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(54) Title: SLURRY AND METHOD FOR PRODUCING REFRACTORY BORIDE BODIES AND COATINGS FOR USE IN ALUMINIUM ELECTROWINNING CELLS

(57) Abstract

A refractory boride body or coating made of a boride of titanium, chromium, vanadium, zirconium, hafnium, niobium, tantalum, molybdenum and cerium is produced from a slurry of the refractory boride or a precursor in a colloidal carrier preferably composed of two or more different grades of the same colloidal carrier selected from colloidal alumina, yttria, ceria, thoria, zirconia, magnesia, lithia, monoaluminum phosphate and cerium acetate. The slurry can also comprise an organic additive selected from polyvinyl alcohol; polyacrylic acid; hydroxy propyl methyl cellulose; polyethylene glycol; ethylene glycol, butyl benzyl phthalate; ammonium polymethacrylate and mixtures thereof. The refractory boride body or coated body is useful as a component of aluminium electrowinning cells.

*(Referred to in PCT Gazette No. 38/1998, Section II)

SLURRY AND METHOD FOR PRODUCING REFRACTORY BORIDE BODIES
AND COATINGS FOR USE IN ALUMINIUM ELECTROWINNING CELLS

Field of the Invention

The invention relates to the production of refractory boride coatings and bodies in particular for use in cells for the electrowinning of aluminium by the electrolysis of alumina dissolved in a molten electrolyte such as cryolite or other fluoride-based electrolytes. The invention more specifically relates to a slurry for producing refractory boride coatings and bodies, as well as bodies coated with or made of refractory boride for use as components of aluminium electrowinning cells.

Background of the Invention

Aluminium is produced conventionally by the Hall-Heroult process, by the electrolysis of alumina dissolved in cryolite-based molten electrolytes at temperatures up to around 950°C. A Hall-Heroult reduction cell typically has a steel shell provided with an insulating lining of refractory material, which in turn has a lining of carbon which contacts the molten constituents. Conductor bars connected to the negative pole of a direct current source are embedded in the carbon cathode substrate forming the cell bottom floor. The cathode substrate is usually an anthracite based carbon lining made of prebaked cathode blocks, joined with a ramming mixture of anthracite, coke, and coal tar, or with glue.

It has long been recognized that it would be desirable to make (or coat or cover) the cathode of an aluminium electrowinning cell with a refractory boride such as titanium diboride that would render the cathode surface wettable to molten aluminium which in turn would

lead to a series of advantages. Many difficulties were encountered in producing refractory boride coatings which meet up to the rigorous conditions in an aluminium electrowinning cell. However, as described in the following patents, such coatings have recently been successfully introduced.

U.S. Patent 5,310,476 (Sekhar et al.) discloses a method of producing a protective refractory coating on a substrate of, *inter alia*, carbonaceous materials by applying to the substrate a micropyretic reaction layer from a slurry containing particulate reactants in a colloidal carrier, and initiating a micropyretic reaction. The micropyretic slurry optionally also contains some preformed refractory material, and the micropyretic slurry may be applied on a non-reactive sub-layer.

U.S. Patent 5,364,513 (Sekhar et al.) discloses a method of producing a protective refractory coating by applying to the substrate a reactive or non-reactive layer from a slurry containing particulate reactants and/or preformed particulate refractory materials in a colloidal carrier, and initiating a micropyretic reaction or non-reactive sintering. The colloidal carrier was selected from the group consisting of colloidal alumina, yttria, ceria, thoria, zirconia, magnesia, lithia, monoaluminum phosphate, cerium acetate and mixtures thereof. Various colloid mixtures were disclosed, such as colloidal alumina-colloidal silica and colloidal alumina-monoaluminium phosphate.

U.S. Patent No. 5,651,874 (de Nora et al.) discloses applying a protective coating of a refractory boride such as TiB_2 to a carbon component of an aluminium electrowinning cell, by applying thereto a slurry of particulate boride in a colloid in several layers with drying between each layer.

These coatings have shown outstanding performance compared to previous attempts to apply refractory coatings

to components of aluminium electrowinning cells. These aluminium-wettable refractory boride coated bodies can be used in conventional cells with a deep aluminium pool and also permit the elimination of the thick aluminium pool
5 required to partially protect the carbon cathode, enabling the cell to operate with a drained cathode.

These refractory boride coated bodies have the following attributes: excellent wettability by molten aluminium, inertness to attack by molten aluminium and
10 cryolite, low cost, environmentally safe, ability to absorb thermal and mechanical shocks, durability in the environment of an aluminium production cell, and ease of production and processing. The boride coating also acts as a barrier to sodium penetration.

15 The refractory boride coated bodies find many applications on account of their excellent resistance, protection, and stability when exposed to the corrosive conditions existing in the cell even when the temperature of operation is low as in the Low Temperature electrolysis
20 process for the production of aluminium, see for example U.S. Patent No 4,681,671 (Duruz).

