (Si₃N₄).

Mixing of the charge is continued until a substantially homogeneous mass is obtained.

15 In step b), the charge is shaped and placed in a mold.

In the next compaction or "pressing" step c), the contents of the mold are compressed by applying a force to the upper surface of the charge which can transform it into a preform that is capable of being sintered. A specific pressure of
20 300 kg/cm² [kilogram/square centimeter] to 600 kg/cm² is appropriate. Pressing is preferably carried out uniaxially or isostatically, for example using a hydraulic press. It may advantageously be preceded by a manual or pneumatic and/or vibrational ramming operation.

25 Next, the preform is unmolded (step d)), then dried (step e)). Drying can be carried out at a moderately high temperature. Preferably, it is carried out at a temperature in the range 110°C to 200°C. It conventionally lasts between 10 hours and one week, depending on the format of the preform,
30 until the residual moisture content of the preform is less than 0.5%.

The dried preform is then fired (step f)). The firing period, between about 3 and 15 days cold to cold, depends on the materials and also on the size and shape of the block. In
35 accordance with the invention, firing is carried out in nitrogen in order to form the nitride by reactive sintering, which nitride acts as the ceramic binder for the grains. The firing cycle is preferably carried out at a temperature in the

range 1100°C to 1700°C. During firing, nitrogen reacts with certain of the constituents of the particulate mixture of the charge to form a matrix of silicon nitride which can bind the grains of said charge, in particular grains of silicon carbide. A monolithic block is produced.

In the various tests below, provided by way of non-limiting illustration, the particle size of the powders used as additives (B_4C , CaB_6 , and $CaSiO_3$) is less than 45 μm . Their respective contents in the starting composition are indicated in Table 1.

Metallic silicon is also added in the proportion indicated in Table 1.

"Black" or "refractory" silicon carbide with different granulometric fractions, sold by Saint-Gobain Ceramic Materials, was also used. This material is essentially constituted by alpha SiC and has a mean chemical analysis, by weight, of 98.5% of SiC .

Table 1 also shows the results of various tests carried out to characterize the products of the invention compared with the reference product (Refrax® type product). All of the measurements were carried out on the core of the specimens.

- The nitrogen (N) contents in the products were measured using LECO (LECO TC 436 DR; LECO CS 300) type analyzers. The values given are percentages by weight.
- The boron (B) and calcium (Ca) contents in the products were measured by X-ray fluorescence spectrometry. The values given are percentages by weight.
- The oxidation tests were carried out in accordance with ASTM C863. To reproduce the oxidation conditions experienced by the blocks of an aluminum electrolysis cell, the specimens (typically with a size of 25 × 25 × 120 mm) underwent a test of at least 100 hours at 900°C in an atmosphere saturated with steam. Oxidation generates an increase in mass ("Om" value, given as a percentage) and/or in volume ("Ov", given as a percentage), which results from the transformation of the silicon nitride and carbide into silica. The increases in mass and volume were thus indicators of the degree of

oxidation. Two materials were considered to be different when their oxidation indicators differed by at least 1% (mean over 3 test specimens).

▪ The variation in open porosity due to plugging by the oxidation products of the reaction was also a measure allowing the degree of oxidation to be determined. The open porosity was measured in accordance with International Standard ISO5017 ("PO-Ox" value, given as a percentage).

▪ The corrosion resistance test allowed the behavior of 25 mm × 25 mm cross section specimens which had already undergone the oxidation test to be determined. These specimens were kept at 1030°C for 22 hours in a bath of molten cryolite. Their corroded length was then measured, i.e. the reduction in their length resulting from corrosion. The value "Ic" provides, as a percentage, the ratio between the corroded length of the test specimen and the corroded length of a reference specimen. The lower the Ic, the better the corrosion resistance.

▪ The crystalline phases present in the refractory products were determined by X ray diffraction. Principally, it was found that silicon nitride Si_3N_4 as well as an oxynitride phase, Si_2ON_2 , were present. The amounts of these phases, as a percentage by weight, are indicated in Table 1. The complement was SiC.

The apparent specific gravity of the products of the invention was in the range 2.4 to 2.7. That of the reference product was 2.6.

The silicon nitride could be in the alpha or beta form. The alpha phase was present in the form of a tangle of silicon nitride fibrils, while the beta phase was in the form of grains with a variable shape.

Analyses carried out over several years by the Applicant have shown that silicon nitride in the beta form is less sensitive to rapid combustion because of its lower specific surface area, than is silicon nitride in the alpha form. During rapid combustion, silicon nitride is oxidized and produces silica which is "consumed" by the molten cryolite.

Those reactions thus result in an increase in the porosity and connectivity of the pores, facilitating the penetration of corrosive materials. Thus, it is advantageous to encourage the formation of the beta form to improve the resistance to attack by molten cryolite.

However, it is known that enrichment of the beta silicon nitride phase is generally accompanied by an enrichment in the oxynitride phase Si_2ON_2 .

However, silicon oxynitride, like residual silicon and Sialon with alumina impurities, conventionally generated during a nitriding process, are unwanted phases which have a lower resistance to cryolite compared with that of silicon nitride, regardless of the form of the silicon nitride. Thus, it is advantageous to limit the quantities thereof.

The inventors have discovered that adding boron and/or calcium, preferably in an oxygen-free form, to the starting charge advantageously stimulates the transformation into beta silicon nitride during the process for nitriding silicon carbides with a nitride binder, without causing deleterious enrichment of the Si_2ON_2 oxynitride phase. Table 1 below illustrates this discovery.

In accordance with the invention, a boron compound is thus added, preferably in a non-oxide form. Advantageously, this addition results in almost complete transformation into beta silicon nitride without major enrichment of the oxynitride phase Si_2ON_2 .

