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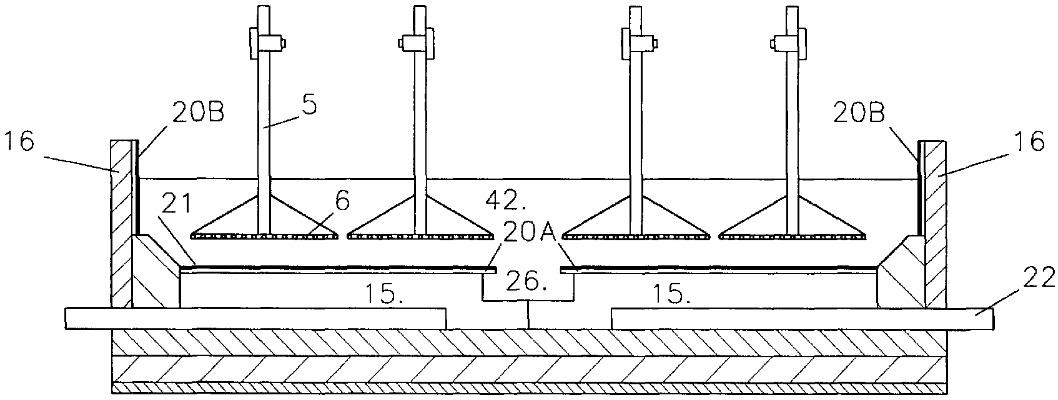
(54) **Title:** CARBON TILES WITH REFRACTORY COATING FOR USE AT ELEVATED TEMPERATURE



(57) **Abstract:** A method of bonding a protective coating on a wear-exposed surface of a carbon tile comprises: applying onto the wear-exposed surface of the carbon tile at least one layer of a slurry of particulate refractory material suspended in a colloidal and/or inorganic polymeric carrier comprising a dispersion of colloidal particles and/or a solution of inorganic polymeric particles of binding metal oxide; and heat treating the slurry-applied layer(s) to consolidate the particulate refractory material in the binding metal oxide to form the protective coating. A hydrophobic carbon compound having a hydrophilic substituent, such as -OH, -SO_3Na or -COOH, is used in the slurry as a bonding agent that bonds the binding metal oxide to the carbon tile by being bonded to the wear-exposed surface of the carbon tile and by having its hydrophilic substituent bonded to the binding metal oxide. Preferably, the protective coating comprises on the layer(s) containing the hydrophobic carbon compound one or more layers of refractory material which are substantially free of any elemental carbon or organic carbon compound.

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.

CARBON TILES WITH REFRACTORY COATING FOR USE AT ELEVATED TEMPERATURE

Field of the Invention

The invention relates to the protection with a refractory coating of carbon tiles, in particular for use in oxidising and/or corrosive environments.

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.

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 WO00/63630 (Holz/Duruz).

During the electrowinning of metals, such as aluminium, some components are exposed to molten electrolyte, molten metal and corrosive gases. In conventional aluminium production cells these components are still made of consumable carbonaceous materials.

Aluminium is produced conventionally by the Hall-Héroult process, by the electrolysis of alumina dissolved in cryolite-based molten electrolytes at temperatures up to around 950°C. A Hall-Héroult 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 and corrosive gases. Conductor bars connected to the negative pole of a direct current source are embedded in the carbon cathode forming the cell bottom floor. The cathode 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.

The use of titanium diboride and other RHM current-conducting elements in electrolytic aluminium production cells has been contemplated for long time and is described in US Patents Nos 2,915,442, 3,028,324, 3,215,615, 3,314,876, 3,330,756, 3,156,639, 3,274,093 and 3,400,061. Despite extensive efforts and the potential advantages of having surfaces of titanium diboride at the cell cathode bottom, such propositions have not been commercially adopted by the aluminium industry.

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. Many difficulties were encountered in producing refractory boride coatings which meet up to the rigorous conditions in an aluminium electrowinning cell. Nevertheless, as described in the following patents, such coatings on carbon bodies have recently been introduced.

WO01/42168 (de Nora/Duruz) and WO01/42531 (Nguyen/Duruz/de Nora) disclose applying a protective coating of a refractory boride such as titanium diboride to a carbon component of an aluminium electrowinning cell, by applying thereto a slurry of particulate boride in a colloid in several layers.

US Patents 4,333,813 and 4,341,611 (both in the name of Kaplan) disclose an aluminium electrowinning cell with a carbon cathode bottom covered with tiles having a refractory hard metal surface, e.g. made of TiB_2.

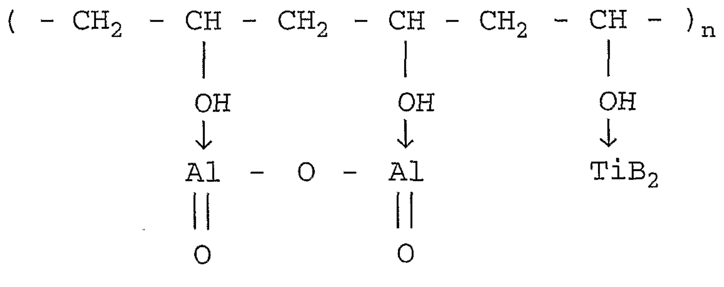
WO 98/17842 (Sekhar/Duruz/Liu) discloses inter-alia tiles that can be fitted together to form an aluminium production cell. The tiles can be made of a carbon substrate covered with a refractory boride coating applied from a colloidal slurry containing a particulate of the refractory boride. To obtain improved coatings without mud-cracks certain organic additives can be added to the colloidal slurry such as polyvinyl alcohol, polyacrylic acid, hydroxy propyl methyl cellulose, polyethylene glycol, ethylene glycol, butyl benzyl phthalate and ammonium polymethacrylate.