For most applications, thin coatings (less than 1 mm thick) are required and the methods for applying such thin coatings in one or more layers from a slurry in a
25 colloidal carrier have proven to be essentially problem-free. Nevertheless, for some special applications, for example coating certain types of drained-cathode surfaces, it would be desirable to have thicker coatings.

When, however, it was attempted to produce thicker
30 coatings, some problems were encountered, in particular undesirable mud-cracking was found to occur in the finished, dried coating when the coating thickness exceeded about 1 mm or even only 0.8 mm depending on the coating formulation. Mud-cracking involves cracks ranging
35 in width from 0.1 mm to 1 mm. Hairline cracks, typically less than 0.1 mm, (generally from 0.03 to 0.09 mm) are

also formed but are more acceptable.

Despite this problem of mud-cracking as the thickness increases, the coatings of U.S. Patent 5,651,874 (de Nora et al) remain outstandingly the best available industrially-applicable coatings.

In WO 97/08114 (Sekhar et al.) filed 21.08.96, priority U.S. 08/519,711 of 28.08.95 which constitutes prior art under PCT Rule 33.1(c), it has been proposed to make bodies of refractory boride, for example by slip casting or pressing a slurry of particulate boride in a colloid.

Summary of the Invention

The invention sets out to improve the production of refractory boride coatings or bodies for use as cell components for aluminium electrowinning cells, especially for use as cathodes.

One object of the invention is to provide an improved slurry for the production of bodies or coatings of refractory boride.

Another object of the invention is to produce refractory boride coated bodies and refractory boride bodies starting from readily available and relatively inexpensive commercial particulate borides or their precursors in a specific colloidal carrier.

A specific object of the invention is to produce bodies coated with refractory borides with coating thicknesses equal to or greater than those previously possible, without mud-cracking, the coatings being aluminium-wettable and electrically conductive so they can serve as coatings for cathodes or other cell components of aluminium production cells.

In the production of "thick" refractory boride coatings, it has been discovered that the mud-cracking problem can be alleviated by utilizing specific colloidal carriers. Moreover, it has been observed that these specific colloidal carriers are also advantageous when producing normal "thin" coatings and even more



advantageous when producing bodies of refractory borides, as opposed to coatings.

According to one main aspect of the invention, a slurry for the production of bodies or coatings of refractory boride comprises particulate preformed refractory boride and/or particulate precursors of refractory boride in a colloidal carrier which comprises colloidal particles with a non-gaussian particle size distribution, comprising a mixture of at least two different grades of the same colloid having mean particle sizes which differ from one another, each grade of colloid having a generally gaussian particle size distribution.

In contrast to the known colloid mixtures of different colloidal components (colloidal alumina and colloidal silica, for example) this colloidal carrier according to the invention is obtainable by mixing two different "grades" of the same colloid, producing a desirable particle size distribution.

"Grade" is to be understood as a range of particle sizes of the colloidal particles, with the mean particle size and at least 50% of the particles within that particular range. Commercially available colloids have a predominant particle size with generally gaussian particle size distribution.

Use of this bi- or multigrade colloidal carrier, advantageously in combination with an organic additive, provides an unexpected combination of properties, namely better homogeneity/bonding without cracking and enhanced protection against sodium penetration when the coating or body is used as a component in an aluminium production cell. Moreover, the slurry with this mixed colloidal carrier has improved thixotropic properties, in particular it remains in suspension much longer than standard colloids, which leads to significant cost savings. The thixotropic mix minimizes sedimentation of the refractory boride powders and the aged dispersion



does not result in dense sediments. The slurry with the mixed colloid thus remains stable, providing increased shelf life, while

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remaining easy to apply, for example by brushing. Surprisingly, use of the modified colloidal carrier also leads to a lowering of the resistivity of the coating or body, thereby increasing the cell efficiency.

5 It should be noted that mixing of different types of colloids is not normally to be recommended because physical and chemical reactions may take place resulting in coagulation, flocculation, rise in pH or irreversible
10 invention, one colloid will generally be of the polymeric type, and the other non-polymeric.

Usually, two distinct fractions of colloidal particles have mean particle sizes which differ from one another by 10-50 nanometers, and the slurry can include a
15 first fraction of colloidal particles with a mean particle size in the range 5-50 nanometers (e.g. 10-30 nanometers), and a second fraction of colloidal particles with a mean particle size in the range 30-100 nanometers (e.g. 40-60 nanometers). This slurry optionally further includes a
20 third distinct fraction of colloidal particles with a mean particle size in the range 100-250 nanometers.

The first and second particle fractions of the slurry can be in a volume ratio from 10:6 to 10:16, for example from 10:8 to 10:14 or more particularly from 10:10
25 to 10:12, i.e. by volume of the colloids in the mixture.

