

Refractory product having high zirconia content**Technical field**

The invention relates to a novel fused and cast refractory product having a high zirconia content.

5 Prior art

Among refractory products, a distinction is made between fused and cast products, which are well known for the construction of glass-melting furnaces, and sintered products.

10 In contrast to sintered products, fused and cast products generally comprise an intergranular vitreous phase binding the crystalline grains together. The problems posed by sintered products and by fused and cast products, and the technical solutions adopted for solving them, are therefore generally different. A composition developed for manufacturing a sintered product therefore cannot be used *a priori* as it is for manufacturing a fused and cast product, and vice versa.

15 The fused and cast products, often called electrocast products, are obtained by melting a mixture of suitable raw materials in an electric arc furnace or by any other technique that is suitable for these products. The molten material is then poured into a mold and then the product obtained undergoes a controlled cooling cycle so that it is brought to ambient temperature without cracking. This operation is called "annealing"
20 by a person skilled in the art.

Among the fused and cast products, the electrocast products with high zirconia content are renowned for their quality of very high corrosion resistance without coloration of the glass produced and without generation of defects.

25 Conventionally, fused and cast products with high zirconia content also comprise sodium oxide (Na_2O) to prevent the formation of zircon from the zirconia and silica present in the product. The formation of zircon is in fact harmful since it is accompanied by a decrease in volume of the order of 20%, thus creating mechanical stresses that give rise to cracking.

30 FR 2 701 022 describes fused and cast products with high zirconia content that contain 7.0 to 11.2 wt.% of SiO_2 , 0.05 to 1.0 wt.% of P_2O_5 , 0.05 to 1.0 wt.% of boron oxide B_2O_3 and 0.01 to 0.12 wt.% of $\text{Na}_2\text{O} + \text{K}_2\text{O}$.

FR 2 723 583 describes fused and cast products with high zirconia content that contain 3 to 8 wt.% of SiO_2 , 0.1 to 2.0 wt.% of Al_2O_3 , 0.05 to 3.0 wt.% of boron oxide B_2O_3 , 0.05 to 3 wt.% of $\text{BaO} + \text{SrO} + \text{MgO}$, and 0.05 to 0.6 wt.% of $\text{Na}_2\text{O} + \text{K}_2\text{O}$ and less than 0.3 wt.% of $\text{Fe}_2\text{O}_3 + \text{TiO}_2$.

- 5 FR 2 836 682 describes fused and cast products with high zirconia content that contain 2 to 8 wt.% of SiO_2 , 0.2 to 2.0 wt.% of Al_2O_3 , 0.12 to 1.0 wt.% of Na_2O and 0.5 to 2.6 wt.% of $\text{Y}_2\text{O}_3 + \text{CaO}$.

The product ER-1195 produced and marketed by the Société Européenne des Produits Réfractaires ("European Refractory Products Company") and covered by
10 patent EP-B-403 387 is now widely used in glass-melting furnaces. Its chemical composition comprises about 94% of zirconia, 4 to 5% of silica, about 1% of alumina, 0.3% of sodium oxide and less than 0.05 wt.% of P_2O_5 . It is typical of the products with high zirconia content used for glassmaking furnaces.

15 These products have good performance but there is still a need for a fused product with high zirconia content offering good feasibility and long service life, notably when it is used in a glassmaking furnace tank.

The present invention aims to satisfy this need.