TABLE 1

N°	Composition					Analysis											
	Si	B ₄ C	CaB ₆	H ₃ BO ₃	CaCO ₃	PO	N	B	Ca	Si ₃ N ₄ a	Si ₃ N ₄ b	b/a	Si ₂ ON ₂	Om	Ov	PO-Ox	IC
R	13.5	0	0	0	0	17.2	5.9	0.0	0.1	12	5	29	3	1.6	1.0	14.0	100
1	13.5	0.2	0.0	0.0	0.0	16.2	6.4	0.1	0.1	10	9	47	3	2.4	0.0	9.4	45
2	11.8	0.5	0.0	0.0	0.0	17.1	7.4	0.5	0.1	8	9	53	3	2.7	0.1	9.5	ND
3	13.5	0.5	0.0	0.0	0.0	15.5	6.1	0.4	0.2	ND	ND	ND	ND	1.3	0.0	8.6	65
4	10.0	0.8	0.0	0.0	0.0	16.8	5.5	0.6	0.1	7	7	50	ND	2.5	0.0	6.7	61
5	13.5	0.8	0.0	0.0	0.9	16.3	7.1	0.5	0.4	1	14	93	4	1.5	0.0	10.0	41
6	13.5	0.8	0.0	0.0	0.0	16.1	7.0	0.5	0.0	2	14	88	4	1.9	0.1	9.4	41
7	13.5	0.8	0.0	0.0	0.0	16.1	7.1	0.6	0.1	7	10	59	2	2.4	0.1	6.2	45
8	14.3	0.8	0.0	0.0	0.0	16.1	7.0	0.5	0.0	1	14	93	4	2.0	0.1	9.5	41
9	13.5	1.0	0.0	0.0	0.0	15.2	6.1	0.6	0.2	ND	ND	ND	ND	1.5	0.1	7.6	72
10	13.5	1.6	0.0	0.0	0.0	16.1	6.9	ND	0.2	2	17	89	0	2.2	0.2	7.1	70
11	14.3	1.6	0.0	0.0	0.0	17.0	7.2	1.0	0.1	1	14	93	4	2.3	0.0	7.3	70
12	13.5	3.0	0.0	0.0	0.0	13.6	4.5	1.9	0.2	ND	ND	ND	ND	1.4	0.0	8.3	60
13	14.3	5.0	0.0	0.0	0.0	14.1	8.1	2.9	0.1	1	14	93	4	1.7	0.3	5.1	73
14	13.5	0.0	0.0	3.5	0.0	20.0	7.1	0.4	0.1	2	9	82	7	1.0	0.0	13.5	86
15	13.5	0.0	0.0	3.5	0.9	20.0	7.8	0.4	0.4	2	13	87	7	1.4	0.3	16.4	88
16	13.5	0.0	0.0	0.0	2.0	19.1	6.7	ND	1.0	9	9	100	0	1.5	0.9	ND	75
17	13.5	0.0	0.2	0.0	0.0	16.6	7.3	0.1	0.2	8	10	56	2	1.9	0.2	10.3	45
18	13.5	0.0	0.5	0.0	0.0	14.3	5.8	0.3	0.5	ND	ND	ND	ND	1.0	0.0	8.3	ND
19	13.5	0.0	1.0	0.0	0.0	16.4	7.7	0.3	0.4	1	18	95	0	1.6	0.3	11.3	35
20	13.5	0.0	1.0	0.0	0.0	15.6	7.1	0.6	0.5	3	15	83	3	1.7	0.0	7.7	47
21	13.5	0.0	3.0	0.0	0.0	14.3	6.0	1.1	1.4	ND	ND	ND	ND	2.0	0.0	7.5	ND

Table 1 indicates that adding boron and/or calcium can improve the corrosion resistance of refractories formed from silicon carbide with a Si₃N₄ matrix binder.

Table 1 indicates that adding boron and/or calcium can advantageously enhance the proportion of beta phase Si₃N₄. However, only adding boron and/or calcium in a non oxide form can limit the amount of silicon oxynitride Si₂ON₂ to values

close to or lower than that of the reference product, as can be seen in Examples 14 and 15.

Table 1 indicates that the open porosity is improved when the amount of boron in the final product is non zero: only examples 14, 15 and 16 have an open porosity that is greater than that of the reference product. For this reason, products containing 0.05% to 3% of boron are preferred.

Further, Table 1 shows that the presence of boron compounds in the starting charge advantageously catalyzes the nitriding reaction (the amount of nitrogen in the products of the invention is enhanced).

Without wishing to be bound by a theory, the inventors have a partial explanation for the improvement in corrosion resistance, namely stabilization of oxidation degradation. As indicated in Table 1 and shown in Figure 2, the oxidation resistance of the products of the invention is improved.

Table 1 shows that the variation in volume due to oxidation is very limited in the products of the invention. Further, the increase in mass after oxidation is limited when the calcium that is added is combined with boron. Thus, adding CaB_6 is advantageous, in particular in amounts between 0.5% and 2%.

Figure 2 shows the change in the resistance to oxidation when the test is extended to 500 hours. The improvement over the reference is confirmed and accentuated.

Table 1 shows that adding boron and/or calcium has an influence on corrosion resistance even for small amounts. It also appears that a minimum amount of 0.8% by weight can produce a substantially maximum corrosion resistance.

Preferably, the percentage by weight of CaB_6 in the starting charge is more than 0.5%.

It appears that the effect of adding B_4C to the starting charge is substantially the same at B_4C contents as low as 0.2%. A reinforced effect is obtained with a content of 0.6%.

Clearly, the present invention is not limited to the implementations described and shown by way of non limiting illustrative examples.

The inventors have also observed that adding boron in the non oxide form, and more specifically CaB_6 or B_4C , also contributes to increasing the thermal diffusivity of the products of the invention, without a specific effect linked to compactness. This is clearly very important in encouraging heat transfer.

Further, it has been found that none of the products of the invention contains Si_3N_4 in the acicular form, including on the surface.

The oxidation performance of the products of the invention indicates that applications other than in electrolysis cells may be envisaged.

But, the inventors have discovered that the material of the refractory block of the invention which has been described here above, called "sintered material of the invention" may be used, with various forms, in quite different applications than in electrolysis cells and, in particular, in applications where it could not be predicted that this material would be appropriate.

The addition of boron in a refractory product usually lowers the melting temperature of this product. The possibility of using of a product of the invention in applications where it may be submitted to temperatures that may reach $1\,500^\circ\text{C}$, $1\,600^\circ\text{C}$ or even $1\,700^\circ\text{C}$ was therefore surprising.

