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(54) SLURRY FOR COATING NON-CARBON METAL-BASED ANODES FOR ALUMINIUM PRODUCTION CELLS

AUFSCHLÄMMUNG ZUM BESCHICHTEN VON KOHLENSTOFFFREIEN ANODEN AUF METALLBASIS FÜR ZELLEN ZUR ALUMINIUMHERSTELLUNG

COULIS DE REVETEMENT D'ANODES METALLIQUES EXEMPTES DE CARBONE POUR CELLULES DE PRODUCTION D'ALUMINIUM

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Description

Field of the Invention

[0001] This invention relates to a slurry for coating anodes for use in cells for the electrowinning of metals from their oxides dissolved in molten salts, and to methods for their fabrication and reconditioning, as well as aluminium electrowinning cells containing coated anodes and their use to produce aluminium.

Background Art

[0002] The production of metals by the electrolysis of their oxides is usually carried out in very chemically aggressive environments. Therefore, the materials used for the manufacture of components of production cells must be resistant to attack by the environment of such cell. Anodes of cells for the production of metals by the electrolysis of their oxides dissolved in molten salts need to be resistant to attack by the electrolyte and by the oxygen which is anodically produced during electrolysis.

[0003] Unfortunately, for the dissolution of the raw material a highly aggressive electrolyte, such as a fluoride-based electrolyte is required.

[0004] The surface of the anode must be electrochemically active, substantially insoluble in the electrolyte and resistant to attacks by the nascent monoatomic oxygen and by the subsequently formed molecular oxygen gas which are anodically produced. Since monoatomic oxygen is far more aggressive than biatomic molecular gaseous oxygen, the constituents of the active surface of the anode should contain electro-catalytic materials for the reaction which forms molecular oxygen from the monoatomic oxygen to reduce monatomic oxygen attack.

[0005] The materials having the greatest resistance to oxidation are metal oxides which are all to some extent soluble in cryolite. Oxides are also poorly electrically conductive, therefore, to avoid substantial ohmic losses and high cell voltages, the use of oxides should be minimal in the manufacture of anodes. Whenever possible, a good conductive material should be utilised for the anode core, whereas the surface of the anode is preferably made of an oxide having a high electrocatalytic activity.

[0006] In the field of aluminium production, it has been described in US Patents 5,069,771, 4,960,494 and 4, 956, 068 (all Nyguen/Lazouni/Doan), 5,510,008 (Sekhar/Liu/Duruz) and WO-A-93/20026 (Sekhar/De Nora) that a metal core could be protected by barrier layers and/or by oxidised metals but these results have not as yet been commercially and industrially applied.

Objects of the Invention

[0007] An object of the invention is to provide a method for coating an anode for metal electrowinning cells, in particular aluminium electrowinning cells, which substantially reduces the consumption of the active anode surface that is attacked by nascent monoatomic oxygen by enhancing the reaction of nascent oxygen to gaseous molecular gaseous oxygen.

[0008] Another object of the invention is to provide a slurry for coating anodes for metal electrowinning cells, in particular aluminium electrowinning cells, which provides a coating with high electrolytic activity, a long life and which can be re-coated onto the anode as soon as such activity decreases or when the coating is worn out.

[0009] A major object of the invention is to provide an anode for metal electrowinning cells, in particular aluminium electrowinning cells, which has no carbon so as to eliminate carbon-generated pollution and reduce the cell voltage and the high cost of cell operation.

Summary of the Invention

[0010] The present invention concerns a method of applying a slurry onto a conductive, heat resistant anode substrate to form an oxide coating on those parts of the substrate which are exposed to oxidising or corrosive cell environments.

[0011] The invention in particular relates to a method of coating an electronically conductive and heat resistant substrate of a non-carbon metal-based anode of a cell for the electrowinning of metals from their oxides dissolved in molten salt, to protect and make the surface of the anode substrate active for the oxidation of the oxygen ions present in the electrolyte. The method comprises applying onto the substrate a slurry comprising at least one oxide or a precursor thereof as a non-dispersed but suspended particulate in a colloidal and/or inorganic polymeric carrier, the slurry is then solidified and made adherent to the substrate upon heat treatment to form an adherent, protective, predominantly oxide-containing coating.

[0012] The essential features to solve the aforementioned objects are defined in claims 1, 20 and 22. Preferred embodiments are defined in dependent claims 2 to 19, 21 and 23 to 30, respectively.

[0013] An oxide may be present in the oxide-containing coating 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.

[0014] A typical application for this method is the coating of anodes for the electrowinning of aluminium by the electrolysis of alumina dissolved in a molten fluoride-containing electrolyte, such as a cryolite-based electrolyte or cryolite.

[0015] The colloidal and/or inorganic polymeric carrier may be selected from alumina, ceria, lithia, magnesia, silica, thoria, yttria, zirconia, tin oxide, zinc oxide and mixtures thereof.

[0016] Advantageously, the colloidal and/or inorganic polymeric carrier forms upon heat treatment the same chemical compound as the non-dispersed particulate.

[0017] The oxides which may be used as a non-dispersed particulate and/or as a carrier may be in the form of spinels and/or perovskites or precursors thereof. Spinels may be doped, non-stoichiometric and/or partially substituted spinels, the doped spinels comprising dopants selected from the group consisting of 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^{+}.