Summary of the Invention

The invention relates to a method of bonding a protective coating on a wear-exposed surface of a carbon tile comprising applying onto the wear-exposed surface of the carbon tile at least one layer of a slurry of particulate refractory material and/or a heat convertible precursor thereof suspended in a colloidal and/or inorganic polymeric carrier comprising a dispersion of colloidal particles and/or a solution of inorganic polymeric particles of binding metal oxide and/or a heat convertible precursor of the binding oxide; and heat treating the slurry-applied layer(s) to consolidate the particulate refractory material in the binding metal oxide to form said protective coating.

According to the invention a hydrophobic (organic) carbon compound, usually a carbon monomer or polymer, having a hydrophilic substituent is used in the slurry as a bonding agent that bonds the binding metal oxide to the carbon tile by being bonded to the wear-exposed surface of the carbon tile and by having its hydrophilic substituent bonded to the binding metal oxide.

The bonding between the hydrophilic substituent and the (hydrophilic) colloidal and/or inorganic polymeric particles 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) carbon compound with hydrophilic substituents, the bonding of the constituents is as follows:



$$\begin{array}{ccccccc} (- CH_2 - & CH & - CH_2 - & CH & - CH_2 - & CH & -)_n \\ & | & & | & & | & \\ & OH & & OH & & OH & \\ & \downarrow & & \downarrow & & \downarrow & \\ & Al & - O - & Al & & TiB_2 & \\ & \| & & \| & & & \\ & O & & O & & & \end{array}$$

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 $-CH_2-$) of the polyvinyl alcohol chain are absorbed by the surface of the (hydrophobic) carbon tile and secure the layer thereon.

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

Suitable hydrophilic substituents of carbon compound(s) may be selected from -OH, $-SO_3Na$ and -COOH, and combinations thereof. The carbon compound(s) can have a carbon/hydrophilic substituent ratio in the range of 2 to 4. For example, the 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.

Usually, the tiles are from 10 to 120 cm long, in particular from 10 to 50 cm long, from 10 to 50 cm wide and from 0.5 to 5 cm thick.

In a preferred embodiment the protective coating comprises on the layer(s) containing the hydrophobic carbon compound (hereinafter called the "bonding layer") one or more hydrophilic layer(s) of refractory material which are substantially free of any elemental carbon or organic carbon compound.

The attachment between the bonding layer(s) and the hydrophilic layer(s) is ensured by the affinity between hydrophilic constituents, e.g. ceramics, present in the layers.

It follows that the or each hydrophilic layer on the bonding layer(s) is well bonded to the carbon tile without containing at its surface organic carbon material that could react during use to form carbides or other compounds, in particular aluminium carbide when exposed to aluminium, thereby damaging the protective coating and impairing its electrical conductivity.

Conveniently, the or each hydrophilic layer is also applied from a slurry of particulate refractory material and/or a heat convertible precursor thereof suspended in a colloidal and/or polymeric carrier comprising a dispersion of particles of a binding metal oxide and/or a heat convertible precursor thereof.

The protective coating, in particular the bonding and/or the hydrophilic layer(s), may comprise a binding metal oxide selected from lithia, beryllium oxide, magnesia, alumina, silica, titania, vanadium oxide, chromium oxide, magnesia, iron oxide, nickel 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. In particular, the slurry can contain 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.

Usually, the hydrophilic colloidal particles are 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 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 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 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 protective coating, in particular the bonding and/or the hydrophilic layer(s), usually comprises a 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.

It is preferable to choose particle size below 100 microns for the non-dispersed 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 $MoSi_2$ as non-dispersed particles it is preferable to choose the particle size of the $MoSi_2$ 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.

Advantageously, the slurry (-ies) producing the protective coating, in particular the bonding and/or the hydrophilic layer(s), comprise(s) a reinforcing metal oxide which reacts with the bonding metal oxide and an integral oxide film on the particles of refractory metal compound to form a mixed oxide matrix embedding the refractory metal compound particles. Suitable combinations of refractory metal compounds, bonding metal oxides and reinforcing metal oxides are disclosed in WO01/42531 (Nguyen/Duruz/de Nora).

The protective coating, in particular the bonding and/or the hydrophilic layer(s), can comprise an aluminium-wetting metal oxide, such as oxides of iron, copper, cobalt, nickel, zinc or manganese, which when exposed to molten aluminium reacts therewith to produce aluminium oxide and the metal of the aluminium-wetting metal oxide, as disclosed in WO01/42168 (de Nora/Duruz).

When the protective coating has hydrophilic and bonding layers, the hydrophilic layer(s) preferably comprise(s) the aluminium-wetting oxide, the bonding layer(s) being made of aluminium-repellent material substantially free of any aluminium-wetting metal oxide. In this way, the protective coating can be well wetted by molten aluminium without exposing the carbon tile to aluminium which would react with the carbon tile to form aluminium carbide and impair the adherence of the protective coating.

Preferably the carbon tile is made of graphite or graphitised carbon material.

The carbon tile can comprise a bottom surface which is not covered with the protective coating.

Another aspect of the invention relates to a slurry for forming a protective coating of particulate refractory material consolidated in a binding metal oxide upon application and heat treatment of the slurry on a wear-exposed surface of a carbon tile for use in an aluminium electrowinning cell. The slurry comprises the particulate refractory material and/or a heat convertible precursor thereof suspended in a colloidal and/or inorganic polymeric carrier comprising a dispersion of colloidal particles and/or a solution of inorganic polymeric particles of binding metal oxide and/or a heat convertible precursor of the binding oxide.

More particularly the invention relates to the use in such a slurry of a hydrophobic carbon compound having a hydrophilic substituent as an agent for bonding the binding metal oxide to the carbon tile by bonding the hydrophobic carbon compound to the wear-exposed surface of the carbon tile and by bonding its hydrophilic substituent to the binding metal oxide.

Another aspect of the invention relates to a tile that comprises a carbon substrate having a wear-exposed surface covered with a protective coating that comprises: at least one bonding layer of particulate refractory material consolidated in a binding metal oxide formed on the wear-exposed surface of the carbon substrate from a heat-treated slurry that comprises the particulate refractory material and/or a heat convertible precursor thereof suspended in a colloidal and/or inorganic polymeric carrier comprising a dispersion of colloidal particles and/or a solution of inorganic polymeric particles of binding metal oxide and/or a heat convertible precursor of the binding oxide; and one or more outer layers of refractory ceramic material.