In another aspect, the slurry according to the invention comprises 30-50 volume% of colloids with a mean particle size less than 20-40 nanometers and 70-50 volume% of colloids with a mean particle size greater than 20-40
30 nanometers. For example the colloid can contain 30-50 volume%, say about 40 volume%, of colloids with a mean particle size less than about 30 nanometers and 70-50 volume%, say about 60 volume% of colloids with a mean particle size greater than about 30 nanometers.

35 In advantageous embodiments, the colloids contain particle fractions wherein the largest fraction has a mean

diameter of 60 nanometres, or even 50 nanometres. Such colloids contain a large spread of particles with diameters less than 50 nanometres.

The slurry's colloidal carrier is usually selected
5 from the group consisting of colloidal alumina, yttria, ceria, thoria, zirconia, magnesia, lithia, monocalcium phosphate, cerium acetate and mixtures thereof. Normally, however, the colloidal particles of the colloidal carrier are all particles of the same colloid. It is surprising
10 that a mixture of one colloid, say colloidal alumina, obtainable by mixing together two grades of colloidal alumina with different mean particle sizes, is advantageous compared to the individual grades.

The colloidal carrier is usually in an aqueous medium
15 but, advantageously, the slurries of the present invention also include at least one organic additive selected from the group consisting of polyvinyl alcohol, polyethylene glycol, ethylene glycol, polyacrylic acid, hydroxy propyl methyl cellulose, butyl benzyl phthalate and aluminium
20 polymethacrylate.

The colloid may be derived from colloid precursors and reagents which are solutions of at least one salt such as chlorides, sulfates, nitrates, chlorates, perchlorates or metal organic compounds such as alkoxides, formates, acetates of aluminium, silicon, yttrium, cerium, thorium
25 zirconium, magnesium and lithium. These colloid precursors or colloid reagents can contain a chelating agent such as acetyl acetone or ethylacetoacetate. The aforesaid solutions of metal organic compounds, principally metal
30 alkoxides, can be of the general formula $M(OR)_z$ where M is a metal or complex cation, R is an alkyl chain and z is a number, preferably from 1 to 12.

It is also possible to include further components in the colloidal slurry, for example powdered aluminium which
35 improves the conductivity of the resulting coating or body.

The pre-formed particulate refractory boride is usually selected from borides of titanium, chromium, vanadium, zirconium, hafnium, niobium, tantalum, molybdenum and cerium. The preferred particulate refractory
5 boride is titanium diboride.

When choosing the refractory boride powder, the particle size selection is of some importance. It is preferable to choose particle size below 100 micrometers and to choose particle sizes which are varied. For example
10 it is preferable to choose particle sizes extending over a range where the smallest particles are at least two times and preferably at least three times smaller than the large ones. Generally, the ratio of the particle sizes will be in the range from 2:1 to 15:1, usually from about 3:1 to
15 10:1, for instance a ratio of about 3:1 with large particles in the range 15 to 30 micrometers and small particles in the range 5 to 10 micrometers, or a ratio of about 10:1 with large particles in the range from 30 to 50 micrometers and small particles in the range from 3 to 5
20 micrometers. Usually, the preformed particulate metal boride has particles with sizes in the range from about 3 micrometers to about 50 micrometers.

It has been ascertained that the choice of the particle size of the metal boride influences the maximum
25 thickness obtainable without mud-cracking and, for all types and mixtures of the refractory boride, use of the mixed colloidal carrier according to the invention increases the maximum obtainable thickness without mud-cracking. Mud-crack-free coatings up to 4, 6 or even 8 mm
30 thick can thus be achieved.

The slurry usually contains 5 - 100 g of the pre-formed particulate refractory boride per 10 ml of colloid and each colloid has a dry colloid content corresponding to up to 50 weight% of the colloid plus liquid carrier,
35 preferably from 5 to 30 weight%, the optimum being from 7-20 weight%.

The Method

According to the invention, there is provided a method of applying a refractory boride to a component of a cell for the production of aluminium by the electrolysis of alumina dissolved in a cryolite-based molten electrolyte, to protect the component from attack by liquid and/or gaseous components of the electrolyte in the form of elements, ions or compounds, the method comprising applying to the surface of the component the previously described mixed bi- or multigrade slurry and drying the coated surface. All previously-described features of the slurry are applicable in the method, such as the inclusion of an organic additive.

The invention also provides a method of producing a body coated with a refractory boride from the group consisting of the borides of titanium, chromium, vanadium, zirconium, hafnium, niobium, tantalum, molybdenum and cerium. The coating according to the invention includes a refractory boride containing a specific grade of colloidal binder or preferably at least two colloids, selected from the group consisting of colloidal alumina, silica, yttria, ceria, thoria, magnesia, lithia, monoaluminium phosphate and cerium acetate, each said colloid having a different grade, and is obtained from a slurry of particulate refractory boride in one or more of said colloids, by forming and drying the slurry.

Drying of the slurry is followed by heat treatment before or after the component is installed in an aluminium production cell.

