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[54] CATHODE FOR AN ALUMINIUM FUSION ELECTROLYSIS CELL AND METHOD OF MAKING THE SAME

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[58] **Field of Search** .... 204/243 R, 244–247, 204/290 R

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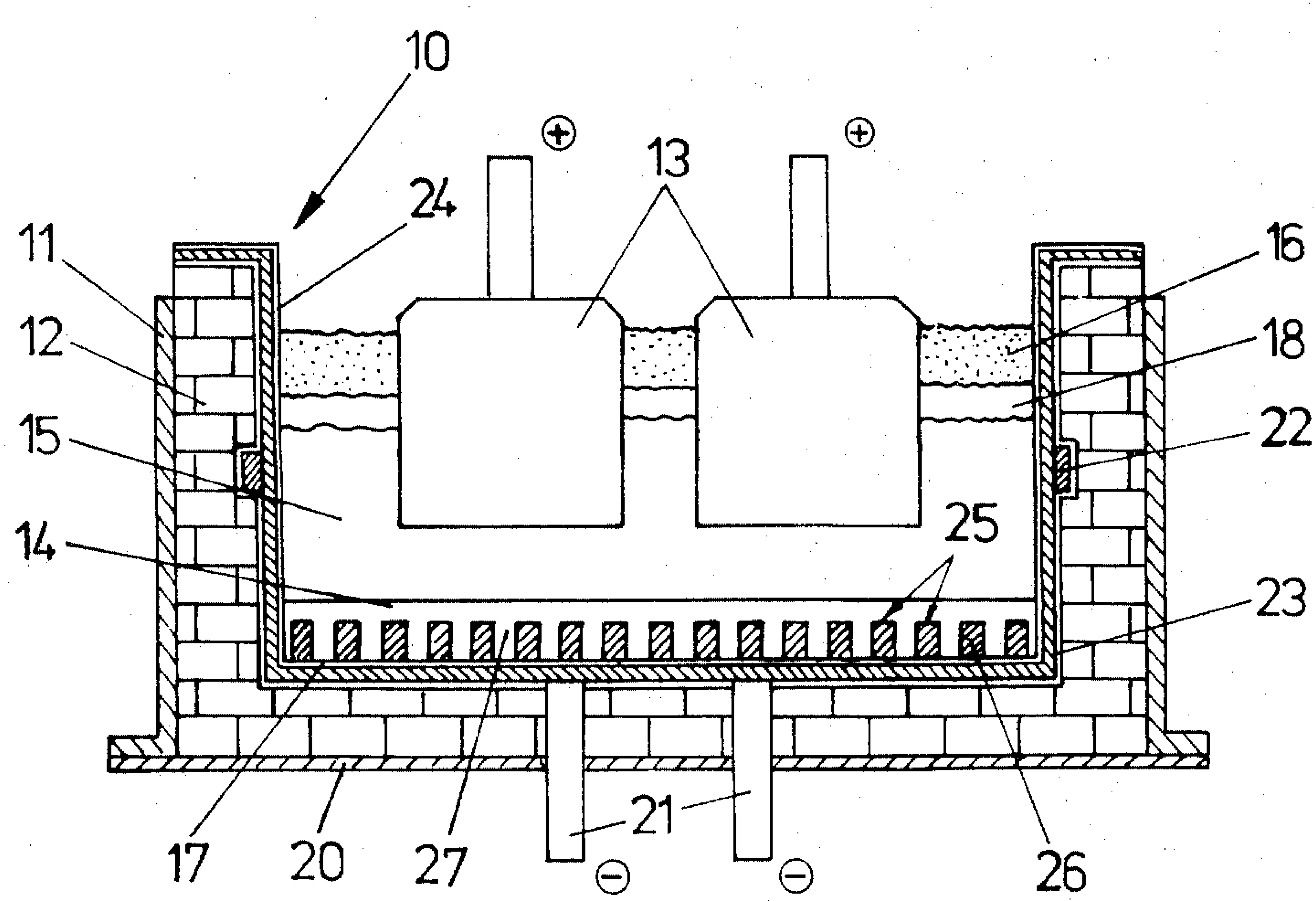
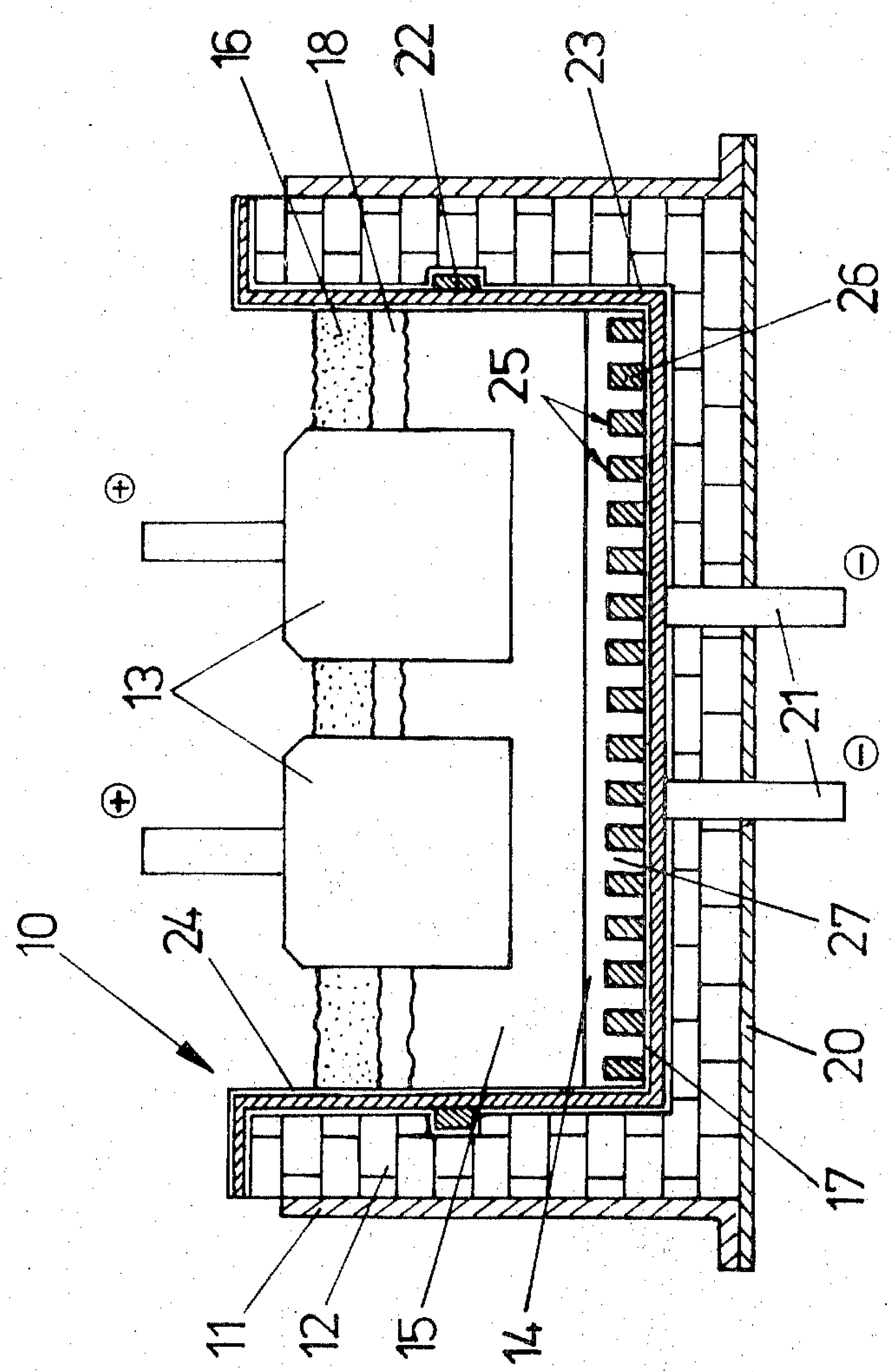
[57] **ABSTRACT**

The invention relates to a cathode for an aluminium fusion electrolysis cell, particularly to a cathode in the form of a pot, comprising walls of electrically conducting material and a coating on the inner surface of the walls of a ceramic material which is electrically conducting and insoluble in fused cryolite and in molten aluminium and further to a method of making a pot in which the ceramic material is applied in finely dispersed form with such energy as to produce adhesion between the ceramic material and the inner surface of the pot and consolidation of the ceramic material.

