ALUMINIUM ELECTROWINNING CELLS WITH METAL-BASED ANODES

Inventor: Vittorio de Nora, Nassau (BS)

Correspondence Address:
J R Deshmukh
458 Cherry Hill Road
Princeton, NJ 08540 (US)

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ABSTRACT

A cell for the electrowinning of aluminium comprises a metal-based anode (10) containing at least one of nickel, cobalt and iron, for example an anode made from an alloy consisting of 50 to 60 weight % in total of nickel and/or cobalt; 25 to 40 weight % iron; 6 to 12 weight % copper; 0.5 to 2 weight % aluminium and/or niobium; and 0.5 to 1.5 weight % in total of further constituents. The anode (10) may have an applied hematite-based coating and optionally a cerium oxyfluoride-based outermost coating. The cell contains a fluoride-containing molten electrolyte (5) at a temperature below 940°C, in which the anode is immersed and which consists of: 5 to 14 weight % dissolved aluminium; 35 to 45 weight % aluminium fluoride; 30 to 45 weight % sodium fluoride; 5 to 20 weight % potassium fluoride; 0 to 5 weight % calcium fluoride; and 0 to 5 weight % in total of one or more further constituents. A nickel-containing anode stem (14b) can be used to suspend the anode (10) in the electrolyte facing a cathode (21, 21A, 25) that has an aluminium-wettable surface (20), in particular a drained horizontal or inclined surface.
ALUMINIUM ELECTROWINNING CELLS WITH METAL-BASED ANODES

FIELD OF THE INVENTION

[0001] This invention relates to aluminium electrowinning cells having metal-based anodes which contain at least one of nickel, iron and copper and which during use are inhibited from passivating and dissolving and from causing unacceptable contamination of the product aluminium.

BACKGROUND ART

[0002] The technology for the production of aluminium by the electrolysis of alumina, dissolved in molten cryolite, at temperatures around 950° C. is more than one hundred years old and still uses carbon anodes and cathodes.

[0003] Using metal anodes in commercial aluminium electrowinning cells would be new and drastically improve the aluminium process by reducing pollution and the cost of aluminium production.

[0004] U.S. Pat. Nos. 4,614,569 (Duruz/Debely/Adorian), 4,680,094 (Duruz), 4,683,037 (Duruz) and 4,966,674 (Bunnochie/Smith) describe non-carbon anodes for aluminium electrowinning coated with a protective coating of cerium oxyfluoride, formed in-situ in the cell or pre-applied, this coating being maintained by the addition of a cerium compound to the molten cryolite electrolyte. This made it possible to have a protection of the anode surface from the electrolyte attack and to a certain extent from the gaseous oxygen but not from the nascent monoatomic oxygen.

[0005] EP Patent application 0 306 100 (Nguyen/Lazouni/Doan) describes anodes composed of a chromium, nickel, cobalt and/or iron based substrate covered with an oxygen barrier layer and a ceramic coating of nickel, copper and/or manganese oxide which may be further covered with an in-situ formed protective cerium oxyfluoride layer. Likewise, U.S. Pat. Nos. 5,069,771, 4,960,494 and 4,956,068 (all Nguyen/Lazouni/Doan) disclose aluminium production anodes with an oxidised copper-nickel surface on an alloy substrate with a protective oxygen barrier layer. However, full protection of the alloy substrate was difficult to achieve.

[0006] U.S. Pat. No. 6,248,227 (de Nora/Duruz) discloses an aluminium electrowinning anode having a metallic anode body which can be made of various alloys, for example a nickel-iron-copper alloy. During use, the surface of the anode body is oxidised by anodically evolved oxygen to form an integral electrochemically active oxide-based surface layer. The oxidation rate of the anode body is equal to the rate of dissolution of the surface layer into the electrolyte. This oxidation rate is controlled by the thickness and permeability of the surface layer which limits the diffusion of anodically evolved oxygen therethrough to the anode body.

[0007] U.S. Pat. No. 6,372,099 (Duruz/de Nora) discloses the use of transition metal species in an electrolyte below 910° C. of an aluminium electrowinning cells to inhibit dissolution of metal-based anodes of the cell.

[0008] WO00/06803 (Duruz/de Nora/Crottaz) and WO00/06804 (Crottaz/Duruz) both disclose an anode produced from a nickel-iron alloy which is surface oxidised to form a coherent and adherent outer iron oxide-based layer whose surface is electrochemically active. WO00/06804 also mentions that the anode may be used in an electrolyte at a temperature of 820° to 870° C. containing 23 to 26.5 weight % AlF₃, 3 to 5 weight % Al₂O₃, 1 to 2 weight % LiF and 1 to 2 weight % MgF₂.

[0009] U.S. Pat. Nos. 5,006,209 and 5,284,562 (both Beck/Brooks), 6,258,247 and 6,379,512 (both Brown/Brooks/Frizzle/Juric), 6,419,813 (Brown/Brooks/Frizzle) and 6,436,272 (Brown/Frizzle) all disclose the use of nickel-copper-iron anodes in an aluminium production electrolyte at 660° to 800° C. containing 6-26 weight % NaF; 7-33 weight % KF; 1-6 weight % LiF and 60-65 weight % Al₂O₃. The electrolyte may contain Al₂O₃ in an amount of up to 30 weight %, in particular 5 to 10 weight %, most of which is in the form of suspended particles and some of which is dissolved in the electrolyte, i.e. typically 1 to 4 weight % dissolved Al₂O₃. In U.S. Pat. Nos. 6,258,247, 6,379,512, 6,419,813 and 6,436,272 such an electrolyte is said to be usable at temperatures up to 900° C. In U.S. Pat. Nos. 6,258,247 and 6,379,512 the electrolyte further contains 0.004 to 0.2 weight % transition metal additives to facilitate alumina dissolution and improve cathode operation.