The inventors have also discovered that the resistance to oxidation of the products of the invention is much less variable from one product to the other in comparison with corresponding products which would not contain any boron.

The invention also concerns a refractory product, in the form of :

- a "shaped product", in particular in the form of a block, for instance a brick or a wall block, a plate, a tile, and a tube,
- a "non shaped product", in particular a lining,

5 comprising, or made of, a sintered material of the invention, said sintered material being manufactured on plant, for instance from a castable or a pumpable composition.

A shaped product is a product which has been given a specific shape with a mold or through a die. On the contrary,
10 an unshaped product is a product which has been applied on a support without being shaped, for instance through a projection of a castable product. An unshaped product is sintered after being applied on the support.

The shaped product may be chosen in the group consisting
15 of kiln furniture or of other firing supports, in particular in the form of a plate, a post, a setter, a beam or a roller, said kiln furniture being covered by a protective coating or not; a block, a tile and a tube of a heat exchanger; a block, a tile and a tube of a heat recuperator; a block, a tile and a
20 tube of a heat regenerator; a block, a tile and a tube of a muffle; a block, a tile and a tube of a domestic incineration furnace; a block, a tile and a tube of a furnace of a glass making factory, in particular in a location where the sintered material of the invention is not in direct contact with the
25 molten glass, a block, a tile and a tube of a metallurgical furnace, in particular a block, a tile and a tube of a holding furnace or a block of a smelting furnace for non ferrous metals, like copper shaft furnaces; a block, a tile and a tube of a protection wall, in particular to protect a heat
30 exchanger; a block of a skid rail of a metallurgical furnace, for example a furnace for the heat treatment of iron or steel bars or of other metallurgical products; a block and a tube of

an immersion heater; a heater tube, a thermocouple protective tube, and a tube for transporting molten metal.

The shaped product may have any shape, depending on the intended application.

5 In particular, it may be massive.

The maximal thickness of a product is usually determined so that the level of residual silicon in the core of the product be less than 1% by weight, as measured for example by X Ray diffraction. It depends on the firing technology.
10 Preferably, the maximal thickness is less than 150mm.

The minimal thickness of a product is mainly depending on the forming technology, the mix formulation and the desired mechanical properties.

Surprisingly, a shaped product of the invention may be
15 thin, for instance substantially flat. Its thickness may be less than 3/10, less than 2/10, less than 1/10, less than 5/100, less than 2/100 or even less than 1/100 or less than 5/1000 of its length and/or of its width.

The invention in particular relates to a refractory
20 product, for instance in the form of a plate, the thickness of which is less than 10 mm, less than 8 mm, or less than 5 mm. It may have a length and/or a width of 5 cm or more, 10 cm or more, 20 cm or more, 50 cm or more or even 100 cm or more. Its surface may be 1 m² or more.

25 Without being bound by a theory, the inventors consider that boron helps to form a stable nitrogen glassy phase that limits the increase of crystallized silica (SiO₂) and therefore avoids a fall of the mechanical resistance in service. A sintered material of the invention may therefore be used in
30 the form of a thin product.

The invention also concerns a device chosen in the group constituted of a heat exchanger, an incineration furnace, in

particular for domestic waste, a heat recuperative furnace, a heat recuperator, a heat regenerator, a furnace for making heat insulation fibre glass, a firing support, and in particular kiln furniture, a glass making factory, a metallurgical furnace, in particular a holding furnace or a smelting furnace, a skid rail for a metallurgical furnace, an immersion heater, an assembled wall, an assembled lining, an assembled muffle and more generally an assembly of shaped products, a non shaped lining, i.e. which does not result of an assembly of shaped products, said device comprising, and possibly being constituted of, a sintered material of the invention.

Kiln furniture

The inventors have discovered that the sintered material of the invention has a very good mechanical resistance in a large range of temperatures, especially from 800°C up to 1,600°C, or even up to 1,750°C. This was not expected because of the low smelting points of current oxide glassy phases containing boron.

They also discovered that the sintered material of the invention can very well withstand cyclic variations of temperature. For instance it can very well withstand more than 100 cycles between 20°C and 1500°C under air, each cycle lasting several hours, as it occurs in tunnel furnaces for firing porcelain articles.

The invention therefore also concerns the use of a refractory product according to the invention (comprising, or made of, a sintered material of the invention), in particular a shaped product of the invention, in an application where said product is submitted to cycling variations of

temperature, each cycle lasting less than 24 hours, in particular in applications where in any cycle, the temperature varies of at least 1000°C, of at least 1300°C or even of at least 1500°C and/or in which any cycle lasts at least 1 hour, at least 5 hours, or at least 10 hours.

They finally discovered that said sintered material presents a very high dimensional stability. In fact, kiln furniture made of the sintered material of the invention has a long service life.

Besides, as described, for example, in US 6,143,239 or EP 603 851, incorporated by reference, it is known that kiln furniture may be made of a support covered by a protective coating (in particular a sol or a glaze), deposited on the fired support. The coating may comprise or be made of metal hydrate, e.g. alumina hydrate, alumina, aluminosilicate, in particular mullite and its precursors, borosilicate, zircona, and mixture of these constituents.

The dilatation coefficients of the support and of the coating are determined to be as close as possible, but the difference of these dilatation coefficients usually increases with time. In addition, the support may react with the coating and swell, which may lead to peeling of the coating. The inventors have observed that supports made of a sintered material of the invention and covered with a coating such as those described in US 6,143,239 or EP 603 851 present a very long service life, without peeling. Without being bound by this theory, they consider that this advantageous property is due to the fact that the sintered material of the invention does not react, or very little, with the coating.

The invention therefore also concerns the use of a refractory shaped product according to the invention (comprising, or made of, a sintered material of the invention), said refractory shaped product being at least

partly covered with a coating, to avoid peeling of said coating, in particular when said product is used as a support to sinter porcelain pieces.

Because of its noteworthy chemical inertness, the sintered material of the invention may be used, very efficiently, without any coating. Advantageously, the manufacturing and maintenance costs of kiln furniture made of a sintered material according to the invention, without being coated, would be reduced.

