

12 **EUROPEAN PATENT APPLICATION**

21 Application number: 83810164.0

51 Int. Cl.³: **C 25 C 3/08**

22 Date of filing: 19.04.83

30 Priority: 21.04.82 US 370565

71 Applicant: **DIAMOND SHAMROCK CORPORATION,**
717 North Harwood Street, Dallas Texas 75201 (US)

43 Date of publication of application: 26.10.83
Bulletin 83/43

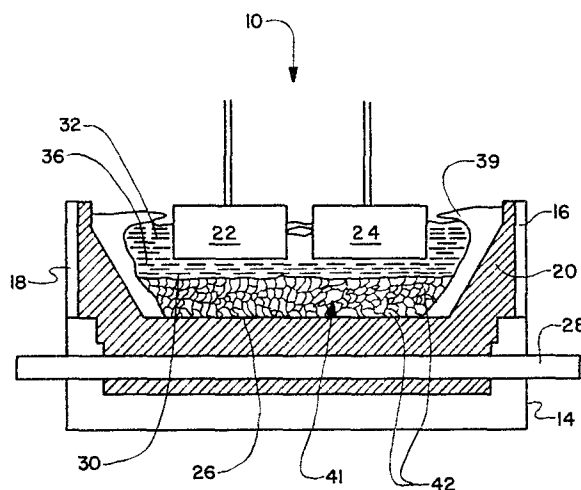
72 Inventor: **Wheeler, D.J., 1159 Oxford Road, Cleveland Heights Ohio 44121 (US)**
Inventor: **Konicek, M.G., 7782 Geramdier Lane, Brecksville Ohio 44141 (US)**
Inventor: **Sen, R.K., 1139 Erieview Road, Cleveland Heights Ohio 44118 (US)**

84 Designated Contracting States: **AT BE CH DE FR GB IT LI LU NL SE**

74 Representative: **Cronin, Brian Harold John, c/o Eltech Systems Corporation 17-19, Chemin du Champ-d'Anier, CH-1209 Le Petit-Saconnex Geneva (CH)**

54 **Non-wettable aluminum cell packing.**

57 An aluminum non-wettable packing for use in aluminum electrowinning cells for dampening wave motion in molten aluminum contained in the cell. Utilizing the packing, anode to cathode spacing within these aluminum electrowinning cells can be decreased with reduced concern for short circuits, allowing cell operation while consuming reduced electrical power.



NON-WETTABLE ALUMINUM CELL PACKING

Technical Field

This invention relates to the metal electrowinning cells, and particularly to cells for the electrowinning of aluminum. More specifically, this invention relates to cathode arrangements for use in these aluminum electrowinning cells.

Background of the Invention

Aluminum is commonly produced by electrowinning aluminum from Al_2O_3 (alumina) at about 900°C to $1,000^\circ\text{C}$. Aluminum oxide being electrowon frequently is dissolved in molten Na_3AlF_6 (cryolite) that generally contains other additives helpful to the electrowinning process such as CaF_2 , AlF_3 and LiF .

In one popular configuration for these electrolytic aluminum cells, anode and cathode are arranged in vertical spaced configuration within the cell, the anode being uppermost. Reduction of aluminum oxide to aluminum occurs at the cathode which customarily is positioned at the bottom or floor of the cell. Oxygen is electrochemically disassociated from Al_2O_3 , in most commercial cells combining with carbonaceous material comprising the cell anode and being emitted from the cell as CO and CO_2 .

Cryolite is an aggressive chemical necessitating use of a cathode material substantially resistant to this

aggressive cryolite. One popular choice is the use of molten aluminum as a cathode. While use of other cathodes such as bare graphite in contact with cryolite has been contemplated, formation of undesirable by-products such as aluminum carbides has discouraged use. In many commercial cells, this cathode often covers substantially the entire floor of the cell which typically can be 6 feet wide by 18 or more feet in length.

In utilizing aluminum for cathode purposes in a cell, typically the cathode is included in an assembly of a cathodic current feeder covered by a pool of aluminum ranging in depth, depending upon the cell, from a few inches to in excess of a foot, but generally about 6 inches. The aluminum pool functions effectively as a cathode and also serves to protect current feeders made from materials less than fully resistant to cell contents.

