Oct. 20, 1959 N. P. NIES 2,909,471

ELECTROLYTIC CELL

Filed June 17, 1958

Fig. 1.

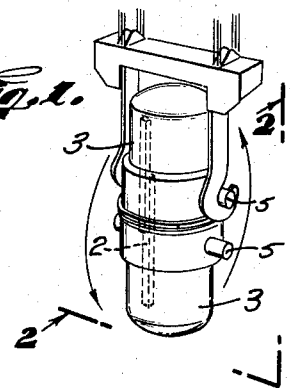


Fig. 3.

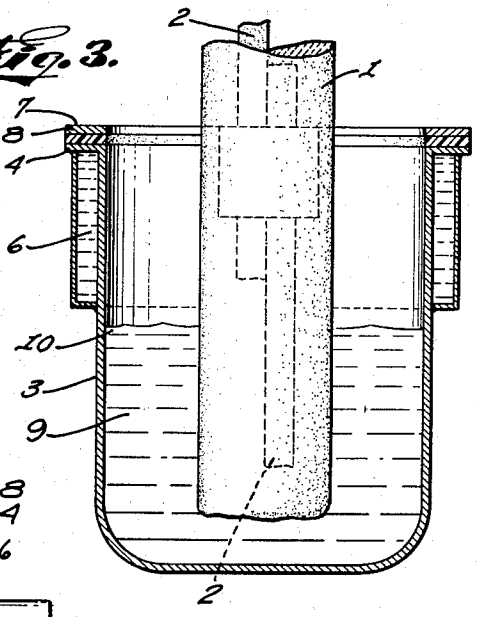


Fig. 2.

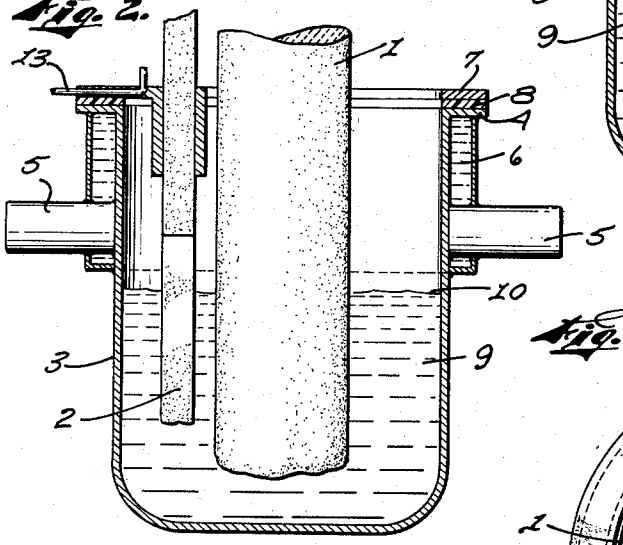


Fig. 4.

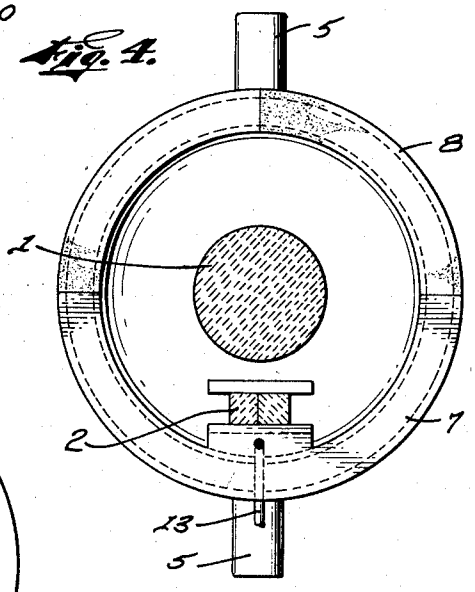
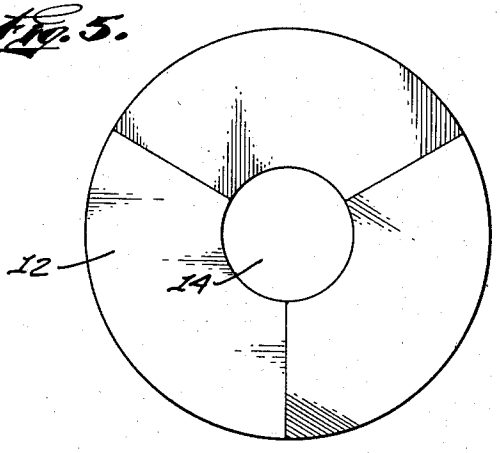


Fig. 5.



INVENTOR.
NELSON P. NIES
BY
Ernest H. Hodo
AGENT

United States Patent Office 2,909,471 Patented Oct. 20, 1959

2,909,471

ELECTROLYTIC CELL

Nelson P. Nies, Laguna Beach, Calif., assignor to United States Borax & Chemical Corporation, a corporation of Nevada

Application June 17, 1958, Serial No. 742,679

7 Claims. (Cl. 204—60)

This invention relates as indicated to an electrolytic cell and more particularly to an improved electrolytic cell of general utility for the production by fused-salt electrolysis of solid products and especially suitable for the production of boron, borides, silicon, silicides, carbides, phosphides, arsenides, metals and alloys.

In prior art methods of producing boron, borides, etc. by electrolysis, the cell generally employs a cathode, an anode and a fused salt electrolyte. Electric current is passed through the cell and the reduced material deposits on the cathode. After a sufficient deposit accumulates on the cathode, the electrolysis is terminated, the cathode is removed and the product stripped from the cathode. In the production of materials as disclosed above, the product is a crystalline mass which clings loosely to the cathode and which during the operation tends to spall off. Additionally as the cathode is removed from the cell more product may fall off into the fused-salt bath, and in order to obtain the product from the bath it is necessary to remove the electrolyte at the end of the run.

