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(54) **AN ELECTRODE FOR ALUMINIUM PRODUCTION AND A METHOD OF MAKING SAME**
ELEKTRODE ZUR ALUMINIUMHERSTELLUNG UND VERFAHREN ZUR HERSTELLUNG DAVON
ÉLECTRODE POUR PRODUCTION D'ALUMINIUM ET SON PROCÉDÉ DE FABRICATION

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Description

[0001] The present invention relates to an electrode for aluminium production and a method for making same.

[0002] Aluminium metal is presently produced by electrolysis of an aluminium containing compound dissolved in a molten electrolyte, and the electrowinning process is performed in smelting cells of conventional Hall-Heroult design. These electrolysis cells are equipped with horizontally aligned electrodes, where the electrically conductive anodes and cathodes of today's cells are made from carbon materials. The electrolyte is based on a mixture of sodium fluoride and aluminium fluoride, with additions of alkaline and alkaline earth halides. The electrowinning process takes place as the current passed through the electrolyte from the anode to the cathode causes the electrical discharge of aluminium ions at the cathode, producing aluminium metal.

[0003] Commonly, for the fixation of steel collector bars in cathode blocks, there are preformed slots in the blocks that allow the bars to be entered into them. The space or void between the wall of the slots and the bars can be filled with melted cast-iron and/or a conductive paste can be applied.

[0004] In a similar way, pre-baked carbon anodes are fixed to steel studs that are part of an anode hanger. The anode has pre-formed bores which allow the steel studs to be entered into them. The fixation of the studs to the anode is commonly performed by pouring melted cast-iron in the annular space between each individual stud and the corresponding bore in the anode.

[0005] In an alternative, conductive particles can be applied for rodding as shown in the Applicant's own patent application WO09/099335.

[0006] In the race toward low specific energy consumption for aluminium production, one well known and potent tool is to aim at the reduction of the cathodic and/or the anodic voltage drop. Indeed, reducing cathodic voltage drop reduces ohmic energy loss in the cathode, allowing operators to either increase potline amperage and/or reduce pot voltage that ultimately results in a reduction of the specific energy consumption per ton of produced aluminium.

[0007] Many means have been used to achieve cathodic voltage drop reduction, and one that is commonly known is the use of copper inserts to improve the conductivity of the commonly used steel collector bars. Many publications shows that the copper insert or element has at least one external side or surface that rest onto one corresponding surface of the steel collector bar.

[0008] Examples are given in WO04031452 which discloses collector bars of steel having a copper core, US5976333A and WO0163014 which both discloses various designs of a copper rod inserted in a steel tube embedded in a slot in a cathode block. US6231745 describes copper and iron diffusion across their interface in a composite conductor. US2006151333 describes a cathode collector separated by a contact zone and divid-

ed longitudinally into two sections of different electrical resistance, separated from one another by a mica sheet insulator.

[0009] It has been demonstrated in tests that copper inserts in the steel collector bars can reduce the cathodic voltage drop by about 60mV with regard to conventional steel collector bars. Another benefit of using copper as a high conducting element in cathodes is the more uniform cathodic current density achieved with such designs. For graphitized cathodes especially, a more uniform current density decreases the maximum erosion rate, thereby increasing cathode life.

[0010] However, each mV saved with solutions involving insertion of highly conductive elements is expensive, because in addition to the expensive copper rods used, assembly (collector bar drilling and copper bar insertion) nearly triples the cost of copper alone.

[0011] In addition, there has been observed by the inventors that at the high temperatures present for this type of composite conductors, Fe in the steel collector bar may diffuse into the Cu metal of an adjacent insert of copper.

[0012] This diffusion can result in an increase of ohmic resistivity of the composite collector bar, and followingly increase in the cathodic voltage drop over time.

[0013] Similar effects with respect to ohmic resistivity can occur when applying composite conductors of the Fe - Cu type for anodes.

[0014] The present invention relates to electrodes, anodes or cathodes, with composite conductors and a method for making same, where these detrimental effects can be reduced or avoided.