[0010] U.S. Pat. No. 5,725,144 (de Nora/Duruz) discloses an aluminium production cell having anodes made of nickel, iron and/or copper in an electrolyte at a temperature from 680° to 880° C. containing 42-63 weight % AlF₃, up to 48 weight % NaF; up to 48 weight % LiF and 1 to 5 weight % Al₂O₃, MgF₂, KF and CaF₂ are also mentioned as possible constituents.

SUMMARY OF THE INVENTION

[0012] One object of the invention is to provide an aluminium electrowinning cell incorporating metal-based anodes which remain substantially insoluble at the cell operating temperature and which can be operated without passivation or excessive contamination of the produced aluminium.

[0013] Another object of the invention is to provide an aluminium electrowinning cell operating with a crustless and ledgeless electrolyte which can achieve high productivity, low contamination of the product aluminium, and whose components resist corrosion and wear.

[0014] The invention relates to a cell for electrowinning aluminium from alumina. The cell comprises: a metal-based anode having an outer part that contains at least one of nickel, cobalt and iron and that has an electrochemically active oxide-based surface; and a fluoride-containing molten electrolyte at a temperature below 940° C., in particular in the range from 880° to 920° C., in which the active anode surface is immersed. The electrolyte consists of: 5 to 14 weight % overall of dissolved alumina; 35 to 45 weight % aluminium fluoride; 30 to 45 weight % sodium fluoride; 5 to 20 weight % potassium fluoride; 0 to 5 weight % calcium fluoride; and 0 to 5 weight % in total of one or more further constituents.

[0015] For instance, the electrolyte consists of: 7 to 10 weight % dissolved alumina; 38 to 42 weight % aluminium fluoride; 34 to 43 weight % sodium fluoride; 8 to 15 weight % potassium fluoride; 2 to 4 weight % calcium fluoride; and 0 to 3 weight % in total of one or more further constituents.
Such an electrolyte composition is well adapted for aluminium electrowinning at reduced temperature, i.e. at a temperature below the conventional aluminium electrowinning temperature of about 950°C, using a metal-based anode containing at least one of nickel, cobalt and iron, usually in metallic and/or oxide form. The electrolyte is particularly adapted for anodes containing at least one of metallic nickel, metallic cobalt and oxides of iron. Oxides of iron include ferrous oxide, hematite, magnetite and ferrites (e.g. nickel ferrite), in stoichiometric and non-stoichiometric form. For example, the anode has a metallic alloy body that contains one or more of these metals — nickel, cobalt and iron — and that is covered with an integral active oxide layer or film.

The presence in the electrolyte of potassium fluoride in the given amount has two effects. On the one hand, it leads to a reduction of the working temperature by up to several tens of degrees without increase of the electrolyte’s aluminium fluoride content or even a reduction thereof compared to standard electrolytes operating at about 950°C, with an aluminium fluoride content of about 45 weight %.

On the other hand, it maintains a high solubility of alumina, i.e. up to above about 14 weight %, in the electrolyte even though the temperature of the electrolyte is reduced by a few tens of degrees compared to conventional temperature.

Hence, in contrast to prior art low temperature electrolytes which carry large amounts of undissolved alumina in particulate form, according to the present invention a large amount of alumina in the electrolyte is in a dissolved form.

Without being bound to any theory, it is believed that combining a high concentration of dissolved alumina in the electrolyte and a limited concentration of aluminium fluoride leads predominantly to the formation of (basic) fluorine-poor aluminium oxyfluoride ions \( \text{[AlF}_2\text{O}]^{2-} \) instead of (acid) fluorine-rich aluminium oxyfluoride ions \( \text{[Al}_2\text{OF}_3]^{3-} \) near the anode. As opposed to acid fluorine-rich aluminium oxyfluoride ions, basic fluorine-poor aluminium oxyfluoride ions do not significantly passivate the anode’s nickel and cobalt, or dissolve the anode’s iron. In particular, basic fluorine-poor aluminium oxyfluoride ions do not significantly passivate metallic nickel and cobalt, or dissolve iron oxides.

The weight ratio of dissolved alumina/aluminium fluoride in the electrolyte should be above 1/7, and often above 1.5 or even above 1/6, to obtain a favourable ratio of the fluorine-poor aluminium oxyfluoride ions and the fluorine-rich aluminium oxyfluoride ions.

It follows that the use of the above described electrolyte with metal-based anodes containing at least one of nickel, cobalt and iron inhibits passivation and corrosion thereof.

In order to maintain the alumina concentration above the given threshold during normal electrolysis, the cell is preferably fitted with means to monitor and adjust the electrolyte’s alumina content.

The abovementioned one or more further constituents of the electrolyte may comprise at least one fluoride selected from magnesium fluoride, lithium fluoride, cesium fluoride, rubidium fluoride, strontium fluoride, barium fluoride and cerium fluoride.

Advantageously, the cell is sufficiently insulated to be operated with a substantially crustless and/or ledgeless electrolyte. Suitable cell insulation is disclosed in U.S. Pat. No. 6,402,928 (de Nora/Sekhar), WO02/070784 and US Application 2003/0102228 (both de Nora/Berclaz).