Summary of the invention

20 The invention proposes a fused and cast refractory product comprising, in percentages by weight based on the oxides and for a total of 100%:

- | | | |
|----|---|--|
| | - ZrO_2 : | complement to 100% |
| | - Hf_2O_3 : | < 5% |
| | - SiO_2 : | 2% to 10% |
| | - $\text{Y}_2\text{O}_3 + \text{CeO}_2 + \text{CaO} + \text{MgO}$: | 0.8% to 4.0% |
| 25 | - B_2O_3 : | $\leq 4.5\%$ |
| | - B_2O_3 : | $\geq 0.09 \times (\text{Y}_2\text{O}_3 + 1/3 (\text{CeO}_2 + \text{CaO} + \text{MgO})) \times \text{SiO}_2$ |
| | - Al_2O_3 : | 0.3% to 2.0% |
| | - $\text{Na}_2\text{O} + \text{K}_2\text{O}$: | $\leq 0.5\%$ |
| | - P_2O_5 : | < 0.05% |
| 30 | - $\text{Fe}_2\text{O}_3 + \text{TiO}_2$: | < 0.55% |
| | - other species: | < 1.5%, |

provided that the Y_2O_3 content is greater than or equal to 0.5%, or greater than or equal to 0.7% or that the content of $CeO_2 + CaO + MgO$ is greater than or equal to 2%.

5 A block of a tank of a glassmaking furnace is subjected in service to a temperature that decreases from its face in contact with the molten glass ("hot face") to its exposed face on the outside of the tank ("cold face"). Now, a product with high zirconia content conventionally has a temperature of maximum expansion between the temperatures of these two faces. Two adjacent blocks are therefore assembled so
10 that they always remain in contact at least in the region where they are subjected to this temperature of maximum expansion. This ensures that at least in this critical region they will be able to provide impermeability of the tank. It is important to limit the corrosion in this critical region.

 However, corrosion by molten glass generally increases with its temperature.
15 The inventors therefore imagined that it could be advantageous to try to reduce the temperature of maximum expansion of the material of the blocks in order to displace said critical region towards the cold face of the blocks. In this way, this critical region can be in contact with molten glass that is more viscous and less corrosive than in the prior art.

20 As will be shown in more detail later in the description, as a result of their research, the inventors discovered that a product of the present invention has remarkable dilatometric behavior, and in particular a reduced temperature of maximum expansion. Moreover, this product retains high industrial feasibility.

 In one embodiment, a product according to the invention comprises less than
25 0.5%, less than 0.3%, or even less than 0.1%, of each of the oxides CeO_2 , CaO and MgO , or even does not comprise these oxides at all. Said oxides may only be present as impurities. The inventors have in fact observed that Y_2O_3 leads to the best results.

 A product according to the invention can further comprise one or more of the following optional characteristics, including when it complies with the particular
30 embodiments described below and these optional characteristics are not incompatible with said particular embodiments:

- Preferably $B_2O_3 \geq 0.095 \times (Y_2O_3 + 1/3 (CeO_2 + CaO + MgO)) \times SiO_2$;
- Preferably $B_2O_3 \geq 0.1 \times (Y_2O_3 + 1/3 (CeO_2 + CaO + MgO)) \times SiO_2$;
- The content by weight of $ZrO_2 + HfO_2$ is less than 97.0%, or even less than 96.5%
35 and/or greater than 85.0%, or greater than 86.0%;

