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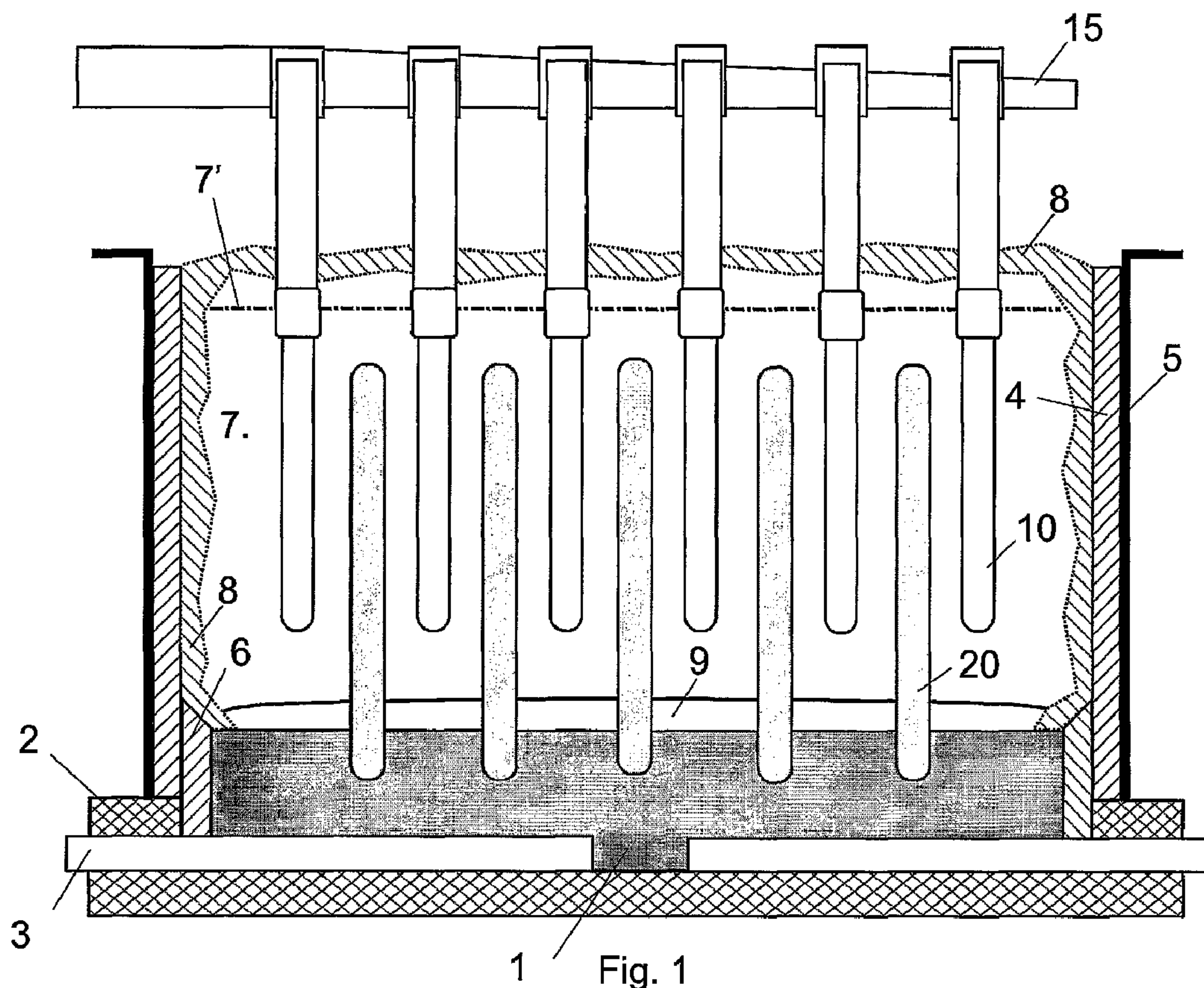
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(54) Titre : CELLULE D'EXTRACTION ELECTROLYTIQUE D'ALUMINIUM AVEC DES CATHODES A BASE DE METAL

(54) Title: ALUMINIUM ELECTROWINNING CELL WITH METAL-BASED CATHODES



(57) **Abrégé/Abstract:**

A cell for the electrowinning of aluminium has one or more anodes (10) facing at least one cathode (20). This cathode comprises: a cathode body (25) made predominantly of at least one hard metal selected from tungsten and molybdenum; and a surface of

(57) **Abrégé(suite)/Abstract(continued):**

carbide (26,27) of this hard metal which is integral with the body or which is formed by a layer bonded to the body. The carbide surface forms a cathodic operative surface on which during use aluminium (9) is produced or forms an anchorage surface for an aluminium-wettable ceramic layer (28,29) on which during use aluminium is produced.

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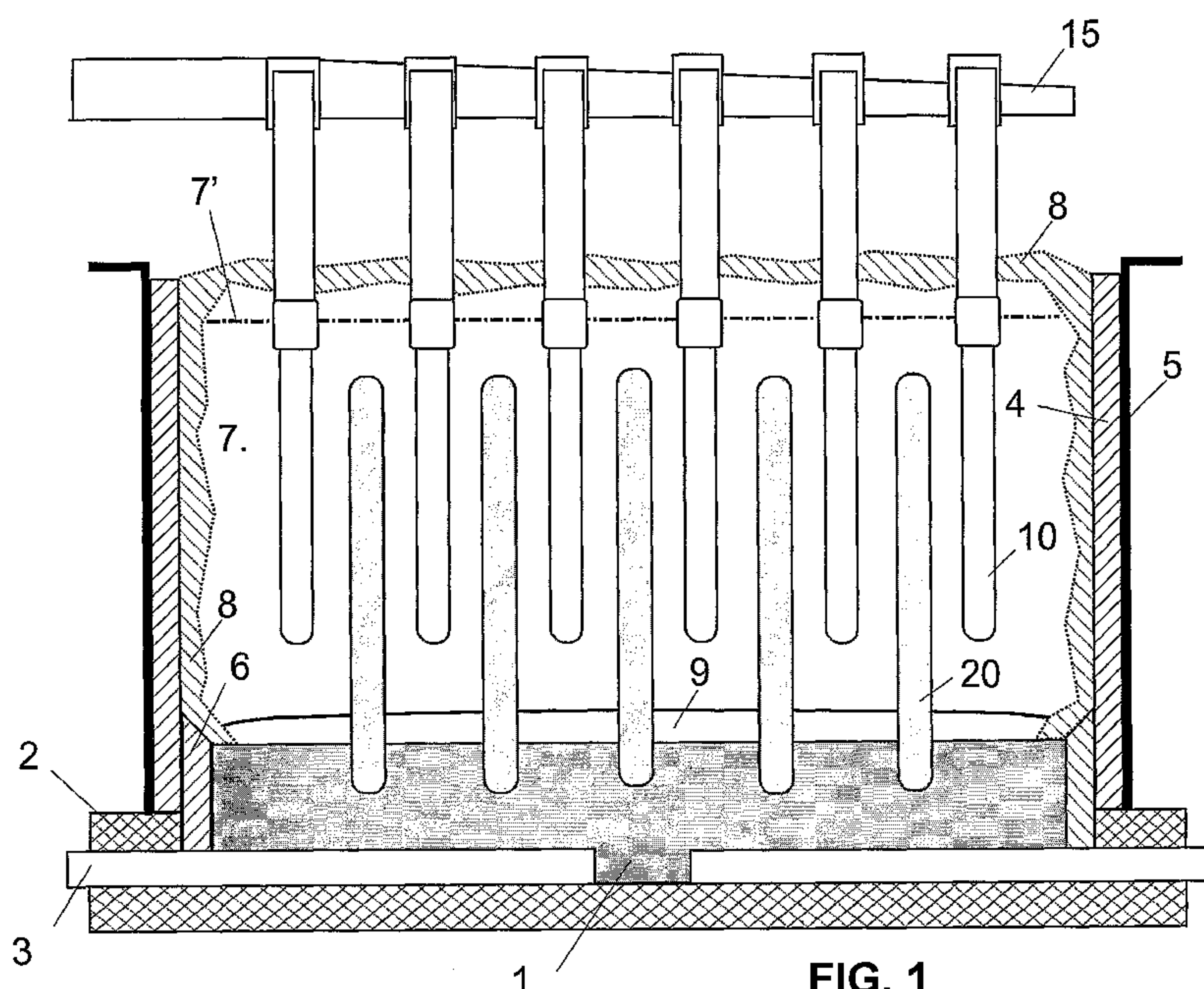


FIG. 1

(57) Abstract: A cell for the electrowinning of aluminium has one or more anodes (10) facing at least one cathode (20). This cathode comprises: a cathode body (25) made predominantly of at least one hard metal selected from tungsten and molybdenum; and a surface of carbide (26, 27) of this hard metal which is integral with the body or which is formed by a layer bonded to the body. The carbide surface forms a cathodic operative surface on which during use aluminium (9) is produced or forms an anchorage surface for an aluminium-wettable ceramic layer (28, 29) on which during use aluminium is produced.