The cell can have a cathode that has an aluminium-wettable surface, in particular a drained horizontal or inclined surface. Suitable cathode designs are for example disclosed in U.S. Pat. Nos. 5,683,559, 5,888,360, 6,093,304 (all de Nora), 6,258,246 (Duruz/de Nora), 6,358,393 (Bercelaz/de Nora) and 6,436,273 (de Nora/Duruz), and in PCT applications WO99/02764 (de Nora/Duruz), WO00/63463 (de Nora), WO01/31086 (de Nora/Duruz), WO01/31088 (de Nora), WO02/070785 (de Nora), WO02/097168 (de Nora), WO02/097168 (de Nora), WO03/023091 (de Nora) and WO03/023092 (de Nora).

The cathode can have an aluminium-wettable coating that comprises a refractory boride and/or an aluminium-wetting oxide. Suitable aluminium-wetting materials are disclosed in WO01/42168 (de Nora/Duruz), WO01/42531 (Nguyen/Duruz/de Nora), WO02/070783 (de Nora), WO02/096831 (Nguyen/de Nora) and WO02/096830 (Duruz/Nguyen/de Nora).

The anode can have a metallic or cermet body and an oxide layer integral with or applied on the anode body.

Usually, the anode body is made from an iron alloy, in particular an alloy of iron with nickel and/or cobalt. Suitable alloys are disclosed in U.S. Pat. Nos. 6,248,227 (de Nora/Duruz), 6,521,115 (Duruz/de Nora/Crottaz), 6,562,224 (Crottaz/Duruz), and in PCT publications WO00/04783 (de Nora/Duruz), WO01/42534 (de Nora/Duruz), WO01/42536 (Duruz/Nguyen/de Nora), WO02/083991 (Nguyen/de Nora), WO03/014420 (Nguyen/Duruz/de Nora) and WO03/078695 (Nguyen/de Nora).

For example, the anode body is made from an alloy consisting of:

- 40 to 80% nickel and/or cobalt, in particular 50 to 60 weight %;
- 9 to 55 weight % iron, in particular 25 to 40 weight %;
- 5 to 15 weight % copper, in particular 6 to 12 weight %;
- 0 to 4 weight % in total of at least one of aluminium, niobium and tantalum, in particular 0.5 to 2 weight %; and
- 0 to 2 weight % in total of further constituents, in particular 0.5 to 1 weight %.

Typically such an alloy is oxidised prior to or during use. This can lead to diffusion of metals in the anode, especially at the alloy’s surface, which locally changes the alloy’s composition.

The anode body can be covered with an integral iron oxide-based layer containing less than about 35 weight % nickel oxide and/or cobalt oxide, in particular from 5 to 10 weight % nickel oxide. Such integral layers are usually obtained by preoxidation of the body before and/or during use in the cell.

The anode may also comprise an applied iron oxide-based coating. Suitable iron oxide-based coatings are disclosed in U.S. Pat. Nos. 6,361,681 (de Nora/Duruz), 6,365,018 (de Nora), 6,379,526 (de Nora/Duruz) and 6,413,406 (de Nora), and in PCT applications PCT/IB03/01479, PCT/IB03/03654 and PCT/IB03/03978 (all Nguyen/de Nora). For example, the anode coating contains Fe₃O₄ and optionally: at least one dopant selected from TiO₂, ZnO and CuO and/or at least one inert material selected from nitrides and carbides.

Especially when used in the upper part of the abovementioned operating temperature range (e.g. 910°C–940°C), the anode can comprise an applied cerium oxyfluoride-based
A nickel-containing stem can be used to suspend the 
anode in the electrolyte, in particular a stem having a 
nickel-containing core covered with an applied oxide coating, 
such as a coating containing aluminium oxide and titanium oxide. 
The core of the stem can comprise a copper inner part and a 
nickel-based outer part. Further details of anode stems are 
disclosed in PCT/IB03/02702 (Crottaz/Duruz).

Suitable anode designs are for example disclosed in 
WO99/02764 (de Nora/Duruz), WO00/04781, WO00/04782, 
WO03/023091, WO03/023092 and WO03/006716 (all de Nora).

Usually, the cell comprises at least one component, 
e.g., the cathode, that contains a sodium-active cathodic 
material, such as elemental carbon. This sodium-active cathodic 
material is preferably shielded from the electrolyte by a 
sodium-inert layer to inhibit the presence in the molten 
electrolyte of soluble cathodically-produced sodium metal that 
constitutes an agent for dissolving the active oxide-based 
anode surface. This mechanism is explained in greater detail 
in US Application 2003/0075454 and WO03/083176 (both de 
Nora/Duruz).

The invention also relates to a cell that comprises:

- a metal-based anode having an outer part that has 
an electrochemically active oxide-based surface and that 
is made from an alloy consisting of: 50 to 60 weight % in 
total of nickel and/or cobalt; 25 to 40 weight % iron; 6 to 
12 weight % copper; 0.5 to 2 weight % aluminium 
and/or niobium; and 0.5 to 1.5 weight % in total of 
other constituents, the anode comprising an applied 
matte-based coating and optionally a cerium oxyfluoride-based 
outermost coating;

- a nickel-containing anode stem for suspending 
the anode in the electrolyte, the stem being covered with 
a coating of aluminium oxide and titanium oxide;

- a fluoride-containing molten electrolyte at a 
temperature in the range from 880°C to 920 or 930°C, 
in which the active anode surface is immersed and which 
consists of: 7 to 10 weight % dissolved alumina; 38 to 42 
weight % aluminium fluoride; 28 to 43 weight % sodium 
fluoride; 8 to 15 weight % potassium fluoride; 2 to 4 
weight % calcium fluoride; and 0 to 3 weight % in total of 
one or more further constituents; and

a cathode having an aluminium-wettable surface, 
in particular a drained horizontal or inclined surface, 
formed by an aluminium-wettable coating of refractory 
hard material and/or aluminium-wetting oxide.

