(54) Title: COMPOSITE STRUCTURE COMPRISING A COMPONENT OF ELECTRO-CAST REFRACTORY AND ELEMENTS HIGHLY RESISTANT TO CORROSION AND EROSION

(57) Abstract

A composite and monolithic refractory structure, particularly adapted for making furnaces for glassmaking or the like, constituted by a block-shaped component made of electro-.cast refractory material based on oxides of aluminum zirconium, silicon and the like, having shapes and dimensions that are adapted for its uses, inside which at least one protective element is monolithically inserted; the protective element is highly resistant to the attack of molten glass baths or the like and is chosen among metals, noble metals, refractory metals, refractory materials, conventional and non-conventional ceramic materials, such as carbides, nitrides, borides, and the like, or graphite-based materials, alloys and/or compounds and/or composites thereof; the element is provided substantially in the shape of a plate that is shaped and sized so as to have a profile that is similar to the peripheral profile of the refractory block and is arranged, inside the block, so that its surfaces are located at, and proximate to, the surfaces of the block that are meant to be exposed to the attack of the bath, so as to constitute an insert that acts as a continuous protective barrier against the attack for the refractory component. The scope of the invention also includes a process for producing the composite refractory structure in conventional molds.
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COMPOSITE STRUCTURE COMPRISING A COMPONENT OF ELECTRO-CAST REFRACTORY AND ELEMENTS HIGHLY RESISTANT TO CORROSION AND EROSION

Technical Field

The present invention relates to a composite refractory structure constituted by an electro-cast refractory component based on ceramic oxides, refractories and other materials, and mineral oxides, which includes at least one variously shaped structural element that is highly resistant to corrosion and/or erosion produced by molten baths and in particular by baths of molten glass and the like.

The scope of the present invention also includes a process for producing said monolithic composite refractory structure, which can be used to make furnaces for glassmaking and particularly in the regions of the furnace that are most intensely subjected to the corrosive action of molten glass.

Background Art

It is known that the technology for building glassmaking furnaces uses appropriately assembled monolithic elements made of electro-cast refractory material which are usually termed "electro-cast blocks". These electro-cast blocks are produced in various shapes, sizes, kinds, and qualities, and are all obtained by casting a mixture of molten refractory oxides in a three-phase electric-arc furnace, as disclosed in Italian

The molten mixture is cast into appropriately designed and shaped molds, where it undergoes a first partial cooling and assumes the intended shape. The electro-cast refractory material then completes its cooling cycle in controlled conditions; at the end of this cycle, it is usually machined and finished mechanically.

This final product is commonly termed "electro-cast refractory block".

It is also known that the electro-cast refractory material is attacked during use, as a consequence of the various mechanical, physical, and chemical conditions that occur in each part of the furnace.

The attack to which the electro-cast refractory is subjected wears it. The extent of the wear determines the duty life of the blocks of electro-cast material and substantially determines the duty life of the glass furnace.

The wear of blocks of electro-cast material is different according to their quality, type, and location in the furnace. In fact, it is known that there are areas in the furnace where wear is more intense than in others. It is widely acknowledged that among the most intense wear which occurs, there is the wear in the electro-cast blocks that compose the throat of the furnace, in particular the covering block at the glass inlet, the anti-blowback wall, or in the area of the blocks that is technically defined as "flux line" or "metal line".

In order to extend the life of a glass furnace as much as possible, good practice selects and assembles together
electro-cast refractories having different qualities and properties in order to balance the extent of wear in every part of the furnace.

In the production of glass furnaces it is in fact now common to simultaneously have blocks of electro-cast refractory having different chemical compositions (Al₂O₃-ZrO₂-SiO₂, alpha and beta Al₂O₃, ZrO₂, Al₂O₃-Cr₂O₃-SiO₂-ZrO₂, etcetera), located in specific areas depending on the quality and type of glass produced and on the stresses that it must withstand.

In the known art, despite using different materials, a satisfactory balance between the wear of the various regions of the glass furnace has not yet been achieved, and therefore the optimum life of said furnace is still not achieved due to the early wear of some parts thereof.

In order to reduce the effects of this disparity in wear and ensure the maximum operating life of the furnace, one generally resorts to other solutions of a mechanical type, such as cooling the structure from outside, or to repairs of the most intensely worn regions while the furnace is hot and running.

**Disclosure of the Invention**

Accordingly, the aim of the present invention is to provide a composite and monolithic refractory structure that is shaped like an electro-cast refractory block having various dimensions and chemical-physical characteristics which has, during use, a high resistance to corrosion/erosion produced by molten baths and particularly by baths of molten glass, and therefore a life that is far longer than that normally achieved with electro-cast
materials of any kind and composition.

