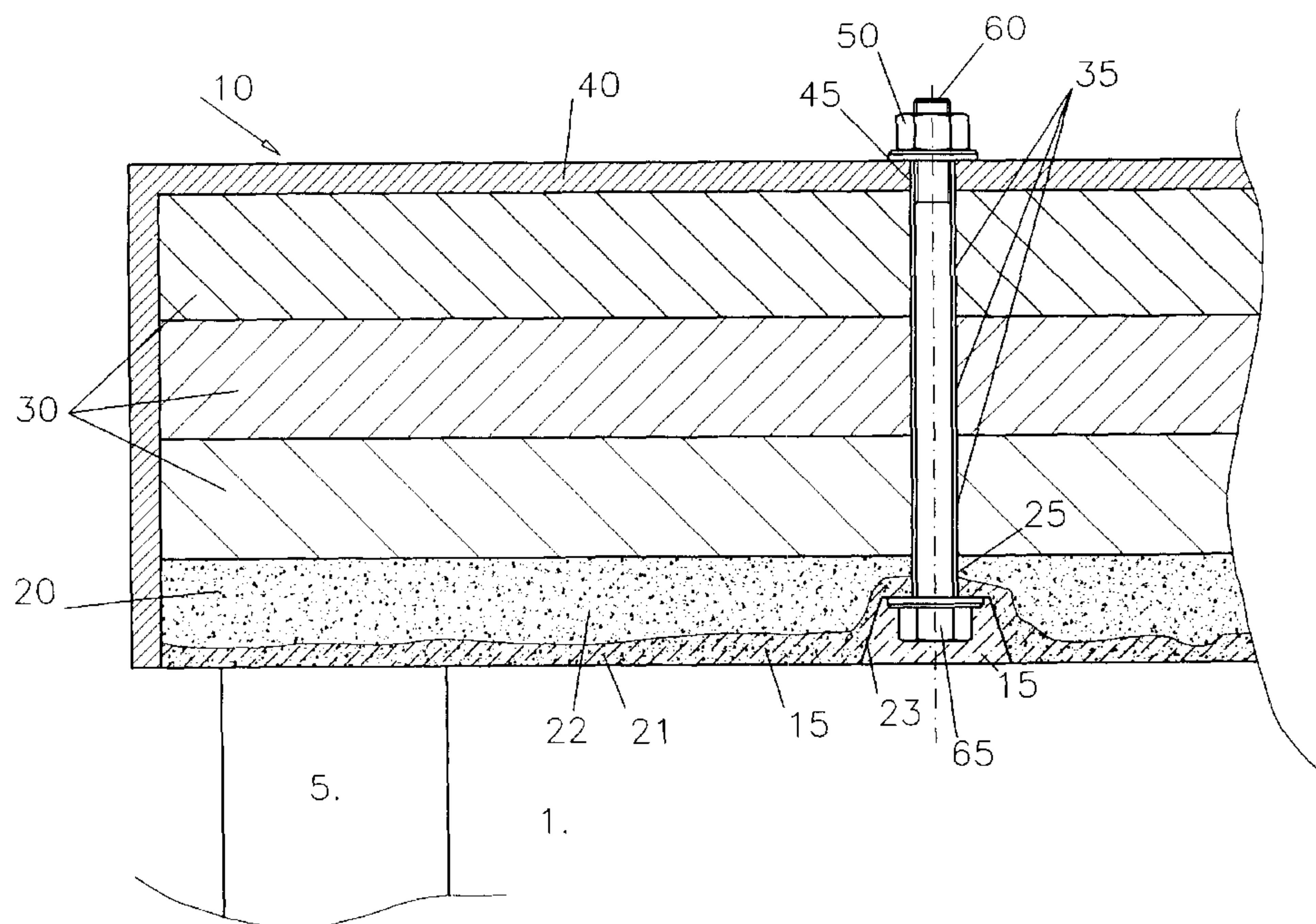




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(71) Demandeur/Applicant:
MOLTECH INVENT S.A., LU
(72) Inventeurs/Inventors:
DE NORA, VITTORIO, BS;
BERCLAZ, GEORGE, CH
(74) Agent: GOWLING LAFLEUR HENDERSON LLP

