United States Patent

[11] 3,622,491

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[73] Assignee **The United States of America as represented by the Secretary of the Interior**

[54] **ELECTROLYTIC APPARATUS FOR MOLTEN SALT ELECTROLYSIS**
8 Claims, 3 Drawing Figs.

[52] **U.S. Cl.** **204/225,** 204/246, 204/247
[51] **Int. Cl.** **B01k 3/00,** C22d 3/02
[50] **Field of Search** 204/225, 243–247

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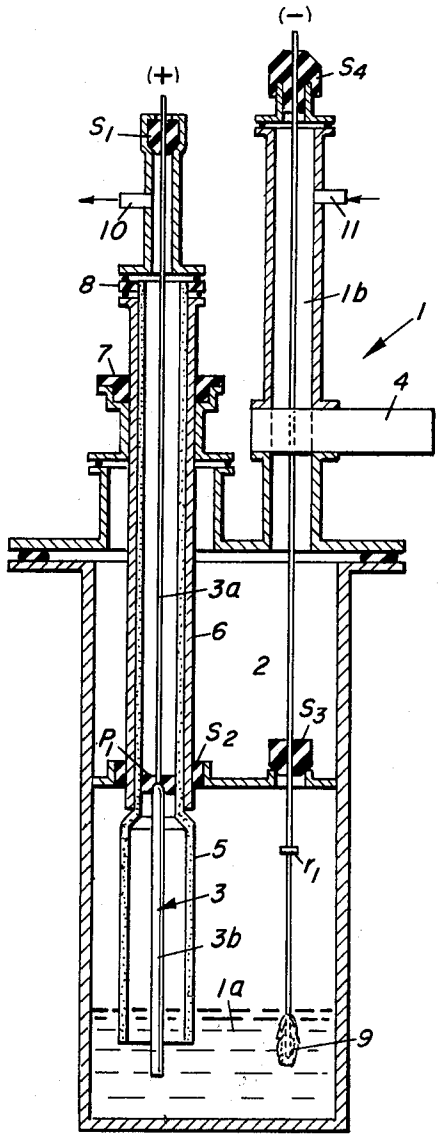
ABSTRACT: In an electrolytic cell a vertically movable hood is provided to capture corrosive gases evolving from the molten electrolyte at the anode. The hood is electrically conductive and can be lowered into the electrolyte and connected up as an anode which surrounds the cathode, or the hood can be completely removed from the electrolyte during, for example, an electrorefining operation.



