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(54) **MULTI-LAYER NON-CARBON METAL-BASED ANODES FOR ALUMINIUM PRODUCTION CELLS**

MEHRSCICHTIGE, KOHLENSTOFFFREIE ANODEN AUF BASIS VON METALLEN FÜR
ALUMINIUM-ELEKTROGEWINNUNGSZELLEN

ANODES MULTICOUCHES NON CARBONEES A BASE DE METAL POUR CELLULES DE
PRODUCTION D'ALUMINIUM

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(56) References cited:
EP-A- 0 306 102 **WO-A-99/36592**

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Description

Field of the Invention

[0001] This invention relates to multi-layer non-carbon, metal-based anodes, for use in cells for the electrowinning of aluminium by the electrolysis of alumina dissolved in a molten fluoride-containing electrolyte, and to methods for their fabrication and reconditioning, as well as to electrowinning cells containing such anodes and their use to produce 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.

[0003] This process, conceived almost simultaneously by Hall and Héroult, has not evolved as many other electrochemical processes.

[0004] The anodes are still made of carbonaceous material and must be replaced every few weeks. During electrolysis the oxygen which should evolve on the anode surface combines with the carbon to form polluting CO₂ and small amounts of CO and fluorine-containing dangerous gases. The actual consumption of the anode is as much as 450 Kg/Ton of aluminium produced which is more than 1/3 higher than the theoretical amount of 333 Kg/Ton.

[0005] Using metal anodes in aluminium electrowinning cells would drastically improve the aluminium process by reducing pollution and the cost of aluminium production.

[0006] US Patent 4,614,569 (Duruz/Derivaz/Debely/Adorian) describes 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 cerium to the molten cryolite electrolyte. This made it possible to have a protection of the surface only from the electrolyte attack and to a certain extent from the gaseous oxygen but not from the nascent monoatomic oxygen.

[0007] EP Patent application 0 306 100 (Nyguen/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.

[0008] 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.

[0009] Metal or metal-based anodes are highly desirable in aluminium electrowinning cells instead of carbon-based anodes.

As mentioned hereabove, many attempts were made to use metallic anodes for aluminium production, however they were never adopted by the aluminium industry.

Objects of the Invention

[0010] An object of the invention is to provide a multi-layer functionally graded coating for metal-based anodes for aluminium electrowinning cells which is substantially impervious to molecular oxygen and also to monoatomic oxygen and is electrochemically active for the oxidation reaction of oxygen ions present at the anode/electrolyte interface into monoatomic oxygen, as well as for subsequent reaction for the formation of biatomic molecular oxygen evolving as gas.

[0011] Another object of the invention is to provide a coating for metal-based anodes for aluminium electrowinning cells which has a high electrochemical activity, a long life and which can easily be applied onto a metal-based anode substrate.

[0012] A further object of the invention is to reduce substantially the consumption of the active anode surface of metal-based anodes for aluminium electrowinning cells which is attacked by the nascent oxygen produced by enhancing the reaction of nascent oxygen to gaseous oxygen which is much less active in oxidising metal anodes of aluminium electrowinning cells.

[0013] A major object of the invention is to provide an anode for aluminium electrowinning cells which has no carbon so as to eliminate carbon-generated pollution and eliminate the high carbon anode cost.

Summary of the Invention

[0014] The invention relates to a composite, high-temperature resistant, non-carbon, metal-based, oxygen-evolving anode of a cell for the electrowinning of aluminium by the electrolysis of alumina dissolved in a molten fluoride-containing electrolyte. The anode comprises a metal-based core structure of low electrical resistance, for connecting the anode to a positive current supply, coated with a series of superimposed, adherent, electrically conductive layers. The conductive layers consist of:

a) at least one layer on the metal-based core structure constituting during electrolysis a barrier substantially impervious to molecular oxygen and also monoatomic oxygen, the barrier comprising at least one of chromium, niobium and nickel oxides;

b) one or more intermediate protective layers containing oxidised, or oxidised and metallic, copper and optionally at least one of nickel and cobalt applied to the oxygen barrier to protect the oxygen barrier against dissolution, which intermediate layer(s) during electrolysis remain inactive in the reactions

for the evolution of oxygen gas; and

c) an electrochemically active layer on the outermost intermediate layer, for the oxidation reaction of oxygen ions present at the anode/electrolyte interface into nascent monoatomic oxygen, as well as for subsequent reaction for the formation of gaseous biatomic molecular oxygen evolving as gas, the active layer protecting the intermediate layer(s) against dissolution.

[0015] The active layer comprises at least one transition metal and/or an oxide thereof (excluding the lanthanides and actinides and their oxides alone), for instance iron, cobalt, nickel, copper, chromium or titanium as metals and/or oxides. The active layer has a surface that is iron oxide-based and that is made of at least one ferrite or consists of an oxidised surface of an alloy which has at least 70 wt% iron before oxidation.

[0016] The active layer may be slowly consumable during electrolysis.

[0017] In this context, metal-based anode means that the anode contains at least one metal in the anode core structure and/or in the protective layers as such or as alloys, intermetallics and/or cermets.

[0018] The core structure may comprise at least one metal selected from nickel, copper, cobalt, chromium, molybdenum, tantalum, niobium or iron. For instance, the core structure may be made of an alloy consisting of 10 to 30 weight% of chromium, 55 to 90% of at least one of nickel, cobalt or iron, and 0 to 15% of aluminium, titanium, zirconium, yttrium, hafnium or niobium. Alternatively, the core may be nickel plated copper.

[0019] Possibly, the core structure may comprise an alloy or intermetallic compound containing at least two metals selected from nickel, cobalt, iron and aluminium.

[0020] Alternatively, the core structure can comprise a cermet containing copper and/or nickel as a metal, and a ceramic phase.

[0021] Advantageously, the oxygen barrier layer may be formed on the core structure by surface oxidation. However, it is also possible to form an oxygen barrier by slurry application techniques, arc spraying or plasma spraying. The oxygen barrier may optionally be formed by applying a precursor which is then converted into a functional barrier by heat treatment, such as applying a layer of chromium, niobium or nickel metal on the core which can then be oxidised.

[0022] One of the intermediate layers may comprise iron cuprate, nickel ferrite and/or cobalt ferrite.

[0023] Typically, one of the intermediate layers comprises an oxidised alloy containing 20 to 60 weight% of copper with one or more further metals forming a solid solution with copper, such metals being generally nickel and/or cobalt.

