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(54) Title: ALUMINIUM PRODUCTION CELLS WITH IRON-BASED METAL ALLOY ANODES

(57) Abstract: An iron-based metal anode for the electrowinning of aluminium by the electrolysis of alumina in a molten fluoride electrolyte has an electrochemically active integral outside oxide layer on an iron-based alloy that consists of 75 to 90 weight % iron; 0.5 to 5 weight % in total of at least one rare earth metal, in particular yttrium; 1 to 10 weight % aluminium; 0 to 10 weight % copper; 0 to 10 weight % nickel; and 0.5 to 5 weight % of other elements. The total amount of aluminium, copper and nickel is in the range from 5 to 20 weight %; and the total amount of rare earth metal(s), aluminium and copper is also in the range from 5 to 20 weight %. The electrochemically active surface layer is predominantly of iron oxide that slowly dissolves into the electrolyte during operation and is maintained by progressive slow oxidation of iron at the interface of the bulk metal of the alloy with the oxide layer. This progressive slow oxidation of iron corresponds to the dissolution of iron into the electrolyte which remains at or below saturation level at the operating temperature, the operating temperature being maintained sufficiently low to limit the contamination of the product aluminium to an acceptable level, and the electrolyte being circulated to maintain a sufficient concentration of alumina in the anode cathode gap.

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ALUMINIUM PRODUCTION CELLS WITH
IRON-BASED METAL ALLOY ANODES

Field of the Invention

This invention relates to iron-based metal anodes for the electrowinning of aluminium by the electrolysis of alumina dissolved in a molten fluoride-containing electrolyte and to a cell and method for the electrowinning of aluminium using such iron-based metal anodes.

Background Art

Using non-carbon anodes in aluminium electrowinning cells should drastically improve the aluminium production process by reducing pollution and the cost of aluminium production. Many attempts have been made to use oxide anodes, cermet anodes and metal-based anodes for aluminium production, however they were never adopted by the aluminium industry.

US Patent 6,248,227 (de Nora/Duruz) discloses a non-carbon, metal-based slow-consumable anode of a cell for the electrowinning of aluminium that self-forms during normal electrolysis an electrochemically-active oxide-based surface layer. The rate of formation of this layer is maintained substantially equal to its rate of dissolution at the surface layer/electrolyte interface thereby maintaining its thickness substantially constant.

In some embodiments, the anode body comprised an iron alloy, in particular an HSLA steel comprising 94 to 98 weight% iron with small amounts of alloying elements and less than 0.5 weight% carbon, which when oxidised formed an oxide-based surface layer containing iron

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oxide, such as hematite or a mixed ferrite-hematite. It was disclosed that the anode body may comprise one or more additives selected from beryllium, magnesium, yttrium, titanium, zirconium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, rhodium, silver, aluminium, copper, nickel, silicon, tin, hafnium, lithium, cerium and other Lanthanides.

A different approach was taken in WO 00/06802 (Duruz/de Nora/Crottaz) where anodes comprising a transition metal-based oxide active surface of iron oxide, cobalt oxide, nickel oxide or combinations thereof, were kept dimensionally stable during electrolysis by continuously or intermittently feeding to the electrolyte a sufficient amount of alumina and transition metal species that are present as oxides at the anode surface. The cell was operated at a sufficiently low temperature so as to limit the solubilisation of the transition metal species.

WO 00/40783 (de Nora/Duruz) further describes the use of HSLA steel with a coherent and adherent oxide surface as an anode for aluminium electrowinning, preferably using an external supply of iron to maintain the anode surface as described in WO 00/06802.

Nickel-iron alloy anodes with various additives are further described in WO 00/06803 (Duruz/de Nora/Crottaz), WO 00/006804 (Crottaz/Duruz), WO 01/42534 (de Nora/Duruz), WO 01/42535, (Duruz/de Nora) and WO 01/42536 (Duruz/Nguyen/ de Nora).

Despite the progress achieved, there is still a need, in particular with iron-rich steels or alloys (>75% iron), to reduce contamination of the product aluminium. For this reason, most effort was directed to alloys with lower iron content, such as 60-40 weight% iron-nickel and 65-35 weight% iron-nickel: see the examples in the above-

mentioned patent publications on nickel-iron alloy anodes.