These aluminum pool type cell cathode assemblies contain conductive current collectors. Where these conductive current collectors are utilized in certain cell configurations, these collectors contribute to an electrical current flow within the cell that is not perpendicular to the cell bottom. These nonperpendicular electrical currents can interact with strong magnetic fields established around cells by current flow through busses and the like to contribute to strong electromagnetic fluxes within the cell.

In cells employing a pool of aluminum covering the cathode floor of the cell, the cryolite, containing Al_2O_3 to be electrolyzed, floats atop this aluminum pool. The cell anodes are immersed in this cryolite layer.

It is important that these anodes do not contact the aluminum pool, for such contact would result in a somewhat dysfunctional short circuit within the cell. The electromagnetic flux within the cell arising from the interaction of nonperpendicular electrical currents with an electromagnetic field surrounding the cell contributes to the formation of wave motion within the aluminum pool

contained in the cell, making prediction of the exact depth of the aluminum pool somewhat imprecise. Therefore, prediction of the minimum necessary spacing between the anode and cathode current collector and between the anode
5 and the interface between molten aluminum and molten cryolite at any particular cell location is somewhat imprecise. Consequentially, cell anodes are generally positioned within the cryolite substantially above the normal or expected level of the interface between molten
10 cryolite and molten aluminum within the cell. Usually, a spacing of $1\frac{1}{2}$ to $2\frac{1}{2}$ inches is utilized.

The combination of a substantial aluminum pool depth susceptible to wave motion and a positioning of the anodes substantially above the cryolite-aluminum normal
15 interface position to forestall short circuits caused, for example, by wave motion in the aluminum establishes a substantial gap between the anode and cathode in most conventional cells. Electrical power consumed in operation of the cell is somewhat proportional to the
20 magnitude of this gap. Substantial reductions in the anode-cathode spacing would result in considerable cost savings via reduced cell electrical power consumption during operation. Additionally, where the thickness of aluminum in the pool could be reduced while reliably
25 maintaining a molten aluminum cover upon the cathodic current feeder, considerable aluminum inventory savings would be realized.

One proposal to reduce spacing between anode and cathode has been to employ so-called "drained cathodes" in
30 constructing aluminum electrolysis cells. In such cells, no pool of aluminum is maintained upon a cathode current feeder to function as a cathode; electrowon aluminum drains from the cathode at the bottom of the cell to be recovered from a collection area. In drained cathode
35 cells, without wave action attendant to a molten aluminum pool, the anode and the cathode may be quite closely arranged, realizing significant electrical power savings.

In these drained cathode cells, however, the cathode, particularly where non wettable by molten aluminum is in generally continuous contact with molten cryolite. This aggressive material, in contact with a
5 graphite or carbon cathode, can contribute to material loss from the cathode and can trigger formation of such undesirables as aluminum carbides. Particularly, carbon or graphite for use as a drained cathode material of construction is therefore of quite limited utility due to
10 possible service life constraints and carbide contaminant formation.

Other longer lived materials are, in theory, available for use in a drained cathode. Generally, these materials are both conductive and aluminum wettable
15 refractory materials such as TiB_2 . It has been found that unless TiB_2 and similar materials are in essentially pure form, they too lose material or corrode at unacceptable rates in the aggressive cell environment.

It is believed that the molten cryolite
20 contributes to TiB_2 corrosion by fluxing reaction products of TiB_2 and aluminum generated near grain boundaries of the material. While it is known that in aluminum electrowinning cells essentially pure TiB_2 does not exhibit as substantial a corrosion susceptibility as does
25 lower purity TiB_2 , cost and availability factors seriously limit the use of TiB_2 sufficiently pure to withstand the aggressive cell environment.

In 'another' proposal, a particular cathodic current feeder configuration has been utilized to reduce
30 significantly non-perpendicular current flow within the cell, thereby reducing wave motion. These solutions have not proven wholly satisfactory however.