- The content by weight of silica SiO_2 is greater than 2.5%, or even greater than 3.0% and/or less than 9.0%, or even less than 8.0%, or even less than 7.0%, or even less than 6.0%;
- The content by weight of MgO is less than 0.7%, less than 0.5%, less than 0.3% and/or greater than 0.1%;
- The content by weight of CeO_2 is less than 0.7%, less than 0.5%, less than 0.3% and/or greater than 0.1%;
- The content by weight of CaO is less than 0.7%, less than 0.5%, less than 0.3% and/or greater than 0.1%;
- The content by weight of each of the oxides MgO , CeO_2 and CaO is less than 0.5%, less than 0.3%, or even less than 0.2%;
- The content by weight of $\text{Y}_2\text{O}_3 + \text{CeO}_2 + \text{CaO} + \text{MgO}$ is greater than 0.9%, and/or less than 3.5%, or even less than 3.0%;
- The content by weight of Y_2O_3 is greater than 0.5%, or even greater than 0.6%, or even greater than 0.7%, or even greater than 0.8%, or even greater than 0.85%, or even greater than 0.9%, and/or less than 3.0%, or even less than 2.5%, or even less than 2.0%, or even less than 1.5%, or even less than 1.3%;
- The content by weight of boron oxide B_2O_3 is greater than 0.2%, or even greater than 0.3%, or even greater than 0.4% and/or less than 3.5%, less than 3%, less than 2.5%, or even less than 2.0%, or even less than 1.5%, or even less than 1.0%;
- The content by weight of alumina Al_2O_3 is less than 1.5%, or even less than 1.2%, or less than 1.0%;
- The content by weight of alumina Al_2O_3 is greater than 0.4%, greater than 0.6%, or even greater than 0.7%;
- The sum of the contents by weight of sodium oxide Na_2O and potassium oxide K_2O is less than 0.4%, or even less than 0.3%, less than 0.2%;
- Sodium oxide Na_2O is only present as impurities and its content by weight is less than 0.2%, or even less than 0.1%;
- Potassium oxide K_2O is only present as impurities and its content by weight is less than 0.2%, or even less than 0.1%;
- The content by weight of iron oxides and/or titanium oxides, $\text{Fe}_2\text{O}_3 + \text{TiO}_2$, is less than 0.4%, preferably less than 0.3%, preferably less than 0.2%;
- The content by weight of BaO is less than 0.1%, or even less than 0.05%;

- The total content by weight of "other species" is less than 1.0%, less than 0.6%, less than 0.5%, or even less than 0.3%;
- The "other species" only consist of impurities;
- The content by weight of any "other species" is less than 0.4%, or even less than 0.3%, or even less than 0.2%;
- The oxides represent more than 98%, more than 99%, or even roughly 100% of the mass of the product.

According to a particular embodiment, the invention proposes a fused and cast refractory product comprising, in percentages by weight based on oxides:

- SiO_2 : < 8%
- Y_2O_3 : < 2.5%
- B_2O_3 : 0.3% to 2.5%
- Al_2O_3 : < 1.5%.

According to a particular embodiment, the invention proposes a fused and cast refractory product comprising, in percentages by weight based on oxides:

- SiO_2 : 3% to 6%
- Y_2O_3 : < 1.5%
- B_2O_3 : 0.4% to 1.0%
- Al_2O_3 : < 1.2%.

The invention also relates to a process for manufacturing a refractory product according to the invention, comprising the following successive steps:

- a) mixing raw materials to form an initial charge,
- b) melting said initial charge until a molten material is obtained,
- c) casting and solidification of said molten material, by cooling, so as to obtain a refractory product,

this process being remarkable in that said raw materials are selected so that said refractory product complies with the invention.

Preferably, the oxides for which a minimum content is necessary, or precursors of these oxides, are added systematically and methodically. Preferably, the contents of these oxides are taken into account in the sources of the other oxides where they are conventionally regarded as impurities.

Preferably, cooling is controlled, preferably so as to be carried out at a rate of less than 20°C per hour, preferably at a rate of about 10°C per hour.

The invention also relates to a glass-melting furnace having a refractory product according to the invention, or a refractory product manufactured or that can be manufactured by a method according to the invention, in particular in regions intended to be in contact with molten glass. In a furnace according to the invention, the refractory product can advantageously form part of a tank for making glass by melting, notably by electric melting, where it may come in contact with molten glass at a temperature above 1200°C.

The invention also relates to a method for limiting corrosion in a region in which two blocks of a tank of a glassmaking furnace are only in contact when the tank contains molten glass. According to the invention, blocks of a product according to the invention are used.

Definitions

The percentages by weight of oxides refer to the total contents for each of the corresponding chemical elements, expressed in the form of the most stable oxide, according to the usual convention in the industry; therefore the suboxides are included and optionally nitrides, oxynitrides, carbides, oxycarbides, carbonitrides, or even the metallic species of the aforementioned elements.

