

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
5 December 2002 (05.12.2002)

PCT

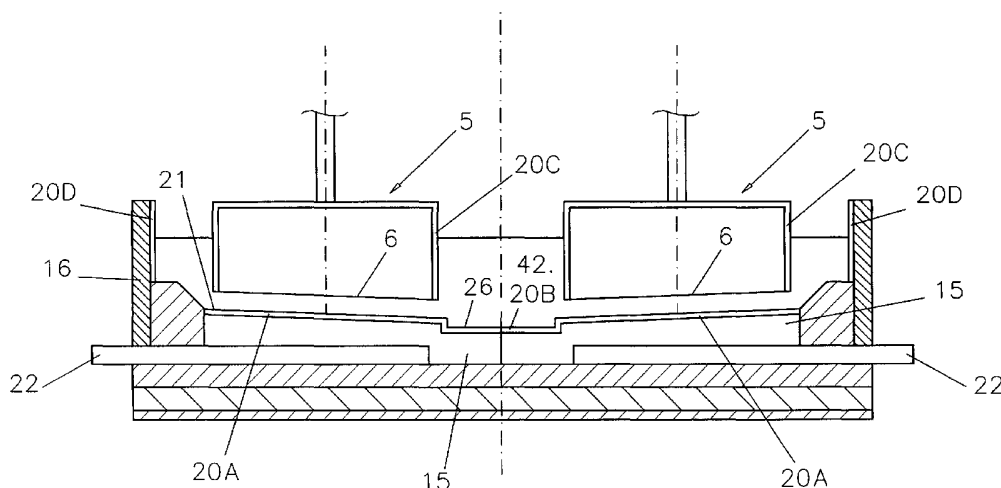
(10) International Publication Number
WO 02/096831 A1

- (51) International Patent Classification⁷: C04B 41/89, (74) Agent: CRONIN, Brian; Moltech S.A, Route de Troinex 9, CH-1227 Carouge (CH).
C25C 3/08, 3/12, F27D 23/04
- (21) International Application Number: PCT/IB02/01932
- (22) International Filing Date: 28 May 2002 (28.05.2002)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: PCT/IB01/00949 30 May 2001 (30.05.2001) IB
- (71) Applicant: MOLTECH INVENT S.A. [LU/LU]; 68-70 Boulevard de la Pétrusse, L-2320 Luxembourg (LU).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): NGUYEN, Thinh, T. [CH/CH]; Rte du Grand-Lancy 165b, CH-1213 Onex (CH). DE NORA, Vittorio [IT/BS]; Sandrigham House, Nassau (BS).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declaration under Rule 4.17:
— of inventorship (Rule 4.17(iv)) for US only

[Continued on next page]

(54) Title: HYDROPHILIC PROTECTIVE LAYERS BONDED ON HYDROPHOBIC SUBSTRATES FOR USE AT ELEVATED TEMPERATURE



(57) Abstract: The invention concerns a method of coating a hydrophobic substrate (5,15,16) with a hydrophilic protective layer free of organic carbon (20A,20B,20C,20D) to protect the substrate (5,15,16) when used at high temperature. The method comprises: applying one or more layers of a slurry comprising hydrophilic colloidal particles and/or hydrophilic inorganic polymeric particles onto the hydrophobic substrate followed by drying to form a heat stable intermediate bonding layer on the hydrophobic substrate. One or more layers of a slurry forming the hydrophilic protective layer are applied onto the intermediate bonding layer followed by drying and/or heat treating to form the hydrophilic protective layer on the intermediate bonding layer. The slurry forming the intermediate bonding layer contains at least one carbon compound selected from hydrophobic carbon monomers and hydrophobic carbon polymers and comprising hydrophilic substituents in an amount sufficient to bond the hydrophilic colloidal/inorganic polymeric particles to the carbon compound(s).

WO 02/096831 A1



Published:

- *with international search report*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

HYDROPHILIC PROTECTIVE LAYERS BONDED ON HYDROPHOBIC
SUBSTRATES FOR USE AT ELEVATED TEMPERATURE

Field of the Invention

The invention relates to the bonding of hydrophilic protective layers, in particular ceramic layers, on hydrophobic substrates, such as carbon substrates, for use at high temperature, in particular in processes for the production, purification or recycling of metals in a molten state during which the protected substrates are exposed to high temperature oxidising and/or corrosive environments.

10 Background of the Invention

The production, purification or recycling of metals, such as aluminium or steel, is usually carried out at high temperature in very aggressive environments, in particular in molten metal, molten electrolyte and/or corrosive gas. Therefore, the materials used for the manufacture of components exposed to such environments must be thermally and chemically stable.

Graphite and other carbonaceous materials are commonly used for components, especially conductive components. Unfortunately, carbon components do not resist oxidation and/or corrosion and must be periodically replaced.

Several proposals have been made to reduce wear of carbon components in such technologies to achieve a higher operation efficiency, reduce pollution and the costs of operation.

In the field of steel recycling using arc electrode furnaces, it has been sought to reduce oxidation wear of inactive lateral faces of carbon arc electrodes, which is caused by exposure to oxygen at the high operating temperature. For instance, in US Patent 5,882,374 (Hendrix) it has been proposed to coat the inactive lateral face of the arc electrode with silica material to avoid consumption of the lateral face.

For the purification of molten metals, in particular molten aluminium, by the injection of a flux removing impurities towards the surface of the molten metal, it

has been proposed to coat carbon components which are exposed to the molten metal with a coating of refractory material as disclosed in W000/63630 (Holz/Duruz).

5 In aluminium production, some components are exposed to molten fluoride-containing electrolyte, molten aluminium and/or anodically produced oxygen. In conventional Hall-Héroult cells these components are still made of consumable carbonaceous materials.

10 It has long been recognised 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.

15 US Patents 5,310,476, 5,364,513 (both in the name of Sekhar/de Nora) and 5,651,874 (de Nora/Sekhar) all disclose applying a protective coating of a refractory material such as titanium diboride to a carbon component of an aluminium electrowinning cell, by applying thereto
20 a slurry of particulate refractory material and/or precursors thereof in a colloid in several layers with drying between each layer.

25 WO98/17842 (Sekhar/Duruz/Liu) discloses another refractory boride coating produced from a slurry of different particle grades of the refractory boride or a precursor in a al carrier which can also comprise an organic carbon-based additive selected from polyvinyl alcohol, polyacrylic acid, hydroxy propyl methyl cellulose, polyethylene glycol, ethylene glycol, butyl
30 benzyl phthalate, ammonium polymethacrylate and mixtures thereof to avoid mud-cracks in the coating.

Summary of the Invention

35 An important object of the invention is to provide a method for coating a hydrophobic substrate, in particular made of carbon, with an hydrophilic protective layer free of organic carbon for use at high temperature.

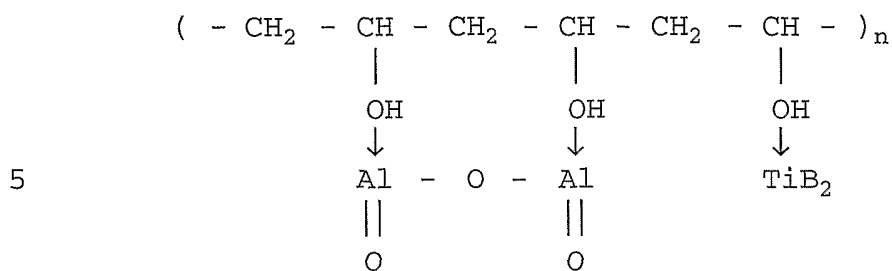
40 Therefore, the invention relates to a method of coating a hydrophobic substrate, in particular made of carbon, with an hydrophilic protective layer free of organic carbon, in particular a metal, ceramic or cermet protective layer, to protect the substrate when used at high temperature in particular in a cell for the electrowinning of aluminium from alumina dissolved in a

fluoride-containing electrolyte. This method comprises:
applying one or more layers of a slurry comprising
hydrophilic colloidal particles and/or hydrophilic
inorganic polymeric particles onto the hydrophobic
5 substrate followed by drying to form a heat stable
intermediate bonding layer on the hydrophobic substrate;
and applying one or more layers of a slurry forming the
hydrophilic protective layer onto the intermediate
bonding layer followed by drying and/or heat treating to
10 form the hydrophilic protective layer on the intermediate
bonding layer.

According to the invention, the slurry forming the
intermediate bonding layer contains at least one organic
carbon compound selected from hydrophobic carbon monomers
15 and hydrophobic carbon polymers and comprising
hydrophilic substituents in an amount sufficient to bond
the hydrophilic colloidal/inorganic polymeric particles
to the monomer and/or polymer carbon compound(s).