According to the invention, the outer layer(s) is/are hydrophilic and substantially free of any elemental carbon or organic carbon compound, and the bonding layer(s) further comprise(s) dispersed particles of elemental carbon and/or a carbon compound derived from a hydrophobic carbon compound having a hydrophilic substituent that is present is the slurry prior to heat treatment and that bonds the binding metal oxide to the carbon tile by being bonded to the wear-exposed surface of the carbon substrate and by having its hydrophilic substituent bonded to the binding metal oxide.

A further aspect of the invention concerns an apparatus for the production, purification or recycling of a metal in a molten state. The apparatus comprises at least one component which is protected against a high temperature environment that is oxidising and/or corrosive, and gaseous and/or molten, by at least one tile as described above.

The apparatus can be a cell for the electrowinning of a metal from a compound thereof dissolved in a molten electrolyte. In this case, the tile protects a cell component against the electrowon metal, the molten electrolyte and/or cell gases.

In one embodiment, the apparatus is an aluminium electrowinning cell, the tile protecting the cell component against at least one of molten aluminium, molten electrolyte and anodically produced gases. The hydrophilic layer(s) of the tile may form a cathodic surface which can be aluminium-wettable and optionally drained.

In another embodiment, the apparatus is an arc furnace for the recycling of steel, the tile protecting a component against oxidising gas and/or molten steel.

In a further embodiment, the apparatus is a device for the purification of a molten metal, in particular molten aluminium, magnesium, iron or steel, by the injection of a purifying fluid into the molten metal to remove impurities towards the surface thereof, the tile protecting a component of the device against the molten metal to be purified, the purifying fluid and/or impurities of the molten metal.

As opposed to direct application of the slurry of refractory material to a component, e.g. a cathode bottom, of an apparatus followed by in-situ heat-treatment to form the coating, the application of the slurry to a tile permits consolidation by heat-treatment of the slurry in a controlled environment on the tile before use of the coating in the apparatus.

The invention also relates to a method of producing, purifying or recycling a metal in one the above mentioned apparatus. The method comprises using the tile described above to protect a component of the apparatus against a high temperature environment which is oxidising and/or corrosive, and gaseous and/or molten.

For the electrowinning of metal, the method comprises electrolysing a metal compound, in particular alumina, in a molten electrolyte of a metal electrowinning cell to produce the metal, in particular aluminium, of the compound cathodically and gas anodically, and using the tile to protect a cell component against at least one of electrolyte, cathodically produced metal and anodically produced gas.

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 having its cathode bottom and sidewalls lined with aluminium-wettable tiles according to the invention;

- Figure 2 schematically shows an arc electrode furnace having sidewalls and bottom lined with the tiles according to the invention;

- Figure 3 shows an apparatus for the purification of a molten metal having sidewalls and bottom lined with the tiles according to the invention;

- Figure 3a is an enlarged schematic sectional view of part of a 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 metal-based anodes 5 having operative surfaces 6 suspended over drained generally horizontal cathode surface 21 in a fluoride-containing molten electrolyte 42 containing dissolved alumina.

The anodes 5 can be of the type disclosed in WO00/40781 or WO00/40782 (both de Nora) and made of the materials disclosed in any one of the following references: WO99/36591 and WO99/36592 (both in the name of de Nora), WO99/36593 and WO99/36594 (both in the name of de Nora/Duruz), WO00/06800 (Duruz/de Nora), WO00/06801 (de Nora/Duruz), WO00/06802 and WO00/06803 (both in the name of Duruz/de Nora/Crottaz), WO00/06804 (Crottaz/Duruz), WO00/06805, WO00/40783 and WO01/42534 (all in the name of de Nora/Duruz), and WO01/42536 (Duruz/Nguyen/de Nora), and WO01/43208 (Duruz/de Nora).

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 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).

The drained cathode surface 21 is formed according to the invention by tiles 20A which have their upper face coated with a bonding layer and an (outer) hydrophilic aluminium-wettable layer (free of any elemental carbon or organic carbon compound) according to the invention and a temporary start-up layer as taught in Example 4 below.

The tiles 20A are placed side-by-side on a series of carbon cathode blocks 15 extending in pairs arranged end-to-end across the cell. As shown in Figure 1, each cathode block 15 is covered by a tile 20A that extends from the side of the cell to the centre of the cell. Alternatively, a plurality of smaller tiles placed side-by-side across the cell could be used to cover such a cathode block.

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.

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 tiles 20A preferably cover a substantial part of the groove 26 to maximise the surface area of the aluminium-wettable cathode surface 21. The tiles 20A leave only a vertical opening, e.g. a gap between two tiles 20A across the cell, above the groove 26 sufficient to let product aluminium drain from the aluminium-wettable cathode surface 21 through the small vertical opening into the aluminium collection groove 26. This vertical opening can also be used to access groove 26 for the tapping of molten aluminium.

The cell comprises carbonaceous sidewalls 16 exposed to molten electrolyte 42 and to the environment above the molten electrolyte 42. These sidewalls 16 are protected against the molten electrolyte 42 and the environment above the molten electrolyte with tiles 20B according to the invention.

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 tiles 20A.

The cathodically-produced molten aluminium flows on the drained cathode surface 21 into the aluminium collection groove 26 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 a sloping cathode bottom, as disclosed in WO99/02764 (de Nora/Duruz), and optionally one or more aluminium collection reservoirs across the cell, each intersecting the aluminium collection groove to divide the drained cathode surface into four quadrants as described in WO00/63463 (de Nora).

The cell's cathodic tiles may be covered with a shallow or deep pool of aluminium as disclosed in US Patent 5,651,874 (de Nora/Sekhar).

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 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 bottom and sidewalls 45 of the furnace are protected with coated carbon tiles 20C according to the invention.