The slurry is usually applied in several layers, for example by brushing, by roller or spraying, each layer being allowed to dry at least partially in the ambient air or assisted by heating before applying the next layer, followed by a final heat treatment to dry the slurry after application of the last layer. Heating at a temperature from 80 to 300°C can for example be carried out each time

an added thickness of about 0.2 to about 0.6 mm is reached by the application of one or more layers.

The resulting coating of refractory boride usually has a dried thickness up to 8.0 mm without mud-cracking.

5 Another aspect of the invention is a method of producing a self-sustaining body of a refractory boride preferably from the group consisting of the borides of titanium, chromium, vanadium, zirconium, hafnium, niobium, tantalum, molybdenum and cerium, in which the body
10 includes a refractory boride and a colloid preferably from the group consisting of colloidal alumina, silica, yttria, ceria, thoria, zirconia, magnesia, lithia, monoaluminium phosphate and cerium acetate, and is obtained from the
15 preformed refractory boride, by forming and drying the slurry.

For example, the slurry is cast into a die or mold on a porous layer and the cast slurry is allowed to dry by draining the liquid through the porous layer. Further
20 methods of forming bodies of refractory boride from slurries are disclosed in WO 97/08114 (Sekhar et al.).

To assist rapid wetting by molten aluminium, the bodies made of or coated with refractory borides may be exposed to molten aluminium in the presence of a flux
25 assisting penetration of aluminium into the refractory boride, the flux for example comprising a fluoride, a chloride or a borate, of at least one of lithium and sodium, or mixtures thereof. Such treatment favors aluminization of the surface of the body by the
30 penetration therein of aluminium.

The invention also applies to methods of producing bodies or coatings from a slurry according to the invention which contains, instead of or in addition to
35 particulate preformed refractory boride, precursor powders which react to form the refractory boride(s). For instance titanium and boron powders can be reacted in the presence

of preformed titanium diboride which moderates the reaction.

Numerous examples of micropyretic reaction mixtures for this purpose are described in the aforementioned U.S. Patents 5,310,476 and 5,364,513 (both Sekhar et al.), the disclosures whereof are incorporated herein by way of reference.

Cell Components

The invention also concerns cell components of aluminium production cells, in particular those which in use of the cell are exposed to contact with molten cryolite and/or molten aluminium. The cell component is for instance a cathode or forms part of a cathodic cell bottom, or may be a tile or a component such as a weir or a baffle or grid immersed in the molten aluminium.

According to the invention, there is provided a component of a cell for the production of aluminium by the electrolysis of alumina dissolved in a cryolite-based molten electrolyte, which cell component is subjected to molten cryolite and/or to molten aluminium. The cell component comprises a body or a coating made from the slurry of the present invention.

In the case of components coated with the refractory boride, the main body or substrate of the component will often be made of carbon or of a carbon-containing composite. It is also possible to coat refractory substrates, such as various types of alumina or other refractory oxycompounds as well as composite materials comprising an electrically conductive and an electrically non-conductive component.

For example, a body can be made including titanium diboride as the reaction product of titanium oxide, boron oxide and aluminium from a slurry according to the invention and/or coated with a refractory boride such as titanium diboride by the method of the invention.

Usually, the component will have a porous surface, which is the case for carbon, but coatings can also be applied successfully to essentially impervious substrates.

The component may be a current-carrying component for
5 example a cathode, a cathode current feeder, or the
cathodic part of a bipolar electrode. Particular
advantages are achieved for drained cathodes where the
produced aluminium continuously drains from the cathode
surface which is made of refractory boride or coated
10 with a relatively thick and crack-free coating of
refractory boride according to the invention.

The bodies may consist of blocks or tiles that can be
fitted together to form a cell bottom of an aluminium
production cell, which acts to carry current to the
15 cathodic pool if there is one, or to a thin layer of
aluminium in drained cells, or they may form a packed bed
of bodies on a cell bottom.

The component advantageously forms part of a cathode
through which the electrolysis current flows, the
20 refractory boride cathodic surface being in contact with
the cathodically-produced aluminium. For example, it is
part of a drained cathode wherein the refractory boride
forms the cathodic surface on which the aluminium is
deposited cathodically, the component's drained surface
25 being arranged usually upright or at a slope to assist
draining of the aluminium. Arrangements with a horizontal
drained surface are also possible.

For example, providing a "thick" and crack-free
refractory boride coating according to the invention is
30 very advantageous when applied to a drained-cathode grid
as described in U.S. Patent 5,472,578 (de Nora).

Electrolytic Cells and Operation

The invention also relates to an aluminium
electrowinning cell comprising a cell component including
35 a body or coating as discussed above as well as a method

of producing aluminium using such cells and methods of operating the cells.

Such cells may comprise a component which in operation of the cell is exposed to molten cryolite or aluminium, said component including a body or coating as
5 discussed above, wherein the product aluminium is in contact with the refractory boride, which may be a cathode or form part of a cathodic cell bottom.