[0015] More specific, the invention relates to an electrode for production of aluminium metal by electrolysis of an aluminium containing compound dissolved in a molten electrolyte, where the electrowinning process is performed in smelting cells of conventional Hall-Heroult design. The electrode comprises a calcinated carbon containing body having fixed thereto at least one composite metallic conductor comprising conducting elements of a Fe containing material and conducting elements of a Cu containing material. The composite conductor comprises a diffusion barrier layer material at the interface between the two conducting materials. Several materials for the diffusion barrier layer have been achieved to as well as methods for application of the layer.

[0016] At least two important objectives of the invention can be mentioned;

- 1) preserve minimum resistivity during lifetime of the cell and
- 2) to make use of thinner Cu-sections in composite conductors, i.e. Cu plates, to enhance the quality and the cost situation of the composite conductor.

[0017] These and more advantages can be achieved in accordance to the invention as claimed in the accompanying claims.

[0018] In the following, the present invention shall be further described by diagrams where:

Fig. 1 is a phase diagram that disclose Fe diffusion into Cu,

Fig. 2 is a diagram showing the increase in resistivity when Fe diffuses into Cu,

Fig. 3 is a diagram showing concentrations of Fe in Cu for composite conductors without and with various barrier materials

[0019] The invention relates to electrodes in general, but when referring to cathodes, there is one problem with collector bars in general, and that is that their operation temperature is well above 900°C, and other elements in contact with the collector bar may diffuse into the material and deteriorate the resistivity of the material. For normal steel collector bars, carbon (C) diffuses into the steel and the resistivity increases.

[0020] For composite collector bars of i.e. Cu and Fe, an additional interdiffusion is occurring. Fe will diffuse into Cu to the content that is given in the phase diagram in Fig 1. Vice versa, Cu will also diffuse into Fe, but this is less critical for the resistivity of the assembly.

[0021] The increase in resistivity when Fe diffuses into Cu is measured, and shown in Fig. 2. The resistivity of Cu increase almost 100% when Cu becomes saturated with Fe. It is therefore desirable to have a barrier preventing the interdiffusion of Fe in Cu.

[0022] The required properties of a barrier preventing Fe to diffuse into Cu in a composite collector bar is:

- 1) A low solubility of the compound in both Fe and Cu
- 2) Stable at the operating temperature of the cell
- 3) Preserve electrical conductivity
- 4) Easy to apply in thin layers

[0023] In a first experiment, a thin coating of TiB₂ powder was applied to a Cu - rod, and the effectiveness was measured in a diffusion experiment. A Cu rod was dipped into TiB₂ slurry and a 100 micron thick layer was applied. The rod was put into a steel hollow and the assembly was heated to 950 °C for 14 days.

[0024] In the next experiments, a Mo and W foil of 100 micron were tested in the same manner, i.e. each applied at the surface of a Cu rod which subsequently was put in a steel hollow and heated correspondingly.

[0025] The concentration profiles are shown in Fig 3. A significant reduction in diffusion is observed. For the TiB₂ coating, a tenfold reduction in diffusion is observed. The Mo and W foil seems to virtually block diffusion in the timescale of the test (14 days).

[0026] There might be other elements/compound that are more (cost) effective and not tested, and a barrier is not limited to the compounds mentioned here. Other conductive metals, intermetallics or materials fulfilling the cri-

teria, are potential barriers.

[0027] When selecting a material with low diffusion coefficient, low solubility is also an important property. The electrical conductivity of copper is very dependent of the impurity level, thus the solubility of a material defines the upper limit of the harm the material can do. The barrier material should be able to block Fe, at the same time the barrier material itself must not enter the copper phase.

[0028] In general, diffusion occurs more rapidly along grain boundaries and over free surfaces than through the interiors of crystals, i.e. impurities will diffuse faster into the metal along grain boundaries. As long as the solubility is low, the accumulation in the copper also should be expected to be low, and thus the potential reduction of the conductivity will be limited. In addition to low diffusivity, a good diffusion barrier also must have low solubility in copper, and possess sufficient electrical conductivity.

Selection criteria of metal barrier materials

[0029] Hume-Rothery (Ref.: Lee J.D.: "Concise Inorganic Chemistry", 4th Ed., Chapman & Hall, London 1991, p. 136) has created a set of simple rules describing conditions to be fulfilled if extensively solid solution between metals should occur:

Atomic size factor rule: The relative difference between the atomic diameters (radii) of the two species should be less than 15%. If the difference is >15%, the solubility is limited.