Disclosure of the Invention

The present invention provides an improved
35 cathode assembly for use in an aluminum electrowinning

cell. The improved cathode is intended for use in an aluminum electrowinning cell having an anode and cathode in vertical spaced relationship within the cell, the anode being immersed in a molten cryolite pool.

5 The improved cathode assembly includes a cathodic current feeder arranged in vertical spaced relationship with the anode. A pool of molten aluminum covers the cathodic current feeder with the molten cryolite in which the anode is immersed being atop the
10 molten aluminum. Immersed in the molten aluminum is a packed bed of loose packing elements. The elements are of a refractory material non-wettable by aluminum, and are substantially resistant to attack by molten aluminum and cryolite while immersed in the aluminum. The loose packed
15 bed elements are disposed atop the current feeder relatively uniformly to a predetermined depth not greater than the depth of the aluminum pool atop the cathodic current feeder.

 Conductivity of the non-wettable bed packing
20 elements is relatively unimportant to its utility in the electrolysis cell. The packing elements should be each sufficiently large to permit continuous electrical current pathways of molten aluminum between the cathodic current feeder and the molten cryolite atop the molten aluminum,
25 notwithstanding the packing elements being non-wettable by molten aluminum. That is, the packing should not be so densely arranged as to preclude the presence of molten aluminum from substantial void volume within the packed bed by virtue of surface tension.

30 Installed in the cell, immersed in the molten aluminum, the packing functions to suppress wave motion in the molten aluminum cathode resulting from magnetic flux from electrical currents flowing non-perpendicularly to the flow of the aluminum electrowinning cell. With wave
35 motion within the cell being suppressed, the anode, immersed in the molten cryolite, can be arranged to be in closer proximity to the molten aluminum cathode. Voltage

required for aluminum electrowinning is reduced by this anode cathode arrangement in close proximity, and power requirements for cell operation are correspondingly reduced.

5 The above and other features and advantages of the invention will become more apparent from the following, detailed description of the invention made with reference to the accompanying drawings forming a part of the specification.

10 Description of the Drawings

Fig. 1 is a cross sectional representation of an aluminum electrowinning cell embodying the loosely packed bed elements of the invention.

Best Embodiments of the Invention

15 Referring to the drawings, Fig. 1 shows in cross section a representation of an aluminum electrowinning cell 10. The cell includes a base 14 and sidewalls 16, 18, generally of steel, surrounding the cell. The cell includes a cathodic current feeder 20 and anodes 22, 24.

20 The base and sidewalls enclose the cathodic current feeder 20 which in this best embodiment functions also as a cell liner. Portions 26 of the liner define a floor of the cell. Well known refractory materials and graphite are suitable for fabricating this current feeder
25 20, as are other suitable or conventional materials. A current buss 28, embedded in the feeder 20 provides electrical current for distribution within the cell 10. The buss 28 is connected to an external source of electrical current (not shown).

30 The anodes 22, 24 are arranged in vertical spaced relationship with the current feeder portions 26 defining the floor of the cell. The anodes 22, 24 are separated from the cathodic current feeder by two pools

30, 32 of molten material. One pool 30 comprises essentially molten aluminum. This molten aluminum pool functions as a cathode for electrowinning of aluminum within the cell. While the pool consists essentially of
5 aluminum, impurities customarily associated with aluminum produced electrolytically may be present.

The remaining pool 32 is comprised of molten cryolite, Na_3AlF_6 , containing dissolved Al_2O_3 . A number of cryolite formulations that include additives such as
10 CaF_2 , LiF , and AlF_3 for enhancing electrolysis of the Al_2O_3 to aluminum are possible and are contemplated as being utilized within the scope of the invention. This cryolite layer, being less dense than the molten aluminum, floats upon the aluminum. An interface 36 separates the
15 molten aluminum 30 from the molten cryolite 32.

An insulating layer 39 is provided to resist heat flow from the cell 10. While a variety of well-known structures are available for making this insulating structure, commonly the insulating layer 39 is
20 crystallized contents of the electrolytic cell.