The invention therefore also concerns a firing method in which an item to be fired is supported by a firing support during firing, said firing support comprising a sintered material of the invention and being free of any coating, at least on the surface in contact with said item.

Besides, in some applications, the firing support is classically fired under air atmosphere, typically between 800°C and 1,600°C in order to passivate the support. A firing under an oxidizing atmosphere, in particular air, in order to passivate the support may be performed during the cooling, and/or in the same furnace, after firing of said support in a reducing atmosphere of nitrogen at a temperature of 1100°C to 1700°C.

The inventors have discovered that the presence of boron in a product according to the invention improves the efficiency of the passivation. Therefore, the invention also concerns a method comprising steps a) to e), and a passivation step between 800°C and 1,600°C.

The inventors have discovered that this operation may be omitted with a product of the invention.

Therefore, the invention also concerns a firing method in which an item to be fired is supported by a firing support during firing, said firing support comprising a refractory

product according to the invention (comprising, or made of, a sintered material of the invention) and being free of any coating, at least on the surface in contact with said item, and wherein said firing support has not been passivated.

5

Heat recuperative furnaces and heat recuperators

Heat recuperative furnaces are used for making glass, as described in the patent application US 4,497,628, incorporated by reference. The blocks of these furnaces, and in particular
10 the bottom blocks, are exposed to corrosive alkali vapours at about 1000-1100°C and to strong mechanical erosion due to high air velocities and to the presence of particles or dust. Usually, the blocks used in heat recuperative furnaces for making glass are therefore oxide products.

15 However, surprisingly, the inventors also discovered that the sintered material of the invention has an excellent thermal stability and a good corrosion resistance in the severe conditions which occur in this application.

The invention also concerns the use of a sintered product
20 of the invention (comprising, or made of, a sintered material of the invention) in a bottom part of an heat regenerator of a heat recuperative furnace for making glass.

Muffle

25 The muffles covering the forming blocks described, for example, in the patent application US 2005/130830, incorporated by reference, are subjected to a strong oxidizing environment during the manufacture of glass. The inventors have discovered that the sintered material of the invention is
30 very stable in these severe conditions. The invention therefore also concerns a muffle, and more generally, any part of a glass making factory which is not in contact with molten

glass, comprising, or made of, a sintered material of the invention.

Refractory tubes

5 The inventors have found that the performances of refractory tubes like heater tubes or thermocouple protective tubes or tubes for transporting molten metal, as described for example in US 5,135,893, incorporated by reference, may be improved by a sintered material of the invention.

10

Incineration furnace and/or heat exchangers

Refractory linings for incineration furnaces are for example described in EP 0 107 520, WO 00/26597 or EP 0 635 678, incorporated by reference.

15 The inventors have discovered that a sintered material of the invention is also very well suited to make the refractory lining of an incineration furnace, in particular for the incineration of domestic waste. It may be shaped into refractory tiles or walls or tubes or bricks or the like. The
20 sintered material of the invention indeed exhibits few cracks and a good corrosion resistance at temperatures up to 1,300 °C in the environment of such incineration furnaces.

 The invention therefore also concerns the use of a refractory product of the invention (comprising, or made of, a
25 sintered material of the invention), in a refractory lining of an incineration furnace in which said product has not been submitted to an oxidative post-treatment at a temperature between 1000° C and 1700° C.

 The inventors have also discovered that the thermal
30 conductivity is very little reduced by the corrosion by alkalis vapours. This is very advantageous in applications where the material of the invention is intended to transfer

the heat by conduction. The inventors have noticed that an amount of boron of 1.5%, in percentage by weight of the sintered material according to the invention, enables a good maintenance of the thermal conductivity.

5 The invention therefore also concerns the use of a refractory product of the invention (comprising, or made of, a sintered material of the invention) in a refractory lining of an incineration furnace to transfer heat by conduction.

10 Moreover, it was also noticed by the inventors that a second firing in an oxidizing atmosphere, for example in air, of a sintered material of the invention, after the first firing in a nitrogen atmosphere (corresponding to the previously described step f)), leads to an excellent resistance against corrosion. In particular, the dimensional
15 stability in an oxidizing atmosphere saturated with moisture is very high. Such a property was not predictable.

 The second firing may be done at a temperature between 1,000°C and 1,700°C. It would usually last between 1 and 10 hours, depending on the dimensions of the sintered product.

20 The second firing under oxidizing atmosphere, in particular air, will passivate the support. It may be performed during the cooling and/or in the same furnace after firing of said support in a reducing atmosphere of nitrogen at a temperature of 1100°C to 1700°C.

25

Fabrication method

 The invention also concerns a method of fabricating a sintered material based on silicone carbide (SiC), with a silicon nitride binder (Si₃N₄), said method comprising the
30 following steps in succession:

 A) preparing a charge comprising a particulate mixture comprising a silicon carbide granulate and at least one

boron and/or calcium compound, a binder optionally being added to said particulate mixture;

B) forming said charge;

C) firing said formed charge in a reducing atmosphere of
5 nitrogen at a temperature in the range 1,100°C to 1,700°C;

said boron and/or calcium compound being added in a quantity which is determined so that the sintered material obtained at the end of step C) includes a total amount of calcium and
10 boron in the range 0.05% to 1.5%.

The composition of the starting charge may be determined so as to obtain, at the end of step C), a sintered material which has one or several of the optional characteristics of a sintered material according to the invention.

15 At step B), any technique known to form a charge to fabricate a ceramics may be used. In particular, step B) may comprise the following operations:

- i) forming the charge by pressing or by casting or slip casting in a porous or non porous mold, to obtain a preform;
- 20 ii) unmolding said preform;
- iii) drying.

The forming operation may comprise, for instance, an additional compacting technique by vibration or tamping

In an embodiment of the invention, the forming operation
25 at step i) may comprise extrusion.

In an embodiment of the invention, the fabrication method according to the invention comprises an additional step, following step C), in which the sintered material obtained at the end of step C) is fired in an oxidizing atmosphere, preferably at a temperature between 1,000°C and 1,700°C, and
30 possibly for a time in the range between 1 and 10 hours, depending on the dimensions of the mass of sintered material.