Usually, the hydrophilic colloidal particles are
20 made of a heat stable ceramic, e.g. oxide, or a precursor
thereof in the form of a metal salt (e.g. hydroxide) and
have a generally spherical or polyhedral shape of
submicronic dimensions, typically having a diameter
between 10 and 100 nanometer, and are dispersed in an
25 aqueous dispersion liquid. The hydrophilic inorganic
polymeric particles are also made of precursors of heat
stable ceramic such as oxides (e.g. in the form of
hydrolysed metal salts), and are in the form of molecular
chains of submicronic length, typically form 1 to 100 nm
30 long, dissolved in a solution. The magnitude of these
dimensions distinguishes colloids/inorganic polymers from
bulk systems in the following way: (a) an extremely large
surface area and (b) a significant percentage of
molecules reside in the surface of colloidal/polymeric
35 systems. Up to 40% of the molecules may reside at the
surface of the colloidal particles and up to 100% of the
molecules may reside at the surface of the polymeric
particle.

The bonding between the hydrophilic substituent and
40 the hydrophilic colloidal/inorganic polymeric particles
in the intermediate bonding layer is of electrostatic
nature. In the case of a slurry of TiB_2 particles
suspended but not dispersed in a colloidal alumina
carrier containing polyvinyl alcohol as a hydrophobic
45 carbon polymer with hydrophilic substituents, the bonding
of the constituents is as follows:



10 The alcohol groups (-OH) of the polyvinyl alcohol chain interact with the hydrophilic constituents, i.e. alumina and titanium diboride, whereas the hydrophobic hydrocarbon sites (-CH- and -CH₂-) of the polyvinyl alcohol chain are absorbed by the surface of the hydrophobic substrate, e.g. carbon, and secure the intermediate bonding layer thereon.

15 The bonding between the hydrophilic protective layer and the intermediate bonding layer is ensured by the affinity of the hydrophilic constituents of both layers.

20 During heat treatment the polymer and/or monomer carbon compound(s) usually decomposes and the hydrophilic substituents may evaporate leaving the hydrophilic colloidal/inorganic polymeric particles in intimate contact with the carbon remaining from the carbon compound.

25 It follows that the hydrophilic protective layer on the intermediate bonding layer is well bonded on the hydrophobic substrate without containing at its surface organic carbon material that could react during use to form carbides, in particular aluminium carbide, thereby damaging the protecting layer and impairing its electrical conductivity.

30 Suitable hydrophilic substituents of the monomer and/or polymer carbon compound(s) may be selected from -OH, -SO₃Na and -COOH, and combinations thereof. The monomer and/or polymer carbon compound(s) can have a carbon/hydrophilic substituent ratio in the range of 2 to 4. For example, the monomer and/or polymer carbon compound(s) is/are selected from ethylene glycol, hexanol, polyvinyl alcohol, polyvinyl acetate, polyacrylic acid, hydroxy propyl methyl cellulose and ammonium polymethacrylate and mixtures thereof.

40 In one embodiment the hydrophilic protective layer is applied from a slurry comprising colloidal and/or

inorganic polymeric particles and non-dispersed suspended particulate refractory material.

The slurry forming the intermediate bonding layer and/or the slurry forming the hydrophilic protective layer may comprise hydrophilic colloidal particles selected from lithia, beryllium oxide, magnesia, alumina, silica, titania, vanadium oxide, chromium oxide, manganese oxide, iron oxide, gallium oxide, yttria, zirconia, niobium oxide, molybdenum oxide, ruthenia, indium oxide, tin oxide, tantalum oxide, tungsten oxide, thallium oxide, ceria, hafnia and thoria, and precursors thereof, all in the form of colloids; and/or hydrophilic inorganic polymeric particles selected from lithia, beryllium oxide, alumina, silica, titania, chromium oxide, iron oxide, nickel oxide, gallium oxide, zirconia, niobium oxide, ruthenia, indium oxide, tin oxide, hafnia, tantalum oxide, ceria and thoria, and precursors thereof, all in the form of inorganic polymers.

The slurry forming the intermediate bonding layer can further comprise non-dispersed suspended particulate refractory material or a precursor thereof, or particulate carbon.

It is preferable to choose particle size below 100 microns for the non-dispersed (organic carbon-free or organic carbon-containing) refractory particles and, when employing combinations of non-dispersed refractory particles, to choose particle sizes which are varied such that the packing of particles is optimised. For example when choosing a composition containing mostly SiC and some MoSi₂ as non-dispersed particles it is preferable to choose the particle size of the MoSi₂ much smaller (at least three times smaller) than the SiC. Generally, the ratio of the particle sizes will be in the range from 2:1 to 5:1, preferably about 3:1, for instance with large particles in the range 15 to 30 micrometers and small particles in the range 5 to 10 micrometers.

The slurry forming the intermediate bonding layer and/or the slurry forming the hydrophilic protective layer usually comprises non-dispersed particulate refractory material selected from borides, silicides, nitrides, oxynitrides, carbides, oxycarbides, phosphides, oxides, aluminides, of titanium, zirconium, hafnium, vanadium, silicon, niobium, tantalum, nickel, molybdenum and iron, and/or a precursor thereof.

Furthermore, the invention relates to a hydrophobic substrate, in particular made of carbon, coated with an hydrophilic protective layer free of organic carbon and protecting the substrate when used at high temperature, in particular in a cell for the electrowinning of aluminium from alumina dissolved in a fluoride-containing electrolyte. The protective layer is bonded to the substrate through an intermediate bonding layer which comprises dried hydrophilic colloidal particles and/or hydrophilic inorganic polymeric particles.

In accordance with the invention, the dried hydrophilic colloidal/inorganic polymeric particles of the intermediate bonding layer are intimately bonded to carbon on the hydrophobic substrate. The intimate bonding between the hydrophilic colloidal/inorganic polymeric particles and carbon on the hydrophobic substrate is obtainable by applying onto the hydrophobic substrate a slurry comprising the hydrophilic colloidal/inorganic polymeric particles and at least one carbon compound selected from hydrophobic carbon monomers and hydrophobic carbon polymers and comprising hydrophilic substituents in an amount sufficient to bond the hydrophilic colloidal/inorganic polymeric particles to the monomer and/or polymer carbon compound(s).

The intermediate bonding layer and/or the protective layer can comprise dried hydrophilic colloidal/inorganic polymeric particles selected from the above lists.

The intermediate bonding layer and/or the protective layer usually comprises particulate refractory material selected from borides, silicides, nitrides, oxynitrides, carbides, oxycarbides, phosphides, oxides, aluminides, of titanium, zirconium, hafnium, vanadium, silicon, niobium, tantalum, nickel, molybdenum and iron, and/or a precursor thereof, in particular particulate titanium diboride.

Advantageously, the intermediate bonding layer and/or the protective layer comprises a particulate refractory metal compound, a dried colloidal metal/inorganic polymeric oxide and a further metal oxide to reinforce the layer(s), the dried colloidal/inorganic polymeric metal oxide and oxide of the metal of the particulate refractory metal compound forming miscible mixed oxides with the reinforcing metal oxide. Suitable combinations of particulate refractory metal compounds, dried colloidal/inorganic polymeric metal oxides and

reinforcing metal oxides are disclosed in WO01/42531 (Nguyen/Duruz/de Nora).

5 The protective layer can comprise an aluminium-wettable metal oxide, such as oxides of manganese, iron, cobalt, nickel, copper, zinc, molybdenum, lanthanum, which when exposed to molten aluminium reacts therewith to produce aluminium oxide and the metal of the aluminium-wettable metal oxide, as disclosed in WO01/42168 (de Nora/Duruz).

10 The invention also relates to a component of a cell for the electrowinning of aluminium from alumina dissolved in a fluoride-containing electrolyte, comprising a coated substrate as described above, and to
15 a component of an apparatus for treating a molten metal which component during use is exposed to the molten metal and which comprises a coated substrate as described above.

Another aspect of the invention relates to an
20 apparatus for the production, purification or recycling of a metal in a molten state comprising at least one component which comprises a coated substrate as described above, and which during use is exposed to an oxidising and/or corrosive gaseous and/or molten environment at elevated temperature.

25 The apparatus can be an aluminium electrowinning cell, comprising at least one component which is part of a cell bottom coated with the hydrophilic protective layer protecting the cell bottom component from molten aluminium and/or molten electrolyte; a cathode having an
30 aluminium-wettable surface, in particular a drained surface, formed by the hydrophilic protective layer which protects the cathode from molten aluminium and/or molten electrolyte; an anode having one or more electrochemically inactive surfaces coated with the
35 hydrophilic protective layer which protects the inactive surface from molten electrolyte and/or anodically produced gas; or a cell sidewall coated with the hydrophilic protective layer which protects the sidewall from molten electrolyte, molten aluminium and/or
40 anodically produced gas.

The apparatus may be an arc furnace for the recycling of steel, the component being an arc-electrode or an arc-electrode holder coated with the hydrophilic

protective layer which protects it from oxidising gas and/or molten steel.