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ALUMINIUM ELECTROWINNING CELLS WITH METAL-BASED CATHODES

Field of the Invention

The invention relates to a cell for the electrowinning of aluminium with a metal-based cathode on which during use aluminium is produced. The invention
5 also relates to a method for electrowinning aluminium in this a cell, to the cathode as such and to a method of manufacturing the cathode.

Background of the Invention

Aluminium is produced conventionally by the Hall-
10 Heroult process, by the electrolysis of alumina dissolved in cryolite-based molten electrolytes at temperatures up to around 950°C. A Hall-Heroult reduction cell typically has a steel shell provided with an insulating lining of refractory material, which in turn has a lining of carbon
15 which contacts the molten constituents. Conductor bars connected to the negative pole of a direct current source are embedded in the carbon cathode substrate forming the cell bottom floor. The cathode substrate is usually an anthracite based carbon lining made of prebaked cathode
20 blocks, joined with a ramming mixture of anthracite, coke, and coal tar, or with glue.

It has long been recognised that it would be desirable to make (or coat or cover) the cathode of an aluminium electrowinning cell with a refractory boride
25 such as titanium diboride that would render the cathode surface wettable by molten aluminium which in turn would lead to a series of advantages.

For example, US Patents 5,310,476, 5,364,513, 5,651,874 and 6,436,250 (all assigned to Moltech Invent
30 S.A.) disclose applying a protective coating of a refractory material such as titanium diboride to a carbon component of an aluminium electrowinning cell, by applying thereto a slurry of particulate refractory material and/or precursors thereof in a colloid in
35 several layers with drying between each layer. WO01/42168, WO01/42531 and WO02/096831 (all assigned to Moltech Invent S.A.) disclose the use of a layer made of particulate oxide of Mn, Fe, Co, Ni, Cu, Zn, Mo or La (-325 mesh) mixed with refractory material and/or on a
40 layer of refractory material. The use of these oxides

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promotes the wetting of the refractory material by molten aluminium. These patents also disclose the use of such materials in an oxidising and/or corrosive environment.

US patents 6,558,525, 6,800,191, 6,811,676 and
5 7,077,945 (all assigned to Northwest Aluminium) disclose aluminium electrowinning cells having vertical foraminated nickel-copper-iron anodes facing vertical cathodes, the cathodes being preferably made of titanium diboride or any suitable material that is substantially inert to
10 molten aluminium, such as zirconium diboride, titanium carbide, zirconium carbide, molybdenum or tungsten.

These materials have not as yet found wide commercial acceptance and there is a need to provide a cathodic material with improved properties for use in an
15 aluminium electrowinning cell.

Summary of the Invention

An object of the invention is to provide a cathode for an aluminium electrowinning cell, which cathode has a high conductivity, permits an enhanced current
20 distribution compared to carbon cathodes and is resistant to molten contents of the cell, in particular sodium.

A particular object of the invention is to provide a long lasting metal-based cathode for aluminium electrowinning cells.

25 Another object of the invention is to provide a metal-based cathode for aluminium electrowinning cell that is resistant to exposure to molten aluminium and has a low wear rate.

It has been observed that there is no substantial
30 inter-diffusion between tungsten or molybdenum and molten aluminium. However, the solubility of tungsten or molybdenum in molten aluminium is not sufficiently low to achieve, when used alone, the objects of the invention. Indeed, when an aluminium electrowinning cell utilises a
35 cathode of metallic tungsten or molybdenum in direct contact with molten aluminium, the corrosion rate of the tungsten or molybdenum cathode is of the order of 2 to 3 micron per hour, which is commercially unacceptable

This drawback has been overcome by providing the
40 cathode with a protective surface of tungsten carbide or molybdenum carbide in accordance with the invention. It has been found that tungsten carbide and molybdenum

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carbide are stable in molten aluminium. Moreover, such carbide is wettable by molten aluminium which makes its use suitable for providing an aluminium-wettable cathode surface.

5 Therefore, the invention relates to a cell for the electrowinning of aluminium from an aluminium compound dissolved in a molten electrolyte. The cell has one or more anodes facing at least one cathode. Such a cathode comprises: a cathode body made predominantly of at least
10 one hard metal selected from tungsten and molybdenum; and a surface of carbide of this hard metal which is integral with the cathode body or which is formed by a layer bonded to the cathode body. This carbide surface forms a cathodic operative surface on which during use aluminium
15 is produced or forms an anchorage surface for an aluminium-wettable ceramic layer on which during use aluminium is produced.

It follows that as opposed to the prior art (US patents 6,558,525, 6,800,191, 6,811,676 and 7,077,945),
20 tungsten and/or molybdenum cathode bodies of a cell of the present invention are covered with a carbide surface that significantly increases the resistance of the cathode body against wear and dissolution in the cell.

Moreover, the tungsten and/or molybdenum body with a
25 carbide surface has been found to resist penetration by sodium. Therefore, the use of such metal-based cathode bodies solves the problem of detrimental penetration of sodium from the electrolyte and thereby-caused swelling and wear that occur with carbon cathodes even when
30 covered with an RHM layer.

Typically, the cathode body contains the hard metal (tungsten and/or molybdenum) in an amount of 50 to 100%, in particular 75 to 98% such as 85 to 95%, by weight of the cathode body.

35 The cathode body may contain silicon in an amount of 0.1 to 30%, in particular 2 to 25% such as 5 to 15%, by weight of the cathode body. The cathode body can contain aluminium in an amount of 0.1 to 10 wt%, in particular 0.5 to 8% such as 2 to 6%, by weight of the cathode body.

40 Optionally, the cathode body contains further constituents such as Fe, Ni, Co, Mn, Cr, N, O, B and compounds thereof in a total amount of 0.1 to 5 wt%, in particular 0.5 to 2 wt%, by weight of the cathode body.

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In one embodiment, the cathode body is predominantly metallic or essentially metallic.

The cathode body may also contain carbon in an amount of 0.1 to 20 wt%, in particular 1 to 15% such as 5 to 10%, by weight of the cathode body. In such a case, a surface of the cathodic body can form the carbide surface of the cathode.

Typically, the carbide surface of the cathode is formed by a layer of the hard metal carbide integral with or bonded to the hard metal body, the carbide layer having a thickness of at least 0.01 mm, in particular in the range of 0.02 to 5 mm, such as 0.03 to 3 mm, typically 0.05 to 1 or 2 mm.

When the carbide surface itself forms the cathodic operative surface on which during use aluminium is produced, the layer of hard metal carbide should be sufficiently thick to provide a long-lasting protection against product aluminium. Usually, a thickness of the order of a couple of millimetres, such as 0.5 to 3 mm, or 1 to 2 mm, will be sufficient. When the carbide surface forms an anchorage surface for an aluminium-wettable ceramic layer on which during use aluminium is produced, the layer of hard metal carbide can be thinner, e.g. 10 to 400 micron, or 20 to 300 micron.

As mentioned above, in one embodiment of the invention, the cathode comprises an aluminium-wettable ceramic layer that is anchored onto the carbide surface and contains a refractory compound. This layer contains optionally an aluminium-wetting agent. The refractory compound can comprise one or more borides, in particular a boride of at least one metal selected from titanium, chromium, vanadium, zirconium, hafnium, niobium, tantalum, molybdenum, cerium, nickel and iron. The aluminium-wettable ceramic layer may contain an aluminium-wetting agent selected from at least one metal oxide and/or at least one partly oxidised metal, such as iron, copper, cobalt, nickel, zinc and manganese, in the form of oxides and partly oxidised metals and combinations thereof.

For instance, the aluminium-wettable ceramic layer is a sintered slurry of a particulate of the refractory compound and, when present, an optional wetting agent in a dried inorganic polymeric and/or colloidal binder. Usually, this slurry is a binder containing alumina,

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beryllium oxide, chromium oxide, silica, yttria, ceria, hafnia, thoria, zirconia, ruthenia, indium oxide, tin oxide, magnesia, lithia, vanadium oxide, titania, tantalum oxide, tungsten oxide, thallium oxide, molybdenum oxide, niobium oxide, gallium oxide, monoaluminium phosphate, cerium acetate, nickel oxide, $\text{FeO}(\text{OH})_2$, FeO , Fe_2O_3 and Fe_3O_4 and combinations and precursors thereof, all in the form of colloids and/or inorganic polymers.

Suitable aluminium-wettable ceramic layers are for example disclosed in US patents 5,364,513, 5,651,874, 6,436,250, and in PCT publications WO01/42168, WO01/42531, WO02/070783, WO02/096830 and WO02/096831, WO2004/092449, WO2005/068390 (all assigned to MOLTECH Invent S.A.).

Even though the cell may be fitted with carbon anodes, this is not preferred and instead the anode(s) are advantageously made of metal and/or ceramic material that is/are active for the evolution of oxygen, in particular having an electrochemically active oxide surface of oxides of at least one of iron, nickel and cobalt.