The anodes 22, 24 are fabricated from any suitable or conventional material and immersed in a cryolite phase 32 contained in the cell. Since oxygen is released in some form at the anode, the anode material
25 must be either resistant to attack by oxygen or should be made of a material that can be agreeably reacted with the evolving oxygen, preferably producing a lower anode half cell voltage by virtue of reactive depolarization. Typically, carbon or graphite is utilized. The anodes 22,
30 24 should be arranged for vertical movement within the cell so that a desired spacing can be maintained between the anode and cathode notwithstanding the anode being consumed by evolved oxygen.

A packed bed 41 of loose elements 42 is
35 positioned in the cell, in the molten aluminum pool 30. These elements are formed of a substance substantially non-wettable by aluminum. The elements are maintained in

the molten aluminum at a level at or below the interface between the molten aluminum and molten cryolite, the depth to which the elements are packed being substantially uniform across the cell. In general, the elements should
5 be not further than 5 centimeters from the interface, but should not extend substantially above the interface, particularly where the elements 42 may be subject to aggressive attack by the cryolite.

The packed bed elements can be of any shape. It
10 is preferred that the shapes provide, when packed, substantial interstices through the packed bed to assure that aluminum fills gaps in the packing to maintain uniform electrical conductivity through the packed pool of aluminum. Particularly, packing in the form of berl
15 saddles, Intalox saddles, Raschig rings and equiaxed shapes such as cylinders and spheres are much preferred; however randomly shaped packing, blocks or bricks may also suffice.

The packing is fabricated from a material
20 substantially non-wettable by molten aluminum, with alumina, Al_2O_3 , being much preferred. Since alumina is soluble in the molten cryolite, and since aluminum is being electrolyzed from alumina dissolved in the cryolite layer 32, it is important that the alumina packing be
25 maintained reliably beneath the interface. Immersion in the molten aluminum shields the packing elements from aggressive attack by the cryolite.

Other suitable materials for fabrication of the packing include AlN , Al_4C_3 , AlB_{12} , BN , SiAlON , AlB_2 , ZrO_2 ,
30 HfO_2 , ThO_2 , mixtures of these refractory materials and mixtures with aluminum oxide. Particularly, preferred are Al_2O_3 , Al_4C_3 , SiAlON , ZrO_2 , HfO_2 and ThO_2 , mixtures thereof, and mixtures thereof with Al_2O_3 .

Electrical conductivity of the packing elements
35 is relatively unimportant. Conductivity pathways through the aluminum immersing the packing provide the substantial current routes between the cathodic current feeder and the

interface 36 where active electrowinning occurs. Where the packing provides interstices too small to permit a substantial number of electrical pathways through the aluminum non-wettable packed bed from the current feeder to the interface, than an unacceptably elevated voltage in
5 operating the cell results.

The packing elements 42 arranged in the cell and immersed in the molten aluminum function to suppress wave formation and propagation in the molten aluminum. Reduced
10 wave action permits quite close anode spacing to the molten aluminum cathode interface 36. This close spacing reduces voltage requirements in operating the cell, thereby reducing power consumption. In order to dampen effectively wave formation in the molten aluminum, it is
15 preferred that the packing be quite close to the interface while remaining immersed in the molten aluminum. Spacings between the packing and the interface of greater than about 5 centimeters generally will provide less than satisfactory performance in dampening wave motion.

Use of non-wettable materials such as alumina for packing materials can offer a substantial cost advantage over the use of expensive wettable materials such as titanium boride. Where interstices between and within the non-wettable packing elements are sufficiently
20 large and numerous to permit required electrical pathways between the current feeder and the interface to support aluminum electrolysis being undertaken, then electrical conductivity in the packing material is not required. In general, suitable packing elements 42 range in size from
25 about .1 centimeters to about 5 centimeters, with packing in a size range of from 1 centimeter to 3 centimeters being preferred.
30

The following examples are offered to further illustrate the invention.