[0018] The spinels may comprise a ferrite which can be selected from cobalt, copper, chromium, manganese, nickel and zinc ferrite, and mixtures and precursors thereof. The ferrites may also be doped with at least one oxide selected from chromium, titanium, tin, zinc and zirconium. Nickel-ferrite is a preferred compound for an electrochemically active coating for its high chemical resistance and may be present as such or partially substituted with Fe^{2+}.

[0019] Alternatively, the spinels may also comprise a chromite which can be selected from iron, cobalt, copper, manganese, beryllium, calcium, strontium, barium, yttrium, magnesium, nickel and zinc chromite, and mixtures and precursors thereof.

[0020] The slurry advantageously comprises one or more electrocatalysts or a precursor thereof, however such a constituent is not always necessary. When an electrocatalyst is used, it may be advantageously selected from iridium, palladium, platinum, rhodium, ruthenium, silicon, tin, zinc, Mischmetal oxides and metals of the Lanthanide series, and mixtures and compounds thereof.

[0021] For the formation of the coating onto the substrate, the oxide constituents of the slurry may react among themselves. Alternatively the constituents of the slurry may react with constituents of the electronically conductive and heat resistant substrate. However, a reaction is not always necessary for the formation of the coating from the slurry.

[0022] The slurry may be applied onto the substrate by conventional techniques such as brushing, spraying dipping, electrodeposition or by using rollers.

[0023] The substrate can be chosen among metals, alloys, intermetallics, cermets, and conductive ceramics. It may for instance comprise at least one of chromium, cobalt, hafnium, iron, molybdenum, nickel, copper, niobium, platinum, silicon, tantalum, titanium, tungsten, vanadium, yttrium and zirconium, and their combinations and compounds.

[0024] The substrates may advantageously have a self-healing effect, i.e. when exposed to electrolyte the substrate passivates under the effect of the electrical current and becomes substantially inert to the electrolyte.

[0025] The adherence of the coating on the substrate may be enhanced by applying onto the substrate a pre-coat before applying the slurry. Several methods are known to obtain an oxide pre-coat on a metal substrate, e.g. heating in air for prolonged periods at high temperatures (>1000°C).

[0026] However, a preferred pre-coat can be formed by applying a metal oxide in a colloidal or polymeric solution onto a clean metal substrate, drying and heat-treating the pre-coat at 500°C. Oxides for the pre-coat may be selected from SiO_2, Al_2O_3, ThO_2, ZrO_2, SnO_2, TiO_2 and CeO_2. Preferably the colloid/polymer contains cerium oxide having a crystallite size of about 5 to 10 nanometer and a NO_3-/CeO_2 mole ratio of approximately 0.25, which can be prepared by following the teachings of US Patent 4,356,106 (Woodhead/Raw).

[0027] The pre-coat can be applied from a colloidal dispersion having a concentration between 25 and 250 g/l. Conventional techniques such as dipping, brushing or spraying can be used prior to drying and/or heat-treating the pre-coat.

[0028] The invention also relates to an anode coating slurry for coating an electronically conductive and heat resistant substrate of a non-carbon metal-based anode for the electrowinning of metals from their oxides dissolved in molten salts, to form an adherent, protective, predominantly oxide-containing coating after heat treatment and to make the surface of the anode active for the oxidation of the oxygen ions present in the electrolyte. The slurry comprises at least one oxide or oxide precursor as a non-dispersed but suspended or suspendable particulate in a colloidal and/or inorganic polymeric carrier.

[0029] This method may also be applied for reconditioning a non-carbon metal-based anode with a slurry as described hereabove, the active coating of which anode has become non-active or worn out. The method comprises clearing and restoring the surface of the conductive substrate before applying the slurry onto the substrate as described hereabove.

[0030] Another aspect of the invention is an anode of a cell for the electrowinning of a metal, in particular of an aluminium electrowinning cell, comprising an electronically conductive substrate and a protective electrochemically active coating obtained from a slurry as described hereabove.

[0031] A further aspect of the invention is a cell for the production of a metal by the electrolysis of its oxide dissolved in a molten salt, in particular for the electrowinning of aluminium or a lanthanide such as neodymium, having at least one anode comprising an electronically conductive substrate and a protective electrochemically active coating obtained from a slurry as described hereabove.

[0032] An aluminium electrowinning cell may advantageously comprise at least one aluminium-wettable cathode. The cell may be in a drained configuration by having at least one drained cathode on which aluminium is produced and from which aluminium continuously drains. 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.

[0033] Preferably, the aluminium electrowinning 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.

[0034] The aluminium electrowinning cell may be operated with the electrolyte at conventional temperatures, such as 950 to 970°C, or at reduced temperatures as low as 750°C.

[0035] Yet another aspect of the invention is a method of electrowinning aluminium in a cell comprising at least one coated non-carbon metal-based anode as described hereabove, the method comprising dissolving alumina in the electrolyte and then electrolysing the dissolved alumina to produce aluminium.