An object of the invention is to provide a composite refractory structure conceived and provided so as to be constituted by components that are chemically and/or physically different from each other and are in intimate and continuous contact with each other, one component being constituted by refractory material that has been electro-cast or cast with other methods, and one or more parts being constituted by a material that is highly resistant to high temperatures and to corrosion and is capable of constituting an effective protective barrier for the refractory component against the continuous attack of a bath of molten glass or the like.

Another object of the invention is to provide a method for manufacturing said composite refractory structure conceived so as to be easy to perform and highly effective without requiring particular and expensive equipment for performing it.

This aim, these objects, and others which will become apparent from the following description are achieved by a composite and monolithic refractory structure, particularly and not exclusively adapted for making furnaces for molten glass, which is constituted, according to the present invention, by a block-shaped component made of electro-cast refractory material based on oxides of aluminum, zirconium, silicon, and the like, having shapes and dimensions that are adapted for its uses, inside which at least one protective element is monolithically inserted, said protective element being highly resistant to the attack of molten glass baths or the like and being chosen among
metals, noble metals, refractory metals, refractory materials, conventional and non-conventional ceramic materials, such as carbides, nitrides, borides, and the like, or graphite-based materials, alloys and/or compounds and/or composites thereof; said element being provided substantially in the shape of a plate that is shaped and sized so as to have a profile that is similar to the peripheral profile of the refractory block and being arranged, inside the block, so that its surfaces are located at, and proximate to, the surfaces of the block that are meant to be exposed to the attack of the bath, so as to constitute an insert that acts as a continuous protective barrier against said attack for the refractory material located behind it.

More particularly, said protective element is provided in the shape of a rigid lamina that is formed so as to have various geometric shapes with "C-", "I-", "L-", "O-", "S-", "U-", "V-" shaped profiles and the like; of cylindrical or conical tubes with a base profile constituted by an open or closed perimeter; of compositions and/or assemblies thereof, so as to constitute open or closed solid or box-like bodies; said laminae or inserts being constituted by at least one metal, chosen preferably among molybdenum, tantalum, tungsten, and platinum, refractory metals, conventional and non-conventional ceramic materials, such as those based on graphite, carbides, nitrides, borides, silicides, and the like, both as such and as alloys and/or compounds and/or composites thereof.

Also according to the invention, a method is provided for the production of said composite refractory structure;
said method is introduced, with particular conditions and operating steps, in a conventional cycle for the production of electro-cast refractory blocks inside appropriate molds, said blocks being preferably meant to build glass furnaces.

The method according to the present invention in fact consists in:

-- preparing a conventional mold for the production of a block of refractory material having the desired dimensions;

-- preparing at least one protective insert that is highly resistant to the attack of molten glass and has shapes and dimensions adapted to constitute a continuous barrier at least for those areas of the refractory block that are meant to be most exposed to said attack;

-- positioning, inside said mold, supporting and/or suspension elements for said insert, which are shaped and arranged so as to keep said insert stably and fully contained within the mold and therefore immersed in the refractory block after casting it, and also so that the surfaces that constitute the protective barrier are in a parallel position and are located proximate to the surfaces of the block that are exposed to the attack of the molten glass; and then

-- casting into said mold refractory material melted according to a method and an equipment for introducing molten material that are capable of avoiding movements of the insert with respect to the walls of the mold; and finally

-- stopping the casting when the mold is filled and then cooling the block of refractory that contains the insert according to successive cycles, so as to achieve an
intimate, continuous, and permanent contact between the insert, the supporting elements, and the refractory part.

More particularly, said refractory material is chosen among those that are electro-cast or cast with other methods, and more specifically among refractory materials whose main components are individual chemical substances or combinations thereof, including $\text{Al}_2\text{O}_3$, $\text{SiO}_2$, $\text{ZrO}_2$, $\text{Cr}_2\text{O}_3$, MgO, and compounds thereof.

Furthermore, said inserts are preferably constituted by materials whose main components are Mo, Pt, Ta, W, noble metals or refractories in general, graphite, ceramic materials, and also particular materials such as nitrides, borides, carbides, silicides, and the like, both as such and as alloys, compounds, and composites thereof.

Likewise, in order to achieve intimate, mutual, and stable contact between the refractory part and the insert, the materials chosen for the refractory part, for the insert, and for the support and/or suspension elements must have a similar dilatometric behavior.