13 Claims, 1 Drawing Figure

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CATHODE FOR AN ALUMINIUM FUSION ELECTROLYSIS CELL AND METHOD OF MAKING THE SAME

A conventional aluminium fusion electrolysis cell consists of a casing consisting of metal or concrete in which is arranged a pot intended to receive cryolite and electrolytically separated aluminium. Between the outer wall of the pot and the inner wall of the casing there is introduced an electrically non-conducting thermal insulation, which at the same time also supports the pot in the casing. For conductwon of the electrical energy for maintaining the electrolysis in progress, there are provided conductors of a ferrous material connected with the pot.

Because of the physical and chemical conditions created by the aluminium fusion electrolysis and acting on the material of the pot, the pot is usually made of carbon. It can be manufactured by moulding of a mass consisting of carbon with a binder, with subsequent thermal treatment. However, it is preferred to assemble pre-fabricated carbon blocks, with sealing of the separating gaps with a carbon mass, and thereafter to treat the pot thermally. In this procedure, the ferrous conductors, otherwise known as cathode bars, are inserted in a previous operation in channel-shape recesses in one side of the preformed carbon bodies, and are cast around with cast iron to produce the electrical contact, whereupon, for embedding the conductors without gaps, the channel-shaped recesses are filled with carbon mass.

The working temperature of (**130**) an aluminium fusion electrolysis cell lies between 950° and 980°C, and consequently the contents of the pot, consisting of cryolite and separated aluminium, exerts extreme thermal conditions on the pot by reason of its high heat content, which limits the working life of the pot by reason of mechanical effects. During the operation of the cell there takes place an impregnation of the material of the pot with alkali fluorides originating from the cryolite, which produces an additional chemical action on the pot material reducing the life of the pot. This action penetrates to the iron cathods bars, and finally has as a consequence a "break through."

At the end of the working life of the pot there appears a degeneration attributable to these conditions, and revealing itself by current and voltage values departing from the normal, as well as by increasing iron content in the electrolytically separated aluminium. At high expenditure the cell must be put out of action, for renewal of the pot with employment of pre-formed blocks and tamping in of a carbon mass for sealing of cracks as well as introduction of cathode bars, as explained above, with subsequent burning of the entire structure. From endeavours towards an economical cell operation, with the objective of as high as possible a working life of the pot, the walls, especially the wall portions between the pot floor and the upper side of the cathode bars, are made of considerable thickness.

However, the additional costs for each unit of aluminium produced are against an unrestricted choice of the vessel wall thickness, and compel a compromise. Thus with the smallest possible cell ground area, and provision of necessary insulation, a pot content as large as possible is to be aimed at, which, with employment of a good insulating material between vessel and casing, is obtainable only through a reduced vessel wall thickness. Usually during the electrolytic process detectable losses of output arise, which can be attributed to the internal resistance of the cell, which is composed of a series of individual resistances. A given internal cell resistance is unavoidable at the starting of the electrolytic process, but at the present state of cell technology the losses to be noted, and pure losses over and above, are in an order of magnitude which justifies all endeavours to form the cell components with smallest possible individual resistance. The pot consisting of carbon, by reason of its wall thickness, produces a resistance which amounts to a not insignificant part of this output loss.

The invention exerts influences on this, in that the pot on its inner surface has a coating consisting of a ceramic material which is electronically conducting and insoluble in fused cryolite and molten aluminium.

By the invention, defects of the known electrolysis cells are eliminated.

With a metal pot the electrolysis space, with equal external measurements of the casing, is increased by about the thickness of the carbon lining hitherto usual. Furthermore repairs are simplified by the omission of the carbon lining.

