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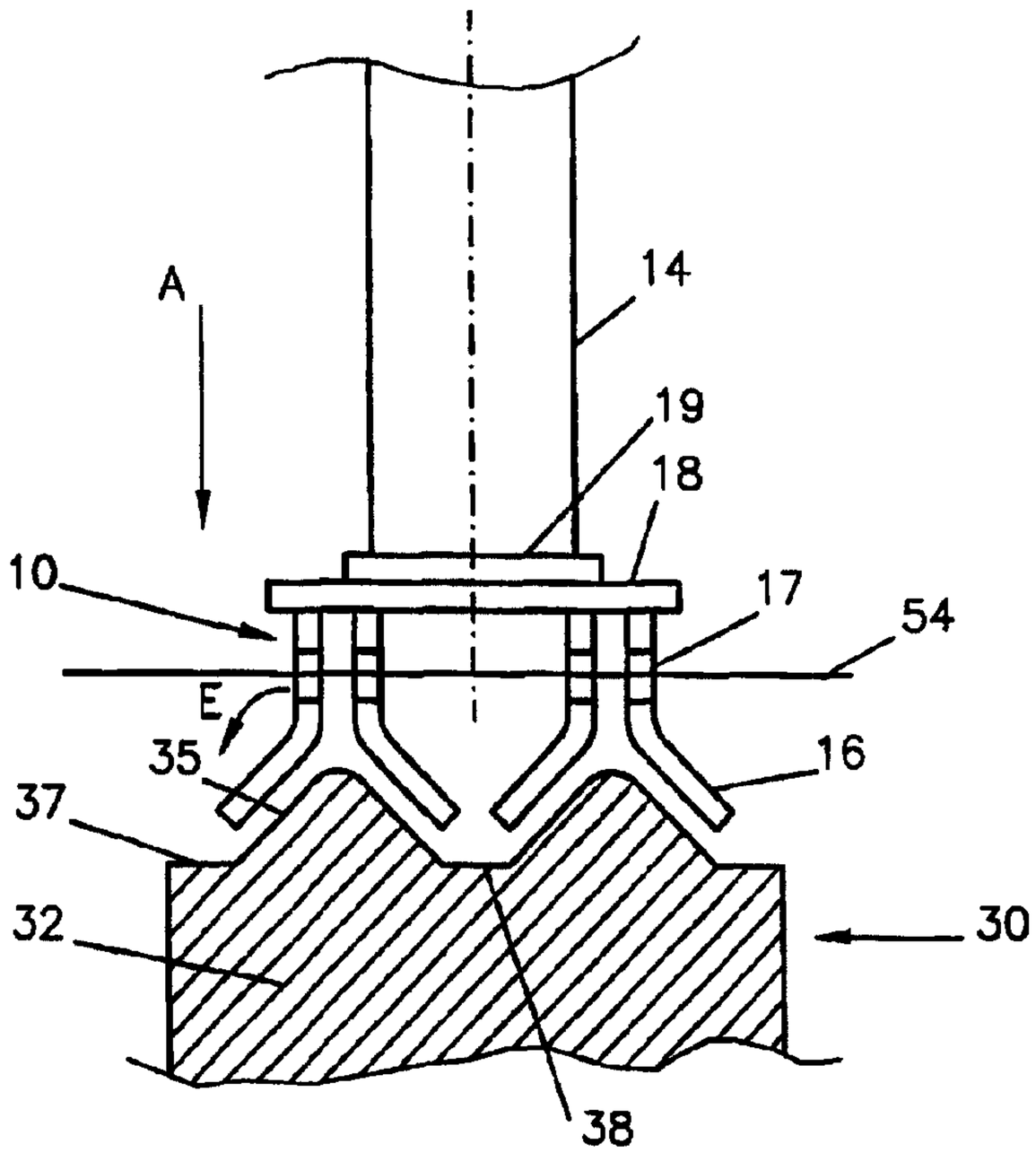
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(54) Title: A DRAINED CATHODE CELL FOR THE PRODUCTION OF ALUMINIUM



(57) Abrégé/Abstract:
A drained cathode cell for the produc-tion of aluminium by the electrolysis of an aluminium compound dissolved in a molten electrolyte, in which a dimensionally stable active cathode surface (35) has a sloping aluminium-wettable surface (37) permitting the produced aluminium to drain from the cathode surface. The anodes (10) are carbon or non-carbon anodes with active faces (16) facing cathode surfaces (35) both at a slope up to about 60°. The anode-cathode gap between the sloping anodes and cathodes is no more than 3 cm and is configured such that an upward circulation of the electrolyte is induced in the anode-cathode space by the anodically-released gases. An alumina-rich melt is fed at the lower part of the anode-cathode gap.

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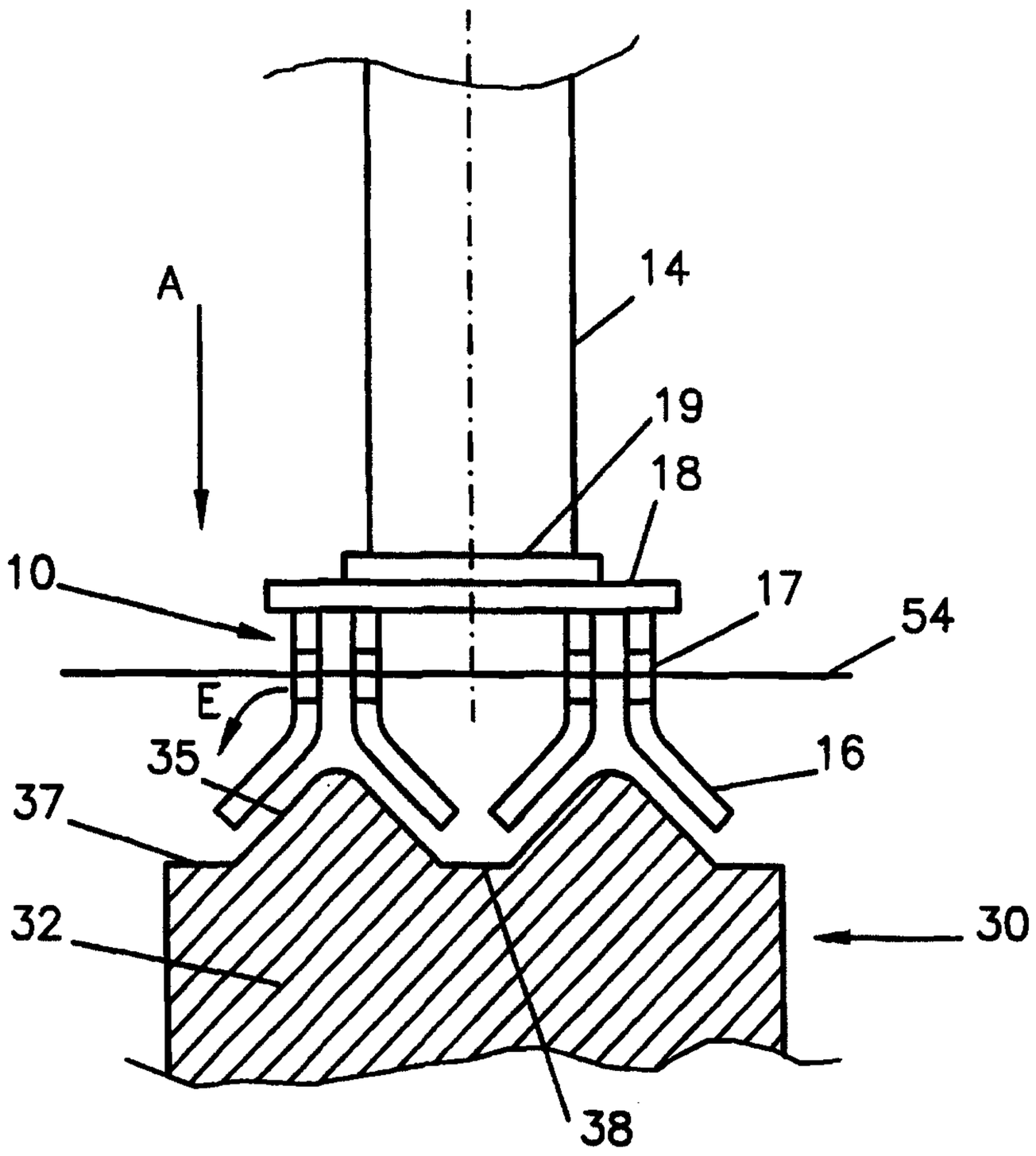
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(57) Abstract

A drained cathode cell for the production of aluminium by the electrolysis of an aluminium compound dissolved in a molten electrolyte, in which a dimensionally stable active cathode surface (35) has a sloping aluminium–wettable surface (37) permitting the produced aluminium to drain from the cathode surface. The anodes (10) are carbon or non–carbon anodes with active faces (16) facing cathode surfaces (35) both at a slope up to about 60°. The anode–cathode gap between the sloping anodes and cathodes is no more than 3 cm and is configured such that an upward circulation of the electrolyte is induced in the anode–cathode space by the anodically–released gases. An alumina–rich melt is fed at the lower part of the anode–cathode gap.



A DRAINED CATHODE CELL FOR THE PRODUCTION OF ALUMINIUM

Field of the Invention

The invention relates to cells for the production of aluminium by the electrolysis of an aluminium compound dissolved in a molten electrolyte, for example alumina dissolved in a molten fluoride-based electrolyte.

It concerns in particular an aluminium production cell of drained configuration in which the aluminium pool protecting the carbon cathodes is no longer required because the carbon cathodes are protected by an aluminium wettable coating or are not made of carbon and are drained whereby the aluminium produced which is formed on the drained surface is collected and tapped.

The invention also concerns a method of producing aluminium in this drained cathode cell.

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.

This process, conceived almost simultaneously by Hall and Héroult, has not evolved as much as other electrochemical processes, despite the tremendous growth in the total production of aluminium that in fifty years has increased almost one hundred fold. The process and the cell design have not undergone any great change or improvement and carbonaceous materials are still used as electrodes and cell linings.

The electrolytic cell trough is typically made of a steel shell provided with an insulating lining of refractory material covered by prebaked anthracite-graphite

or all graphite carbon blocks at the cell floor bottom which acts as cathode and to which the negative pole of a direct current source is connected by means of steel conductor bars embedded in the carbon blocks. The side walls are also covered with prebaked anthracite-graphite carbon plates or silicon carbide plates.

The anodes are still made of carbonaceous material and must be replaced every few weeks. The operating temperature is still approximately 950°C in order to have a sufficiently high rate of dissolution of alumina which decreases at lower temperatures and to have a higher conductivity of the electrolyte.

The carbonaceous materials used in Hall-Héroult cells as cell lining deteriorate under the existing adverse operating conditions and limit the cell life.