[0030] Crystal structure rule: For appreciable solid solubility, the crystal structures of the two elements must be identical.

[0031] Valence rule: A metal will dissolve a metal of higher valence to a greater extent than one of lower valence. The solute and solvent atoms should typically have the same valence in order to achieve maximum solubility.

[0032] Electronegativity rule: Electronegativity difference close to 0 gives maximum solubility. The more electropositive one element and the more electronegative the other, the greater is the likelihood that they will form an intermetallic compound instead of a substitutional solid solution. The solute and the solvent should lie relatively close in the electrochemical series.

[0033] A barrier metal in accordance to the present invention should fall outside the above rules in comparison with Cu and Fe, since it should not interfere with them.

Selection criteria for ceramics barrier materials

[0034] When applying ceramics such as Refractory Hard Materials (RHM), as barrier material, interstitial solid solution can form if the smaller atom can be accommodated between the atoms in the metal lattice. According to Hagg's rule (see below) interstitial solid solution forms only if the atomic radius ratio of the two components $r_i/r_m < 0.59$.

[0035] Ref.: Hägg G.: Gesetzmässigkeiten in Kristallbau by Hydriden, Boriden, Carbiden und Nitriden" der

Übergangselemente", S. Phys. Chem. B12 (1931) 33-56 and Hägg G.: "Eigenschaften der Phasen von Übergangselementen in binären Systemen mit Bor, Kohlenstoff und Stickstoff", Z. Phys. Chem. B12 (1931) 221-232.

[0036] Based upon these criterions, it has been assessed that in contact with Cu, metals like Ta, Mo and W look promising. B containing ceramics seem to be the a good candidate to prevent the barrier material from entering Cu. Moreover, Refractory Hard Materials (RHM) may provide good candidates as well such as nitrides and borides, more specific TiN, TaN, ZrN, and ZrB₂, TiB₂ and possibly borides in general.

[0037] Regarding the ability of the barrier material's ability to block Fe, it was found that W looks most promising, and possibly Mo and Ru. W diffusion data from CRC handbook 58th Ed, 1977-1978, F-63-F-71, indicates that Fe diffuses four orders of magnitude slower into W than it does into Cu.

[0038] As mentioned above, the composite conductor in the electrode comprises a diffusion barrier layer material at the interface between the two conducting materials. It has been demonstrated that;

[0039] The diffusion barrier layer can be made of a ceramic material or a RHM material.

[0040] Diffusion barrier layers of Nitrides or Borides such as TiN, TaN, ZrN, ZrB₂, or TiB₂ may also be applied.

[0041] Methods for applying these diffusion barrier layer materials can comprise to prepare it as a slurry and apply it to the conducting elements by dipping at least one of the two conducting elements in said slurry followed by drying, or it can be applied by powder coating.

[0042] Further, a method for application of the diffusion barrier material may comprise that the barrier layer is applied by a Plasma coating technique.

[0043] Preferred barrier layers of a metallic material includes; Mo, W, Ta or Ru.

[0044] These diffusion barrier layers can be prepared as a foil, by Chemical Vapor Deposition or Electroplating, and applied onto at least one of the two conducting elements before bringing these parts together.

[0045] The thickness of the barrier layer can preferably be in the range 1-1000 µm.

Claims

1. Electrode for production of aluminium metal by electrolysis of an aluminium containing compound dissolved in a molten electrolyte, where the electrowinning process is performed in smelting cells of conventional Hall-Heroult design, where the electrode comprises a calcinated carbon containing body having fixed thereto at least one composite metallic conductor comprising conducting elements of a Fe containing material and conducting elements of a Cu containing material,
characterised in that
the composite conductor comprises an electronic

conductive diffusion barrier layer material at the interface between the two conducting materials wherein the barrier layer is constituted by a ceramic material or a metallic material of Mo, W or Ru.