A method of operating the cells comprises producing a
10 cell component which includes a body or a coating made from a slurry as described above; optionally subjecting the coated component to heat treatment; placing the component in the cell so that it will be contacted by the cathodically produced aluminium, and/or the molten
15 electrolyte; and operating the cell to produce molten aluminium.

As mentioned previously, in the case of cell components coated with the refractory boride, the main
20 body or substrate of the component can be made of carbon or of a carbon-containing composite or a refractory material as well as composite materials comprising an electrically conductive and an electrically non-conductive component.

Advantageously, the cell includes a component
25 comprising a body including titanium diboride as the reaction product of titanium oxide, boron oxide and aluminium using a slurry according to the invention and/or coated with a refractory boride by the method of the invention.

30 The cell component may be a current-carrying component for example a cathode, in particular a drained cathode.

Operation of the cell can be at normal operating
35 temperatures (about 950°C) or in a low temperature process, with the molten fluoride-based electrolyte containing dissolved alumina at a temperature below 900°C,

usually at a temperature from 680°C to 880°C. The low temperature electrolyte may be a fluoride melt or a mixed fluoride-chloride melt. This low temperature process is operated at low current densities on account of the low alumina solubility.

Detailed Description

The invention will be further described in the following Examples.

Example I

10 A slurry was prepared from a dispersion of 25 g TiB₂, 99.5% pure, -325 mesh (<42 micrometer), with 7 ml of one grade of colloidal alumina (NYACOL® Al-20, a milky liquid with a colloidal particle size grade of about 40 to 60 nanometers, i.e. mean particle size in the range 40 to 60
15 nanometers) and 6 ml of another grade of colloidal alumina (CONDEA® 10/2 Sol, a clear, opalescent liquid with a colloidal particle size grade of about 10 to 30 nanometers, i.e. mean particle size in the range 10 to 30 nanometers).

20 Carbon cathode samples measuring 50 x 20 mm were prepared, coated with the above slurry and allowed to dry naturally. The slurry was easy to apply by brush. The slurry was gel-free for a period of at least 5 days after preparation, which is considerably longer than for the
25 individual grades of colloid.

The dried coatings were adherent and mud-crack free with thicknesses of about 0.80 mm.

The thickness of the coatings can be increased without causing mud-cracking by applying multiple layers and drying the layers prior to application of the next
30 layer at a temperature ranging from 80 to 300°C. Preferably, the drying is undergone after each applied layer as a thickness from about 0.2 to 0.7 mm, preferably from 0.3 to 0.6 mm. Alternatively, for multi-layer
35 coatings, each layer of slurry can be allowed to dry for

several minutes before applying the next with optionally a final drying by baking in an oven or with warm air at 100-150°C.

5 Various TiB_2 powders selected from Advanced Ceramics "HCT-30", Advanced Refractory Technologies Inc. "TGF", and Starck Grades "C" and "D", were used in the slurries. Mud-crack free coatings 4.0 to 6.0 mm thick were obtainable depending on the type of TiB_2 used (best results with Starck Grade "C").

10 Instead of a single grade of TiB_2 , advantageously at least two grades of TiB_2 may be used, each with differing particle sizes. The use of a mixture of TiB_2 powders assists preventing the onset of mud-cracking of thick coatings.

15 The amount of TiB_2 in the slurry was varied from 20 to 30 g and the amount of the colloidal alumina mixture was varied from 10-20 ml total (from 3-10 ml of the NYACOL and from 3-10 ml of the CONDEA). For more dilute slurries a longer drying time was required. For all coatings
20 excellent adhesion to carbon, excellent strength and excellent resistivity was noted.

A coated carbon body produced as above, was subjected to heat treatment at 1250°C for 10 hours under argon, and subjected to a sodium penetration test by connecting it as
25 a cathode in a NaF/NaCl bath (67.7 wt%/32.3 wt%) at 720°C for 4.5 hours at a current density of 0.15 A/cm². Non-coated carbon cathodes subjected to the same treatment show signs of deterioration due to sodium penetration. Improved sodium resistance was obtained the greater the
30 amount of the larger particle size colloid compared to the lower particle size.

The green strength of the coatings or bodies was found to improve the greater the amount of the smaller particles compared to the larger particles.

35 Overall, best results were obtained with a volume ratio of the CONDEA (smaller colloidal particles) to

NYACOL (larger colloidal particles) in the ratio 10:10 to 10:12.

EXAMPLE II (COMPARATIVE)

A slurry was prepared from a dispersion of 25 g TiB_2 ,
5 99.5% pure, -325 mesh (<42 micrometer), per 10 ml of
colloidal alumina containing about 20 weight% of solid
alumina, using the same NYACOL or CONDEA grade as in
Example I, but singly and not mixed. If several coats were
applied, as in Example I, each layer of slurry was allowed
10 to dry for several minutes before applying the next, with
an optional final drying by baking in an oven at 100-
150°C. Coating thicknesses of about 0.15 to about 0.55 mm
were obtainable without mud-cracking. However, for thicker
coatings, mud-cracking was observed.