Another major drawback, however, is due to the fact that irregular electromagnetic forces create waves in the molten aluminium pool and the anode-cathode distance (ACD), also called interelectrode gap (IEG), must be kept at a safe minimum value of approximately 50 mm to avoid short circuiting between the aluminium cathode and the anode or reoxidation of the metal by contact with the CO_2 gas formed at the anode surface, leading to a lower current efficiency.

The high electrical resistivity of the electrolyte, which is about 0.4 ohm. cm., causes a voltage drop which alone represents more than 40% of the total voltage drop with a resulting high energy consumption which is close to 13kWh/kgAl in the most modern cells. The cost of energy consumption has become an even bigger item in the total manufacturing cost of aluminium since the oil crisis, and has decreased the rate of growth of this important metal.

In the second largest electrochemical industry following aluminium, namely the caustic and chlorine industry, the invention of the dimensionally stable anodes (DSA®) based on noble metal activated titanium metal, which were developed around 1970, permitted a revolutionary progress in the chlorine cell technology resulting in a

substantial increase in cell energy efficiency, in cell life and in chlorine-caustic purity. The substitution of graphite anodes with DSA® increased drastically the life of the anodes and reduced substantially the cost of operating the cells. Rapid growth of the chlorine caustic industry was retarded only by ecological concerns.

In the case of aluminium production, pollution is not due to the aluminium produced, but to the materials and the manufacturing processes used and to the cell design and operation.

However, progress has been reported in the operation of modern aluminium plants which utilize cells where the gases emanating from the cells are in large part collected and adequately scrubbed and where the emission of highly polluting gases during the manufacture of the carbon anodes and cathodes is carefully controlled.

While progress has been reported in the use of carbon cathodes to which have been applied coatings or layers of new aluminium wettable materials which are also a barrier to sodium penetration during electrolysis, very little progress has been achieved in design of cathodes for aluminium production cells with a view to improving the overall cell efficiency, simplifying assembly of the cathodes in the cell, simplifying the removal and disposal of used cathodes, as well as restraining movement of the molten aluminium in order to reduce the interelectrode gap and the rate of wear of its surface.

U.S. Patent 3,202,600 (Ransley) proposed the use of refractory borides and carbides as cathode materials, including a drained cathode cell design wherein a wedge-shaped consumable carbon anode was suspended facing a cathode made of plates of refractory boride or carbide in V-configuration.

U.S. Patents 3,400,061 (Lewis et al) and 4,602,990 (Boxall et al) disclose aluminium electrowinning cells with sloped drained cathodes arranged with the cathodes and facing anode surfaces sloping across the cell. In these cells, the molten aluminium flows down the sloping cathodes

into a median longitudinal groove along the centre of the cell, or into lateral longitudinal grooves along the cell sides, for collecting the molten aluminium and delivering it to a sump.

U.S. Patent 4,544,457 (Sane et al) proposed a drained cathode arrangement in which the surface of a carbon cathode block was covered with a sheath that maintained stagnant aluminium on its surface in order to reduce wear. In this design, the cathode block stands on the cell bottom.

U.S. Patent 5,203,971 (de Nora et al) discloses an aluminium electrowinning cell having a partly refractory and partly carbon based cell lining. The carbon-based part of the cell bottom may be recessed in respect to the refractory part, which assists in reducing movement of the aluminium pool.

An improvement described in U.S. Patent 5,472,578 (de Nora) consisted in using grid-like bodies which could form a drained cathode surface and simultaneously restrain movement in the aluminium pool.

U.S. Patent 5,316,718 and WO 93/25731 (both in the name of Sekhar et al) proposed coating components with a slurry-applied coating of refractory boride, which proved excellent for cathode applications. These publications included a number of novel drained cathode configurations, for example including designs where a cathode body with an inclined upper drained cathode surface is placed on or secured to the cell bottom.

In U.S. Patent 5,362,366 (de Nora et al), a double-polar anode-cathode arrangement was disclosed wherein cathode bodies were suspended from the anodes permitting removal and reimmersion of the assembly during operation, such assembly also operating with a drained cathode.

U.S. Patent 5,368,702 (de Nora) proposed a novel multimonopolar cell having upwardly extending cathodes facing and surrounded by or in-between anodes having a relatively large inwardly-facing active anode surface area.

In some embodiments, electrolyte circulation was achieved using a tubular anode with suitable openings.

WO 96/07773 (de Nora) proposed a new cathode design for a drained cathode, where grooves or recesses were incorporated in the surface of blocks forming the cathode surface in order to channel the drained product aluminium.

In summary, since commercial production of aluminium begun the cells have characteristics which have permitted an increase in the total production and a reduction of cost.

Aluminium is present in the electrolyte as a suspension of small particles, soluble in small amounts, and reacts with the anode gas which contains mainly CO_2 formed by the reaction of oxygen with carbon. This is facilitated by the fact that the bubbles of CO_2 which form on the anode escape with difficulty from under the anode, through the electrolyte, before the gas is collected and purified to recover fluorides and eliminate other dangerous polluting impurities.

The reaction between aluminium and CO_2 which reduces considerably the current efficiency of the process is facilitated by the movement of the electrolyte due to the intermittent escape of big bubbles formed, and by the movement of the aluminium pool maintained on top of the carbon cathode to protect the cathode from chemical corrosion by the formation of aluminium carbide. Such movement of the aluminium pool, due to the electromagnetic forces which become violent when the current distribution is not uniform, additionally leads to erosion of the cathode surface.

Attempts have been made to improve the situation such as by decreasing the size of the active surface of each anode - see the above-mentioned U.S. Patent 5,368,702 (de Nora) - in order to have a more uniform current distribution.

Of course, an improvement could be obtained if the active surface of the cathode and of the anode would be at a slope to facilitate the escape of the bubbles of the

released gas. Moreover, to have a cathode at a slope and obtain an efficient operation of the cell would be possible only if the surface of the cathode were aluminium-wettable so that the production of aluminium ions would take place on a film of aluminium. So far, attempts to achieve this have failed.

Only recently has it become possible to coat carbon cathodes with a slurry which adheres to the carbon and becomes aluminium-wettable and very hard when the temperature reaches 700-800°C or even 950-1000°C, as disclosed in the aforementioned U.S. Patent 5,316,718 and WO 93/25731 (both in the name of Sekhar et al). Though application of these coating to drained cathode cells has been proposed, so far the commercial-scale application of this technology has been confined to coating carbon bottoms of cells operating with the conventional deep pool of aluminium. Further design modifications in the cell construction could lead to obtaining more of the potential advantages of these coatings.

While the foregoing references indicate continued efforts to improve the operation of molten cell electrolysis operations, none suggest the invention and there have been no acceptable proposals for improving the efficiency cell, and at the same time facilitating the implementation of a drained cathode configuration.

Objects of the Invention

One object of the present invention is to provide a drained cathode cell for the production of aluminium which has characteristics which make the cell efficient from the point of high current efficiency but also from the point of view of reduced energy consumption.

Another object of the invention is to overcome problems inherent in known designs of drained cathode cells used in the electrowinning of aluminium wherein electrolyte circulation is induced by anodically-released gases with feeding of an alumina-rich melt at the lower part of the anode-cathode gap.

Yet another object of the invention is to provide a drained cathode cell in which the product aluminium can be better moved and collected.

A further object of the invention is to enhance the circulation of electrolyte in a drained cathode cell by using non-carbon oxygen-evolving anodes designed to favour the escape of the anodically-produced gas while promoting circulation of the electrolyte.

A yet further object of the invention is to provide a drained cathode cell in which the cell sidewall also acts as an active cathode whereby the cell can operate at low current densities.

An even further object of the invention is to implement a drained cathode cell design that can operate without formation of a crust of solidified electrolyte, possibly by operating at high current densities from 1 to 2 Amp/cm^2.

Another object of the invention is to provide a cell of drained cathode configuration having non-carbon non-consumable anodes of shapes which permit the rapid escape of bubbles when they are still small.

Yet another object of the invention is to provide a cell of drained cathode configuration wherein a small inter-electrode distance of several centimeters (typically 3cm or less) can be maintained while reducing contact between the produced aluminium and the anodically-released gases, by avoiding a deep pool of aluminium with waves and by facilitating release of the bubbles of anodically-produced gas.

Summary of the Invention

The invention proposes a drained cathode cell for the production of aluminium by the electrolysis of an aluminium compound dissolved in a molten electrolyte, in which the active cathode surfaces are dimensionally stable and have an aluminium-wettable surface and are at a slope, and in which anode surfaces parallel to the cathode surfaces are spaced by a reduced anode-cathode gap and are

configured to induce an upward release of the anode gas and an upward circulation of the electrolyte with a downward draining of the aluminium produced.

The drained cell of the invention is further characterized by the fact that it utilizes one or more of the following features :

1) An alumina-rich melt is fed at the lower part of the anode-cathode gap.

2) The anode-cathode gap between the sloping anode and cathode surfaces is up to 3 cm, possibly about 2 cm.

3) The entire cell bottom or part of it is at a slope so that the aluminium can be better moved and collected. Preferably, the slope is such that it is sufficient to ensure an efficient release of bubbles of the anodically-released gas before these bubbles become too big, thereby avoiding or considerably reducing reaction with particles of aluminium.

4) The cell bottom is sloped without moving the center of the cell (i.e. one end is raised, the other end is lowered).

5) The tapping of the aluminium is made from a storage located inside or outside the cells, at an end of the cell or at the side, or in the middle.

6) The active cathode surface is made dimensionally stable by a slurry-applied coating of aluminium-wettable refractory material which controls the sodium penetration.

7) The active cathode surface as well as the remaining bottom of the cells is protected by an aluminium-wettable titanium diboride coating, or titanium diboride plates, or a fiber cloth or a porous sheath filled with a titanium diboride slurry.

8) The cell side wall also acts as an active cathode and is protected by an aluminium-wettable titanium diboride coating, or titanium diboride plates, or a fiber cloth or a

porous sheet filled with a titanium diboride slurry, on which aluminium is also formed.

9) The entire side face inside the cell, whether it is in contact with aluminium or cryolite or anodically-generated gases, is lined with an aluminized titanium diboride coating, or titanium diboride plates, or a carbon fiber cloth or foraminous copper filled with a titanium diboride slurry.

10) The main active cathode surface has a slope. This slope is for example from 5° to 60° to horizontal, preferably from 5° to 45°.

11) The cathode slope is obtained using the cross-section of the cathode blocks, as disclosed in PCT publication WO96/07773 (de Nora).

12) The cathode slope is obtained by providing a wedge-shaped member ("wedge"), which is solid or is made of vertical plates spaced apart, on a flat cathode bottom, the wedge being made of carbon or of "heavy" materials, i.e. having a specific weight greater than the molten aluminium and cryolite, or incorporating internal ballast, this wedge also being coated with an aluminium-wettable titanium diboride coating, see for example U.S. Patent 5,472,578 (de Nora).