[0036] The slurry as described hereabove can be used for coating a non-carbon metal-based anode for the production of aluminium in a cell for the electrowinning of aluminium by the electrolysis of alumina dissolved in a fluoride-containing electrolyte, on which anode oxygen ions in the electrolyte are oxidised and released as biatomic molecular gaseous oxygen by the electrochemically active anode slurry-obtained coating.

Detailed Description

[0037] The invention will be further described in the following Examples:

Example 1

[0038] A polymeric slurry was prepared from: a non-dispersable but suspendable particulate consisting of a nickel-ferrite powder and a nickel aluminate ($NiOAl_2O_3$) precursor material acting as a polymeric carrier and binder for the nickel ferrite powder. The nickel-ferrite powder was specially prepared; however, commercially-available products could also have been used. The precursor $NiOAl_2O_3$ materials, solution and gel powder reacted to form the spinel $NiAl_2O_4$ at < 1000°C.

[0039] When applied to a suitably prepared substrate such as nickel, this slurry produced an oxide coating made from the pre-formed or the in-situ formed nickel ferrite which adhered well onto the substrate and formed a coherent coating when dried and heated. The slurry could be applied by a simple technique such as brushing or dipping to give a coating of pre-determined thickness.

Example 2

[0040] A carrier consisting of a nickel aluminate polymeric solution containing a non-dispersed but suspended particulate of nickel aluminate was made by heating 75 g of $Al(NO_3)_3.9\ H_2O$ (0.2 moles Al) at 80°C to give a concentrated solution which readily dissolved 12 g of $NiCO_3$ (0.1 moles). The viscous solution (50 ml) contained 200 g/l Al_2O_3 and 160 g/l NiO (total oxide, >350 g/l).

[0041] This nickel-rich polymeric concentrated anion deficient solution was compatible with commercially-available alumina sols e.g. NYACOL™.

[0042] A stoichiometrically accurate $NiO.Al_2O_3$ mixture was prepared by adding 5 ml of the anion deficient solution to 2.0 ml of a 150 g/l alumina sol; this mixture was stable to gelling and could be applied to smooth metal and ceramic surfaces by a dip-coating technique. When heated to 450-500°C, X-ray diffraction showed nickel-aluminate had formed in the coating.

[0043] Other non-dispersable particulate than nickel aluminate could be suspended in the anion-deficient nickel aluminate precursor solution and applied as coatings which when heat-treated would form nickel-aluminate containing the added oxides.

Example 3

[0044] A colloidal solution containing a metal ferrite precursor (as required for $NiONiFe_2O_4$) was prepared by mixing 20.7 g Ni $(NO_3)_2.6\ H_2O$ (5.17 g NiO) with 18.4 g $Fe(NO_3)_3.9\ H_2O$ (4.8 g Fe_2O_3) and dissolving the salts in water to a volume of 30 ml. The solution was stable to viscosity changes and to precipitation when aged for several days at 20°C.

[0045] An organic solvent such as PRIMENE™ JMT (R_3CNH_2 molecular weight -350) is immiscible with water and extracts nitric acid from acid and metal nitrate salt solutions. An amount of 75 ml of the PRIMENE™ JMT (2.3 M) diluted with an inert hydrocarbon solvent was mixed with 10 ml of the colloidal nickel-ferrite precursor solution. Within a few minutes the spherical droplets of feed were converted to a mixed oxide gel; they were filtered off, washed with acetone and dried to a free-flowing powder. When the gel was heated in air, nickel-ferrite formed at < 800°C and the powder could be used as a non-dispersable but suspended particulate in colloidal and/or inorganic polymeric slurries as described in Example 1 or 2. Commercially-available nickel-ferrite powder could also have been used.

Example 4

[0046] An amount of 5 g of $NiCO_3$ was dissolved in a solution containing 35 g $Fe(NO_3)_3.9\ H_2O$ to give a mixture (40 ml) having the composition required for the formation of $NiFe2O_4$. The solution was converted to gel particles by solvent extracting the nitrate with PRIMENE™ JMT as described in Example 3. The nickel-ferrite precursor gel was calcined in air to give a non-dispersable but suspended particulate in the form of a nickel-ferrite powder, which could be hosted into nickel-aluminate carrier for coating applications from colloidal and/or polymeric slurries.

Example 5

[0047] An amount of 100 g of $Cr(NO_3)_3.9\ H_2O$ was heated to dissolve the salt in its own water of crystallisation to form a solution containing 19 g Cr_2O_3. The solution was heated to 120°C and 12.5 g of magnesium-hydroxy carbonate containing the equivalent of 5.0 g MgO was added. Upon stirring a solution was obtained in the form of an anion-deficient polymer mixture with a density of approximately 1.5 g/cm^3 suitable to act as a carrier. An amount of 50 g of this carrier was evaporated to dryness to convert the solution into a fine oxide powder. The oxides were then calcined at 600°C into a magnesium chromite powder to form a non-dispersable but suspended particulate.

[0048] After grinding to a fine powder, the magnesium chromite particulate was suspended in the polymer carrier to form a slurry suitable for coating treated metal substrates.

Example 6

[0049] An amount of 150 g of $Fe(NO_3)_3.9\ H_2O$ was heated to dissolve the salt in its own water of crystallisation to form a solution containing 29 g Fe_2O_3. The solution was heated to 120°C and 18.9 g of magnesium hydroxy-carbonate dissolved in the hot solution to form 7.5 g MgO in form of an inorganic polymer together with Fe_2O_3. An amount of 50 g of the polymer solution was evaporated to dryness and then calcined at 600°C yielding approximately 13 g of magnesium ferrite powder.