EXAMPLE 1

Alumina tubes, fabricated from McDanel Grade 998 alumina, some tubes 39 millimeter (mm) O.D. x 90 mm tall, having a 2 mm wall and some 12.7 mm O.D. x 90 mm tall and having a 2 mm wall were inserted vertically into a laboratory cell containing 600 grams of molten aluminum interfacing with a thin layer of molten cryolite mix. The tubes protruded slightly through the interface. The cell was held at 1,000°C for one hour; then cooled to room temperature and the solid aluminum containing the alumina tubes was cross-sectioned. It was found that aluminum had completely encapsulated the alumina and filled the tubes. Some of the alumina had fractured, it is believed, due to thermal shock and a small section of the 12.7 mm O.D. tubing was found laying horizontally at the bottom of the cell, completely filled by aluminum. Sections of the alumina tubes protruding through the aluminum into the cryolite had the typical appearance of poor wetting by aluminum with an apparent contact angle greater than 90°.

Although aluminum does not normally wet alumina under the experimental conditions described, good contact between the alumina and aluminum was observed at a depth 0.5 cm and greater below the aluminum cryolite interface. The good contact between the alumina and aluminum was attributed to both a thin intermediate layer of cryolite mix and the head pressure of the aluminum and cryolite above the tube samples. The confinement of aluminum in the alumina tubes reduced the movement of the aluminum pad within the cell.

EXAMPLE 2

Raschig rings of alumina, McDanel Grade 998, 29 mm O.D. x 7 mm with a wall thickness of 2 mm were placed in an alumina crucible 54 mm O.D. x 45 mm deep and covered with 150 grams of aluminum shot, Alfa 3.2 mm. The crucible was fitted with an alumina covered graphite current feeder to form a cathode assembly. The cathode

assembly was inserted into a larger alumina crucible, 73 mm I.D. x 152 mm tall, with a 4 mm wall, and 500 grams of cryolite mix was added to cover the cathode assembly. A carbon anode was attached to the larger crucible in contact with the cryolite, thereby forming an aluminum electrowinning cell which was then inserted into a crucible furnace. At 1,000°C, electrowinning of aluminum was undertaken with an average cell voltage of 3.52 V and at a cathode current density of 0.5 A/cm² for 5.5 hours.

Initial adjustment of the cathode current feeder was necessary to insure good contact with the aluminum cathode pad in the first 30 minutes of the electrolysis. For the electrolysis run as a whole, the current efficiency was in a range of 60 - 70%.

Inspection of the packed cathode bed, after cooling, clearly showed the aluminum completely covering the alumina Raschig rings. No cryolite or sludge was observed within the solidified packed cathode bed upon sectioning of the sample. Frozen cryolite mix was found in areas between walls of the cathode crucible container and the packed cathode bed. Wetting of the alumina packing by aluminum was not observed

EXAMPLE 3

Stability of alumina aluminum-non-wettable elements in a commercial cell was evaluated by insertion of packing elements into a commercial cell for controlled periods of time. Packing elements utilized were fused-cast alumina bricks, preheated for four hours prior to insertion into a 60 kiloampere vertical stud Soderberg cell. The fused-cast bricks, some measuring 95 x 110 x 148 mm and some 110 x 148 x 187 mm, were lowered into the cell at the edge of the anode shadow and placed on the bottom of the cell. The bricks were exposed to the commercial cell environment for periods of 15 minutes, 1 week, and 4½ months.

Evaluation of the fused-cast alumina bricks after the 15 minute and 1 week tests identified no change in the bulk dimensions. The corners of the samples remained square. There was no evidence of bulk
5 dissolution; however, large cracks were observed in the sample tested for 1 week. These cracks were attributed to thermal stress. The brick retained in the cell for 4½ months fractured into 3 pieces. Bulk dissolution of this 4½ month sample was not observed.

10 Wetting of the alumina by aluminum was not observed. Penetration of the bath along the cracks in the samples was observed. Some local dissolution was found on crack faces. Discoloration of the fused-cast alumina bricks was observed, the depth of discoloration being
15 dependent upon the length of exposure, i.e., the brick immersed for 4½ months having the greatest discoloration. Penetration of bath as evidenced by alumina discoloration was greatest at a layer of columnar grains on the samples. Greater localized dissolution was also observed at these
20 columnar grains. The fused-cast alumina packing bricks did not produce a perceptible change in the current efficiency of the commercial cell as no anode-cathode spacing adjustments were effected. Estimated life of the fused-cast alumina is in excess of two years.