The second firing step may be done as a post-treatment, after partial or complete cooling of the sintered material obtained at the end of the first firing step.

It could also be done in the continuity of the first firing step, through the injection of an oxidizing gas, for example air, without any substantial cooling between the two firing steps. The fabrication method according to this embodiment is therefore particularly efficient.

The oxidizing atmosphere preferably contains at least 20% by weight of oxygen

Examples

The samples of the following examples A to D were shaped by slip casting in a gypsum mould to form plates.

The ceramic slip was prepared from the constituents according to Table 2. After removal from the mould, the green plates were dried at up to 100°C and fired at 1,420°C under nitrogen atmosphere. The green plates were thus sintered by reaction with nitrogen to form silicon nitride bond.

The samples of the examples E to H are plates, tiles or bricks which were prepared by pressing a mix inside a mould at a pressure of about 500 kg/cm² in order to obtain green compacts with the desired dimensions. The ceramic mix was prepared from the constituents according to the Table 2'.

After removal from the mould, the plates or tiles or bricks of all the examples except G were dried at up to 100°C and fired at 1,420°C under nitrogen atmosphere.

The product G is a brick made of sintered chromium oxide called Zirchrom 60® delivered by Saint-Gobain SEFPRO

30

Bulk density and open porosity were measured in accordance with ISO5017 Standard.

The modulus of rupture in bending (MOR) was evaluated according to the ISO5014 Standard.

The steam oxidation test 5 was performed in accordance with ASTM C863 at 1000°C.

5 The corrosion test 6 for reproducing the corrosion in heat recuperative furnaces for fibre glass making was obtained in the following manner. Three cylindrical samples of 22 mm diameter and 100 mm length were cut from the core of each brick, tile or plate to be tested. The samples, placed in a
10 furnace crucible, were immersed in a slag of rasorite (which is a kind of sodium boride) at a temperature of 1000°C for 48 hours under air atmosphere. The samples were rotated at a speed of 6 rpm. The volume was measured before and after corrosion. The corrosion indicator is equal to the reverse of
15 the average volume loss of the three samples of the tested brick, tile or plate. The volume loss results from the corrosive attack by the melt and the vapours. Higher is the corrosion indicator, higher is the corrosion resistance. The Zirchrom 60® is the reference product. Its corrosion indicator
20 is therefore 100.

The thermal conductivity was measured according to test 7. First, the thermal diffusivity $a(600^{\circ}\text{C})$ was measured by laser flash method at 600°C under argon in accordance with EN821.2 recommendation. The thermal conductivity $\lambda(600^{\circ}\text{C})$ was
25 evaluated according to the relation

$$\lambda(600^{\circ}\text{C}) = \rho * a(600^{\circ}\text{C}) * C_p(600^{\circ}\text{C})$$

where ρ is the bulk density measured in accordance with ISO5017 and C_p is the thermal heat capacity measured by a calorimeter.

30

Test 8 is a creep test under flexion at high temperature.

The piece of material to be tested is cut in order to obtain a sample of dimensions $70 \times 20 \times 4 \text{ mm}^3$ extracted from pieces of $100 \text{ mm} \times 100 \text{ mm} \times 4 \text{ mm}$, previously fired or passivated under air at 1400°C , during a soak time of 5 hours after a first firing in a reducing atmosphere of nitrogen.

After grinding, the sample is placed in a furnace equipped with a 3 point bending system. The sample is placed on two supports spaced by 50 mm, as represented in Figure 3. A force F is applied on a top part of dimensions 1 cm width and 2 cm long (width of the sample to be tested) placed at the middle length of the sample. A load of 2 MPa (F divided by the surface of said top part) is applied at room temperature and the temperature of the furnace is then increased to 1450°C at a rate of 10 K/min. At the temperature of 1450°C , the load is increased to 50 MPa and maintained during 10 hours. A measurement system with a dial gauge allows measuring the deflection (or the vertical deformation) of the sample at the mid length of the sample. This deflection is measured in mm, at 1450°C under the load of 50 MPa. The deflection result is an average of 10 samples i.e. 10 tests.

The test 9 is similar to the test 5, but is performed on samples which have been fired or passivated under air at 1400°C , during a soak time of 5 hours after a first firing in a reducing atmosphere of nitrogen.

The test results in the tables 3 and 3' show that the products B and D are much more stable in dimension after an oxidation according a very long duration compared to the reference products A and B, respectively.

It was also found that the D product of the invention exhibits a better abrasion resistance compared to the reference product C.

The product F of the invention exhibits a smaller decrease of its thermal conductivity compared to the reference product E.

The product H of the invention exhibits a really high corrosion resistance in accordance with the test 6 compared to
5 the reference product G.

The Modulus of Rupture of the products according to the invention is also noteworthy. Therefore, the invention also concerns the use of a refractory shaped product according to the invention (comprising, or made of, a sintered material of
10 the invention) to increase the modulus of rupture in bending. The standard for measurement is ISO5014.

Table 2

	A According to US4990469	B Product of the invention	C Reference product	D Product of the invention
Mix formulation (pourcentages in weight)				
SiC grains and powder 0.2 to 1mm			81	80.2
SiC Grains and powder 20 to 150µm	40	39.6		
SiC Grains and powder 0. 1 to 10µm	37.5	37.2		
Silicon metal powder 0.5 to 50µm	17	16.9	16	16
Calcined Refractory Clay			3	3
Boron carbide powder(B4C >95%) diameter of grains : 95%less than 45µm		0.8		0.8
Iron oxide powder 1 to 75µm	0.5	0.5		
Calcined alumina powder 0.4 to 10µm	5	5		
Mineral formulation	100	100	100	100
Additives (pourcentages in weight relative to total mineral formulation)				
Fluidizer such as water and sodium hydroxide	0.3	0.3	0.2	0.2
Water	12. 5	12. 5	6	6

Table 2'