Furthermore, the apparatus can be an apparatus for the purification or treatment of a molten metal, such as aluminium, molten magnesium, cast iron or molten steel, in particular by the injection of a purifying fluid into the molten metal to remove impurities towards the surface thereof. The component can be a rotatable stirrer or a vessel for containing molten metal to be purified or treated which is protected from the molten metal to be purified or treated and optionally the purifying fluid and impurities of the molten metal by the hydrophilic protective layer. Further details of such a purification or treatment apparatus are disclosed in WO00/63630 (Holz/Duruz).

A further aspect of the invention is a method of producing, purifying, treating or recycling a metal in an apparatus as described above and which comprises at least one component coated with the hydrophilic protective layer. The method comprises exposing the coated substrate to an oxidising and/or corrosive gaseous and/or molten environment at elevated temperature.

Yet a further aspect of the invention relates to a method of bonding a heat stable layer applied from a slurry comprising hydrophilic colloidal particles and/or hydrophilic inorganic polymeric particles onto a hydrophobic substrate for use at high temperature in particular in a cell for the electrowinning of aluminium from alumina. This method comprises: adding to the slurry at least one carbon compound selected from hydrophobic carbon monomers and hydrophobic carbon polymers and which comprises hydrophilic substituents in an amount sufficient to bond the hydrophilic colloidal/inorganic polymeric particles to the carbon compound(s); and thereafter applying one or more layers of the slurry onto the hydrophobic substrate followed by drying and/or heat treating to bond hydrophilic colloidal/inorganic polymeric particles to the hydrophobic substrate by carbon from the carbon compound(s) and thereby bond said heat stable layer on the hydrophobic substrate.

Yet another aspect of the invention relates to the use, in a slurry comprising hydrophilic colloidal particles and/or hydrophilic inorganic polymeric particles for producing upon drying and/or heat treatment a heat stable layer on a hydrophobic substrate for use at

high temperature in particular in a cell for the electrowinning of aluminium from alumina, of at least one carbon compound selected from hydrophobic carbon monomers and hydrophobic carbon polymers and which comprises hydrophilic substituents, as an agent for improving bonding of the heat stable layer on the hydrophobic substrate.

Brief Description of the Drawings

Embodiments of the invention will now be described by way of example with reference to the accompanying schematic drawings, wherein:

- Figure 1 shows a schematic cross-sectional view of an aluminium production cell with carbonaceous drained cathodes having an aluminium-wettable hydrophilic protective layer in accordance with the invention;

- Figure 2 schematically shows an arc electrode furnace incorporating hydrophilic protective layers according to the invention;

- Figure 3 shows an apparatus for the purification of a molten metal having a carbonaceous stirrer protected with an aluminium-wettable hydrophilic protective layer according to the invention;

- Figure 3a is an enlarged schematic sectional view of part of the stirrer shown in Figure 3; and

- Figure 4 schematically shows a variation of the stirrer shown in Figure 3.

Detailed Description

Aluminium Electrowinning Cell:

Figure 1 shows an aluminium electrowinning cell comprising a series of carbonaceous anode blocks having operative surfaces suspended over drained sloping flattened generally V-shaped cathode surface in a fluoride-containing molten electrolyte containing dissolved alumina.

The drained cathode surface 21 is formed by the surface of an aluminium-wettable hydrophilic protective layer 20A applied to the upper surfaces of a series of juxtaposed hydrophobic carbon cathode blocks extending in pairs arranged end-to-end across the cell. The

protective layer 20A is bonded to the carbon cathode blocks 15 by an intermediate layer applied from compounds according the invention from a slurry comprising hydrophilic colloidal and/or inorganic polymeric particles and one or more monomer and/or polymer carbon.

The cathode blocks 15 comprise, embedded in recesses located in their bottom surfaces, current supply bars 22 of steel or other conductive material for connection to an external electric current supply.

10 The drained cathode surface 21 is divided by a central aluminium collection groove 26 located in or between pairs of cathode blocks 15 arranged end-to-end across the cell. The aluminium collection groove 26 is situated at the bottom of the drained cathode surface 21 and is arranged to collect the product aluminium draining from the cathode surface 21. The aluminium collection groove 26 is coated according to the invention with an intermediate bonding layer and the aluminium-wettable hydrophilic refractory protective layer 20B.

20 The anode blocks 5 too are coated with a hydrophilic refractory protective layer 20C on their inactive surfaces, but not on the operative anode surfaces 6 which are immersed as such in the molten electrolyte 42.

25 The cell comprises carbonaceous sidewalls 16 exposed to molten electrolyte 42 and to the environment above the molten electrolyte, but protected against the molten electrolyte 42 and the environment above the molten electrolyte with a hydrophilic refractory protective layer 20D according to the invention.

30 In operation of the cell illustrated in Figure 1, alumina dissolved in the molten electrolyte 42 at a temperature of 750° to 960°C is electrolysed between the anodes 5 and the cathode blocks 15 to produce gas on the operative anodes surfaces 6 and molten aluminium on the aluminium-wettable drained cathode layer 20A.

40 The cathodically-produced molten aluminium flows down the inclined drained cathode surface 21 into the aluminium collection grooves 26 onto the aluminium-wettable hydrophilic protective layer 20B from where it flows into an aluminium collection reservoir for subsequent tapping.

Figure 1 shows a specific aluminium electrowinning cell by way of example. It is evident that many

alternatives, modifications, and variations will be apparent to those skilled in the art. For instance, the cell may have one or more aluminium collection reservoirs across the cell, each intersecting the aluminium
5 collection groove to divide the drained cathode surface into four quadrants as described in W000/63463 (de Nora).

The cell bottom may have a horizontal aluminium-wettable cathode surface which is in a drained configuration or which is covered with a shallow or deep
10 pool of aluminium.

The anodes may be made of inert materials and have an electrochemically active structure of grid-like design to permit electrolyte circulation, as for example disclosed in W000/40781, W000/40782 (both in the name of
15 de Nora) and W001/31086 (de Nora/Duruz).

The anodes may be coated with a protective layer of one or more cerium compounds, in particular cerium oxyfluoride. The protective layers can be maintained by maintaining an amount of cerium species in the
20 electrolyte. Further details of such coatings and cell operation therewith can be found in the above mentioned US Patents 4,614,569 (Duruz/Derivaz/Debely/Adorian), 4,680,094, 4,683,037 (both in the name of Duruz) and 4,966,674 (Bannochie/Sheriff).

25 Arc Furnace:

The arc furnace shown in Figure 2 comprises three consumable electrodes 15A arranged in a triangular relationship. For clarity, the distance between the electrodes 15A as shown in Figure 2 has been
30 proportionally increased with respect to the furnace. Typically, the electrodes 15A have a diameter between 200 and 500 mm and can be spaced by a distance corresponding to about their diameter.

The electrodes 15A are connected to an electrical power supply (not shown) and suspended from an electrode
35 positioning system above the cell which is arranged to adjust their height.

The consumable electrodes 15A are made of a hydrophobic carbon substrate laterally coated with a hydrophilic protective layer 20 protecting the carbon
40 substrate from oxidising gas. The protective layer 20 is bonded to the carbon substrate 15A by an intermediate bonding layer applied according to the invention from a

slurry comprising hydrophilic colloidal/inorganic polymeric particles and one or more monomer and/or polymer carbon compounds.

5 The bottom of electrodes 15A which is consumed during operation and constitutes the electrodes' operative surface is uncoated. The hydrophilic protective layer 20 protects only the electrodes' lateral faces against premature oxidation.

10 The electrodes 15A dip in an iron source 41, usually containing iron oxide or oxidised iron, such as scrap iron, scrap steel and pig iron. Preferably, the iron source 41 further comprises reductants selected from gaseous hydrogen, gaseous carbon monoxide or solid carbon bearing reductants. The reductants may also comprise non-iron minerals known as gangue which include silica, 15 alumina, magnesia and lime.

The iron source 41 floats on a pool of liquid iron or steel 40 resulting from the recycling of the iron source 41.

20 During use, a three phase AC current is passed through electrodes 15A, which directly reduces iron from the iron source 41. The reduced iron is then collected in the iron or steel pool 40. The gangue contained in the reduced iron is separated from the iron by melting and 25 flotation forming a slag (not shown) which is removed, for example through one or more apertures (not shown) located on sidewalls of the arc furnace at the level of the slag.

30 The pool of iron or steel 40 is periodically or continuously tapped for instance through an aperture (not shown) located in the bottom of the arc furnace.

Molten Metal Purification Apparatus:

35 The molten metal purification apparatus partly shown in Figure 3 comprises a vessel 45 containing molten metal 40', such as molten aluminium, to be purified. A rotatable stirrer 10 made of carbon-based material, such as graphite, is partly immersed in the molten metal 40' and is arranged to rotate therein.

40 The stirrer 10 comprises a shaft 11 whose upper part is engaged with a rotary drive and support structure 30 which holds and rotates the stirrer 10. The lower part of shaft 11 is carbon-based and dips in the molten metal 40'

contained in vessel 45. At the lower end of the shaft 11 is a rotor 13 provided with flanges or other protuberances for stirring the molten metal 40'.

