ELECTRODE WITH PROTECTIVE COATING

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ABSTRACT OF THE DISCLOSURE

An electrode, especially an anode for electrolytic production of aluminium, is protected against oxidation in service by means of a coating consisting of a material which has been applied as particles at least partly molten at high temperature, and has solidified in situ, so that in the coating the said particles are bonded together over at least a part of their exterior. The coating material includes aluminium oxide and facultatively aluminium, both then being applied simultaneously as a cermet or as successive layers in sandwich structure. The coating has preferably a thickness of 0.1 to 1.0 mm, and has suitably been applied by means of a plasma burner.

The invention relates to electrodes, especially anodes intended for cooperation with an electrolyte of a cell for production of aluminium by fusion electrolysis. The electrodes have, on surface parts not intended for passage of current, a coating for hindering any oxidation of the electrode material.

The cathodically connected pot of a fusion electrolysis cell for production of aluminium contains molten aluminium, and an electrolyte floating on the aluminium and containing aluminium oxide; the electrolyte on its side directed towards the atmosphere forms a solid crust, which in turn is covered with a layer of alumina (aluminium oxide) for periodical enrichment of the electrolyte and thermal insulation of the bath in the pot. Anodes consisting of artificial carbon penetrate the alumina layer and the crust and extend into the electrolyte, for conduction of the electric current which maintains the electrolysis in progress. The crust and the aluminium oxide deposited on it usually do not sealingly enclose the circumference of each anode, but a gap forms around the anode circumference owing to rising gases and other influences. For enrichment of the electrolyte with alumina, the crust is periodically broken in. The gases released from the electrolytic process, which primarily rise through the cracks around the anode circumferences, form above the tank a mixture with the surrounding air which is destructive of the longest possible working life of the anodes.

The consumption of an anode during the operation of the anode, also known as burning away, which is made up of a primary and secondary burning, is based upon two oxidation mechanisms which should be considered separately for present purposes.

In the primary burning, the oxygen released from the aluminium oxide during the fusion electrolysis attacks the carbon of the anode with formation of a gas mixture of carbon dioxide and monoxide, which rises from the tank, and this reaction, which causes the majority of the burning away, proceeds exothermically with heating of the electrolyte and reduction of the energy necessary for the electrolysis. This primary burning is unavoidable with carbon anodes.

The invention concerns means by which influence is exerted on the oxidation mechanism which produces the secondary burning away of an anode and which impairs economic cell operation.

The temperature of the bath, that is of the electrolyte in the cathode pot, lies at about 950 to 980° C., and this heat source imparts a heat content to the carbon anodes, so that a gradient occurs between the side of the anode facing towards the bath and that facing away from the bath. Corresponding to this heat content of the anodes, the surfaces of the anodes exhibit a temperature gradient between a maximum of 980° C., and 400° C. The part of the anode extending out of the bath is surrounded by a gas mixture consisting of workshop air and gases rising from the cell, which, promoted by the temperature of the anode, acts on it in an oxidizing manner and thus in a manner hastening burning away. The burning reactions which then take place produce, in contrast to the oxidation mechanism which causes the primary burning, no contribution to the bath heating and thus to the reduction of energy, but they produce unproductive losses of carbon, which can amount to up to 8% of the total consumption of anode carbon.

To reduce the losses brought about by secondary burning, it is known to provide anodes with a coating on their upper end lateral faces, the anodes consisting of carbon and being intended for insertion in a fusion electrolysis cell for production of aluminium. From the requirement that the material of the coating must not contaminate the electrolyte and hence the electrolytically separated aluminium, in the present state of the art aluminium is chosen as material, which can be applied by spraying or casting on. Various defects are characteristic of coatings of this kind. Sprayed aluminium coatings are applied in a thickness of about 0.3 to 0.5 mm—cast coatings have a thickness of at least 1 cm, but preferably of several cms., which, multiplied by the total surface of all the anodes dipping into the cell, gives a total volume which, as a continuously circulating quantity of metal, is disproportionately large in relation to the rate of raw aluminium output of the cell. The most significant defect lies however in the fact that the aluminium coating melts on an isotherm on the anode surfaces of about 650° C, so that the anode surface in its lower free zone, several cms. high, between the bath and this isotherm of about 650° C, is exposed to the oxidising attack of the surrounding air mixture. Even if the aluminium coating when melting away leaves beneath it a natural aluminium oxide skin, this skin also tears away and adheres not at all or badly to the carbon surface, so that it cannot ensure any effective protection against burning away.