5

	E Reference product	F Product of the invention	H Product of the invention
Mix formulation (pourcentage in weight)			
SiC grains and powder 0.2 to 3mm	65	64.5	72
SiC Grains and powder 90% <200µm %	21	20.8	14.5
Silicon metal powder 0.5 to 75µm	14	13.9	13
Boron carbide powder (B4C >95%) diameter of grains 95%lower than 45µm		0.8	0.5
Iron oxide powder 1 to 75µm			
Calcined alumina powder 0.4 to 10µm			
Mineral formulation	100	100	100
Additives (pourcentages in weight relative to total mineral formulation)			
Calcium lignosulfonate binder	+2.0	+2.0	+2.0
Cellulose binder	+0.5	+0.5	+0.5
Water	+3.0	+3.0	+3.0

Table 3

examples		A According to US4990469	B Product of the invention	C Reference product	D Product of the invention
Shape of the product		50*50*4mm plates	50*50*4mm plates	50*50*4mm plates	50*50*4mm plates
Test 1	Bulk density	2.82	2.83	2.65	2.67
Test 1	Open porosity %	12.0	12.1	15.0	15.0
Test 2	Modulus of rupture MPa at ambient	175	180	40	42
Test 3	Si ₃ N ₄ α	8	5		
	Si ₃ N ₄ β	14	17		
	SiAlON β'				
	Si ₂ ON ₂	3	2		
Test 4	N LECO analysis	8.5	8.7	8	8.2
	SiC LECO analysis	72	71	75	76
	O LECO analysis			1.5	1.6
Test 5	Δ m/m(%) after 500h	+3.0+	+1.9		
	Δ v/v (%) after 500h	+2.5	+0.2	+3.5	+0.5
Test 8	Measurement after firing under air 1400°C / 5h soak : Creep tests under flexion at 1450°C / 50 MPa load ; Deflection after 10 h in mm	0.35 +/-0.1	0.25 +/-0.05		
Test 9	Measurement after firing under air 1400°C / 5 h soak : Δ m/m(%) after 800h at 1000°C	+1.5%	+0.7%		

Table 3'

examples		E Reference product	F Product of the invention	G =Zirchrom 60 Reference product	H Product of the invention
Shape of the product		Tile Dim 20*10 0*100mm	Tile Dim 20*10 0*100mm	bricks 75*230*230mm	bricks 75*230*230 mm
Test 1	Bulk density	2.70	2.70	3.85	2.62
Test 1	Open porosity %	14.0	14.0	14.0	16.5
Test 2	Modulus of rupture MPa at ambient	55	50		
test 3	Si ₃ N ₄ α	8	4		1
	Si ₃ N ₄ β	12	18		15
	SiAlON β'				
	Si ₂ ON ₂	<2	<2		
Test 4	N LECO analysis	7.9	7.7		8
	SiC LECO analysis	79	78.5		78
	CR ₂ O ₃ chemical analysis			62	
	ZrO ₂ chemical analysis			10	
	O LECO analysis	0.5	0.5		0.9
test 5	Δ m/m(%) after 500h	+4.0	+1.8		
	Δ v/v (%) after 500h	+1.6	+0.2		
Test 6	corrosion test with rasorite at 1000°C/48h Corrosion index Id			100	400
Test 7	Thermal conductivity at 600°C in w/m.K by laser flash method	20	25		
	Loss in % after steam oxidation according to test 5 but after 300h	8	18		

CLAIMS

1. A refractory shaped product based on silicon carbide (SiC) reactively sintered between 1,100°C and 1,700°C to form a silicon nitride binder Si₃N₄, including 0.05% to 1.5% of boron, the Si₃N₄/SiC weight ratio being in the range 0.05 to 0.45, wherein said shaped product is chosen in the group consisting of kiln furniture or other firing supports; a block, a tile and a tube of an heat exchanger; a block, a tile and a tube of a heat recuperator; a block, a tile and a tube of a heat regenerator; a block and a tube of a muffle; a block, a tile and a tube of a domestic incineration furnace; a block, a tile and a tube of a furnace of a glass making factory; a block, a tile and a tube of a metallurgical furnace; a block, a tile and a tube of a protection wall; a block of a skid rail of a metallurgical furnace; a block and a tube of an immersion heater; a heater tube; a thermocouple protective tube; and a tube for transporting molten metal.
2. A refractory product according to the preceding claim, wherein said shaped product is chosen in the group consisting of a plate; a post; a setter; a beam; a roller; a block, a tile or a tube of a furnace of a glass making factory in a location where it is not in direct contact with molten glass; a block, a tile or a tube of a holding furnace; a block, a tile or a tube of a smelting furnace for non ferrous metals; a block, a tile or a tube of a protection wall; a block of a skid rail of a furnace for the heat treatment of iron or steel bars or of other metallurgical products.
3. A refractory product according to any one of the preceding claims, wherein said shaped product is kiln furniture or other firing support on which a coating comprising or made of metal hydrate, alumina, alumina silicate borosilicate, zirconia and mixture of these is deposited.

4. A refractory product according to any one of claims 1 to 2, wherein said shaped product is kiln furniture or other firing support free of any coating.
- 5 5. A refractory product according to any one of the preceding claims, presenting a thickness less than 1/10 of its length and/or of its width.
6. A refractory product according to the preceding claim, presenting a thickness less than 2/100 of its length and/or of its width.
- 10 7. A refractory product according to any one of the preceding claims, presenting a thickness less than 10 mm.
8. A refractory product according to any one of the preceding claims, in which the percentage by weight of boron is in the range 0.05% to 1.2%.
- 15 9. A refractory product according to any one of the preceding claims, in which the $\text{Si}_3\text{N}_4/\text{SiC}$ weight ratio is in the range 0.1 to 0.2.
10. A refractory product according to the preceding claim, in which the silicon nitride Si_3N_4 in the beta form represents, as a percentage by weight, at least 80% of the whole of the silicon nitride Si_3N_4 in the beta form and in the alpha form.
20
11. A refractory product according to any one of the preceding claims, in which the amount of Si_2ON_2 , as a percentage by weight, is less than 5%.
25
12. A refractory product according to any one of the preceding claims, in which the percentage by weight of calcium is in the range 0.05% to 1.2%.
13. A refractory product according to any one of the preceding claims, including at least 0.3% by weight of boron, as a percentage by weight.
30