Brief description of the drawings

Further characteristics and advantages of the present invention will become apparent from the following detailed description, given with reference to the accompanying drawings, which are provided only by way of non-limitative example and wherein:

figures 1, 1b and 1a are respectively a perspective view, a front view, and a side view of a type of metallic insert that is shaped like a metallic lamina with an L-shaped profile;

figures 2 and 2a are a side view and a front view of a
metallic plate-like insert;
figures 3 and 3a are a side view and a front view of another insert shaped like a metallic lamina;
figures 4 and 4a are a side view and a front view of a laminar insert that substantially has a U-shaped profile;
figures 5, 5b, 5a are respectively a perspective view, a front view, and a side view of another laminar insert folded so as to be L-shaped;
figure 6 is a view of an insert constituted by a solid cylindrical bar;
figures 6 bis to 11a are views of a series of elements for supporting and/or suspending an insert (shown in the previous figures) inside a mold; said elements can be made of metal, graphite, or refractory or ceramic material, or of other adapted materials in various dimensions and shapes;
figure 12 is a median sectional view of a conventional mold for producing a block of electro-cast refractory material, inside which an L-shaped metallic laminar insert is positioned by using supporting elements chosen among those shown in figures 6 bis to 11a;
figures 12a and 12b are respectively a transverse sectional view of the mold, taken along the plane XII-XII of figure 12, and a view of figure 12 taken from "A";
figure 13 is instead a schematic view of an example of use of the composite structures provided according to the invention, and more precisely of a shape of the glass flow region, termed "throat", and of the direction (F) of the molten glass flow from the melting tank to the forming tank; and
figure 14 is a time-based plot of the corrosion of a block and more precisely of the progressive corrosion profile compared with the initial profile of the refractory block.

Ways of carrying out the Invention

With reference to the above figures and to the preceding description, the composite refractory structure according to the present invention is substantially constituted by a monolithic component made of refractory material that is electro-cast (or cast with other methods), is based on ceramic oxides, particularly oxides of the AZS system, and includes at least one metallic insert that is fully immersed so as to be concealed, said insert acting as a barrier for protecting the refractory material from the attack of the molten glass or similar corrosive product.

Depending on the type of block of electro-cast material and most of all on its relative position in the structure that composes a furnace for molten glass, metal inserts such as for example those shown in figures 1 to 6 or any other adapted shape are used, and various kinds of support, such as for example those shown in figures 6 bis to 11a, or similar ones, are used to support said inserts inside a mold for an electro-cast block.

Thus, for example, a first type of insert is constituted by a rectangular metallic lamina (figures 1, 25 1a, 1b) that is folded so as to be L-shaped and have two identical (or optionally different) wings 1a, 1b along a preset radius of curvature R; at the opposite ends, for example, of the wing 1a, there is a recess or notch 2 that is semicircular (or has another kind of profile) and is
meant to interrupt the continuity of the insert external perimeter.

Likewise, the metallic insert of figure 2 is also constituted by a metallic lamina 2 that is folded so as to be L-shaped and form the two wings 2a and 2b. The wing 2a ends with a part 2c that is folded at an angle and is provided with a semicircular recess 2e. The wing 2b also ends with a portion that is folded like the portion 2c.

Likewise, the inserts of figures 3, 4, and 5 are constituted by a metallic plate that is folded so as to be L-shaped or U-shaped, are respectively designated by the reference numerals 3, 4, and 5, and are also provided with a recess 3a, 4a, and 5a.

Only the ends of the insert 4 are not folded.

Said inserts are generally constituted by metals such as Mo, Pt, Ta, W, and the like; they can also be constituted by materials including, for example, ceramic materials, graphite, carbides, nitrides, borides, silicides, and other similar materials, both as such and as alloys or compounds and/or composites thereof. They can also be treated by means of chemical, physical, or mechanical processes to adapt them to the operating requirements; likewise, their dimensions in length, width, and thickness can vary according to the dimensions of the block for which said inserts must constitute the protective barrier.

The shape of said inserts reproduces the peripheral shape of the part of the block that is protected against the attack of the molten glass bath.

Various kinds of supporting elements, such as those
shown by way of example in figures 6 bis to 11a, are used to stably position the various inserts inside the mold.

Thus, for example, figures 6 bis and 7 illustrate dowels or pins made of metal, graphite, refractory or ceramic materials, or other adapted material, that can be used to position the insert of figure 6, constituted by a solid cylindrical bar, inside the mold.