[0024] Usually, the electrochemically active layer comprises at least one oxide which may slowly wear away during electrolysis. Optionally but not necessarily

the electrochemically active layer comprises (an) oxide (s) throughout its thickness.

[0025] An oxide may be present in the electrochemically active layer as such, or in a multi-compound mixed oxide and/or in a solid solution of oxides. The oxide may be in the form of a simple, double and/or multiple oxide, and/or in the form of a stoichiometric or non-stoichiometric oxide.

[0026] The electrochemically active layer may for instance comprise a metal, alloy, intermetallic compound or cermet which during normal operation in the cell is slowly consumable by oxidation of its surface and dissolution into the electrolyte of the formed surface oxide. In this case the rate of oxidation may be substantially equal to the rate of dissolution.

[0027] Advantageously, the electrochemically active layer containing metals is pre-oxidised prior to electrolysis. The metals of the electrochemically active layer may be iron with at least one metal selected from nickel, copper, cobalt, aluminium and zinc.

[0028] Optionally, the electrochemically active layer may further comprise at least one additive selected from beryllium, magnesium, yttrium, titanium, zirconium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, rhodium, silver, hafnium, lithium, cerium and other Lanthanides.

[0029] Advantageously, the electrochemically active layer may also comprise at least one electrocatalyst for the anode reaction selected from iridium, palladium, platinum, rhodium, ruthenium, silicon, tin, mischmetal and metals of the Lanthanide series, and mixture, oxides and compounds thereof, for example as disclosed in WO99/36592 (de Nora).

[0030] The electrochemically active layer may be a surface oxidised iron-nickel layer, the surface containing iron oxide, nickel oxide or a mixture thereof.

[0031] Alternatively, the electrochemically active layer comprises spinels and/or perovskites. In particular, the electrochemically active layer may comprise ferrites, such as ferrites selected from the group consisting of cobalt, copper, manganese, magnesium, nickel and zinc ferrite, and mixtures thereof, in particular nickel ferrite partially substituted with Fe^{2+} . Additionally, the ferrite may be doped with at least one oxide selected from chromium, titanium, tin and zirconium oxide.

[0032] The electrochemically active layer can also comprise ceramic oxides containing combinations of divalent nickel, cobalt, magnesium, manganese, copper and zinc with divalent/trivalent nickel, cobalt, manganese and/or iron. The electrochemically active layer may for instance have doped, non-stoichiometric and/or partially substituted spinels, the doped spinels comprising dopants selected from Ti^{4+} , Zr^{4+} , Sn^{4+} , Fe^{4+} , Hf^{4+} , Mn^{4+} , Fe^{3+} , Ni^{3+} , Co^{3+} , Mn^{3+} , Al^{3+} , Cr^{3+} , Fe^{2+} , Ni^{2+} , Co^{2+} , Mg^{2+} , Mn^{2+} , Cu^{2+} , Zn^{2+} and Li^{+} .

[0033] Further materials which may be used for forming the electrochemically active layer include high-strength low-alloy (HSLA) steels.

[0034] It has been observed that low-carbon HSLA steels such as Cor-Ten™, even at high temperature, form under oxidising conditions an iron oxide-based surface layer which is dense, electrically conductive, electrochemically active for oxygen evolution and, as opposed to oxide layers formed on standard steels or other iron alloys, is highly adherent and less exposed to delamination and limits diffusion of ionic, monoatomic and molecular oxygen.

[0035] HSLA steels are known for their strength and resistance to atmospheric corrosion especially at lower temperatures (below 0°C) in different areas of technology such as civil engineering (bridges, dock walls, sea walls, piping), architecture (buildings, frames) and mechanical engineering (welded/bolted/riveted structures, car and railway industry, high pressure vessels). However, these HSLA steels have never been proposed for applications at high temperature, especially under oxidising or corrosive conditions, in particular in cells for the electrowinning of aluminium.

[0036] It has been found that the iron oxide-based surface layer formed on the surface of a HSLA steel under oxidising conditions limits also at elevated temperatures the diffusion of oxygen oxidising the surface of the HSLA steel. Thus, diffusion of oxygen through the surface layer decreases with an increasing thickness thereof.

[0037] If the HSLA steel is exposed to an environment promoting dissolution or delamination of the surface layer, in particular in an aluminium electrowinning cell, the rate of formation of the iron oxide-based surface layer (by oxidation of the surface of the HSLA steel) reaches the rate of dissolution or delamination of the surface layer after a transitional period during which the surface layer grows or decreases to reach an equilibrium thickness in the specific environment.

[0038] High-strength low-alloy (HSLA) steels are a group of low-carbon steels (typically up to 0.5 weight% carbon of the total) that contain small amounts of alloying elements. These steels have better mechanical properties and sometimes better corrosion resistance than carbon steels.

[0039] The surface of a high-strength low-alloy steel electrochemically active layer may be oxidised in an electrolytic cell or in an oxidising atmosphere, in particular a relatively pure oxygen atmosphere. For instance the surface of the high-strength low-alloy steel layer may be oxidised in a first electrolytic cell and then transferred to an aluminium production cell. In an electrolytic cell, oxidation would typically last 5 to 15 hours at 800 to 1000°C. Alternatively, the oxidation treatment may take place in air or in oxygen for 5 to 25 hours at 750 to 1150°C.

[0040] In order to prevent thermal shocks causing mechanical stresses, a high-strength low-alloy steel layer may be tempered or annealed after pre-oxidation. Alternatively, the high-strength low-alloy steel layer may be maintained at elevated temperature after pre-oxidation until immersion into the molten electrolyte of an alumin-

ium production cell.

[0041] The high-strength low-alloy steel layer may comprise 94 to 98 weight% iron and carbon, the remaining constituents being one or more further metals selected from chromium, copper, nickel, silicon, titanium, tantalum, tungsten, vanadium, zirconium, aluminium, molybdenum, manganese and niobium, and optionally a small amount of at least one additive selected from boron, sulfur, phosphorus and nitrogen.

[0042] Advantageously, the electrochemically active layer is initially sufficiently thick to constitute an impermeable barrier to gaseous oxygen penetration, and even to nascent, mono-atomic oxygen.

[0043] Any of these layers may be slurry applied, for instance by applying a precursor slurry. The layers may also be applied in the form a precursor powder followed by heat-treating.