" $Y_2O_3 + CeO_2 + CaO + MgO$ " means conventionally Y_2O_3 and/or CeO_2 and/or CaO and/or MgO .

A "molten material" is a liquid mass which, to maintain its shape, must be contained in a container. It can contain some solid particles, but in an insufficient amount for them to be able to structure said mass.

"Impurities" means unavoidable constituents, introduced unintentionally and necessarily with the raw materials or resulting from reactions with these constituents. The impurities are not necessary constituents, but are merely tolerated. For example, the compounds forming part of the group of oxides, nitrides, oxynitrides, carbides, oxycarbides, carbonitrides and metallic species of iron, titanium, and chromium are impurities.

Unless stated otherwise, all the amounts of oxides in the products described and claimed are percentages by weight based on the oxides.

Detailed description of the invention

In the fused and cast products according to the invention, the high content of zirconia ZrO_2 makes it possible to meet the requirements of high corrosion resistance without coloration of the glass produced or generating defects impairing the quality of said glass.

5 The hafnium oxide, HfO_2 , present in the product according to the invention is the hafnium oxide naturally present in sources of zirconia. Its content in a product according to the invention is therefore less than 5%, generally less than 2%.

10 The presence of silica SiO_2 notably permits the formation of an intergranular vitreous phase that can efficiently accommodate the volume changes of zirconia during its reversible allotropic transformation, i.e. during transition from the monoclinic phase to the tetragonal phase. The content by weight of silica must be greater than 2%. Conversely, the addition of silica must not exceed 10% as said addition is made at the expense of the zirconia content and can therefore impair the corrosion resistance.

15 The presence of B_2O_3 notably makes it possible to improve the feasibility of the products. Conversely, the addition of boron oxide must not exceed 4.5% as this addition is made at the expense of the zirconia content and can therefore impair the corrosion resistance.

20 The presence of alumina Al_2O_3 is notably necessary for the formation of a stable vitreous phase and for good castability of the molten material in the mold. However, the addition of alumina must not exceed 2% as a higher content by weight can lead to instability of the vitreous phase (formation of mullite crystals), in particular owing to the presence of boron oxide.

25 The content by weight of $Na_2O + K_2O$ must not exceed 0.50% in order to limit the fly-off of raw materials, in particular of boron oxide. In a product according to the invention, the oxides Na_2O and K_2O are considered to have similar effects.

According to the invention, the content by weight of $Fe_2O_3 + TiO_2$ is less than 0.55% and that of P_2O_5 is less than 0.05%. In fact, these oxides are harmful and their content must be limited to traces introduced as impurities with the raw materials.

30 The "other species" are species that are not listed above, namely species other than ZrO_2 , Hf_2O , SiO_2 , Y_2O_3 , CeO_2 , CaO , MgO , B_2O_3 , Al_2O_3 , Na_2O , K_2O , P_2O_5 , TiO_2 , and Fe_2O_3 . In one embodiment, the "other species" are limited to species whose

presence is not particularly desirable and which are generally present as impurities in the raw materials.

Conventionally, the sources of the oxides listed above do not comprise Ta_2O_5 . The Ta_2O_5 content of a product according to the invention can be less than 5 0.9%, or less than 0.5%, or less than 0.2%.

In another embodiment, the "other species" can also comprise species whose presence is advantageous. Thus, in one embodiment, the product advantageously comprises at least 0.05% of barium oxide BaO. This oxide can be an impurity or can be added deliberately in the initial charge, if required. Preferably its 10 content is less than 0.5%, as percentage by weight based on the oxides.

A product according to the invention can be manufactured conventionally following steps a) to c) described below:

- a) mixing raw materials to form an initial charge,
- b) melting of said initial charge until a molten material is obtained,
- 15 c) solidification of said molten material, by cooling, so as to obtain a refractory product according to the invention.