The active anodic surface can be the surface of an anode body that has a plurality of through passages for the flow of circulating electrolyte through the anode body from below to above the anode body and/or from above to below the anode body. The anode body may comprise a series of elongated members spaced apart by inter-member gaps which form said through passages, or the anode body may comprise a solid body, in particular a plate, which has through holes that form said through passages. Suitable anodes are disclosed in WO00/40781, WO00/40782, WO03/006716, WO03/023091, WO03/023091 and WO2005/118916 (all assigned to MOLTECH Invent S.A.).

Suitable materials for metal-based, in particular oxygen-evolving, anodes include at least one metal selected from nickel, iron, cobalt and copper. For instance the anode has a metal oxide surface, in particular a surface containing at least one of iron oxide, nickel oxide and cobalt oxide. Suitable anode materials are disclosed in WO99/36591 and WO99/36592, WO99/36593 and WO99/36594, WO00/06800, WO00/06801, WO00/06802 and WO00/06803, WO00/06804, WO00/06805, WO00/40783 and WO01/42534, WO01/42536, and WO01/43208, WO02/070786, WO02/083990, WO02/083991, WO03/078695,

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WO03/087435, WO2004/018731, WO2004/024994, WO2004/044268, WO2004/050956, WO2005/090641 and WO2005/090643 (all assigned to MOLTECH Invent S.A.). Oxygen-evolving anodes may be coated with a protective layer made of one or more cerium compounds, in particular cerium oxyfluoride, as disclosed in US Patents 4,614,569, 4,680,094, 4,683,037 and 4,966,674 (all assigned to MOLTECH Invent S.A.).

Another aspect of the invention relates to a method of electrowinning aluminium in a cell as described above. The method comprises passing an electrolysis current from the cathode(s) to the anode(s) through the molten electrolyte to electrolyse the dissolved alumina whereby gas is evolved anodically and aluminium is produced on the carbide surface of the cathode or on an aluminium-wettable ceramic layer anchored on said carbide cathode surface.

Advantageously the cell is in a drained configuration, aluminium being drained on the cathode. The aluminium can be drained on an upright or inclined cathode surface.

The cell's molten electrolyte is usually a fluoride-containing molten electrolyte, the electrolyte being at a temperature below 960°C, such as in the range from 900° to 950°C. The electrolyte may consist of: 6.5 to 11 weight% dissolved alumina, in particular 7 to 10 weight%; 35 to 44 weight% aluminium fluoride, in particular 36 to 42 weight%, such as 36 to 38 weight%; 38 to 46 weight% sodium fluoride, in particular 39 to 43 weight%; 2 to 15 weight% potassium fluoride, in particular 3 to 10 weight%, such as 5 to 7 weight%; 0 to 5 weight% calcium fluoride, in particular 2 to 4 weight%; and 0 to 5 weight% in total of one or more further constituents, in particular up to 3 weight%. Such further constituents may comprise at least one fluoride selected from magnesium fluoride, lithium fluoride, cesium fluoride, rubidium fluoride, strontium fluoride, barium fluoride and cerium fluoride.

The electrolyte can be a fluoride-containing electrolyte, for example as disclosed in WO00/06802, WO01/42535, WO02/097167, WO03/083176, WO2004/035871, WO2004/074549 and WO2005/090642 (all assigned to MOLTECH Invent S.A.).

A further aspect of the invention relates to a cathode for the electrowinning of aluminium from an

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aluminium compound dissolved in a molten electrolyte. The cathode comprises: a cathode body made predominantly of at least one hard metal selected from tungsten and molybdenum; and a surface of carbide of said hard metal which is integral with the cathode body or which is formed by a layer bonded to the cathode body, the carbide surface forming a cathodic operative surface on which during use aluminium is produced or forming an anchorage surface for an aluminium-wettable ceramic layer on which during use aluminium is produced.

The cathode may be shaped to be embedded in a cell bottom and protrude therefrom, or it can be suspended in the electrolyte. The cathode may comprise a connector for connection to a cathodic busbar, the connector optionally including a stem for suspending the cathode body in the molten electrolyte from a busbar located thereabove.

Yet another aspect of invention relates to a method of manufacturing such cathodes. The method comprises providing a cathodic body made predominantly of at least one hard metal selected from tungsten and molybdenum; and forming a surface of carbide of said hard metal which is integral with the body or formed by a layer bonded to the body.

The cathodic body can be made predominantly of at least one hard metal selected from metallic tungsten and molybdenum by carburizing the metallic surface. For instance, carburization can be carried out by heating the hard metal in the presence of carbon powders and/or in a methane-hydrogen atmosphere.

For instance, the cathodic body surface is carburized by contacting the surface with a carbon mass and subjecting the cathodic body in contact with the carbon mass to a carburization heat treatment, in particular at a temperature above 900°C. Such carbon mass may comprise: a mixture of carbon powder and pitch that is applied onto the cathode body's surface and dried; and a carbon powder bed into which the body with the applied and dried mixture is immersed. Optionally, a particulate refractory compound, in particular a boride, is added into or onto this mixture of carbon powder and pitch prior to drying.

In one embodiment, the carbide surface of the cathode body is covered by applying a layer of an aluminium-wettable ceramic layer, this layer containing

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optionally an aluminium-wetting agent, as mentioned above.

In a variation of the invention, it is also contemplated to use this hard metal (tungsten and/or molybdenum) having a carbide surface which is integral with the hard metal or which is formed by a layer bonded to the hard metal, with or without an applied aluminium-wettable ceramic top layer as a non-cathodic material, in particular a cell material that is exposed to molten aluminium during use. Such a protected hard metal can be used as part of a sidewall, sidewall lining or an aluminium collection reservoir or channel.

Brief Description of the Drawings

Embodiments of the invention will now be described by way of example with reference to the accompanying schematic drawings, wherein:

- Figures 1 and 2 show two aluminium electrowinning cells of the invention having vertical tungsten and/or molybdenum-based cathodes, Figure 1 in diagrammatic section along the cell and Figure 2 in diagrammatic section across the cell;

- Figures 3a, 3b, 4a and 4b show cut-away vertical tungsten and/or molybdenum-based cathodes according to the invention; and

- Figures 5 to 7 schematically show cut-away cross-sectional views of the external part of three different tungsten and/or molybdenum-based cathodes according to invention.

Detailed Description

Figures 1 and 2, in which the same numeric references designate the same elements, show two aluminium electrowinning cells according to the invention. The cells have a trough formed by: a conductive carbon bottom 1 that is embedded in a layer of insulating material 2 and that is connected via metal bars 3 to an external current supply; and insulating sidewalls 4 contained in an outer shell 5 connected to bottom 1 via ramming paste joint 6. The cell troughs enclose a molten electrolyte 7 that contains dissolved alumina, sidewalls 4 being protected from molten electrolyte 7 by a ledge and crust of frozen electrolyte 8 that extends along the entire sidewalls 4 and above

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molten electrolyte 7. Bottom 1 is protected from molten electrolyte 7 by a layer or pool of product molten aluminium 9.

5 The cells have vertical anodes 10,10' suspended from busbar 15 in molten electrolyte 7 to face vertical cathode rods 20. Such rods 20 have their bottom end mechanically secured and electrically connected to carbon bottom 1 as shown in greater detail in Figure 3a and 3b which are, respectively, a side view and a view from
10 above of a cathode rod 20 in a partly-shown bottom 1.

Anodes 10 shown in Figure 1 are in the form of vertical rods facing cathode rods 20. Anodes 10' shown in Figure 2 are vertically suspended plates that face rows of cathode rods 20. The anodes can have an
15 electrochemically active oxide surface of oxides of at least one of iron, nickel and cobalt, as mentioned above.

In accordance with the invention, the cathode rods 20 comprise: a cathode body made predominantly of at least one hard metal selected from tungsten and
20 molybdenum; and a surface of carbide of this hard metal which is integral with the body or which is formed by a layer bonded to the body. The carbide surface forms a cathodic operative surface on which during use aluminium 9 is produced or forms an anchorage surface for an
25 aluminium-wettable ceramic layer on which during use aluminium 9 is produced.

During use of the cells shown in Figures 1 and 2, an electrolysis current is supplied to bottom 1 via conductor bars 3 and fed into the bottom end of cathode
30 rods 20. The current is passed from the surfaces of cathode rods 20 through electrolyte 7 to anodes 10,10' so as to electrolyse dissolved alumina contained in electrolyte 7. Gas is evolved on anodes 10 and aluminium is produced on the carbide surface of the cathode 10 or
35 on an aluminium-wettable ceramic layer anchored on the carbide cathode surface. The product aluminium 9 is collected on bottom 1. Alumina is intermittently or continuously supplied to surface 7' at the top of electrolyte 7.

40 Figures 4a and 4b, in which the same numeric references designate the same elements, show a side view and a view from above, respectively, of another cathode 20' according to the invention. The cathode has a general pyramidal active part with inclined active faces 21. Such

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a cathode 20' is suitable for use with inclined anodes, for example in an anode-cathode arrangement as disclosed in US 6,797,148 and WO03/023096 (both assigned to MOLTECH INVENT S.A.).