2. Electrode in accordance to claim 1,
characterised in that
the diffusion barrier layer is made out of a Refractory Hard Material (RHM).
3. Electrode in accordance to claim 2,
characterised in that
the diffusion barrier layer is made of Nitrides or Borides selected among TiN, TaN, ZrN, ZrB₂, or TiB₂
4. Electrode in accordance to any preceding claim,
characterised in that
the diffusion barrier layer has a thickness in the range 1-1000 µm.
5. Method of making an electrode in accordance to claim 1 - 4,
characterised in that
the ceramic diffusion barrier layer is applied by powder coating, by plasma coating or in the state of a slurry.
6. Method of making an electrode in accordance to claim 5,
characterised in that
the ceramic diffusion barrier layer is prepared as a slurry and is applied to the conducting elements by dipping at least one of the two conducting elements in said slurry followed by drying.
7. Method of making an electrode in accordance to claim 1,
characterised in that
the metallic diffusion barrier layer is applied as a foil, by Chemical Vapor Deposition, or by Electroplating and applied onto at least one of the two conducting elements before bringing these parts together.

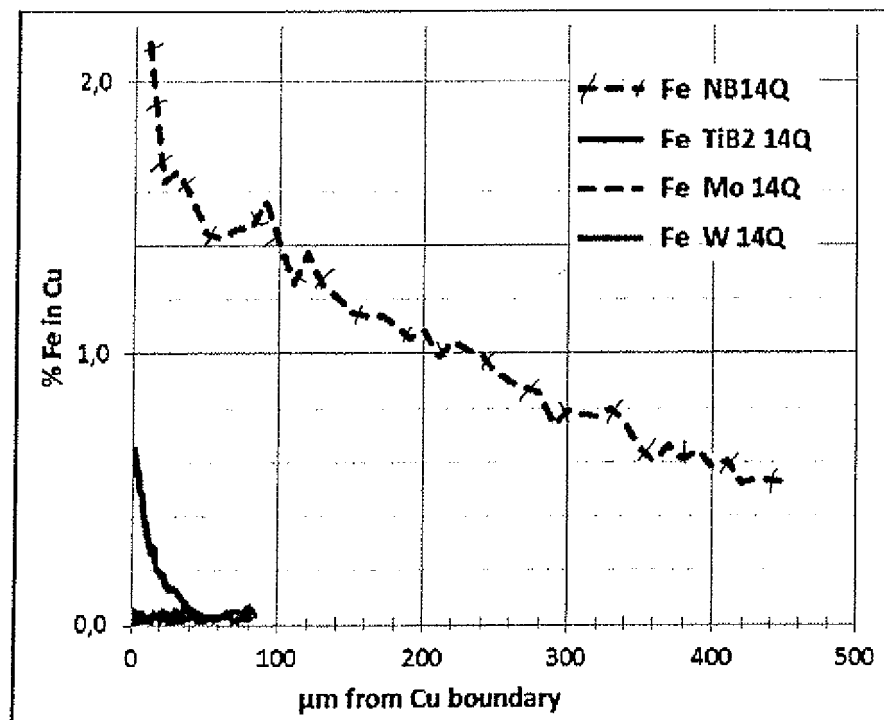
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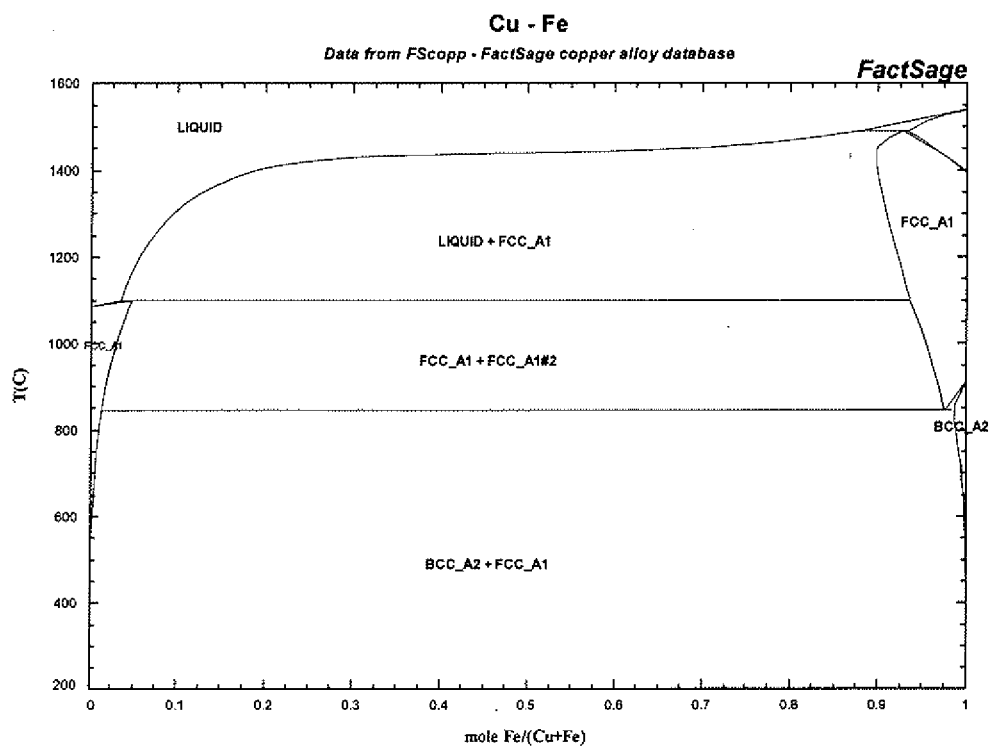
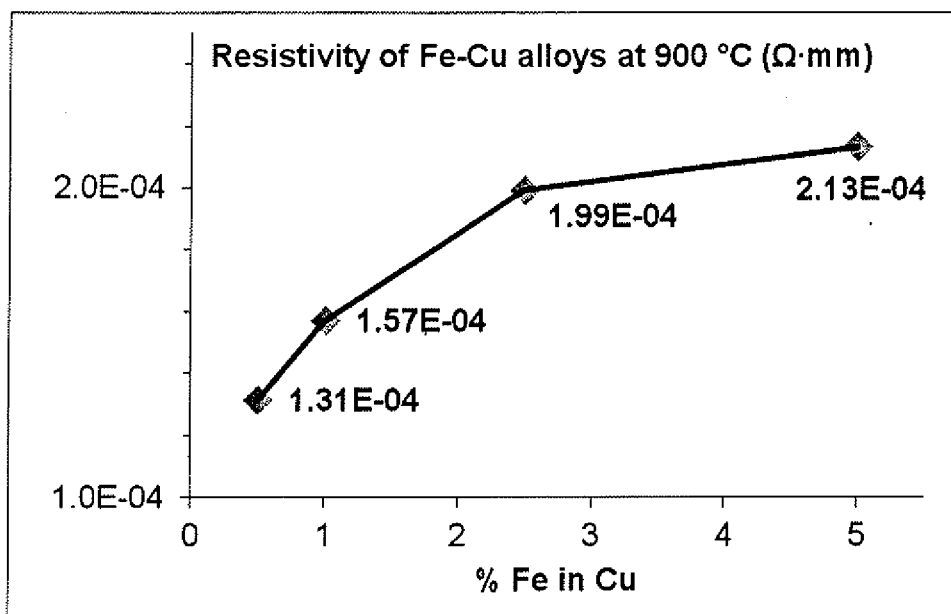
1. Elektrode zur Herstellung von Aluminiummetall durch Elektrolyse einer aluminiumhaltigen Verbindung, die in einem Schmelzflusselektrolyten aufgelöst ist, wobei der elektrolytische Metallgewinnungsprozess in Schmelzzellen einer konventionellen Hall-Heroult-Ofen-Ausführung ausgeführt wird, wobei die Elektrode einen kalzinierten kohlenstoffhaltigen Körper umfasst, an dem mindestens ein metallischer Zweimetalleiter befestigt ist, der leitende Elemente eines Fe-haltigen Materials und leitende Elemente eines Cu-haltigen Materials umfasst,
dadurch gekennzeichnet, dass