(54) Titre : COMPOSANTS STRUCTURELS ISOLANTS THERMIQUEMENT RESISTANT A UN MILIEU CORROSIF A
HAUTE TEMPERATURE
(54) Title: THERMALLY INSULATING STRUCTURAL COMPONENTS RESISTANT TO HIGH TEMPERATURE
CORROSIVE MEDIA



(57) **Abrégé/Abstract:**

The invention relates to a thermally insulating structural component (10) such as a cover of a container (5), in particular a molten salt electrolytic cell which component (10) is inert and resistant to corrosive media (1) at high temperature in the form of liquids, vapours and/or gases, in particular NaAlF₄, AlF₃, HF or O₂, and which during use is exposed to such corrosive media (1). The component (10) comprises thermal insulating material (30) shielded from the corrosive media (1) by an openly porous or reticulated alumina structure (20) which is made impermeable by a compact filler material (15) resistant and inert to the corrosive media and comprising compacted particles of refractory material, in particular alumina cement. The structural component (10) can have a top metallic shell (40) which extends over the thermal insulating material (30) and downwards along lateral sides of the component (10). The insulating material (30) can be secured to the alumina structure (20) through nuts (50) and bolts (60).



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MOLTECH INVENT S.A. [LU/LU]; 68-70 Boulevard de la Pétrusse, L-2320 Luxembourg (LU).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **DE NORA, Vittorio** [IT/BS]; Sandrigam House, Nassau (BS).
BERCLAZ, George [CH/CH]; Av. St.-François, CH-3968 Veyras/Sierre (CH).(74) Agent: **CRONIN, Brian**; Moltech S.A., Route de Troinex 9, CH-1227 Carouge (CH).(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).**Declarations under Rule 4.17:**

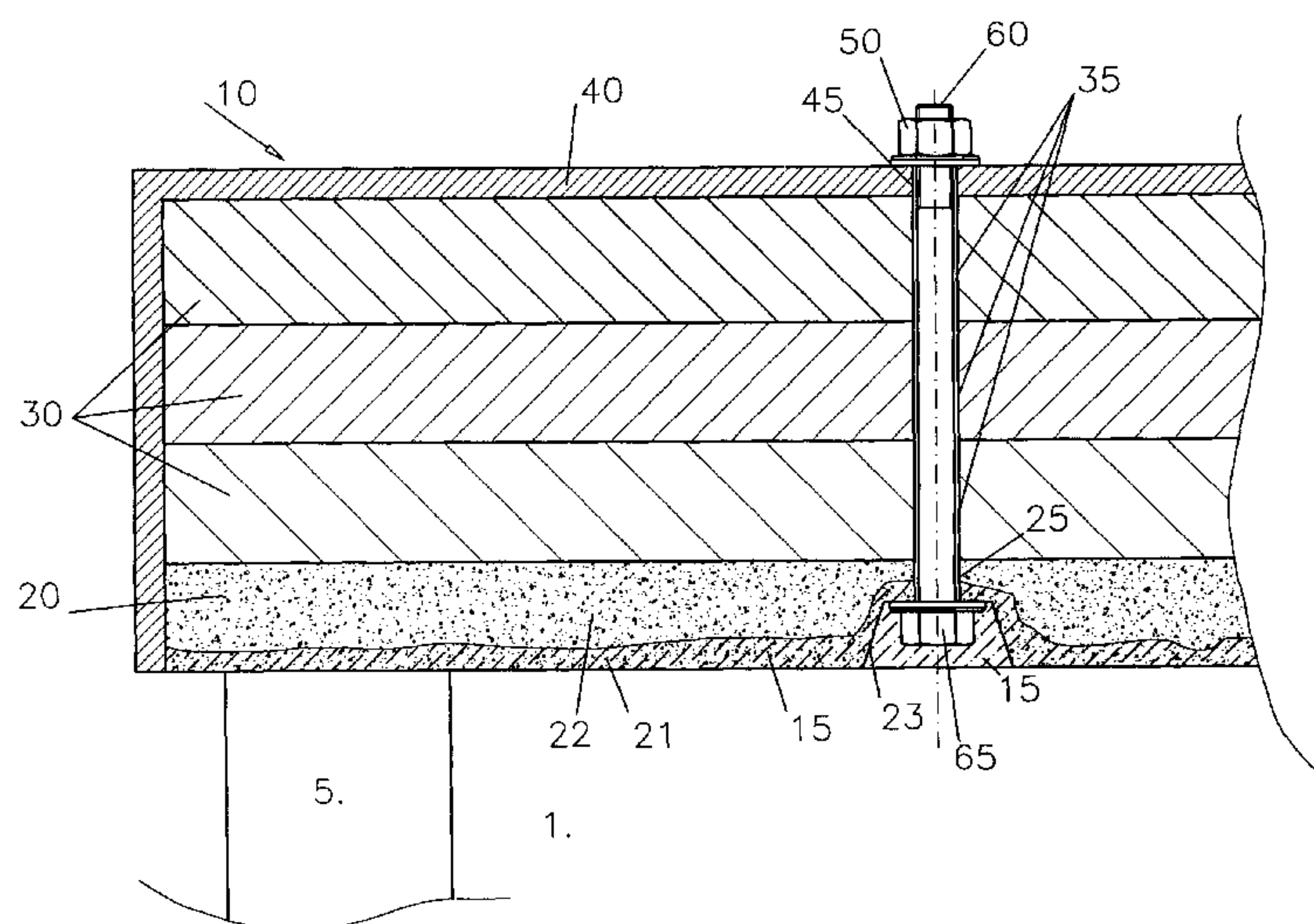
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(54) Title: THERMALLY INSULATING STRUCTURAL COMPONENTS RESISTANT TO HIGH TEMPERATURE CORROSIVE MEDIA