[0044] Several techniques may be used to apply the layers, such as dipping, spraying, painting, brushing, arc spraying, plasma spraying, electro-chemical deposition, physical vapour deposition, chemical vapour deposition or calendar rolling.

[0045] The invention also relates to a method of manufacturing an anode as described above. The method comprises the steps of formation of the oxygen barrier layer(s), of the intermediate layer(s) and of the electrochemically active layer. It is possible to form the oxygen barrier by substrate oxidation after the intermediate barrier has been applied onto the substrate.

[0046] The method for manufacturing such an anode may also be used for reconditioning an anode whose electrochemically active layer is worn or damaged. The method comprises clearing at least worn and/or damaged parts of the active surface from the core structure or from the outermost intermediate layer to which it adheres and then reconstituting at least the electrochemically active layer.

[0047] Another aspect of the invention is a cell for the production of aluminium by the electrolysis of alumina dissolved in a molten fluoride-containing electrolyte comprising at least one composite anode as described above.

[0048] Advantageously, the cell may comprise at least one aluminium-wettable cathode which can be a drained cathode on which aluminium is produced and from which it continuously drains.

[0049] Usually, the cell is in a monopolar, multi-monopolar or in a bipolar configuration. Bipolar cells may comprise the anodes as described above as the anodic side of at least one bipolar electrode and/or as a terminal anode.

[0050] In such a bipolar cell an electric current is passed from the surface of the terminal cathode to the surface of the terminal anode as ionic current in the electrolyte and as electronic current through the bipolar electrodes, thereby electrolysis the alumina dissolved in the electrolyte to produce aluminium on each cathode surface and oxygen on each anode surface.

[0051] Preferably, the cell comprises means to improve the circulation of the electrolyte between the anodes and facing cathodes and/or means to facilitate dissolution of alumina in the electrolyte. Such means can for instance be provided by the geometry of the cell as described in co-pending application PCT/IB99/00222 (de Nora/Duruz) or by periodically moving the anodes as described in co-pending application PCT/IB99/00223 (Duruz/Bellò).

[0052] The cell may be operated with the electrolyte at conventional temperatures, such as 950 to 970°C, or at reduced temperatures as low as 700°C.

[0053] Yet another aspect of the invention is a method of producing aluminium in such an aluminium electrowinning cell, wherein alumina is dissolved in the molten fluoride-containing electrolyte and then electrolysed to produce aluminium.

[0054] Advantageously, during electrolysis the active layer of the anode may be protected by an electrolyte-generated oxyfluoride-containing layer, such as cerium oxyfluoride self-formed on the electrochemically active layer as described in US Patent 4,614,569 (Duruz/Derivaz/Debely/Adorian).

Detailed Description

[0055] The invention will be further described in the following Examples:

Example 1

[0056] A test anode was made by coating by electrodeposition a core structure in the shape of a rod having a diameter of 12 mm consisting of 74 weight% nickel, 17 weight% chromium and 9 weight% iron, such as Inconel®, first with a nickel layer about 200 micron thick and then a copper layer about 100 micron thick.

[0057] The coated structure was heat treated at 1000°C in argon for 5 hours. This heat treatment provides for the interdiffusion of nickel and copper to form an intermediate layer. The structure was then heat treated for 24 hours at 1000°C in air to form a chromium oxide (Cr₂O₃) barrier layer on the core structure and oxidising at least partly the interdiffused nickel-copper layer thereby completing formation of the intermediate layer.

[0058] A nickel-ferrite powder was made by drying and calcining at 900°C the gel product obtained from an inorganic polymer precursor solution consisting of a mixture of molten Fe(NO₃)₃·9 H₂O with a stoichiometric amount of Ni(CO₃)₂·6 H₂O. A thick paste was made by mixing 1 g of this nickel-ferrite powder with 0.85 g of a nickel aluminate polymer solution containing the equivalent of 0.15 g of nickel oxide. This thick paste was then diluted with 1 ml of water and ground in a pestle and mortar to obtain a suitable viscosity to form a ferrite-based paint.

[0059] An electrochemically active oxide layer was obtained on the core structure by applying the ferrite-

based paint onto the core structure with a brush. The painted structure was allowed to dry for 30 minutes before heat treating it at 500°C for 1 hour to decompose volatile components and to consolidate the oxide coating.

[0060] The heat treated coating layer was about 15 micron thick. Further coating layers were applied following the same procedure in order to obtain a 200 micron thick electrochemically active coating covering the intermediate layer and barrier layer on the core structure.

[0061] The anode was then tested in a cryolite melt containing approximately 6 weight% alumina at 970°C by passing a current at a current density of about 0.8 A/cm². After 100 hours the anode was extracted from the cryolite and showed no significant internal corrosion after microscopic examination of a cross-section of the anode sample.

[0062] The Example can be repeated with an electrochemically active layer obtained from a feed prepared by slurring nickel ferrite powder in an inorganic polymer solution having the required composition for the formation of NiFe₂O₄. The powder to polymer ratio was 1 to 0.25. Several layers of the coating feed can be brushed onto the nickel-copper layer and heat treated to form the electrochemically active layer on the intermediate layer.

[0063] Alternatively, the Example can be repeated with an electrochemically active layer obtained from an amount of 1 g of commercially available nickel ferrite powder slurried with 1 g of an inorganic polymer consisting of a precursor of 0.25 g equivalent nickel-ferrite per 1 ml. An amount corresponding to 5 weight% of IrO₂ acting as an electrocatalyst for the rapid conversion of oxygen ions into monoatomic oxygen and subsequently gaseous oxygen can be added to the slurry as IrCl₄, as described in WO99/36592 (de Nora). The slurry can be brush-coated onto the interdiffused and at least partly oxidised nickel copper alloy layer by applying 3 successive 50 micron thick layers of the slurry, each slurry-applied layer should be allowed to dry by heat-treating the anode at 500°C for 15 minutes between each layer application.

Example 2

[0064] A nickel metal core structure was heated in air at 1100°C for 16 hours to form an oxidised surface layer having a thickness of about 35 micron. The surface layer was black showing the presence of nickel oxide (NiO_{1+x}) which is known to act as an oxygen barrier layer and to be electrically conductive.

[0065] An interdiffused nickel-copper layer was then applied onto the oxygen barrier and oxidised as described in Example 1.