14. A refractory shaped product comprising a sintered material sintered between 1100°C and 1700°C based on silicon carbide SiC with a silicon nitride binder Si₃N₄, said sintered material including an anti-corrosion agent selected from boron, calcium and mixtures thereof, the total amount of calcium and boron being in the range 0.05% to 1.5%, the Si₃N₄/SiC weight ratio being in the range 0.1 to 0.2, wherein said shaped product is chosen in the group consisting of kiln furniture or other firing supports; a block, a tile and a tube of an heat exchanger; a block, a tile and a tube of a heat recuperator; a block, a tile and a tube of a heat regenerator; a block and a tube of a muffle; a block, a tile and a tube of a domestic incineration furnace; a block, a tile and a tube of a furnace of a glass making factory; a block, a tile and a tube of a metallurgical furnace; a block, a tile and a tube of a protection wall; a block of a skid rail of a metallurgical furnace; a block and a tube of an immersion heater; a heater tube; a thermocouple protective tube; and a tube for transporting molten metal.

15. A fabrication method to fabricate a sintered material based on silicone carbide, with a silicon nitride binder, said method comprising the following steps in succession:

A) preparing a charge comprising a particulate mixture comprising a silicon carbide granulate and at least one boron and/or calcium compound, a binder optionally being added to said particulate mixture;

B) forming said charge;

C) firing said formed charge in a reducing atmosphere of nitrogen at a temperature in the range 1,100°C to 1,700°C;

said boron and/or calcium compound being added in a quantity which is determined so that the sintered material obtained at the end of step C) includes a total amount of calcium and boron in the range 0.05% to 1.5%, said method comprising, after step C), a second firing step wherein the refractory product obtained at the end of step C) is fired

in an oxidizing atmosphere at a temperature between 1,000°C and 1,700°C.

16. A fabrication method according to the preceding claim, in which said boron and/or calcium compound is added in a quantity which is determined so as to obtain a refractory product according to any one of claims 1 to 14.

17. A firing method in which an item to be fired is supported by a firing support during firing, said firing support comprising a refractory product according to any one of claims 1 to 3 and 5 to 14 and being free of any coating, at least on the surface in contact with said item, and wherein said firing support has not been passivated.

18. Use of a refractory shaped product according to any one of claims 1, and 3 to 14, said refractory shaped product being at least partly covered with a coating, to avoid peeling of said coating when said product is used as a support to sinter porcelain pieces.

19. Use of refractory product according to any one of claims 1 to 14, in an application where said product is submitted to cycling variations of temperature, each cycle lasting less than 24 hours.

20. Use according to the preceding claim, in which in any cycle, the temperature varies of at least 1000° C and/or in which any cycle lasts at least 1 hour.

21. Use of a refractory product according to any one of claims 1 to 14, in a bottom part of an heat regenerator of a heat recuperative furnace for making glass.

22. Use of a refractory shaped product according to any one of claims 1 to 14 to increase the modulus of rupture in bending.

23. Use a refractory product according to any one of claims 1 to 14 in a refractory lining of an incineration furnace to transfer heat by conduction.

- 5 24. Use of a refractory product according to any one of the claims 1 to 14, in an refractory lining of an incineration furnace in which said product has not been submitted to an oxidative post-treatment at a temperature between 1000° C and 1700° C.

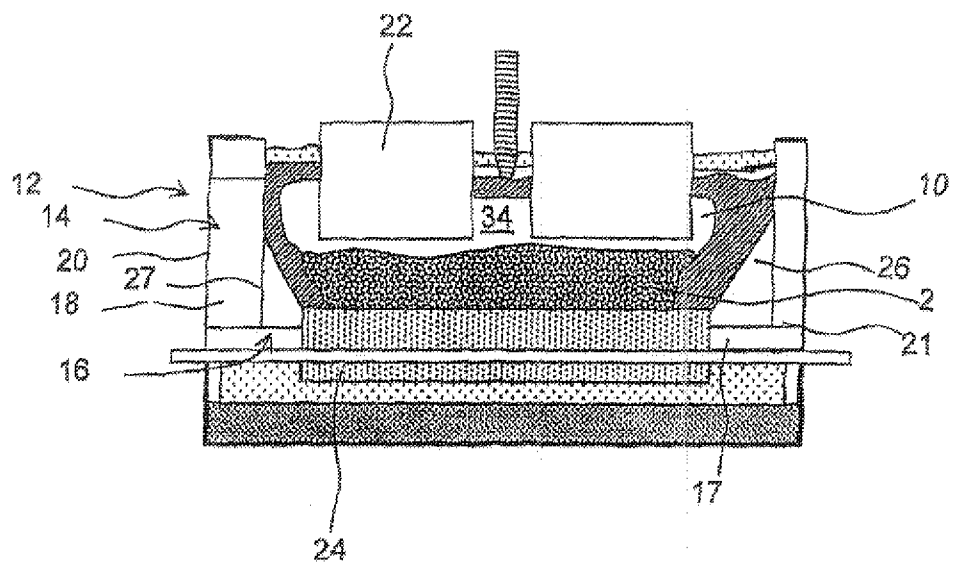


Fig. 1

volume increase in % as a function of oxidation time using the ASTM C 843 test at 900°C with steam