15 The TiB_2 in the slurry was varied from 5 to 15 g and
the colloidal alumina was varied from 10-40 ml. For more
dilute slurries a longer drying time was required.
Increasing the colloidal alumina content increases the
electrical resistivity by increasing the volume percentage
20 of non-conducting material in the sample.

After the sodium-resistance test as in Example I, the
non mud-cracked "thin" samples showed no sign of
deterioration and were wetted by aluminium. However, the
sodium resistance was not as good as the coating of
25 Example I. The thicker mud-cracked samples displayed
inferior performance.

EXAMPLE III

In order to obtain improved coatings without mud-
cracks (in particular to enable use of lesser-performing
30 grades of TiB_2 and to reduce the need to use two grades of
 TiB_2) certain organic additives were added to the slurry of
Example I. The organic additives tested were: polyvinyl
alcohol; polyacrylic acid; hydroxy propyl methyl
cellulose; polyethylene glycol; ethylene glycol; butyl
35 benzyl phthalate; and ammonium polymethacrylate. The
results are reported in Table I below.

Powder	Coating Thickness (mm)	Weight load (g/cm ²)	Room dry	200° dry	Average flexural strength, (MPa.) (baked at 900°C for 2 hours)	Electrical Resistivity ($\mu\Omega\text{m}$)		
						25°C dried	200°C dried	900°C baked
Example I + 1 ml PEG400	Approx. 1.7	Approx. 0.40	no crack	no crack	3.58	high	2889	108
Example I + 0.5 ml PEG400	Approx. 2.0	Approx. 0.49	no crack	no crack	6.72	5667	1297	30
Example I + 0.25 ml PEG 400	Approx. 1.8	Approx. 0.50	no crack	no crack	8.92	2519	1036	25
Example I + 0.25 ml PEG400	Approx. 1.8	Approx. 0.45	no crack	hairline crack				
Example I + 0.25 ml PEG300	Approx. 1.6	Approx. 0.40	no crack	no crack	10.52	4572	1182	31
Example I + 0.25 ml PEG200	Approx. 1.9	Approx. 0.38	no crack	no crack	8.85	2845	1545	28
Example I + 0.5 ml EG	Approx. 1.4	Approx. 0.20	no crack	hairline crack	5.87	high	7700	116
Example I + 0.5 ml Santicizer	Approx. 2.4	Approx. 0.30	no crack	no crack				
Example I + 1 ml MC (1%)	Approx. 2.4	Approx. 0.35	no crack	hairline crack				
Example I + 0.5 ml MC (2%)	Approx. 1.0	Approx. 0.20	no crack	hairline crack				
Example I + 0.5 ml DAXAD 32	Approx. 2.4	Approx. 0.40	no crack	hairline crack				

PEG400 = CARBOWAX PEG400, UNION CARBIDE; MC = Methocel by DOW Chemical

PEG300 = CARBOWAX PEG300, UNION CARBIDE; DAXAD 32 = Ammonium polymethacrylate by WRGrace Co.

PEG200 = CARBOWAX PEG200, UNION CARBIDE; EG = Ethylene Glycol by FISHER Co.

Santicizer 261 = Butyl benzyl phthalate by MONSANTO; Weight load g/cm² - gms of dry TiB₂ per surface area in g/cm²

Example IV

A slurry was prepared from a dispersion of TiB_2 powder, - 325 mesh (<42 micrometer), in colloidal alumina (CONDEA) ranging from particle size grades of 15
5 nanometers through 200 nanometers consisting of a mixture of three grades (Grade 10/2, mean particle size in the range 10 - 30 nanometers; Grade 20/2, mean particle size in the range 30 - 50 nanometers; Grade 25/5, mean particle size in the range 170 - 230 nanometers). Comparative
10 samples were made with the individual grades of colloid. The slurry was prepared by mixing the TiB_2 powder with the colloidal alumina. All the slurries are made with about 9 weight percent colloidal alumina and the rest TiB_2 powder.

The slurry is then coated onto cathode samples as in
15 Example I or slip cast into block-shaped samples.

The electrical resistivity of block samples was measured by the four point probe method according to the ASTM C611-84 standard, both for the green body and after bonding by heat treatment ("sintering"). A constant
20 current of 1 ampere (generated by a Keithly™ 228A voltage/current apparatus) was passed through the sample and the voltage drop recorded.

The flexural strength of the green and "sintered" composite samples was measured by the four point bending
25 test, performed with an Instron™-4206 machine according to the standard method from the ASTM mechanical property handbook. The crosshead speed of loading was kept at a constant rate of 0.1 mm/min for all samples.

For measurement of the interfacial bonding strength, the "sintered" samples were arranged precisely under the
30 Instron-4206 machine. A small load was applied with the crosshead speed at 1 mm/min. The maximum load was recorded for the calculation of the interfacial bonding strength by strength $(S) = F(\text{maximum load}) / \pi dh$ (Area).