25 While a preferred embodiment of the invention has been shown and described in detail, it should be apparent that various alterations and modifications may be made without departing from the scope of the appended claims.

What is claimed is:

1. In an aluminum electrowinning cell having an anode mounted in a vertical spaced relationship to a cathode assembly, the anode being immersed in a molten cryolite pool, the improved cathode assembly comprising:

an electrically conductive cathodic current feeder arranged in vertical spaced relationship with the anode;

a pool cathode of molten aluminum covering the cathodic current feeder, the molten cryolite pool being atop the molten aluminum pool; and

a packed cathode bed of loose elements consisting essentially of an aluminum-non-wettable refractory material substantially resistant to attack by the molten aluminum and cryolite while immersed in molten aluminum, the bed elements being disposed atop the current feeder to a predetermined depth not greater than the depth of the aluminum pool covering the current feeder.

2. The improved cathode assembly of claim 1 wherein the bed elements are formed from a material selected from a group consisting essentially of Al_2O_3 , AlN , Al_4C_3 , AlB_{12} , BN , SiAlON , AlB_2 , ZrO_2 , HfO_2 , ThO_2 and mixtures thereof.

3. The improved cathode assembly of claim 1 wherein the aluminum cathode pool covering the cathodic current feeder is maintained to be not greater than 5 cm in depth beyond the depth of the loose bed of packing elements.

4. In an aluminum electrowinning cell having an anode mounted in a vertical spaced relationship with a cathode assembly, the anode being immersed in a cryolite pool, the improved cathode assembly comprising:

an electrically conductive cathodic current feeder arranged in vertical spaced relationship with the anode;

5 a pool cathode of molten aluminum covering the cathodic current feeder, the molten cryolite being atop the molten aluminum pool; and

10 a packed cathode bed of loose elements consisting essentially of an aluminum-non-wettable refractory material substantially resistant to attack by the molten aluminum and cryolite while immersed in the molten aluminum, the bed elements being disposed atop the current feeder to a predetermined depth not greater than the depth of the aluminum pool covering the current feeder, the bed elements being formed from a material
15 selected from a group consisting essentially of Al_2O_3 , Al_4C_3 , SiAlOn , ZrO_2 , HfO_2 , ThO_2 , and mixtures thereof, and the molten aluminum pool depth being not more than 5 centimeters in excess of the depth of the loose bed of packing elements.

20 5. An electrolytic cell for electrowinning aluminum from a fused cryolite-alumina bath having at least one anode immersed in the bath, the cell further comprising:

25 a cathodic current feeder, and a molten aluminum cathode covering the current feeder and in a spaced vertical relationship to the anode, the cathode further including a packed bed of aluminum-non-wettable loose elements formed of a refractory material substantially resistant to attack by molten aluminum and
30 cryolite while immersed in molten aluminum, the packing elements being arranged upon the current feeder to a depth not exceeding the depth of molten aluminum covering the current feeder, the the loose packing elements being formed from a material selected from a group consisting
35 essentially of Al_2O_3 , Al_4C_3 , SiAlOn , ZrO_2 , HfO_2 , ThO_2 , and mixtures thereof.