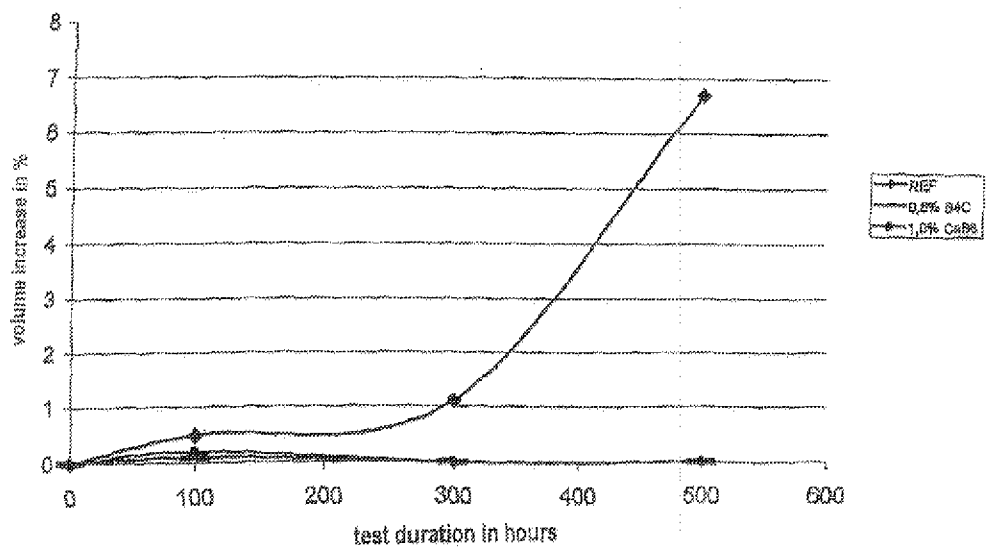


Fig. 2

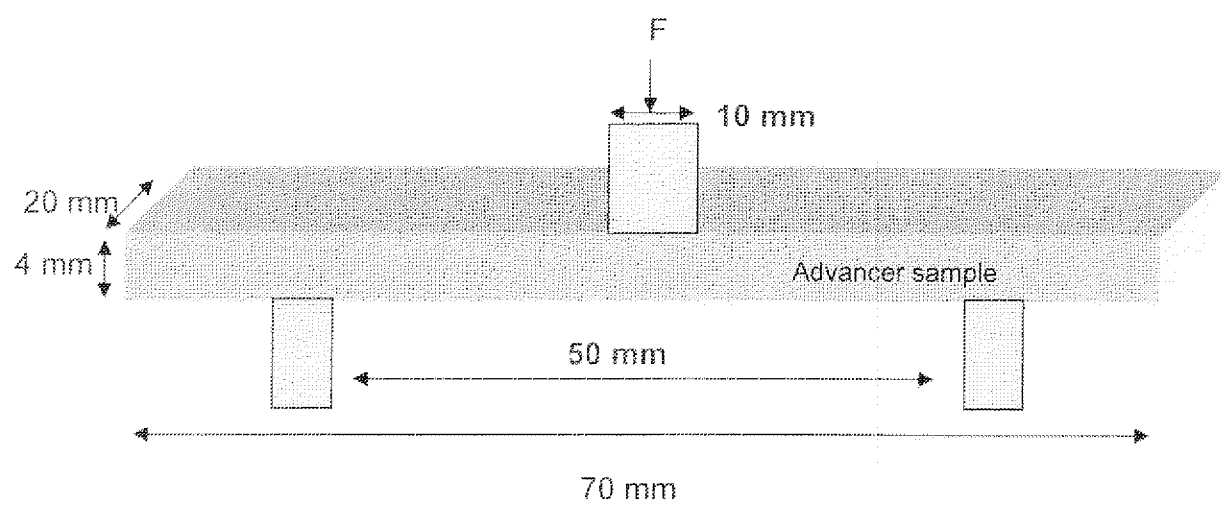


Fig. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2009/050480

A. CLASSIFICATION OF SUBJECT MATTER

INV. C04B35/573 C04B35/66 C04B35/64 F27D1/16 C04B35/63

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C04B F27D

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

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

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2006/056698 A (PEEN SAINT GOBAIN CT DE RECH S [FR]; JORGE ERIC [FR]; MARGUIN OLIVIER) 1 June 2006 (2006-06-01) page 7 - page 8	1,2, 5-14, 17-24
Y	page 3 - page 4; claims 1,7,13; examples 7,8; table 1	3,4,15, 16
Y	US 6 143 239 A (SONNTAG ANDREAS [DE]) 7 November 2000 (2000-11-07) cited in the application claim 26	3,4
X	JP 03 223166 A (NGK INSULATORS LTD; NGK ADREC CO LTD) 2 October 1991 (1991-10-02) abstract; example 6; table 1	14
	-/--	

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

20 May 2009

Date of mailing of the international search report

05/06/2009

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Bonneau, Sébastien

INTERNATIONAL SEARCH REPORT

International application No

PCT/IB2009/050480

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2000 302554 A (OSAKA YOGYO FIRE BRICK) 31 October 2000 (2000-10-31) abstract paragraph [0008] -----	14,23,24
A	GB 728 306 A (ARTHUR ABBEY) 20 April 1955 (1955-04-20) page 2, line 32 - line 65 page 3, line 112 - page 4, line 9; example 1 page 3, line 72 - line 92 -----	14
Y	US 2005/008878 A1 (BRYDEN RAYMOND H [US]) 13 January 2005 (2005-01-13) paragraphs [0007], [0026] -----	15,16
A	US 3 968 194 A (PROCHAZKA SVANTE) 6 July 1976 (1976-07-06) column 2, line 27 - line 47; table 1 -----	1,2,8-14
A	EP 0 417 292 B (OSAKA GAS CO LTD [JP]; NIPPON CRUCIBLE CO [JP]) 20 April 1994 (1994-04-20) tables 1,2 -----	1-24

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2009/050480

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 2006056698	A	01-06-2006	AU 2005308712 A1	01-06-2006
			BR PI0518679 A2	02-12-2008
			CA 2586783 A1	01-06-2006
			CN 101068758 A	07-11-2007
			EP 1828077 A2	05-09-2007
			FR 2878520 A1	02-06-2006
			US 2007264576 A1	15-11-2007
US 6143239	A	07-11-2000	AT 208749 T	15-11-2001
			DE 19634855 A1	19-03-1998
			EP 0826651 A1	04-03-1998
			ES 2167654 T3	16-05-2002
JP 3223166	A	02-10-1991	JP 2781440 B2	30-07-1998
JP 2000302554	A	31-10-2000	NONE	
GB 728306	A	20-04-1955	NONE	
US 2005008878	A1	13-01-2005	NONE	
US 3968194	A	06-07-1976	NONE	
EP 0417292	B	20-04-1994	DE 68914834 D1	26-05-1994
			DE 68914834 T2	04-08-1994
			EP 0417292 A1	20-03-1991
			WO 9011981 A1	18-10-1990
			US 5135893 A	04-08-1992