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

The consumable electrodes 15A are made of a carbon substrate laterally coated with a protective layer 20 protecting the carbon substrate from oxidising gas. The bottom of electrodes 15A which is consumed during operation and constitutes the electrodes' operative surface is uncoated. The protective layer 151 protects only the electrodes' lateral faces against premature oxidation. Suitable protective layers are disclosed in WO01/42168 (de Nora/Duruz), WO01/42531 (Nguyen/Duruz/de Nora) and PCT/IB01/00949 (Nguyen/de Nora).

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, 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. The iron source 41 and the liquid iron or steel 40 contact the tiles 20C.

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 flotation forming a slag (not shown) which is removed, for example through one or more apertures (not shown) located on the tiles 20C and sidewalls of the arc furnace at the level of the slag.

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, through the tiles 20C.

Molten Metal Purification Apparatus:

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. The sidewalls and bottom of the vessel 45 are protected with coated carbon tiles 20D according to the invention.

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'.

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.

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.

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 a protective layer 111 which improves the resistance to erosion, oxidation and/or corrosion of the stirrer during operation.

As shown in Figure 3, the upper part of shaft 11 is protected against oxidation and/or corrosion with a protective layer 112. The upper part of the carbon-based shaft 11 is coated with a thin layer of refractory material 112 protection against oxidation and corrosion, whereas the layer 111 protecting the immersed part of the shaft 11 and the rotor 13 is a thicker layer of refractory material against erosion, oxidation and corrosion.

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 tiles 20C protect the sidewalls and bottom of the vessel 45 against molten metal, the reactive or non-reactive fluid and air.

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 a protective layer.

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 113, 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 113 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 covered with a protective layer 113. The lateral surface of rotor 13 is covered with a protective layer 131 and the bottom surface of the rotor 13 is coated with a protective layer 132.

For each specific stirrer design, the layer or different protective layers on different parts of the stirrer, such as layers 113, 114, 131 and 132 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.

Suitable coatings for protecting the shaft 11 and the rotor 13 are described in WO00/63630 (Holz/Duruz), WO01/42168 (de Nora/Duruz), WO01/42531 (Nguyen/Duruz/de Nora) and PCT/IB01/00949 (Nguyen/de Nora).

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.

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, 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. Such a composite shaft would preferably be 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 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. 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-pending application WO97/26626 (de Nora/Duruz/Berclaz).

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

Further details of such a purification or treatment apparatus are disclosed in WO00/63630 (Holz/Duruz).

The invention will be further described in the following examples.

Example 1

A slurry for use on a carbon tile in accordance with 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 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/or Polymeric Oxides	Suspended Reinforcing Metal Oxides	Suspended Surface-Oxidised Refractory Metal Compounds
Al_2O_3	TiO_2, MgO or SiO_2	TiB_2, SiC, TiC or TiN
TiO_2	Al_2O_3 or MgO	SiC or SiN
SiO_2	Al_2O_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 a hydrophilic layer free of organic carbon (elemental or in the form of a compound) which can be bonded through a bonding layer to a carbon tile in accordance with the invention was prepared by suspending 2.5 g particulate Fe_2O_3 (-325 mesh), a refractory hard metal boride consisting of 92.5 g particulate needle-shaped surface-oxidised TiB_2 (-325 mesh) having a TiO_2 surface oxide film, and 2.5 g particulate TiO_2 (-325 mesh) in a colloid consisting of a combination of two grades of colloidal Al_2O_3, namely 28 ml of a first grade of colloidal Al_2O_3 (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 Al_2O_3 (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 TiO_2, Fe_2O_3 and Al_2O_3. This matrix contains and bonds the TiB_2 and Fe_2O_3 particles.

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

Example 2a

Example 2's slurry composition consists of Fe_2O_3 and a reaction mixture made of the colloid (Al_2O_3), the suspended refractory metal boride (TiB_2) the suspended metal oxide (TiO_2). 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.

Example 3

A further slurry for producing a highly aluminium-wettable hydrophilic start-up layer free of organic carbon which can be bonded through a bonding layer to a carbon tile 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).

Example 4

Three graphite tiles for use on a cathode bottom of a drained-cathode cell for the production of aluminium were covered with a multi-layer coating produced from the slurries of Examples 1, 2 and 3 as follows:

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

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

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

The coating formed by the bonding layer, the permanent aluminium-wettable hydrophilic layers and the temporary start-up layer on the tile was allowed to dry for 24 hours.

Two of the three coated tiles 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 coated tile 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 bonding layer was intimately bonded to the (hydrophobic) carbon tile.

The second coated tile 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 hydrophilic layers. 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 bonding layer for lack of oxide reactable with aluminium.

The aluminium metal infiltration into the start-up layer and the permanent aluminium-wettable hydrophilic layers 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 tiles showed a continuous matrix of titanium-aluminium mixed oxides between the bonding layer and the permanent aluminium-wettable hydrophilic layers which guarantees an excellent adherence between the layers. In both cases the particles of TiB_2 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.

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

The graphite tile with the dried coating according to the invention was placed on the cell cathode bottom and covered 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.

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.

The cell was further heated to 960°C at which temperature the cell was operated under an electrolysis current density of 0.8 A/cm^2 to produce aluminium under conventional steady state conditions.

Example 5

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.

(A) An amount of 150 g of $Fe(NO_3)_3.9\ H_2O$ was heated to dissolve the salt in its own water of crystallisation to form a solution containing 29 g Fe_2O_3. The solution was heated to 120°C and 18.9 g of magnesium hydroxy-carbonate dissolved in the hot solution to form 7.5 g MgO in form of an inorganic polymer together with Fe_2O_3 suitable for use as an inorganic polymeric carrier.

(B) An amount of 100 g of $Cr(NO_3)_3.9\ H_2O$ was heated to dissolve the salt in its own water of crystallisation to form a solution containing 19 g Cr_2O_3. 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/cm^3 suitable to act as an inorganic polymeric carrier.