Summary of the Invention

An object of the invention is to provide an iron-based metal anode with an iron-rich alloy having an integral outside oxide layer which can be progressively formed during use at a rate corresponding to a controlled dissolution into the electrolyte at the operating temperature, or which can even be stabilised by maintaining an amount of iron species in the electrolyte, leading to an acceptably low contamination of the product aluminium.

According to the invention, an iron-based metal anode for the electrowinning of aluminium by the electrolysis of alumina in a molten fluoride electrolyte has an electrochemically active integral outside oxide layer on an iron-based alloy that consists of:

- 75 to 90 weight% iron, preferably 80 to 90 weight%;
- 0.5 to 5 weight% in total of one or more rare earth metals, in particular yttrium preferably in an amount of 0.5 to 3 weight%;
- 1 to 12 weight% aluminium, usually 2 to 10 weight% and preferably 4 to 8 weight%;
- 0 to 10 weight% copper, preferably 0.5 to 8 weight%;
- 0 to 10 weight% nickel, preferably 0.5 to 8 weight%; and
- 0 to 5 weight% of other elements, usually at least one of molybdenum, manganese, titanium, tantalum, tungsten, vanadium, zirconium, niobium, chromium, cobalt, silicon and carbon, and preferably up to 2 weight%.

In this iron-based alloy according to the invention, the total amount of aluminium, copper and nickel is in

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the range from 5 to 20 weight%, and the total amount of rare earth metal(s), aluminium and copper is also in the range from 5 to 20 weight%.

5 The electrochemically active oxide-based surface layer on the iron-based metal anode is predominantly iron oxide, in the form of hematite, or in a multi-compound mixed oxide and/or in solid solution of oxides, depending on the additive metals included in the bulk of the alloy. The oxide can be in the form of a simple, double and/or
10 multiple oxide, and/or in the form of a stoichiometric or non-stoichiometric oxide.

Suitable rare earth metals include Actinides, such as scandium or yttrium, and Lanthanides, such as cerium and ytterbium. The preferred rare earth metal is yttrium
15 and preferably the iron-based metal anode contains yttrium in an amount of 0.5 to 3 weight%.

The rare earth metals - which are substantially insoluble in iron - are present in the grain boundaries of the metal bulk of the anode in an amount which
20 provides during use controlled diffusion of oxygen into the metal bulk, and hence the controlled oxidation and dissolution rate of the anode. When the iron alloy is cast, the presence of the rare earth metal refines the structure of the alloy by reducing the grain size, for
25 example from about 0.5-1 cm to about 50-100 micron when yttrium is used as an additive.

Such a rare earth metal migrates predominantly to the grain boundaries of the iron or iron alloy and acts as a barrier against diffusion of oxygen. At the grain
30 boundaries, the rare earth metals can be present before oxidation as a substantially distinct metal phase and after oxidation as oxides, in particular mixed oxides with iron and the other alloying metals. To be effective, oxidation of the rare earth metal should be avoided

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during casting before it has reached the grain boundaries.

When cerium is included as a rare earth (preferably in combination with yttrium), it is oxidised to ceria in the formation of the oxide-based surface layer to provide on the surface of the layer a nucleating agent for the in-situ formation of an electrolyte-generated protective layer. Such electrolyte-generated protective layer usually comprises cerium oxyfluoride when cerium ions are contained in the electrolyte and may be obtained by following the teachings of US Patent No. 4,614,569 (Duruz/Derivaz/Debely/Adorian) which describes a protective anode coating of cerium oxyfluoride, formed in-situ in the cell or pre-applied, and maintained by the addition of small amounts of cerium to the molten electrolyte.

The further metals in the iron-rich alloy include aluminium and usually at least one of copper and/or nickel.

Aluminium, copper and nickel are soluble in iron and can form alloys therewith, and in addition may form intermetallic compounds or mixed oxides with the rare earth metals.

The presence of aluminium in an amount up to 10 or 12 weight%, normally up to about 8 weight% of the iron-rich alloy and preferably from 2 to 6 weight%, has the effect of controlling the oxidation of the bulk iron by reinforcing the oxygen barrier at the grain boundaries through forming stable intermetallics with the rare earths.