As stated above, the secondary burning away amounts to up to 8% of the total consumption of carbon for a given quantity of aluminium produced. If an economic advantage is to be obtained from elimination of the secondary burning, the cost expended for this purpose must be kept within the scope of the above-mentioned component of carbon cost. By reason of the production of a cast body, the care to be employed in the choice of the coating material, the large quantity of continuously circulating metal, with the additional expenditure of electrical energy for fusion electrolysis which necessarily results from it, as well as the only restricted anode protection arising from melting of the coating below the isotherm of 650° C., the expenditure on the coatings known from the state of the art is high. This known method is economically unattractive.

The invention starts from this, and the object underlying it is to produce on an electrode a coating which is neutral to the surroundings, and does not melt at operating temperatures, especially a coating on an anode consisting of carbon, intended for cooperation with an electrolyte of a fusion electrolysis cell for production of
aluminium, the material consumption necessary for the production of which coating amounts to a minimum in relation to the advantage achievable by elimination of secondary burning away. This object is achieved according to the invention in that the coating consists of a flame-sprayed particulate material, at least a part of which is aluminium oxide, and the individual particles of the coating are at least partly connected together by solidification which has taken place in situ.

Preferably, for production of such a coating, the grains of the material to form the coating are heated in a high temperature gas jet at least into the plastic condition, and preferably into the melted condition, and by means of this gas jet are thrown against the surface to be coated. These molten drops then solidify in succession on the surface to be coated, after they have come into contact with one another and have melted more or less together. Usually the individual particles of aluminium oxide which have been more or less flattened by the impact are still distinguishable in the coating at high magnification. The chilled aluminium oxide agglomerated in this way exists crystallographically primarily in the gamma modification. Any overheating of the coating applied is to be avoided, because the gamma progressively transforms itself into the alpha modification, which in operation shows the disadvantage that, if present in too great quantity in the coating, it does not dissolve again in the cryolite electrolyte and leads to the production of bottom crust.

By reason of the high melting point of the material, and the very great temperature drop on solidification caused by this, and further also because of the surface roughness of the underlying carbon body, it may occur that, on impingement, individual molten drops unite insufficiently with those already applied and leave interstices, or that in consequence of the very rapid solidification and the internal stresses arising from it, cracks arise within or between the individual solidified grains, which can lead to a certain porosity of the coating. This porosity can, when the anode is in operation, have as consequence a restricted secondary burning. To dispose of this defect by means of a statistical closing of the pores, the coating preferably has a thickness of 0.1 to 1.0 mm., preferably from 0.2 to 0.5 mm. When anodes coated in this way with a cermet-type material are in operation in a cell, then in their relatively cold parts the protection against burning off is ensured by the impermeable metal constituent. In the hotter zones in the neighborhood of the bath the aluminium oxide is partly oxidised to aluminium oxide, which closes the interstices impermeably.

The choice of aluminium oxide of industrial quality for the coating on the surface of the anode has the advantage that this product without more ado can be employed for topping up of the electrolyte. Thus for the purely ceramic coating the material costs can be reckoned as zero.

With combined coatings the same is true with reference to the aluminium oxide component; the quantity of aluminium required at the same time for fulfilling the desired purpose can also be kept very small, in particular significantly smaller than in a case of known pure aluminium coatings, so that also from this point of view the material costs can be kept very low. One must consider in this connection that the aluminium introduced into the bath with the coating in the neighborhood of the anode is re-oxidised at least in part and thus must be re-electrolysed. The quantity of aluminium supplied is thus in practice to be taken account of at the price of the metal, but can as explained restricted to a minimum.

Finally the coating of alumina and aluminium dissolves easily in the electrolyte when the anode is lowered in known manner, so that also in this respect no disturbance of operation can be created.

In summary, a coating according to the invention brings significant advantages both in the technical and in the commercial respect.

Preferred embodiments of the invention and a device for producing coatings according to the invention are shown by way of example in the drawings. These show:

FIG. 1, an anode provided with a simple coating;
FIGS. 2, 3, 4, 5 and 6, special arrangements of combination coatings;
FIG. 7, a device for forming the coatings.

For clarity the thickness of the protective layers are shown greatly exaggerated in these figures.