In step a), the raw materials are selected so as to guarantee the contents of oxides in the finished product.

In step b), melting is preferably carried out by the combined action of a fairly 20 long electric arc, not producing reduction, and stirring, promoting reoxidation of the products.

To minimize the formation of nodules of a metallic appearance and avoid the formation of slits or splits in the final product, it is preferable to conduct the melting operation in oxidizing conditions.

25 The long-arc melting process described in French patent No. 1 208 577 and its additions No. 75893 and 82310 is preferably used.

This process consists of using an electric arc furnace in which the arc is struck between the charge and at least one electrode at a distance from this charge and controlling the length of the arc so that its reducing action is minimized, while 30 maintaining an oxidizing atmosphere above the molten bath, and mixing said bath, either by the action of the arc itself, or by bubbling an oxidizing gas (air or oxygen, for example) in the bath or by adding substances to the bath that release oxygen, such as peroxides or nitrates.

In step c), cooling is preferably carried out at a rate of less than 20°C per hour, preferably at a rate of about 10°C per hour.

Any conventional method of manufacture of fused products based on zirconia intended for applications in glass-melting furnaces can be employed, provided that the composition of the initial charge enables products to be obtained that have a composition complying with that of a product according to the invention.

Examples

The following nonlimiting examples are given for the purpose of illustrating the invention.

- 10 In these examples, the following raw materials were used:
- zirconia containing principally, on average by weight, 98.5% of $\text{ZrO}_2 + \text{HfO}_2$, 0.2% of SiO_2 and 0.02% of Na_2O ,
 - zircon sand at 33% silica,
 - yttrium and boron oxides of purity above 99%,
 - 15 - alumina of type AC44 sold by the company Pechiney and containing on average 99.4% of alumina Al_2O_3 .

The products were prepared according to the conventional process of arc furnace melting, then cast to obtain blocks of dimensions 220 mm x 450 mm x 150 mm.

- 20 The chemical analysis of the products obtained is given in Table 1; this is an average chemical analysis, given in percentages by weight.

Feasibility

- For each of these examples, the feasibility of the product is evaluated using a feasibility index FI. A value of FI equal to 1 corresponds to excellent feasibility (optimal manufacturing yield, no flaws on the parts obtained), and a value of FI equal to 0 corresponds to unacceptable feasibility for industrial manufacture (through-cracks, parts broken up, etc.).

Samples for carrying out tests were taken from the various examples of blocks produced.

30 Measurement of the temperature of maximum expansion before phase change

The curve of expansion as a function of temperature is constructed and the temperature corresponding to maximum expansion, before the transformation (monoclinic to quadratic) of the zirconia, is noted, designated "T" in Table 1.

Example 1 corresponds to the product ER1195, which serves as reference.

Table 1

Ex.	ZrO ₂	SiO ₂	Y ₂ O ₃	Al ₂ O ₃	Na ₂ O	B ₂ O ₃	0.09 x Y ₂ O ₃ x SiO ₂	FI	T
1	95.1	3.45	0.00	1.15	0.30	0.00	0.00	1	1140°C
2	95.1	3.14	0.72	0.65	0.00	0.39	0.20	1	1083°C
3	93.5	4.20	0.83	0.96	0.00	0.51	0.31	1	1032°C
4	92.9	5.00	0.85	0.93	0.04	0.28	0.38	0	1034°C
5	90.9	6.26	0.86	1.16	0.00	0.84	0.48	1	1040°C
6	92.7	4.87	0.88	0.90	0.04	0.66	0.39	1	1029°C
7	95.1	2.59	0.97	1.03	0.05	0.28	0.23	1	1011°C
8	94.6	3.06	1.20	0.77	0.05	0.37	0.33	1	983°C
9	92.3	5.00	1.20	0.90	0.00	0.60	0.54	1	980°C
10	93.9	3.81	1.23	0.79	0.00	0.25	0.42	0	957°C

The results show the positive role of yttrium oxide. It is considered that a minimum content of 0.8% of yttrium oxide in the product is necessary for significantly lowering the temperature of maximum expansion before phase change, in particular so that this temperature is below 1050°C. Thus, it becomes possible, advantageously, to reduce the temperature of the molten glass in contact with the critical region, thus to increase its viscosity and therefore the corrosion that it produces. Advantageously, the risks of escapes of glass are therefore limited.

