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(54) **ELECTROLYTIC CELL FOR PRODUCTION OF RARE EARTH METALS**

ELEKTROLYSEZELLE ZUR HERSTELLUNG VON SELTENERDMETALLEN

CELLULE ÉLECTROLYTIQUE POUR LA PRODUCTION DE MÉTAUX DES TERRES RARES

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(73) Proprietor: **Lynas Services Pty Ltd**

Sydney, New South Wales 2000 (AU)

(72) Inventors:

• **KENIRY, Jeffrey**
Mount Macedon, Victoria 3441 (AU)

• **KJAR, Anthony Rudland**

Blackburn, Victoria 3130 (AU)

(74) Representative: **Zinkler, Franz et al**

Schoppe, Zimmermann, Stöckeler

Zinkler, Schenk & Partner mbB

Patentanwälte

Radlkoferstrasse 2

81373 München (DE)

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Description

Field

[0001] The present disclosure relates generally to electrolytic cells, in particular electrolytic cells adapted to produce rare earth metals, such as neodymium, praseodymium, cerium, lanthanum and mixtures thereof, by an electrolysis process in a molten fluoride or chloride electrolyte bath.

Background

[0002] Electrolytic cells for production of aluminium in a molten fluoride or chloride salt bath are well known and many of their design features address important considerations. In particular, it is important to maintain a stable and low anode-cathode distance (ACD) as an energy saving measure in a highly energy intensive process. Maintaining a constant ACD may prove difficult where molten aluminium pools on the surface of the cathode and is under hydrodynamic forces imposed by strong magnetic fields. Accordingly, in some cell configurations, the cathodes may be suspended above the cell floor onto which the molten aluminium pools. In other configurations, the cathodes may be provided with channels into which the molten aluminium may collect, thereby draining the molten aluminium from the cathode surface as soon as it forms to maintain a constant ACD.

[0003] It is also important that the electrolytic cell is configured to liberate carbon dioxide gas, which evolves at the anode surface during the electrolysis, from the interelectrode space to substantially prevent 'back reaction' with the aluminium metal as it forms on the cathode surface, thereby reducing the efficiency of the electrolysis process.

[0004] Neodymium and praseodymium, mixtures thereof, and other rare earth metals, are also currently made commercially by an electrolysis process in a molten mixed fluoride salt bath. In contrast to the electrolytic production of aluminium, the anodes and cathodes are disposed in a vertical orientation and the molten metal is collected into a receiving vessel on the floor of the cell. The interelectrode space is not affected by the molten metal accumulation, but it is nevertheless subject to change by the continuous electrolytic consumption of the carbon anode surfaces. The cathodes are typically comprised of an inert metal, such as molybdenum or tungsten.

[0005] As the anodes are consumed, there is no effective means to keep anode-cathode separation distance uniform. As the major part of the process heat is delivered by the ohmic resistance of the electrode spacing, the process temperature is highly variable and generally controlled by reduction in current supplied to the cell. This is impractical in larger scale operations where a number of cells would be connected in electrical series. Furthermore, deterioration in current throughout the electrolysis

process is also undesirable since it decreases the production capacity of the cell. Most importantly, failure to closely control the process temperature reduces the process yield, or Faraday efficiency, and results in the formation of insoluble sludge which settles on the floor of the cell. Consequently, the electrolysis has to be periodically halted to remove the sludge from the cell, thereby inhibiting continuous electrolysis.

[0006] Poor control of the process temperature also increases the vapour emissions from the cell, which are harmful to the working atmosphere and the environment if they are not contained.

[0007] Additionally, as the anodes are consumed, their displaced volume in the electrolyte decreases and the electrolyte level in the cell falls. This reduces the working area of the anode immersed in the electrolyte, to the detriment of process efficiency including power consumption and increased possibility of 'anode effects' generating highly polluting gases.

[0008] Moreover, the product rare earth metal is reactive with carbon at the process temperature. Carbon is a highly undesirable impurity for certain rare earth metal product applications. Decreasing the possibility of contact between fugitive carbon in the cell and the metal and/or the residence time of product metal in the cell are desirable design attributes that are not apparent in the current commercial cell designs. This particular problem is not a factor in the design of electrolytic cells for aluminium production because aluminium does not react with carbon under these conditions.

[0009] Additionally, in current electrolytic cell designs for rare earth metals, it is difficult to maintain the product rare earth metals in a molten state because the operating temperatures are preferably only 10-30 °C above the freezing point of the product rare earth metals. This problem is not an issue and is not addressed in electrolytic cells for electrolytic production of aluminium because the process temperature is about 300 °C above the freezing point of aluminium.

[0010] Current commercial activities for electrolytic production of rare earth metals are small in scale, labour intensive and operated in a semi-batch manner. Several deficiencies prevent the process from being scaled up to allow higher productivity, continuous electrolysis, and high standards of environmental performance, occupational health and safety to be achieved.

[0011] Firstly, the electrolysis cells generally operate in a limited current range of 5-10 kiloamperes, commensurate with low production capacity.

[0012] There is poor control of a rare earth oxide feed material to the cell, resulting in the accumulation of insoluble sludges that require frequent cell clean-out thereby hindering continuous electrolysis. Additionally, feed material is delivered to the cell manually, without a known reference to the current oxide concentration in the cell.

[0013] The existing technology uses vertical electrode arrangements. Such arrangements are not amenable to achieving a high Faraday efficiency. For example, gas

bubbles which evolve and rise from the anode surface are likely to be entrained in the electrolyte flows and make contact with the product metal forming on the cathode plates, thereby reducing the process yield consequent to back-oxidation of the product metal.

[0014] US 5 810 993 A describes a method of producing neodymium in an electrolytic cell designed to operate without the occurrence of anode effects, therefore avoiding the generation and release of highly polluting perfluorinated carbon (PFC) gases. In this invention, the objectives are achieved firstly by providing a multitude of anode plates such that the anodic current density remains well below that at which the anode effect may occur, and secondly by physically separating the vertical cathodes from the vertical anodes using an inert barrier material which remains porous to neodymium ions, such that a higher concentration of dissolved neodymium oxide can be maintained in the anode region than in the cathode region. The disclosed invention has a number of deficiencies and impracticalities however. There is no demonstration in the cited examples that the barrier material (boron nitride) is indeed permeable to neodymium ions as would be required for a continuous electrolysis process. Further, the proposed anode design is complex and the wear rate of the anode plates may be expected to be highly non-uniform and wasteful. The compartmental separation of the anodic and cathodic zones further results in a large interelectrode separation distance, and a resulting inefficient energy consumption. Further, the invention proposes use of carbon as the inert cathode material, while it is well known that carbon will react with and contaminate the product metal.