FIG. 1 shows an anode already inserted in an electrolytic cell. This anode hangs on its anode rod 11 and
dips with its lower part into the molten cryolite 12 of a fusion electrolysis cell. On the cryolite floats a crust 13 which in turn is covered with an alumina layer 14 for periodical enrichment of the cryolite 12 and control of the heat content of the cell. In general the crust 13 does not touch the surface 19 of the anode 10, so that a gap 16 remains between the anode and the crust. After dipping from the fusion electrolysis, with formation of a surrounding atmosphere acting in an oxidising manner on the surfaces 19 of the anode 10. For protection of the anode surfaces 19 against oxidising constituents of the surroundings, the anode 10 is provided with a coating 15 of flame sprayed aluminium oxide. Before the anode is put into operation, an overvoltage is applied across the anode 10 that directed towards the molten cryolite 12. Upon insertion of the anode in a cell, the molten cryolite 12 dissolves the coating 15 to an extent corresponding to the depth of immersion of the anode 10 into the cryolite 12, so that the coating is maintained down to the surface of the molten cryolite 13, that is to say also in the gap 16. By this means an effective protection is ensured in the hottest zone of the anode and thus at the place of most severe secondary burning. With progressive displacement of the anode 10 downwards, in the usual manner, to compensate for the primary burning away of carbon, the coating is gradually melted, but continues to extend down to the surface of the cryolite. The thickness of the coating 15 amounts suitably to 0.1 to 1.0 mm, preferably 0.2 to 0.5 mm. Layers of ceramic materials as for example aluminium oxide, are however not limited to the values given, but can depart both upwards and downwards. The layer thickness in fact requires to be sufficient to ensure that, as a consequence of the statistical distribution of particles, there are no continuous pores penetrating the coating. The thicknesses given have been found to be satisfactory for achievement of the purpose sought by the invention, namely the provision of a coating 15 which is thoroughly impermeable to gas and well matches to the thermal expansion of the anode 10 for avoidance of crack formation and fragmentation. According to FIG. 2 a further layer 17 of aluminium is superimposed onto the coating 15 of alumina oxide applied to the anode 10. During the operation of the anode the aluminium of the layer 17 also oxidises and its oxidation products close the pores in the coating 15. The thickness of the coating 15 can in this case likewise amount to 0.1 to 1.0 mm, preferably 0.2 to 0.5 mm, while the thickness of the layer 17 can amount to between 0.05 to 1.0 mm. With the combined layer of ceramic and metal materials one can take account of the statistical pore closure and the pore closure with help of oxidation products in an advantageous manner, as being additive in effect. FIG. 3 shows a further arrangement in which, between the surface 19 of the anode 10 and the coating 15 of alumina oxide, there is provided a basis layer 18 consisting of aluminium which is in engagement with the carbon of the anode 10. Here components from the surrounding atmosphere, which produce oxidation after penetration through the coating 15, produce a modification of the material of the basis layer 18 and hence closure of the pores of the coating 15. With such a construction, in which the coating 15 has the thickness given above, the covering layer 18 can have a thickness like that of layer 17 of aluminium in FIG. 2, or one can choose, as regards the thickness of the basis layer 18, outside the lower value, because the flow of gas through the pores of the coating 15 is reduced. The embodiment according to FIG. 4 is suited for use in surroundings with large amounts of constituents which are oxidising in action, and are gaseous, or present in other aggregate conditions. A coating 15 of aluminium oxide is applied on the anode surfaces 19. This carries a layer 17 of metallic aluminium, which in its turn is covered with a covering 20 of aluminium oxide. The layer 17 of aluminium is suited for the same mode of operation as has been described in connection with FIG. 2. The thickness of the covering 20 can amount to 0.1 to 1.0 mm., preferably 0.2 to 0.5 mm., and this layer thickness can also be chosen in these circumstances for the coating 15. Values between 0.05 to 1.0 mm. in one or more passes are advantageous for the case described of the layer 17. In practice the thickness of the single layers or of the deposits of the single passes cannot be held uniform, but it is possible at the end to obtain a coating with a regular thickness. FIG. 5 shows a development of FIG. 4. The surfaces 19 of the anode 10 are provided with a basis layer 21, on which a coating 15 is applied, with a layer of aluminium 17 arranged on it, while the layer 17 has a covering 20. The coating 15 and the covering 20 consist of aluminium oxide as in the embodiment according to FIG. 4, or as already described in connection with FIG. 1. The layer 17, the covering 18, the layer 17 in the embodiment according to FIGS. 4 and 5, as well as the basis layer 21, consist of aluminium. Aluminium is a preferred means of attaining the object of the invention, but the invention is not limited to it, and other metallic material can be brought into use, also as addition to aluminium as long as they do not influence cryolite and the melt produced from it, and have the same action as described. In FIG. 6 the protection of the anode 10 is by means of a layer 23 of cermet-type material, i.e. a ceramic-metallic material in mixed condition. Advantageously the material consists of aluminium oxide and aluminium with a ratio by weight of 10:1 to 2:1. The choice of ratio within this range depends on the level of the components having an oxidising action and the total porosity of the applied layer, which in turn depends on the statistical distribution of the particles of the layer. The layer thickness also ranges on economic grounds suitably in a thickness of 0.1 to 1.0 mm. With a layer thickness at the lower limit of the range identified, one will choose a weight ratio of aluminium oxide to aluminium which is nearer to 2:1 than to 10:1, while with increasing layer thickness the weight ratio will come nearer to the value 10:1. The coatings 15 and coverings 20 described in connection with the embodiments according to FIGS. 1, 2, 3, 4 and 5 can also be formed of the cermet-type material. Here also other cermet-type materials are suitable for use, if they satisfy the requirements of solution free of impurity in cryolite, no influence on the electrolytically separated aluminium, and the absence of influence on the cell covering, with simultaneous ability to form a coating impermeable to gas and compatible with the thermal expansion of the anode. Coatings of ceramic and of ceramic-metallic material according to the invention are preferably applied in finely dispersed form and compacted to a coherent layer with employment of thermal energy, where the coatings of metallic kind can be applied, for example by flame spraying, with the help of an acetylene burner. This kind of layer formation produces results which are commercially satisfactory compared with the state of the art. In this connection, for production of the optimum advantage attainable from elimination of secondary burning away, the device shown in FIG. 7 is preferably used for formation of the coatings. This device is a so-called plasma burner 23, which applies the coating material 24 in the melted condition onto the anode surface 19 while finely dispersed, with simultaneous formation of a relatively impermeable layer. An arc burns in a cavity of the plasma burner 23, and a gas is introduced into the cavity, which is ionised by the arc, and, according to the adjustment of the burner 23, is brought to a high energy content in the order of magnitude up to 10⁸ Kcal/kg. The coating material 24 is introduced into the ionised gas jet 26 through a passage 25, either in powder, rod or melted form, is converted therein into a fine dispersion, and is applied onto the anode surface by means of the high thermal and kinetic energy pres-
ent in the gas jet 26. The device presents the advantage that the application of the material 24 and the formation of a non-permeable layer take place simultaneously. The simultaneous heating of the anode surface 19, that is of a zone around the point of application, hinders any rebound of the applied layer, and, on the basis of shock heating, excludes oxidation of the carbon, or of a possible metallic layer, e.g. an aluminium layer applied previously.