[0066] A mixture of nickel-ferrite and copper-ferrite powder was slurried in an inorganic polymer solution having the required composition for the formation of CuFe₂O₄ and NiFe₂O₄. The polymer solution had a concentration of 350g/l oxide equivalent and the powder to

polymer ratio was 1 to 0.25. The slurry was used as a coating feed and brushed onto the nickel oxide surface layer of the core structure to form a ferrite-based electrochemically active layer on the nickel oxide layer. After drying the ferrite-based layer at 105°C, the core structure was submitted to a heat treatment at 500°C in air to consolidate the coating.

[0067] Several ferrite-based layers were applied, with each applied layer being heat treated before applying a subsequent layer, to form a consolidated coating of more than 100 micron thick.

Example 3

[0068] A steel core structure was coated with a slurry prepared by suspending chromium oxide (Cr_2O_3) in an inorganic Cr^{3+} polymer solution. The feed concentration was greater than 500 g/l of Cr_2O_3 .

[0069] After heat-treating to consolidate the chromium oxide (Cr_2O_3) applied layer, thereby forming a barrier layer on the steel structure, a second intermediate layer of interdiffused nickel-copper was applied as described in Example 1 on the barrier layer. Finally the intermediate layer was coated with several electrochemically active layers of CuFe_2O_4 and NiFe_2O_4 as described in Example 2.

Example 4

[0070] A test anode was obtained by coating an Inconel® metal core structure with a nickel copper alloy layer and heat-treating it as described in Example 1 to form a barrier layer and an intermediate layer on the metal core structure.

[0071] A further layer of a nickel-iron based alloy consisting of 30 weight% nickel, 70 weight% iron of a thickness of approximately 0.5 mm can then applied on the interdiffused and at least partly oxidised nickel copper layer by plasma spraying.

[0072] This alloy layer can then pre-oxidised at 1100°C for 6 hours for the formation of a dense iron oxide-based electrochemically active oxide layer on the alloy layer. Although pre-oxidation of the alloy layer is preferred, the treatment is not necessary before using the anode in the cell to produce aluminium.

[0073] The test anode can then tested in a cell as described in Example 1. During electrolysis the alloy layer will further oxidised at the alloy layer/active layer interface, self-forming the electrochemically active layer. Simultaneously, the active layer will slowly dissolved into the electrolyte at the active layer/electrolyte interface at substantially the same rate as its rate of formation at the alloy layer/active layer interface, thereby maintaining the thickness of the oxide layer substantially constant, as the alloy layer wears away.

[0074] When the alloy layer is worn or damaged, the anode can be reconditioned by clearing at least the worn or damaged parts and reconstituting at least the alloy

layer.

Example 5

[0075] A test anode was obtained by electrodepositing onto a copper metal core structure a series of successive metallic layers consisting of a nickel layer (10 micron thick) which is known to be well adherent to copper and chromium, a chromium layer (25 micron thick), a nickel layer (50 micron thick) and a copper layer (50 micron thick) and heat treating first in argon and then in oxygen as described in Example 1 to interdiffuse and oxidise the nickel and the copper layers to form an intermediate layer, and oxidise the chromium layer to form an oxygen barrier layer.

[0076] An iron layer (200 micron thick) was then electrodeposited onto the interdiffused nickel-copper layer and pre-oxidised at 1100°C in air for 6 hours to form a dense iron oxide-based electrochemically active outer surface layer on the intermediate layer.

[0077] The anode was then tested in molten electrolyte containing approximately 6 weight% alumina at 850°C at a current density of about 0.8 A/cm². The anode was extracted from the cryolite after 100 hours and showed no sign of significant internal or external corrosion after microscopic examination of a cross-section of the anode sample.

Example 6

[0078] Examples 1 to 5 have been repeated by replacing the electrochemically active layer by a Cor-Ten™ type low-carbon high-strength (HSLA) steel layer doped with niobium, titanium, chromium and copper in a total amount of less than 4 weight% which is also electrochemically active upon oxidation. The anodes were pre-oxidised in air at about 1050°C for 15 hours for the formation of a dense hematite-based outer layer constituting an oxide-based surface layer on an un-oxidised anode body.

[0079] The anodes were then tested in a fluoride-containing molten electrolyte at 850°C containing cryolite and 25 weight% excess of AlF_3 and approximately 3 weight% alumina at a current density of about 0.7 A/cm².

[0080] To maintain the concentration of dissolved alumina in the electrolyte, fresh alumina was periodically fed into the cell. The alumina feed contained sufficient iron oxide to slow down the dissolution of the hematite-based electrochemically active anode layer.

[0081] After 140 hours electrolysis was interrupted and the anode extracted. Upon cooling the anode was examined externally and in cross-section. No corrosion was observed at or near the surface of the anode.

[0082] The produced aluminium was also analysed and showed an iron contamination of about 700 ppm which is below the tolerated iron contamination in commercial aluminium production.

[0083] The Example can be repeated with different HSLA steel layers such as an HSLA steel layer doped with manganese 0.4 weight%, niobium 0.02 weight%, molybdenum 0.02 weight%, copper 0.3 weight%, nickel 0.45 weight% and chromium 0.8 weight%, or an HSLA steel layer doped with nickel, copper and silicon in a total amount of less than 1.5 weight%.

Claims

1. A composite, high-temperature resistant, non-carbon, metal-based oxygen-evolving anode of a cell for the electrowinning of aluminium by the electrolysis of alumina dissolved in a molten fluoride-containing electrolyte, the anode comprising a metal-based core structure of low electrical resistance, for connecting the anode to a positive current supply, coated with a series of superimposed, adherent, electrically conductive layers consisting of:

a) at least one layer on the metal-based core structure constituting during electrolysis a barrier substantially impervious to molecular oxygen and also monoatomic oxygen, said barrier comprising at least one oxide selected from chromium, niobium and nickel oxide;

b) one or more intermediate protective layers containing oxidised, or oxidised and metallic, copper and optionally at least one of nickel and cobalt applied to the oxygen barrier to protect the oxygen barrier against dissolution, which intermediate layer(s) during electrolysis remain inactive in the reactions for the evolution of oxygen gas; and

c) an electrochemically active layer on the outermost intermediate layer, for the oxidation reaction of oxygen ions present at the anode/electrolyte interface into nascent monoatomic oxygen, as well as for subsequent reaction for the formation of gaseous biatomic molecular oxygen evolving as gas, the active layer protecting the intermediate layer(s) against dissolution and comprising at least one transition metal and/or an oxide thereof,

wherein the electrochemically active layer has a surface that is iron oxide-based and that is made of at least one ferrite or consists of an oxidised surface of an alloy that contains at least 70 weight% iron before oxidation.