13) The cathode is made of a solid body of titanium-diboride-based material made by consolidating preformed titanium diboride, for example as described in PCT publication WO7/08114 (Sekhar et al) or by micropyretic reaction for example as described in U.S. Patents 5,217,583 and 5,316,718 (both in the name of Sekhar et al), possibly coated with an aluminium-wettable titanium diboride coating, for example as described in U.S. Patent 5,534,119 (Sekhar et al), or coated with titanium diboride plates, or a fiber cloth or a porous sheet filled with a titanium diboride slurry.

14) The anode is a consumable carbon anode.

15) The anode is a non-carbon oxygen evolving anode.

16) The non-carbon oxygen evolving anode comprises an assembly of plates, rods, elongated members such as strips, with a cross-section and spacing so as to favour gas escape, for example rods in so-called "spaghetti" configuration.

17) The non-carbon oxygen evolving anode is a double-faced structure with louvers or other openings in its surface for directing the anodically-produced gas inside the anode structure.

18) The anode has a cross-section to favour escape of the anodically-produced gas and circulation of the electrolyte.

19) The conventional wedge of ramming paste located between the bottom of the side walls and the edges of the cell bottom is eliminated. This permits the anodes to be near to the side wall, and the side wall can operate as a cathode i.e. facing a vertical part of the anodes. (See point 5). The cell can thus operate with low current density.

20) With cathodes in sloping wedge configuration, the alumina is fed to the lowest point of the wedge. This facilitates circulation of the electrolyte enriched with dissolved alumina.

21) The cell side wall is provided with sufficient internal and/or external insulation that the cell operates without formation of a crust of frozen electrolyte.

22) The cell operates at a high current density, from 0.5 to 2 Amp/cm^2.

23) An aluminium-wettable coating is applied to components of the cell as a slurry containing an "active" powder of aluminium-wettable material (like titanium diboride), wherein fibers are added to the slurry :

a) The fibers are made of electrically-conductive and non-conductive materials such as carbonaceous, metals, carbides, nitrides, borides, alumina etc.

b) The active aluminium-wettable powder is titanium diboride and similar materials, preformed or formed in situ.

c) The fibers form a woven or non-woven cloth.

Further features of the invention are set out in the claims.

Brief Description of the Drawings

The invention will be further decribed with reference to the accompanying schematic drawings, in which :

Fig. 1 is a cross-sectional view through part of a drained cathode aluminium production cell according to the invention;

Fig. 2 is a plan view of the anode of the cell of Fig. 1;

Fig. 3 is a side elevational view of the part of the anode of Fig. 2;

Fig. 3A is a cross-section along line 3A-3A of Fig. 3;

Fig. 4 is a cross-sectional view through part of the drained cathode aluminium production cell of Fig. 1.

Fig. 5 is a cross-sectional view through part of another drained cathode aluminium production cell according to the invention.

Figs 6, 7 and 8 are longitudinal cross-sectional views through part of three further embodiments of drained cathode cells; and

Fig. 8A shows a detail of Fig. 8.

Detailed Description

Fig. 1 shows part of a drained-cathode aluminium production cell comprising a plurality of non-carbon oxygen-evolving anodes 10 suspended over a cathode 30

comprising a cathode mass 32 having inclined cathode surfaces 35 and coated with an aluminium-wettable coating 37, for example a slurry-applied titanium diboride coating according to U.S. Patent 5,316,718 (Sekhar et al).

The cathode mass 32 is advantageously a composite alumina-aluminium-titanium diboride material, for example produced by micropyretic reaction of TiO_2, B_2O_3 and Al. Such composite materials exhibit a certain plasticity at the cell operating temperature and have the advantage that they can accommodate for thermal differences during cell start up and operation, while maintaining good conductivity required to effectively operate as cathode mass.

Alternatively the cathode mass 32 can be made of carbonaceous material, for example packed carbon powder, graphitized carbon, or stacked plates or slabs of carbon imbricated with one another and separated by layers of a material that is impermeable to the penetration of molten aluminium. When the cathode is made of carbon, the cathode slope can be obtained using the cross-section of the assembled cathode blocks, the sloping top surface of the assembled cathode blocks forming the active cathode surface, as further described in international patent application WO 96/07773 (de Nora).

Advantageously, the cathode mass 32 is supported in a metal cathode holder shell or plate 31 (see Fig. 4) as disclosed in Applicant's international patent application WO98/53120, to which current is supplied by one or more current collector bars extending through the electric and thermic insulation in the bottom of the cell, or through the sides of the cell.

As shown, the inclined active cathode surfaces 35 are arranged in a series of parallel rows of approximately triangular cross-section, extending along (or across) the cell. These surfaces 35 are inclined at an angle of for example 30° to 60° to horizontal, for instance about 45°. This slope is such that the produced aluminium drains efficiently, avoiding the production of a suspension of particles of aluminium in the electrolyte 54.

Between the adjacent inclined surfaces 35 is a trough 38 into which aluminium from the surfaces 35 can drain. Conveniently, the entire aluminium production cell is at a slope longitudinally, so the aluminium collected in the troughs 38 can drain to one end of the cell where it is collected in a storage inside or outside the cell.

The anodes 10 are suspended above the cathode 30 with a series of active inclined anode surfaces on plates 16 facing corresponding inclined cathode surfaces 35 leaving a narrow anode-cathode space, which can be less than 3cm, for example about 2cm. The active parts of the anodes are formed by plates 16 which for example are made of nickel-iron-aluminium or nickel-iron-aluminium-copper with an oxide surface as described in U.S. Patent No. 5,510,008 (de Nora et al). As shown in Fig. 1, these plates 16 are arranged in facing pairs forming a roof-like configuration.

The sloping inner active faces of the anode plates 16 assist in removing the anodically-evolved gases, principally oxygen. The chosen slope - which is the same as that of the cathode surfaces 35, for example about 45° - is such that the bubbles of anodically-released gas are efficiently removed from the active anode surface before the bubbles become too big. The risk of these gas bubbles interacting with any particles of aluminium in the electrolyte 54 is thus reduced or eliminated.

Each anode 10 comprises an assembly of metal members that provides an even distribution of electric current to the active anode plates 16. For this, the active anode plates 16 are suspended from transverse plates 18 fixed under a central longitudinal plate 19 by which the anode is suspended from a vertical current lead-in and suspension rod 14, for example of square cross-section.

For example, each anode 10 is made up of four pairs of active anode plates 16 held spaced apart and parallel to one another and symmetrically disposed around the current lead-in rod 14. As shown in Fig. 1, each active anode plate 16 is bent more-or-less about its center at about 45°, the opposite plates 16 of each pair being spaced apart from one

another with their bent lower ends projecting outwardly, so they fit over the corresponding inclined cathode surfaces 35.

As seen in plan in Fig. 2, pairs of transverse plates 18 which each carry two pairs of the active anode plates 16 are symmetrically disposed about the current lead-in rod 14 so that, overall, the active anode plates 16 are equally distributed about the axis of the current lead-in rod 14. On each side of the current lead-in rod 14, two side-by-side pairs of active anode plates 16 are carried by two transverse plates 18 spaced apart lengthwise along the plates 16/19.

In their vertical upper parts, the active anode plates 16 have a series of apertures 17 of sufficient height that the level of the molten electrolyte 54 intersects these apertures 17 about mid-way along (as shown in Fig. 1), allowing for passage of the anodically-released gases and circulation of the electrolyte 54 induced by gas-lift. As shown in the left hand part of Fig. 3, these apertures 17 are of oblong shape equally spaced apart from one another along the length of the plates 16, but other shapes are possible, for example circular or oval and possibly with unequal spacing. For example, circular apertures 17 are illustrated in the right hand part of Fig. 3.

In a variation, the illustrated active anode plates 16 could be replaced by a series of bent vertical rods, or a grid structure having through-spaces for gas release.

Fig. 4 shows part of the drained-cathode aluminium production cell of Fig. 1, comprising a plurality of non-carbon oxygen-evolving anodes 10 suspended over a cathode 30 comprising a cathode mass 32A,32B having inclined cathode surfaces 35 and coated with an aluminium-wettable coating 37, for example a slurry-applied titanium diboride coating according to U.S. Patent 5,316,718 (Sekhar et al).

The lower part 32B of the cathode mass is advantageously a composite alumina-aluminium-titanium diboride material, for example produced by micropyretic

reaction of TiO_2, B_2O_3 and Al. Such composite materials exhibit a certain plasticity at the cell operating temperature and have the advantage that they can accommodate for thermal differences during cell start up and operation, while maintaining good conductivity required to effectively operate as cathode mass.

The top part 32A of the cathode mass can be made of carbonaceous material, for example packed carbon powder, graphitized carbon, or stacked plates or slabs of carbon imbricated with one another and separated by layers of a material that is impermeable to the penetration of molten aluminium. The cathode slope can be obtained using the cross-section of the assembled cathode blocks, the sloping top surface of the assembled cathode blocks forming the active cathode surface, as further described in international patent application WO 96/07773 (de Nora).

As illustrated, each carbon block making up the top part 32A of the cathode mass has in its bottom surface two metal current conductors 42 for evenly distributing electric current in the blocks. At its edges, the top part 32A of the cathode mass is surrounded by a mass of ramming paste 32C which could alternatively be replaced by silicon carbide plates.

The lower part 32B of the cathode mass is supported on a metal cathode holder shell or plate 31 as disclosed in Applicant's international patent application WO98/53120, to which current is supplied by one or more current collector bars extending through the electric and thermic insulation 40 in the bottom of the cell, or through the sides of the cell.

Above the active parts of the anodes 10 is supported a horizontal removable insulating cover 60 which rests above the level of the electrolyte 54 and which is located underneath an outer cover 70. This cover 60 is made in sections which are removable individually with the respective anodes 10, optionally leaving gas-release gaps 63' around the anode rods 14.

In operation, the described cell can operate at a current density from 0.5 to 2 Amp/cm^2 of the projected

surface area of the active anode plates 16. Due to the slope of the active surfaces of the anode plates 16, for example at about 45°, the bubbles of oxygen generated during electrolysis on these sloping surfaces escape by moving rapidly up, and are released from the top of the active sloping surfaces while the size of the bubbles remains small. This upward escape of the tiny bubbles of oxygen creates a lift in the molten electrolyte 54 adjacent to the inclined anode surfaces.

As indicated in Fig. 1, the level of the molten electrolyte 54 intersects the apertures 17 about half-way up, so that anodically-released gas (oxygen) can escape by passing through these apertures 17. Also, the molten electrolyte 54 circulated upwardly by gas lift can pass out through the apertures 17, from where it circulates down outside the inclined surface of the anode plates 16, as indicated by arrow E in Fig. 1.