(57) **Abstract:** The invention relates to a thermally insulating structural component (10) such as a cover of a container (5), in particular a molten salt electrolytic cell which component (10) is inert and resistant to corrosive media (1) at high temperature in the form of liquids, vapours and/or gases, in particular NaAlF₄, AlF₃, HF or O₂, and which during use is exposed to such corrosive media (1). The component (10) comprises thermal insulating material (30) shielded from the corrosive media (1) by an openly porous or reticulated alumina structure (20) which is made impermeable by a compact filler material (15) resistant and inert to the corrosive media and comprising compacted particles of refractory material, in particular alumina cement. The structural component (10) can have a top metallic shell (40) which extends over the thermal insulating material (30) and downwards along lateral sides of the component (10). The insulating material (30) can be secured to the alumina structure (20) through nuts (50) and bolts (60).

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THERMALLY INSULATING STRUCTURAL COMPONENTS RESISTANT
TO HIGH TEMPERATURE CORROSIVE MEDIA

Field of the Invention

The invention relates to thermally insulating structural components such as a cover of a container, in particular of a molten salt electrolytic cell. The structural components are inert and resistant to high temperature corrosive media in the form of liquids, vapours and/or gases, such as NaAlF_4 , AlF_3 , HF or O_2 .

Background of the Invention

The technology for the production of aluminium by the electrolysis of alumina, dissolved in molten cryolite containing salts, at temperatures around 950°C is more than one hundred years old.

Conventional aluminium production cells are constructed so that in operation a crust of solidified molten electrolyte forms around the inside of the cell sidewalls. At the top of the cell sidewalls, this crust is extended by a ledge of solidified electrolyte which projects inwards over the top of the molten electrolyte. The solid crust in fact extends over the top of the molten electrolyte between the carbon anodes. To replenish the molten electrolyte with alumina in order to compensate for depletion during electrolysis, this crust is broken periodically at selected locations by means of a crust breaker, fresh alumina being fed through the hole in the crust.