[0015] US 4 684 448 A discloses a process and an apparatus for producing a neodymium-iron alloy by electrolysis reduction of neodymium fluoride in a bath of molten electrolyte conducted between one or more iron cathode and one or more carbon anode.

[0016] US 3 909 375 A discloses production of metals by electrolysis of their respective metal halides wherein the metals are deposited on one of a pair of spaced substantially parallel electrodes, the opposed surfaces of which are inclined at an angle of between 5° and 30° to the vertical. Gas liberated in the inter-electrode space is discharged upwardly into a gas separation chamber disposed above the inter-electrode space.

[0017] There is therefore a need for alternative or improved electrolytic cells and processes for producing rare earth metals.

[0018] The above references to the background art do not constitute an admission that the art forms a part of the common general knowledge of a person of ordinary skill in the art. The above references are also not intended to limit the electrolytic cell as disclosed herein.

Summary of the Disclosure

[0019] The invention provides an electrolytic cell according to claim 1. Further developments of the invention

are defined in the dependent claims.

[0020] In a first aspect there is disclosed an electrolytic cell for production of rare earth metals comprising:

- 5 a cell housing provided with one or more inclined channels disposed in a floor of the cell housing along which channel(s) molten rare earth metals produced in the electrolytic cell can drain;
- 10 one or more cathodes suspended within the cell housing in substantially vertical alignment with the one or more channels, respective opposing surfaces of the one or more cathodes being downwardly and outwardly inclined at an angle from the vertical;
- 15 one or more pairs of consumable anodes suspended within the cell housing, each anode in the one or more pairs having a facing surface inclined from the vertical and spaced apart in parallel alignment with respective opposing inclined surfaces of the one or more cathodes to define a substantially constant anode-cathode distance therebetween;
- 20 a sump for receiving molten rare earth metals from the channel, wherein the sump is spaced apart and isolated from the one or more cathodes and the one or more pairs of anodes; and
- 25 a device operatively associated with the one or more anodes to control the distance between the anodes and the opposing sides of the cathode in response to anode consumption.

30 **[0021]** In a further aspect there is disclosed a system for electrolytically producing rare earth metals comprising:

- 35 an electrolytic cell in accordance with the first aspect as defined above;
- a feed material comprising one or more rare earth metal compounds capable of undergoing electrolysis to produce rare earth metals;
- 40 an electrolyte in which molten state the feed material is soluble; and,
- a source of direct current configured to pass a current between an anode and a cathode of the electrolytic cell to electrolyse the feed material and thereby produce molten rare earth metal product in the electrolytic cell.
- 45

[0022] In another aspect there is disclosed a process for electrolytically producing rare earth metals comprising:

- 50 providing an electrolytic cell in accordance with the first aspect;
- charging the electrolytic cell with a feed material comprising one or more rare earth metal compounds capable of undergoing electrolysis to produce rare earth metals and an electrolyte bath comprising molten electrolyte in which the feed material is soluble;
- 55 passing a direct current between at least one con-

sumable anode and a cathode in the electrolytic cell to electrolyse the feed material and thereby produce molten rare earth metal product; and, displacing the molten electrolyte in the electrolytic cell to maintain a height of the electrolyte bath in the electrolytic cell.

[0023] In a still further aspect there is disclosed a process for electrolytically producing rare earth metals comprising:

providing an electrolytic cell in accordance with the first aspect;
charging the electrolytic cell with a feed material comprising one or more rare earth metal compounds capable of undergoing electrolysis to produce rare earth metals and a molten electrolyte in which the feed material is soluble;
passing a direct current between at least one consumable anode and a cathode in the electrolytic cell to electrolyse the feed material and thereby produce molten rare earth metal product on the cathode; and, translating the or each consumable anode toward the cathode in response to a rate of anode consumption to maintain a constant anode-cathode distance in the electrolytic cell.

[0024] Embodiments disclosed allow improved control capability for anode-cathode distance (ACD) and consequently process temperature, improved control of electrolyte bath height in the electrolytic cell and anode immersion, better mixing of the electrolyte to enhance dissolution of the feed material, and higher Faraday efficiency by limiting opportunity for back reaction of anode gas with produced metal.

Brief Description of the Figures

[0025] Notwithstanding any other forms which may fall within the scope of the disclosure as set forth in the Summary, specific embodiments will now be described, by way of example only, with reference to the accompanying drawings in which:

Figure 1 is side view of an electrolytic cell in accordance with one specific embodiment; and

Figure 2 is a cross-sectional view of the electrolytic cell shown in Figure 1.

Detailed Description of Specific Embodiments

[0026] The description broadly relates to an electrolytic cell arranged to produce rare earth metals by an electrolysis process in a molten electrolytic salt bath.

[0027] The rare earth metals produced in the electrolytic cell disclosed herein include those rare earth metals having a melting point less than 1100 °C. Exemplary rare

earth metals include, but are not limited to, Ce, La, Nd, Pr, Sm, Eu, and alloys thereof including didymium and mischmetal. The electrolytic cell disclosed herein is also suitable for the production of alloys of rare earth metals with iron.

[0028] The molten electrolytic salt bath behaves as a solvent for the feed material. The electrolyte for use in the molten electrolytic salt bath may comprise halide salts, in particular fluoride salts. Examples of 'fluoride salts' include, but are not limited to, metal fluoride salts including rare earth metal fluorides such as LaF₃, CeF₃, NdF₃, and PrF₃, alkali metal fluorides such as LiF, KF, and alkaline earth metal fluorides such as CaF₂, BaF₂.

[0029] Selection of a feed material for the electrolysis process will depend on the desired rare earth metal product and the composition of the electrolyte. Where the electrolyte is composed of fluoride salts, the feed material that is subjected to the electrolysis process may comprise oxides of the rare earth metals.

[0030] The term 'rare earth metal oxide' broadly refers to any oxide or any precursors of such oxides of a rare earth metal, including rare earth metal hydroxides, carbonates or oxalates. Rare earth metals are a set of seventeen chemical elements in the periodic table, specifically the fifteen lanthanides plus scandium and yttrium. Scandium and yttrium are considered rare earth metals since they tend to occur in the same ore deposits as the lanthanides and exhibit similar chemical properties. The lanthanides include lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium.