The inclusion of copper in an amount up to 10 weight%, normally from 1 to 8 weight% of the iron-rich alloy, has the effect of improving the compactness of the oxide layer formed, thereby reducing its imperviousness

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and improving its resistance to further oxidation. The migration of copper to the surface inhibits the formation of a non-conductive layer of fluoride compounds such as NiF_2 on the surface of the iron bulk under the desired
5 hematite layer which is dense and protective, and further reduces the inward migration of oxygen.

The inclusion of nickel in amounts up to 10 weight% stabilises the iron against oxidation by the formation of stable intermetallics with aluminium and the rare earth
10 metals in particular yttrium.

In embodiments with copper and nickel, the weight ratio of copper to nickel is preferably in the range 1:3 to 3:1. The combination of copper with nickel, in particular copper from 2 to 6 weight % and nickel from 2
15 to 8 weight%, produces copper-nickel alloys that inhibit the formation of unwanted nickel fluoride (NiF_2).

Usually the total amount of aluminium, copper and nickel is in the range from 8 to 18 weight%, and the total amount of rare earth metal, aluminium and copper is
20 also in the range from 8 to 18 weight%.

In one embodiment of the anode, the iron-based alloy consists of:

- 80 to 90 weight% iron;
- 0.5 to 3 weight% yttrium;
- 25 - 2 to 6 weight% aluminium;
- 1 to 8 weight% copper;
- 1 to 8 weight% nickel; and
- 0 to 5 weight% (usually 0.5 to 2 weight%) of other elements,

30 subject to the aforesaid minimum and maximum combined amounts of the groups of additives.

Possible additives constituting these other alloying elements in amounts up to 5 weight% and preferably below 2 weight% in total of the iron-based alloy, include:

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- molybdenum (usually up to 1 weight%);
 - manganese, titanium, tantalum, tungsten, vanadium, zirconium, and niobium (usually each up to 1 weight%);
 - 5 - chromium and cobalt (usually each up to 2 weight%);
 - silicon up to about 2 weight %;
 - as well as traces of carbon and of the usual impurities.
- 10 In a variation of the invention, an iron-based metal anode for the electrowinning of aluminium by the electrolysis of alumina in a molten fluoride electrolyte has an electrochemically active integral outside oxide layer on an iron-based alloy that consists of:
- 15 - 75 to 90 weight% iron;
 - 1 to 12 weight% aluminium, usually 2 to 10 weight%;
 - 1 to 10 weight% copper;
 - 1 to 10 weight% nickel; and
 - 1 to 10 weight% of one or more additional elements
 - 20 selected from:
 - 0 to 5 weight% in total of one or more rare earth metals, in particular yttrium; and
 - 0 to 5 weight% of other elements, as listed above.
- 25 In this modified composition and the previous compositions, the total amount of copper and nickel is preferably at least 4 weight%; the weight ratio of copper to nickel is in the range 1:3 to 3:1; and the weight ratio of the total amount of (a) copper and nickel to (b)
- 30 the total amount of said additional elements is in the range (a):(b) from 20:1 to 4:10; preferably from 10:1 to 4:6.

The anode is preferably made by casting iron containing the specified metals as additives, i.e. where

the final anode shape is produced by casting the molten iron with additives in a mould, usually a sand mould. As mentioned above, when the iron alloy is cast, the presence of a rare earth metal refines the structure of the alloy by reducing the grain size. Moreover, casting is particularly advantageous for forming the anodes into structures of the desired shape.

The anode may have an active part consisting of a body made of the described iron-rich alloy, however its active part can comprise a layer of the iron-rich alloy on an electronically conductive, inert, inner core made of a different electronically conductive material, such as metals, alloys, intermetallics, cermets and conductive ceramics. Such inner core can be selected from metals, alloys, intermetallic compounds, cermets and conductive ceramics or combinations thereof and may be covered with an oxygen barrier layer, as described in US Patent 6,248,227 (de Nora/Duruz).