With pots consisting of carbon or of carbon with ceramic materials, advantages are also achieved. As compared with conventional wall thicknesses, the coating permits ones of smaller dimensions, with enlargement of the cell space. Furthermore in a pot consisting of carbon of usual wall thickness a deformation of the pot which is based upon an interaction of the pot material with constituents of the pot content is through hindered, which means a significant extension of the working life of the pot.

If the pot is of carbon, the coating protects the inner surfaces of the pot, and especially protects the pot material against impregnation with alkali fluorides. By this means the chemical conditions which have to be regarded in selecting the pot wall thickness are so far diminished in effect, that slighter wall thickness for a comparable or longer working life of the pot become possible, with simultaneous increase of its capacity and reduction of its internal resistance.

This result can also be achieved to an increased extent if the pot consists of a metal resistant to high temperature, for example Cr Ni-steel.

Another possibility is to make the pot of a mixture of carbon with titanium boride, titantium carbide or silicon carbide or of carbon with mixtures of titanium boride, titanium carbide or silicon carbide. This permits a further reduction of the wall thickness as compared with pots consisting of carbon, but without the employment of metallic materials for formation of the pot.

Preferably the ceramic material is applied in finely dispersed form with such energy as to produce adhesion between the ceramic material and the inner surface of the pot and consolidation of the ceramic material.

A construction of electrolytic cell embodying the invention will now be explained in more detail by way of example with reference to the accompanying drawing, which shows a section through the cell.

The cathodically connected part of the aluminium fusion electrolysis cell consists of a pot **10** and a casing **11** surrounding the pot **10**, while an insulating layer **12** is provided between the casing **11** and the pot **10** for maintenance of a desired balance in the pot. On the floor **17** of the pot **10** there collects a layer **14** of electrolytically separated aluminium, on which floats the fused electrolyte consisting of fused cryolite in which alumina is dissolved. At its surface, the fused electrolyte **15** solidifies to a crust **18**, which is covered with a layer **16** of alumina intended for introduction into the electrolyte **15** from time to time. For conduction of electrical energy, anodes **13** extend into the electrolyte **15**, penetrating the alumina and crust.

The base of the housing **11** is formed by a floor plate **20**, which, according to whether the casing consists of metal or concrete, can be made of the same material. Cathodically connected current conductors **21**, consisting of a ferrous material, extend through the base plate **20** and the insulation **12**, and are secured to the pot **10**.

In the embodiment shown in the drawing the pot **10** of rectangular shape is prepared from a heat-resistant steel which still has an adequate mechanical rigidity at the working temperature of the aluminium fusion electrolysis cell of 1,000°C max. The wall thickness of the pot **10** depends on the kind of steel employed, but amounts to at least 5 mm, and reinforcing ribs **22** are fitted on the outer face of the pot. With employment of a metallic pot material, it is suitable to connect the current conductor **21** directly to the floor **17** of the pot.

The outer face of the pot **10** is in contact with the porous insulating layer **12**, which for example can consist of fire-clay blocks. This outer face is preferably coated with a protective coating **23** for the purpose of supression of scaling effects. According to the tendency of the metallic pot material to scaling, the protective coating **23** applied on the outer surface of the pot can consist of an aluminium layer applied by means of flame spraying with a layer of fire-proof cement on it, of iron aluminite/chromium aluminite or nickel aluminite.