To replenish alumina consumed during electrolysis, a supply of fresh alumina is periodically fed to the space outside the bottom of the anode-cathode gap, as indicated by arrow A. This fresh alumina is then entrained in the flow of electrolyte 54 into the anode-cathode gap so that the electrolyte 54 in this gap never becomes depleted of alumina during operation.

During electrolysis, ionic aluminium is converted to metallic aluminium on the aluminium-wettable surface 37 of the inclined cathode surfaces 35. Because of the slope of this cathode surface, for example at about 45°, the aluminium produced drains as a thin film and is collected in the troughs 38. This downflow of molten aluminium takes place under gravity and is not interfered with by the upward flow of gas and entrained electrolyte 54 adjacent to the inclined surfaces of the anode plates 16. The formation of a suspension of tiny particles of aluminium is minimized or avoided.

As a result, the inclined active surfaces of the anode plates 16 and the inclined active cathode surfaces 35 can be spaced apart with a small anode-cathode gap, less

than 3cm and possibly only 2cm, while maintaining a high efficiency of the electrolysis.

Fig.5 illustrates part of another cell according to the invention including an anode structure of modified design, the same references being used to designate the same elements as before, or their equivalents, which will not be described again in full.

In the cell of Fig. 5, above a cathode cell bottom 20 enclosed in an outer steel shell 21 and containing the cathode 30 is suspended a series of non-carbon substantially non-consumable oxygen evolving anodes 10, each anode 10 comprising a series of inclined active lower plates 16 suspended by a vertical current lead-in rod 14 via current distribution members 18.

In this example, the current distribution members 18 are formed by a series of side-by-side inclined metal plates 16 connected by cross-plates, not shown. The active parts of the anodes are formed by the inclined plates 16 which for example are made of nickel-iron-aluminium or nickel-iron-aluminium-copper with an oxide surface as described in U.S. Patent No. 5,510,008 (de Nora et al). These plates 16 are arranged in facing pairs forming a roof-like configuration. The sloping inner active faces of the anodes 10 assist in removing the anodically-evolved gases, principally oxygen.

The illustrated anode 10 has three pairs of inclined plates 16 in roof-like configuration. However, the anode 10 can include any suitable number of these pairs of inclined plates.

Instead of being full, the plates 16 could be replaced by a series of rods or fingers spaced apart from one another and also inclined. In this case, the anodically-evolved gases can escape between the rods or fingers.

In the embodiment of Fig. 5, the cathode 30 comprises a metal cathode carrier 31 in the form of a shell or dished plate to which current is supplied by current distribution bars 42 which in this case are horizontal and lead through the side of the cell. Alternatively, the

current collector bars 42 could be vertical and extend through the bottom of the cell. The inner shell 31 has a flat bottom and inclined side walls 33, and forms an open-topped container for a cathode mass 32 which advantageously is a composite alumina-aluminium-titanium diboride material, for example produced by micropyretic reaction of TiO_2, B_2O_3 and Al and which wraps around the edges of the cathode carrier 32's inclined side walls 33.

Advantageously, an air or gas space (not shown) can be provided between the underside of the cathode carrier shell 31 and the top of the bricks 40, in the spaces left between the horizontal current distribution bars 42 wherein a plurality of additional spacers such as girders are provided. This space under the central flat part of the cathode carrier 31 acts as a thermic insulating space by means of which it is possible to adjust the temperature of the cathode 30 (shell 31 and cathode mass 32) by supplying a heating or cooling gas to the space. For example, during cell start up, the cathode 30 can be heated by passing hot gas through the space. Or during operation, the surface of the cathode mass 32 can be cooled to make the electrolyte 54 contacting it form a protective paste.

The central part of the top of the cathode 32 mass has a flat surface which can be inclined longitudinally along the cell and leads down into a channel or a storage for draining molten aluminium, situated at one end of the cell. On top of the cathode mass 32 is a coating 37 of aluminium-wettable material, preferably a slurry-applied boride coating as described in U.S. Patent 5,316,718 (Sekhar et al). As shown in Fig, 4, on top of the cathode mass 32 are arranged a plurality of active cathode bodies 39 having inclined surfaces also coated with the aluminium-wettable coating 37 and which face the inclined faces of the active anode plates or rods 16.

Above each anode 10, resting on the current distribution members 18, it is possible to place a thermic insulating cover (not shown). With this anode-cathode arrangement, when the anode 10 is lowered to its operating position the inclined active plates or rods 16 of the anode 10 are held with a small spacing above the inclined cathode

surface 35. In this operating position of the anodes, such thermic insulating cover can be held level with or slightly below the top of the cell sidewalls 22 and just above the level of the electrolyte 54.

The described cell of Fig. 5 employs inclined non-carbon oxygen-evolving anodes 10 facing a dimensionally-stable drained cathode 30 with inclined aluminium-wettable operative surfaces 35/37, enabling the cell to operate with a narrow anode-cathode gap, say about 3cm or less (particularly because of the improved gas release with the inlined anode-cathode surfaces), instead of about 4 to 5 cm for conventional cells. This smaller anode-cathode gap means a substantial reduction in the heat produced during electrolysis, leading to a need for extra insulation to prevent freezing of the electrolyte.

In operation of the cell of Fig. 4 or Fig. 5, it is advantageous to preheat each anode 10 before it is installed in the cell in replacement of an anode 10 that has become disactivated or requires servicing. In particular, this inhibits the formation of an electrolyte crust which could lead to part of an anode being disactivated until the electrolyte crust has melted.

Figs 6 to 8 show three further embodiments of drained cathode cells with consumable carbon anodes 10'.

In the cell of Fig. 6, the cathode is made up of a series of carbon blocks 82 of generally rectangular cross-section assembled together side-by-side on a layer of refractory insulating material 40. These carbon blocks 82 are joined by ramming paste or glue. Each carbon block 82 has a centrally-located current collector bar 42 extending transverse to the cell.

On the flat top face of blocks 82 are arranged wedge-shaped carbon bodies 83 having sloping top surfaces 84 inclined at about 5° to horizontal. As illustrated, these top surfaces 84 are oppositely inclined to one another to provide a series of shallow V-shaped recesses forming the active cathode surfaces.

These bodies 83 are also joined by ramming paste or glue to the blocks 82, advantageously using a TiB_2-containing slurry, as described in U.S. Patent N°. 5,320,717 (Sekhar).

The exposed inclined top surfaces 84 of the bodies 83 are coated with an aluminium-wettable refractory coating, preferably the slurry-applied TiB_2 as described in U.S. Patent N°. 5,534,119 (Sekhar et al).

The lower active faces of the anodes 10' have corresponding V-shaped inclined surfaces facing the inclined active cathode surfaces 84. The anode surfaces have exactly the same angle of inclination as the cathode surfaces, e.g. about 5°. The anode-cathode gap is held at a reduced value, about 3cm or less. This is sufficient to promote efficient removal of the bubbles of anodically-generated gas. This also promotes an upward (and sideward) circulation of the electrolyte 54 in the anode-cathode gap, whereas the produced aluminium is drained to the center of the V-shaped recesses and collected by inclining the cell to one side, where the aluminium is collected.

Fig. 7 illustrates a similar design, but where the cathode blocks 82 are of trapezoidal cross-section and have integral inclined surfaces 84, arranged alternately to form the shallow V-shaped recesses. In this case, the sloping cathode surfaces 84 are provided by the modified cross-sectional shape of the carbon blocks 82.

Fig. 8 illustrates a modification of the drained cathode cell of Fig. 6 wherein the solid cathode wedges 83 are replaced by wedge-shaped members made of a series of side-by-side spaced-apart plates 85 connected by cross-bars 86. As illustrated, each wedge-shaped cathode member is made up of eight vertical plates 85 joined by two cross-bars 86. However, any suitable number of plates 85 can be connected by any suitable number of cross-bars 86, of round cross-section or any other suitable cross-section.

These plates 85 can be made of carbon, in which case they are secured to the cathode blocks 82 or loaded with ballast. Advantageously, however, the plates 85 can be

made of a refractory material, such as alumina, having a specific weight greater than molten aluminium. In both cases, the entire surface of the wedge-shaped plates 85, or at least their top parts including the sloping surfaces, will be coated with an aluminium-wettable refractory material, preferably slurry-applied TiB_2.

In this design, the produced aluminium can drain in the spaces between the plates 85. The height of the lower end of the wedge-shaped plates 85 is such that it is possible to allow a fluctuation of the level of the produced aluminium to facilitate tapping of the aluminium by a batch process. As before, the cell floor is advantageously inclined to promote collection of the aluminium at the side/end of the cell.

Of course, the cells of Figs 6, 7 and 8 could employ non-carbon oxygen-evolving anodes instead of carbon anodes.

CLAIMS

1. A drained cathode cell for the production of aluminium by the electrolysis of an aluminium compound dissolved in a molten electrolyte, comprising at least one non-carbon oxygen-evolving anode facing at least one cathode, the or each cathode having one or more dimensionally stable sloped aluminium-wettable cathode surfaces, the or each anode having a plurality of active anode surfaces parallel to the cathode surfaces, the anode and cathode surfaces being spaced by an anode-cathode gap and configured to induce an upward release of the anode gas and an upward circulation of the electrolyte with a downward draining of the aluminium produced, wherein the or each anode comprises an assembly of plates, spaced apart parallel rods or strips with a cross-section and spacing so as to favour gas escape and supported by at least one current distribution member transverse thereto, said plurality of anode surfaces being formed by surfaces of said plates, rods or strips.

2. The drained cathode cell of claim 1, wherein an alumina-rich melt is fed at the lower part of the anode-cathode gap.

3. The drained cathode cell of claim 1 or 2, wherein the anode-cathode gap between the sloping anode and cathode surfaces is up to 3 cm.

4. The drained cathode cell of claim 1, 2 or 3, wherein the entire cell bottom or part of it is at a slope to assist movement and collection of the molten aluminium.

5. The drained cathode cell of claim 4, wherein the cell bottom is sloped without moving the centre of the cell by raising one end relative to the cell, and lowering the other end relative to the cell.

6. The drained cathode cell of any one of claims 1 to 5, comprising a storage located inside or outside the cell, for tapping of the product aluminium.

7. The drained cathode cell of any one of claims 1 to 6, wherein the active cathode surface is made dimensionally

stable by a slurry-applied coating of aluminium-wettable refractory material which controls the sodium penetration.

8. The drained cathode cell of any one of claims 1 to 7, wherein the active cathode surface as well as the remaining bottom of the cell is protected by an aluminium-wettable titanium diboride coating, or titanium diboride plates, or a fibre cloth or a porous sheath filled with a titanium diboride slurry.