[0031] Suitable examples of feed material for electrolytic production of neodymium or praseodymium include neodymium oxide (Nd₂O₃) or praseodymium oxide (Pr₆O₁₁). Where an alloy, such as didymium, is the desired product the feed material may comprise two or more oxides of rare earth metals (e.g. Nd₂O₃ and Pr₆O₁₁) in the desired stoichiometric ratio of the desired alloy. Mischmetal may be prepared from oxides of several rare earth metals, such as Ce, La, Nd, Pr, wherein the ratio of rare earth metals in the mischmetal corresponds to the ratio of rare earth metal oxides in the feed material.

[0032] Alternatively, where the electrolyte is composed of chloride salts, the feed material may comprise chloride salts of the rare earth metals.

[0033] In one embodiment the electrolyte comprises one or more rare earth metal fluorides and lithium fluoride. The one or more rare earth metal fluorides may be present in the electrolyte in a range of about 70-95 wt% with the balance as lithium fluoride. Optionally, the electrolyte may further comprise up to 20 wt% calcium fluoride and/or barium fluoride.

[0034] It will be appreciated by persons skilled in the art that the operating temperature of the electrolytic cell will depend on the target rare earth metal product or rare earth metal alloy, the composition of the electrolyte, and consequently the respective freezing points of the rare

earth metal, alloy and electrolyte. In one embodiment, the operating temperature of the electrolytic cell may be in the range of 5 - 50 °C above the freezing point of the electrolyte, and preferably 10 - 20 °C above the melting point of the electrolyte. The composition of the electrolyte is selected so that the liquidus of the electrolyte may be in a range of 5 - 50 °C above the freezing point of the metal.

[0035] In some embodiments, where the target rare earth metal product is mischmetal (a mixture of cerium, lanthanum, neodymium and praseodymium), the freezing point is variable depending on the composition of the mischmetal and the relative ratios of the rare earth metals therein, but nonetheless is around 800 °C. In these embodiments, the electrolyte may include barium or calcium fluorides as described above to achieve an electrolyte liquidus in the range of 5 - 50 °C above the freezing point of the mischmetal.

[0036] In other embodiments, where the freezing points of the rare earth metal alloys or mixtures are 800 °C or lower, the electrolyte may optionally comprise one or more rare earth metal chloride and lithium chloride salts.

[0037] Referring to Figures 1 and 2, where like numerals refer to like parts throughout, there is shown an embodiment of an electrolytic cell 10 for production of rare earth metals. The cell 10 includes a housing 12 having a floor 14, a sump 16, one or more cathodes 18, and one or more pairs of anodes 20.

[0038] The housing 12 is formed from anti-corrosive materials which are inert in view of the electrolyte composition and operating conditions, as has been described in the preceding paragraphs. In particular, the anti-corrosive materials used to internally line the housing 12 should be resistant to forming an alloy with the rare earth metals produced therein. In one embodiment the housing 12 may be lined internally with refractory materials. Suitable refractory materials include, but are not limited to, carbon, silicon carbide, silicon nitride, boron nitride, or certain stainless steels such as will be well known to those skilled in the art.

[0039] The inclined floor 14 has one or more inclined channels 22 disposed therein along which molten rare earth metals produced in the electrolytic cell 10 can drain. In one embodiment, the one or more inclined channels 22 are inclined from the horizontal at an angle α of up to about 10°.

[0040] In the embodiment shown in Figure 2, the channel 22 has a rectangular cross-section. It will be appreciated, however, that in alternative embodiments, the cross-section of the channel 26 may take other forms, such as a V-shape or a U-shape.

[0041] In some forms of the invention the floor 14 may be provided with more than one inclined channel 22, as shown in Figure 2. In these particular forms the channels 22 are configured in adjacent lateral parallel alignment with one another. In general, the channel(s) 22 may be aligned along or spaced equidistantly from a central lon-

gitudinal axis of the floor 14 in the housing 12. In this arrangement, the channel(s) 22 in the floor 14 may be located proximal to an underside 24 of the one or more cathodes 18 to receive molten rare earth metals produced on the one or more cathodes 18.

[0042] The floor 14, or an upper surface of the floor 14, may be formed from anti-corrosive materials similar to or the same as those materials selected for the lining of the cell housing 12. All surfaces having direct contact with the rare earth metal product, including the channel(s) 22 and the sump 16 should be resistant to forming alloys with the rare earth metals produced in the electrolytic bath. Suitable lining materials for the channel(s) 22 and the sump 16 include, but are not limited to, metals such as tungsten, molybdenum, or tantalum.

[0043] The sump 16 is configured to receive, in use, molten rare earth metal produced on the one or more cathodes 18 which collects in the channel and drains towards the lower end 26 of the channel 22. The sump 16 is spaced apart and isolated from the one or more cathodes 18 and the one or more anodes 20.

[0044] The sump 16 may be provided with a heater to maintain a temperature above the liquidus of the molten rare earth metal. The sump 16 may also be provided with a port (not shown) from which molten rare earth metal may be tapped as required. The sump 16 may be formed from inert metals similar to those used for the housing 12.

[0045] The arrangement allows for continuous removal of molten rare earth metal product from the floor 14 of the cell 10 which prevents pooling of the molten rare earth metal product and consequently provides several advantages. In prior art electrolytic cells where a pool of molten rare earth metal product is allowed to form, particularly on the floor of the cell or at a cathodic surface, it is common for the molten rare earth metal product to become contaminated with 'sludge' which comprises undissolved and partially molten rare earth feed material, reaction intermediates, and byproducts. In the electrolytic cell 10 disclosed herein, in the absence of molten rare earth metal product, the sludge remains in contact with the molten electrolyte and is thereby provided with an opportunity for re-dissolution in the molten electrolyte.

[0046] The molten rare earth metal product collected in the sump 16 is spaced apart from and isolated from the one or more cathodes 18 and the one or more anodes 20. Consequently, the molten rare earth metal is protected from reaction and/or contamination with fugitive carbon arising from the one or more anodes 20, and back reactions with off gases from the one or more anodes 20.

[0047] The one or more cathodes 18 are suspended in the electrolyte bath 11 contained within the cell housing 12 above the channel 22 in substantially vertical alignment therewith. In the form as illustrated, the cathodes 18 comprise plates of cathodic material having an upper surface 28 and opposing elongate surfaces 30, with the underside 24 being disposed above the channel 22 in so that molten rare earth metal produced on the opposing surfaces 30 may fall under gravity directly into the under-

lying channel 22. The opposing surfaces 30 of the cathodes 18 are supported by an inert refractory filler material 32 which further avoids the formation of an inactive electrolyte zone in the cell 10.