5 Figures 5 to 7 illustrate cut-away sections of the outer portion of cathodes 20 according to the invention.

10 Figure 5 shows part of a cathode 20 having a metallic tungsten and/or molybdenum substrate 25 that has an integral surface layer 26 of tungsten and/or molybdenum carbide. Such surface layer 26 has a thickness of 10 micron to 1 mm and can be obtained by plasma spraying the components, e.g. tungsten and/or molybdenum carbide, of layer 26 or heat treatment of substrate 25 in a methane-containing environment. When the surface layer is thin (e.g. a few tens or hundreds of microns), it can be used as an anchorage layer for a ceramic cathodic layer or, when thicker, as a cathodic operative surface layer without an additional ceramic top layer. This cathode 20 can be manufactured by the method disclosed in
20 Example 1.

 The cathodes 20 shown in Figures 6 and 7 have both a substrate 25 of tungsten or molybdenum that is covered with a thin carbide anchorage layer 27. This anchorage layer 27 serves to anchor aluminium-wettable top layers
25 28 and 29 to substrate 25.

 In Figure 6, top layer 28 is made of particulate TiB_2 in a pitch binder optionally containing a wetting agent such as an oxide of iron, which can be produced by the method disclosed in Example 2 below. The top layer 29 shown in Figure 7 is made of a sintered particulate RHM, such as TiB_2 , applied in a colloidal binder and optionally containing a wetting agent, for example as disclosed in WO01/42168, WO01/42531 and WO02/096831 (all assigned to MOLTECH Invent S.A.). Top layers 28 and 29
35 are suitable to be used as an active operative cathode surface.

 The invention will be further described in the following examples.

Example 1

40 A tungsten cathode according to the invention was prepared as follows:

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A rod of metallic tungsten having a diameter of 10 mm and a length of 50 mm was submitted to a carburization treatment in a carbon powder bed, at 950 °C in air. After 16 hours of this carburization treatment, the rod was
5 allowed to cool down.

After cooling the rod was examined and showed a hard and black carburized tungsten surface. No oxidation was observed. Based on the weight gain of the rod, the thickness of the tungsten carbide layer was estimated to
10 be about 1 micron.

The carburized tungsten rod was tested as a hanging cathode facing a cobalt-based anode rod in a molten electrolyte of an aluminium electrowinning cell. The electrolyte was at a temperature of 930°C and made of
15 62.4 wt% Na_3AlF_6 , 11 wt% NaF , 7 wt% KF , 4% wt% CaF and 9.6 wt% Al_2O_3 . A current was passed between the anode and the cathode at a cathodic current density of 0.8 A/cm².

During electrolysis, the cell voltage showed over time a very regular saw tooth profile indicating that the
20 cathodic tungsten rod was well wetted by product aluminium. After 200 hours, the electrolysis was stopped and the cathode was removed from the cell to be examined.

The carburized tungsten cathodic rod showed no sign of wear. Its surface was covered with a layer of
25 aluminium indicating that it had been well wetted by molten aluminium during use. The change of dimension of the tungsten cathodic rod was less than 150 micron in the rod radius after 200 hours, or about 0.7 microns per hour which was at least 20 times less than the non carburized
30 cathode.

Compared to a non-carburized metallic tungsten cathode having a wear rate of 2 to 3 micron per hour during use, this test demonstrated that carburizing a
tungsten cathode prior to use is an appropriate pre-
35 treatment for improving the corrosion resistance of the cathode during use.

The corrosion resistance can be improved by forming at the surface of the tungsten cathodic rod a thicker carburized layer, for instance having a thickness in the
40 range of 0.05 to 1 mm, in particular 0.1 to 0.5 mm, for example by heat treating the tungsten cathodic rod in a methane-hydrogen atmosphere.

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Example 2

The starting point of this Example is based on two experimental observations:

5 - A titanium diboride-based coating can be obtained from a slurry of TiB_2 powders in carbon pitch (H. Oye et al.: TMS 2006 - pp. 262).

10 - A tungsten carbide layer that is formed by reaction between a metallic tungsten surface and a carbon source can be used as a diffusion bonding between the tungsten structure and the carbon matrix.

This Example therefore describes a cathodic tungsten rod which is coated with a TiB_2 -based coating as follows:

15 A layer of commercial cathode glue consisting essentially of a mixture of graphite powder and pitch was applied on a sandblasted surfaces of a tungsten rod.

Dry particulate TiB_2 was sprayed and incorporated into the still-humid cathode glue. The excess TiB_2 powder was eliminated by brushing. The applied TiB_2 -glue layer was dried for 30 minutes at 150 °C in air.

20 The application of a TiB_2 -glue layer was repeated five times overall. The five applied layers formed a green coating having a thickness of about 0.5 mm was obtained on the tungsten cathodic rod.

25 After application of the TiB_2 -glue coating the tungsten cathodic rod was placed in a graphite powder bed and submitted to a carburization reaction at 950 °C during 24 hours in air.

30 After carburization, the coated tungsten cathodic rod was allowed to cool down to room temperature and examined. The TiB_2 -based coating was coherent and showed no sign of any surface oxidation. The coating was hard and adhered well to the cathodic tungsten rod, i.e. resisting sandblasting.

35 Aluminium-wettability of the coating was improved by applying a layer of a copper slurry thereon, as taught in WO01/42168 (assigned to MOLTECH Invent SA), e.g. oxidised Cu particles in colloidal Al_2O_3 . As an alternative, this copper-based layer can be applied before carburization.

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The coated tungsten cathodic rod was then tested as a hanging cathode in a cell under the same conditions as described in Example 1.

5 After 200 hours, the electrolysis was stopped and the cathode was removed from the cell to be examined.

10 The TiB_2 -based coating had been fully impregnated by aluminium during electrolysis. The tungsten carbide layer underneath the TiB_2 -based coating formed a barrier layer on the metallic tungsten substrate so that this substrate contained no aluminium and showed no sign of diffusion or dissolution. No signs of wear were observed on the cathodic rod whose dimension had remained unchanged.

CLAIMS

1. A cell for the electrowinning of aluminium from an aluminium compound dissolved in a molten electrolyte, said cell having one or more anodes facing at least one cathode, said cathode comprising: a cathode body made predominantly of at least one hard metal selected from tungsten and molybdenum; and a surface of carbide of said hard metal which is integral with the cathode body or which is formed by a layer bonded to the cathode body, the carbide surface forming a cathodic operative surface on which during use aluminium is produced or forming an anchorage surface for an aluminium-wettable ceramic layer on which during use aluminium is produced.
2. The cell of claim 1, wherein the cathode body contains said hard metal(s) in an amount of 50 to 100%, in particular 75 to 98% such as 85 to 95%, by weight of the cathode body.
3. The cell of claim 1 or 2, wherein the cathode body contains silicon in an amount of 0.1 to 30%, in particular 2 to 25% such as 5 to 15%, by weight of the cathode body.
4. The cell of any preceding claim, wherein the cathode body contains aluminium in an amount of 0.1 to 10 wt%, in particular 0.5 to 8% such as 2 to 6%, by weight of the cathode body.
5. The cell of any preceding claim, wherein the cathode body contains further constituents such as Fe, Ni, Co, Mn, Cr, N, O, B and compounds thereof in a total amount of 0.1 to 5 wt%, in particular 0.5 to 2 wt%, by weight of the cathode body.
6. The cell of any preceding claim, wherein the cathode body under said cathode surface is predominantly metallic or essentially metallic.
7. The cell of any preceding claim, wherein the cathode body contains carbon an amount of 0.1 to 20 wt%, in particular 1 to 15% such as 5 to 10%, by weight of the cathode body.
8. The cell of claim 7, wherein a surface of the cathodic body forms said carbide surface.

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9. The cell of any preceding claim, wherein said carbide surface is formed by a layer of said hard metal carbide integral with or bonded to the hard metal body, the carbide layer having a thickness of at least 0.01 mm, in particular in the range of 0.02 to 5 mm, such as 0.03 to 3 mm, typically 0.05 to 1 or 2 mm.

10. The cell of any preceding claim, comprising an aluminium-wettable ceramic layer that is anchored onto the carbide surface and contains a refractory compound, said layer containing optionally an aluminium-wetting agent.

11. The cell of claim 10, wherein said refractory compound in the ceramic layer comprises one or more borides, in particular a boride of at least one metal selected from titanium, chromium, vanadium, zirconium, hafnium, niobium, tantalum, molybdenum, cerium, nickel and iron.

12. The cell of claim 10 or 11, wherein the aluminium-wettable ceramic layer also contains an aluminium-wetting agent selected from at least one metal oxide and/or at least one partly oxidised metal, such as iron, copper, cobalt, nickel, zinc and manganese, in the form of oxides and partly oxidised metals and combinations thereof.

13. The cell of any one of claims 10 to 12, wherein the aluminium-wettable ceramic layer is a sintered slurry of a particulate of the refractory compound and, when present, the optional wetting agent in a dried inorganic polymeric and/or colloidal binder, in particular a binder containing alumina, beryllium oxide, chromium oxide, silica, yttria, ceria, hafnia, thoria, zirconia, ruthenia, indium oxide, tin oxide, magnesia, lithia, vanadium oxide, titania, tantalum oxide, tungsten oxide, thallium oxide, molybdenum oxide, niobium oxide, gallium oxide, monoaluminium phosphate, cerium acetate, nickel oxide, $\text{FeO}(\text{OH})_2$, FeO , Fe_2O_3 and Fe_3O_4 and combinations and precursors thereof, all in the form of colloids and/or inorganic polymers.