By "high energy content" of the gas jet 26 there is to be understood an energy content which has been adjusted to be the maximum possible for the material in question and has to be sufficient for melting the material. This can amount to as much as 10^6 Kcal./kg. For the application of a layer of aluminium oxide one will so adjust the energy content of the ionised gas jet that the energy is optimum for coating, but not so great that the aluminium oxide vapourizes before it reaches the surface to be coated.

To improved the adhesion and stability of the layer consisting of aluminium oxide or of a cermet-type material, the gas jet should act in an oxidising manner on the material of the layer. With employment of a non-oxidising ionised gas jet, one can arrive at the formation and presence of aluminium suboxide and free oxygen, so that, just where they are required, an optimum adhesion and stability cannot be attained. With the presence of nitrogen in the ionised gas jet, aluminium nitrides can be formed, which likewise oppose the stability and adhesion of the applied layer. For production of an ionised gas jet both gas-stabilised and also water-stabilised plasma burners can be employed. A burner is water-stabilised by introduction of water through an opening into the cavity.

The plasma burner 23 is water-stabilised, and should have a minimum input of 40 kw. preferably of about 150 kw., or higher. Inputs in this order of magnitude are attainable according to the present state of technology exclusively with water-stabilised burners; as already mentioned, such burners enable the simultaneous rapid heating up of a sufficiently large zone around the point of application so that any rebound of an applied layer, or any oxidation of the carbon and of a possible aluminium layer already applied to the carbon, is avoided.

Burners 23 of this kind are not restricted by their construction to the introduction of only one material 24 in the ionised gas jet 26. Thus it is possible to introduce one or more materials 24 into the plasma burner 23, that is into the ionised gas jet 26, while according to the handling of the device a homogenous or heterogeneous material becomes applied as the coating. Therefore a device for ionisation of a gas jet, by reason of the adjustability of its output, is suitable for the production of anodes according to the constructions according to FIGS. 1 to 6 which are neutral to the surroundings in operation.

The cost of the devices for ionisation of a gas jet, that is for the burner 23, is relatively slight in proportion to the advantages flowing from them by suppression of the secondary burning away, so that the purpose of the invention is still attained if, for example, two devices of the kind mentioned are employed for production of a coating consisting of an aluminium layer with a layer of aluminium oxide applied over it, one producing aluminium layer and the other that of aluminium oxide.