The narrower end of the pin of figure 6 bis is inserted in the wall of the mold, whereas one end of the cylindrical bar-shaped insert of figure 6 is arranged in the seat of the protruding part having a larger diameter. The support of figure 7 is substantially constituted by a plate 7 made of metal or other material which is provided with an adapted hole 7a, in which the free end of the cylindrical bar-shaped insert is inserted; the part 7b shown in dashed lines is instead inserted snugly in the wall of the mold. Figures 8 to 11a illustrate other supports having a cylindrical or frustum-like shape and provided with laterally formed notches 8b and 10b or with recesses 9b and 11b that are formed at their ends. Said recesses or notches are meant to snugly accommodate the edge of the wings of the various laminar inserts so as to position them stably.

Figures 12, 12a and 12b illustrate a complete example of the positioning of an insert inside a mold which is shaped like a rectangular parallelepiped, shown in figure 12, prior to the casting of the molten refractory.

The insert arranged therein is of the type of the one designated by the reference numeral 1 in figure 1, that is to say, a lamina with an L-shaped profile and with wings 1a
and 1b vertically arranged. The lower edge of the wing 1a is accommodated in the recess 9b of two vertical cylindrical supports 9 (figure 9), in which the ends that lie opposite to the one provided with the recess are inserted snugly in the back wall of the mold 12; the wing 1b is likewise arranged on two identical supports 9 which are also snugly inserted in the back wall of the mold, as shown by the sectional view of figure 12a. Said wings 1a and 1b are furthermore retained at the top of the mold by means of two cylindrical elements 8 that are horizontally inserted snugly in the contiguous walls of the mold (figure 12b).

The arrangement of the wings of the insert 1 is such as to allow said insert to remain fully contained inside the mold and thus also inside the finished refractory block, and is also such as to keep its wings stably parallel and close to the inside surfaces of the mold walls.

Of course, the other kinds of support can be used to position and support the other kinds of insert, such as those shown merely by way of example in the accompanying figures.

The method for casting the molten refractory material inside the mold to achieve the composite structure according to the invention therefore entails the following operating steps:

-- positioning, supporting, and/or suspending at least one insert inside the casting mold with the aid of said appropriately structured and configured supporting elements, so that said insert is fully immersed in the part
made of electro-cast refractory so that the surfaces that must constitute the barrier against the attack of the molten glass bath are located at, and proximate to, the surfaces of the block that will be exposed to said attack;

-- casting the molten refractory material inside the mold with an appropriate method and equipment ensuring control of the flow-rate and of the adequate directionality of the casting flow, in order to introduce the molten material in the planned time, prevent relative movements of the insert or inserts with respect to the mold, and thus achieve uniform and complete filling of said mold.

The importance of choosing the materials constituting the elements that position and support the insert or inserts, their shape, and their dimensions, is evident during this step.

The definition of these correlated characteristics must be performed in accordance with the nature of the insert and of the refractory part and is essential to:

-- prevent, during casting, the elements from undergoing an alteration of any nature that might cause a movement of the insert from its original planned position;

-- produce permanent structural continuity between the elements and the refractory part of the composite structure after the block has cooled; and

-- produce permanent, intimate, and mutual contact without discontinuities between the elements and the insert at their interface after the block has cooled.

It is furthermore necessary to cool the composite structure constituted by the refractory part and by the insert according to an appropriate thermal cycle, so as to
ensure the formation of a uniform microcrystalline structure of the refractory part and permanent intimate contact between said refractory part and the insert.

For this purpose, it is indispensable that the choice of the nature of the refractory part, of the insert, and of the supports be such that they have a consistent dilatometric behavior.

The block produced according to the described method can be used for example for each one of the positions numbered 1 to 9 of figure 13. Said figure 13 illustrates one of the possible embodiments of the region of the glass furnace technically termed "throat".

Intense corrosion of the electro-cast refractory material occurs in this region and mostly affects the blocks in positions 1, 2, and 3, and particularly the block in position 1, which is the most critical element, also from the point of view of its structural function in the throat of figure 13.

The throat is an essential element of the structure of the furnace, and its wear in practice determines the duty life of said furnace, sometimes entailing an early shutdown. Corrosion of the blocks that constitute the throat occurs according to the typical profile shown in figure 14, where F designates the direction of the flow of molten glass, B designates the profile of the initial block, and t₁ and t₂ designate the progressive corrosion profiles in the times t₁ and t₂, where t₂ is subsequent to t₁.

The insert I, shown in dashed lines inside the block in position 1, by interposing itself between the molten
glass bath and the refractory material, acts as a protective barrier for the refractory body, preventing said body from making contact with the molten glass, thus avoiding its corrosion and/or erosion and in practice increasing the working life of the block.