Resistance to oxygen may be at least partly achieved by forming an oxygen barrier layer on the surface of the inner core by surface oxidation or application of a precursor layer and heat treatment. Known barriers to oxygen are chromium oxide, niobium oxide and nickel oxide in particular non-stoichiometric nickel oxide. As described in US Patent 6,248,227 (de Nora/Duruz), the inner core may be covered with an oxygen barrier layer which is in turn covered with at least one protective layer consisting of copper, or copper and at least one of nickel and cobalt, and/or oxide(s) thereof to protect the oxygen barrier layer by inhibiting its dissolution into the electrolyte.

The anode according to the invention can be pre-oxidised prior to its immersion into an electrolyte where the electrolysis of alumina takes place, by oxidation in an oxidising atmosphere or by electrolysis in a

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conditioning molten electrolyte before being transferred in a production molten electrolyte containing dissolved alumina for the electrowinning of aluminium. However, in general with the anode compositions according to the invention, it is possible to self-form the electrochemically active integral outside oxide layer on the alloy during use.

Another aspect of the invention is a cell for the electrowinning of aluminium by the electrolysis of alumina in a molten fluoride electrolyte utilising an iron-based metal anode with an electrochemically active integral outside layer predominantly of iron oxide as discussed above.

This integral outside layer can slowly dissolve into the electrolyte during operation and be maintained by progressive slow oxidation of iron at the interface of the metal bulk of the alloy with the oxide layer. Alternatively, such a layer can be inhibited from dissolving by maintaining an amount of iron species in the electrolyte as disclosed in the abovementioned WO 00/06802.

The cell preferably comprises at least one aluminium-wettable cathode. Even more preferably, the cell is in a drained configuration by having a drained cathode on which aluminium is produced and from which aluminium continuously drains, as described in US Patents 5,651,874 (de Nora/Sekhar) and 5,683,559 (de Nora).

The cell may be of monopolar, multi-monopolar or bipolar configuration. A bipolar cell may comprise the anodes as described above as a terminal anode or as the anode part of a bipolar electrode.

During operation of the cell, the concentration of alumina dissolved in the electrolyte is below 10 weight%, preferably between 5 weight% and 8 weight%.

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
5 be provided by the geometry of the cell as described in co-pending applications WO 99/41429 (de Nora/Duruz) and WO 01/31088 (de Nora), or by periodically moving the anodes as described in co-pending application WO 99/41430 (Duruz/Bellò). Preferably, the iron-based metal anodes
10 have a foraminate electrochemically active structure provided with openings to permit circulation of the electrolyte therethrough, as disclosed in WO 00/40782 (de Nora), which is advantageously fitted with a funnel-like arrangement to guide the molten electrolyte from and to
15 the electrochemically active anode surfaces as described in WO00/40781 (de Nora).

According to one mode of operation of the invention, the progressive slow oxidation of iron at the interface of the bulk of the alloy with the oxide layer corresponds
20 to the dissolution of iron into the electrolyte at a rate such that the maximum concentration of iron species in the electrolyte does not exceed the saturation level of iron species in the electrolyte at the operating temperature.

During operation, the progressive slow oxidation of iron at the interface of the metal alloy with the oxide layer provides a compensation for dissolution of iron into the electrolyte which takes place at a rate depending on the electrolyte composition, the temperature
30 of the electrolyte and the composition of the oxide layer. On the other hand, the rate of dissolution of iron can be so low that contamination of the aluminium can be kept at an acceptable level and so that the rate of oxidation can be controlled. To achieve this, the
35 operating temperature should be maintained sufficiently

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low to control the dissolution of iron into the electrolyte.

The anode with the specified additives provides a slow oxidation which corresponds to the slow controlled dissolution of iron into the electrolyte from the anodes that supply current for the electrolysis of alumina.

Whether the anode is operated as discussed above in a slow dissolution mode or in a dimensionally stable mode, the operating temperature is preferably maintained sufficiently low to control the solubility of iron in the electrolyte and to limit the contamination of the product aluminium to an acceptable level, for example the operating temperature is below 930°C, preferably between 840°C and 890°C.

The operating temperature can also be in the range of 930° to 960°C, preferably around 940°C.