On its inner surface the vessel **10** carries the coating **24** according to the invention, which consists of a ceramic material which is electrically conducting and insoluble with reference to the contents of the pot, namely cryolite and aluminium. It is to be particularly required of the ceramic material that, at the working temperature of the aluminium fusion electrolysis cell of 1,000°C max., it still has electric conductivity as far as possible unaffected, and the resistance to attack by the contents of the pot is ensured, even when the pot is cathodically connected. Materials suitable for the coating **24** include the carbides, nitrides, borides and silicides of elements of the 4th to 6th groups of the periodic table, and also silicon carbide, as well as their combinations in intimate mixture and also in successive coatings. Preferred are titanium boride ($Ti\ B_2$), zirconium boride (ZrB_2) or eventually silicon carbide (SiC), because these compounds have the least solubility in molten aluminium and cryolite. Preferably the thickness of the coating amounts to at least 0.1 mm. The coating thickness is determined from the electrical properties of the material employed for formation of the coating, the magnitude of the chemical and thermal actions on the pot material and what residual porosity of the applied coating can be accepted. A coating thickness of 0.5 to 1.0 mm has appeared as suitable, because the thickness ensures an electrical resistance which can be disregarded, and a sufficient statistical pore closure for protection of the material of the pot. During operation the pot undergoes deformations released by heat, which the coating has to match for the purpose of remaining free of fracture. With a coating thickness in the advantageous range, there forms a layer arranged adjacent to the pot material which, after the manner of a buffer coating, equalises a differing movement behaviour of the pot and coating under thermal action.

During its operation an aluminium fusion electrolysis cell continuously undergoes recurrent working operations. To enrich the cryolite with aluminium oxide a crust floating on the cryolite has to be broken through by means of mechanical tools, to eliminate an anode effect the melt has to be set in motion by a stirring tool, the anodes have to be adjusted in the direction towards the cathode to balance their burning away, and separated aluminium has to be removed periodically from the pot by means of a suction pipe. Thus for example during the adjustment of the anodes fragments of anode may fall into the pot contents. Additionally there exists the possibility that, with unskilled handling of the suction pipe the suction pipe mouth may knock against the floor of the pot.

For protection against mechanical effects on the coating **24**, the floor **17** is provided with a grating **25**, which consists of a material insoluble in fused aluminium. Preferably the grating **25** is formed out of rows of tile-like plates **26**, the rows being spaced apart and extending parallel to one another along the floor **17**. Thus channels **27** arise between the rows of tile-like plates **26**, the shape and dimensions of which are so chosen that a suction pipe mouth, large fragments from the anodes **13**, and also parts of tools for servicing of the cell, cannot knock against the floor **17** and thus cannot cause destruction or damage to the coating **24**. For conduction of current, electrolytically separated aluminium is received in the channels **27**. Between each pair of tiles arranged successively, considered in the longitudinal direction of the rows, an expansion gap is provided for avoidance of thermal stresses between the individual plates **26** and the pot **10** or the pot floor **17**.

As material for the tile-like plates **26** there come into consideration both electrically conducting and also non-conducting materials, which are resistant to aluminium and inert at a temperature of the separated aluminium, preferably with a safety margin upwards, and have a greater specific gravity than the aluminium. Sintered corundum or silicon carbide have proved themselves especially suitable.

The coating **24** on the inner surface of the pot **10** can suitably be formed in that the ceramic material of the coating is applied in finely dispersed form with such energy as to produce adhesion between the material and the inner surface of the pot **10** and consolidation of the ceramic material.

The coating **24** can be formed by applying the ceramic material to the inner surface with production of adhesion, and thereafter consolidating the material, for example by a sintering process. However, for coating of a pot formed of carbon or of a ferrous material, it is preferred to carry out the formation of the coating with bonding of the material to the surface to be coated and with simultaneous consolidation of the coating material. Suitably an ionised gas stream, which can be produced in a plasma spray pistol, supplied the energy necessary for this. The gas stream carries the coating material in finely dispersed form, and the output of the plasma generator or plasma burner is adjustable, matching the material to be applied, so that material of the coating **24** is applied molten, between tacky and liquid.

According to the kind of material to be applied, the energy content of the ionised gas stream suitable for formation of the coating can amount to up to 10^5 Kcal./kg gas. For the application of a coating of titanium boride one would adjust the energy content of the ionised gas stream to match the technological properties of the titanium boride and of the layer **24** to be produced in such a way that the energy for application and for consolidation is optimal, but not so great that the titanium boride, which has arrived at application well melted, should vaporise before it has reached the surface of the pot **10** to be coated.

The construction of devices operating with plasma is such that no difficulties arise in applying materials for formation of the coating **23** as mixtures or in mixed form.