CLAIMS

1. A method of bonding a protective coating on a wear-exposed surface of a carbon tile comprising:

- applying onto the wear-exposed surface of the carbon tile at least one layer of a slurry of particulate refractory material and/or a heat convertible precursor thereof suspended in a colloidal and/or inorganic polymeric carrier comprising a dispersion of colloidal particles and/or a solution of inorganic polymeric particles of binding metal oxide and/or a heat convertible precursor of the binding oxide; and
- heat treating the slurry-applied layer(s) to consolidate the particulate refractory material in the binding metal oxide to form said protective coating,

characterised by using in said slurry a hydrophobic carbon compound having a hydrophilic substituent as a bonding agent that bonds the binding metal oxide to the carbon tile by being bonded to the wear-exposed surface of the carbon tile and by having its hydrophilic substituent bonded to the binding metal oxide.

2. The method of claim 1, wherein said hydrophilic substituent is selected from -OH, $-SO_3Na$ and -COOH.

3. The method of claim 2, wherein said carbon compound having a hydrophilic substituent is selected from ethylene glycol, hexanol, polyvinyl alcohol, polyvinyl acetate, polyacrylic acid, hydroxy propyl methyl cellulose and ammonium polymethacrylate.

4. The method of any preceding claim, wherein the protective coating comprises on the layer(s) containing the hydrophobic carbon compound (hereinafter called the "bonding layer(s)") one or more hydrophilic layers of refractory material which are substantially free of any elemental carbon or organic carbon compound.

5. The method of claim 4, wherein the hydrophilic layer(s) is/are applied from a slurry of particulate refractory material and/or a heat convertible precursor thereof suspended in a colloidal and/or inorganic polymeric carrier comprising a dispersion of colloidal particles and/or a solution of inorganic polymeric

particles of binding metal oxide and/or a heat convertible precursor of the binding oxide.

6. The method of any preceding claim, wherein the protective coating comprises a binding metal oxide selected from lithia, beryllium oxide, magnesia, alumina, silica, titania, vanadium oxide, chromium oxide, magnesia, iron oxide, nickel 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.

7. The method of any preceding claim, wherein the protective coating comprises a 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.

8. The method of any preceding claim, wherein the protective coating comprises an aluminium-wetting metal oxide which when exposed to molten aluminium reacts therewith to produce alumina and the metal of said aluminium-wetting metal oxide.

9. The method of claim 8, wherein the aluminium-wetting metal oxide is selected from oxides of iron, copper, cobalt, nickel, zinc and manganese.

10. The method of claim 8 or 9 when depending on claim 4, wherein the hydrophilic layer(s) comprise(s) the aluminium-wetting oxide, the bonding layer(s) being made of aluminium-repellent material substantially free of any aluminium-wetting metal oxide.

11. The method of any preceding claim, wherein the carbon tile is made of graphite or graphitised carbon material.

12. The method of any preceding claim, wherein the carbon tile comprises a bottom surface which is not covered with the protective coating.

13. Use, in a slurry for forming a protective coating of particulate refractory material consolidated in a binding metal oxide upon application and heat treatment of said slurry on a wear-exposed surface of a carbon tile for use in an aluminium electrowinning cell, which slurry comprises the particulate refractory material and/or a

heat convertible precursor thereof suspended in a colloidal and/or inorganic polymeric carrier comprising a dispersion of colloidal particles and/or a solution of inorganic polymeric particles of binding metal oxide and/or a heat convertible precursor of the binding oxide,

of a hydrophobic carbon compound having a hydrophilic substituent as an agent for bonding the binding metal oxide to the carbon tile by bonding the hydrophobic carbon compound to the wear-exposed surface of the carbon tile and by bonding its hydrophilic substituent to the binding metal oxide.

14. A tile comprising a carbon substrate having a wear-exposed surface covered with a protective coating comprising:

- at least one bonding layer of particulate refractory material consolidated in a binding metal oxide formed on the wear-exposed surface of the carbon substrate from a heat-treated slurry that comprises the particulate refractory material and/or a heat convertible precursor thereof suspended in a colloidal and/or inorganic polymeric carrier comprising a dispersion of colloidal particles and/or a solution of inorganic polymeric particles of binding metal oxide and/or a heat convertible precursor of the binding oxide; and

- one or more outer layers of refractory material on the bonding layer(s),

characterised in that the outer layer(s) is/are hydrophilic and substantially free of any elemental carbon or organic carbon compound, and that the bonding layer further comprises dispersed particles of elemental carbon and/or a carbon compound derived from a hydrophobic carbon compound having a hydrophilic substituent that is present is said slurry prior to heat treatment and that bonds the binding metal oxide to the carbon tile by being bonded to the wear-exposed surface of the carbon substrate and by having its hydrophilic substituent bonded to the binding metal oxide.

15. The tile of claim 14, wherein the hydrophilic layer(s) is/are applied from a slurry of particulate refractory material and/or a heat convertible precursor thereof suspended in a colloidal and/or inorganic polymeric carrier comprising a dispersion of colloidal particles and/or a solution of inorganic polymeric

particles of binding metal oxide and/or a heat convertible precursor of the binding oxide.

16. The tile of claim 14 or 15, wherein the protective coating comprises a binding metal oxide selected from lithia, beryllium oxide, magnesia, alumina, silica, titania, vanadium oxide, chromium oxide, magnesia, iron oxide, nickel 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.

17. The tile of any one of claims 14 to 16, wherein the protective coating comprises a 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.

18. The tile of any one of claims 14 to 17, wherein the protective coating comprises an aluminium-wetting metal oxide which when exposed to molten aluminium reacts therewith to produce alumina and the metal of said aluminium-wetting metal oxide.

19. The tile of claim 18, wherein the aluminium-wetting metal oxide is selected from oxides of iron, copper, cobalt, nickel, zinc and manganese.

20. The tile of claim 18 or 19, wherein the hydrophilic layer(s) comprise(s) the aluminium-wetting oxide, the bonding layer(s) being made of aluminium-repellent material substantially free of any aluminium-wetting metal oxide.

21. The tile of any one of claims 14 to 20, wherein the carbon substrate is made of graphite or graphitised carbon material.

22. The tile of any one of claims 14 to 21, wherein the carbon substrate comprises a bottom surface which is not covered with the bonding and hydrophilic layers.