A further aspect of the invention relates to a method 
of electrowinning aluminum in a cell as described above. 
The method comprises electrowining the dissolved alumina to 
produce oxygen on the anode and aluminium cathodically, and 
supplying alumina to the electrolyte to maintain therein a 
concentration of dissolved alumina of 5 to 14 weight %, in 
particular 7 to 10 weight %.

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

FIGS. 1a and 1b schematically show respectively a side 
elevation and a plan view of an anode for use in a cell 
according to the invention;

FIGS. 2a and 2b show a schematic cross-sectional 
view and a plan view, respectively, of an aluminium produc- 
tion cell for equipment with a potassium fluoride-containing 
electrolyte and a metal-based anode according to the inven- 
tion; and

FIG. 3 shows a schematic cross-sectional view of 
another aluminium production cell for equipment with a 
potassium fluoride-containing electrolyte and a metal-based 
anode according to the invention.

The invention also relates to a cell that comprises:

- a metal-based anode having an outer part that has 
an electrochemically active oxide-based surface and that 
is made from an alloy consisting of: 50 to 60 weight % in 
total of nickel and/or cobalt; 25 to 40 weight % iron; 6 to 
12 weight % copper; 0.5 to 2 weight % aluminium 
and/or niobium; and 0.5 to 1.5 weight % in total of 
other constituents, the anode comprising an applied 
matte-based coating and optionally a cerium oxyfluoride-based 
outermost coating;

- a nickel-containing anode stem for suspending 
the anode in the electrolyte, the stem being covered with 
a coating of aluminium oxide and titanium oxide;

- a fluoride-containing molten electrolyte at a 
temperature in the range from 880°C to 920 or 930°C, 
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weight % aluminium fluoride; 28 to 43 weight % sodium 
fluoride; 8 to 15 weight % potassium fluoride; 2 to 4 
weight % calcium fluoride; and 0 to 3 weight % in total of 
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- a cathode having an aluminium-wettable surface, 
in particular a drained horizontal or inclined surface, 
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hard material and/or aluminium-wetting oxide.

A further aspect of the invention relates to a method 
of electrowinning aluminum in a cell as described above. 
The method comprises electrowining the dissolved alumina to 
produce oxygen on the anode and aluminium cathodically, and 
supplying alumina to the electrolyte to maintain therein a 
concentration of dissolved alumina of 5 to 14 weight %, in 
particular 7 to 10 weight %.
The anodes 10 are similar to the anode shown in FIGS. 1a and 1b. Suitable alternative anode designs are disclosed in WO00/40781, WO00/40782 and WO03/006716 (all de Nora).

The drained cathode surface 20 is formed by tiles 21A which have their upper face coated with an aluminium-wettable layer. Each anode 10 faces a corresponding tile 21A. Suitable tiles are disclosed in greater detail in WO02/096830 (Duruz/Nguyen/de Nora).

Tiles 21A are placed on upper aluminium-wettable faces 22 of a series of carbon cathode blocks 25 extending in pairs arranged end-to-end across the cell. As shown in FIGS. 2a and 2b, pairs of tiles 21A are spaced apart to form aluminium collection channels 36 that communicate with a central aluminium collection groove 30.

The central aluminium collection groove 30 is located in or between pairs of cathode blocks 25 arranged end-to-end across the cell. The tiles 21A preferably cover a part of the groove 30 to maximise the surface area of the aluminium-wettable cathode surface 20.

As explained hereafter, the cell is thermally sufficiently insulated to enable ledgeless and crustless operation.

The cell comprises sidewalls 40 made of an outer layer of insulating refractory bricks and an inner layer of carbonaceous material exposed to molten electrolyte 5 and to the environment thereafter. These sidewalls 40 are protected against the molten electrolyte 5 and the environment thereafter with tiles 21B of the same type as tiles 21A. The cathode blocks 25 are connected to the sidewalls 40 by a peripheral wedge 41 which is resistant to the molten electrolyte 5.

Furthermore, the cell is fitted with an insulating cover 45 above the electrolyte 5. This cover inhibits heat loss and maintains the surface of the electrolyte in a molten state. Further details of suitable covers are disclosed in the above-mentioned references.

In operation of the cell illustrated in FIGS. 2a and 2b, alumina dissolved in the molten electrolyte 5 at a temperature of 880°C to 940°C is electrolysed between the anodes 10 and the cathode surface 20 to produce gas on the operative anodes surfaces 16 and molten aluminium on the aluminium-wettable drained cathode tiles 21A.

The cathodically-produced molten aluminium flows on the drained cathode surface 20 into the aluminium collection channels 36 and then into the central aluminium collection groove 30 for subsequent tapping.

The cell shown in FIG. 3 comprises a plurality of metal-based anodes 10 dipping in a molten electrolyte 5 according to the invention.

The anodes 10 are similar to the anode shown in FIGS. 1a and 1b. Suitable alternative anode designs are disclosed in WO00/40781, WO00/40782, WO03/006716 and WO03/023092 (all de Nora).

The cell bottom comprises a series of pairs of spaced apart carbon cathode blocks 25 placed across the cell and having an aluminium-wettable upper surface 22 formed by an aluminium-wettable layer. The upper surfaces 22 are covered with aluminium-wettable openly porous plates 21 which are filled with molten aluminium to form an aluminium-wettled drained active cathode surface 20 above the upper surfaces 22 of the carbon cathode blocks 25. Further details of such a cathode bottom are disclosed in WO02/097168 and WO02/097169 (both de Nora).