2. The anode of claim 1, wherein the core structure comprises a metal, an alloy, an intermetallic compound or a cermet.

3. The anode of claim 2, wherein the core structure comprises at least one metal selected from nickel,

copper, cobalt, chromium, molybdenum, tantalum, niobium or iron.

4. The anode of claim 3, wherein the core structure is nickel plated copper.

5. The anode of claim 3, wherein the core structure comprises an alloy consisting of 10 to 30 weight% of chromium, 55 to 90% of at least one of nickel, cobalt or iron, and 0 to 15% of aluminium, titanium, zirconium, yttrium, hafnium or niobium.

6. The anode of claim 3, wherein the core structure comprises an alloy or intermetallic compound containing at least two metals selected from nickel, cobalt, iron and aluminium.

7. The anode of claim 3, wherein the core structure comprises a cermet containing copper and/or nickel as a metal, and a ceramic phase.

8. The anode of claim 1, wherein said intermediate layer(s) comprise an oxidised alloy containing 20 to 60 weight% of copper with one or more further metals forming a solid solution with copper.

9. The anode of claim 8, wherein said further metal is selected from nickel and/or cobalt.

10. The anode of claim 1, wherein the electrochemically active layer comprises oxides which may slowly wear away during electrolysis.

11. The anode of claim 1, wherein the electrochemically active layer is an oxidised layer of high-strength low-alloy steel that comprises 94 to 98 weight% iron and carbon, the remaining constituents being one or more further metals selected from chromium, copper, nickel, silicon, titanium, tantalum, tungsten, vanadium, zirconium, aluminium, molybdenum, manganese and niobium, and optionally a small amount of at least one additive selected from boron, sulfur, phosphorus and nitrogen.

12. The anode of claim 1, wherein the electrochemically active layer is pre-oxidised prior to electrolysis.

13. The anode of claim 1, wherein the electrochemically active layer is a layer of iron with: at least one metal selected from nickel, copper, cobalt, aluminium and zinc; and at least one electrocatalyst selected from iridium, palladium, platinum, rhodium, ruthenium, silicon, tin, mischmetal and metals of the Lanthanide series, and mixture, oxides and compounds thereof.

14. The anode of claim 1, wherein the electrochemically active layer is a surface oxidised iron-nickel layer,

the oxidised surface containing iron oxide and/or nickel oxide.

15. The anode of claim 15, wherein the electrochemically active layer comprises ferrites. 5
16. The anode of claim 1, wherein the electrochemically active layer comprises ceramic oxides containing combinations of divalent nickel, cobalt, magnesium, manganese, copper and zinc with divalent/trivalent nickel, cobalt, manganese and/or iron. 10
17. The anode of claim 1, wherein at least one of said layers is slurry applied. 15
18. A method of manufacturing a composite, high-temperature resistant, non-carbon, metal-based, oxygen-evolving anode according to claim 1, comprising a series of superimposed, adherent, electrically conductive layers on a metal-based core structure of low electrical resistance for connecting the anode to a positive current supply, said method comprising the following steps: 20
 - a) forming by surface oxidation or by direct application at least one layer on the metal-based core structure constituting during electrolysis a barrier substantially impervious to molecular oxygen and also monoatomic oxygen; 25
 - b) applying on the oxygen barrier or on the core structure prior to forming said oxygen barrier one or more intermediate protective layers to protect the oxygen barrier against dissolution, which intermediate layer(s) during electrolysis remain inactive in reactions for the evolution of oxygen gas; and 30
 - c) forming on the outermost intermediate layer an electrochemically active layer for the oxidation reaction of oxygen ions present at the anode/electrolyte interface into nascent monoatomic oxygen, as well as for subsequent reaction for the formation of gaseous biatomic molecular oxygen, the active layer protecting the intermediate layer(s) against dissolution and comprising at least one transition metal and/or an oxide thereof. 35 40 45
19. The method of claim 18, comprising applying at least one of said layers as a precursor slurry. 50
20. The method of claim 18, comprising applying at least one of said layers as a precursor powder followed by a heat-treatment. 55
21. The method of claim 18, comprising applying at least one layer as a metallic layer which is subse-

quently oxidised.

22. The method of claim 18, comprising applying at least one of said layers by dipping, spraying, painting, brushing, arc spraying, plasma spraying, electro-chemical deposition, physical vapour deposition, chemical vapour deposition or calendar rolling.
23. The method of claim 18, for reconditioning an anode according to claim 1 whose electrochemically active layer is worn or damaged, the method comprising clearing at least worn and/or damaged parts of the active surface from the core structure or from the outermost intermediate layer to which it adheres and then reconstituting at least the electrochemically active layer.
24. A cell for the production of aluminium by the electrolysis of alumina dissolved in a molten fluoride-containing electrolyte comprising at least one composite anode according to claim 1 facing a cathode.
25. The cell of claim 24, comprising an aluminium-wettable cathode.
26. The cell of claim 25, comprising a drained cathode.
27. The cell of claim 24, which is in a bipolar configuration.
28. A method of producing aluminium in an aluminium electrowinning cell according to claim 24 containing alumina dissolved in a molten fluoride-containing electrolyte, the method comprising electrolysis of alumina to produce aluminium on the cathode and oxygen on the facing anode.
29. The method of claim 28, wherein during electrolysis the or each anode is protected by an electrolyte-generated oxyfluoride-containing layer formed on the electrochemically active layer.