[0048] The cathodes 18 are configured in adjacent alignment with one another whereby opposing elongate surfaces 30 of adjacent cathodes 18 are respectively longitudinally aligned with one another and respective opposing end surfaces of adjacent cathodes 18 face one another. It will be appreciated by persons skilled in the art that spacing between facing opposing end surfaces of adjacent cathodes 18 is as narrow as possible.

[0049] The plates of cathodic material are correspondingly sized so that, in the arrangement as described above, an effective length of the adjacently disposed cathodes 18 is substantially the same as or marginally shorter than the length of the channel 22.

[0050] Alternatively, a single cathode 18 having a similar length as the channel 22 may be employed in the electrolytic cell 10 as disclosed herein.

[0051] The opposing elongate surfaces 30 of the cathodes 18 are downwardly and outwardly inclined at an angle from the vertical, whereby a cross-sectional shape of the cathode 18 is substantially triangular. The opposing elongate surfaces 30 may be inclined from the vertical by angle β of up to about 45° , and preferably from 2° to 10° .

[0052] The angle of inclination is selected on the basis of optimised bubble-driven flow of electrolyte to achieve good mixing with feed material, and maintenance of high Faraday yield. The desired angle β may be determined by computational modelling for the specific cell geometry.

[0053] In embodiments where a single rare earth metal or an alloy of rare earth metals is the desired electrolytic product, the cathodes 18 may be formed from an electrically conductive material with sufficient resistive heat properties to ensure free flow of the molten rare earth metals at temperatures marginally greater than their melting points. Such materials should be resistant to forming alloys with the rare earth metals produced in the electrolytic bath. Suitable materials include, but are not limited to, metals such as tungsten, molybdenum, or tantalum.

[0054] In alternative embodiments where an alloy of iron with one or more rare earth metals is desired, the cathode 18 may be formed from iron. It will be appreciated by persons skilled in the art that in these particular embodiments, the cathode 18 will be consumed during the electrolytic process for production of the iron-rare earth metal alloy.

[0055] In the embodiment shown in Figures 1 and 2, a plurality of pairs of anodes 20 are suspended within the cell housing 12. Each anode 20 in the pair is spaced apart from respective opposing elongate surfaces 30 of the cathodes 18. In the form as illustrated, the anodes 20 comprise plates of consumable anodic material having an upper surface 32, a lower surface 34, opposing distal and proximal elongate surfaces 36a, 36b and opposing

ends 38. Distal elongate surface 36a of each anode 20 may be substantially vertical or may be inclined from the vertical. The proximal elongate surface 36b is inclined from the vertical. The proximal elongate side 36b may be inclined from the vertical by angle β' of up to about 45° , and preferably from 2° to 10° , tapering toward the lower surface 34 of the anode 20.

[0056] The proximal elongate surfaces 36b of the anodes 18 face respective opposing elongate surfaces 30 of the cathodes 18. Both surfaces 36b and 30 are inclined from the vertical by corresponding angle β' such that the said surfaces 36b and 30 are spaced apart in parallel alignment with one another so as to define a substantially constant anode-cathode distance therebetween.

[0057] The anodes 20 are configured in adjacent alignment with one another whereby opposing elongate surfaces 36a, 36b of adjacent anodes 20 are respectively longitudinally aligned with one another and respective opposing ends 38 of adjacent anodes 20 face one another. It will be appreciated by persons skilled in the art that spacing between facing opposing ends 38 of adjacent anodes 20 is as narrow as possible.

[0058] The plates of anodic material are correspondingly sized so that, in the arrangement as described above, an effective length of the adjacently disposed anodes 20 is substantially the same as or marginally shorter than the length of the channel 22.

[0059] Alternatively, a single pair of anodes 20 having a similar length as the channel 22 may be employed in the electrolytic cell 10 as disclosed herein.

[0060] Suitable examples of consumable anodic material include, but are not limited to, carbon-based materials in particular high purity carbon, electrode grade graphite, calcined petroleum coke-coal tar pitch formulations. Such formulations will be well known to those skilled in electrolytic production of rare earth metals and other metals such as aluminium.

[0061] The anodes are consumed as the electrolysis process progresses and the angle of inclination β of proximal elongate side 36b remains substantially constant. Gas bubbles released from the anode 20 are therefore retained close to the proximal elongate surface 36b as the gas bubbles rise to the electrolyte surface, by virtue of the inclined profile of proximal elongate surface 36b, as illustrated in Figure 2. Advantageously, this reduces the opportunity for contact of the evolved gas with metal forming on the cathode 18, hence improving Faraday efficiency and avoiding insoluble sludges formed by back reaction therewith.

[0062] Under most operating conditions the ACD in the electrolytic cell, as disclosed herein, may be between about 30 mm to about 200 mm, although an ACD of between about 50 mm to about 100 mm is preferred. The person skilled in the art may readily determine an appropriate ACD depending on the desired heat generation in the electrolyte zone, electrolyte flows for optimum solubility of the feed material, and optimisation of the process yield (Faraday efficiency).

[0063] The anode is consumed during electrolysis and consequently the ACD may increase as electrolysis progresses. The electrolysis cell 10 disclosed herein may be provided with a device 40 operatively associated with the one or more anodes 20 to control the ACD, in particular to maintain a substantially constant ACD. Said device 40 may comprise a horizontal positioning apparatus in operative communication with the one or more anodes 20. In use, the horizontal positioning apparatus may laterally translate the one or more anodes 20 toward the cathode 18 in response to a rate at which the anode 20 is consumed so that the ACD may remain substantially constant. The rate of anode consumption may be determined by reference to current flow. Alternatively, the horizontal positioning apparatus may translate the one or more anodes 20 in response to variation in cell resistance from a predetermined value.

[0064] Consequent to anode consumption, the volume occupied by the anodes 20 in the electrolytic cell 10 decreases thereby lowering the height of the electrolyte bath in the housing 12. Similarly, the intermittent cell operations such as the replacement of spent anodes with new anodes, and the removal of rare earth metal product from the cell, will result in substantial and undesirable variation in the height of the electrolyte bath and the electrode immersion depth. The electrolysis cell 10 disclosed herein may be provided with a displacement device 42 to control the height of the electrolyte bath in the housing 12, in particular to maintain a substantially constant height of the electrolyte bath in the housing 12. The displacement device 42 may comprise an inert body which is suspended in the housing 12 and positionable in a vertical direction. In use, the inert body may be downwardly or upwardly translated in response to specific cell operation so that the height of the electrolyte bath may remain substantially constant. The inert body may take any suitable form, for example a bar as illustrated in the Figures.

