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54 **Alumina reduction cell, methods of producing such a cell, and use thereof in the manufacture of aluminium.**

57 Alumina reduction cells are used to prepare aluminium metal by the electrolytic reduction of alumina dissolved in molten cryolite. The molten aluminium formed collects at the bottom of the cell. When the cell floor serves as cathode and is of carbon, the molten aluminium does not wet the carbon making it necessary to increase the inter-electrode distance and reducing efficiency.

The invention provides a cell wherein a floor cathode comprises a carbon substrate having an adherent surface layer of electrodeposited titanium diboride which is readily wettable by molten aluminium and which makes possible considerable savings in the expense of running the cell. The titanium diboride layer can be formed *in situ* in the cell or can be formed outside the cell on carbonaceous elements which are subsequently installed in the cell.

EP 0 021 850 A1

- 1 -

DESCRIPTION"ALUMINA REDUCTION CELL, METHODS OF PRODUCING SUCH A CELL, AND USE THEREOF IN THE MANUFACTURE OF ALUMINIUM"

This invention relates to an improved alumina reduction cell, to methods of producing such a cell, and to the use of the cell in the manufacture of aluminium.

5 Aluminium metal is prepared electrolytically by the reduction of alumina. Conventional alumina reduction cells comprise a vessel having a refractory lining, frequently of carbon, containing, as molten electrolyte, alumina dissolved in fused cryolite. The
10 floor of the cell or vessel is typically made of a carbonaceous material, which not only provides thermal insulation, but also serves as part of the cathode. At least one anode is disposed within the vessel spaced apart from the cathode. Upon the passage of an electric
15 current between anode and cathode, aluminium is formed by electrolytic reduction of the alumina. The molten aluminium formed is denser than the cryolite electrolyte and collects as a pool of metal on the floor of the cell. Molten aluminium metal is drained from the cell in order
20 to prevent too deep a pool of aluminium metal forming on the floor of the cell. Quite clearly, the molten aluminium on the floor of the cell cannot be allowed to touch the anodes or short-circuiting of the cell would take place.

25 Molten aluminium does not readily wet carbonaceous materials. This can quite easily be demonstrated by allowing a drop of molten aluminium to contact an untreated surface of a carbonaceous substrate whereupon the aluminium will form a bead or globule and
30 will not spread over the surface of the carbonaceous

- 2 -

substrate. The fact that molten aluminium metal does not readily wet or spread over the floor of an alumina reduction cell can cause operating problems. The deeper is the layer of molten aluminium at the bottom of a cell, the greater necessarily must be the inter-electrode distance. The greater is the inter-electrode distance the lower is the operating efficiency of the cell and the greater is the power requirement of the cell. Not only this, but the layer of molten aluminium formed upon an untreated carbonaceous cell floor is of sufficient thickness to permit thermal or magnetic currents to develop therein, making the layer somewhat unstable and liable to turbulence, so that waves can form in the layer and which can touch an anode and short-circuit the cell. The depth of the layer of molten aluminium at the bottom of a cell may vary from cell to cell, but typically is in the range from 3 to 8 centimetres.

Proposals have been made to modify the floor of an alumina reduction cell. For example, it is known that titanium and zirconium carbides are strongly wetted by molten aluminium and have good electrical conductivity and low solubility in molten aluminium. U.S. Patent Specification No. 3,471,380 (Bullough - issued 7th October 1969) describes a method of improving the performance of an alumina reduction cell by the formation of a coating of a beneficial metal carbide, in particular of titanium or zirconium, on the carbon cathode surface of the cell. The coating is produced by adding to the electrolyte within the cell a refractory metal or compound thereof so that, during operation of the cell, a coating of a carbide of the metal forms upon the carbon cathode surface. However, refractory metal carbides do not provide ideal coatings for carbon substrates in an alumina reduction cell since they are susceptible to thermal shock.



- 3 -

U.S. Defensive Publication T993002 (Kaplan et al - issued 1st April 1980) discloses the provision of a titanium diboride surface to contact molten aluminium at the bottom of an alumina reduction cell.

5 The titanium diboride surface is provided by refractory tiles secured to a carbonaceous substrate. The tiles are stated to be wettable by molten aluminium and to be chemically inert under the conditions of the electrolytic process. Although titanium
10 diboride is less susceptible to thermal shock than titanium carbide and a titanium diboride surface would make possible considerable energy savings during operation of the alumina reduction cell, the tiles proposed for use in the Defensive Publication are of
15 considerable thickness and therefore necessarily wasteful of titanium diboride, a very expensive material. Also problems arise from the need to bond the tiles to the carbonaceous substrate. The method of the Defensive Publication is considered to be so expensive in terms
20 of the tiles required, that the ostensible cure would be worse than the complaint since greater expense would be incurred in fabricating and installing the tiles than could be saved by virtue of the reduced energy consumption of the alumina reduction process.