14. The cell of any preceding claim, wherein the anode(s) is/are made of metal and/or ceramic material that is/are active for the evolution of oxygen, the anodes comprising in particular an electrochemically active oxide surface of oxides of at least one of iron, nickel and cobalt.

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15. A method of electrowinning aluminium in a cell as defined in any preceding claim, which method comprises passing an electrolysis current from the cathode(s) to the anode(s) through the molten electrolyte to electrolyse the dissolved alumina whereby gas is evolved anodically and aluminium is produced on the carbide surface of the cathode or on an aluminium-wettable ceramic layer anchored on said carbide cathode surface.
16. The method of claim 15, wherein aluminium is drained on the cathode.
17. The method of claim 16, wherein the aluminium is drained on an upright or inclined cathode surface.
18. The method of any one of claims 15 to 17, wherein the molten electrolyte is a fluoride-containing molten electrolyte, the electrolyte being at a temperature below 960°C, such as in the range from 900° to 950°C, and optionally consisting of:
- 6.5 to 11 weight% dissolved alumina, in particular 7 to 10 weight%;
 - 35 to 44 weight% aluminium fluoride, in particular 36 to 42 weight%, such as 36 to 38 weight%;
 - 38 to 46 weight% sodium fluoride, in particular 39 to 43 weight%;
 - 2 to 15 weight% potassium fluoride, in particular 3 to 10 weight%, such as 5 to 7 weight%;
 - 0 to 5 weight% calcium fluoride, in particular 2 to 4 weight%; and
 - 0 to 5 weight% in total of one or more further constituents, in particular up to 3 weight%.
19. The method of claim 18, wherein the electrolyte comprises, as said further constituent(s), at least one fluoride selected from magnesium fluoride, lithium fluoride, cesium fluoride, rubidium fluoride, strontium fluoride, barium fluoride and cerium fluoride.
20. A cathode for the electrowinning of aluminium from an aluminium compound dissolved in a molten electrolyte, comprising: a cathode body made predominantly of at least one hard metal selected from tungsten and molybdenum; and a surface of carbide of said hard metal which is integral with the cathode body or which is formed by a layer bonded to the cathode body, the carbide surface forming a cathodic operative surface on which during use aluminium is produced or forming an anchorage surface for an

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aluminium-wettable ceramic layer on which during use aluminium is produced.

21. A method of manufacturing a cathode as defined in claim 20, comprising providing a cathode body made
5 predominantly of at least one hard metal selected from tungsten and molybdenum; and forming a surface of carbide of said hard metal which is integral with the cathode body or formed by a layer bonded to the cathode body.

22. The method of claim 21, comprising providing a
10 cathodic body made predominantly of at least one hard metal selected from metallic tungsten and molybdenum and carburizing the metallic surface.

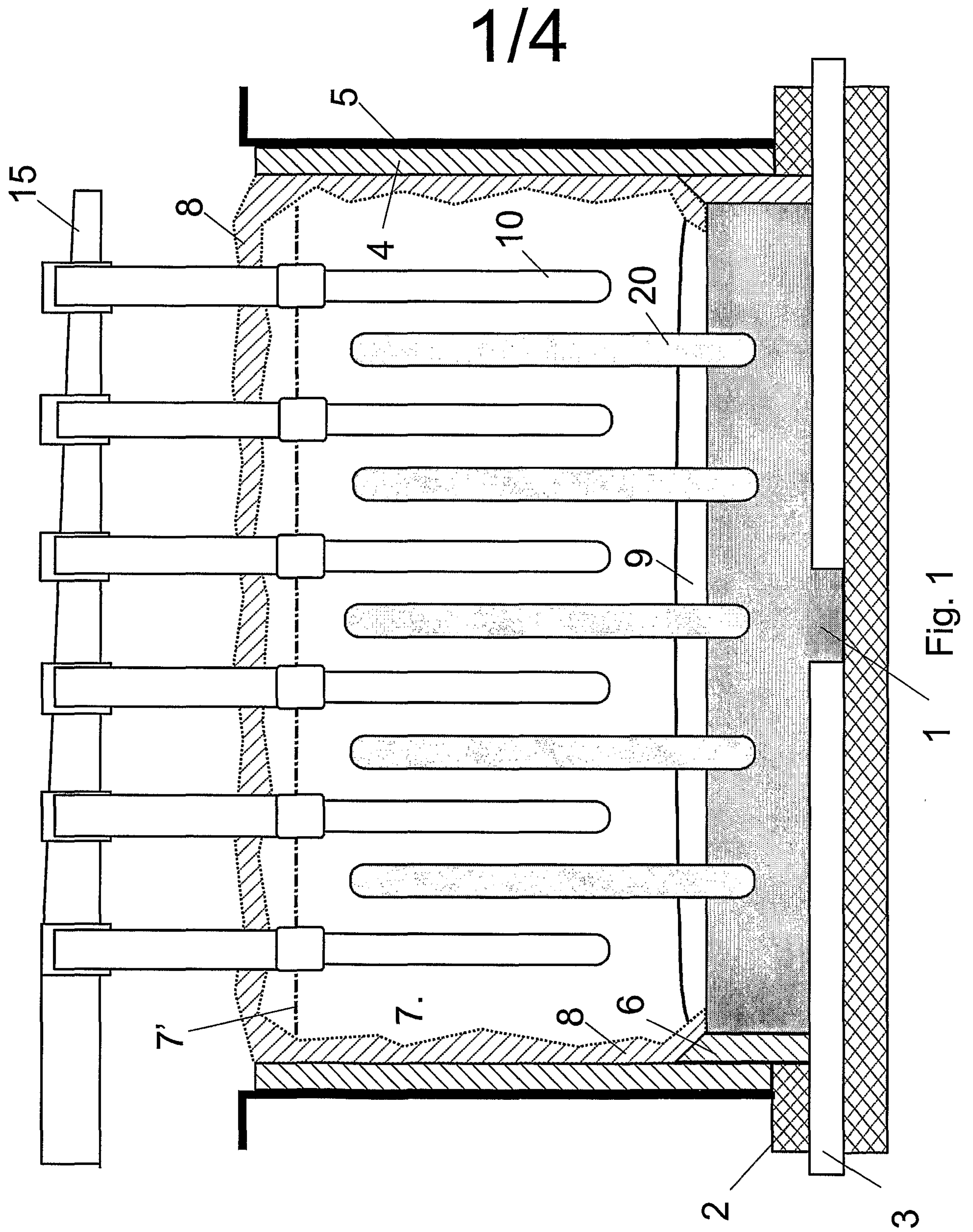
23. The method of claim 22, wherein the cathode body's surface is carburized by contacting the surface with a
15 carbon mass and subjecting the cathode body in contact with the carbon mass to a carburization heat treatment, in particular at a temperature above 900°C.

24. The method of claim 23, wherein the carbon mass comprises: a mixture of carbon powder and pitch that is
20 applied onto the cathode body's surface and dried; and a carbon powder bed into which the body with the applied and dried mixture is immersed.