Two devices for ionisation of a gas jet are also suitable for manufacture of a coating consisting of an aluminium layer with a cermet layer applied onto it. In that case, first aluminium is applied to the anode surface from one device, and then the cermet-type layer is built up with switching in of the second device, with combination of their discharges of aluminium and aluminium oxide, while the latter arrangement is also suitable for formation of a cermet-type layer alone by employment of one burner for aluminium and the other for aluminium oxide. Alternatively, equally good results have been attained with reference to the economics of the method, if the aluminium layer is applied to the anode surface or as intermediate layer of a sandwich coating, by flame spraying by means of an acetylene-oxygen mixture.

Below are some examples of manufacture of anodes embodying the invention. These examples also involve use of methods which are the subject of:

Example 1

On a carbon anode for aluminium electrolysis, the surfaces are first preferably lightly sand sprayed with corundum sand. A layer about 0.4 mm. thick of aluminium oxide is applied by means of a water-stabilised plasma burner of 150 kw. power input and a spray output of about 20 kg. per hour. This produces successive traverses with cross-wise coverage of the surface. The distance of the anode of the plasma burner from the surface of the carbon anode amounts to 25 to 30 cm. The rate of deposition of the aluminium oxide amounts to about 16 kg. per hour. The aluminium oxide which is not deposited is sucked up, collected and delivered back to the process. The grain size of the aluminium oxide amounts to 75 to 100%.

Example 2

The surface to be protected is a usual carbon anode for aluminium electrolysis is preferably lightly sand sprayed with corundum sand. A layer of aluminium about 0.1 mm. thick is applied with the help of a metallisation burner i.e. an oxyacetylene burner. Directly thereupon a layer of Al_2O_3 about 0.3 mm. thick is applied with the help of a water-stabilised plasma burner with a power input of 150 kg. and a spray output of 20 kg. per hour by successive traversing of the surface three times with the plasma flame, while the distance of the anode of the plasma assembly from the surface of the carbon anode 25 amounts to 25 to 30 cm. The deposition efficiency of the Al_2O_3 amounts to about 80%. The applied Al_2O_3 (industrial alumina) has a grain size of 75 to 150%.

Example 3

The surface to be protected is provided, as described in Example 2, with a layer about 0.1 mm. thick of aluminium metal. Then a quantity of about 20 kg. Al_2O_3 and about 5 kg. aluminium metal per hour is applied with the help of a water-stabilised plasma burner of 150 kw. power input, which is supplied with a continuously-fed aluminium wire anode of 3.5 mm. diameter, with formation of a cermet-type layer of about 0.4 mm. thickness. The remaining conditions correspond entirely with those given in Example 2.

Example 4

The surface to be protected is sand sprayed as described in Example 1, and thereupon is plasma coated with a quantity of about 7 kg. aluminium and about 20 kg. Al_2O_3 per hour with the help of a water-stabilised plasma burner of 150 kw. power input, which is provided with a continuously-fed aluminium wire anode of 3.5 mm. diameter, with formation of a cermet-type layer of 0.5 mm. thickness. The separation between the surface and the aluminium wire anode amounts to 20 to 25 cm.; the layer is applied by traversing of the plasma flame four times over the surface. As in the other examples, care must here also be taken, that the plasma jet is directed as perpendicularly as possible onto the surface of the carbon anode.

What is claimed is:

1. An electrode for use in electrolysis, the surface of which electrode is provided with a coating for hindering oxidation of the anode material, wherein the coating consists of aluminium oxide and aluminium, and the aluminium oxide has been applied as particles at least partly molten in a plasma burner, and has solidified in situ, so that in the coating the said particles are bonded together at least over a part of their exterior.

2. An electrode according to claim 1, wherein the coating has a thickness of 0.1 to 1.0 mm.
3. An electrode according to claim 1, including a layer of aluminium applied over the said coating.

4. An electrode according to claim 3, wherein the layer of aluminium has a thickness of 0.05 to 1.0 mm.

5. An electrode according to claim 1, including a basis layer of aluminium between the surface of the anode and the said coating.

6. An electrode according to claim 5, wherein the basis layer has a thickness of 0.05 to 1.0 mm.

7. An electrode according to claim 1, wherein the said coating consists of a cermet-type material.

8. An electrode according to claim 7, wherein the cermet-type material consists of aluminium oxide and aluminium with a weight ratio of between 10:1 and 2:1.

9. An electrode according to claim 1, wherein the coating includes a small portion of cryolite added to the aluminium oxide as a melting point depressing additive.

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