25 U.S. Patent Specifications Nos. 3,697,390 and 3,827,954 (McCawley et al - issued 10th October 1972 and 6th August 1974, respectively) disclose the formation of platings of titanium, zirconium or hafnium borides on substrates by electrodeposition from fused borate baths.
30 The anodes to be used comprise a metal of the desired boride or the boride itself. No mention is made in either Patent Specification of the deposition of metallic boride coatings on carbonaceous substrates, and the cathodes used in the Examples are all metallic, for
35 example being of molybdenum, nickel or "Inconel".



- 4 -

Japanese Laid-Open Patent Application 1974-67844 (Toyota -
published 1st July 1974) discloses a method of coating
ferrous metals or their alloys with a titanium diboride
layer by electrodeposition from a molten bath of a
5 borate salt containing dissolved titanium. The reference
states that the metal or alloy cathode to be used in
the method must have a carbon content of less than 0.1
percent if a titanium carbide layer is not to be
formed.

10 While therefore the prior art has recognised
the desirability of providing an alumina reduction cell
with a cathode, or cathode coating, that is readily
wettable by molten aluminium and has suggested titanium
diboride in this context, it has hitherto been considered
15 that a layer of titanium diboride could not be formed
on a carbonaceous substrate by electrodeposition without
the formation of titanium carbide. We have now found
surprisingly that a layer of titanium diboride can be
formed upon a carbonaceous substrate by electrodeposition.

20 The invention accordingly provides an
aluminium reduction cell comprising a vessel having a
refractory lining and at least one anode disposed within
said vessel, wherein at least part of the vessel floor
serves as a cathode and said cathode comprises a carbon
25 substrate having an adherent surface layer of
electrodeposited titanium diboride.

The alumina reduction cell of the invention
can be prepared by-electrodepositing the titanium
diboride layer on a carbonaceous cathode in situ in the
30 cell, or by electrodepositing a layer of titanium
diboride on at least one of the surfaces of carbonaceous
blocks or elements externally of the cell and then
installing the blocks or elements in a cell to provide
the coated cathode surface. In the latter case the
35 coated blocks or elements are positioned on the floor of



- 5 -

cell and secured thereto with, for example, pitch.

An adherent surface layer of titanium diboride is formed in accordance with the invention, either on a carbonaceous cell floor or on constituent
5 carbonaceous blocks or elements, by electrodeposition from a molten electrolyte containing a source of boron and having titanium or a compound thereof dissolved therein. The carbonaceous cell floor or the blocks or
10 elements serve as cathode and a firmly adherent surface layer forms thereon, with the electrodeposit of titanium diboride faithfully following the surface contours of the cathode. The anode preferably is of carbon since it has been found that better quality electrodeposits are formed with carbon anodes. It is, however, possible to
15 use consumable titanium anodes which dissolve anodically to provide titanium values in the molten electrolyte. When using titanium anodes it is not necessary separately to dissolve a source of titanium in the molten electrolyte. If, however, a source of titanium is to be dissolved in
20 the electrolyte, as for example when using carbon anodes, it is preferred to use titanium dioxide or a titanate as such a source. It is particularly preferred to use an electrolyte containing 2 to 10% by weight of titanium dioxide as a source of titanium. The molten
25 electrolyte must contain a source of boron, and it is preferred to use an anhydrous borate as such a source, more particularly sodium tetraborate (borax) or potassium tetraborate. In general the molten electrolyte should be sufficiently conductive as to provide adherent
30 electrodeposits of titanium diboride on the carbonaceous cathode and also sufficiently fluid as to permit ready removal from an electrolytic cell. When the electrodeposit of titanium diboride is formed in situ in an alumina reduction cell, the electrolyte
35 should be removed and the cell cleaned.

- 6 -

The conditions of the electrolysis for the deposition of the titanium diboride layer are not particularly critical, but it has been found that the cell voltage should not exceed 2 volts if good quality electrodeposits are to be formed. At voltages above 2 volts the electrodeposit tends to become powdery and less adherent. Preferred voltages are from 1.2 to 1.8 volts. The current density can vary over a wide range and suitable values are from 5 to 100 milliamps per cm^2 . The temperature should clearly be one at which the electrolyte is molten and of the requisite conductivity. Suitable temperatures are in the region of 900 to 1000°C. If necessary a flux can be added to the electrolyte to assist in operating at a desired temperature. The electrolyte desirably is agitated to assist in the formation of good quality deposits and agitation can conveniently be provided by means of a rotating anode. The duration of the electrolysis will be dependent to a large extent upon the thickness desired for the titanium diboride surface layer. Prolonging the electrolysis, replenishing the electrolyte as required, will result in the production of thicker electrodeposits. If desired, successive layers can be built up by repeated electrodepositions.

The titanium diboride layer can be electrodeposited directly onto an untreated carbonaceous cathode, but an underlayer of a titanium carbide electrodeposit can be provided if desired.