9. The drained cathode cell of any one of claims 1 to 8, wherein the cell side wall also acts as an active cathode and is protected by an aluminium-wettable coating on which aluminium is also formed.

10. The drained cell of claim 9, wherein the aluminium-wettable coating of the cell side wall is a titanium diboride coating, or titanium diboride plates, or a fibre cloth or a porous sheet filled with a titanium diboride slurry.

11. The drained cathode cell of claim 1, wherein the entire side face inside the cell, whether it is in contact with aluminium or cryolite or anodically-generated gases, is lined with an aluminised titanium diboride coating, or aluminised titanium diboride plates, or aluminised carbon fibre cloth or foraminous copper filled with a titanium diboride slurry.

12. The drained cathode cell of any one of claims 1 to 11, wherein the main active cathode surface has a slope from 5° to 45° to horizontal.

13. The drained cathode cell of any one of claims 1 to 12, wherein the cathode slope is obtained using the cross-section of assembled cathode blocks of modified design, the sloping top surface of the assembled cathode blocks forming the active cathode surface.

14. The drained cathode cell of claim 1, wherein the cathode slope is obtained by providing a wedge-shaped member on a flat cathode bottom, the wedge-shaped member being made of carbon or of refractory materials having a specific weight greater than the molten aluminium and cryolite or

containing ballast, the wedge-shaped member also being coated with an aluminium-wettable titanium diboride coating.

15. The drained cathode cell of claim 14, wherein the wedge-shaped member is solid.

16. The drained cathode cell of claim 14, wherein the wedge-shaped member is made of vertical plates spaced apart from one another.

17. The drained cathode cell of claim 1, wherein the cathode is made of a solid body of titanium-diboride based material.

18. The drained cathode cell of claim 17, wherein said solid cathode body of titanium-diboride based material is made by consolidating preformed titanium diboride.

19. The drained cathode cell of claim 17, wherein said solid cathode body of titanium-diboride based material is made by reaction of reactants compacted into the form of the body.

20. The drained cathode cell of claim 17, 18 or 19, wherein said solid cathode body of titanium-diboride is coated with an additional aluminium-wettable titanium diboride coating, or coated with titanium diboride plates, or a fibre cloth or a porous sheet filled with a titanium diboride slurry.

21. The drained cathode cell of claim 1, wherein the anode is made of an assembly of inclined plates in spaced-apart parallel configuration supported by at least one current distribution member transverse to the inclined plates.

22. The drained cathode cell of claim 1, wherein the non-carbon oxygen evolving anode is a double-faced open structure with louvers or other openings in its surface for directing the anodically-produced gas inside the anode structure.

23. The drained cathode cell of any one of claims 1 to 22, wherein the anode has a cross-section to favour escape of the anodically-produced gas and circulation of the electrolyte.

24. The drained cathode cell of claim 23, wherein the anode is a non-carbon oxygen-evolving anode with an inclined operative surface and a substantially vertical top part having therein apertures for circulation of the electrolyte.

25. The drained cathode cell of claim 8, wherein the bottom of the side walls joins together with the edges of the cell bottom without any wedge of ramming paste between them, whereby the anodes are near to the cell side walls which operate as a cathode facing a vertical part of the anodes.

26. The drained cathode cell of any one of claims 1 to 25, wherein the cell side wall is provided with sufficient internal and/or external thermic insulation that the cell operates without formation of a crust of solidified electrolyte.

27. The drained cathode cell of any one of claims 1 to 26, which operates at a current density from 0.5 to 2 Amp/cm^2 of the projected anode surface area.

28. The drained cathode cell of any one of claims 1 to 27, wherein an aluminium-wettable coating is applied to components of the cell as a slurry containing a powder of aluminium-wettable material.

29. The drained cathode cell of claim 28, wherein the aluminium-wettable material is a powder of titanium diboride and similar materials, preformed or formed in situ.

30. The drained cathode cell of claim 28 or 29, wherein fibres are added to the slurry.

31. The drained cathode cell of claim 30, wherein the fibres are made of electrically conductive and non conductive materials such as carbonaceous, metals, carbides, nitrides, borides, alumina.

32. The drained cathode cell of claim 30 or 31, wherein the fibres are metallic or carbonaceous.

33. The drained cathode cell of claim 30, 31 or 32, wherein the fibres form a cloth.

34. The drained cathode cell of any one of claims 1 to 33, wherein the cathode comprises a cathode mass made mainly of an electrically conductive non-carbon material.

35. The drained cathode cell of claim 34, wherein the cathode mass is made of a composite material made of an electrically conductive material and an electrically non-conductive material.

36. The drained cathode cell of claim 35, wherein the non-conductive material is alumina, cryolite, or other refractory oxides, nitrides, carbides or combinations thereof.

37. The drained cathode cell of claim 35 or 36, wherein the conductive material is at least one metal from Groups IIA, IIB, IIIA, IIIB, IVB, VB and the Lanthanide series of the Periodic Table and alloys and intermetallic compounds thereof.

38. The drained cathode cell of claim 37, wherein the conductive material is at least one metal from aluminium, titanium, zinc, magnesium, niobium, yttrium and cerium.

39. The drained cathode cell of claim 37 or 38, wherein the bonding metal has a melting point from 650°C to 970°C.

40. The drained cathode cell of any one of claims 35 to 39, wherein the composite material is a mass comprising alumina bonded with aluminium or an aluminium alloy.

41. The drained cathode cell of claim 40, wherein the composite material is a mass made of alumina and titanium diboride bonded with aluminium.

42. The drained cathode cell of claim 41, wherein the composite material is obtained by reaction in which the reactants are TiB_2, B_2O_3 and Al.

43. The drained cathode cell of any one of claims 1 to 42, wherein the cathode mass is impervious to molten aluminium and to the molten electrolyte.

44. The drained cathode cell of any one of claims 1 to 43, wherein the upper surface of the cathode mass is coated with a coating of refractory aluminium-wettable material.

45. The drained cathode cell of any one of claims 1 to 44, comrising at least one non-carbon oxygen-evolving anode immersed in the molten electrolyte, and a removable thermic insulating cover just above the level of the molten electrolyte.

46. The drained cathode cell of claim 45, wherein the thermic insulating cover is removable with at least one anode.

47. The drained cathode cell of any one of claims 1 to 46, comprising an air or gas space between the cathode and an electric and thermic insulating mass forming a cell lining.

48. A method of producing aluminium in a cell of any one of claims 1 to 47, comprising passing electrolysis current at a current density of 0.5 to 2 Amp/cm2 per projected area of the anode to induce an upward circulation of the electrolyte in the anode-cathode gap by gas release.