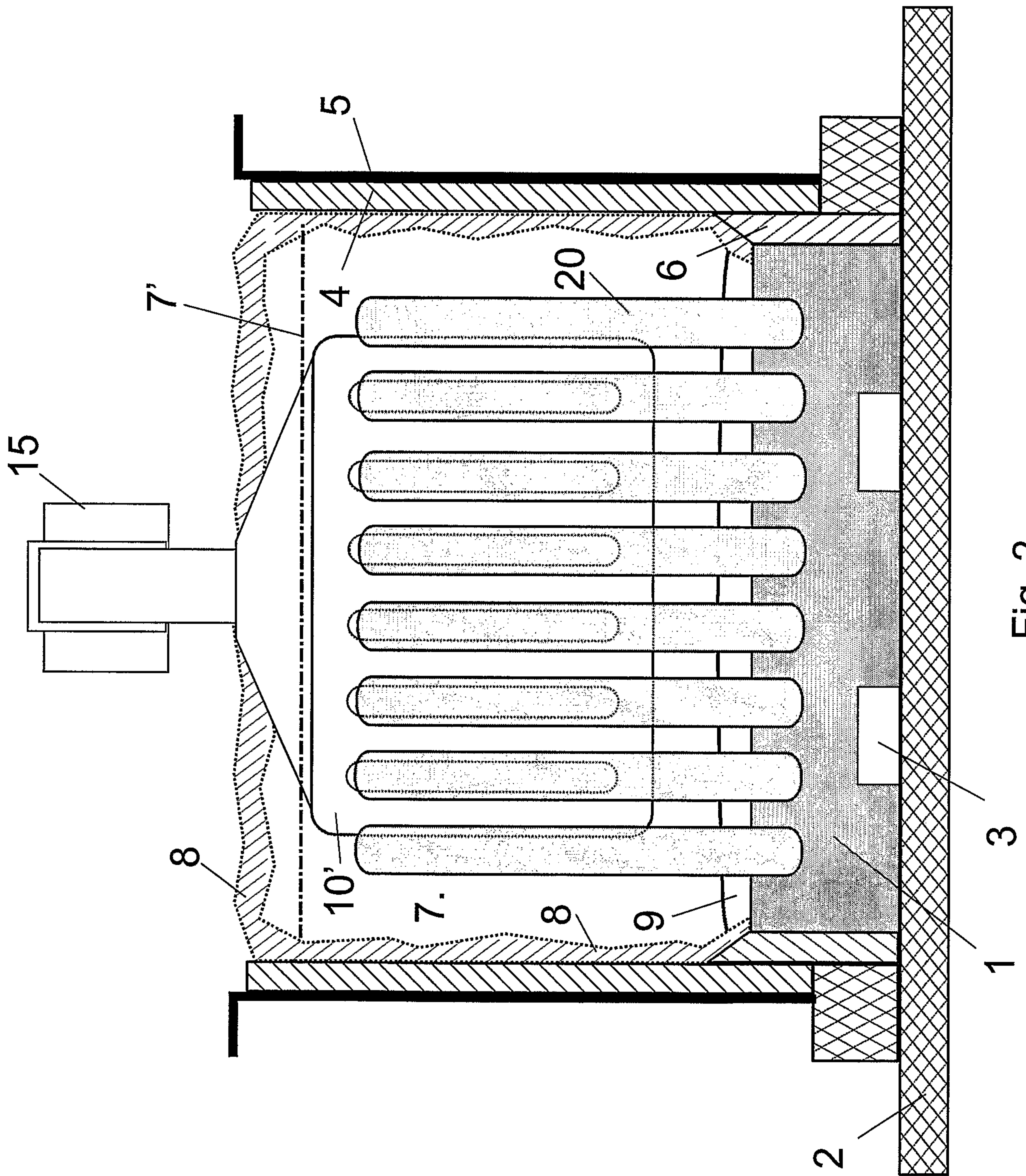
26. The method of claim 25, wherein a particulate refractory compound, in particular a boride, is added
25 into or onto said mixture prior to drying.

27. The method of any one of claims 22 to 26, wherein the carbide surface of the cathode body is covered with a layer of an aluminium-wettable ceramic layer, said layer containing optionally an aluminium-wetting agent.

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Fig. 3a

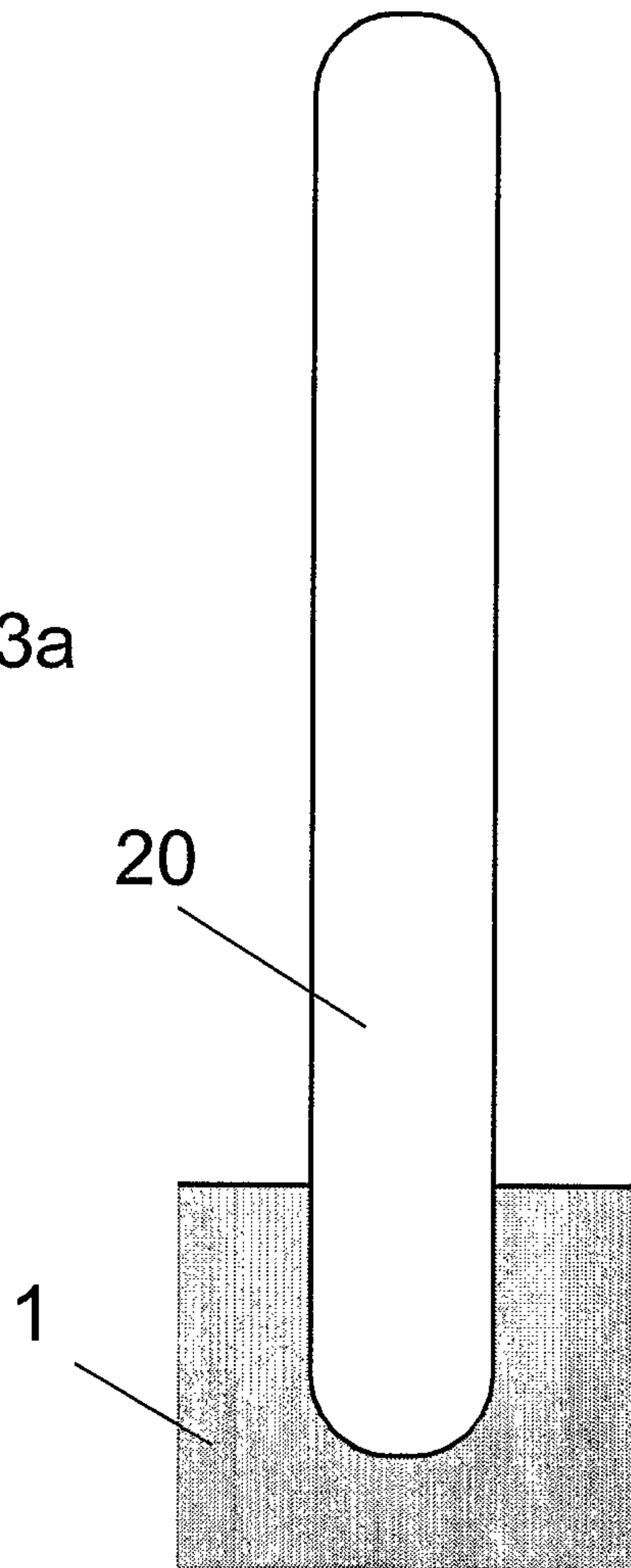


Fig. 4a

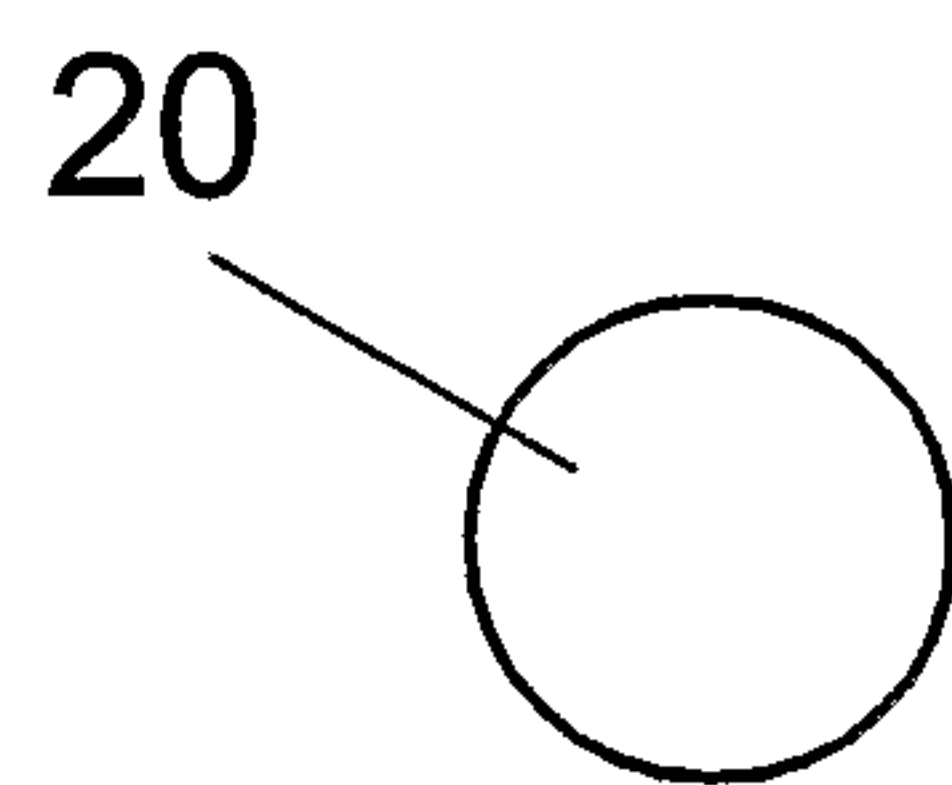
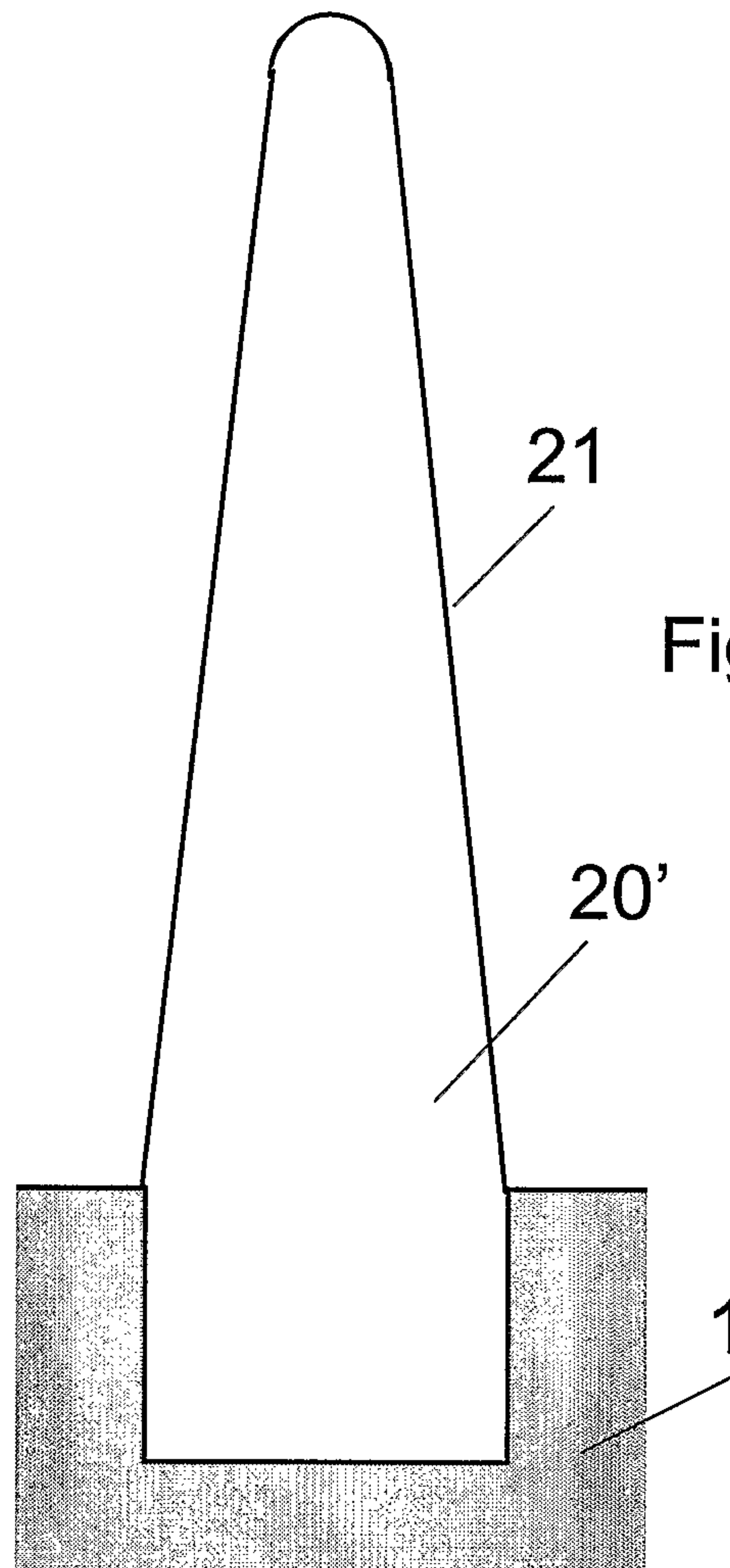