5 Inside the shaft 11, along its length, is an axial duct 12, as shown in Figure 3a, which is connected at the stirrer's upper end through a flexible tube 35 to a gas supply (not shown), for instance a gas reservoir provided with a gas gate leading to the flexible tube 35.

10 The axial duct 12 is arranged to supply a fluid to the rotor 13. The rotor 13 comprises a plurality of apertures connected to the internal duct 12 for injecting the gas into the molten metal 40', as shown by arrows 51.

15 The lower part of the shaft 11, i.e. the immersed part and the interface region at or about the meltline 14 of the shaft, as well as the rotor 13 are coated according to the invention with an intermediate bonding layer and a hydrophilic protective layer 20E which improves the resistance to erosion, oxidation and/or corrosion of the stirrer during operation.

20 As shown in Figure 3, the upper part of shaft 11 is also protected against oxidation and/or corrosion by an intermediate bonding layer and a hydrophilic protective layer 20F according to the invention. The upper part of the carbon-based shaft 11 is coated with a thin layer of refractory material 20F providing protection against oxidation and corrosion, whereas the layer 20E protecting the immersed part of the shaft 11 and the rotor 13 is a thicker layer of refractory material providing protection against erosion, oxidation and corrosion.

30 Likewise, surfaces of the vessel 45 which come into contact with the molten metal may be protected with an hydrophilic protective layer according to the invention or possibly with a protective layer as described in WO00/63630 (Holz/Duruz) in the case when the vessel is made of hydrophilic material.

40 During operation of the apparatus shown in Figure 3, a reactive or non-reactive fluid, in particular a gas 50 alone or a flux, such as a halide, nitrogen and/or argon, is injected into the molten metal 40' contained in the vessel 45 through the flexible tube 35 and stirrer 10 which dips in the molten metal 40'.

The stirrer 10 is rotated at a speed of about 100 to 500 RPM so that the injected gas 50 is dispersed

throughout the molten metal in finely divided gas bubbles. The dispersed gas bubbles 50, with or without reaction, remove impurities present in the molten metal 40' towards its surface, from where the impurities may be separated thus purifying the molten metal.

The stirrer 10 schematically shown in Figure 4 dips in a molten metal bath 40' and comprises a shaft 11 and a rotor 13. The stirrer 10 may be of any type, for example similar to the stirrer shown in Figure 3 or of conventional design as known from the prior art. The rotor 13 of stirrer 10 may be a high-shear rotor or a pump action rotor.

In Figure 4, instead of coating the entire shaft 11 and rotor 13, parts of the stirrer 10 liable to erosion are selectively coated with an intermediate bonding layer and an aluminium-wettable protective layer according to the invention.

The interface portion at and about the meltline 14 of the carbon-based lower part of the shaft 11 is coated with a refractory interface layer 20E₁ consisting of an intermediate bonding layer and a hydrophilic protective layer according to the invention, for instance over a length of up to half that of the shaft 11. Excellent results have been obtained with a layer over a third of shaft 11. However, the length of layer 20E₁ could be a quarter of the length of shaft 11 or even less, depending on the design of stirrer 10 and the operating conditions.

In addition to the interface portion of such stirrers, other areas may be liable to erode, again depending on the design and operating conditions of the stirrers. The schematically shown stirrer 10 in Figure 4 illustrates further coated surfaces which are particularly exposed to erosion. The lower end of the shaft 11 adjacent to the rotor 13 is protected with a layer 20E₂ consisting of an intermediate bonding layer and a hydrophilic protective layer according to the invention. The lateral surface of rotor 13 is protected with a layer 20E₃ and the bottom surface of the rotor 13 is coated with a layer 20E₄, both consisting of an intermediate bonding layer and a hydrophilic protective layer according to the invention.

For each specific stirrer design, the layer or different protective layers on different parts of the stirrer, such as layers 20E₁, 20E₂, 20E₃ and 20E₄ shown in Figure 4, may be adapted as a function of the expected

lifetime of the stirrer. For optimal use, the amount and location of such layers can be so balanced that they each have approximately the same lifetime.

5 In an alternative embodiment (not shown), the layer on such stirrers may be continuous as illustrated in Figure 3 but with a graded thickness or composition so as to adapt the resistance against erosion to the intensity of wear of each part of the stirrer, thereby combining the advantages of the different layers shown in Figure 4.

10 Various modifications can be made to the apparatus shown in Figures 3, 3a and 4. For instance, the shaft shown in Figure 3 may be modified so as to consist of an assembly whose non-immersed part is made of a material other than carbon-based, such as a metal and/or a ceramic,
15 which is resistant to oxidation and corrosion and which, therefore, does not need any protective layer, whereas the immersed part of the shaft is made of carbon-based material protected with a protective layer according to the invention. Such a composite shaft would preferably be
20 designed to permit disassembly of the immersed and non-immersed parts so the immersed part can be replaced when worn.

Likewise, a carbon-based non-immersed part of the shaft may be protected from oxidation and corrosion with
25 a layer and/or impregnation of a phosphate of aluminium, in particular applied in the form of a compound selected from monoaluminium phosphate, aluminium phosphate, aluminium polyphosphate, aluminium metaphosphate, and mixtures thereof as disclosed in US Patent 5,534,119
30 (Sekhar). It is also possible to protect the non-immersed part of the shaft with a layer and/or impregnation of a boron compound, such as a compound selected from boron oxide, boric acid and tetraboric acid as disclosed in US Patent 5,486,278 (Manganiello/Duruz/Bellò) and in co-
35 pending application WO97/26626 (de Nora/Duruz/Berclaz).

In a modification, the protective layer of the invention may simply be applied to any part of the stirrer in contact with the molten metal, to be protected
40 against erosion, oxidation and/or corrosion during operation.

The invention will be further described in the following examples.

Example 1

A slurry for use as an intermediate bonding layer for bonding a hydrophilic protective layer onto a hydrophobic substrate according to the invention was prepared as follows.

A refractory hard metal boride consisting of 47.5 g surface-oxidised particulate spherical TiB_2 (-325 mesh) having a TiO_2 surface film and a particulate reinforcing metal oxide in the form of 2.5 g TiO_2 (-325 mesh) were stirred and suspended in a colloidal carrier consisting of 20 ml colloidal Al_2O_3 (NYACOL® Al-20, a milky liquid with a colloidal particle size of about 40 to 60 nanometer) to form an colloidal slurry.

After the particulate titanium diboride and oxide had been suspended in the colloidal carrier, an amount of 1 ml of an aqueous solution containing 15 weight% polyvinyl alcohol (PVA), a hydrophobic carbon polymer comprising hydrophilic substituents (-OH), was added to the colloidal slurry.

This slurry produces upon heat treatment an oxide matrix of titanium-aluminium mixed oxide from the reaction of the colloidal oxide Al_2O_3 and TiO_2 present as suspended oxide particles and oxide film covering the suspended TiB_2 particles intimately mixed with carbon from the hydrophobic carbon polymer. The oxide matrix contains and bonds TiB_2 particles.

This slurry is suitable for the manufacture of a composite coating according to the invention as described in Example 4.

Example 1a

The constituents of the slurry of Example 1 may be changed as shown in the following Table in which each line represents possible combinations of constituents which are combined with one or more carbon compounds in the form of hydrophobic carbon monomers and/or polymers that comprise hydrophilic substituents, such as ethylene glycol, hexanol, polyvinyl alcohol, polyvinyl acetate, polyacrylic acid, hydroxy propyl methyl cellulose and ammonium polymethacrylate.

Colloidal and Polymeric Oxides	Suspended Reinforcing Metal Oxides	Suspended Surface-Oxidised Refractory Metal Compounds
Al ₂ O ₃	TiO ₂ , MgO or SiO ₂	TiB ₂ , SiC, TiC or TiN
TiO ₂	Al ₂ O ₃ or MgO	SiC or SiN
SiO ₂	Al ₂ O ₃ or MgO	TiB ₂ , TiC or TiN

In a variation, the suspended refractory metal compound does not need to be surface oxidised and the suspended reinforcing metal oxide may be replaced by the suspended surface-oxidised refractory metal compounds in the same weight percentage.

Example 2

A slurry for producing an hydrophilic protective layer free of organic carbon which can be bonded through an intermediate bonding layer to a hydrophobic substrate in accordance with the invention was prepared by suspending 2.5 g particulate Fe₂O₃ (-325 mesh), a refractory hard metal boride consisting of 92.5 g particulate needle-shaped surface-oxidised TiB₂ (-325 mesh) having a TiO₂ surface oxide film, and 2.5 g particulate TiO₂ (-325 mesh) in a colloid consisting of a combination of two grades of colloidal Al₂O₃, namely 28 ml of a first grade of colloidal Al₂O₃ (NYACOL® Al-20, a milky liquid with a colloidal particle size of about 40 to 60 nanometer) and 24 ml of a second grade of colloidal Al₂O₃ (CONDEA® 10/2 Sol, a clear, opalescent liquid with a colloidal particle size of about 10 to 30 nanometer).

