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(54) Title: OPERATION OF ALUMINIUM ELECTROWINNING CELLS HAVING METAL-BASED ANODES

(57) Abstract: The present invention relates to a method of inhibiting fluorination and passivation of a metal-based anode having an alloy outer portion made of iron with nickel and/or cobalt and covered with an integral oxide surface layer facing a cathode in an aluminium fluoride-comprising molten electrolyte. This method comprises maintaining an amount of at least one basic fluoride, such as calcium or lithium fluoride, in the electrolyte to reduce the acidic activity of aluminium fluoride thereby inhibiting fluorination, corrosion of iron and passivation of nickel and/or cobalt of the alloy outer portion.



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OPERATION OF ALUMINIUM ELECTROWINNING
CELLS HAVING METAL-BASED ANODES

Field of the Invention

This invention relates to operation of aluminium electrowinning cells with anodes made of an alloy of iron with nickel and/or cobalt whereby anode passivation by
5 fluorination or oxidation of nickel and/or cobalt or anode corrosion by fluorination and dissolution of iron is inhibited or prevented, as well as aluminium production cells permitting such operation.

Background Art

10 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.

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

US Patents 4,614,569 (Duruz/Derivaz/Debely/
Adorian), 4,680,094 (Duruz), 4,683,037 (Duruz) and
20 4,966,674 (Bannochie/Sherriff) 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
25 electrolyte. This made it possible to have a protection of the surface from the electrolyte attack and to a certain extent from the gaseous oxygen but not from the nascent monoatomic oxygen.

EP Patent application 0 306 100 (Nyguen/Lazouni/
30 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

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an in-situ formed protective cerium oxyfluoride layer. Likewise, US Patents 5,069,771, 4,960,494 and 4,956,068 (all Nyguen/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.

WO00/06805 (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.

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% AlF_3 , 3 to 5 weight% Al_2O_3 , 1 to 2 weight% LiF and 1 to 2 weight% MgF_2 .

WO 01/31086 (de Nora/Duruz) discloses a cell having oxidised nickel-iron alloy anodes and operating with an aluminium fluoride-comprising electrolyte at reduced temperature, e.g. 730° to 910°C. It is mentioned that the electrolyte may contain MgF_2 and/or LiF in an amount of up to 5 weight% each.

Metal or metal-based anodes are highly desirable in aluminium electrowinning cells instead of carbon-based anodes. Many attempts were made to use metallic anodes for aluminium production, however they were never adopted by the aluminium industry for commercial aluminium production

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because their lifetime was too short and needs to be increased.

Summary of the Invention

The invention relates to a method of inhibiting
5 fluorination, corrosion and passivation of a metal-based
anode having a nickel-iron alloy outer portion covered
with an integral oxide surface layer facing a cathode in
an aluminium fluoride-comprising molten electrolyte. This
method comprises maintaining an amount of at least one
10 basic fluoride in the electrolyte to reduce the acidic
activity of aluminium fluoride thereby inhibiting
fluorination, corrosion of iron and passivation of nickel
of the nickel-iron alloy outer portion.

In a modification of the invention the nickel of
15 the nickel-iron alloy outer portion of the anode is wholly
or predominantly substituted by cobalt which behaves
substantially like nickel under the cell operating
conditions discussed hereafter.

This method is particularly appropriate when
20 operating with an electrolyte at reduced temperature, in
particular to reduce the solubility of metal oxides when
using metal-based anodes as disclosed in WO00/06802
(Duruz/de Nora/Crottaz). Indeed, to reduce the temperature
of a cryolite-based molten electrolyte aluminium fluoride
25 is added to the electrolyte. However, the addition of
aluminium fluoride increases the acidity of the
electrolyte and promotes fluorination, corrosion of iron
and passivation of nickel of the nickel-iron alloy outer
portion by exposure to fluorides and/or fluorine which are
30 derived from the aluminium fluoride and which diffuse in
the integral oxide surface layer.