49. The method of claim 48, further comprising feeding an alumina-rich melt at the lower end of the anode-cathode gap.

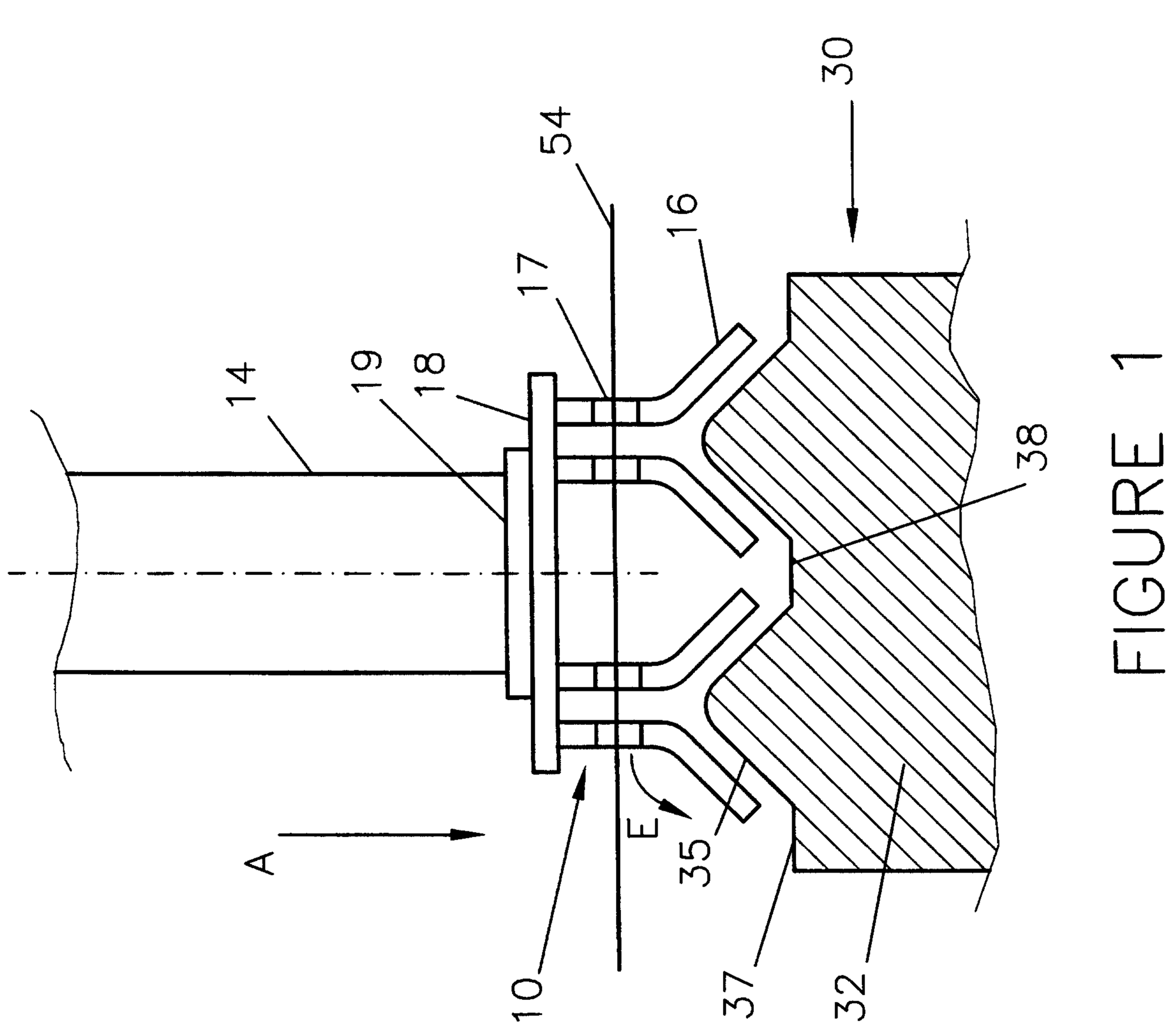


FIGURE 1

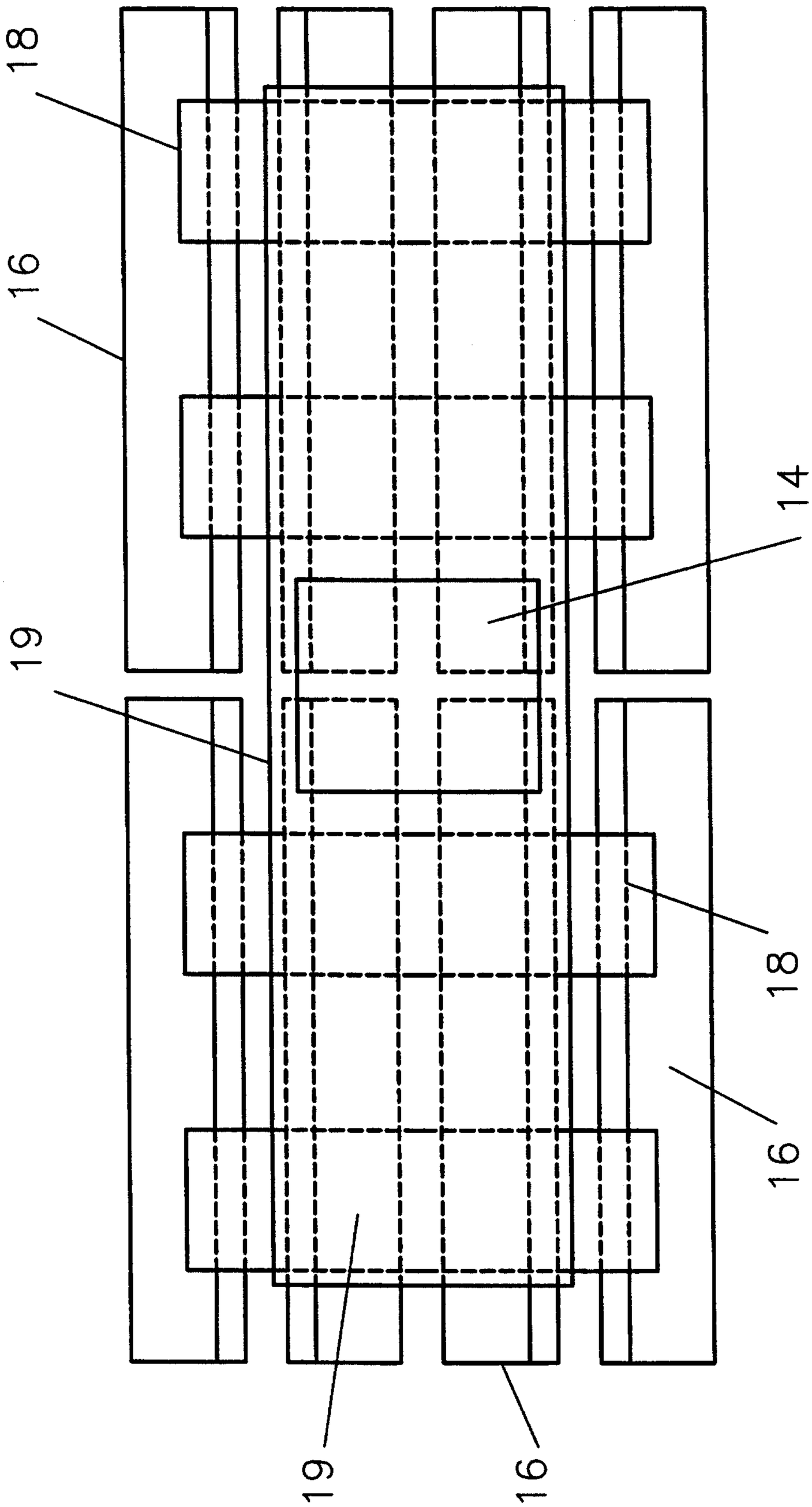


FIGURE 2