Fig. 3b

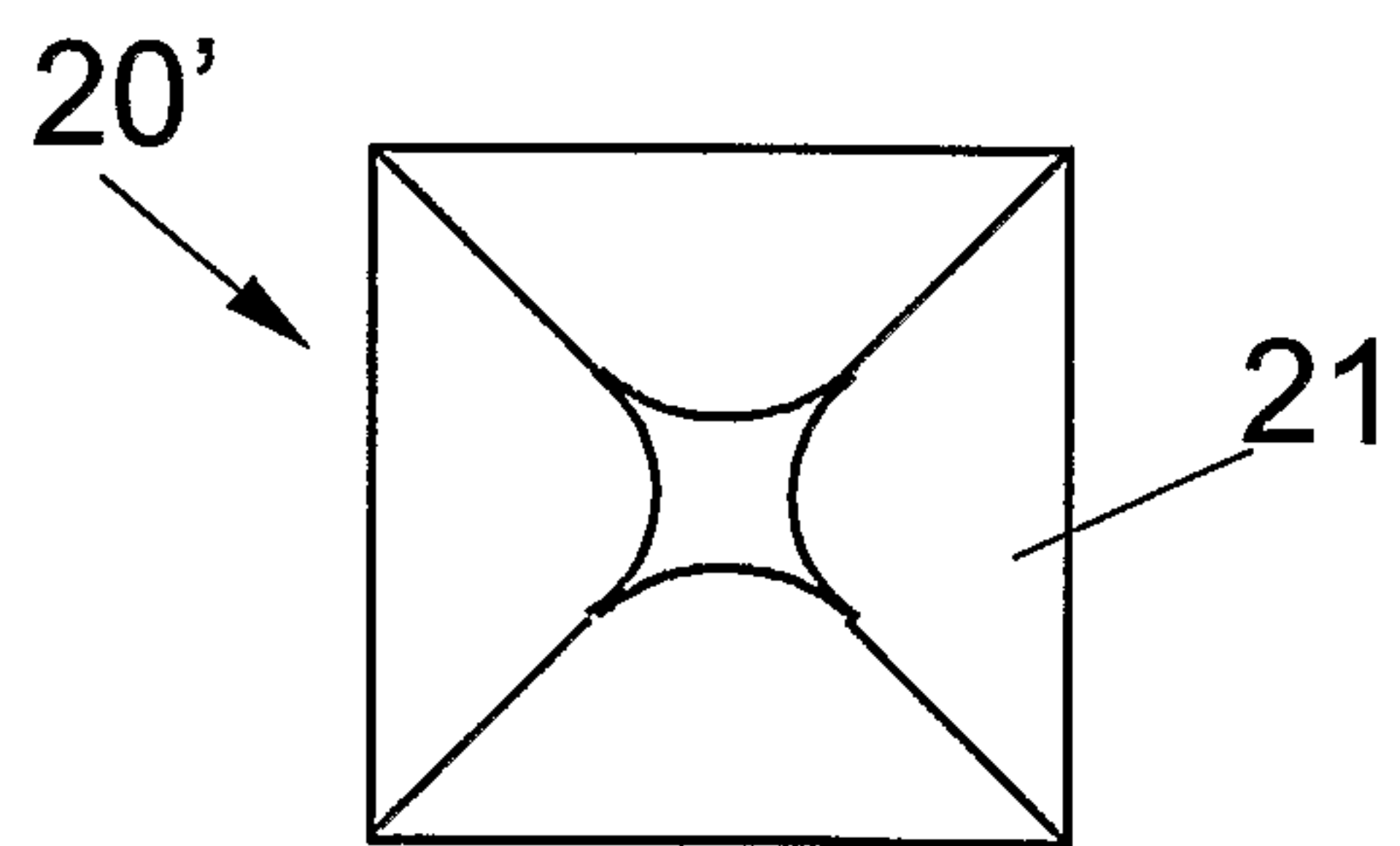


Fig. 4b

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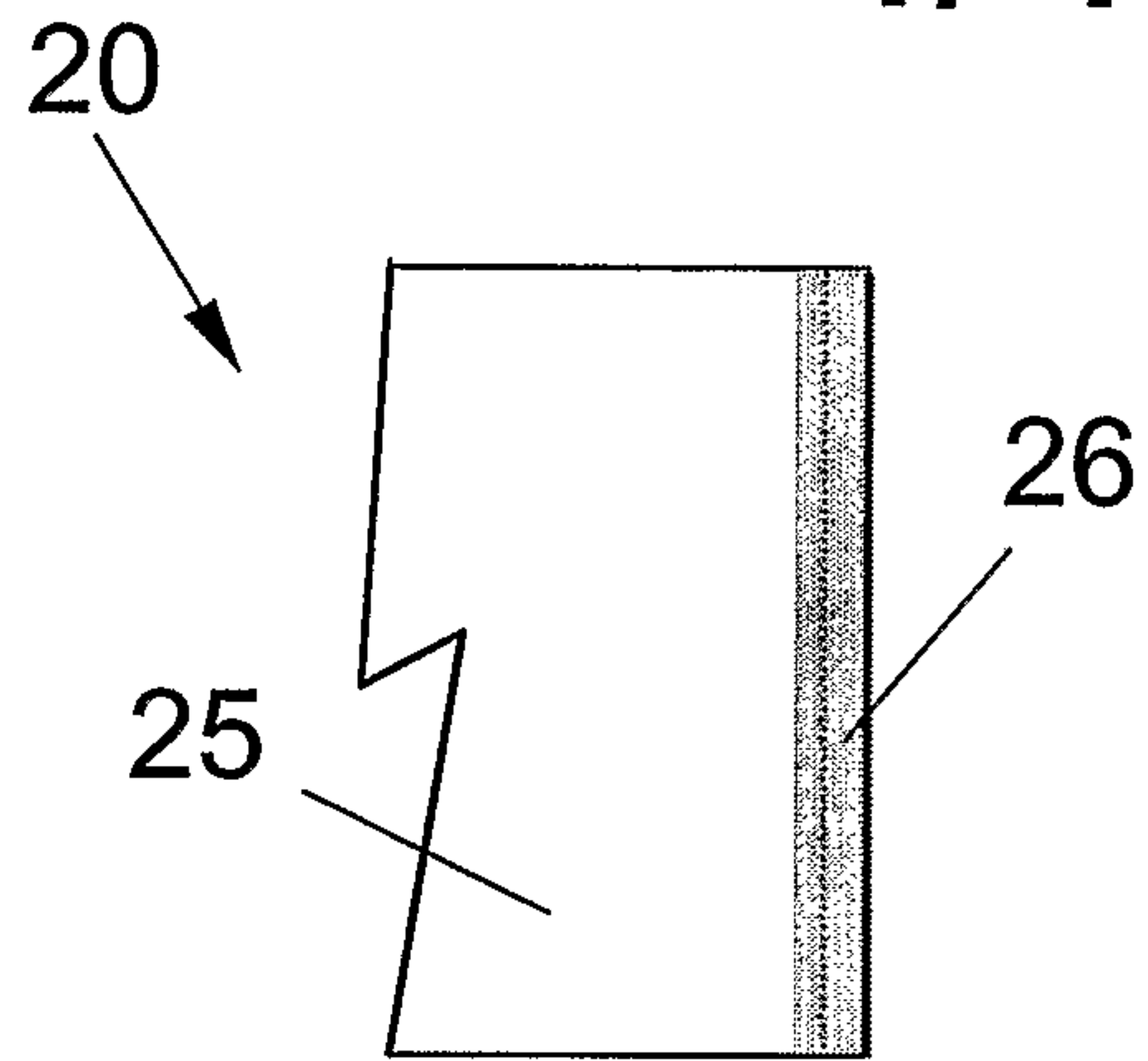