Patentansprüche

1. Hochtemperaturbeständige, metallbasierte, sauerstoffentwickelnde Nicht-Kohlenstoff-Verbundanode für eine Zelle zur elektrolytischen Gewinnung von Aluminium durch die Elektrolyse von Aluminium, das in geschmolzenes Fluorid enthaltendem Elektrolyten gelöst ist, wobei die Anode eine metallbasierte Kernstruktur mit geringem elektrischem Widerstand zum Anschließen der Anode an eine positive Stromquelle umfasst, welche mit einer Reihe von übereinanderliegenden, fest haftenden, elektrisch leitfähigen Schichten beschichtet ist, bestehend aus:

a) mindestens einer Schicht auf der metallbasierten Kernstruktur, die während der Elektrolyse eine für molekularen Sauerstoff und auch für monoatomaren Sauerstoff im Wesentlichen undurchlässige Barriere bildet, wobei die Barriere mindestens ein Oxid ausgewählt aus Chrom-, Niob- und Nickeloxid umfasst,

b) einer oder mehreren schützenden Zwischenschichten, die oxidiertes, oder oxidiertes und metallisches, Kupfer und gegebenenfalls, zum Schutz der Sauerstoffbarriere gegen Auflösung, aufgebracht auf die Sauerstoffbarriere mindestens eines von Nickel und Kobalt enthalten, welche Zwischenschicht bzw. welchen Zwischenschichten während der Elektrolyse in den Reaktionen zur Entwicklung von Sauerstoffgas inaktiv sind, und

c) einer elektrochemisch aktiven Schicht auf der äußersten Zwischenschicht für die Oxidationsreaktion von Sauerstoffionen, die an der Grenzfläche von Anode/Elektrolyt vorhanden sind, zu naszierendem monoatomaren Sauerstoff, sowie für die anschließende Reaktion für die Bildung von gasförmigem monoatomaren molekularen Sauerstoff, der sich als Gas entwickelt, wobei die aktive Schicht die Zwischenschicht bzw. die Zwischenschichten gegen Auflösung schützt und mindestens ein Übergangsmetall und/oder ein Oxid davon umfasst,

wobei die elektrochemisch aktive Schicht eine Oberfläche aufweist, die auf Eisenoxid basiert und die hergestellt ist aus mindestens einem Ferrit, oder die aus einer oxidierten Oberfläche einer Legierung besteht, die vor der Oxidation mindestens 70 Gew. % Eisen enthält.

2. Anode nach Anspruch 1, wobei die Kernstruktur ein Metall, eine Legierung, eine intermetallische Verbindung oder ein Cermet umfasst.
3. Anode nach Anspruch 2, wobei die Kernstruktur mindestens ein Metall ausgewählt aus Nickel, Kupfer, Kobalt, Chrom, Molybdän, Tantal, Niob oder Eisen umfasst.
4. Anode nach Anspruch 3, wobei die Kernstruktur mit Nickel platiertes Kupfer ist.
5. Anode nach Anspruch 3, wobei die Kernstruktur eine Legierung umfasst, die aus 10 bis 30 Gew. % Chrom, 55 bis 90 Gew. % von mindestens einem von Nickel, Kobalt oder Eisen und 0 bis 15% Aluminium, Titan, Zirkonium, Yttrium, Hafnium oder Niob besteht.

6. Anode nach Anspruch 3, wobei die Kernstruktur eine Legierung oder intermetallische Verbindung umfasst, die mindestens zwei Metalle ausgewählt aus Nickel, Kobalt, Eisen und Aluminium enthält.

7. Anode nach Anspruch 3, wobei die Kernstruktur ein Cermet umfasst, das Kupfer und/oder Nickel als Metall und eine keramische Phase enthält.

8. Anode nach Anspruch 1, wobei die Zwischenschicht bzw. die Zwischenschichten eine oxidierte Legierung umfasst bzw. umfassen, die 20 bis 60 Gew. % Kupfer enthält, wobei ein oder mehrere weitere Metalle eine feste Lösung mit Kupfer bilden.

9. Anode nach Anspruch 8, wobei das weitere Metall ausgewählt ist aus Nickel und/oder Kobalt.

10. Anode nach Anspruch 1, wobei die elektrochemisch aktive Schicht Oxide umfasst, die während der Elektrolyse langsam abgetragen werden können.

11. Anode nach Anspruch 1, wobei die elektrochemisch aktive Schicht eine oxidierte Schicht aus hochfestem, niedrig legierten Stahl, der 94 bis 98 Gew. % Eisen und Kohlenstoff umfasst, wobei die übrigen Bestandteile eines oder mehrere der weiteren Metalle sind, die ausgewählt sind aus Chrom, Kupfer, Nickel, Silicium, Titan, Tantal, Wolfram, Vanadium, Zirkonium, Aluminium, Molybdän, Mangan und Niob, und gegebenenfalls eine kleine Menge mindestens eines Zusatzstoffes ausgewählt aus Bor, Schwefel, Phosphor und Stickstoff.

12. Anode nach Anspruch 1, wobei die elektrochemisch aktive Schicht vor der Elektrolyse voroxidiert wird.

13. Anode nach Anspruch 1, wobei die elektrochemisch aktive Schicht eine Schicht aus Eisen mit mindestens einem Metall ausgewählt aus Nickel, Kupfer, Kobalt, Aluminium und Zink, und mindestens einem Elektrokatalysator ausgewählt aus Iridium, Palladium, Platin, Rhodium, Ruthenium, Silicium, Zinn, Mischmetall und Metallen der Lanthanidenreihe und Mischungen, Oxiden und Verbindungen derselben ist.

14. Anode nach Anspruch 1, wobei die elektrochemisch aktive Schicht eine an der Oberfläche oxidierte Eisen-Nickelschicht ist, wobei die oxidierte Oberfläche Eisenoxid und/oder Nickeloxid enthält.

15. Anode nach Anspruch 15, wobei die elektrochemisch aktive Schicht Ferrite umfasst.

16. Anode nach Anspruch 1, wobei die elektrochemisch aktive Schicht Keramikoxide umfasst, die Kombinationen aus zweiwertigem Nickel, Kobalt, Magnesi-

um, Mangan, Kupfer und Zink mit zweiwertigem/dreiwertigem Nickel, Kobalt, Mangan und/oder Zink enthalten.