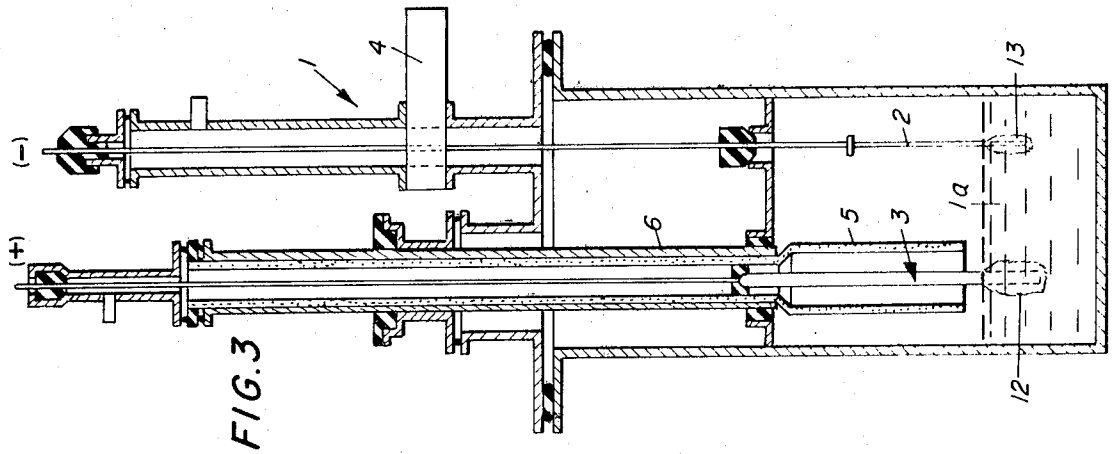


FIG. 3

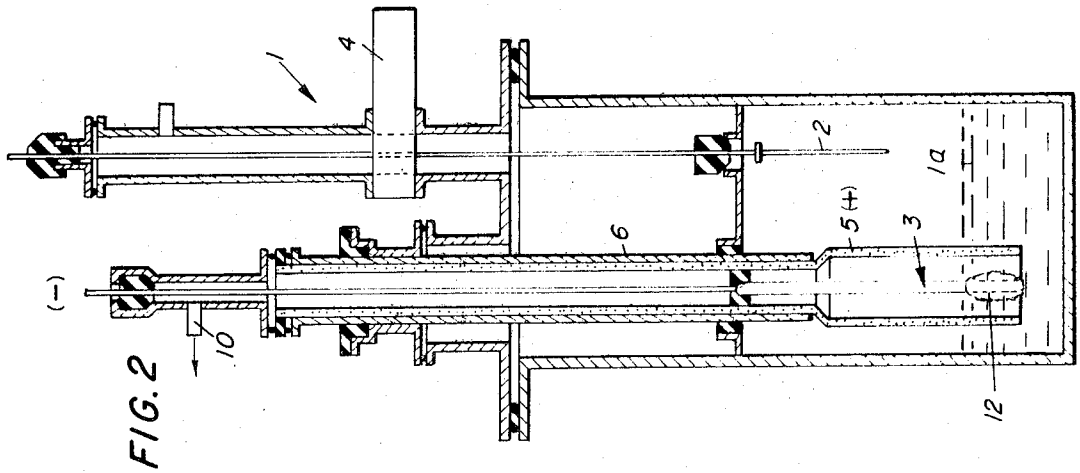


FIG. 2

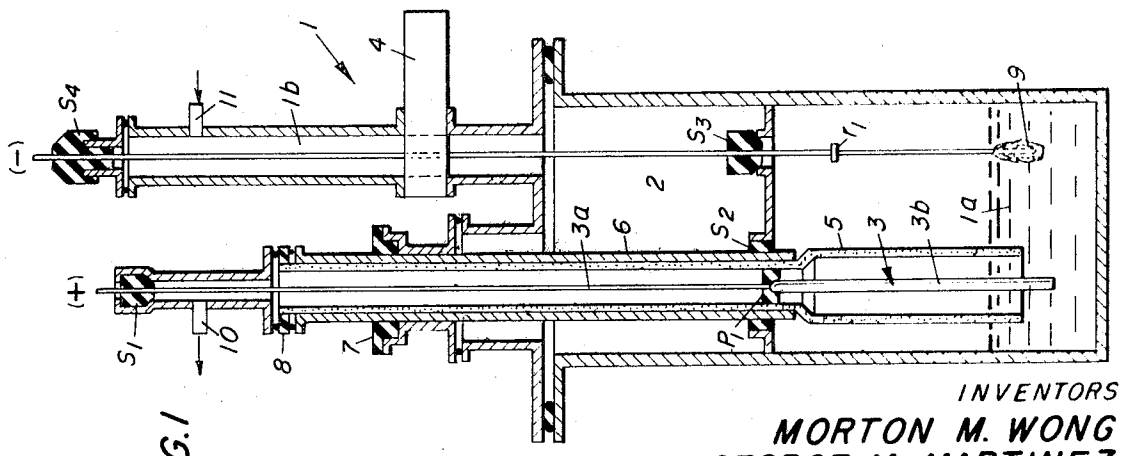


FIG. 1

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ELECTROLYTIC APPARATUS FOR MOLTEN SALT ELECTROLYSIS

This invention relates to cells for molten salt electrolysis.

In the winning of metals by molten salt electrolysis, many times it is necessary to provide a hood partially submerged in the electrolyte and surrounding the anode so that corrosive gases evolving from the electrolyte at the anode will pass directly into the hood and will not come into contact with and corrode other parts of the cell.