This crust/ledge of solidified electrolyte forms part of the cell's heat dissipation system in view of the need to keep the cell in operation at constant temperature despite changes in operating conditions, as when anodes are replaced, or due to damage/wear to the sidewalls, or due to over-heating or cooling as a result of great fluctuations in the operating conditions. In conventional cells, the crust is used as a means for automatically maintaining a satisfactory thermal

balance, because the crust/ledge thickness self-adjusts to compensate for thermic unbalances. If the cell overheats, the crust dissolves partly thereby reducing the thermic insulation, so that more heat is dissipated through the sidewalls leading to cooling of the cell contents. On the other hand, if the cell cools the crust thickens which increases the thermic insulation, so that less heat is dissipated, leading to heating of the cell contents.

10 The presence of a crust of solidified electrolyte is considered to be important to achieve satisfactory operation of commercial cells for the production of aluminium on a large scale. In fact, the heat balance is one of the major concerns of cell design and energy consumption, since only about 25% of such energy is used for the production of aluminium. Optimization of the heat balance is needed to keep the proper bath temperature and heat flow to maintain a frozen electrolyte layer (side ledge) with a proper thickness.

 In conventional cells, the major heat losses occur at the sidewalls, the current collector bars and the cathode bottom, which account for about 35%, 8% and 7% of the total heat losses respectively, and considerable attention is paid to providing a correct balance of these losses.

 Further losses of 33% occur via the carbon anodes, 10% via the crust and 7% via the deck on the cell sides. This high loss via the anodes is considered inherent in providing the required thermal gradient through the anodes.

 In the literature, there have been suggestions for cells operating without a crust of solidified electrolyte.

35 US Patent 5,368,702 (de Nora) discloses a multimonopolar aluminium production cell operating with tubular anodes in a crustless molten electrolyte which is thermally insulated by a cover. The cover is lined underneath with a layer of thermally insulating

material. US Patent 5,415,742 (La Camera/Tomaswick/Ray/Ziegler) disclose another aluminium production cell operating with a crustless molten electrolyte which is thermally insulated by a cover.

5 Despite previous efforts to develop a cell design for operation with a crustless molten electrolyte, there is still a need to provide a thermic insulating material for cell covers which is resistant to electrolyte vapours and gases evolved during
10 electrolysis and which is sufficiently lightweight but mechanically resistant to be used for removable covers.

Summary of the Invention

 The invention proposes a thermally insulating cover of a container, in particular a molten salt
15 electrolytic cell, which cover is inert and resistant to corrosive media at high temperature in the form of liquids, vapours and/or gases contained in the container, in particular NaAlF_4 , AlF_3 , HF or O_2 , and which during use is exposed to such corrosive media. The
20 cover comprises thermal insulating material shielded from the corrosive media by an openly porous or reticulated alumina structure which is made impermeable by a compact filler made of material resistant and inert to said corrosive media. The filler material comprises
25 compacted particles of refractory material.

 The thermal insulating material may consist of or include a part of the openly porous or reticulated alumina structure that contains no filler. The thermal
30 insulting material may also include or be formed of an entirely different body above the openly porous or reticulated filled alumina structure.

 The filler may extend throughout the alumina structure. Alternatively, the alumina structure may be only partly filled by the filler, leaving a filler-free
35 part of the alumina structure, in particular a filler-free top part.

 For example, the filled part forms a layer which may form an outer surface of the cover, in particular an outer surface of a bottom part of the cover.

In addition, the alumina structure may be covered with an outside layer made of the same filler material, the outside layer forming an outer surface of the cover.

Usually, the alumina structure is a plate having a thickness in the range of 20 to 150 mm. A layer inside the alumina structure may have a thickness in the range of 10 to 100 mm. An outside layer covering the alumina structure can be 2 to 10 mm thick.

Usually, the refractory material of the filler comprises at least one compound selected from metal oxides, carbides and nitrides. For instance, the filler comprises a mixture of metal oxide particles with particles of at least one compound selected from carbides and nitrides. These particles may be applied in a colloidal metal oxide carrier.