In accordance with the invention, the Lewis
acidity of the electrolyte and thus the activity of
fluorides is reduced. Hence corrosion of iron and
35 passivation of nickel of the anode can be inhibited and
even stopped by replacing at least part of the aluminium
fluoride by a basic fluoride.

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In other words, usually, the acid aluminium fluoride (AlF_3) of a conventional electrolyte vaporises and corrodes the iron of the anode to form volatile FeAlF_5 and attacks the nickel of the anode to form in the presence of anodically evolved oxygen alumina (Al_2O_3) and nickel fluoride (NiF) that passivates the surface of the anode. However, by adding an adjusted amount of a basic fluoride (MF) to the electrolyte, the acidity of the aluminium fluoride is neutralised by combination therewith ($\text{AlF}_3 + \text{MF} \rightarrow \text{AlF}_4^- + \text{M}^+$), which inhibits vaporisation of aluminium fluoride and the resulting corrosion and/or passivation of the anode.

Suitable basic fluorides of the invention are fluorides of metals of group IA and IIA of the Periodic Tables, in particular fluorides of calcium, lithium and magnesium. For instance, the electrolyte may comprise calcium fluoride, preferably in such an amount that the density of the electrolyte is below the density of molten aluminium, typically up to 7 weight%, preferably from 1 to 6%, in particular 3 to 5%, calcium fluoride. The electrolyte can alternatively or additionally comprise up to 4 weight%, preferably 1 to 3 weight% in particular 1.5 to 2.5 weight%, of lithium fluoride.

The addition of calcium fluoride reduces the melting point of the electrolyte: each added weight percent of calcium fluoride reduces the temperature of the electrolyte by about 1°C . Likewise, each added weight percent of lithium fluoride reduces the electrolyte's melting point by about 5°C .

The electrolyte should not comprise more than 24 weight% aluminium fluoride, in addition to cryolite. Preferably, the aluminium fluoride-content (in addition to cryolite) is comprised in the range from 14 to 22 weight%. Depending on the temperature used, an adjusted amount of basic fluorides must be added to reduce the melting point of the electrolyte and de-acidify the electrolyte.

The melting point of the electrolyte is lowered even more by adding aluminium fluoride. Each additional weight percent of aluminium fluoride in the electrolyte

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corresponds to a reduction of about 10°C of the electrolyte's melting point. Lowering the electrolyte's temperature increases the required amount of aluminium fluoride and thus increases the required amount of one or more basic fluorides to neutralise the electrolyte.

The method of the invention may be used with an electrolyte which is at a temperature in the range from 880° to 940°C, preferably from 890° to 930°C. The electrolyte may consist essentially of sodium fluoride, aluminium fluoride and the basic fluoride(s), containing dissolved alumina. With an electrolyte at 880°C the cumulated amount of basic fluorides should be of at least about 5 to 7 weight% to avoid corrosion (iron) and passivation (nickel), whereas at about 930°-940°C the required cumulated amount of basic fluorides is much lower, typically from 3 to 5 weight%.

The dissolution of the integral surface layer of the anode can be inhibited by permanently and uniformly substantially saturating the electrolyte with alumina.

In one embodiment, the anode is coated with a protective layer of one or more cerium compounds, in particular cerium oxyfluoride. In this case, the method of the invention advantageously comprises maintaining an amount of cerium species in the electrolyte to maintain the protective layer, as disclosed in the above-mentioned US Patents 4,614,569, 4,680,094, 4,683,037 and 4,966,674.

The nickel-iron alloy outer portion may comprise up to or even more than 50 weight% iron. Also, the nickel-iron alloy outer portion can have an iron/nickel weight ratio in the range of 1 to 3.