The cathode blocks 25 are made of graphite and have a reduced height, e.g. 30 cm, and are coated with an aluminium-wettable layer which forms the upper surface and which protects the graphite from erosion and wear. Suitable aluminium-wettable layers are disclosed in U.S. Pat. No. 5,651,874, WO98/17842, WO01/42168 and WO01/42531. The aluminium-wettleable openly porous plates 21 covering the coated cathode blocks 25 can be made of the material disclosed in WO02/070783 (de Nora).

The cell bottom further comprises a centrally-located recess 35 which extends at a level below the upper surfaces 22 of the carbon cathode blocks 25 and which during use collects molten aluminium 60 drained from the aluminium-wettleable drained active cathode surface 20.

The aluminium collection recess 35 is fitted in a reservoir body 30 which is placed below the blocks 25 of each pair of cathode blocks and spaces them apart across the cell. As shown in FIG. 3, the recess 35 formed in the reservoir body 30 is generally U-shaped with rounded lower corners and an outwardly curved upper part.

The reservoir body 30 is made of two generally L-shaped sections 31 assembled across the cell. The reservoir sections 31 are made of an anthracite-based material. The aluminium-wettleable layer forming the upper surfaces 22 extends in the recess 35 to protect the reservoir body 30 during use against wear and sodium or potassium intercalation.

As shown in FIG. 3, the reservoir body 30 extends below the cathode blocks 25 into the refractory and insulating material 26 of the cell bottom permitting maximisation of the capacity of the aluminium collection recess 35.

Furthermore, the reservoir body 30 has a solid base 32 which extends from above to below the bottom face of the cathode blocks 25 and provides sufficient mechanical resistance to keep the blocks 25 properly spaced apart across the cell when exposed to thermal expansion during start-up of the cell and normal operation. As shown in dotted lines in the upper part of the reservoir body 30, longitudinally spaced apart spacer bars 33 placed across the reservoir body 30 may provide additional mechanical strength to the reservoir body 30. Such spacer bars 33 can be made of carbon material coated with an aluminium-wettleable protective layer.

The openably porous plates 21 placed on the upper surfaces 22 of the carbon cathode blocks 25 and located in the central region of the cell bottom extend over part of the aluminium collection recess 35 so that during use the protruding part of the aluminium-wettleable drained active cathode surface 20 is located over the recess 35.

The openably porous plates 21 are spaced apart over the aluminium collection recess 35 to leave an access for the tapping of molten aluminium through a conventional tapping tube. The spacing between the openably porous plates 21 over the aluminium collection recess can be much smaller along the remaining parts of the recess 35, thereby maximising the surface area of the active cathode surface 20.

The cell shown in FIG. 3 comprises a series of corner pieces 41 made of the same openably porous material as plates 21 and filled with aluminium and placed at the periphery of the cell bottom against sidewalls 40. The sidewalls 40 and the surface of the electrolyte 5 are covered with a ledge and a small crust of frozen electrolyte 6. The cell is fitted with an insulating cover 45 above the electrolyte crust 6. Further details of suitable covers are disclosed in the above-mentioned references.
The cell is also provided with exhaust pipes (not shown) that extend through the cover 45 for the removal of gases produced during electrolysis.

The cell comprises alumina feeders 50 with feeding tubes 51 that extend through the insulating cover 45 between the anodes 10. The alumina feeders 50 are associated with a crust breaker (not shown) for breaking the crust 6 underlying the feeding tube 51 prior to feeding.

In a variation, the insulating material of the sidewalls 40 and cover 45 may be sufficient to prevent formation of any ledge and crust of frozen electrolyte. In such a case, the sidewalls 40 are preferably completely shielded from the molten electrolyte 5 like in the cell of FIGS. 2a and 2b or by a lining of the aforementioned openly porous material filled with aluminium.

Enhanced alumina dissolution may be achieved by utilising an alumina feed device which sprays and distributes alumina particles over a large area of the surface of the molten electrolyte 5. Suitable alumina feed devices are disclosed in U.S. Pat. No. 6,572,757 (de Nora/Bercelaz) and in WO03/006771 (Bercelaz/Duruz). Furthermore, the cell may comprise means (not shown) to promote circulation of the electrolyte 5 from and to the anode-cathode gap to enhance alumina dissolution in the electrolyte 5 and to maintain in permanence a high concentration of dissolved alumina close to the active surfaces of anodes 10, for example as disclosed in WO00/40767 (de Nora).

During operation of the cell shown in FIG. 3, alumina dissolved in the electrolyte 5 is electrolysed to produce oxygen on the anodes 10 and aluminium 60 on the drained cathode surfaces 20. The product aluminium 60 drains from the cathode surfaces 20 over the open porous plates 21 that extend over part of the reservoir 30 into the reservoir 30 from where it can be tapped.

Hence, aluminium is produced on the drained active cathode surface 20 which covers not only the cathode blocks 25 but also part of the reservoir 30, thereby maximising the useful aluminium production area (i.e. the drained cathode surface 22) of the cell.

FIGS. 2a, 2b and 3 show specific aluminium electro-winning cells by way of example. It is evident that many alternatives, modifications, and variations will be apparent to those skilled in the art.

For instance, the cell may have a sloping cathode bottom, as disclosed in WO99/02764 (de Nora/Duruz), and optionally one or more aluminium collection reservoirs across the cell, each intersecting the collection groove to divide the drained cathode surface into four quadrants as described in WO00/63463 (de Nora).