[0065] The displacement device 42 may be formed from similar refractory materials as the inner linings of the housing 12 as described previously.

[0066] In use, the electrolysis process may be performed by charging the molten electrolyte to the electrolytic cell 10 as described herein. An alternating current may be supplied between the cathodes 18 and the anodes 20 and the resistance of the electrodes 18, 20 raises the operating temperature of the electrolytic cell 10 to a predetermined temperature. The feed material is then charged to the electrolytic cell 10 and dissolves in the molten electrolyte. A direct current in a range of 5-100 kiloamperes is supplied to the anodes 20, whereupon electrolysis of the dissolved feed material commences. In the electrolytic reaction the feed material is reduced to molten rare earth metal(s) on the opposing elongate surfaces 30 of the cathode 18. The molten rare earth metal(s) subsequently fall into the channel 22 and drain along the channel 22 into the sump 16, which is tapped as required. Feed material may be regularly charged to

the electrolytic cell 10 into areas of high electrolyte flow, at a rate corresponding more or less to the consumption rate. It will be appreciated by those familiar with the art that the feed rate may be finely controlled to achieve a target cell resistance corresponding to the desired concentration of feed in the electrolyte.

[0067] The electrolysis process may be performed under an inert or low oxygen atmosphere within the electrolytic cell 10. The inert atmosphere may be established and maintained by supplying an inert gas or gas mixtures to the electrolytic cell 10 to exclude air therefrom and thereby prevent undesirable reactions with the molten electrolyte and/or the electrodes 18, 20. Suitable examples of inert gases include, but are not limited to, helium, argon, and nitrogen.

[0068] Numerous variations and modifications will suggest themselves to persons skilled in the relevant art, in addition to those already described, without departing from the basic inventive concepts. All such variations and modifications are to be considered within the scope of the present invention, the nature of which is to be determined from the preceding description.

[0069] In the claims which follow, and in the preceding description, except where the context requires otherwise due to express language or necessary implication, the word "comprise" and variations such as "comprises" or "comprising" are used in an inclusive sense, i.e. to specify the presence of the stated features but not to preclude the presence or addition of further features in various embodiments of the apparatus and method as disclosed herein.

Claims

1. An electrolytic cell for production of rare earth metals comprising:

a cell housing provided with one or more inclined channels disposed in a floor of the cell housing along which channel(s) molten rare earth metals produced in the electrolytic cell can drain;
 one or more cathodes suspended within the cell housing in substantially vertical alignment with the one or more channels, respective opposing surfaces of the one or more cathodes being downwardly and outwardly inclined at an angle from the vertical;
 one or more pairs of consumable anodes suspended within the cell housing, each anode in the one or more pairs having a facing surface inclined from the vertical and spaced apart in parallel alignment with respective opposing inclined surfaces of the one or more cathodes to define a substantially constant anode-cathode distance therebetween;
 a sump for receiving molten rare earth metals from the channel, wherein the sump is spaced

- apart and isolated from the one or more cathodes and the one or more anodes; and a device operatively associated with the one or more anodes to control the distance between the anodes and the opposing sides of the cathode in response to anode consumption. 5
2. The electrolytic cell as defined in claim 1 further comprising a displacement device to control a height of the electrolyte bath contained in the cell housing. 10
3. The electrolytic cell as defined in claim 2, wherein displacement device comprises an inert body which is suspended in the housing and positionable in a vertical direction. 15
4. The electrolytic cell as defined in claim 1, wherein the device operatively associated with the one or more anodes comprises a horizontal positioning apparatus. 20
5. The electrolytic cell as defined in claim 4, wherein the horizontal positioning apparatus is configured, in use, to laterally translate the one or more anodes towards the cathode in response to a rate at which the anodes are consumed. 25
6. The electrolytic cell as defined in any one of the preceding claims, wherein the one or more channels therein are inclined from the horizontal at an angle of up to about 10°. 30
7. The electrolytic cell as defined in any one of the preceding claims, wherein the one or more channels have a cross-sectional shape that is rectangular, V-shaped or U-shaped. 35
8. The electrolytic cell as defined in any one of the preceding claims, wherein the opposing sides of the cathode and the facing sides of the anode are inclined from the vertical by up to 45°. 40
9. The electrolytic cell as defined in claim 8, wherein the opposing sides of the cathode and the facing sides of the anode are inclined from the vertical by 2° to 10°. 45
10. A system for electrolytically producing rare earth metals comprising:
an electrolytic cell as defined in any one of the preceding claims; 50
- a feed material comprising one or more rare earth metal compounds capable of undergoing electrolysis to produce rare earth metals; 55
- a molten electrolyte in which the feed material is soluble; and,
- a source of direct current configured to pass a

current between an anode and a cathode in the electrolytic cell to electrolyse the feed material and thereby produce molten rare earth metal product in the electrolytic cell.

11. A process for electrolytically producing rare earth metals comprising:

providing an electrolytic cell as defined in any one of claims 2 to 10;
charging the electrolytic cell with a feed material comprising one or more rare earth metal compounds capable of undergoing electrolysis to produce rare earth metals and an electrolyte bath comprising molten electrolyte in which the feed material is soluble;
passing a direct current between at least one consumable anode and a cathode in the electrolytic cell to electrolyse the feed material and thereby produce molten rare earth metal product on the cathode; and,
displacing the molten electrolyte in the electrolytic cell to maintain a height of the electrolyte bath in the electrolytic cell.

12. A process for electrolytically producing rare earth metals comprising:

providing an electrolytic cell according to any one of claims 1 to 10;
charging the electrolytic cell with a feed material comprising one or more rare earth metal compounds capable of undergoing electrolysis to produce rare earth metals and a molten electrolyte in which the feed material is soluble;
passing a direct current between at least one consumable anode and a cathode in the electrolytic cell to electrolyse the feed material and thereby produce molten rare earth metal product on the cathode; and,
translating the or each consumable anode toward the cathode in response to a rate of anode consumption to maintain a constant cathode-anode distance in the electrolytic cell.