We have now developed an improvement in regard to such cell structures. Basically, our cell incorporates a vertically movable hood constructed of an electrically conductive material such as graphite. In one position the hood acts in the usual manner as an exit passage for corrosive gases escaping at the anode. Alternatively, the hood is lowered further into the molten electrolyte and connected as the anode while still functioning as an exit passage for corrosive gases. The electrode surrounded by the hood is then connected as the cathode for the purpose of, for example, depositing a metal thereon by electrowinning. If it is then desired to electrorefine the deposited metal, the hood is electrically disconnected and moved upwards out of the electrolyte. Subsequently, the electrode with the metal deposit thereon is connected as the anode, and another electrode is lowered into the melt as the cathode for the purpose of electrorefining the anode deposit.

It is therefore an object of the present invention to provide a new and improved cell for molten salt electrolysis which provides for corrosive gas removal during electrowinning and which also provides for combined electrowinning-electrorefining operations. Another object is to provide an electrolyte cell with a vertically movable hood for directing corrosive gases from the cell.

Further objects and advantages will be obvious from the following more detailed description of the invention taken in conjunction with the drawings in which

FIG. 1 shows a schematic cross section of a cell in which a movable hood provides for exit of corrosive gases escaping in the area of the anode;

FIG. 2 shows the cell of FIG. 1 with the hood extending further into the melt so that it not only provides for exit of corrosive gases but also acts as the anode.

FIG. 3 shows the cell of FIG. 1 in which the hood is removed from the bath so that an electrorefining operation can be conducted.

Referring to FIG. 1, reference numeral 1 generally designates the electrolytic cell of the present invention containing melt 1*a* and generally comprising an electrode rod 2 which is connected as a cathode, and an electrode rod 3 connected as an anode. Cathode 2 can be fabricated of nickel while anode 3 can be constructed of an upper nickel rod 3*a* and lower graphite rod 3*b*. Both electrodes are attached to the cell in the prior art manner so as to be vertically movable. A slide valve assembly 4 is provided so as to prevent the ingress of undesirable gases during movement of electrode rod 2.

Surrounding electrode 3 is a cylindrically shaped hood 5 fabricated of an electrically conductive material such as graphite. Hood 5 is encased in cylindrical jacket 6 (e.g., a stainless steel tube), and jacket 6 is slidably engaged through O-ring packing seal 7. Graphite hood 5 is slidably engaged through O-ring packing seal 8.

In the usual manner, other insulated slidably engaged seals s_1–s_4 are provided at the requisite positions in the cell structure. Rod 2 is also provided with a retainer r_1 for plug seal s_3. Rod 3 includes an insulated spacer p_1 to maintain the rod out of contact with hood 5. Although not shown, cooling jackets can be provided on the cell, if desired.

In the operation of the cell shown in FIG. 1 for the purpose of, for example, electrowinning a refractory metal, the metal forms as a deposit 9 at electrode rod 2 (cathode) while corrosive gases such as chlorine escape from the melt in the area surrounding electrode rod 3 (anode). These gases then pass up hood 5 and exit from the cell through conduit 10 without contacting other portions of the cell structure.

After the electrodeposition cycle, the deposit is lifted just above the electrolyte surface to allow the salt to drain, and the deposit is then sealed in receiver section 1*b* by closing slide valve assembly 4. After the deposit is cooled to room temperature, it is removed from receiver section 1*b* while slide valve assembly 4 seals the cell from the outside air. Before the slide valve is opened to reintroduce electrode rod 2 into the cell, the receiver compartment 1*b* is evacuated and backfilled with inert gas through conduit 11. Deposited metal, after being stripped from the cathode, is leached in, for example, dilute HCl and then filtered, washed and dried.

Referring now to FIG. 2, therein hood 5 is lowered further into melt 1*a* so that the hood and electrode rod 3 extend into the melt approximately the same distance. Rod 2 is removed from the melt. Hood 5 is then connected as the anode and rod 3 as the cathode. This arrangement is used in the same manner as the FIG. 1 arrangement, i.e., for electrowinning purposes. Metal forms as a deposit 12 on rod 3 while corrosive gas evolves from the melt in close proximity to the inner walls of the hood which is now the anode. As such, corrosive gases are conducted from the cell through the hood and conduit 10.