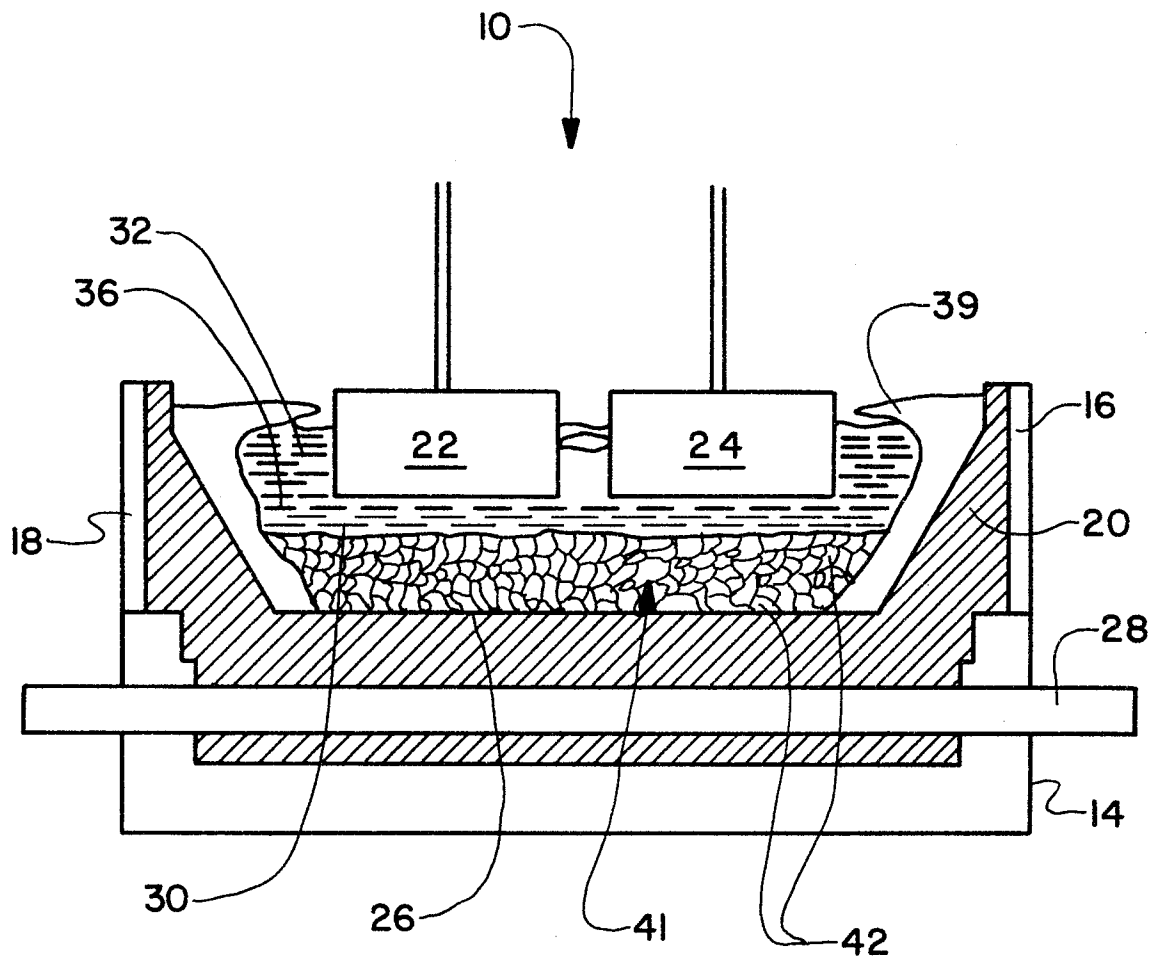


FIG. 1



EP 83810164.0

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 2)
X	EP - A1 - 0 033 630 (DIAMOND SHAMROCK) * Claims 1,8,9 *	1-5	C 25 C 3/08
X	DE - A1 - 3 041 680 (SCHWEIZE-RISCHE ALUMINIUM AG) * Claim 1; fig. 2 *	1-5	
A	DE - A1 - 3 110 490 (SCHWEIZE-RISCHE ALUMINIUM AG) * Page 5, lines 28-30; page 6, line 25-32; page 8, lines 12-30; fig. 2 *	1-5	
P,A	FR - A - 2 508 496 (ALUMINIUM PECHINEY) * Page 3, lines 6-15; fig. 1 *	1,4	TECHNICAL FIELDS SEARCHED (Int. Cl. 2)
A	DE - A1 - 3 024 172 (SCHWEIZE-RISCHE ALUMINIUM AG) * Page 7, line 6 - page 8, line 10 *	1,4	C 25 C
A	US - A - 4 308 115 (ALUMINIUM COMPANY OF AMERICA) * Abstract; fig. 1 *	1,4	
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 22-07-1983	Examiner ONDER
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			