[0050] After calcination, the ferrite powder was ground in a pestle and mortar and then suspended as a non-dispersable particulate in the same inorganic polymer acting as a carrier to give a slurry that was used to coat a treated metal substrate.

Example 7

[0051] A cleaned surface of an Inconel™ billet (typically comprising 76 weight% nickel - 15.5 weight% chromium - 8 weight% iron) was pre-coated with a ceria colloid as described in US Patent 4,356,106 (Woodhead/Raw), dried and heated in air at 500°C. The pre-coated billet was then further coated with the polymeric slurry described in Example 1 or 2, dried and heated in air at 500°C. The ferrite coating was very adherent and successive layers of the slurry could be applied to build up a coating of ferrite/aluminate having a thickness above 100 micron.

[0052] A similar untreated Inconel™ billet was coated with a 10 micron thick layer using the polymeric slurry described in Example 1 or 2 but without pre-coating the billet with ceria colloid. After heat-treatment the coating was cracked and easily broke away from the substrate, which demonstrated the effect of the ceria pre-coat.

Claims

1. A method of coating an electronically conductive and heat resistant substrate of a non-carbon metal-based anode of a cell for the electrowinning of metals from their oxides dissolved in molten salt, to protect and make the surface of the anode substrate active for the oxidation of the oxygen ions present in the electrolyte, the method comprising applying onto the substrate a slurry comprising:

   - a colloidal and/or inorganic polymeric carrier; and
   - a particulate non-dispersed but suspended in the carrier, the particulate being made of at least one oxide or a precursor thereof and comprising spinels or precursors thereof,

   said slurry being solidified and made adherent to the substrate upon heat treatment to form an adherent, protective, predominantly oxide-containing coating comprising spinels.

2. The method of claim 1, wherein the slurry is applied to an anode for the electrowinning of aluminium by the electrolysis of alumina dissolved in a molten fluoride-containing electrolyte.

3. The method of claim 1, wherein the colloidal and/or inorganic polymeric carrier comprises at least one of alumina, ceria, lithia, magnesia, silica, thoria, yttria, zirconia, tin oxide and zinc oxide.

4. The method of claim 1, wherein the colloidal and/or inorganic polymeric carrier forms upon heat treatment the same chemical compound as the non-dispersed particulate.

5. The method of claim 1, comprising applying to the substrate spinels or precursors thereof as a non-dispersed particulate and/or as a carrier.

6. The method of claim 5, wherein the spinels are doped, non-stoichiometric and/or partially substituted spinels, the doped spinels comprising dopants selected from the group consisting of 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^{+}.

7. The method of claim 5, wherein the spinels comprises a ferrite, in particular a ferrite selected from cobalt, copper, chromium, manganese, nickel and zinc ferrites, and mixtures and precursors thereof.

8. The method of claim 7, wherein the ferrite is doped with at least one oxide selected from chromium, titanium, tin, zinc and zirconium oxide.

9. The method of claim 7, wherein the ferrite comprises nickel ferrite or nickel ferrite partially substituted with Fe^{2+}.

10. The method of claim 5, wherein the spinels comprises a chromite.

11. The method of claim 10, wherein the chromite is selected from iron, cobalt, copper, manganese, beryllium, calcium, strontium, barium, yttrium, magnesium, nickel and zinc chromite.

12. The method of claim 1, wherein the slurry further comprises at least one electrocatalyst or a precursor thereof, in particular electrocatalyst(s) selected from iridium, palladium, platinum, rhodium, ruthenium, silicon, tin, zinc, Mischmetal oxides and metals of the Lanthanide series, and mixtures and compounds thereof.

13. The method of claim 1, wherein constituents of the slurry react together to form the coating or react with constituents of the conductive substrate to form the coating.

14. The method of claim 1, wherein the colloidal and/or inorganic polymeric carrier forms upon heat treatment the same chemical compound as the non-dispersed particulate.

15. The method of claim 1, wherein the slurry is applied by brush, spraying, dipping, electrodeposition or rollers onto the substrate.

16. The method of claim 1, wherein the substrate is selected from metals, alloys, intermetallics, cermets, and conductive ceramics.

17. The method of claim 1, comprising applying the slurry onto a conductive substrate which is passivatable during electrolysis to become substantially nonconductive and inert to the electrolyte.

18. The method of claim 1, wherein the substrate is precoated prior to applying the slurry, in particular with a colloidal and/or polymeric solution containing at least one oxide selected from SiO_2, Al_2O_3, ThO_2, ZrO_2, SnO_2, TiO_2 and CeO_2.

19. The method of claim 1 for reconditioning a coated anode, the active coating of which has become nonactive or is worn, wherein the surface of the conductive substrate is cleared and restored before applying said slurry onto the substrate.