This slurry produces upon heat treatment a matrix of mixed oxides consisting of titanium-aluminium mixed oxide and a small amount of iron-titanium-aluminium mixed oxide from the reaction of TiO₂, Fe₂O₃ and Al₂O₃. This matrix contains and bonds the TiB₂ and Fe₂O₃ particles.

This slurry is suitable for the manufacture of a composite coating according to the invention as described in Example 4.

30

Example 2a

Example 2's slurry composition consists of Fe₂O₃ and a reaction mixture made of the colloid (Al₂O₃), the suspended refractory metal boride (TiB₂) the suspended metal oxide (TiO₂). This Example can be modified by

completely or partly substituting Fe_2O_3 with partly oxidised or oxides of copper and/or nickel, and/or by varying the composition of the reaction mixture as in Example 1a.

5

Example 3

A further slurry for producing a highly aluminium-wettable hydrophilic protective start-up layer free of organic carbon which can be bonded through an intermediate bonding layer to a hydrophobic substrate in accordance with the invention, was prepared as follows. An amount of 60 g of surface oxidised copper particles (-325 mesh) was suspended in a carrier consisting of 13 ml of colloidal Al_2O_3 (7 ml NYACOL® Al-20, a milky liquid with a colloidal particle size of about 40 to 60 nanometer and 6 ml CONDEA® 10/2 Sol, a clear, opalescent liquid with a colloidal particle size of about 10 to 30 nanometer).

Upon heat treatment the slurry produces an alumina matrix containing and bonding the oxidised copper particles.

As a modification, oxidised or partly oxidised particles of nickel and/or iron may be used to substitute in part or completely the oxidised copper particles in colloidal alumina (CONDEA 25/5 with a pH > 7).

25

Example 4

Three carbon cathodes for use in a drained cell for the production of aluminium were each coated with the slurries of Examples 1, 2 and 3 as follows:

First, an intermediate bonding layer having a thickness of about 100 micron was painted onto the exposed surface of the hydrophobic carbon cathode from the slurry of Example 1. The intermediate bonding layer was allowed to dry for 30 minutes.

The intermediate bonding layer was covered with a permanent aluminium-wettable hydrophilic protective layer obtained by painting 8 layers of the slurry of Example 2. Each applied layer was allowed to dry for 30 minutes before application of the next layer. The final aluminium-wettable protective layer had a thickness of about 1.8 mm.

The permanent aluminium-wettable hydrophilic protective layer was then covered with a temporary hydrophilic protective start-up layer obtained by painting one layer of the slurry of Example 3. The hydrophilic start-up layer had a thickness of about 100 to 150 micron.

The coating formed by the intermediate bonding layer, the permanent aluminium-wettable hydrophilic protecting layer and the temporary hydrophilic protective start-up layer on the carbon cathode was allowed to dry for 24 hours.

Two of the three cathodes were then covered with an aluminium sheet having a thickness of about 1.5 cm and heated in an oven at a temperature of about 850-900°C in air.

The first cathode was extracted from the oven after 30 minutes and allowed to cool down to ambient temperature. Examination of a cross-section of the coating showed that aluminium had infiltrated the start-up layer so that the coating was superficially wetted by molten aluminium. No reaction between aluminium and iron oxide had yet taken place. The intermediate bonding layer was intimately bonded to the hydrophobic carbon substrate.

The second cathode was extracted from the oven after 24 hours and allowed to cool down to ambient temperature. Examination of a cross-section of the coating showed that aluminium had infiltrated the start-up layer and the permanent aluminium-wettable layer. Part of the aluminium had reacted with Fe_2O_3 to form Al_2O_3 and Fe metal. Aluminium infiltration had been stopped on the intermediate bonding layer for lack of oxide reactable with aluminium.

The aluminium metal infiltration into the start-up layer and the permanent aluminium-wettable layer enhanced the conductivity of the coating. At ambient temperature, the perpendicular electrical resistance through the coating was less than 1 ohm after infiltration versus more than 500 ohm before infiltration.

The coatings on both cathodes showed a continuous matrix of titanium-aluminium mixed oxides between the intermediate bonding layer and the permanent aluminium-wettable layer which guarantees an excellent adherence between the two layers. In both cases the particles of

TiB₂ had not been oxidised by the heat treatment and wettability of the coating by aluminium was very good. The angle of wettability was less than 10 deg.

5 The third coated carbon cathode was used in an aluminium production drained cell as follows:

10 The cathode covered with the dried coating according to the invention was covered in the cell with a 1.5 cm thick sheet of aluminium. The cell was heated to a temperature of about 850-900°C by passing an electrical current between the cathode and facing anodes through carbon powder. Other start-up heating procedures could also have been used, e.g. using gas burners to generate heat.

15 After 30 minutes at 850-900°C, the start-up coating was superficially wetted by molten aluminium which constitutes a barrier against damaging fluoride-based molten electrolyte constituents, such as sodium compounds, and a cryolite based electrolyte was filled into the cell.

20 The cell was further heated to 960°C at which temperature the cell was operated under an electrolysis current density of 0.8 A/cm² to produce aluminium under conventional steady state conditions.

Example 5

25 Any of the layers of Examples 1 to 4 can be modified using inorganic polymeric carriers, such as the polymeric solutions (A) and (B) prepared as set out below, in replacement of the layer's colloidal carriers.

30 (A) An amount of 150 g of Fe(NO₃)₃.9 H₂O was heated to dissolve the salt in its own water of crystallisation to form a solution containing 29 g Fe₂O₃. The solution was heated to 120°C and 18.9 g of magnesium hydroxy-carbonate dissolved in the hot solution together with Fe₂O₃ in form of an inorganic polymer together with Fe₂O₃ suitable for use as an inorganic polymeric carrier.

40 (B) An amount of 100 g of Cr(NO₃)₃.9 H₂O was heated to dissolve the salt in its own water of crystallisation to form a solution containing 19 g Cr₂O₃. The solution was heated to 120°C and 12.5 g of magnesium-hydroxy carbonate containing the equivalent of 5.0 g MgO was added. Upon stirring a solution was obtained in the form

of an anion-deficient polymer mixture with a density of approximately 1.5 g/cm³ suitable to act as an inorganic polymeric carrier.

CLAIMS

1. A method of coating a hydrophobic substrate with an hydrophilic protective layer free of organic carbon to protect the substrate when used at high temperature in particular in a cell for the electrowinning of aluminium from alumina dissolved in a fluoride-containing electrolyte, said method comprising:
- 5
- applying one or more layers of a slurry comprising hydrophilic colloidal particles and/or hydrophilic inorganic polymeric particles onto the hydrophobic substrate followed by drying to form a heat stable intermediate bonding layer on the hydrophobic substrate; and
 - 10
 - applying one or more layers of a slurry forming the hydrophilic protective layer onto the intermediate bonding layer followed by drying and/or heat treating to form the hydrophilic protective layer on the intermediate bonding layer,
 - 15
- characterised in that the slurry forming the intermediate bonding layer contains at least one carbon compound selected from hydrophobic carbon monomers and hydrophobic carbon polymers and comprising hydrophilic substituents in an amount sufficient to bond said hydrophilic colloidal and/or inorganic polymeric particles to the carbon compound(s).
- 20
- 25
2. The method of claim 1, wherein said hydrophilic substituents are selected from -OH, -SO₃Na and -COOH, and combinations thereof.
3. The method of claim 1 or 2, wherein said carbon compound(s) has/have a carbon/hydrophilic substituent ratio in the range of 2 to 4.
- 30
4. The method of any preceding claim, wherein said carbon compound(s) is/are selected from ethylene glycol, hexanol, polyvinyl alcohol, polyvinyl acetate, polyacrylic acid, hydroxy propyl methyl cellulose and ammonium polymethacrylate and mixtures thereof.
- 35
5. The method of any preceding claim, wherein said hydrophilic protective layer is applied from a slurry

comprising colloidal and/or inorganic polymeric particles and non-dispersed particulate refractory material.

6. The method of any preceding claim, wherein at least one of the slurry forming the intermediate bonding layer and the slurry forming the hydrophilic protective layer comprises hydrophilic colloidal particles selected from lithia, beryllium oxide, magnesia, alumina, silica, titania, vanadium oxide, chromium oxide, manganese oxide, iron oxide, gallium oxide, yttria, zirconia, niobium oxide, molybdenum oxide, ruthenia, indium oxide, tin oxide, tantalum oxide, tungsten oxide, thallium oxide, ceria, hafnia and thoria, and precursors thereof, all in the form of colloids; and/or hydrophilic inorganic polymeric particles selected from lithia, beryllium oxide, alumina, silica, titania, chromium oxide, iron oxide, nickel oxide, gallium oxide, zirconia, niobium oxide, ruthenia, indium oxide, tin oxide, hafnia, tantalum oxide, ceria and thoria, and precursors thereof, all in the form of inorganic polymers.