Examples of electrolyte compositions according to the invention are given in Table 1, which shows the weight percentages of the indicated constituents for each specimen electrolyte A1-11 at a given temperature.

<table>
<thead>
<tr>
<th>AIF₃</th>
<th>NaF</th>
<th>KF</th>
<th>CaF₂</th>
<th>Al₂O₃</th>
<th>T °C</th>
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<td>A1</td>
<td>40.4</td>
<td>42.6</td>
<td>6</td>
<td>3</td>
<td>8</td>
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<tr>
<td>B1</td>
<td>40.6</td>
<td>41.4</td>
<td>7</td>
<td>3</td>
<td>8</td>
</tr>
<tr>
<td>C1</td>
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<td>39.6</td>
<td>9</td>
<td>3</td>
<td>8</td>
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<tr>
<td>D1</td>
<td>40.2</td>
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<td>2.5</td>
<td>8</td>
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<tr>
<td>E1</td>
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<td>8</td>
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<td>13</td>
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<td>8</td>
</tr>
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<td>G1</td>
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<td>33.0</td>
<td>8</td>
<td>2</td>
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<p>| TABLE 2 |</p>
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<th>Al</th>
<th>Nb</th>
<th>Ta</th>
<th>other</th>
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<td>A2</td>
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<td>2</td>
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<td>1</td>
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<td>B2</td>
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<td>—</td>
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<td>—</td>
<td>—</td>
<td>1</td>
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<tr>
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<td>—</td>
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<td>1</td>
<td>—</td>
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The "other" elements refer to minor additives such as manganese, silicon and yttrium which may be present in individual amounts of 0.2 to 1.5 weight %. Usual impurities, such as carbon, have not been listed in Table 2.

Examples of alloy compositions of suitable metal-based anode are given in Table 2, which shows the weight percentages of the indicated metals for each specimen alloy A2-K2.

<p>| TABLE 3 |</p>
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<tr>
<th>Fe₂O₃</th>
<th>BN</th>
<th>AlN</th>
<th>ZrC</th>
<th>TiO₂</th>
<th>ZrO₂</th>
<th>ZrO</th>
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<td>10</td>
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<td>5</td>
<td>5</td>
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<td>3</td>
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</tbody>
</table>

Comparative Example

A metal-based anode was tested in a potassium fluoride-free electrolyte at 900° C.

The anode was manufactured from a rod of diameter 20 mm and total length of 20 mm made from a cast nickel-iron alloy having the composition of sample A2 of Table 2. The anode rod was supported by a stem made of an alloy containing nickel, chromium and iron, such as Inconel, protected with an alumina sleeve. The anode was suspended for 16 hours over the molten fluoride-based electrolyte whereby its surface was oxidised prior to immersion into the electrolyte.
Electrolysis was carried out by fully immersing the anode rod in the molten electrolyte. The potassium fluoride-free electrolyte contained 49 weight % aluminium fluoride (AlF₃), 43 weight % aluminium fluoride (NaF), 4 weight % calcium fluoride (CaF₂) and 4 weight % alumina (Al₂O₃). The saturation concentration of alumina in such an electrolyte, unattainable in practice, is at 5 weight %.

The current density was about 0.8 A/cm² and the cell voltage was at 3.6-3.8 volt for 24 hours. The concentration of dissolved alumina in the electrolyte was maintained during the entire electrolysis by periodically feeding fresh alumina into the cell.

After 32 hours the cell voltage increased to 10 volt and electrolysis was interrupted. The anode was extracted. Upon cooling the anode was examined externally and in cross-section.

The anode’s outer dimensions had remained substantially unchanged. The anode’s oxide outer part had grown from an initial thickness of about 70 micron to a thickness after use of about up to 1000 micron. A yellow-green layer of nickel fluoride (NiF₂) was observed between the oxide outer part and the metallic inner part of the anode. Such a nickel fluoride layer is substantially non-conductive and passivates the anode, which caused the voltage increase.

Furthermore, a vermicular structure was observed in the metallic inner part immediately underneath the nickel fluoride layer over a depth of about 2 to 3 mm. The vermicular structure had mainly empty pores that had an average diameter of about 20 to 30 micron.

Example 1

A test was carried out with a cell according to the invention comprising: a molten potassium fluoride-containing electrolyte at 900°C having the composition of sample D1 of Table 1, i.e. rich in dissolved alumina, and an anode made from a nickel-iron alloy having the composition of sample A2 of Table 2.

The anode was manufactured like in the Comparative Example and suspended for 16 hours over the molten electrolyte.

Electrolysis was carried out in the same potassium fluoride-containing electrolyte: The current density was about 0.8 A/cm² and the cell voltage was stable at 3.8 volt during the entire test. The dissolved alumina-content was maintained around 8 weight % by periodically feeding fresh alumina into the cell.

After 50 hours electrolysis was interrupted and the anode extracted. Upon cooling the anode was examined externally and in cross-section.

The anode’s outer dimensions had remained substantially unchanged. The anode’s oxide outer part had grown from an initial thickness of about 70 micron to a thickness after use of about up to 500 micron, instead of the 1000 micron observed in the Comparative Example. Also, no passivating yellow-green layer of nickel fluoride (NiF₂) was observed.

Immediately underneath the oxide outer part, a vermicular structure was observed in the metallic inner part over a depth of about 0.5 to 1 mm, instead of the 2 to 3 mm of the Comparative Example. The vermicular structure had pores which were partly filled with oxides, in particular iron oxides, and which had an average diameter of about 2 to 5 micron.