20. Use of a slurry for coating an electronically conductive and heat resistant substrate of an anode for the electrowinning of metals from their oxides dissolved in molten salts, forming upon heat treatment an adherent, protective, predominantly oxide-containing coating comprising spinels and which makes the surface of the anode substrate active for the oxidation of the oxygen ions present in the electrolyte, the slurry comprising:

- a colloidal and/or inorganic polymeric carrier comprising at least one of alumina, ceria, lithia, magnesia, silica, thoria, yttria, zirconia, tin oxide and zinc oxide; and
- a particulate non-dispersed but suspended in the carrier, the particulate being made of at least one oxide or a precursor thereof, said oxide comprising: a ferrite selected from cobalt, copper, chromium, manganese, nickel and zinc ferrite, and mixtures and precursors thereof; and/or a chromite selected from iron, cobalt, copper, manganese, beryllium, calcium, strontium, barium, yttrium, magnesium, nickel and zinc chromite, and mixtures and precursors thereof.

21. Use of a slurry in accordance to claim 20, for producing a coating on a non-carbon metal-based anode for the electrowinning of aluminium by the electrolysis of alumina dissolved in a fluoride-containing electrolyte, on which slurry-obtained coating oxygen ions of the molten electrolyte are oxidised to monoatomic oxygen and released as biatomic molecular gaseous oxygen.

22. A method of electrowinning a metal, comprising coating an anode substrate by the method of claim 1 and producing said metal by using the coated anode substrate to electrolyse an oxide of said metal that is dissolved in a molten salt of a cell.

23. The method of claim 22, wherein the anode substrate has coating-free areas which become passive and substantially inert to the electrolyte and nonconductive.

24. The method of claim 22, comprising electrowinning aluminium by the electrolysis of alumina dissolved in a fluoride-containing electrolyte.

25. The method of claim 24, comprising electrowinning aluminium on at least one aluminium-wettable cathode.

26. The method of claim 22, comprising producing aluminium on at least one drained cathode from which aluminium continuously drains.

27. The method of claim 22, wherein the cell is in a bipolar configuration and wherein the coated anode substrate forms the anodic side of a bipolar electrode or a terminal anode.

28. The method of claim 22, comprising circulating the electrolyte between the coated anode substrate and a facing cathode.

29. The method of claim 22, wherein the electrolyte is at an operating temperature of 750°C to 970°C

30. The method of claim 22, for the electrowinning of a lanthanide, in particular neodymium.

Patentansprüche

1. Verfahren zum Beschichten eines elektronisch leitfähigen und hitzebeständigen Substrats einer kohlenstofffreien, auf Metall basierenden Anode einer Zelle zur elektrolytischen Gewinnung von Metallen aus deren in geschmolzenem Salz gelösten Oxiden, um die Oberfläche des Anodensubstrats zu schützen und hinsichtlich der Oxidation der in dem Elektrolyten vorhandenen Sauerstoffionen zu aktivieren, wobei das Verfahren die Aufbringung einer Aufschlämmung auf das Substrat umfasst, die:

- einen kolloidalen und/oder anorganischen, polymeren Träger, und
- einen teilchenförmigen Stoff umfasst, der in dem Träger nicht dispergiert aber suspendiert ist, wobei der teilchenförmige Stoff aus mindestens einem Oxid oder einem Vorläufer desselben hergestellt worden ist und Spinelle oder Vorläufer derselben umfasst,

wobei die Aufschlämmung verfestigt wird und an dem Substrat durch Hitzebehandlung haftend gemacht wird, um eine haftende, schützende, überwiegend Oxid-enthaltende Beschichtung zu bilden, die Spinelle umfasst.

2. Verfahren nach Anspruch 1, bei dem die Aufschlämmung auf eine Anode zur elektrolytischen Gewinnung von Aluminium durch Elektrolyse von in geschmolzenem, Fluorid-enthaltenden Elektrolyten gelöstes Aluminiumoxid aufgebracht wird.

3. Verfahren nach Anspruch 1, bei dem der kolloidale und/oder anorganische, polymere Träger mindestens eines von Aluminiumoxid, Ceroxid, Lithiumoxid, Magnesiumoxid, Siliciumdioxid, Thoriumoxid, Yttriumoxid, Zirkoniumdioxid, Zinnoxid und Zinkoxid umfasst.

4. Verfahren nach Anspruch 1, bei dem der kolloidale und/oder anorganische, polymere Träger durch Hitzebehandlung die gleiche chemische Verbindung wie der nicht-dispergierte teilchenförmige Stoff bildet.

5. Verfahren nach Anspruch 1, bei dem auf das Substrat Spinelle oder Vorläufer derselben als nicht-dispergierter, teilchenförmiger Stoff und/oder als Träger aufgebracht wird.

6. Verfahren nach Anspruch 5, bei dem die Spinelle dotierte, nicht-stöchiometrische und/oder partiell substituierte Spinelle sind, wobei die dotierten Spinelle Dotiermittel ausgewählt aus der Gruppe bestehend aus 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+} und Li^{2+} umfassen.

7. Verfahren nach Anspruch 5, bei dem die Spinelle ein Ferrit, insbesondere ein Ferrit ausgewählt aus Kobalt-, Kupfer-, Chrom-, Mangan-, Nickel- und Zinkferriten sowie Mischungen und Vorläufern derselben umfassen.

8. Verfahren nach Anspruch 7, bei dem der Ferrit mit mindestens einem Oxid ausgewählt aus Chrom-, Titan-, Zinn-, Zink- und Zirkoniumoxid dotiert ist.