A further aspect of the invention is a method for the electrowinning of aluminium by the electrolysis of alumina in a molten fluoride electrolyte. This method comprises dissolving alumina in the electrolyte and electrolysing the alumina-containing electrolyte to produce aluminium on the cathode and oxygen on the facing anodes utilising iron-based metal anodes as discussed above.

The method can be implemented by immersing the metallic anode having an oxide-free or a pre-oxidised surface into a molten fluoride-containing electrolyte, self-forming an electrochemically active oxide-based surface layer as described previously and then, as mentioned above, electrolysing the dissolved alumina to produce aluminium in the same or a different fluoride-based electrolyte.

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The anode has an electrochemically active surface layer predominantly of iron oxide that during operation slowly dissolves into the electrolyte. The surface layer is maintained by progressive slow oxidation of iron at the interface of the bulk of the alloy. There is a corresponding controlled dissolution of iron into the electrolyte at such a low rate that the contamination of the product aluminium by iron is at an acceptable level.

For example, the operating temperature is below 930°C, preferably between 840°C and 890°C and typically the electrolyte contains NaF and AlF₃ in a molar ratio comprised between 1.2 and 2.4. The electrolyte may also contain other fluorides such as LiF, CaF₂ or MgF₂. The concentration of alumina dissolved in the electrolyte is below 10 weight%, preferably between 5 weight% and 8 weight%.

During operation, alumina-depleted electrolyte is circulated away from the electrochemically active oxide layer of the anode(s), enriched with alumina, and alumina-enriched electrolyte is circulated towards the electrochemically active oxide layer of the anode(s) to provide a constant supply of alumina to be electrolysed (i.e. maintain a sufficient concentration of alumina in the anode-cathode gap) and to reduce dissolution of the anode.

The aluminium is preferably produced on an aluminium-wettable cathode from which the product aluminium is continuously drained. As the consumption of the non-carbon, metal-based anodes according to the invention is at a very slow rate, these slow consumable anodes in drained cell configurations do not need to be regularly repositioned in respect of their facing cathodes since the anode-cathode gap does not substantially change.

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In summary the anode, cell and method according to the invention all provide or make use of an iron-based metal anode with an iron-rich alloy containing selected additives in the given ranges whereby the anode's integral outside oxide layer can be formed during use at a rate corresponding to a controlled dissolution into the electrolyte at the operating temperature, or can be stabilised during use by maintaining an amount of iron species in the electrolyte, leading to an acceptably low contamination of the product aluminium. In either case, such an anode has a long lifetime. The alloy can be produced economically in particular by casting. Its high iron content further contributes to its economic attractiveness. Moreover, the contamination of the product aluminium associated with prior iron-rich anodes has been reduced.

Detailed Description

Examples of anode compositions according to the invention are given in Table I, which shows the weight percentages of the indicated metals for each specimen A-J.

TABLE I

	Fe	Y	Al	Cu	Ni	Mn
A	82	2	10	6	--	--
B	88	2	10	--	--	--
C	87	4.5	4	4	--	0.5
D	84	1	10	4.5	--	0.5
E	88	2	6	4	--	--
F	84	2	6	6	2	--
G	80	2	6	6	6	--
H	81.5	0.5	2	8	8	--
I	84	1	3	5	7	--
J	86	1	4	4	5	--

The invention will be further described in the
 5 following Examples.

Example 1

An anode rod of diameter 20 mm and total length 200 mm was prepared by casting the composition of Sample D of Table I, using a sand mould.

10 Electrolysis was carried out in a laboratory scale cell equipped with this anode immersed to a depth of 50 mm in a fluoride-containing molten electrolyte at 880°C. The electrolyte contained cryolite with 24 weight% excess of AlF_3 and further containing 4 weight% of CaF_2 .

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The current density was about 0.7 A/cm² and the concentration of dissolved alumina in the electrolyte was 6 weight%. This concentration of alumina was maintained during the entire electrolysis by periodically feeding
5 fresh alumina into the cell.

After 22 hours electrolysis was interrupted and the anode extracted. Upon cooling the anode was examined externally and in cross-section. The anode was covered by an external scale of Fe₂O₃ about 10-15 micron thick on
10 top of a layer of Fe aluminate (probably Fe(FeAl)₂O₄ spinel phase) about 150-200 micron thick. No corrosion was observed at or near the surface of the anode. The presence of the Fe(FeAl)₂O₄ phase indicates the mechanism of internal oxidation at the interface of the Fe-Al core
15 during the anode operation.