Example 2

Example 1 was repeated with an anode made from the nickel-cobalt-iron alloy composition of sample D2 of Table 2 which was prepared, like in Example 1, over a potassium fluoride-containing electrolyte having the composition of sample D1 of Table 1, i.e. rich in dissolved alumina. The anode was then tested in the electrolyte like in Example 1 and showed similar results.

Example 3

Example 1 was repeated with an anode made from the nickel-iron alloy composition of sample H2 of Table 2 prepared, like in Example 1, over a potassium fluoride-containing electrolyte having the composition of sample D1 of Table 1, i.e. rich in dissolved alumina. The anode was then tested in the electrolyte like in Example 1.

After 50 hours electrolysis was interrupted and the anode extracted. Upon cooling the anode was examined externally and in cross-section.

The anode’s outer dimensions had remained substantially unchanged. The anode’s oxide outer part had grown from an initial thickness of about 70 micron to a thickness after use of about up to 1000 micron like in the Comparative Example. However, no passivating yellow-green layer of nickel fluoride (NiF₂) was observed.

A vermicular structure was observed in the metallic inner part immediately underneath the oxide outer part over a depth of about 1.5 to 2 mm, instead of the 2 to 3 mm of the Comparative Example. The vermicular structure had pores which were partly filled with oxides, in particular iron oxides, and which had an average diameter of about 2 to 5 micron.

Example 4

Example 1 was repeated with an anode made from the nickel-iron alloy composition of sample A2 of Table 2 which was prepared, like in Example 1, over a potassium fluoride-containing electrolyte having the composition of sample A1 of Table 1, i.e. rich in dissolved alumina. The anode was then tested in the electrolyte like in Example 1 and showed similar results.

Example 5

Examples 1 to 4 can be repeated using different combinations of electrolyte compositions (A1-H1) selected from Table 1 and anode alloy compositions (A2-K2) selected from Table 2.

Example 6

Another aluminium electrowinning anode was prepared as follows:

A slurry for coating an anode was prepared by suspending in 32.5 g of an aqueous solution containing 5 weight % polyvinyl alcohol (PVA) 67.5 g of a particle mixture made of hematite Fe₂O₃ particles, boron nitride particles, TiO₂ particles and CuO particles (with particle size of ~325 mesh, i.e. smaller than 44 micron) in a weight ratio corresponding to sample A3 of Table 3.

An anode made of the nickel-iron alloy of sample A2 of Table 2 was covered with ten layers of this slurry that
were applied with a brush. The applied layers were dried for 10 hours at 140°C in air and then consolidated at 950°C for 16 hours to form a protective hematite-based coating which had a thickness of 0.4 to 0.45 mm.

[0116] During consolidation, the Fe₂O₃ particles were sintered together into a microporous matrix with a volume contraction. The TiO₂ particles and CuO particles were dissolved in the sintered Fe₂O₃. The boron nitride particles remained substantially inert during the sintering but prevented migration and agglomeration of the micro pores into cracks.

[0117] Underneath the coating, an integral oxide scale mainly of iron oxide had grown from the anode's alloy during the heat treatment and combined with iron oxide and titanium oxide from the coating to firmly anchor the coating to the oxidised alloy. The integral oxide scale contained titanium oxide in an amount of about 10 metal weight %. Minor amounts of copper, aluminium and nickel were also found in the oxide scale (less that 5 metal weight % in total).

[0118] Electrolysis was carried out in a potassium fluoride-containing electrolyte at 900°C having the composition of sample D1 of Table 1, i.e. rich in dissolved alumina. The current density was about 0.8 A/cm² and the cell voltage was stable at 3.6 volt during the entire test, instead of the 3.8 volt observed in Examples 1 to 4. The dissolved alumina-content was maintained around 8 weight % by periodically feeding fresh alumina into the cell.

[0119] After 50 hours electrolysis was interrupted and the anode extracted. Upon cooling the anode was examined externally and in cross-section.

[0120] The anode's outer dimensions as well as the anode's coating had remained substantially unchanged. However, TiO₂ had selectively been dissolved in the electrolyte from the coating. The anode's structure underneath the coating was similar to the structure observed in Examples 1 to 4.

[0121] Samples of the used electrolyte and the product aluminium were also analysed. It was found that the electrolyte contained less that 70 ppm nickel and the produced aluminium contained less than 300 ppm nickel which is significantly lower than with an uncoated anode that can cause a typical nickel contamination of 1000 ppm in the product aluminium.

Example 7

[0122] Example 6 can be repeated using different combinations of electrolyte compositions (A1-11) selected from Table 1, anode alloy compositions (A2-K2) selected from Table 2 and coating compositions (A3-1.3) selected from Table 3.

[0123] Further details on the application of such anode coatings and suitable compositions are disclosed in PCT/IB03/01479, PCT/IB03/03654 and PCT/IB03/03978 (all Nguyen/de Nora).

[0124] In summary, as can be seen by comparing Example 1-5 to the Comparative Example, using the potassium fluoride electrolyte of the invention containing about 8 weight % dissolved alumina instead of a potassium fluoride free electrolyte containing only 4 weight % dissolved alumina, inhibits fluorination and passivation of the nickel and/or cobalt of the anode and reduces wear (oxidation and dissolution of the anode's iron).

[0125] Furthermore, as can be observed from Examples 6-7, use of a crack-free nickel-free hematite-based protective coating on a nickel-iron anode alloy reduces the cell voltage and significantly inhibits contamination of the product aluminium by nickel from the anode, compared to an uncoated nickel-iron anode operated in the same type of electrolyte.