Patentansprüche

1. Eine Elektrolysezelle zur Erzeugung von Seltene-Erden-Metallen, die folgende Merkmale aufweist:

ein Zellengehäuse, das mit einem oder mehreren geneigten Kanälen versehen ist, die in einem Boden des Zellengehäuses angeordnet sind, wobei geschmolzene Seltene-Erden-Metalle, die in der Elektrolysezelle erzeugt werden, entlang dieses Kanals oder dieser Kanäle abfließen können;

- eine oder mehrere Kathoden, die in dem Zellengehäuse in im Wesentlichen vertikaler Ausrichtung mit dem einen oder den mehreren Kanälen aufgehängt sind, wobei jeweilige gegenüberliegende Oberflächen der einen oder mehreren Kathoden in einem Winkel von der Vertikalen nach unten und nach außen geneigt sind, ein oder mehrere Paare verzehrbaren Anoden, die in dem Zellengehäuse aufgehängt sind, wobei jede Anode in dem einen oder den mehreren Paaren eine zugewandte Oberfläche aufweist, die von der Vertikalen geneigt ist, und in Parallelausrichtung mit jeweiligen gegenüberliegenden geneigten Oberflächen der einen oder der mehreren Kathoden beabstandet ist, um eine im Wesentlichen konstante Entfernung zwischen Anode und Kathode dazwischen zu definieren;
- 20 einen Sammelbehälter zum Aufnehmen von geschmolzenen Seltene-Erden-Metallen aus dem Kanal, wobei der Sammelbehälter von der einen oder den mehreren Kathoden und der einen oder den mehreren Anoden beabstandet und getrennt ist; und
- 25 eine Vorrichtung, die der einen oder den mehreren Anoden wirksam zugeordnet ist, um die Entfernung zwischen den Anoden und den gegenüberliegenden Seiten der Kathode ansprechend auf ein Anodenverzehren zu steuern.
- 30
2. Die Elektrolysezelle gemäß Anspruch 1, die ferner eine Verschiebungsvorrichtung aufweist, um eine Höhe des Elektrolytbads, das in dem Zellengehäuse beinhaltet ist, zu steuern.
3. Die Elektrolysezelle gemäß Anspruch 2, bei der die Verschiebungsvorrichtung einen trägen Körper aufweist, der in dem Gehäuse aufgehängt und in einer vertikalen Richtung positionierbar ist.
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4. Die Elektrolysezelle gemäß Anspruch 1, bei der die Vorrichtung, die der einen oder den mehreren Anoden wirksam zugeordnet ist, ein Horizontalpositionierungsgerät aufweist.
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5. Die Elektrolysezelle gemäß Anspruch 4, bei der das Horizontalpositionierungsgerät ausgebildet ist, um bei Verwendung die eine oder die mehreren Anoden ansprechend auf eine Rate, mit der die Anoden verzehrt werden, seitlich in Richtung der Kathode zu verschieben.
- 50
6. Die Elektrolysezelle gemäß einem der vorherigen Ansprüche, bei der der eine oder die mehreren Kanäle in derselben von der Horizontalen in einem Winkel von bis zu etwa 10° geneigt sind.
- 55
7. Die Elektrolysezelle gemäß einem der vorherigen Ansprüche, bei der der eine oder die mehreren Kanäle eine Querschnittsform aufweisen, die rechteckig, V-förmig oder U-förmig ist.
- 5 8. Die Elektrolysezelle gemäß einem der vorherigen Ansprüche, bei der die gegenüberliegenden Seiten der Kathode und die zugewandten Seiten der Anode von der Vertikalen um bis zu 45° geneigt sind.
- 10 9. Die Elektrolysezelle gemäß Anspruch 8, bei der die gegenüberliegenden Seiten der Kathode und die zugewandten Seiten der Anode von der Vertikalen um 2° bis 10° geneigt sind.
- 15 10. Ein System zum Erzeugen von Seltene-Erden-Metallen durch Elektrolyse, das folgende Merkmale aufweist:
- 20 eine Elektrolysezelle gemäß einem der vorherigen Ansprüche;
- ein Zuführmaterial, das eine oder mehrere Seltene-Erden-Metall-Verbindungen aufweist, das einer Elektrolyse unterzogen werden kann, um Seltene-Erden-Metalle zu erzeugen;
- 25 ein geschmolzenes Elektrolyt, in dem das Zuführmaterial löslich ist; und
- eine Gleichstromquelle, die ausgebildet ist, um einen Strom zwischen einer Anode und einer Kathode in der Elektrolysezelle hindurchzuleiten, um das Zuführmaterial einer Elektrolyse zu unterziehen und dadurch ein geschmolzenes Seltene-Erden-Metall-Produkt in der Elektrolysezelle zu erzeugen.
- 35 11. Ein Verfahren zum Erzeugen von Seltene-Erden-Metallen durch Elektrolyse, das folgende Schritte aufweist:
- 40 Bereitstellen einer Elektrolysezelle gemäß einem der Ansprüche 2 bis 10;
- Beladen der Elektrolysezelle mit einem Zuführmaterial, das eine oder mehrere Seltene-Erden-Metall-Verbindungen aufweist, das einer Elektrolyse unterzogen werden kann, um Seltene-Erden-Metalle zu erzeugen, und einem Elektrolytbad, das geschmolzenes Elektrolyt aufweist, in dem das Zuführmaterial löslich ist;
- 45 Hindurchleiten eines Gleichstroms zwischen zumindest einer verzehrbaren Anode und einer Kathode in der Elektrolysezelle, um das Zuführmaterial einer Elektrolyse zu unterziehen und dadurch ein geschmolzenes Seltene-Erden-Metall-Produkt an der Kathode zu erzeugen; und
- 50 Verschieben des geschmolzenen Elektrolyts in der Elektrolysezelle, um eine Höhe des Elektrolytbads in der Elektrolysezelle aufrechtzuerhalten.

12. Ein Verfahren zum Erzeugen von Seltene-Erden-Metallen durch Elektrolyse, das folgende Schritte aufweist:

Bereitstellen einer Elektrolysezelle gemäß einem der Ansprüche 1 bis 10;
 Beladen der Elektrolysezelle mit einem Zuführmaterial, das eine oder mehrere Seltene-Erden-Metall-Verbindungen aufweist, das einer Elektrolyse unterzogen werden kann, um Seltene-Erden-Metalle zu erzeugen, und einem geschmolzenen Elektrolyt, in dem das Zuführmaterial löslich ist;
 Hindurchleiten eines Gleichstroms zwischen zumindest einer verzehrbaren Anode und einer Kathode in der Elektrolysezelle, um das Zuführmaterial einer Elektrolyse zu unterziehen und dadurch ein geschmolzenes Seltene-Erden-Metall-Produkt an der Kathode zu erzeugen; und
 Verschieben der oder jeder verzehrbaren Anode in Richtung der Kathode ansprechend auf eine Rate eines Anodenverzehrns, um eine konstante Entfernung zwischen Kathode und Anode in der Elektrolysezelle aufrechtzuerhalten.