7. The method of any preceding claim, wherein the slurry forming the intermediate bonding layer further comprises non-dispersed particulate refractory material or a particulate precursor thereof.

8. The method of claim 7, wherein the slurry forming the intermediate bonding layer further comprises particulate carbon.

9. The method of any preceding claim, wherein at least one of the slurry forming the intermediate bonding layer and the slurry forming the hydrophilic protective layer comprises non-dispersed particulate refractory material selected from borides, silicides, nitrides, oxynitrides, carbides, oxycarbides, phosphides, oxides, aluminides, of titanium, zirconium, hafnium, vanadium, silicon, niobium, tantalum, nickel, molybdenum and iron, and/or a precursor thereof.

10. The method of any preceding claim, wherein the hydrophobic substrate is made of carbon.

11. A hydrophobic substrate coated with an hydrophilic protective layer free of organic carbon protecting the substrate when used at high temperature, in particular in a cell for the electrowinning of aluminium from alumina dissolved in a fluoride-containing electrolyte, wherein the protective layer is bonded to the substrate through an intermediate bonding layer which comprises dried

hydrophilic colloidal particles and/or dried hydrophilic inorganic polymeric particles,

characterised in that dried hydrophilic colloidal and/or inorganic polymeric particles of the intermediate bonding layer are intimately bonded to carbon on the hydrophobic substrate, the intimate bonding between the hydrophilic colloidal and/or inorganic polymeric particles and carbon on the hydrophobic substrate being obtainable by applying onto the hydrophobic substrate a slurry comprising the hydrophilic colloidal and/or inorganic polymeric particles and at least one carbon compound selected from hydrophobic carbon monomers and hydrophobic carbon polymers and comprising hydrophilic substituents in an amount sufficient to bond the hydrophilic colloidal and/or inorganic polymeric particles to the carbon compound(s).

12. The coated substrate of claim 11, wherein at least one of the intermediate bonding layer and the hydrophilic protective layer comprises dried hydrophilic lithia, beryllium oxide, magnesia, alumina, silica, titania, vanadium oxide, chromium oxide, manganese oxide, iron oxide, gallium oxide, yttria, zirconia, niobium oxide, molybdenum oxide, ruthenia, indium oxide, tin oxide, tantalum oxide, tungsten oxide, thallium oxide, ceria, hafnia and thoria, and precursors thereof, all in the form of colloids; and/or hydrophilic inorganic polymeric particles selected from lithia, beryllium oxide, alumina, silica, titania, chromium oxide, iron oxide, nickel oxide, gallium oxide, zirconia, niobium oxide, ruthenia, indium oxide, tin oxide, hafnia, tantalum oxide, ceria and thoria, and precursors thereof, all in the form of inorganic polymers.

13. The coated substrate of claim 11 or 12, wherein at least one of the intermediate bonding layer and the hydrophilic protective layer comprises particulate refractory material selected from borides, silicides, nitrides, oxynitrides, carbides, oxycarbides, phosphides, oxides, aluminides, of titanium, zirconium, hafnium, vanadium, silicon, niobium, tantalum, nickel, molybdenum and iron, and/or a precursor thereof.

14. The coated substrate of claim 13, wherein at least one of the intermediate bonding layer and the hydrophilic protective layer comprises particulate titanium diboride.

15. The coated substrate of any preceding, wherein at least one of the intermediate bonding layer and the hydrophilic protective layer comprises a particulate refractory metal compound, a dried colloidal metal and/or inorganic polymeric oxide and a further metal oxide to reinforce said layer(s), the dried colloidal and/or inorganic polymeric metal oxide and oxide of the metal of the particulate refractory metal compound forming miscible mixed oxides with the reinforcing metal oxide.
16. The coated substrate of any one of claims 11 to 15, wherein the hydrophilic protective layer comprises an aluminium-wettable metal oxide which when exposed to molten aluminium reacts therewith to produce aluminium oxide and the metal of the aluminium-wettable metal oxide.
17. The coated substrate of claim 16, wherein the aluminium-wettable metal oxide is selected from oxides of manganese, iron, cobalt, nickel, copper, zinc, molybdenum, lanthanum and combinations thereof.
18. The coated substrate of any one of claims 11 to 17, wherein the hydrophobic substrate is made of carbon.
19. A component of a cell for the electrowinning of aluminium from alumina dissolved in a fluoride-containing electrolyte, comprising a coated substrate as defined in any one of claims 11 to 18.
20. A component of an apparatus for treating a molten metal which component during use is exposed to the molten metal, comprising a coated substrate as defined in any one of claims 11 to 18.
21. An apparatus for the production, purification or recycling of a metal in a molten state comprising at least one component which comprises a coated substrate as defined in any one of claims 11 to 18, and which during use is exposed to an oxidising and/or corrosive gaseous and/or molten environment at elevated temperature.
22. The apparatus of claim 21, which is an aluminium electrowinning cell, comprising at least one component which is part of a cell bottom coated with said hydrophilic protective layer protecting the cell bottom component from molten aluminium and/or molten electrolyte; a cathode having an aluminium-wettable surface formed by the hydrophilic protective layer which protects the cathode from molten aluminium and/or molten electrolyte;

an anode having one or more electrochemically inactive surfaces coated with said hydrophilic protective layer which protects the inactive surface from at least one of molten electrolyte and anodically produced gas; or a cell
5 sidewall coated with said hydrophilic protective layer which protects the sidewall from at least one of molten electrolyte, molten aluminium and anodically produced gas.

23. The apparatus of claim 22, wherein said component is a cathode which has an aluminium-wettable drained surface.

10 24. The apparatus of claim 21, which is an arc furnace for the recycling of steel, said component being an arc-electrode or an arc-electrode holder coated with the hydrophilic protective layer which protects it from oxidising gas and/or molten steel.

15 25. The apparatus of claim 21, which is an apparatus for the purification or treatment of a molten metal, in particular by the injection of a purifying fluid into the molten metal to remove impurities towards the surface thereof, said component being a rotatable stirrer or a
20 vessel for containing molten metal to be purified or treated, which component is protected from the molten metal to be purified or treated and optionally the purifying fluid and impurities of the molten metal by the hydrophilic protective layer.

25 26. The apparatus of claim 25, which is an apparatus for the purification of molten aluminium, molten magnesium, cast iron or molten steel.

27. A method of producing, purifying or recycling a metal in an apparatus as defined in any one of claims 21 to 26,
30 which apparatus comprises at least one component coated with said hydrophilic protective layer, the method comprising exposing said coated substrate to an oxidising and/or corrosive gaseous and/or molten environment at elevated temperature.

35 28. A method of bonding a heat stable layer applied from a slurry comprising hydrophilic colloidal particles and/or hydrophilic inorganic polymeric particles onto a hydrophobic substrate for use at high temperature in particular in a cell for the electrowinning of aluminium
40 from alumina, said method comprising:

- adding to the slurry at least one carbon compound selected from hydrophobic carbon monomers and hydrophobic carbon polymers and which comprises hydrophilic

substituents in an amount sufficient to bond the hydrophilic colloidal and/or inorganic polymeric particles to the carbon compound(s); and thereafter

- 5 - applying one or more layers of the slurry onto the hydrophobic substrate followed by drying and/or heat treating to bond hydrophilic colloidal and/or inorganic polymeric particles to the hydrophobic substrate by carbon from the carbon compound(s) and thereby bond said heat stable layer on the hydrophobic substrate.
- 10 29. Use, in a slurry comprising hydrophilic colloidal particles and/or hydrophilic inorganic polymeric particles for producing upon drying and/or heat treatment a heat stable layer on a hydrophobic substrate for use at high temperature in particular in a cell for the
- 15 electrowinning of aluminium from alumina, of at least one carbon compound selected from hydrophobic carbon monomers and hydrophobic carbon polymers and which comprises hydrophilic substituents, as an agent for improving bonding of the heat stable layer onto the hydrophobic
- 20 substrate.