9. Verfahren nach Anspruch 7, bei dem der Ferrit Nikkelferrit oder teilweise mit Fe^{2+} dotierter Nickelferrit ist.

10. Verfahren nach Anspruch 5, bei dem die Spinelle ein Chromit umfassen.

11. Verfahren nach Anspruch 10, bei dem der Chromit aus Eisen-, Kobalt-, Kupfer-, Mangan-, Beryllium-, Calcium-, Strontium-, Barium-, Yttrium-, Magnesium-, Nikkel- und Zinkchromit ausgewählt ist.

12. Verfahren nach Anspruch 1, bei dem die Aufschlämmung ferner mindestens einen Elektrokatalysator oder einen Vorläufer desselben umfasst, insbesondere (einen) Elektrokatalysator(en) ausgewählt aus Iridium, Palladium, Platin, Rhodium, Ruthenium, Silicium, Zinn, Zink, Mischmetalloxiden und Metallen der Lanthanidenreihe sowie Mischungen und Verbindungen derselben.

13. Verfahren nach Anspruch 1, bei dem Bestandteile der Aufschlämmung miteinander unter Bildung der Beschichtung reagieren oder mit Bestandteilen des leitfähigen Substrats unter Bildung der Beschichtung reagieren.

14. Verfahren nach Anspruch 1, bei dem der kolloidale und/oder anorganische, polymere Träger durch Hitzebehandlung die gleiche chemische Verbindung wie der nicht-dispergierte, teilchenförmige Feststoff bildet.

15. Verfahren nach Anspruch 1, bei dem die Aufschlämmung durch Bürsten, Sprühen, Tauchen, Elektroablagerung und/oder Walzen auf das Substrat aufgebracht wird.

16. Verfahren nach Anspruch 1, bei dem das Substrat ausgewählt ist aus Metallen, Legierungen, intermetallischen Verbindung, Cermeten, und leitfähigen Keramiken.

17. Verfahren nach Anspruch 1, bei dem die Aufschlämmung auf ein leitfähiges Substrat aufgebracht wird, das während der Elektrolyse passivierbar ist, um im Wesentlichen nichtleitfähig und gegenüber dem Elektrolyten inert zu werden.

18. Verfahren nach Anspruch 1, bei dem das Substrat vor der Aufbringung der Aufschlämmung vorbeschichtet wird, insbesondere mit einer kolloidalen und/oder polymeren Lösung, die mindestens ein Oxid ausgewählt aus SiO_2, Al_2O_3, ThO_2, ZrO_2, SnO_2, TiO_2 und CeO_2 enthält.

19. Verfahren nach Anspruch 1 zur Rekonditionierung einer beschichteten Anode, deren wirksame Beschichtung inaktiv oder verschlissen worden ist, bei dem die Oberfläche des leitfähigen Substrats gereinigt und wiederhergestellt wird, bevor die Aufschlämmung auf das Substrat aufgebracht wird.

20. Verwendung einer Aufschlämmung für die Beschichtung eines elektronisch leitfähigen und hitzebeständigen Substrats einer Anode zur elektrolytischen Gewinnung von Metallen aus deren in geschmolzenen Salzen gelösten Oxiden, die durch Hitzebehandlung eine haftende, schützende, überwiegend Oxid enthaltende Beschichtung bilden, die Spinelle umfasst und die Oberfläche des Anodensubstrats hinsichtlich der Oxidation der in dem Elektrolyten vorhandenen Sauerstoffionen aktiviert, wobei die Aufschlämmung umfasst:

- einen kolloidalen und/oder anorganischen, polymeren Träger, der mindestens eines von Aluminiumoxid, Ceroxid, Lithiumoxid, Magnesiumoxid, Siliciumdioxid, Thoriumoxid, Yttriumoxid, Zirkoniumdioxid, Zinnoxid und Zinkoxid umfasst, und
- einen teilchenförmigen Stoff umfasst, der in dem Träger nicht dispergiert aber suspendiert ist, wobei der teilchenförmige Stoff aus mindestens einem Oxid oder einem Vorläufer desselben hergestellt worden ist, wobei das Oxid einen Ferrit ausgewählt aus Kobalt-, Kupfer-, Chrom-, Mangan-, Nickel- und Zinkferrit und Mischungen und Vorläufern derselben und/oder einem Chromit ausgewählt aus Eisen-, Kobalt-, Kupfer-, Mangan-, Beryllium-, Calcium-, Strontium-, Barium-, Yttrium-, Magnesium-, Nickel- und Zinkchromit und Mischungen und Vorläufern derselben umfasst.

21. Verwendung einer Aufschlämmung nach Anspruch 20 für die Herstellung einer Beschichtung auf einer kohlenstofffreien, auf Metall basierenden Anode zur elektrolytischen Gewinnung von Aluminium durch Elektrolyse von in einem Fluorid enthaltenden Elektrolyten gelöstem Aluminiumoxid, wobei an der mittels der Aufschlämmung erhaltenen Beschichtung Sauerstoffionen des geschmolzenen Elektrolyten zu einatomigem Sauerstoff oxidiert werden und als zweiatomiger molekularer gasförmiger Sauerstoff freigesetzt werden.