At the operating temperature 880°C, the saturation limit of iron in the electrolyte is approximately 450 ppm.

The produced aluminium was analysed and showed an
20 iron contamination of approximately 800 ppm which is below the tolerated iron contamination in commercial aluminium production.

Example 2

This Example illustrates the wear rate of the iron-
25 based metal anode of Example 1.

An estimation of the wear rate is based on the following parameters and assumptions:

With a current density of 0.7 A/cm² and a current efficiency of 90% an aluminium electrowinning cell
30 produces daily approximately 50 kg aluminium per square meter of active cathode surface.

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Assuming a contamination of the produced aluminium by 800 ppm of iron, which corresponds to the experimentally measured quantities in typical tests, the wear rate of an iron sample corresponds to approximately 5 micron/day.

Example 3

An anode rod of diameter 20 mm and total length 20 mm was prepared by casting the composition of Sample F of Table I, using a sand mould.

10 The anode was subjected to testing as in Example 1 but with electrolysis during 72 hours with the cell voltage maintained stable at 3.8 to 4.0 volts. After 72 hours, the electrolysis was stopped, the anode was extracted and, upon cooling, was examined externally and
15 in cross-section. The anode was covered by a coherent and dense external scale of Fe_2O_3 20 to 30 micron thick, over a cermet zone about 50 micron thick composed of a Ni-Al and Ni-Fe network with inclusions of $\text{Ni}_x\text{Fe}_{2-x}\text{O}_3$ and Al_2O_3 , or a mixture thereof.

20 Comparing with the results described in Example 1, the decrease of the Al content from 10 to 6 weight% and the presence of nickel increased the oxidation resistance of the alloy core by formation of protective scales of $\text{Ni}_x\text{Fe}_{2-x}\text{O}_3$ and Al_2O_3 .

CLAIMS

1. An iron-based metal anode for the electrowinning of aluminium by the electrolysis of alumina in a molten fluoride electrolyte, having an electrochemically active integral outside oxide layer on an iron-based alloy that consists of:
- 75 to 90 weight% iron;
 - 0.5 to 5 weight% in total of one or more rare earth metals, in particular yttrium;
 - 1 to 12 weight% aluminium;
 - 0 to 10 weight% copper;
 - 0 to 10 weight% nickel; and
 - 0 to 5 weight% of other elements,
- wherein the total amount of aluminium, copper and nickel is in the range from 5 to 20 weight%; and the total amount of rare earth metal(s), aluminium and copper is in the range from 5 to 20 weight%.
2. The anode of claim 1, wherein the iron-based alloy contains yttrium in an amount of 0.5 to 3 weight%.
3. The anode of claim 1 or 2, wherein the iron-based alloy contains aluminium in an amount of 2 to 10 weight%, preferably 4 to 8 weight%.
4. The anode of claim 1, 2 or 3, wherein the iron-based alloy contains copper in an amount of 0.5 to 8 weight%.
5. The anode of any preceding claim, wherein the iron-based alloy contains nickel in an amount of 0.5 to 8 weight%.

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6. The anode of any preceding claim, wherein the iron-based alloy contains, as said other element(s), at least one of molybdenum, manganese, titanium, tantalum, tungsten, vanadium, zirconium, niobium, chromium, cobalt,
5 silicon and carbon.

7. The anode of any preceding claim, wherein the iron-based alloy contains said other element(s) in an amount up to 2 weight%.

8. The anode of any preceding claim, wherein the iron-based alloy contains copper in an amount of 2 to 6 weight% and/or nickel in an amount of 2 to 8 weight%.

9. The anode of any preceding claim, wherein the iron-based alloy contains aluminium in an amount of 4 to 6 weight%.

10. The anode of any preceding claim, wherein the total amount of aluminium, copper and nickel is in the range from 8 to 18 weight%.

11. The anode of any preceding claim, wherein the total amount of rare earth metal, aluminium and copper is in
20 the range from 8 to 18 weight%.