For avoidance of oxide formations during the cooling of the material of the coating **23** applied in molten condition, one advantageously works in a protective gas atmosphere. Instead of a complete protective gas atmosphere the ionised gas stream can be surrounded with a protective sheath of inert or reducing gas, as for example hydrogen, carbon monoxide or argon, beneath which, upon progressive movement of the plasma spray pistol, the applied material solidifies without formation of oxides. This bell of gas is advantageously employed during the coating of complete pots, while in the coating of individual carbon blocks an atmosphere surrounding the block can also be used.

Preferably the coating thickness is formed in a single pass of the ionised gas stream loaded with the material over the surface to be coated. If the coating thickness is produced in several passes, i.e., coating operations, then oxides could form on the surface of the individual partial coating, which would hinder a bonding of the next following coating with the underlying one.

With the help of an ionised gas stream not only can the coating **23** be applied to the inner face of the vessel **10,** but also the protective coating can be applied on the outer face. For example if the protective coating **23** consists of a flame-sprayed aluminium coating bonded with the metallic pot and covered with fire-proof cement, then the coating can be applied with an ionised gas stream by reason of the wide range of adjustability of the plasma generator.

Following are further details of particular examples of materials:

EXAMPLE 1

The pot **10** was made of a steel of composition according to ASRM 347 (Mn 2%, Si 1%, Cr 17%, Ni 9–12%, Nb 1%, C O, 1% and remainder Fe). The protective coating **23** consisted of a flame-sprayed aluminuium coating of 0.4 mm thickness, which was covered with fire-proof cement. The inner surface of the pot **10** was throughly sand-sprayed with a corundum sand of particle size 0.5 to 1.0 mm and directly thereafter provided with the coating **24.** The coating consisted of titanium boride applied by means of an ionised gas stream and its thickness amounted to 0.5 mm. During application of the coating **24** the energy of the ionised gas stream was so adjusted that all titanium boride particles melted, and so that the inner surface of the pot **10** was brought to a temperature which permitted a bonding of the titanium boride with the pot material. The ionised gas stream loaded with titanium boride was surrounded with a protective sheath of an inert or reducing gas, for example hydrogen, carbon monoxide or argon. The total thickness of the coating **24** was applied in one pass without oxide inclusions. The height, breadth and lenth of the tile-like plates amounted to 10 × 125 × 250 mm. Sintered corundum was employed as material for the plates **26.** The channels **27** had a clear width of 25 mm. The insulating layer **12** consisted of fire-clay blocks and the casing **11** was formed of steel plates welded together.

EXAMPLE 2

Another pot **10** was formed of a steel of composition Cr 20%, Ni 24%, remainder Fe, which is resistant to scaling up to 1,100°C. In this case an outer scale-resisting protective coating **23** was unnecessary. After the sand-spray, a coating 0.1 mm thick of Ni—-Cr—B—Si alloy was applied with a welding pistol. This coating served for improvement of the adheson of the coating **24** on the pot walls and for equalisation of the thermal stresses between the pot walls and the protective coating **24.** The protective coating **24** consisted of titanium carbide. The titanium carbide was supplied to a plasma generator in powder form with a particle size of 30 to 45 and was applied by means of the ionised gas stream. To hinder a depletion of the carbon content of the titanium carbide during the application process, the part of the ionised gas stream loaded with titanium carbide powder and also the gas protective sheath must consist of a carbonising gas, i.e. C_xH_y, C_2H_5OH. The thickness of the coating **24** amounted to 0.4 mm. Apart from this the pot was formed as in Example

EXAMPLE 3

A further pot was formed of a steel of the composition Cr 21%, Ni 33%, (Al Ti Si Mn), 0.08% C, remainder Fe. As outer protective coating **23** there was applied a layer of iron aluminite chrome/aluminite, which was produced by spraying of a 0.1 mm thick aluminium coating on the outer side with subsequent reaction under influence of heat. The sand-sprayed inner surface of the pot **10** was provided, by coating by means of a plasma burner, with a 0.2 mm thick NiAl under coating for resistance to diffusion and improvement of ahesion. On this under coating there was further applied a combined coating of NbB_2—TiB_2 of composition 20:80 by plasma spraying. By reason of a certain solubility with respect to aluminium, the NbB_2 causes a closing of the pores for formation of a diffusion barrier. The remainder of the cell is formed as already explained in Example 1.