22. Verfahren zur elektrolytischen Gewinnung eines Metalls, bei dem ein Anodensubstrat nach dem Verfahren von Anspruch 1 beschichtet wird und das Metall hergestellt wird, indem das beschichtete Anodensubstrat verwendet wird, um ein Oxid des Metalls zu elektrolysieren, das in einem geschmolzenen Salz einer Zelle gelöst ist.

23. Verfahren nach Anspruch 22, bei dem das Anodensubstrat beschichtungsfreie Bereiche aufweist, die passiv und im Wesentlichen inert gegenüber dem Elektrolyten sowie nichtleitfähig werden.

24. Verfahren nach Anspruch 22, bei dem Aluminium durch Elektrolyse von in einem Fluorid-enthaltenden Elektrolyten gelöstem Aluminiumoxid elektrolytisch gewonnen wird.

25. Verfahren nach Anspruch 24, bei dem Aluminium an mindestens einer mit Aluminium benetzbaren Kathode elektrolytisch gewonnen wird.

26. Verfahren nach Anspruch 22, bei dem Aluminium an mindestens einer drainierten Kathode gewonnen wird, von der Aluminium kontinuierlich abläuft.

27. Verfahren nach Anspruch 22, bei dem die Zelle eine bipolare Konfiguration aufweist und das beschichtete Anodensubstrat die anodische Seite einer bipolaren Elektrode oder einer Terminalelektrode bildet.

28. Verfahren nach Anspruch 22, bei dem der Elektrolyt zwischen dem beschichteten Anodensubstrat und einer gegenüberliegenden Kathode zirkuliert.

29. Verfahren nach Anspruch 22, bei dem der Elektrolyt bei einer Betriebstemperatur von 750 °C bis 970 °C vorliegt.

30. Verfahren nach Anspruch 22 für die elektrolytische Gewinnung eines Lanthanids, insbesondere von Neodym.

Revendications

1. Procédé de revêtement d'un substrat électroniquement conducteur et résistant à la chaleur d'une anode à base de métal sans carbone d'une cellule pour l'électro-obtention de métaux à partir de leurs oxydes dissous dans un sel fondu, pour protéger et rendre la surface du substrat anodique active pour l'oxydation des ions oxygène présents dans l'électrolyte, le procédé consistant à appliquer sur le substrat un coulis comprenant :

- un support colloïdal et/ou polymère inorganique ; et
- un matériau particulaire non dispersé mais suspendu dans le support, le matériau particulaire étant réalisé en au moins un oxyde ou un précurseur de celui-ci et comprenant des spinelles ou des précurseurs de ceux-ci ;

ledit coulis étant solidifié et rendu adhérant au substrat lors de traitement thermique pour former un revêtement adhérant, protecteur, contenant de façon prédominante un oxyde, comprenant des spinelles.

2. Procédé de la revendication 1, dans lequel le coulis est appliqué à une anode pour l'électro-obtention d'aluminium par l'électrolyse d'alumine-dissoute dans un électrolyte fondu contenant du fluorure.

3. Procédé de la revendication 1, dans lequel le support colloïdal et/ou polymère inorganique comprend au moins l'un de l'alumine, oxyde de cérium, lithine, magnésie, silice, thorine, yttria, zircone, oxyde d'étain et oxyde de zinc.

4. Procédé de la revendication 1, dans lequel le support colloïdal et/ou polymère inorganique forme, lors de traitement thermique, le même composé chimique que le matériau particulaire non dispersé.

5. Procédé de la revendication 1, consistant à appliquer au substrat, des spinelles ou des précurseurs de ceux-ci en tant que matériau non dispersé et/ou en tant que support.

6. Procédé de la revendication 5, dans lequel les spinelles sont des spinelles dopés, non stoechiométriques et/ou partiellement substitués, les spinelles dopés comprenant des dopants choisis parmi le groupe constitué de Ti^{4+}, Zr^{4+}, Sn^{4+}, Fe^{4+}, Hf^{4+}, Mn^{4+}, Fe^{3+}, Ni^{3+}, Co^{3+}, Mn^{3+}, Al^{3+}, C^{r3+}, Fe^{2+}, Ni^{2+}, Co^{2+}, Mg^{2+}, Mn^{2+}, Cu^{2+}, Zn^{2+} et Li^{+}.

7. Procédé de la revendication 5, dans lequel les spinelles comprennent un ferrite, en particulier un ferrite choisi parmi des ferrites de cobalt, cuivre, chrome, manganèse, nickel et zinc, et des mélanges et précurseurs de ceux-ci.

8. Procédé de la revendication 7, dans lequel le ferrite est dopé avec au moins un oxyde choisi parmi l'oxyde de chrome, titane, étain, zinc et zirconium.

9. Procédé de la revendication 7, dans lequel le ferrite comprend un ferrite de nickel ou un ferrite de nickel partiellement substitué avec Fe^{2+}.

10. Procédé de la revendication 5, dans lequel les spinelles comprennent une chromite.

11. Procédé de la revendication 10, dans lequel la chromite est choisie parmi la chromite de fer, cobalt, cuivre, manganèse, béryllium, calcium, strontium, baryum, yttrium, magnésium, nickel et zinc.