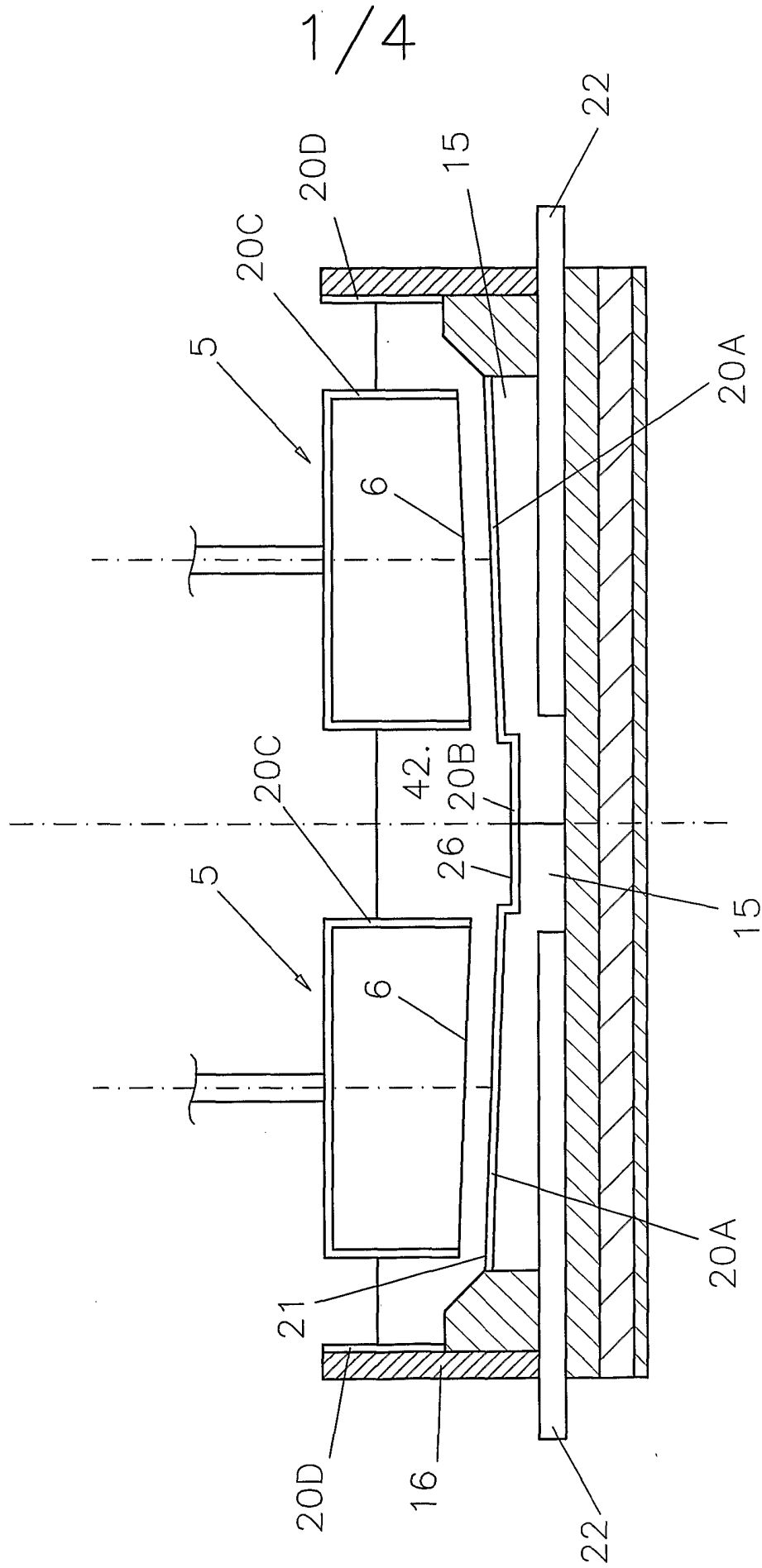


FIGURE 1

2/4

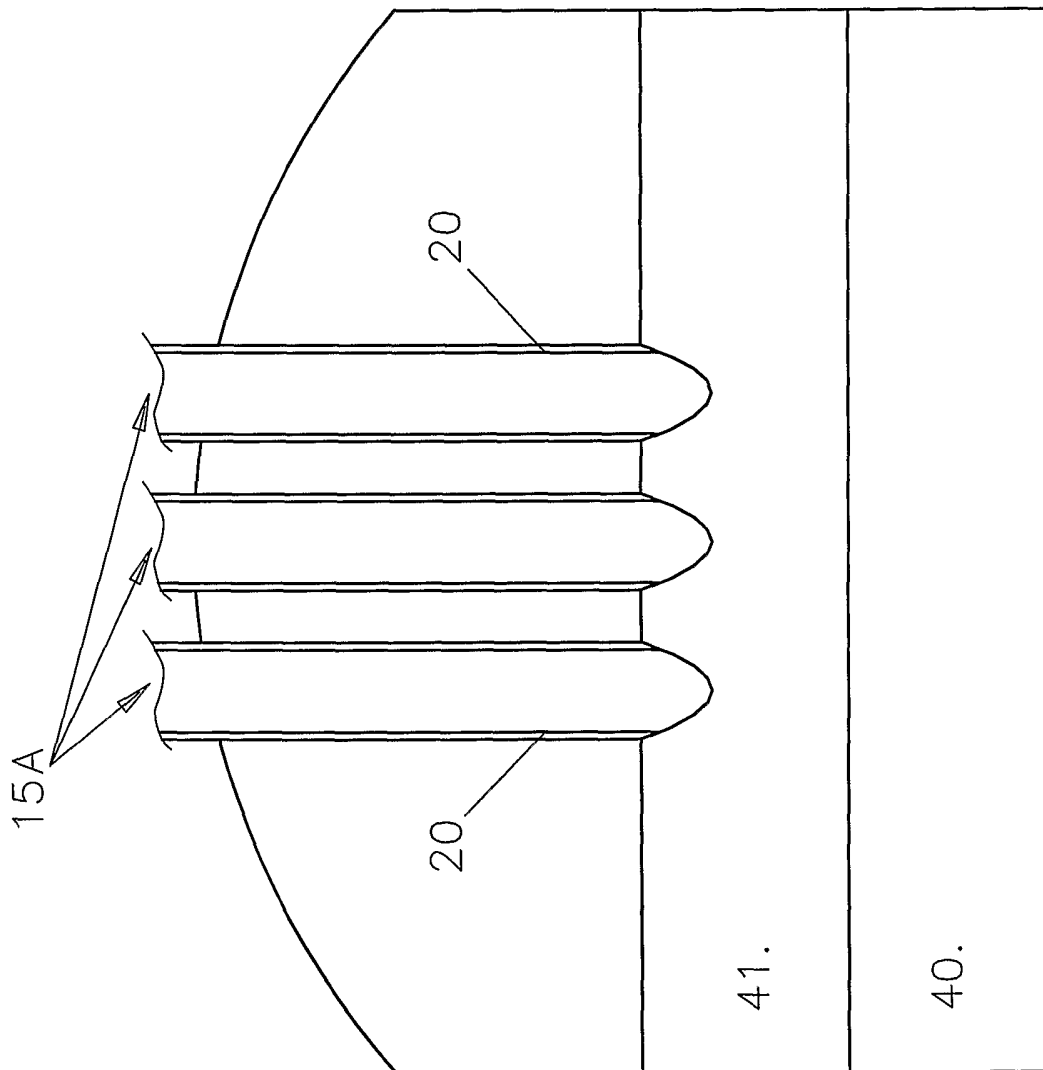


FIGURE 2

3/4

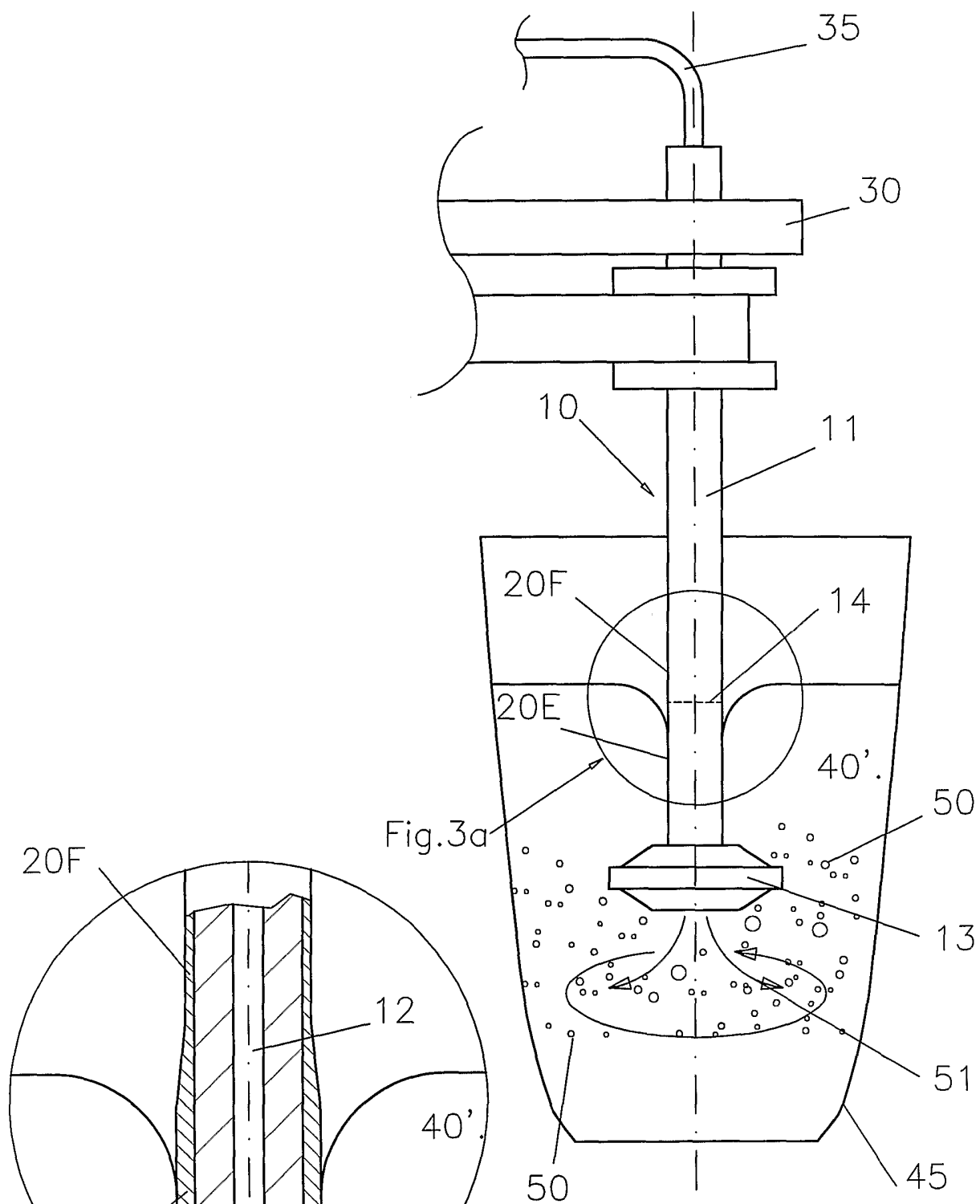


FIG.3

FIG.3a

4/4

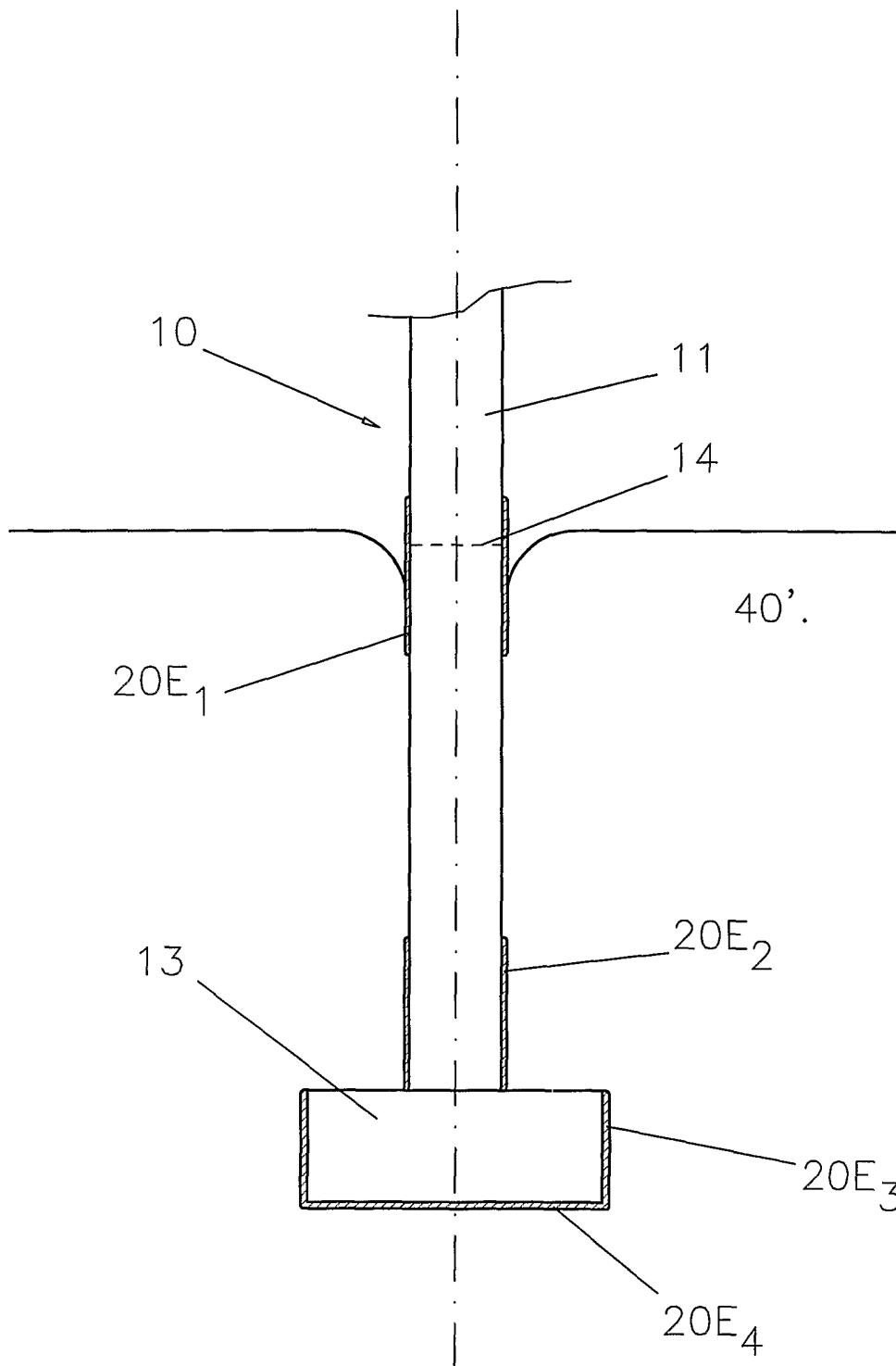


FIGURE 4

INTERNATIONAL SEARCH REPORT

International Application No
PCT/IB 02/01932

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C04B41/89 C25C3/08 C25C3/12 F27D23/04		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) IPC 7 C04B C25C		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, PAJ		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; HAKUTO KAGAKU K. K., JAPAN ET AL: "Coating carbon electrodes" retrieved from STN Database accession no. 102:118464 CA XP002213169 abstract	1-7, 9-13,15, 18-29
Y	& JP 59 184781 A (HAKUTO KAGAKU K. K., JAPAN;NISSHIN STEEL CO., LTD.) 20 October 1984 (1984-10-20) ----- -/--	14
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : *A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *&* document member of the same patent family		
Date of the actual completion of the international search 11 September 2002	Date of mailing of the international search report 30/09/2002	
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Rosenberger, J	

INTERNATIONAL SEARCH REPORT

International Application No

PCT/IB 02/01932

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 17842 A (DURUZ JEAN JACQUES ;MOLTECH INVENT SA (LU); LIU JAMES JENQ (US); S) 30 April 1998 (1998-04-30) cited in the application	28, 29