The surface layer of titanium diboride on the carbonaceous cathode of the alumina reduction cell of the invention not only is readily wetted by molten aluminium with the advantages referred to above, but also reduces the penetration of the cathode by sodium metal which can be formed during the alumina reduction. When sodium penetrates a carbonaceous cathode it can cause breakdown of the cathode.

- 7 -

The invention will now be illustrated by the reference to the following Examples.

EXAMPLE 1

5 An electrolyte consisting of 5% by weight TiO_2 and 95% by weight $\text{K}_2\text{B}_4\text{O}_7$ was electrolysed using graphite electrodes. The anode was also used as a stirrer. Electrolysis was continued for four hours at 950°C at 1.3 to 1.8 volts and a current density of 36 to 56 milliamps per cm^2 (m.a. cm^{-2}).

10 After electrolysis the residual electrolyte was removed and the cathode was washed with water. X-ray diffraction showed the presence of titanium diboride and optical microscopy showed it to be present as a layer about 50 microns thick. Wetting tests showed that
15 it was readily wetted by molten aluminium.

EXAMPLE 2

An electrolyte containing 5% TiO_2 by weight and 95% by weight $\text{Na}_2\text{B}_4\text{O}_7$ was electrolysed using a carbon cathode and a graphite anode for 3.5 hours at
20 950°C and at 1.3 volts and a current density of 60 to 100 m.a. cm^{-2} . After electrolysis the cathode was washed clean of electrolyte and examination by X-ray diffraction and optical microscopy showed the presence of an adherent titanium diboride layer.

25 EXAMPLE 3

$\text{Na}_2\text{B}_4\text{O}_7$ was electrolysed using a graphite cathode and a rotating titanium anode for 5 hours at 950°C at 1.5 volts and current density of 30 m.a. cm^{-2} . After electrolysis the cathode was washed clean of
30 electrolyte and X-ray diffraction and optical microscopy showed the presence of an adherent titanium diboride layer.

EXAMPLE 4

An electrolyte containing 2% by weight TiO_2
35 and 98% by weight $\text{K}_2\text{B}_4\text{O}_7$ was electrolysed using a graphite

- 8 -

cathode and a titanium anode for five hours at 950°C at a voltage of 1.2 volts and a current density 5 m.a. cm⁻². After electrolysis the remaining electrolyte was removed and X-ray diffraction and optical microscopy showed the graphite cathode to be coated with a layer of titanium diboride with an estimated thickness 20 microns.

EXAMPLE 5

K₂B₄O₇ was used as an electrolyte with a graphite cathode and titanium anode. This was electrolysed for 4.5 hours at 950°C at 1.5 volts and a current density of 35 m.a. cm⁻². After electrolysis the remaining electrolyte was washed off. X-ray diffraction and optical microscopy showed the presence of a layer of titanium diboride on the surface of the graphite cathode with an estimated thickness of about 50 microns.

- 9 -

C L A I M S

1. An alumina reduction cell comprising a vessel having a refractory lining and at least one anode disposed within said vessel, wherein at least part of the vessel floor serves as a cathode characterised in that said cathode comprises a carbon substrate having an adherent surface layer of electrodeposited titanium diboride.
2. A method of producing an alumina reduction cell as claimed in claim 1 characterised by electrolysing within an alumina reduction cell comprising a vessel having a refractory lining and at least one anode disposed within said vessel, at least part of the vessel floor being formed of carbon and serving as a cathode, a molten electrolyte containing a source of boron and having titanium or a compound thereof dissolved therein, to form an adherent surface layer of titanium diboride on said cathode by electrodeposition.
3. A method of producing an alumina reduction cell as claimed in claim 1 characterised by electrodepositing an adherent surface layer of titanium diboride on at least one surface of a plurality of carbonaceous blocks from a molten electrolyte containing a source of boron and having titanium or a compound thereof dissolved therein, and installing the resulting carbonaceous blocks in the vessel floor of an alumina reduction cell, said at least-one surface of the blocks serving as the cathode surface of the cell.
4. A method according to claim 2 or 3 characterised in that the molten electrolyte contains an anhydrous borate as a source of boron.
5. A method according to claim 4 characterised in that the borate is sodium or potassium tetraborate.
6. A method according to claim 4 or 5 characterised in that the electrolyte has titania or a titanate

- 10 -

dissolved therein and electrolysis is conducted using a carbon anode.

7. A method according to claim 4 or 5 characterised in that the electrolysis is conducted using a consumable titanium anode which dissolves anodically in a melt initially consisting essentially of an anhydrous borate.

8. A method according to any one of claims 2 to 7 characterised in that electrolysis is conducted at a voltage not exceeding 2 volts.

9. Use of an alumina reduction cell as claimed in claim 1 or as produced by a method as claimed in any one of claims 2 to 8 in the production of aluminium metal by the electrolysis of a molten electrolyte comprising alumina and cryolite.

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