The invention as described and illustrated according to some preferred embodiments is of course susceptible, in its practical execution, of further structurally and functionally equivalent modifications and variations, especially in the molten refractory materials, in the inserts, and in the supports, as well as in the number and relative position of said inserts and supports, without abandoning the scope of the protection of the invention.
CLAIMS

1. Composite and monolithic refractory structure, particularly adapted for making furnaces for glassmaking and the like, characterized in that it is constituted by a block-shaped component made of electro-cast refractory material based on oxides of aluminum, zirconium, silicon, and the like, having shapes and dimensions that are adapted to its uses, inside which at least one protective element is monolithically inserted, said protective element being highly resistant to the attack of molten glass baths or the like and being selected from among metals, noble metals, refractory metals, refractory materials, conventional and non-conventional ceramic materials, such as carbides, nitrides, borides, and the like, or graphite-based materials, alloys and/or compounds and/or composites thereof; said element being provided substantially in the shape of a plate that is shaped and sized so as to have a profile that is similar to the peripheral profile of the refractory block and being arranged, inside the block, so that its surfaces are located at, and proximate to, the surfaces of the block that are meant to be exposed to the attack of the bath, so as to constitute an insert that acts as a continuous protective barrier against said attack for the refractory component located behind it.

2. Refractory structure according to claim 1, characterized in that said protective element is provided in the shape of a rigid plate or lamina formed so as to have various geometric shapes with "C-", "I-", "L-", "O-", "S-", "U-", "V-" shaped profiles and the like; of
cylindrical or conical tubes with a base profile
constituted by an open or closed perimeter; of compositions
and/or assemblies thereof, so as to constitute open or
closed solid or box-like bodies; said laminae or inserts
being constituted by at least one metal, chosen preferably
among molybdenum, tantalum, tungsten, and platinum,
refractory metals, conventional and non-conventional
ceramic materials, such as those based on graphite,
carbides, nitrides, borides, silicides, and the like, both
as such and as alloys and/or compounds and/or composites
thereof.

3. Method for producing a monolithic composite
refractory structure according to claims 1 and 2, using
conventional molds for producing blocks made of electro-
cast refractory material or the like, characterized in that
it consists in:

-- preparing a conventional mold for the production of a
block of electro-cast refractory material having the
desired dimensions;

-- preparing at least one protective insert that is highly
resistant to the attack of molten glass and has shapes and
dimensions that are adapted to constitute a continuous
protective barrier at least for those regions of the
refractory block that are meant to be most exposed to said
attack;

-- positioning, inside said mold, the supporting and/or
suspension elements for said insert, which are shaped and
arranged so as to keep said insert stably and fully
immersed within the mold and therefore in the refractory
block after casting it, and also so that its surfaces are
in a parallel position and are located proximate to the
surfaces of the block that are exposed to the attack; and
then
-- casting, with clearly determined and planned timings,
molten refractory material into said mold according to a
method and an equipment for introducing molten material
that are capable of avoiding movements of the insert with
respect to the walls of the mold; and finally
-- stopping the casting when the mold is filled and then
cooling the block of refractory that contains the insert
according to successive cycles, so as to achieve an
intimate, continuous, and permanent contact between the
insert, the supporting elements, and the refractory part.

4. Method according to claim 3, characterized in that
said casting step comprises casting of refractory material
being selected among materials that are castable
electrically or with other methods and in particular among
refractory materials whose main components are individual
chemical substances or combinations thereof, including
Al₂O₃, SiO₂, ZrO₂, Cr₂O₃, MgO, and compounds or composites
thereof.

5. Method according to claims 3 and 4, characterized
in that in said preparing step, inserts are prepared which
are preferably constituted by materials whose main
components are Mo, Pt, Ta, W, refractory metals in general,
graphite-based materials, conventional and non-conventional
ceramic materials, and also particular materials such as
nitrides, borides, carbides, silicides, both as such and as
alloys or compounds and/or composites thereof, that have
undergone partial or total chemical, physical, mechanical
10 treatments or processes adapted to partially or totally alter their nature, appearance, size, shape, or surface conditions.

6. Method according to claims 3 to 5, characterized in that in said preparing and casting step in order to achieve stable, intimate, and mutual contact between the refractory part and the inserts, the materials selected for the refractory part, for the inserts, and for the supporting and/or suspension elements must have a consistent dilatometric behavior.
INTERNATIONAL SEARCH REPORT

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

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C04B C03B F27D F27B

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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>EP,A,0 008 261 (PRODUITS REFRACTAIRES) 20 February 1980 see page 3, line 22 - page 5, line 11; claims; figures</td>
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Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

Date of the actual completion of the international search: 13 October 1995

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Name and mailing address of the ISA
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