Advantageously, the filler is a slurry-applied filler comprising dried colloidal and/or non-colloidal particles of at least one compound selected from metal oxides, carbides and nitrides, in particular selected from oxides, carbides and nitrides of titanium, zirconium, hafnium, vanadium, silicon, niobium, tantalum, nickel, molybdenum and iron. Suitable colloids may be selected from colloidal alumina, ceria, lithia, magnesia, silica, thoria, yttria, zirconia, tin oxide, zinc oxide and mixtures thereof. Colloidal precursors of such oxides, in particular hydroxides, may also be used. Further colloidal slurries which may be used as a filler material are disclosed in US Patents 5,310,476 and 5,364,513 (both in the name of Sekhar/de Nora).

For instance, the filler comprises a cement that consists predominantly of at least one of alumina, silica and titania particles. The filler may be made of alumina and silica, in particular with an alumina content of at least 80 weight%, in particular at least 90 or even 95 weight%. The filler may comprise a mixture of alumina and titania.

In one embodiment, the thermally insulating cover comprises an insulating layer and a protective layer that shields the insulating layer(s) from the corrosive media, the protective layer being made of the openly porous or reticulated filled alumina structure. Preferably, the insulating layer(s) and the protective

layer are mechanically secured together, in particular by means of one or more metallic attachment members extending through vertical holes of the protective layer and the insulating layer. The hole(s) in the insulating layer(s) may extend into recess(es) located in a bottom face of the alumina structure. Each recess can be arranged to embed a head of one or more of the attachment members and can be filled with the filler to protect the attachment member from the corrosive media. Usually, a top metallic shell extends over the insulating layer(s) and downwards along lateral sides of the cover.

The thermally insulating cover of the invention may be used on any container containing high temperature oxidising and/or corrosive media, in particular vapours and/or gases. In particular, the cover is used for aluminium electrowinning cells. The cover can also be used for other molten salt electrolytic cells, for example for the production of magnesium or other metals produced electrolytically. The cover may also be used in furnaces, such as arc furnaces for the production of steel or molten metal treatment apparatus, such as metal degassing apparatus. Further details of such apparatus may be found in WO00/63630 (Holz/Duruz), WO01/42168 (de Nora/Duruz) and WO01/42531 (Nguyen/Duruz/de Nora).

More generally, the invention relates to a thermally insulating structural component which is inert and resistant to corrosive media at high temperature in the form of liquids, vapours and/or gases, in particular NaAlF_4 , AlF_3 , HF or O_2 , and which during use is exposed to such corrosive media. In accordance with the invention, the component is made an openly porous or reticulated alumina structure which is made impermeable by a compact filler made of material resistant and inert to said corrosive media. The component may comprise any of the above described features or combination thereof.

The component may be a rigid, fire-resistant, lightweight panel, wall, door, lid, beam, balk or girder, housing or other structural component that can be utilised in the construction of containers, pressure vessels, reservoirs, ovens or furnaces etc.

The invention will be further described in the following Example.

Brief Description of The Drawing

5 The invention will be further described with reference to the accompanying schematic drawing which shows a section of a composite thermally insulating cell cover in accordance with the invention.

Detailed Description

10 Figure 1 shows part of a composite thermally insulating cover 10 according to the invention which during use can be placed above a molten salt electrolyte of an electrolytic cell, in particular a cell for the electrowinning of aluminium from alumina dissolved in a fluoride-based crustless molten electrolyte.

15 The composite thermally insulating cover 10 comprises a plurality of superimposed layers 20,30 secured in a steel outer shell 40 which extends over the superimposed layers 20,30 and downwards along lateral sides of the cover 10.

20 As shown in Figure 1, the superimposed layers consist of three upper insulating layers 30 which can be made of known insulating material, for example CERABOARD™ material, and a lower protective layer 20. The protective layer 20 is made of the openly porous or
25 reticulated filled alumina structure according to the invention and shields the insulating layers 30 from corrosive media, such as NaAlF_4 , AlF_3 , HF or O_2 , present as vapours in an aluminium production cell above the molten electrolyte.