All of the mixed-colloid slurries of Examples I and
35 IV were found to be non-Newtonian, and the viscosity of

the slurry is noted to decrease with an increasing shear rate.

5 Surprisingly and unexpectedly, the electrical resistivity of the green composites was found to be lower (better) and the strength was found to be higher (better). The green resistivity for the CONDEA Disperal 25/5 based slurry composite alone was found to be unexpectedly high. Similar results were obtained for the "sintered" (2 hours at 900°C) composites as well.

10 For coated samples, interfacial bonding strengths were observed to be very low for the CONDEA Disperal Grade 25/5 based slurry alone. The Grade 20/2 based slurry displayed the best interfacial bonding strength.

15 The slurries with a mixture of the Grades 10/2 and 20/2 colloidal alumina and a mixture of Grades 10/2, 20/2 and 25/5 colloidal alumina showed best all round properties: no mud-crack formation, low electrical resistivity and good interfacial bonding.

20 It will be understood that modifications may be made in the present invention without departing from scope of the following claims.

Example V

25 The slurry of Example I was cast into a rectangular die on a plaster of Paris base and was allowed to dry in ambient conditions by draining of the liquid through the plaster. After drying for several hours, the "green" body was removed from the die. It formed a self-sustaining body which was then subjected to heat treatment at 1200°C for 24 hours under Argon. The resulting body of TiB₂ bonded by
30 the dried colloid was mechanically stronger than a comparable body made by slip casting a slurry with the individual grades of colloid and its electrical resistivity was lower. This slip-casting procedure was much more convenient using the mixed-colloid slurry
35 according to the invention, than when using a slurry with the individual grades of colloid.

Where the terms "comprise", "comprises", "comprised" or "comprising" are used in this specification, they are to be interpreted as specifying the presence of the stated features, integers, steps or components referred to, but not to preclude the presence or addition of one or more other feature, integer, step, component or group thereof.

5



The claims defining the invention are as follows:

1. A slurry for the production of bodies or coatings of refractory boride, the slurry comprising particulate preformed refractory boride and/or particulate precursors of refractory boride in a colloidal carrier, wherein the colloidal carrier comprises colloidal particles with a non-gaussian particle size distribution, comprising a mixture of at least two different grades of the same colloid having mean particle sizes which differ from one another, each grade of colloid having a generally gaussian particle size distribution.

2. The slurry of claim 1, wherein said two different grades of colloidal particles have mean particle sizes which differ from one another by 10-50 nanometers.

3. The slurry of claim 2, wherein said two different grades of colloidal particles have mean particle sizes which differ from one another by 10-30 nanometers.

4. The slurry of claim 2, including a first grade of colloidal particles with a mean particle size in the range 5-50 nanometers, and a second grade of colloidal particles with a mean particle size in the range 30-100 nanometers.

5. The slurry of claim 4, including a first grade of colloidal particles with a mean particle size in the range 10-30 nanometers, and a second grade of colloidal particles with a mean particle size in the range 40-60 nanometers.

6. The slurry of claim 4, further including a third different grade of colloidal particles with a mean particle size in the range 100-250 nanometers.

7. The slurry of any one of claims 1 to 6, wherein the first and second particle grade are in a volume ratio from 10:6 to 10:16.



8. The slurry of claim 4, wherein the first and second particle grade are in a volume ratio between 10:8 to 10:14.

9. The slurry of claim 5, wherein the first and second particle grade are in a volume ratio from 10:10 to 10:12.

5 10. The slurry of any one of claims 1 to 9, wherein the colloidal carrier is selected from the group consisting of colloidal alumina, yttria, ceria, thoria, zirconia, magnesia, lithia, monoaluminum phosphate, cerium acetate and mixtures thereof.

10 11. The slurry of any one of claims 1 to 10, wherein the pre-formed particulate refractory boride is selected from borides of titanium, chromium, vanadium, zirconium, hafnium, niobium, tantalum, molybdenum and cerium.

12. The slurry of claim 11, wherein the pre-formed particulate refractory boride is titanium diboride.

15 13. The slurry of claim 12, wherein the colloidal carrier is colloidal alumina.

14. The slurry of any one of claims 1 to 13, comprising 5-100 g of the pre-formed particulate refractory boride per 10 ml of total colloid.

20 15. The slurry of any one of claims 1 to 14, wherein the colloid has a dry colloid content corresponding to up to 50 weight % of the colloid plus liquid carrier.

16. The slurry of claim 15, wherein the colloidal carrier has a dry colloid content corresponding to from 5 to 30 weight % of the colloid plus liquid carrier.

25 17. The slurry of any one of claims 1 to 16, further comprising an organic additive selected from the group consisting of polyvinyl alcohol; polyacrylic acid; hydroxy propyl methyl cellulose; polyethylene glycol; ethylene glycol; butyl benzyl phthalate; ammonium polymethacrylate and mixtures thereof.