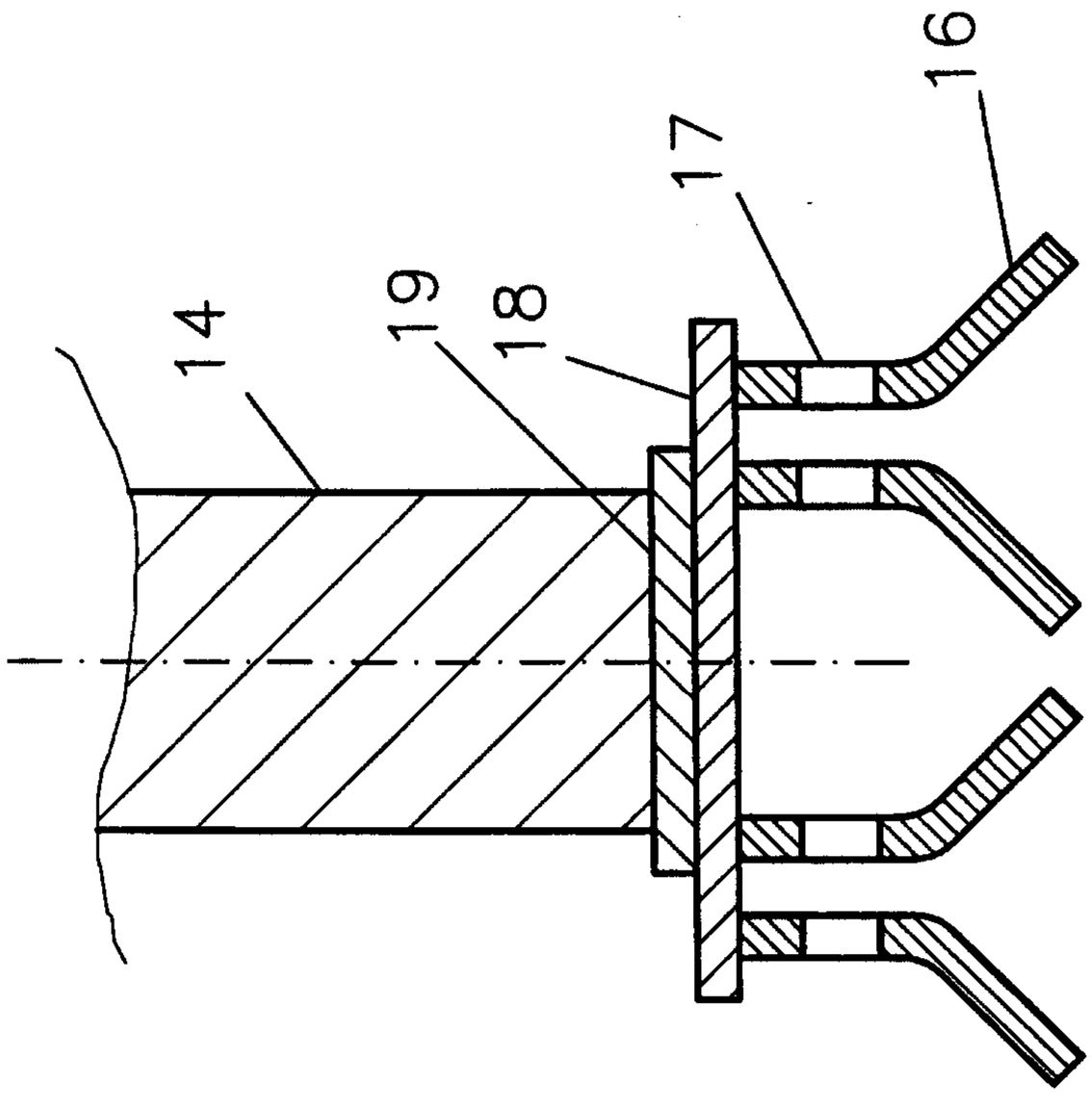


FIGURE 3A

FIGURE 3

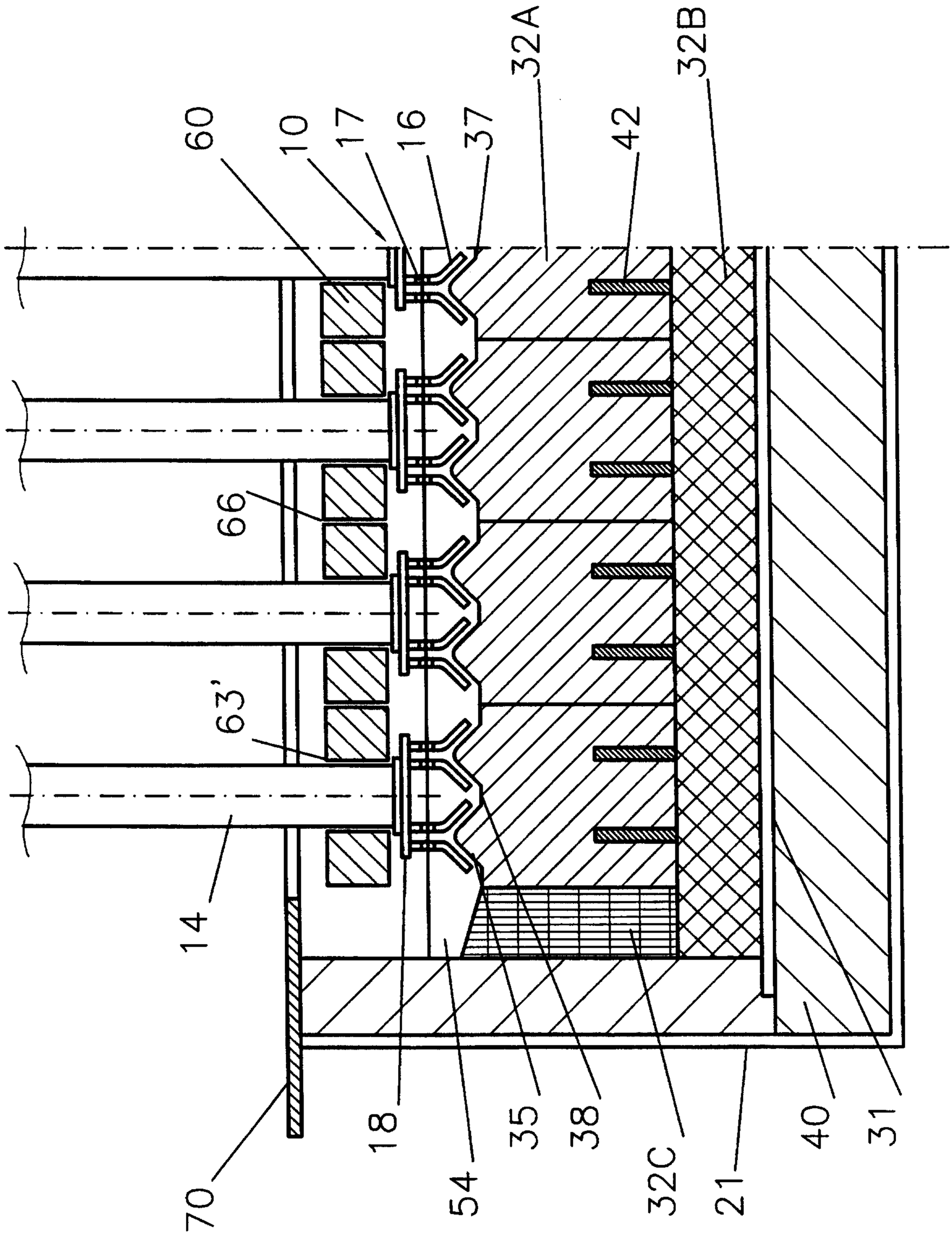


FIGURE 4

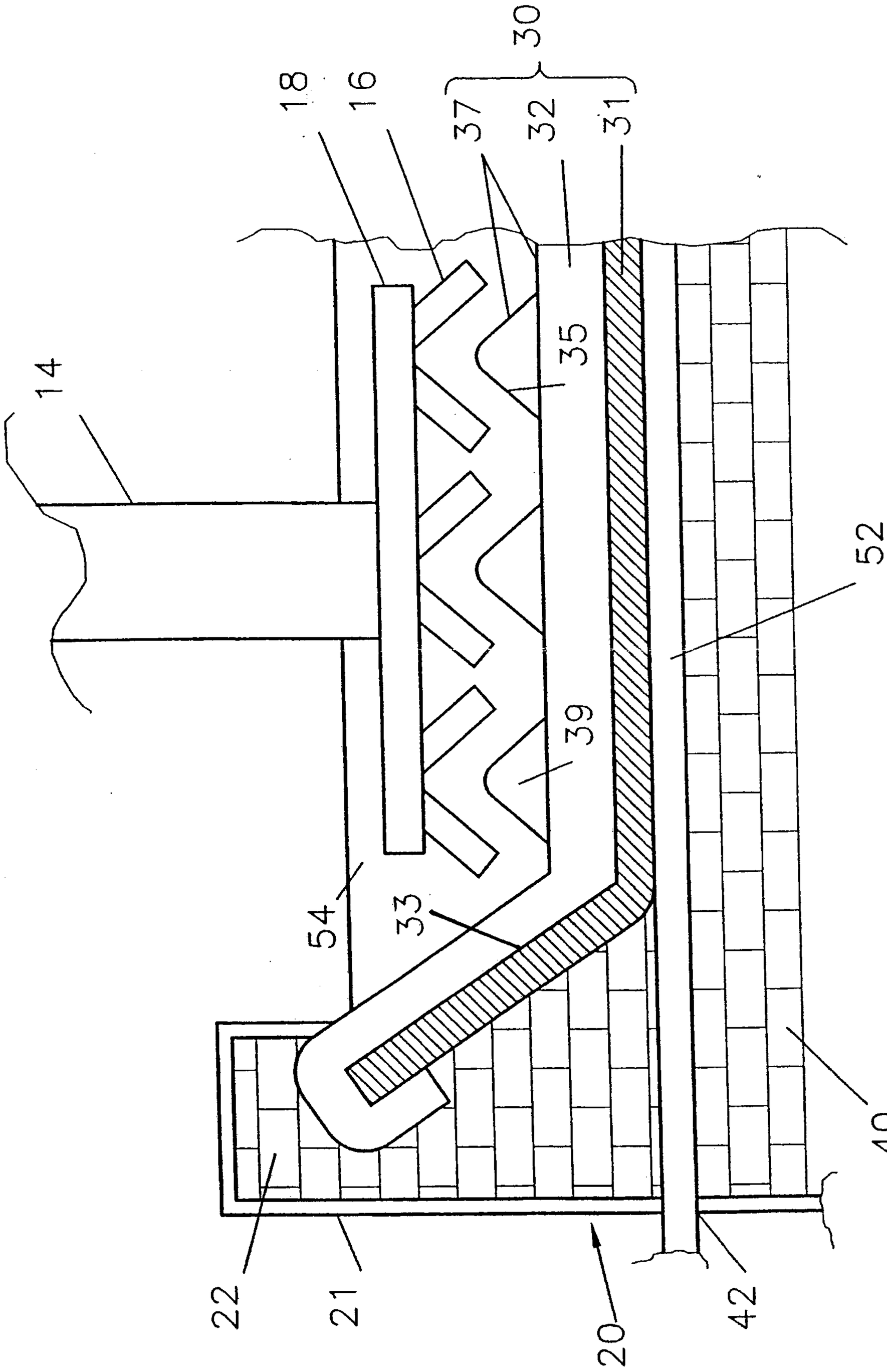


FIGURE 5

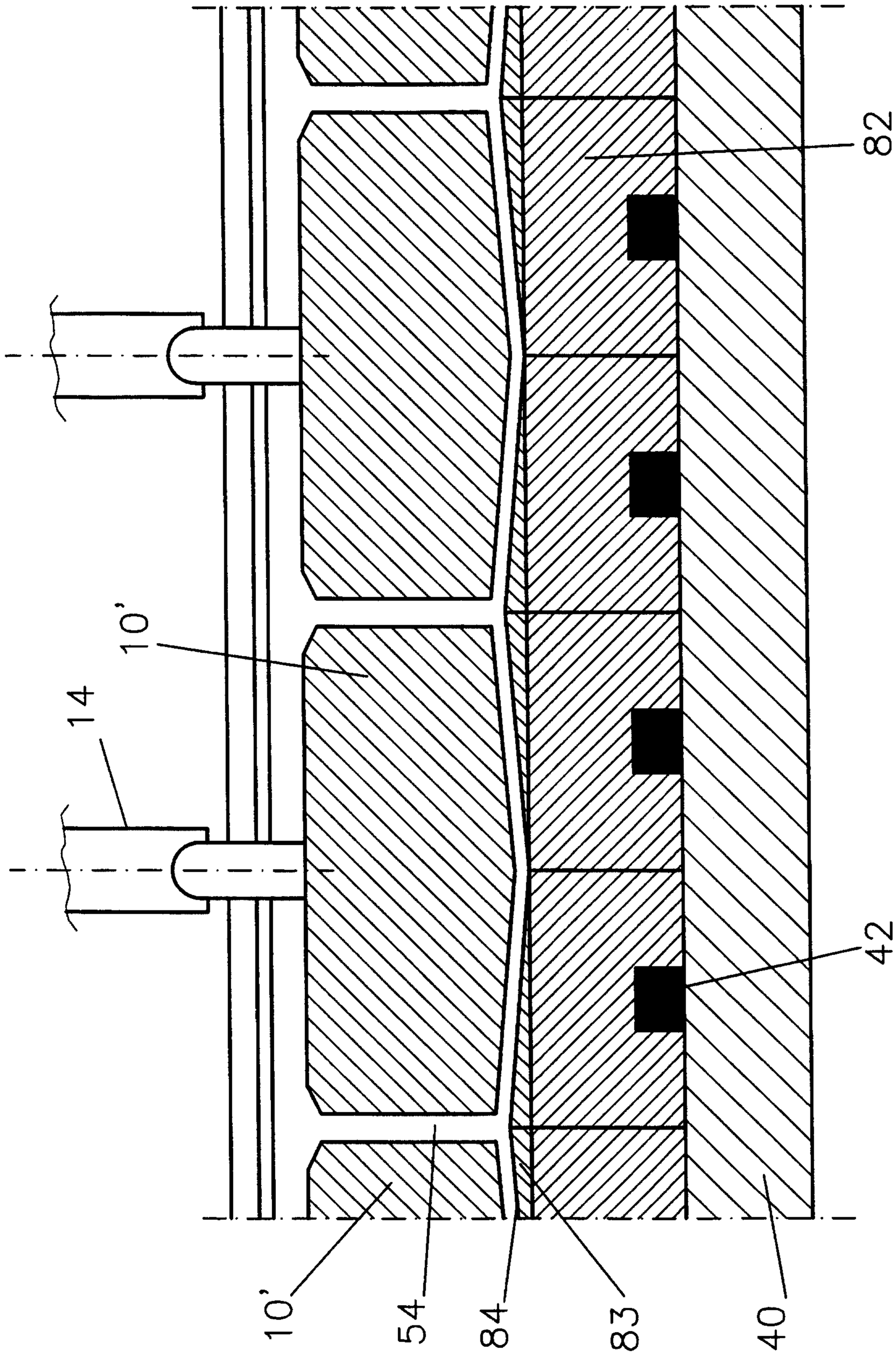


FIGURE 6