- der Zweimetalleiter ein elektronisches leitfähiges Diffusionssperrschichtmaterial an der Grenzfläche zwischen den zwei leitenden Materialien umfasst, wobei die Sperrschicht durch ein Keramikmaterial oder ein metallisches Material aus Mo, W oder Ru gebildet ist. 5
2. Elektrode nach Anspruch 1, **dadurch gekennzeichnet, dass** die Diffusionssperrschicht aus einem feuerfesten Hartmaterial (Refractory Hard Material; RHM) hergestellt ist. 10
3. Elektrode nach Anspruch 2, **dadurch gekennzeichnet, dass** die Diffusionssperrschicht aus Nitriden oder Boriden hergestellt ist, die ausgewählt sind zwischen TiN, TaN, ZrN, ZrB₂ oder TiB₂. 15
4. Elektrode nach einem vorstehenden Anspruch, **dadurch gekennzeichnet, dass** die Diffusionssperrschicht eine Dicke im Bereich von 1 bis 1000 µm aufweist. 20
5. Verfahren zum Herstellen einer Elektrode nach Anspruch 1 bis 4, **dadurch gekennzeichnet, dass** die Keramikdiffusionssperrschicht durch Pulverbeschichtung, Plasmabeschichtung oder im Zustand eines Schlamms aufgebracht wird. 25
6. Verfahren zum Herstellen einer Elektrode nach Anspruch 5, **dadurch gekennzeichnet, dass** die Keramikdiffusionssperrschicht als ein Schlamm hergestellt und auf die leitenden Elemente durch Eintauchen von mindestens einem von den zwei leitenden Elementen in den Schlamm gefolgt von Trocknen aufgebracht wird. 30
7. Verfahren zum Herstellen einer Elektrode nach Anspruch 1, **dadurch gekennzeichnet, dass** die metallische Diffusionssperrschicht durch chemische Gasphasenabscheidung oder galvanische Beschichtung als ein Film aufgebracht und vor dem Zusammenfügen dieser Teile auf mindestens eines der zwei leitenden Elemente aufgebracht wird. 35
- un corps contenant du carbone calciné ayant fixé sur celle-ci au moins un conducteur métallique composite comprenant des éléments de conduction d'un matériau contenant du Fe et des éléments de conduction d'un matériau contenant du Cu, **caractérisée en ce que** le conducteur composite comprend un matériau en couche de barrière de diffusion à conduction électronique au niveau de l'interface située entre les deux matériaux de conduction, dans laquelle la couche de barrière est constituée d'un matériau en céramique ou d'un matériau métallique à base de Mo, W ou Ru. 40
2. Électrode selon la revendication 1, **caractérisée en ce que** la couche de barrière de diffusion est fabriquée à partir d'un matériau dur réfractaire (RHM). 45
3. Électrode selon la revendication 2, **caractérisée en ce que** la couche de diffusion de barrière est constituée de nitrures ou de borures choisis parmi TiN, TaN, ZrN, ZrB₂ ou TiB₂. 50
4. Électrode selon l'une quelconque des revendications précédentes, **caractérisée en ce que** la couche de diffusion de barrière présente une épaisseur dans la gamme comprise entre 1 et 1 000 µm. 55
5. Procédé de fabrication d'une électrode quelconque des revendications 1 à 4, **caractérisé en ce que** la couche de diffusion de barrière céramique est appliquée par revêtement en poudre, par céramisation au plasma ou dans l'état d'une bouillie. 60
6. Procédé de fabrication d'une électrode selon la revendication 5, **caractérisé en ce que** la couche de diffusion de barrière céramique est préparée en tant que bouillie et est appliquée aux éléments de conduction par trempage d'au moins un des deux éléments de conduction dans ladite bouillie, suivi du séchage. 65
7. Procédé de fabrication d'une électrode selon la revendication 1, **caractérisé en ce que** la couche de diffusion de barrière métallique est appliquée en tant qu'une feuille, par dépôt chimique en phase vapeur ou par dépôt électrolytique, et est appliquée sur au moins un des deux éléments de conduction avant de mettre ces parties ensemble. 70

Revendications

1. Électrode destinée à la production d'aluminium métallique par l'électrolyse d'un composé contenant de l'aluminium dissous dans un électrolyte fondu, où le processus d'extraction par voie électrolytique est effectué dans des cellules de fusion d'un concept conventionnel de Hall-Héroult, où l'électrode comprend 55

**Fig. 3**

**Fig. 1****Fig. 2**

REFERENCES CITED IN THE DESCRIPTION

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