18. The slurry of claim 1, wherein the mean particle size of all colloidal particles in the colloidal carrier is in the range from about 15 to about 50 nanometers.

19. The slurry of claim 1, comprising at least two different particle size grades of particulate refractory boride.

20. A component of a cell for the production of aluminium by the electrolysis of alumina dissolved in a cryolite-based molten electrolyte, which cell component is made of or coated with refractory boride obtained from the slurry of any one of claims 1 to 19, the refractory boride being bonded with at least two different grades of colloidal particles having mean particle sizes which differ from one another.

21. The component of claim 20, wherein the colloidal carrier is selected from the group consisting of colloidal alumina, yttria, ceria, thoria, zirconia, magnesia, lithia, monoaluminum phosphate, cerium acetate and mixtures thereof.

22. The component of claim 20 or claim 21, wherein the particulate refractory boride is selected from borides of titanium, chromium, vanadium, zirconium, hafnium, niobium, tantalum, molybdenum and cerium.

23. The component of claim 22, wherein the pre-formed particulate refractory boride is titanium diboride.

24. The component of claim 23, wherein said colloid is colloidal alumina.

25. The component of claim 20, wherein the two colloidal carriers have mean colloidal particle sizes which differ from each other by 10-50 nanometers.

26. The component of any one of claims 20 to 25, wherein the coating further comprises an organic additive selected from the group consisting of polyvinyl alcohol; polyacrylic acid; hydroxy propyl methyl cellulose;



polyethylene glycol; ethylene glycol; butyl benzyl phthalate; ammonium polymethacrylate and mixtures thereof.

27. The component of any one of claims 20 to 26, comprising a non mud-cracked coating of refractory boride having a dried thickness up to 8.0
5 mm.

28. The component of any one of claims 20 to 27, wherein the mean particle size of all colloidal particles in the colloidal carrier is in the range from about 15 to about 50 nanometers.

29. The component of any one of claims 20 to 28, which
10 comprises a carbon-containing body coated with a refractory boride coating.

30. The component of any one of claims 20 to 29, which is a cathode or forms part of or is fitted on a cathodic cell bottom.

31. A method of applying a refractory boride to a component of a cell for the production of aluminium by the electrolysis of alumina dissolved in
15 a cryolite-based molten electrolyte, to protect the component from attack by liquid and/or gaseous components of the electrolyte in the form of elements, ions or compounds, the method comprising applying to the surface of the component the slurry of any one of claims 1 to 19 and drying said coated
20 surface.

32. The method of claim 31, wherein the drying is followed by heat treatment before or after the component is installed in an aluminium production cell.

33. The method of claim 31 or claim 32, wherein the slurry is applied in several layers, each layer being allowed to dry at least partially in the
25 ambient air or assisted by heating before applying the next layer, followed by a final heat treatment to dry the slurry after application of the last layer.

34. The method of any one of claims 31 to 33, comprising heating at a temperature from 100 to 300°C each time an added thickness of about 0.2 to about 0.6 mm is reached.



35. A method of producing a self-sustaining body of refractory boride from the group consisting of the borides of titanium, chromium, vanadium, zirconium, hafnium, niobium, tantalum, molybdenum and cerium, in which the body includes a refractory boride and a colloid from the group
5 consisting of colloidal alumina, silica, yttria, ceria, thoria, zirconia, magnesia, lithia, monoaluminium phosphate and cerium acetate, and is obtained from the slurry of any one of claims 1 to 19 containing preformed refractory boride, by forming and drying the slurry.

36. The method of claim 35, wherein the slurry is cast into a die
10 or mould on a porous layer and the cast slurry is allowed to dry by draining the liquid through the porous layer.

37. A self-sustaining body of refractory boride obtainable by the method of claim 35, the body comprising refractory boride particles bonded with colloidal particles comprising at least two different grades of colloidal particles
15 having mean particle sizes which differ from one another.

38. An aluminium production cell comprising a component which in operation of the cell is exposed to molten cryolite or aluminium, which cell component is made of or coated with refractory boride obtained from the slurry of any one of claims 1 to 19, the refractory boride being bonded with at least
20 two different grades of colloidal particles having mean particle sizes which differ from one another.

39. The aluminium production cell of claim 38, wherein said component is a cathode or forms part of or is fitted on a cathodic cell bottom.

40. A slurry for the production of bodies or coatings of refractory
25 boride according to any one of claims 1 to 19, substantially as hereinbefore described with reference to any one of the accompanying Examples.

41. A component of a cell for the production of aluminium by the electrolysis of alumina dissolved in a cryolite-based molten electrolyte according



to any one of claims 20 to 30 substantially as hereinbefore described with reference to any one of the accompanying Examples.

43. Use of the slurry according to any one of claims 1 to 19, substantially as hereinbefore described.

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DATED this 11th day of October, 1999

10 **MOLTECH INVENT S.A.**

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