23. An apparatus for the production, purification or recycling of a metal in a molten state comprising at least one component which is protected against a high temperature environment that is oxidising and/or corrosive, and gaseous and/or molten, by at least one tile as defined in any one of claims 14 to 22.

24. The apparatus of claim 23, which is a cell for the electrowinning of a metal from a compound thereof dissolved in a molten electrolyte, the tile protecting said component against at least one of the electrowon metal, the molten electrolyte and cell gases.

25. The apparatus of claim 24, which is an aluminium electrowinning cell, the tile protecting said component against at least one of molten aluminium, molten electrolyte and anodically produced gases.

26. The apparatus of claim 25, wherein the hydrophilic layer(s) of the tile form(s) a cathodic surface.

27. The cell of claim 26, wherein the cathodic surface is an aluminium-wettable surface, in particular a drained surface.

28. The apparatus of claim 23, which is an arc furnace for the recycling of steel, the tile protecting said component against oxidising gas and/or molten steel.

29. The apparatus of claim 23, which is a device for the purification of a molten metal by the injection of a purifying fluid into the molten metal to remove impurities towards the surface thereof, the tile protecting said component against at least one of the molten metal to be purified, the purifying fluid and impurities of the molten metal.

30. The apparatus of claim 29, which is a device for the purification of molten aluminium, molten magnesium, cast iron or molten steel.

31. A method of producing, purifying or recycling a metal in an apparatus as defined in any one of claims 23 to 29, the method comprising using said tile to protect a component of the apparatus against a high temperature environment which is oxidising and/or corrosive, and gaseous and/or molten.

32. The method of claim 31, which comprises electrolysing a metal compound, in particular alumina, in a molten electrolyte of a metal electrowinning cell to produce the metal, in particular aluminium, of the compound cathodically and gas anodically, and using said tile to protect a component of the cell against at least one of electrolyte, cathodically produced metal and anodically produced gas.