17. Anode nach Anspruch 1, wobei mindestens eine der Schichten in einer Aufschlämmung aufgebracht wird. 5
18. Verfahren zur Herstellung einer hochtemperaturbeständigen, metallbasierten, Sauerstoff entwickelnden Nicht-Kohlenstoff-Verbundanode gemäß Anspruch 1, die eine Reihe von übereinanderliegenden, fest haftenden, elektrisch leitfähigen Schichten auf einer metallbasierten Kernstruktur mit geringem elektrischen Widerstand zum Anschließen der Anode an eine positive Stromquelle umfasst, wobei das Verfahren die folgenden Schritte umfasst:

a) das Bilden mindestens einer Schicht auf der metallbasierten Kernstruktur, welche während der Elektrolyse eine für molekularen Sauerstoff und auch für monoatomaren Sauerstoff im Wesentlichen undurchlässige Barriere bildet, durch Oberflächenoxidation oder durch direkte Aufbringung, 20

b) das Aufbringen einer oder mehrerer schützender Zwischenschichten auf die Sauerstoffbarriere oder auf die Kernstruktur vor der Bildung der Sauerstoffbarriere, um die Sauerstoffbarriere gegen Auflösung zu schützen, wobei die Zwischenschicht bzw. die Zwischenschichten während der Elektrolyse in Reaktionen für die Entwicklung von Sauerstoffgas inaktiv bleiben, und 30

c) die Bildung einer elektrochemisch aktiven Schicht für die Oxidationsreaktion von Sauerstoffionen, die an der Grenzfläche von Anode/Elektrolyt anwesend sind, zu naszierendem monoatomaren Sauerstoff sowie für die anschließende Reaktion für die Bildung von gasförmigem monoatomaren molekularen Sauerstoff, auf der äußersten Zwischenschicht, wobei die aktive Schicht die Zwischenschicht bzw. die Zwischenschichten gegen Auflösung schützt und mindestens ein Übergangsmetall und/oder ein Oxid davon umfasst. 40

19. Verfahren nach Anspruch 18, bei dem mindestens eine der Schichten als Vorläuferaufschlämmung aufgebracht wird. 50

20. Verfahren nach Anspruch 18, bei dem mindestens eine der Schichten als Vorläuferpulver aufgebracht wird, gefolgt von einer Wärmebehandlung. 55

21. Verfahren nach Anspruch 18, bei dem mindestens

eine Schicht als metallische Schicht aufgebracht wird, die anschließend oxidiert wird.

22. Verfahren nach Anspruch 18, bei dem mindestens eine der Schichten durch Eintauchen, Sprühen, Aufstreichen, Aufbürsten, Lichtbogensprühen, Plasmasprühen, elektrochemische Abscheidung, physikalische Dampfabcheidung, chemische Dampfabcheidung oder Kalanderauftragung aufgebracht wird.
23. Verfahren nach Anspruch 18, zur Rekonditionierung einer Anode gemäß Anspruch 1, deren elektrochemisch aktive Schicht abgenutzt oder beschädigt ist, bei dem zumindest die abgenutzten und/oder beschädigten Teile der aktiven Oberfläche aus der Kernstruktur oder der äußersten Zwischenschicht, an die sie haftet, beseitigt werden und dann zumindest die elektrochemisch aktive Schicht wieder aufgebaut wird.
24. Zelle für die Herstellung von Aluminium durch Elektrolyse von Aluminium, das in geschmolzenes Fluorid enthaltenden Elektrolyten gelöst ist, die zumindest eine Verbundanode gemäß Anspruch 1 gegenüber einer Kathode umfasst.
25. Zelle nach Anspruch 24, die eine Aluminium benetzbare Kathode umfasst.
26. Zelle nach Anspruch 25, die eine Ablaufkathode umfasst.
27. Zelle nach Anspruch 24, die sich in einer bipolaren Konfiguration befindet.
28. Verfahren zur Herstellung von Aluminium in einer Zelle zur elektrolytischen Gewinnung von Aluminium gemäß Anspruch 24, die Aluminium in einem geschmolzenen Fluorid enthaltenden Elektrolyt gelöst enthält, wobei das Verfahren das Elektrolysieren von Aluminium zur Erzeugung von Aluminium an der Kathode und Sauerstoff an der gegenüberliegenden Anode umfasst.
29. Verfahren nach Anspruch 28, wobei während der Elektrolyse die oder jede Anode durch eine elektrolytisch erzeugte Oxyfluorid enthaltende Schicht geschützt wird, die auf der elektrochemisch aktiven Schicht gebildet wird.

Revendications

1. Anode composite, résistante à haute température, non-carbonée, à base de métal, à dégagement d'oxygène d'une cuve pour l'électro-obtention d'aluminium par l'électrolyse d'alumine dissoute dans un

électrolyte contenant du fluorure en fusion, l'anode comprenant une structure de noyau à base de métal de faible résistance électrique, pour relier l'anode à une alimentation en courant positive, revêtue d'une série de couches superposées, adhérentes, électriquement conductrices composées de :

a) au moins une couche sur la structure de noyau à base de métal constituant, pendant l'électrolyse, une barrière sensiblement imperméable à l'oxygène moléculaire et également à l'oxygène monoatomique, ladite barrière comprenant au moins un oxyde choisi à partir d'oxyde de chrome, de niobium et de nickel ;

b) une ou plusieurs couches protectrices intermédiaires contenant du cuivre oxydé, ou oxydé et métallique, et éventuellement au moins l'un de nickel et de cobalt appliquée sur la barrière à l'oxygène pour protéger la barrière à l'oxygène contre la dissolution, laquelle couche(s) intermédiaire(s) pendant l'électrolyse reste inactive dans les réactions pour le dégagement de gaz oxygène ; et

c) une couche électrochimiquement active sur la couche intermédiaire la plus extérieure, pour la réaction d'oxydation d'ions oxygène présents au niveau de l'interface anode/électrolyte en oxygène monoatomique naissant, ainsi que pour la réaction subséquente pour la formation d'oxygène gazeux biatomique moléculaire se dégageant comme gaz, la couche active protégeant la couche(s) intermédiaire(s) contre la dissolution et comprenant au moins un métal de transition et/ou un oxyde de celui-ci,

dans laquelle la couche électrochimiquement active a une surface qui est à base d'oxyde de fer et qui est réalisée au moins en ferrite ou se compose d'une surface oxydée d'un alliage qui contient au moins 70% en poids de fer avant oxydation.

2. Anode selon la revendication 1, dans laquelle la structure de noyau comprend un métal, un alliage, un composé intermétallique ou un cermet.
3. Anode selon la revendication 2, dans laquelle la structure de noyau comprend au moins un métal choisi à partir de nickel, cuivre, cobalt, chrome, molybdène, tantale, niobium ou fer.
4. Anode selon la revendication 3, dans laquelle la structure de noyau est du cuivre plaqué de nickel.
5. Anode selon la revendication 3, dans laquelle la structure de noyau comprend un alliage composé de 10 à 30% en poids de chrome, 55 à 90% d'au moins l'un de nickel, cobalt ou fer, et 0 à 15% d'aluminium, de titane, de zirconium, d'yttrium,

d'hafnium ou de niobium.