12. The anode of any preceding claim, wherein the iron-based alloy consists of:

- 80 to 90 weight% iron;
- 0.5 to 3 weight% yttrium;
- 25 - 2 to 6 weight% aluminium;
- 1 to 8 weight% copper;
- 1 to 8 weight% nickel; and
- 0 to 5 weight% of other elements.

13. The anode of any preceding claim wherein the iron-based alloy contains copper and nickel in a weight ratio
30 Cu:Ni in the range 1:3 to 3:1.

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14. The anode of any preceding claim, wherein the iron-based alloy is made by casting iron together with said metals as additives.
15. A cell for the electrowinning of aluminium by the electrolysis of alumina in a molten fluoride electrolyte utilising an iron-based metal anode having an electrochemically active integral outside oxide layer according to any one of the preceding claims.
16. The cell of claim 15, wherein during operation the electrochemically active integral outside oxide layer of the anode slowly dissolves into the electrolyte and is maintained by progressive slow oxidation of iron at the interface of the metal bulk of the alloy with the oxide layer.
17. The cell of claim 15 or 16, wherein the concentration of alumina dissolved in the electrolyte is below 10 weight%, preferably between 5 weight% and 8 weight%.
18. The cell of claim any one of claims 1 to 17, comprising an aluminium-wettable cathode.
19. The cell of any one of claims 16 to 18, wherein the progressive slow oxidation of iron at the interface of the bulk of the alloy with the oxide layer corresponds to the dissolution of iron into the electrolyte at a rate such that the maximum concentration of iron species in the electrolyte is at or below the saturation level of iron species in the electrolyte at the operating temperature.
20. The cell of claim 19, wherein the operating temperature is maintained sufficiently low to control the dissolution of iron into the electrolyte and limit the contamination of the product aluminium to an acceptable level.

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21. The cell of claim 20, wherein the operating temperature is below 930°C, preferably between 840°C and 890°C.

5 22. The cell of any one of claims 15 to 21, wherein the electrolyte contains NaF and AlF₃ in a molar ratio in the range from 1.2 to 2.4.

23. The cell of any one of claims 15 to 22, which is arranged to circulate alumina-depleted electrolyte away from the electrochemically active oxide layer of the
10 anode(s), enrich the electrolyte with alumina, and circulate alumina-enriched electrolyte towards the electrochemically active oxide layer of the anode(s).

24. A method for the electrowinning of aluminium by the electrolysis of alumina in a molten fluoride electrolyte,
15 comprising dissolving alumina in the electrolyte and electrolysing the alumina-containing electrolyte to produce aluminium on a cathode and oxygen on an iron-based metal anode as claimed in any one of claims 1 to 14.

20 25. The method of claim 24, wherein the electrochemically active integral outside oxide layer of the anode slowly dissolves into the electrolyte and is maintained by progressive slow oxidation of iron at the interface of the metal bulk of the alloy with the oxide
25 layer providing a dissolution of iron into the electrolyte at a rate such that the maximum concentration of iron species in the electrolyte is at or below the saturation level of iron species in the electrolyte at the operating temperature.

30 26. The method of claim 24 or 25, wherein the operating temperature is maintained sufficiently low to control the dissolution of iron into the electrolyte and limit the contamination of the product aluminium to an acceptable level.

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27. The method of claim 26, wherein the operating temperature is below 930°C, preferably between 840°C and 890°C.

28. The method of any one of claims 24 to 27, wherein
5 the electrolyte contains NaF and AlF₃ in a molar ratio in the range from 1.2 to 2.4.

29. The method of any one of claims 24 to 28, wherein the concentration of alumina dissolved in the electrolyte is below 10 weight%, preferably between 5 weight% and 8
10 weight%.

30. The method of any one of claims 24 to 29, wherein alumina-depleted electrolyte is circulated away from the electrochemically active oxide layer of the anode(s), enriched with alumina, and alumina-enriched electrolyte
15 is circulated towards the electrochemically active oxide layer of the anode(s).

31. The method of any one of claims 24 to 30, wherein aluminium is produced on an aluminium-wettable cathode.

32. The method of claim 31, wherein the product
20 aluminium is continuously drained from the aluminium-wettable cathode.