EXAMPLE 4

A pot was assembled of a steel of composition Cr 24%, Ni 20%, C O,0.6%, remainder Fe. The inner surface of the pot **10,** the wall thickness of which as of all previously described ones amounted to at least 0.5 cm, was provided with a diffusion resisting coating of NiAl. Onto this coating was applied a 0.3 mm thick coating of ZrN_2 by spraying of ZrN powder with a particle size of 30 to 45 $\mu$by means of an ionised gas stream. As gas, nitrogen was used, while NH_3 was supplied as surrounding protective gas. The remaining cell construction corresponded to Example 1.

As indicated earlier, the present invention is not limited to the employment of metallic pots, but aluminium fusion electrolysis cells can also be advantageously developed, the pots of which are formed of carbon with or without admixtures of ceramic materials. The current conductors **21** are then embedded in the vessel wall as in conventional cells. The pots may be moulded, or built up of blocks.

For formation of pre-formed blocks intended for formation of a vessel, consisting of carbon or of carbon with titanium boride, titanium carbide or silicon carbide or their mixtures with carbon and provided with the coating according to the invention, it can be advisable to let the necessary working operations and energy expenditure for application, bonding of the coating material to the pot material, and consolidation of the coating material follow one another.

The drawing shows a vessel **10** with a horizontally extending floor **17**. This only shown by way of example. The invention can also advantageously be employed in cells the floor of which is inclined, and formed with a collecting gutter for molten aluminium, either centrally or at one side.

What we claim is:

1. A pot suitable for use as the cathode of an aluminum fusion electrolysis cell, comprising a heat insulating outer shell and, on the interior thereof, an inner chamber having walls of electrically conductive material, and an inner protective thin lining comprising compacted interfused particles strongly adhering to the inner surface of said chamber walls and adapted to be in contact with the melt, said lining being composed of a ceramic material which is electrically conductive and insoluble in a melt of fused cryolite and in molten aluminum.

2. The pot according to claim **1**, in which said walls are of a metal resistant to the service temperature of the cell.

3. The pot according to claim **2**, in which said walls are Cr-Ni steel.

4. The pot as claimed in claim **1**, wherein said ceramic material is selected from the group consisting of borides, carbides, nitrides and silicides of a metal in the 4th to 6th groups of the periodic system.

5. The pot according to claim **4**, in which the ceramic material is either titanium diboride or zirconium diboride.

6. The pot according to claim **1**, in which the thickness of the lining amounts to at least 0.1 mm.

7. The pot according to claim **6**, in which the thickness of the lining is between 0.5 and 1.0 mm.

8. The pot according to claim **1**, further comprising a grating of material insoluble in molten aluminum and cryolite, supported on the floor of the chamber.

9. The pot according to claim **8**, in which the grating consists of rows of tile-like plates, the rows being space apart and extending parallel to one another along the floor.

10. The pot according to claim **9**, in which the grating consists of a ceramic material.

11. The pot according to claim **10**, in which the grating consists of sintered corundum.

12. In a method of lining with ceramic material the inner surface of the conductive inner chamber of a cell pot adapted for use as the cathode of an aluminum fusion electrolysis cell, the steps comprising

introducing said ceramic material in finely dispersed form into a plasma high speed high temperature stream, and

subsequently discharging said stream towards said inner surface with sufficient energy to produce adhesion between said ceramic material and said inner surface of said inner chamber and consolidation of said ceramic material.

13. The method as claimed in claim **12**, wherein said ceramic material is supplied in an ionized gas stream of high energy content, and, by means of the energy existing in the gas stream, the ceramic material being discharged in molten condition whereby the ceramic material is bonded to said inner surface and simultaneously is consolidated.

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