Advantageously, the nickel-iron alloy outer portion of the anode comprises inclusions at the grain boundaries of the nickel-iron alloy for providing a controlled diffusion of iron from the outer portion to the integral oxide surface layer. The inclusions at the grain boundaries may comprise at least one oxide of a rare earth metal that is substantially insoluble with nickel and iron, in particular an oxide of an Actinide, such as scandium or yttrium, and/or of a Lanthanide, such as

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cerium or ytterbium. The inclusions at the grain boundaries may also comprise at least one oxide of a transition metal that has an affinity for oxygen which is greater than the oxygen affinity of iron and nickel, such as an oxide of aluminium, titanium, tantalum and chromium. The inclusions at the grain boundaries can comprise at least one metal oxide, in particular the above rare earth metal oxide or the above transition metal oxide, that is present as one or more mixed oxides with iron and/or nickel.

The nickel-iron alloy outer portion of the anode may further comprise copper which improves the adherence and coherence of the integral oxide surface layer.

The anode can have an electrically conductive inner core, in particular made of nickel, or a nickel-iron alloy body which is covered with the integral oxide layer.

The invention also relates to a method of producing aluminium using a metal-based anode having a nickel-iron alloy outer portion covered with an integral oxide surface layer facing a cathode, in particular a drained cathode, in an aluminium fluoride-comprising molten electrolyte. This method comprises dissolving alumina in the electrolyte, passing an electrolysis current between the metal-based anode and the cathode to evolve oxygen on the anode and produce aluminium on the cathode, and inhibiting fluorination, corrosion of iron and passivation of nickel of the metal-based anode by the above described method.

A further aspect of the invention relates to the use in an aluminium fluoride-comprising electrolyte for the electrowinning of aluminium from alumina dissolved in the electrolyte, of at least one basic fluoride for inhibiting fluorination, corrosion of iron and passivation of nickel of a nickel-iron alloy outer portion of a metal-based anode used in the electrolyte.

As mentioned above the basic fluoride(s) may be selected from fluorides of calcium and lithium.

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Yet a further aspect of the invention relates to a cell for the electrowinning of aluminium from alumina dissolved in a molten electrolyte comprising aluminium fluoride and at least one basic fluoride. This cell
5 comprises a metal-based anode having a nickel-iron alloy outer portion covered with an integral oxide surface layer in the molten electrolyte, and means for monitoring the amount of basic fluoride(s) in the electrolyte and for adjusting this amount such that it reduces the acidic
10 activity of aluminium fluoride and inhibits fluorination, corrosion of iron and passivation of nickel of the nickel-iron alloy outer portion.

For example, these means comprise a device for measuring the composition of the electrolyte, in
15 particular the aluminium fluoride and the basic fluoride content, and/or a system or feeder for supplying aluminium fluoride as well as the basic fluoride as required according to the measured electrolyte composition.

Detailed Description

20 The invention will be further described in the following Examples:

Example 1

An anode was made from a nickel-iron alloy rod which consisted of 50 weight% nickel, 0.3 weight%
25 manganese, 0.5 weight silicon and 1.7 weight% yttrium, the balance being iron, and which was pre-oxidised in air at a temperature of 1100°C for 3 hours.

The anode was immersed in an electrolytic bath at 930°C of a laboratory scale cell consisting of 18 weight%
30 aluminium fluoride, 6 weight% calcium fluoride, 4 weight% alumina, the balance being cryolite (melting point at 906°C).

The alumina concentration was maintained at a substantially constant level throughout the test by adding
35 alumina at a rate adjusted to compensate the cathodic aluminium reduction. The test was run at a current density of about 0.6 A/cm², and the electrical potential of the

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anode remained substantially constant at 4.2 volts throughout the test.

During electrolysis aluminium was cathodically produced while oxygen was anodically evolved which was
5 derived from the dissolved alumina present near the anodes.

After 100 hours, electrolysis was interrupted and the anode was extracted from the cell. The external dimensions of the anode had remained unchanged during the
10 test and the anode showed no external signs of damage.