6. Anode selon la revendication 3, dans laquelle la structure de noyau comprend un alliage ou un composé intermétallique contenant au moins deux métaux choisis à partir de nickel, cobalt, fer et aluminium.
7. Anode selon la revendication 3, dans laquelle la structure de noyau comprend un cermet contenant du cuivre, et/ou du nickel comme métal, et une phase céramique.
8. Anode selon la revendication 1, dans laquelle ladite couche(s) intermédiaire(s) comprend un alliage oxydé contenant 20 à 60% en poids de cuivre avec un ou plusieurs autres métaux formant une solution solide avec du cuivre.
9. Anode selon la revendication 8, dans laquelle ledit autre métal est choisi à partir de nickel et/ou de cobalt.
10. Anode selon la revendication 1, dans laquelle la couche électrochimiquement active comprend des oxydes qui peuvent lentement s'user pendant l'électrolyse.
11. Anode selon la revendication 1, dans laquelle la couche électrochimiquement active est une couche oxydée d'acier faiblement allié à haute résistance qui comprend 94 à 98% en poids de fer et de carbone, les constituants restants étant un ou plusieurs autres métaux choisis à partir de chrome, cuivre, nickel, silicium, titane, tantale, tungstène, vanadium, zirconium, aluminium, molybdène, manganèse et niobium, et éventuellement une petite quantité d'au moins un additif choisi à partir de bore, soufre, phosphore et azote.
12. Anode selon la revendication 1, dans laquelle la couche électrochimiquement active est pré-oxydée avant électrolyse.
13. Anode selon la revendication 1, dans laquelle la couche électrochimiquement active est une couche de fer avec : au moins un métal choisi à partir de nickel, cuivre, cobalt, aluminium et zinc ; et au moins un électrocatalyseur choisi à partir d'iridium, palladium, platine, rhodium, ruthénium, silicium, étain, mischmétal et de métaux de la série des lanthanides, et mélange, oxydes et composés de ceux-ci.
14. Anode selon la revendication 1, dans laquelle la couche électrochimiquement active est une couche fer-nickel oxydée en surface, la surface oxydée contenant de l'oxyde de fer et/ou de l'oxyde de nic-

kel.

15. Anode selon la revendication 1, dans laquelle la couche électrochimiquement active comprend des ferrites.

16. Anode selon la revendication 1, dans laquelle la couche électrochimiquement active comprend des oxydes céramiques contenant des combinaisons de nickel, cobalt, magnésium, manganèse, cuivre et zinc divalent avec du nickel, cobalt, manganèse et/ou fer divalent/trivalent.

17. Anode selon la revendication 1, dans laquelle au moins l'une desdites couches est du coulis appliqué.

18. Procédé de fabrication d'une anode composite, résistante à haute température, non-carbonée, à base de métal, à dégagement d'oxygène selon la revendication 1, comprenant une série de couches superposées, adhérentes, électriquement conductrices sur une structure de noyau à base de métal de faible résistance électrique pour relier l'anode à une alimentation en courant positive, ledit procédé comprenant les étapes suivantes :

a) former par oxydation de surface ou par application directe au moins une couche sur la structure de noyau à base de métal constituant, pendant l'électrolyse, une barrière sensiblement imperméable à l'oxygène moléculaire et également à l'oxygène monoatomique ;

b) appliquer sur la barrière à l'oxygène ou sur la structure de noyau avant de former ladite barrière à l'oxygène, une ou plusieurs couches protectrices intermédiaires pour protéger la barrière à l'oxygène contre la dissolution, laquelle couche(s) intermédiaire(s) pendant l'électrolyse reste inactive dans les réactions pour le dégagement de gaz oxygène ; et

c) former sur la couche intermédiaire la plus extérieure, une couche électrochimiquement active pour la réaction d'oxydation d'ions oxygène présents au niveau de l'interface anode/électrolyte en oxygène monoatomique naissant, ainsi que pour la réaction subséquente pour la formation d'oxygène gazeux biatomique moléculaire, la couche active protégeant la couche(s) intermédiaire(s) contre la dissolution et comprenant au moins un métal de transition et/ou un oxyde de celui-ci.

19. Procédé selon la revendication 18, consistant à appliquer au moins l'une desdites couches en tant que coulis précurseur.

20. Procédé selon la revendication 18, consistant à ap-

pliquer au moins l'une desdites couches en tant que poudre précurseur suivie par un traitement thermique.

21. Procédé selon la revendication 18, consistant à appliquer au moins une couche en tant que couche métallique qui est oxydée subséquentement.

22. Procédé selon la revendication 18, consistant à appliquer au moins l'une desdites couches par immersion, pulvérisation, peinture, brossage, projection à l'arc, projection par plasma, dépôt électrochimique, dépôt physique en phase vapeur, dépôt chimique en phase vapeur ou cylindrage.

23. Procédé selon la revendication 18, pour rénover une anode selon la revendication 1 dont la couche électrochimiquement active est usée ou endommagée, le procédé consistant à enlever au moins les parties usées et/ou endommagées de la surface active à partir de la structure de noyau ou à partir de la couche intermédiaire la plus extérieure à laquelle elle adhère et ensuite à reconstituer au moins la couche électrochimiquement active.

24. Cuve pour la production d'aluminium par l'électrolyse d'alumine dissoute dans un électrolyte contenant du fluorure en fusion comprenant au moins une anode composite selon la revendication 1 faisant face à une cathode.

25. Cuve selon la revendication 24, comprenant une cathode mouillable par l'aluminium.

26. Cuve selon la revendication 25, comprenant une cathode de drainage.

27. Cuve selon la revendication 24, qui est dans une configuration bipolaire.

28. Procédé pour produire de l'aluminium dans une cuve d'électro-obtention d'aluminium selon la revendication 24 contenant de l'alumine dissoute dans un électrolyte contenant du fluorure en fusion, le procédé consistant à électrolyser l'alumine pour produire de l'aluminium sur la cathode et de l'oxygène sur l'anode en vis-à-vis.

29. Procédé selon la revendication 28, dans lequel pendant l'électrolyse la ou chaque anode est protégée par une couche contenant de l'oxyfluorure engendré par l'électrolyte, formée sur la couche électrochimiquement active.