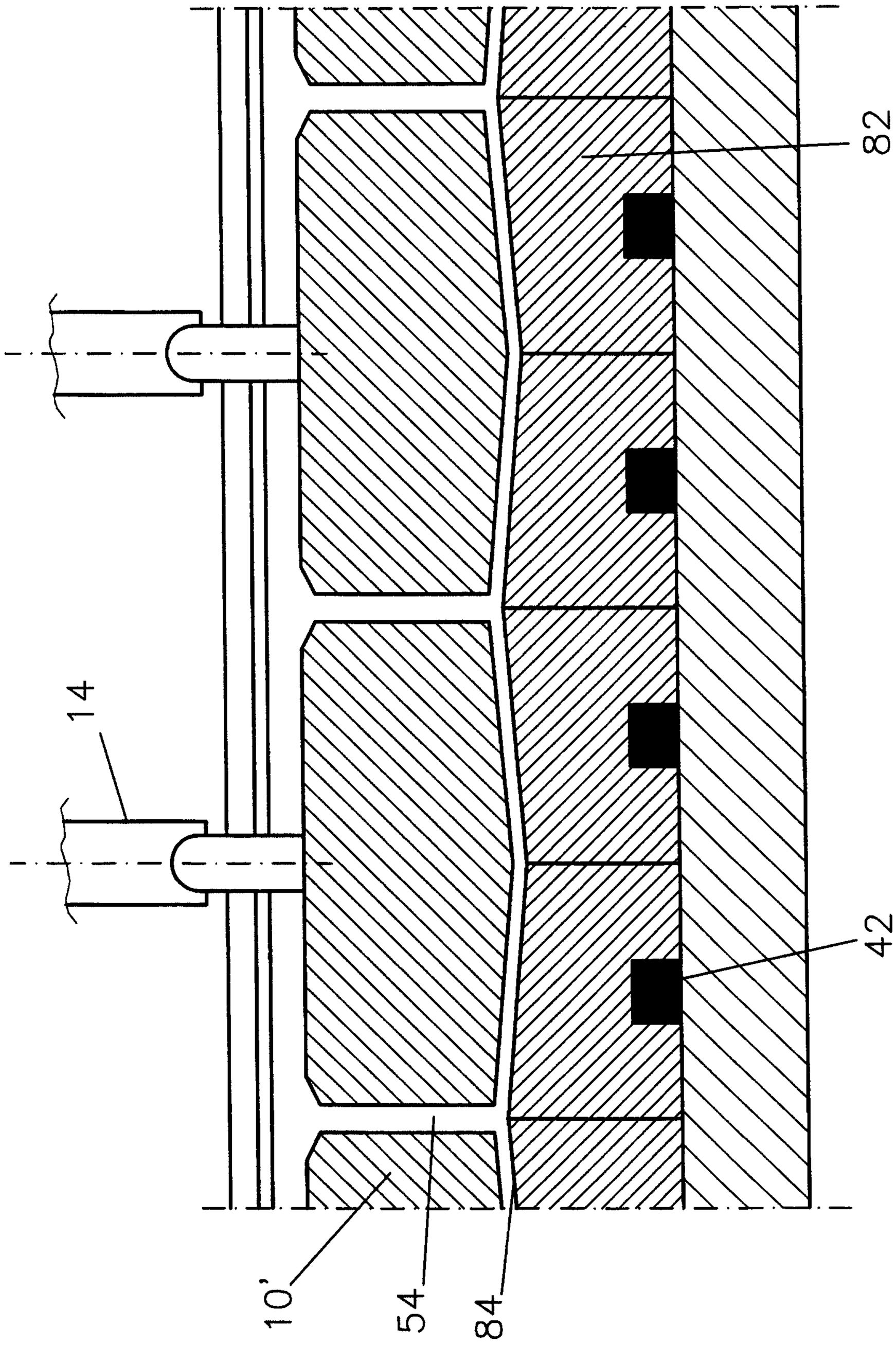


FIGURE 7

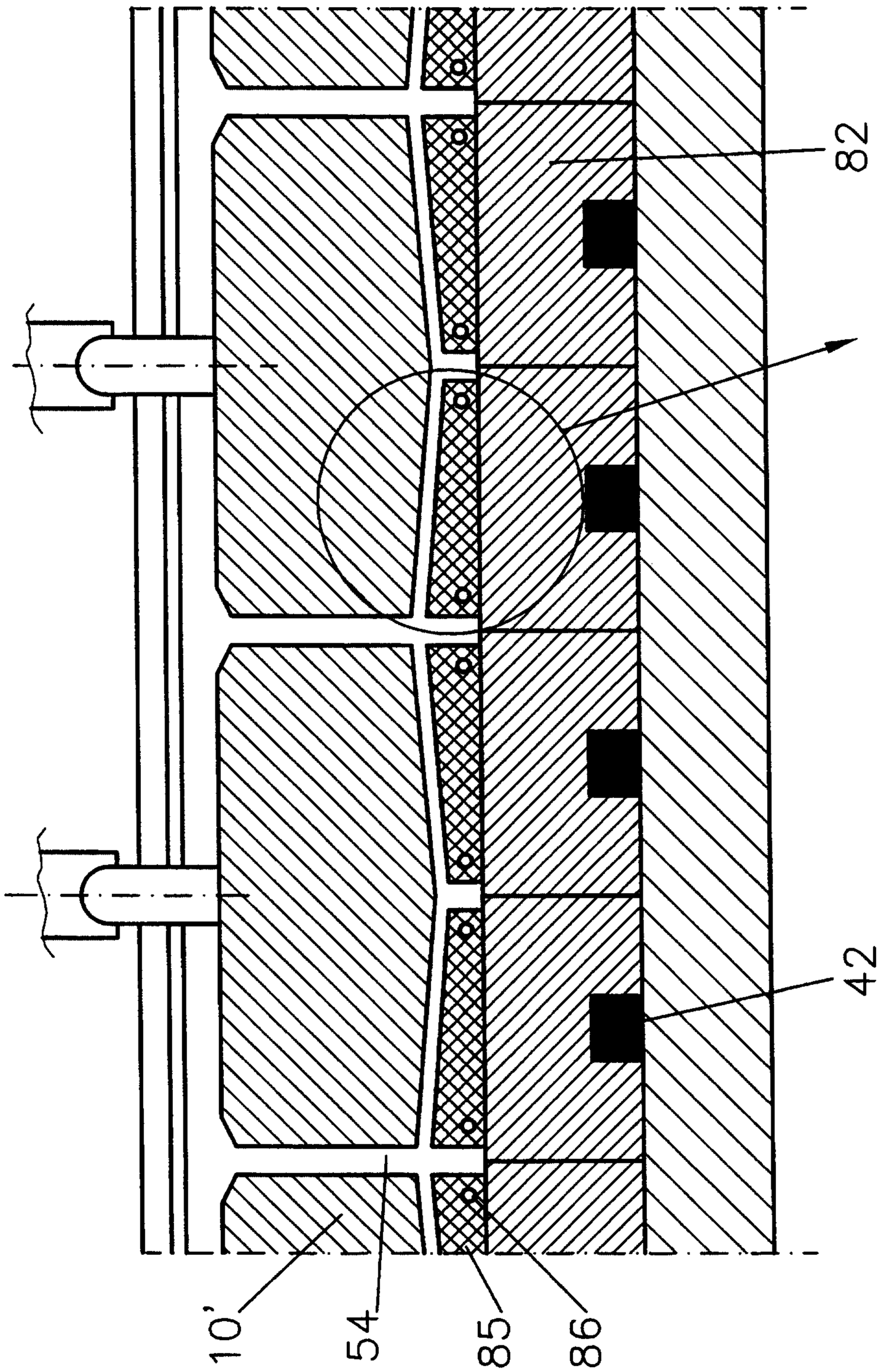


FIGURE 8

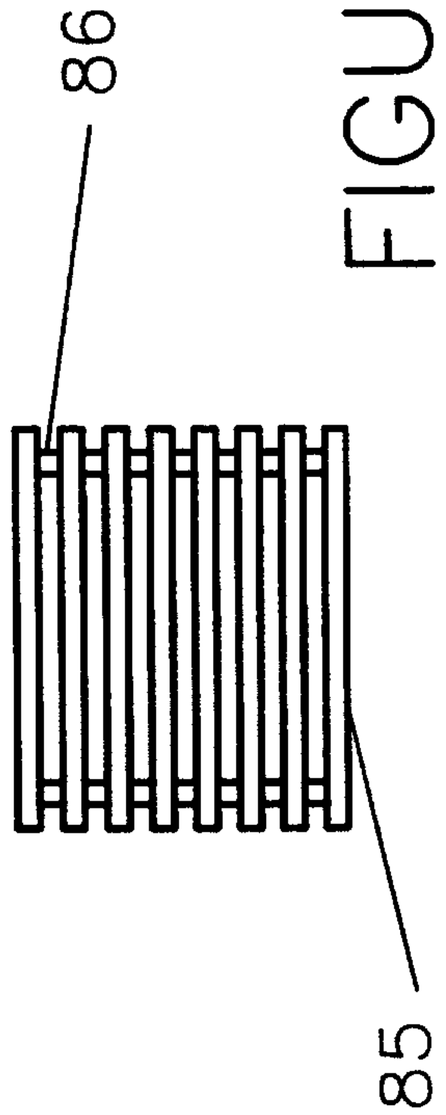
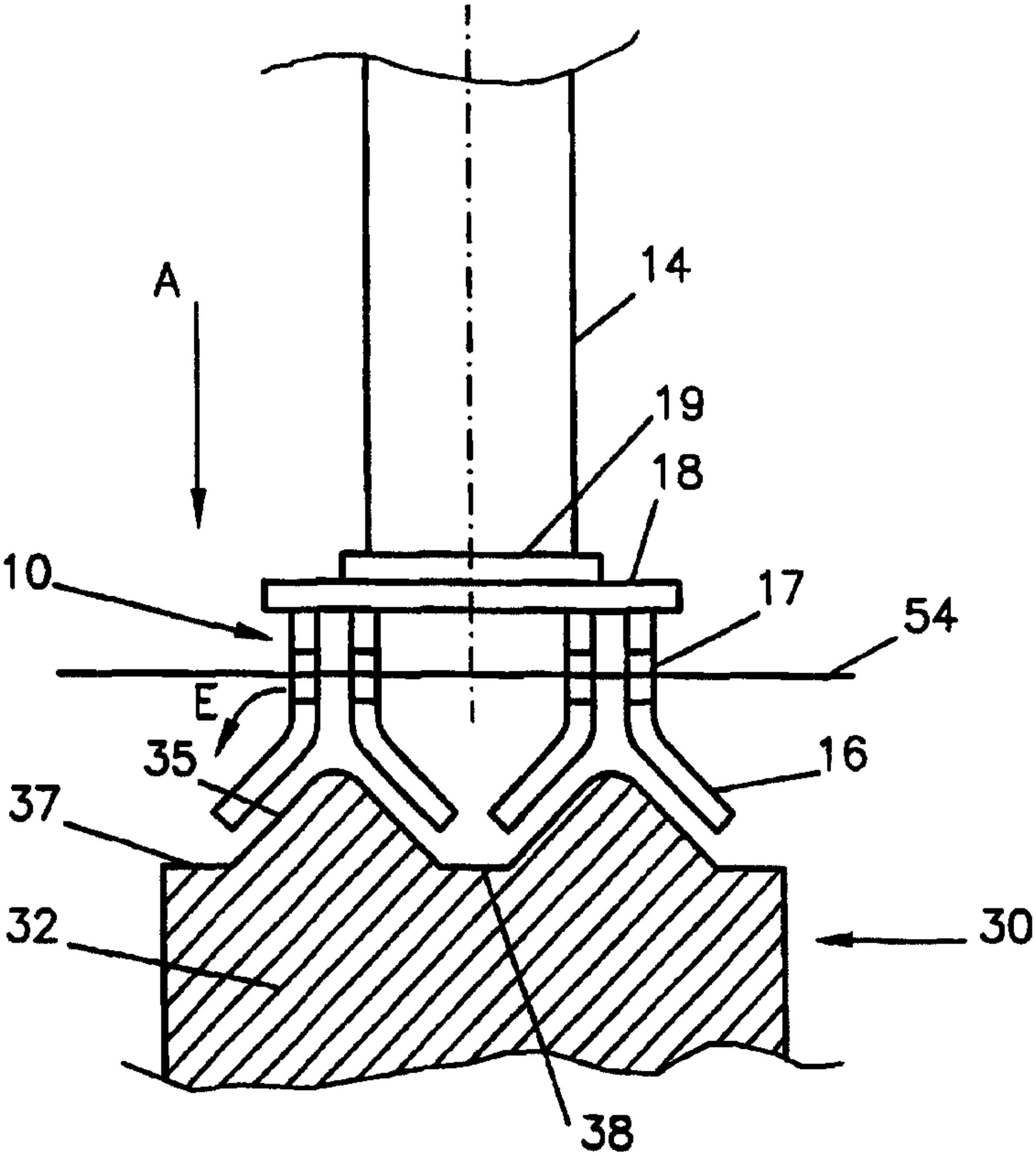


FIGURE 8A


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