The used anode was cut perpendicularly to the anode operative surface and the resulting section of the used anode was subjected to microscopic examination.

It was observed that an integral oxide surface
15 layer of about 20 micron had formed on the anode.

Some small inclusions of iron oxide were also found in a vermicular metallic outer portion of the nickel-iron alloy underlying the integral oxide surface layer. This vermicular outer portion had a thickness of
20 about 100 micron.

During the test the diameter of the overall metallic inner part underlying the integral oxide surface layer of the anode had been reduced by 50 micron. This corresponds to a wear rate by oxidation of about 6 micron
25 per day.

Example 2 (Comparative)

An anode as in Example 1 was immersed in an electrolytic bath at 930°C of a laboratory scale cell consisting of 18 weight% aluminium fluoride, 6 weight%
30 alumina, the balance being cryolite (melting point at 911°C), i.e. without calcium fluoride, and tested as in Example 1.

After 100 hours, electrolysis was interrupted and the anode was extracted from the cell. The external
35 dimensions of the anode had remained unchanged during the test and the anode showed no external signs of damage.

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The used anode was cut perpendicularly to the anode operative surface and the resulting section of the used anode was subjected to microscopic examination.

5 It was observed that a poorly adherent oxide surface layer of about 150-250 micron had formed on the anode.

10 The outer portion of the nickel-iron alloy underlying the oxide surface layer had a corrosion-porosity produced by internal oxidation and reaction with AlF_3 forming volatile FeAlF_5 . This outer portion had a thickness of about 1000 micron.

15 During the test, the diameter of the overall metallic inner part underlying the oxide surface layer of the anode had been reduced by 400 micron. This corresponds to a wear rate by oxidation of about 50 micron per day.

Example 3

20 The Electrolyte composition and temperature of Example 1 can be modified as shown in the following table, each line showing at a given temperature a suitable composition, the balance being cryolite (Na_3AlF_6) and alumina (Al_2O_3):

| Temperature of use | LiF weight% | CaF_2 weight% | AlF_3 weight% |
|--------------------|-------------|------------------------|------------------------|
| 880°C | 4 | 7 | 21 |
| 890°C | 3 | 4 | 21 |
| 900°C | 3 | 4 | 20 |
| 930°C | 1.5 | 3 | 17 |

CLAIMS

1. A method of inhibiting fluorination, corrosion and passivation of a metal-based anode having a nickel-iron alloy outer portion covered with an integral oxide surface layer facing a cathode in an aluminium fluoride-comprising molten electrolyte, said method comprising maintaining an amount of at least one basic fluoride in the electrolyte to reduce the acidic activity of aluminium fluoride thereby inhibiting fluorination, corrosion of iron and passivation of nickel of the nickel-iron alloy outer portion.
2. The method of claim 1, wherein the basic fluoride(s) comprises at least one fluoride selected from fluorides of calcium and lithium.
3. The method of claim 2, wherein the electrolyte comprise(s) calcium fluoride in such an amount that the density of the electrolyte is below the density of molten aluminium.
4. The method of claim 3, wherein the electrolyte comprises up to 7 weight% calcium fluoride, preferably from 1 to 6 weight%, in particular 3 to 5 weight%.
5. The method of any one of claims 2 to 4, wherein the electrolyte comprises up to 4 weight%, preferably 1 to 3 weight% in particular 1.5 to 2.5 weight%, of lithium fluoride.
6. The method of any preceding claim, wherein the electrolyte consists essentially of sodium fluoride, aluminium fluoride and the basic fluoride(s).
7. The method of any preceding claim, wherein the electrolyte comprises up to 24 weight%, preferably 14 to 22 weight%, aluminium fluoride in addition to cryolite.
8. The method of any preceding claim, comprising permanently and uniformly substantially saturating the electrolyte with alumina to inhibit dissolution of the integral surface layer.