Revendications

1. Cellule électrolytique pour la production de métaux des terres rares, comprenant:

un boîtier de cellule pourvu d'un ou plusieurs canaux inclinés disposés dans un fond du boîtier de cellule, canal ou canaux le long desquels peuvent s'écouler les métaux de terres rares fondus produits dans la cellule d'électrolyse;
 une ou plusieurs cathodes suspendues à l'intérieur du boîtier de cellule en alignement sensiblement vertical avec les un ou plusieurs canaux, les surfaces opposées respectives des une ou plusieurs cathodes étant inclinées vers le bas et vers l'extérieur suivant un angle par rapport à la verticale;
 une ou plusieurs paires d'anodes consommables suspendues à l'intérieur du boîtier de cellule, chaque anode dans les une ou plusieurs paires présentant une surface se faisant face inclinée par rapport à la verticale et espacée en alignement parallèle avec les surfaces inclinées opposées respectives des une ou plusieurs cathodes pour définir une distance anode-cathode sensiblement constante entre ces dernières;
 un puisard destiné à recevoir les métaux des terres rares fondus du canal, où le puisard est espacé et isolé des une ou plusieurs cathodes et des une ou plusieurs anodes; et

un dispositif associé fonctionnement associé aux une ou plusieurs anodes pour réguler la distance entre les anodes et les côtés opposés de la cathode en réponse à la consommation d'anode.

2. Cellule électrolytique selon la revendication 1, comprenant par ailleurs un dispositif de déplacement destiné à réguler une hauteur du bain d'électrolyte contenu dans le boîtier de cellule.
3. Cellule électrolytique selon la revendication 2, dans laquelle le dispositif de déplacement comprend un corps inerte qui est suspendu dans le boîtier et qui peut être positionné selon une direction verticale.
4. Cellule électrolytique selon la revendication 1, dans laquelle le dispositif associé en fonctionnement aux une ou plusieurs anodes comprend un appareil de positionnement horizontal.
5. Cellule électrolytique selon la revendication 4, dans laquelle l'appareil de positionnement horizontal est configuré, lors de l'utilisation, pour déplacer en translation latérale les une ou plusieurs anodes vers la cathode en réponse à un taux selon lequel sont consommées les anodes.
6. Cellule électrolytique selon l'une quelconque des revendications précédentes, dans laquelle les un ou plusieurs canaux y présents sont inclinés par rapport à l'horizontale suivant un angle de jusqu'à environ 10°.
7. Cellule électrolytique selon l'une quelconque des revendications précédentes, dans laquelle les un ou plusieurs canaux présentent une forme de section transversale qui est rectangulaire, en forme de "V" ou en forme de "U".
8. Cellule électrolytique selon l'une quelconque des revendications précédentes, dans laquelle les côtés opposés de la cathode et les côtés se faisant face de l'anode sont inclinés par rapport à la verticale de jusqu'à 45°.
9. Cellule électrolytique selon la revendication 8, dans laquelle les côtés opposés de la cathode et les côtés se faisant face de l'anode sont inclinés par rapport à la verticale de 2° à 10°.
10. Système de production électrolytique de métaux des terres rares, comprenant:
 une cellule électrolytique telle que définie dans l'une quelconque des revendications précédentes;

un matériau d'alimentation comprenant un ou plusieurs composés de métaux des terres rares

à même de subir une électrolyse pour produire des métaux des terres rares;
 un électrolyte fondu dans lequel est soluble le matériau d'alimentation; et
 une source de courant continu configurée pour faire passer un courant entre une anode et une cathode dans la cellule électrolytique pour électrolyser le matériau d'alimentation et produire ainsi un produit de métaux des terres rares fondus dans la cellule électrolytique.

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11. Procédé de production électrolytique de métaux des terres rares, comprenant le fait de:

prévoir une cellule électrolytique telle que définie dans l'une quelconque des revendications 2 à 10;
 charger la cellule électrolytique d'un matériau d'alimentation comprenant un ou plusieurs composés de métaux des terres rares à même de subir une électrolyse pour produire des métaux de terres rares et un bain d'électrolyte comprenant un électrolyte fondu dans lequel est soluble le matériau d'alimentation;
 faire passer un courant continu entre au moins une anode consommable et une cathode dans la cellule électrolytique pour électrolyser le matériau d'alimentation et produire ainsi un produit de métaux des terres rares fondu sur la cathode;
 et
 déplacer l'électrolyte fondu dans la cellule électrolytique pour maintenir une hauteur du bain d'électrolyte dans la cellule électrolytique.

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12. Procédé de production électrolytique de métaux des terres rares, comprenant le fait de:

prévoir une cellule électrolytique selon l'une quelconque des revendications 1 à 10;
 charger la cellule d'électrolyse d'un matériau d'alimentation comprenant un ou plusieurs composés de métaux des terres rares à même de subir une électrolyse pour produire des métaux des terres rares et un électrolyte fondu dans lequel est soluble le matériau d'alimentation;
 faire passer un courant continu entre au moins une anode consommable et une cathode dans la cellule électrolytique pour électrolyser le matériau d'alimentation et produire ainsi un produit de métaux des terres rares fondus sur la cathode; et
 déplacer en translation la ou chaque anode consommable vers la cathode en réponse à un taux de consommation d'anode pour maintenir une distance cathode-anode constante dans la cellule électrolytique.