Y A	claims 1,12,13,17,19,30-33 page 11, line 9 - line 15 page 11, line 23 - line 26 page 12, line 4 - line 17 examples 1,3; table I	14 1-7, 9-13,15, 18-27
A	WO 93 20027 A (NORA VITTORIO DE ;MOLTECH INVENT SA (LU); SEKHAR JAINAGESH A (US)) 14 October 1993 (1993-10-14) cited in the application claims	
A	WO 00 63630 A (DURUZ JEAN JACQUES ;HOLZ K JACQUELINE (FR); MOLTECH INVENT SA (LU)) 26 October 2000 (2000-10-26) cited in the application claims	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/IB 02/01932

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
JP 59184781	A	20-10-1984	NONE	
WO 9817842	A	30-04-1998	AU 713415 B2 AU 5084898 A DE 69711900 D1 EP 0932589 A2 NO 991841 A WO 9817842 A2	02-12-1999 15-05-1998 16-05-2002 04-08-1999 18-06-1999 30-04-1998
WO 9320027	A	14-10-1993	US 5310476 A AU 677777 B2 AU 3950993 A AU 3951093 A CA 2131287 A1 CA 2131288 A1 DE 69319721 D1 DE 69319721 T2 DE 69327095 D1 DE 69327095 T2 WO 9320026 A1 WO 9320027 A1 EP 0633870 A1 EP 0633871 A1 ES 2141764 T3 NO 943656 A NO 943657 A WO 9325731 A1 US 5340448 A US 5527442 A US 6139704 A US 6287447 B1 US 6402926 B1 US 6001236 A US 2002043469 A1	10-05-1994 08-05-1997 08-11-1993 08-11-1993 14-10-1993 14-10-1993 20-08-1998 25-03-1999 30-12-1999 27-04-2000 14-10-1993 14-10-1993 18-01-1995 18-01-1995 01-04-2000 30-09-1994 30-09-1994 23-12-1993 23-08-1994 18-06-1996 31-10-2000 11-09-2001 11-06-2002 14-12-1999 18-04-2002
WO 0063630	A	26-10-2000	AU 4135900 A EP 1190203 A1 WO 0063630 A1 AU 1544201 A AU 1544301 A WO 0142531 A1 WO 0142168 A1	02-11-2000 27-03-2002 26-10-2000 18-06-2001 18-06-2001 14-06-2001 14-06-2001