9. The method of any preceding claim, wherein the electrolyte is at a temperature of 880° to 940°C, preferably from 890° to 930°C.

10. The method of any preceding claim, wherein the anode is coated with a protective layer of one or more cerium compounds, in particular cerium oxyfluoride, said method comprising maintaining an amount of cerium species in the electrolyte to maintain the protective layer.

11. The method of any preceding claim, wherein the nickel-iron alloy outer portion comprises at least 50 weight% iron.

12. The method of any preceding claim, wherein the nickel-iron alloy outer portion has an iron/nickel weight ratio in the range of 1 to 3.

13. The method of any preceding claim, wherein the nickel-iron alloy outer portion of the anode comprises inclusions at the grain boundaries of the nickel-iron alloy for providing a controlled diffusion of iron from the outer portion to the integral oxide surface layer.

14. The method of claim 13, wherein said inclusions at the grain boundaries comprise at least one oxide of rare earth metal that is substantially insoluble with nickel and iron.

15. The method of claim 14, wherein said inclusions at the grain boundaries comprise at least one oxide of an Actinide, such as scandium or yttrium oxide.

16. The method of claim 14 or 15, wherein said inclusions at the grain boundaries comprise at least one oxide of a Lanthanide, such as cerium or ytterbium oxide.

17. The method of any one of claims 13 to 16, wherein said inclusions at the grain boundaries comprise at least one oxide of a transition metal that has an affinity for oxygen which is greater than the oxygen affinity of iron and nickel.

18. The method of claim 17, wherein said inclusions at the grain boundaries comprise at least one oxide selected from aluminium, titanium, tantalum and chromium oxides.

19. The method of any one of claims 13 to 18, wherein said inclusions comprise at least one metal oxide that is present as one or more mixed oxides with iron and/or nickel.

20. The method of any preceding claim, wherein the nickel-iron alloy outer portion of the anode further comprises copper which improves the adherence and coherence of the integral oxide surface layer.

21. The method of any preceding claim, wherein the anode has an electrically conductive inner core, in particular made of nickel, underneath the outer portion.

22. The method of any one of claims 1 to 20, wherein the anode is made of a nickel-iron alloy body which is covered with the integral oxide layer.

23. The method of any preceding claim, wherein the anode is modified in that the nickel of the nickel-iron alloy outer portion is wholly or predominantly substituted by cobalt.

24. A method of producing aluminium using a metal-based anode having a nickel-iron alloy outer portion covered with an integral oxide surface layer facing a cathode in an aluminium fluoride-comprising molten electrolyte, said method comprising dissolving alumina in the electrolyte, passing an electrolysis current between the metal-based anode and the cathode to evolve oxygen on the anode and produce aluminium on the cathode, and inhibiting fluorination, corrosion of iron and passivation of nickel of the metal-based anode by a method as defined in any preceding claim.

26. The method of claim 25, wherein aluminium is produced on an aluminium-wettable cathode, in particular a drained cathode.

27. Use in an aluminium fluoride-comprising electrolyte for the electrowinning of aluminium from alumina dissolved in the electrolyte, of at least one basic fluoride for inhibiting fluorination, corrosion of iron and passivation of nickel of a nickel-iron alloy outer portion of a metal-based anode used in the electrolyte.

28. The use of claim 27, wherein the basic fluoride(s) comprises at least one fluoride selected from fluorides of calcium and lithium.

29. A cell for the electrowinning of aluminium from alumina dissolved in a molten electrolyte comprising aluminium fluoride and at least one basic fluoride, said cell comprising a metal-based anode having a nickel-iron alloy outer portion covered with an integral oxide surface layer in the molten electrolyte, and means for monitoring the amount of basic fluoride(s) in the electrolyte and for adjusting said amount such that it reduces the acidic activity of aluminium fluoride and inhibits fluorination, corrosion of iron and passivation of nickel of the nickel-iron alloy outer portion.