Fig. 5

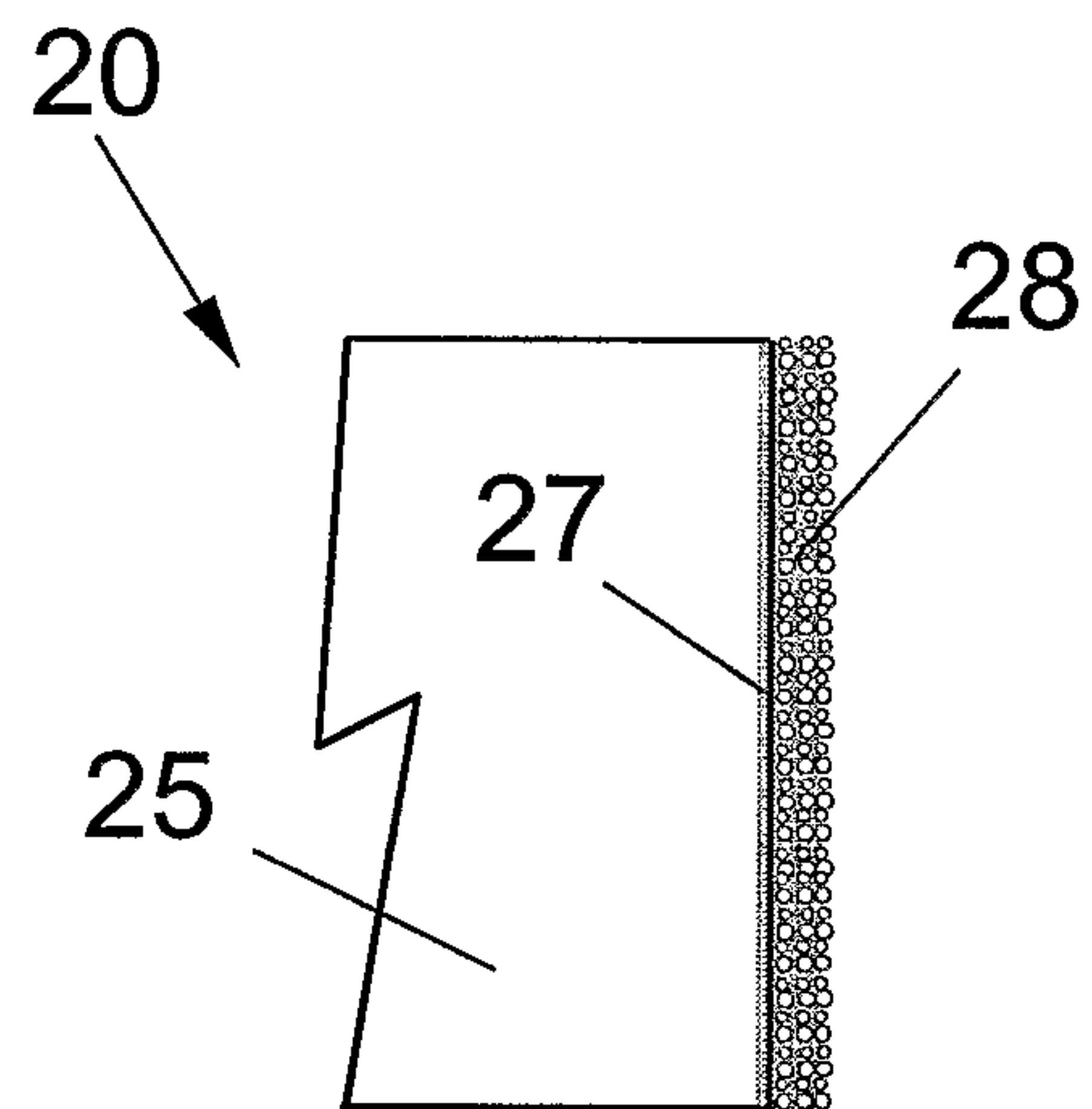


Fig. 6

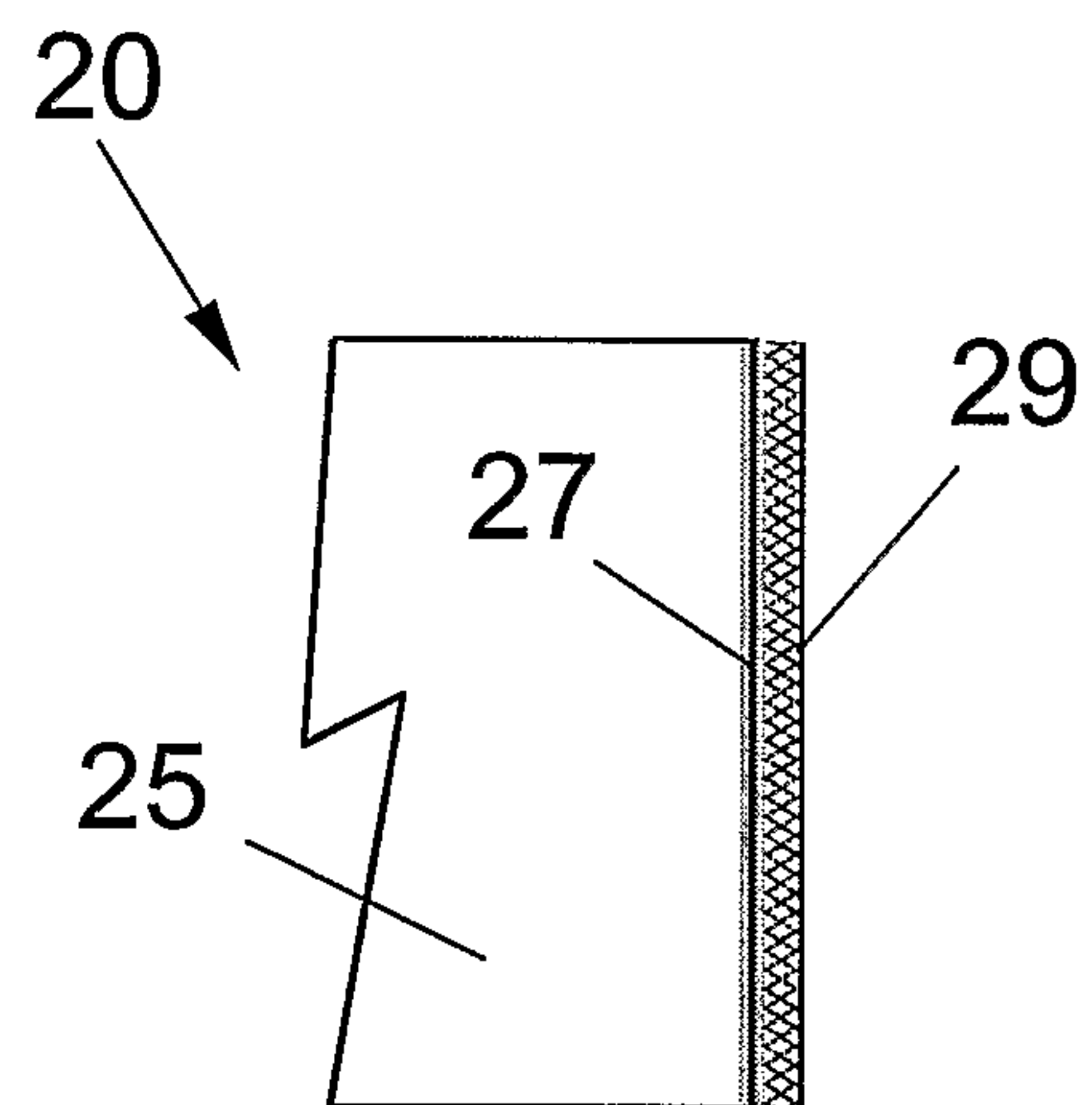


Fig. 7