12. Procédé de la revendication 1, dans lequel le coulis comprend de plus au moins un électrocatalyseur ou un précurseur de celui-ci, en particulier un-électrocatalyseur(s) choisi(s) parmi l'iridium, le palladium, le platine, le rhodium, le ruthénium, le silicium, l'étain, le-zinc, les oxydes de mischmétal et les métaux de la série des lanthanides, et des mélanges et composés de ceux-ci.

13. Procédé de la revendication 1, dans lequel les constituants du coulis réagissent ensemble pour former le revêtement ou réagissent avec des constituants du substrat conducteur pour former le revêtement.

14. Procédé de la revendication 1, dans lequel le support colloïdal et/ou polymère inorganique forme, lors de traitement thermique, le même composé chimique que le matériau particulaire non dispersé.

15. Procédé de la revendication 1, dans lequel-le coulis est appliqué par brossage, pulvérisation, immersion, électrodéposition ou rouleaux sur le substrat.

16. Procédé de la revendication 1, dans lequel le substrat est choisi parmi des métaux, des alliages, des composés intermétalliques, des cermets et des céramiques conductrices.

17. Procédé de la revendication 1, consistant à appliquer le coulis sur un substrat conducteur qui peut être passivé durant l'électrolyse pour devenir sensiblement non conducteur et inerte vis-à-vis de l'électrolyte.

18. Procédé de la revendication 1, dans lequel le substrat est pré-revêtu avant d'appliquer le coulis, en particulier avec une solution colloïdale et/ou polymère contenant au moins un oxyde choisi parmi SiO_2, Al_2O_3, ThO_2, ZrO_2, SnO_2, TiO_2 et CeO_2.

19. Procédé de la revendication 1, pour reconditionner une anode revêtue, dont le revêtement actif est devenu non actif ou est usé, dans lequel la surface du substrat conducteur est clarifiée et restaurée avant d'appliquer ledit coulis sur le substrat.

20. Utilisation d'un coulis pour revêtir un substrat électroniquement conducteur et résistant à la chaleur d'une anode pour l'électro-obtention de métaux à partir de leurs oxydes dissous dans des sels fondus, formant lors de traitement thermique un revêtement adhérant, protecteur contenant de façon prédominante un oxyde, comprenant des spinelles et qui rend la surface du substrat anodique active pour l'oxydation des ions oxygène présents dans l'électrolyte, le coulis comprenant :

- un support colloïdal et/ou polymère inorganique comprenant au moins l'un de l'alumine, oxyde de cérium, lithine, magnésie, silice, thorine, yttrium, zircone, oxyde d'étain et oxyde de zinc ; et
- un matériau particulaire non dispersé mais suspendu dans le support, le matériau particulaire étant réalisé en au moins un oxyde ou un précurseur de celui-ci, ledit oxyde comprenant : un ferrite choisi parmi du ferrite de cobalt, cuivre, chrome; manganèse, nickel et zinc, et des mélanges et des précurseurs de ceux-ci ; et/ou une chromite choisie parmi une chromite de fer, cobalt, cuivre, manganèse, béryllium, calcium, strontium, baryum, yttrium, magnésium, nickel et zinc, et des mélanges et des précurseurs de ceux-ci.

21. Utilisation d'un coulis selon la revendication 20 pour produire un revêtement sur une anode à base de métal sans carbone pour l'électro-obtention d'aluminium par l'électrolyse d'alumine dissoute dans un électrolyte contenant du fluorure, sur lequel revêtement obtenu par coulis des ions oxygène de l'électrolyte fondu sont oxydés en oxygène monoatomique et libérés en tant qu'oxygène gazeux moléculaire biatomique.

22. Procédé d'électro-obtention d'un métal, consistant à revêtir un substrat anodique par le procédé de la revendication 1 et à produire ledit métal en utilisant le substrat anodique revêtu pour électrolyser un oxyde dudit métal qui est dissous dans un sel fondu d'une cellule.

23. Procédé de la revendication 22, dans lequel le substrat anodique a des zones dépourvues de revêtement qui deviennent passives et sensiblement inertes vis-à-vis de l'électrolyte et non conductrices.

24. Procédé de la revendication 22, comprenant l'électro-obtention d'aluminium par l'électrolyse d'alumine dissoute dans un électrolyte contenant du fluorure.

25. Procédé de la revendication 24, comprenant l'électro-obtention d'aluminium sur au moins une cathode mouillable par l'aluminium.

26. Procédé de la revendication 22, consistant à produire de l'aluminium sur au moins une cathode drainée à partir de laquelle s'écoule de façon continue l'aluminium.

27. Procédé de la revendication 22, dans lequel la cellule est dans une configuration bipolaire et dans lequel le substrat anodique revêtu forme le côté anodique d'une électrode bipolaire ou d'une anode de borne.

28. Procédé de la revendication 22, consistant à faire circuler l'électrolyte entre le substrat anodique revêtu et une cathode en vis-à-vis.

29. Procédé de la revendication 22, dans lequel l'électrolyte est à une température de fonctionnement de 750°C à 970°C.

30. Procédé de la revendication 22, pour l'électro-obtention d'un lanthanide, en particulier de néodyme.