30 Superimposed layers 20,30 are secured in the steel outer shell 40 by pairs of nuts 50 and bolts 60, one pair of which is shown in Figure 1. The nuts 50 and bolts 60 can be made of ceramic material resistant to the corrosive media 1, such as fused alumina, or steel
35 preferably coated with this ceramic material. Each bolt 60 extends through vertically aligned holes 25,35,45 of steel shell 40, insulating layers 30 and protective layer 20 with the bolt 60's head 65 anchored in a recess 23 located in the bottom face of protective layer 20.

In accordance with the invention, the protective layer 20 is made of an openly porous or reticulated alumina structure which is impermeabilized by a compact filler 15 made of material resistant and inert to corrosive media 1 and comprising packed particles of at least one compound selected from metal oxides, carbides and nitrides, for instance an alumina cement.

The alumina structure of protective layer 20 is partly filled with filler 15, leaving on top a filler-free part 22 of the alumina structure. As shown in Figure 1, the filled part 21 of the alumina structure forms the outer bottom surface of cover 10. Filler 15 is also used to fill the recess 23, so the bolt's heads 65 are completely embedded in filler 15 and protected from corrosive media 1 contained in the aluminium production cell.

In a variation, the filler material of the protective layer 20 may extend outside the openly porous or reticulated structure, forming a surface layer on the bottom of cover 10. In another variation, the filler material extends throughout protective layer 20.

In a further variation, the head 65 of the bolt 60 can be anchored with cement in a recess (having similar dimensions as recess 23) located in the upper face of the protective layer 20. In this case, the bolt 60 does not extend through the protective layer 20 and no through hole is needed in the protective layer 20 whose bottom face is continuous.

The invention will be further described in the following Example.

Example 1

An openly porous alumina plate with a porosity of 20 ppi (equivalent to about 8 pores per centimetre) having a thickness of 5 cm and a surface of 25 x 25 cm was made impermeable to corrosive vapours by impregnating and coating its bottom face with an alumina slurry.

The slurry used to impermeabilize the porous alumina plate was KERATHIN HATM produced by RATH GmbH. This slurry is made of an aqueous binder containing

5 Layers of the slurry were successively applied to
the plate's bottom face. Each layer of the slurry was
allowed to dry for several minutes before applying the
next. After several layers of the slurry had been
applied, the dried and compacted slurry formed a filler
10 layer of 5 to 10 mm inside the plate and a coating of
about 3 mm outside the plate leaving the impregnated and
coated plate's bottom face with no surface porosity.
Typically, this can be achieved with three to six
applied layers of the slurry depending on its rheology.

An openly porous alumina plate with a porosity of 80 ppi (equivalent to about 32 pores per centimetre) having a thickness of 5 cm and a surface of 25 x 25 cm was made impervious by filling it throughout with a titania-alumina filler and then sealing it as in Example 1 by applying a coating on its bottom.

The titania-alumina filling was produced from a slurry made of 40 g TiO_2 particles (-325 mesh or <42 micrometer) in colloidal aluminium hydroxide consisting of 200 ml Nyacol® (Al-20, a milky liquid with a colloidal particle size grade of about 40 to 60 nanometer) and 20 ml CONDEA® (10/2 Sol, a clear, opalescent liquid with a colloidal particle size grade of about 10 to 30 nanometer), the aluminium hydroxide forming alumina upon heat treatment.

The porous alumina plate was immersed into the titania slurry to infiltrate it with the slurry and then dried for 20 minutes at 60°C. The infiltration was repeated followed by drying for 10 hours at 60°C (alternatively it can be dried for 24 hours at room temperature) and heat treating for 10 hours between about 780° and 800°C.

During heat treatment, the titania reacted with the aluminium hydroxide to form a stable titanium-aluminium mixed oxide which increase the stability of the alumina plate.

The filled alumina plate was then sealed off by coating its bottom face with an alumina slurry (KERATHIN HA™) as in Example 1.

Example 3

5 The impervious plates of Example 1 and 2 were tested as lids on top of crucibles containing a molten cryolite-based electrolyte at 870°C. The electrolyte comprised, in addition to cryolite, an excess of aluminium fluoride in an amount of 28% of the cryolite
10 weight.