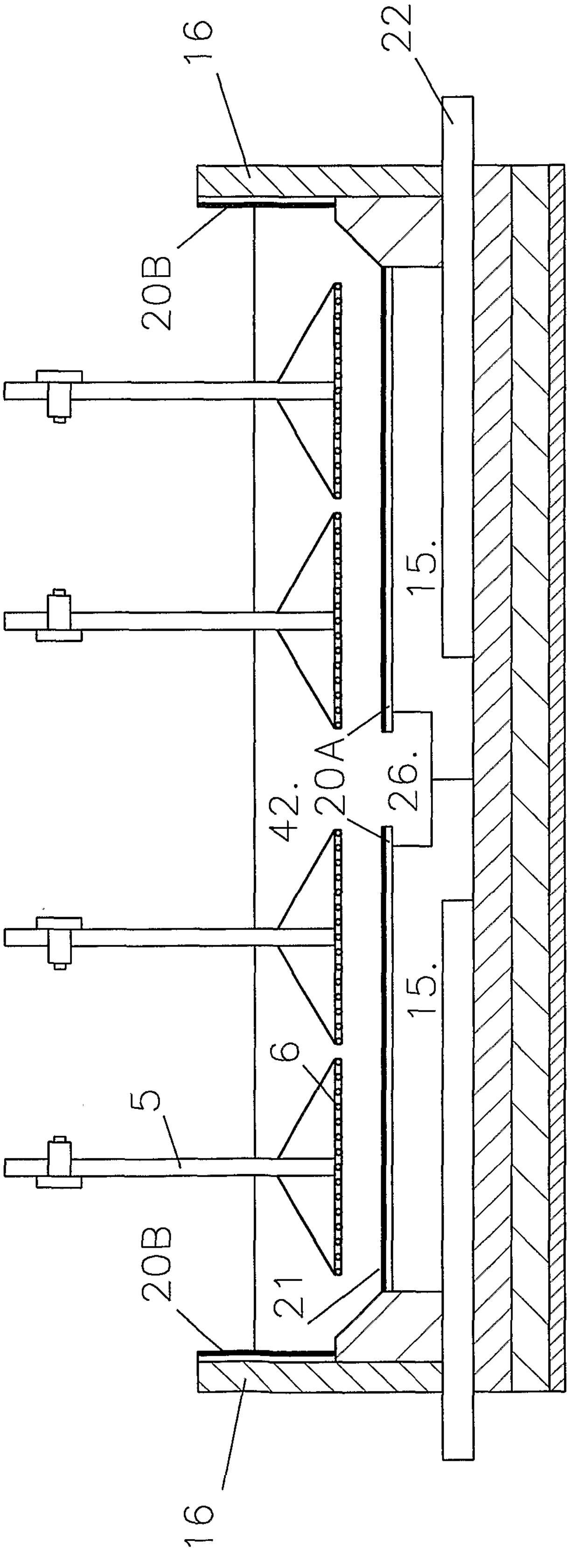


FIGURE 1

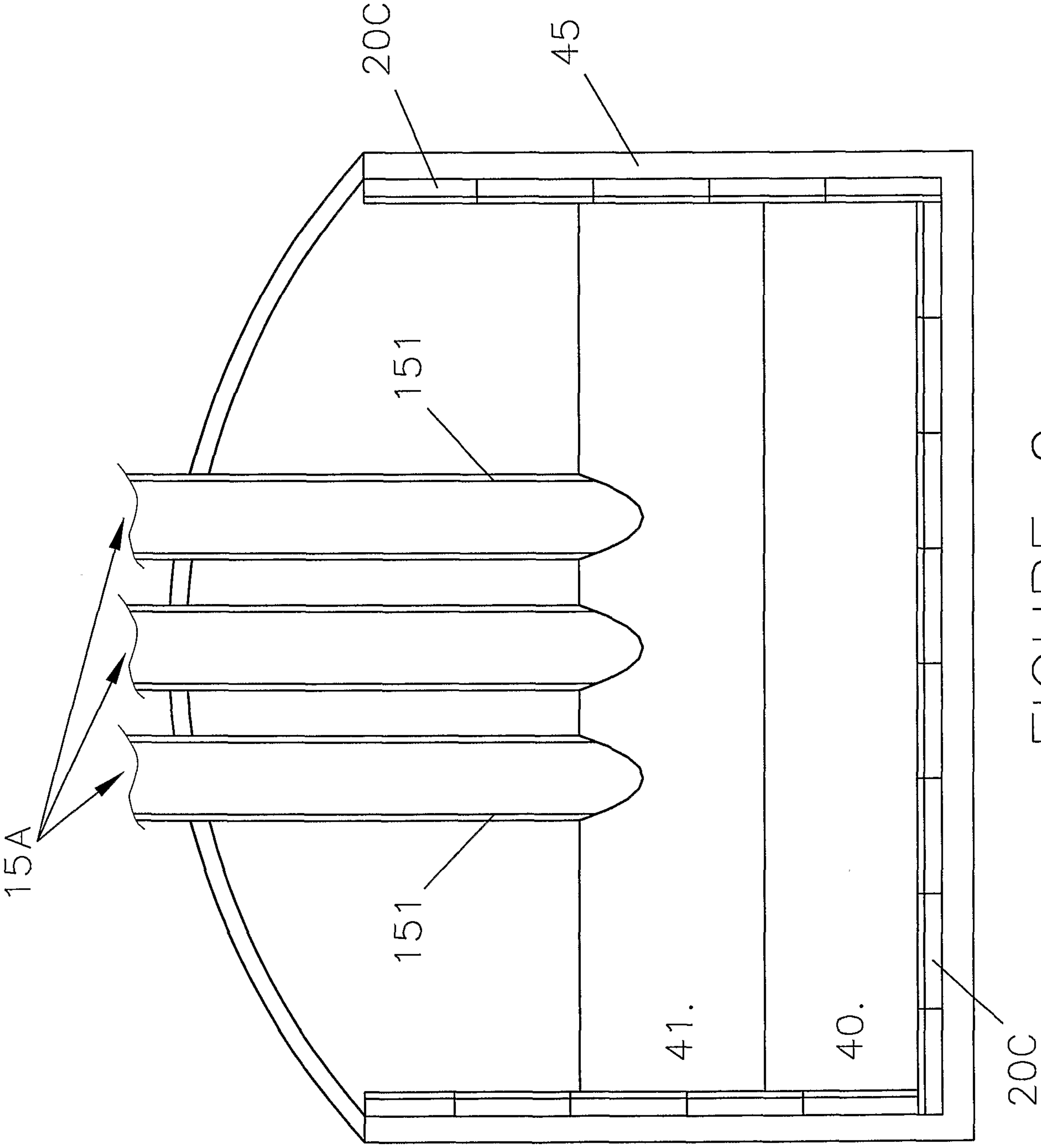


FIGURE 2

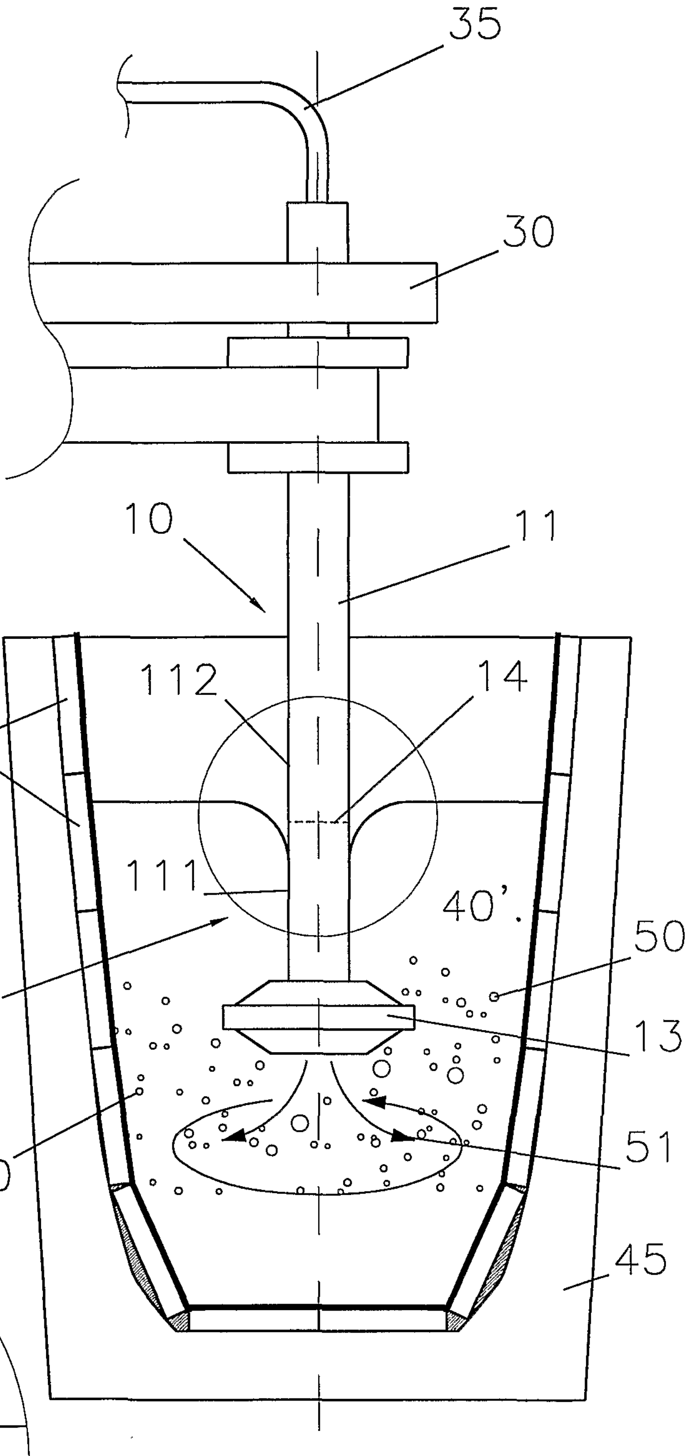


FIG.3

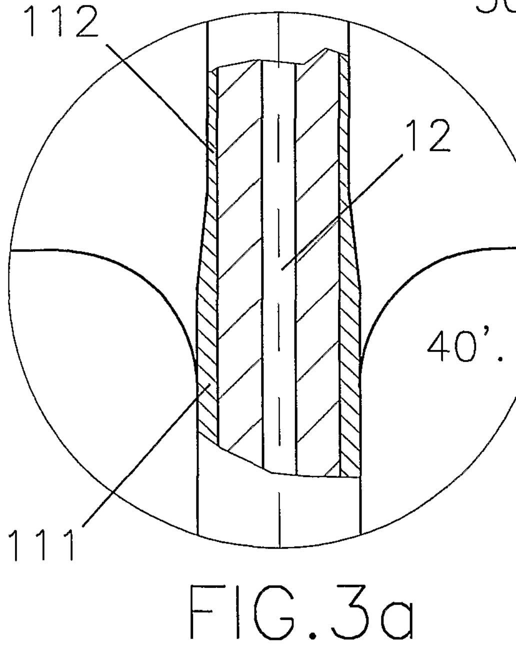


FIG.3a

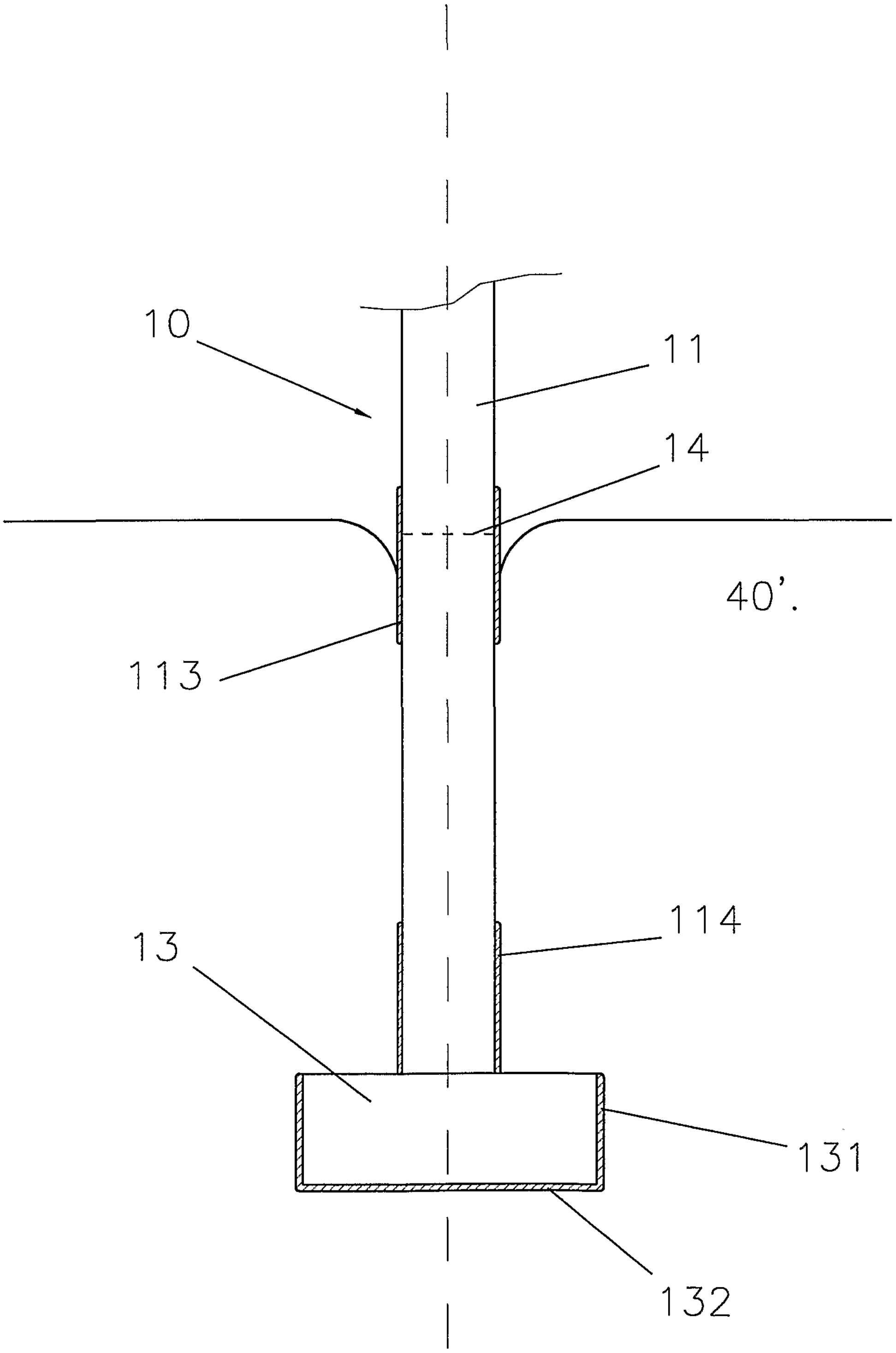


FIGURE 4

INTERNATIONAL SEARCH REPORT

Inte[illegible]onal Application No
PCT/IB 02/01908

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C04B41/89 C25C3/08 C25C3/12

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 & JP 59 184781 A (HAKUTO KAGAKU K. K., JAPAN;NISSHIN STEEL CO., LTD.) 20 October 1984 (1984-10-20) --- -/--	1-7, 11-17, 21-32

☒ Further documents are listed in the continuation of box C.

☒ 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

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"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

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"&" 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

Inte[illegible]onal Application No
PCT/IB 02/01908

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	1-3,6,7, 11-13
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 -----	5,14-17, 21-32

INTERNATIONAL SEARCH REPORT

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Inter[illegible]onal Application No
PCT/IB 02/01908

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WO 9817842	A	30-04-1998	AU	713415	B2	02-12-1999
			AU	5084898	A	15-05-1998
			DE	69711900	D1	16-05-2002
			EP	0932589	A2	04-08-1999
			NO	991841	A	18-06-1999
			WO	9817842	A2	30-04-1998