1. A cell for electrowinning aluminium from alumina, comprising:
   a metal-based anode having an outer part that has an electrochemically active oxide-based surface and that contains at least one of nickel, cobalt and iron;
   a fluoride-containing molten electrolyte in which the active anode surface is immersed and which is at a temperature below 940°C., in particular in the range from 880° to 920°C., and which consists of:
   5 to 14 weight % dissolved alumina;
   35 to 45 weight % aluminium fluoride;
   30 to 45 weight % sodium fluoride;
   5 to 20 weight % potassium fluoride;
   0 to 5 weight % calcium fluoride; and
   0 to 5 weight % in total of one or more further constituents.

2. The cell of claim 1, wherein the electrolyte contains 7 to 10 weight % alumina.

3. The cell of claim 1 or 2, wherein the electrolyte contains 38 to 42 weight % aluminium fluoride.

4. The cell of any preceding claim, wherein the electrolyte contains 34 to 43 weight % sodium fluoride.

5. The cell of any preceding claim, wherein the electrolyte contains 8 to 15 weight % potassium fluoride.

6. The cell of any preceding claim, wherein the electrolyte contains 2 to 4 weight % calcium fluoride.

7. The cell of any preceding claim, wherein the electrolyte contains 0 to 3 weight % of said one or more further constituents.

8. The cell of any preceding claim, wherein said one or more further constituents comprise at least one fluoride selected from magnesium fluoride, lithium fluoride, cesium fluoride, rubidium fluoride, strontium fluoride, barium fluoride and cerium fluoride.

9. The cell of any preceding claim, comprising a cathode that has an aluminium-wettable surface, in particular a horizontal or inclined drained surface.

10. The cell of claim 9, wherein the cathode has an aluminium-wettable coating that comprises a refractory boride and/or an aluminium-wetting oxide.

11. The cell of any preceding claim, wherein the anode has a metallic or cermet body and an oxide layer on the anode body.

12. The cell of any preceding claim, wherein the anode body is made from an iron alloy containing nickel and/or cobalt.

13. The cell of claim 12, wherein the anode body is made from an alloy consisting of:
   40 to 80% nickel and/or cobalt, in particular 50 to 60 weight %;
   9 to 55 weight % iron, in particular 25 to 40 weight %;
   5 to 15 weight % copper, in particular 6 to 12 weight %;
   0 to 4 weight % in total of at least one of aluminium, niobium and tantalum, in particular 0.5 to 2 weight %; and
   0 to 2 weight % in total of further constituents, in particular 0.5 to 1 weight %.

14. The cell of claim 12 or 13, wherein the anode body is covered with an integral iron oxide-based layer containing up to 35 weight % nickel oxide and/or cobalt oxide, in particular from 5 to 10 weight % nickel oxide.
15. The cell of any preceding claim, wherein the anode comprises an applied iron oxide-based coating.

16. The cell of claim 15, wherein the anode coating contains $\text{Fe}_2\text{O}_3$ and optionally: at least one dopant selected from $\text{TiO}_2$, $\text{ZnO}$ and $\text{CuO}$ and/or at least one inert material selected from nitrides and carbides.

17. The cell of any preceding claim, wherein the anode comprises a cerium oxyfluoride-based outermost coating.

18. The cell of any preceding claim, wherein the anode is suspended in the electrolyte by a nickel-containing stem, in particular a stem having a nickel-containing core covered with an applied oxide coating.

19. The cell of claim 18, wherein the nickel containing stem is covered with an applied coating containing aluminium oxide and titanium oxide.

20. The cell of claim 18 or 19, wherein the core of the stem comprises a copper inner part and a nickel-based outer part.

21. The cell of any preceding claim, comprising at least one component that contains a sodium-active cathodic material, such as elemental carbon, said sodium-active cathodic material being shielded from the electrolyte by a sodium-inert layer to inhibit the presence of the molten electrolyte of soluble cathodically-produced sodium metal that constitutes an agent for dissolving the active oxide-based anode surface.

22. A cell according to claim 1, comprising:
   a metal-based anode having an outer part that has an electrochemically active oxide-based surface and that is made from an alloy consisting of:
   - 50 to 60 weight % in total of nickel and/or cobalt;
   - 25 to 40 weight % iron;
   - 6 to 12 weight % copper;
   - 0.5 to 2 weight % aluminium and/or niobium; and
   - 0.5 to 1.5 weight % in total of further constituents,
   the anode comprising an applied hematite-based coating and optionally a cerium oxyfluoride-based outermost coating;
   a nickel-containing anode stem for suspending the anode in the electrolyte, the stem being covered with a coating of aluminium oxide and titanium oxide;
   a fluorode-containing molten electrolyte in which the active anode surface is immersed and which is at a temperature in the range from 880° to 930°C, and which consists of:
   - 7 to 10 weight % dissolved alumina;
   - 38 to 42 weight % aluminium fluoride;
   - 34 to 43 weight % sodium fluoride;
   - 8 to 15 weight % potassium fluoride;
   - 2 to 4 weight % calcium fluoride; and
   - 0 to 3 weight % in total of one or more further constituents;
   and
   a cathode having an aluminium-wettable surface, in particular a drained horizontal or inclined surface, formed by an aluminium-wettable coating of refractory hard material and/or aluminium-wetting oxide.

23. A method of electrowinning aluminium in a cell as defined in any preceding claim, comprising electrolysising the dissolved alumina to produce oxygen on the anode and aluminium cathodically, and supplying alumina to the electrolyte to maintain therein a concentration of dissolved alumina of 5 to 14 weight %, in particular 7 to 10 weight %.

* * * * *