During the test, the impermeabilized plates inhibited evaporation of the electrolyte and dissipation of heat.

15 After 3 weeks, the impermeabilized plates were removed from the crucibles. Visual examination of the impermeabilized plates showed that they had not been damaged by chemical attack or otherwise.

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CLAIMS

1. A thermally insulating cover of a cell for the electrowinning of aluminium from alumina dissolved in a fluoride-based molten electrolyte, which cover is inert and resistant to high temperature corrosive media in the form of liquids, vapours and/or gases that are contained in the cell and that comprise vapours from the electrolyte, and which cover during use is exposed to such corrosive media, said cover comprising thermal insulating material shielded from the corrosive media by an openly porous or reticulated alumina structure which is made impermeable by a compact filler made of material resistant and inert to said corrosive media, the filler material comprising compacted particles of refractory material.
2. The thermally insulating cover of claim 1, wherein said filler completely fills an outermost part of the structure, in particular a outermost bottom part.
3. The thermally insulating cover of claim 2, wherein the filler extends throughout the alumina structure.
4. The thermally insulating cover of claim 1 or 2, wherein the alumina structure is partly filled by the filler, leaving a filler-free part of the alumina structure, in particular a filler-free top part.
5. The thermally insulating cover of claim 4, wherein the filled part forms a layer in the alumina structure.
6. The thermally insulating cover of any preceding claim, wherein the alumina structure is a plate having a thickness in the range of 20 to 150 mm.
7. The thermally insulating cover of claim 6 when depending on claim 5, wherein the filler forms a layer in the plate, the layer having a thickness in the range of 10 to 100 mm.
8. The thermally insulating cover of any preceding claim, wherein the alumina structure is covered with a layer made of the filler material.

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9. The thermally insulating cover of claim 8, wherein the layer covering the alumina structure has a thickness in the range of 2 to 10 mm.

10. The thermally insulating cover of any preceding claim, wherein the refractory material of the filler comprises at least one compound selected from metal oxides, carbides and nitrides.

11. The thermally insulating cover of claim 10, wherein the filler comprises a mixture of metal oxide particles with particles of at least one compound selected from carbides and nitrides.

12. The thermally insulating cover of any preceding claim, wherein the filler is a slurry-applied filler comprising dried colloidal and/or non-colloidal particles of at least one compound selected from metal oxides, carbides and nitrides and precursors thereof.

13. The thermally insulating cover of claim 12, wherein the filler comprises a cement that consists predominantly of at least one of alumina, silica and titania particles.

14. The thermally insulating cover of claims 13, wherein the cement comprises a mixture of silica and alumina, preferably containing at least 80 weight% alumina.

15. The thermally insulated cover of claim 12, wherein the filler comprises a mixture of alumina and titania.

16. The thermally insulating cover of claim 12, wherein the filler comprises particles of at least one compound selected from carbides and nitrides in a dried colloidal metal oxide carrier.

17. The thermally insulating cover of any preceding claim, which comprises one or more insulating layers and a protective layer that shields the insulating layer(s) from said corrosive media, the protective layer being made of said openly porous or reticulated filled alumina structure.

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18. The thermally insulating cover of claim 17, wherein the insulating layer(s) and the protective layer are mechanically secured together.

5 19. The thermally insulating cover of claim 18, wherein the insulating layer(s) and the protective layer are mechanically secured together by means of one or more metallic attachment members extending through vertical holes of the protective layer and the insulating layer.

10 20. The thermally insulating cover of claim 19, wherein the or each vertical hole in the insulating layer(s) extends into a recess located in a bottom face of the alumina structure, said recess being arranged to embed a head of one or more of the attachment members, said recess being filled with said filler to protect the
15 attachment member from said corrosive media.

21. The thermally insulating cover of claim 17, 18, 19 or 20, which comprises a top metallic shell which extends over the insulating layer(s) and downwards along lateral sides of the cover.

20 22. A cell for the electrowinning of aluminium from alumina dissolved in a fluoride-based molten electrolyte, comprising a thermally insulating cover as defined in any preceding claim.

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