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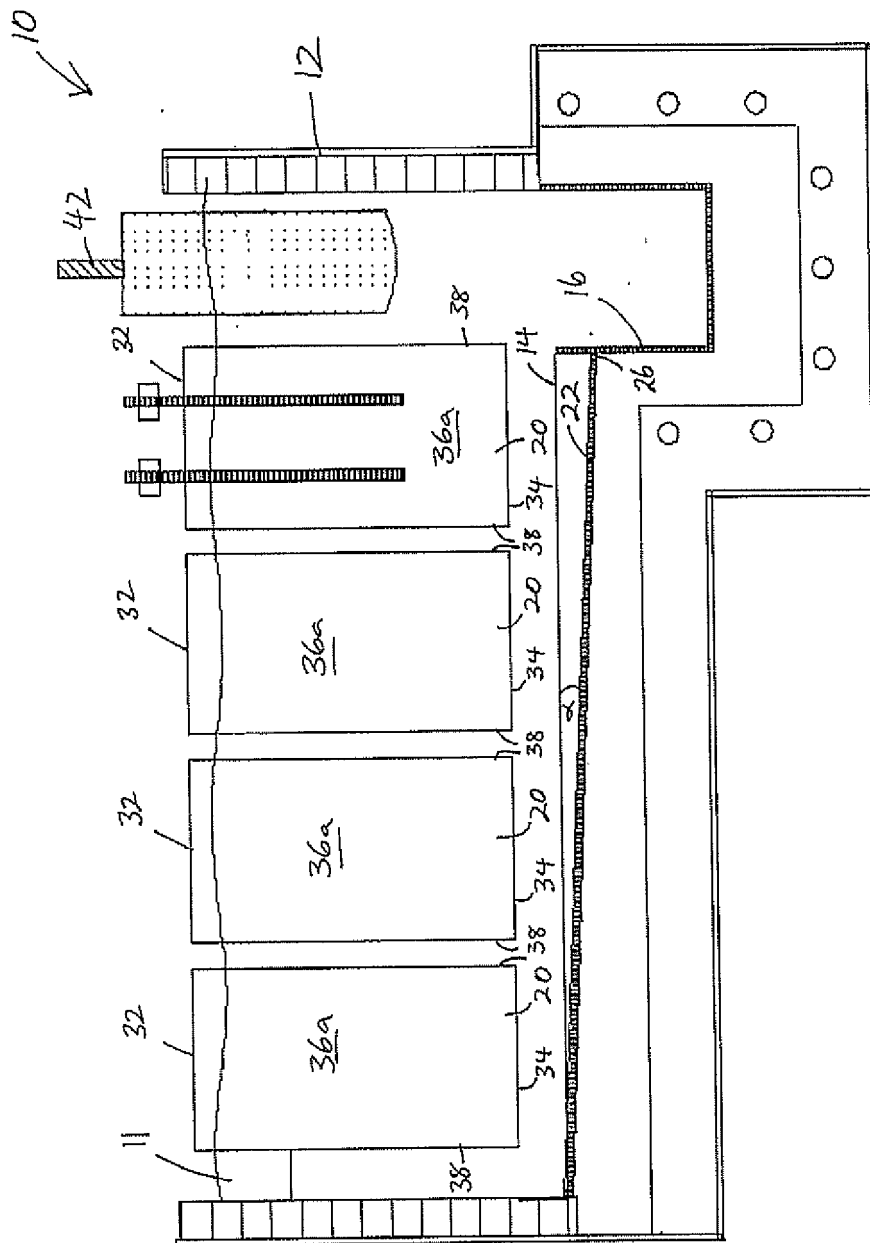


Figure 1

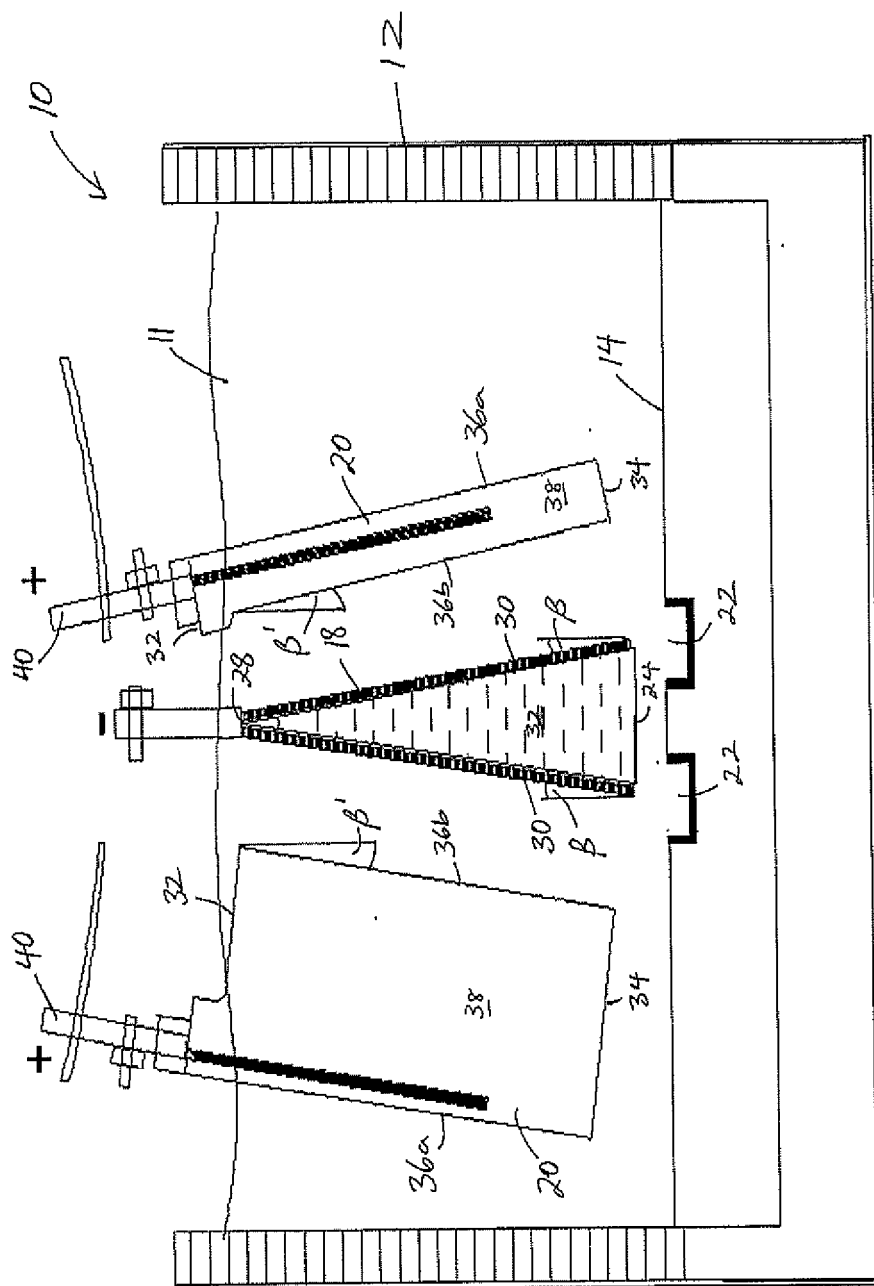


Figure 2

REFERENCES CITED IN THE DESCRIPTION

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