Metallic deposit 12 on rod 3 can now be electrorefined in the system shown in FIG. 3. Referring thereto, rod 2 is again lowered into the melt 1*a* and connected as the cathode, and rod 3 is connected as the anode. Hood 5 is now electrically disconnected and raised up out of the melt so as not to surround deposit 12. Since corrosive gases are not evolved during electrorefining, the hood is not required. After refined metal has coated rod 2 as deposit 13, rod 2 is removed and the deposit 13 is processed in the manner set forth above with regard to the operation of the cell in FIG. 1.

Thus, it can be seen that the apparatus of the present invention can readily be employed for a direct electrowinning operation as shown in FIG. 1, or for an electrowinning-electrorefining operation as shown in FIGS. 2 and 3.

The apparatus of the present invention is particularly suitable for electrowinning or electrowinning-electrorefining hafnium wherein the hafnium is added as hafnium tetrachloride and wherein the electrolyte contains KCl or RbCl or CsCl or combinations thereof.

What is claimed is:

1. In a substantially closed cell for electrowinning metal by molten salt electrolysis in which means are provided in said cell for trapping anodically produced corrosive gases as they egress from molten electrolyte in said cell so as to prevent said gases from contacting and thereby corroding the inner wall surfaces of said cell and conduit means are provided for conveying said trapped gases out of said cell, the improvement comprising the combination of

a. elongated, vertically disposed first electrode means in said cell;

b. means to connect said first electrode means as an anode during a first operation of said cell;

c. second electrode means in said cell;

d. means to connect said second electrode means as a cathode during said first operation of said cell whereby said second electrode means is coated with metal during said first operation;

e. said gas trapping means consisting essentially of a hood in said cell disposed around said first electrode to trap any of said anodically produced gases egressing from said electrolyte during said first operation, said hood being vertically movable, said hood being fabricated of electrically conductive material;

f. means to maintain said hood in an uncharged state during said first operation of said cell;

g. means to vertically move said hood to a position where the bottom of said hood is at least as low as the bottom of said first electrode means during a second operation of said cell; said hood moving means further including means to move said hood to a position where it is out of contact with electrolyte in said cell during a third operation of said cell;

h. means to maintain said second electrode means in an uncharged state during said second operation;

i. means to connect said hood as an anode during said second operation;

j. means to connect said first electrode means as a cathode during said second operation whereby said first electrode means is coated with metal during said second operation;

k. means to connect said metal-coated first electrode means as an anode during said third operation;

l. means to maintain said hood in an uncharged state during said third operation; and

m. means to connect said second electrode means as a cathode during said third operation so as to electrorefine said metal coating on said first electrode means.

2. The apparatus of claim 1 wherein said hood is cylindrically shaped and surrounds said first electrode means so that said first electrode means is concentric therewith.

3. The apparatus of claim 1 wherein said means to move said hood comprises a jacket around and in contact with said hood, and a seal fixed to said cell through which said jacket slidably extends.

4. The apparatus of claim 1 wherein said second electrode means is a vertically disposed, elongated electrode which is vertically movable; wherein means are provided to vertically move said second electrode means to a position where it is out of contact with electrolyte in said cell during said second operation.

5. The apparatus of claim 2 wherein said means to move said hood comprises a jacket around and in contact with said hood, and a seal fixed to said cell through which said jacket slidably extends.

6. The apparatus of claim 2 wherein said second electrode means is a vertically disposed, elongated electrode which is vertically movable; wherein means are provided to vertically move said second electrode means to a position where it is out of contact with electrolyte in said cell during said second operation.

7. The apparatus of claim 3 wherein said second electrode means is a vertically disposed, elongated electrode which is vertically movable; wherein means are provided to vertically move said second electrode means to a position where it is out of contact with electrolyte in said cell during said second operation.

8. The apparatus of claim 5 wherein said second electrode means is a vertically disposed, elongated electrode which is vertically movable; wherein means are provided to vertically move said second electrode means to a position where it is out of contact with electrolyte in said cell during said second operation of said cell.

* * * * *

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,622,491 Dated November 23, 1971

Inventor(s) Morton M. Wong et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

On the cover sheet, the inventor's name "Marginez" should read -- Martinez --.

Signed and sealed this 31st day of October 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

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