Comparison of examples 3 and 4 or 9 and 10 shows the importance of the presence of a minimum amount of boron oxide to obtain optimal feasibility in the presence of yttrium oxide. Comparison of examples 4 and 7 shows, however, that this minimum amount depends on the contents of yttrium oxide and of silica.

Moreover, other tests have also verified that the products according to the invention also display the other properties recognized for materials with high zirconia content, in particular resistance to corrosion by molten glass.

Of course, the present invention is not limited to the embodiments described and represented, supplied as nonlimiting examples for purposes of illustration.

11
CLAIMS

1. A fused and cast refractory product comprising, in percentages by weight based on the oxides and for a total of 100%:
- 5 - ZrO₂: complement to 100%
- Hf₂O: < 5%
- SiO₂: 2% to 10%
- 0.9% < Y₂O₃ + CeO₂ + CaO + MgO ≤ 4.0%
- B₂O₃: ≤ 4.5%
- 10 - B₂O₃: ≥ 0.09 x (Y₂O₃ + 1/3 (CeO₂ + CaO + MgO)) x SiO₂
- Al₂O₃: 0.3% to 2.0%
- Na₂O + K₂O: ≤ 0.5%
- P₂O₅: < 0.05%
- Fe₂O₃ + TiO₂: < 0.55%
- 15 - other species: < 1.0%,
- provided that the Y₂O₃ content is greater than or equal to 0.5% or that the content of CeO₂ + CaO + MgO is greater than or equal to 2%.

2. The product as claimed in the preceding claim, wherein

$$\text{B}_2\text{O}_3 \geq 0.095 \times (\text{Y}_2\text{O}_3 + 1/3 (\text{CeO}_2 + \text{CaO} + \text{MgO})) \times \text{SiO}_2$$

- 20 3. The product as claimed in the preceding claim, wherein

$$\text{B}_2\text{O}_3 \geq 0.1 \times (\text{Y}_2\text{O}_3 + 1/3 (\text{CeO}_2 + \text{CaO} + \text{MgO})) \times \text{SiO}_2$$

4. The product as claimed in any one of the preceding claims, wherein the content of boron oxide is greater than 0.4%.
5. The product as claimed in any one of the preceding claims, wherein the content of boron oxide is less than 2.5%.
6. The product as claimed in any one of the preceding claims, wherein the content of yttrium oxide Y_2O_3 is greater than or equal to 0.7%.
7. The product as claimed in any one of the preceding claims, wherein the content of yttrium oxide Y_2O_3 is less than 2.5%.

8. The product as claimed in any one of the preceding claims, wherein the content of silica is less than 8.0%.
9. The product as claimed in any one of the preceding claims, wherein the content of alumina is less than 1.5%.
- 5 10. The product as claimed in any one of the preceding claims, wherein the content of alumina is greater than 0.7%.
11. The product as claimed in any one of the preceding claims, wherein $(\text{Na}_2\text{O} + \text{K}_2\text{O}) < 0.3\%$.
- 10 12. The product as claimed in any one of the preceding claims, wherein the total content by weight of "other species" is less than 0.5%.
13. The product as claimed in any one of the preceding claims, comprising less than 0.5% of each of the oxides CeO_2 , CaO and MgO .
- 15 14. A glass-melting furnace comprising, in a region intended to be in contact with molten glass, a refractory product as claimed in any one of the preceding claims.