An object of the present invention is to provide an improved electrolytic cell and method for the production of solid materials by fused salt electrolysis.

A further object of this invention is to provide a simple means of preventing contact of the hot product from contact with the air on removal of the product from the fused electrolyte bath.

A still further object is to provide means for rapidly transferring a corrosive fused electrolyte from one container to another with a minimum of heat loss.

Other objects will appear as the description proceeds.

To the accomplishment of the foregoing and related ends, said invention then comprises the features hereinafter fully described and particularly pointed out in the claims, the following description and the annexed drawings setting forth in detail certain illustrative embodiments of the invention, these being indicative, however, of but a few of the various ways in which the principle of the invention may be employed.

In said annexed drawings:

Fig. 1 is a perspective of the present apparatus in assembled form;

Fig. 2 is a section through line 2—2 of Fig. 1;

Fig. 3 is a transverse cross section of the electrolytic cell of the invention;

Fig. 4 is a top plan view of the electrolytic cell of the invention; and

Fig. 5 is a top plan view of a cover for the electrolytic cell of the invention.

Referring more particularly to the drawings the cell comprises metal pot 3 in which the electrolyte is fused. Pot 3 comprises the cathode of the present electrolytic cell and is preferably made from iron or a heat resistant alloy. Pot 3 is provided with a segmented refractory lid 12, having opening 14 through which anode 1 is inserted. Anode 1 is movably suspended through opening 14 of lid 12 as by a crane or other holding device (not shown) so that it can be lowered into pot 3 as it becomes consumed. The upper portion of pot 3 is cooled as by cooling jacket 6 which terminates slightly above the level of the fused salt bath 9 as shown at 10. Cooling means 6 is particularly useful when corrosive electrolytes are used, for example, in the production of boron and borides. Cooling means 6 keeps the upper portion of the walls of pot 3 below the temperature at which corrosion from the salt bath would occur. Trunnions 5 are permanently fixed to pot 3 so that the pot can be lifted as by a crane or other lifting device and inverted. The top of pot 3 is provided with flange 4 so that an identical pot can be clamped thereto (as will later be explained) as by adjustable toggle clamps (not shown) or other well-known clamping devices.

In operation, pot 3 is placed in a pot furnace (not shown) to a depth of about the top level 10 of electrolyte 9. The pot furnace is provided with heating means (not shown) for the initial fusing of the electrolyte at the commencement of the electrolysis. While in the preferred embodiment of my invention I use a pot furnace for heating and fusing the electrolytic salts, it is to be clearly understood that other heating means are entirely within the contemplation of this invention. For example, other heating means such as induction heating, heating by electrical resistance, etc., are applicable to the present invention. Pot 3 is covered with lid 12, which is divided into sections which can be removed for inspection during the electrolysis and also can be removed while anode 1 is in place (as will be later described). Water is circulated through cooling jacket 6 and anode 1 is lowered into the fused-salt bath through opening 14 of lid 12. The current is supplied through anode 1 (pot 3 being the cathode) and the material undergoes electrolysis and deposits on the sides and bottom of pot 3. When sufficient deposit has collected on the inside walls and bottom of pot 3 the current is reduced in anode 1, lid 12 removed from around anode 1, and electric insulator 8 is placed on flange 4. Electric insulator 8 is only used when "protective anodes" 2 and support 7 are used. In case an electrolyte is used which would tend to attack the pot, provision is made for continuing a small current during the period when anode 1 is removed so as to cathodically protect the pot from attack by the electrolyte. Additionally a small current present during the change over (which is later explained) has been found to help keep the deposit more securely held to the walls of the pot. Insulator 8 is a ring of about the same width and diameter as flange 4 and can be made from any well-known insulating material such as, for example, transite. "Temporary anode" support 7 is then placed on top of electric insulator 8. From Fig. 4 it will be seen that support 7 and insulator 8 are made in two halves so that they can be placed around flange 4 without removing anode 1. "Temporary anode" support 7 holds "protective anodes" 2 in place in the electrolyte 9. "Protective anodes" 2 can comprise two vertically disposed electrodes in side-by-side contact, one extending downwardly and the other extending upwardly for approximately an equal distance as shown in the accompanying drawings, or the protective anode could comprise a single elongated vertically disposed electrode. I prefer two electrodes so that either can be separately adjusted when desired. Insulator 8 is placed on top of flange 4 and support 7 placed on top of insulator 8. Protective anodes 2 are now in the bath and insulated from the pot 3. A second insulator, not shown since it is identical with insulator 8, is placed on top of temporary anode support 7. This serves to insulate the empty pot which is later placed over the pot containing the deposit. A small current is supplied to protective anodes 2 and anode 1 is removed from the cell. An empty pot (not shown since it is identical with pot 3) is clamped to pot 3 in an inverted position, i.e., mouth to mouth. If desired, an inert gas such as nitrogen is blown into the combined pots through inlet 13 to displace the air, if

the air tends to react with the pot deposit. A crane or other well-known lifting device is attached to trunnions 5 of the upper pot and the pair are inverted thus transferring the electrolyte to the new pot. The pair are now lowered into the pot furnace and the new pot is ready for continuing the electrolysis by removal of the top pot and protective anodes and insertion of large anode 1, after the upper pot has cooled to the point where oxygen will not react with the deposit.

The pot containing the deposit is unclamped from the new pot and the deposit subsequently removed from its walls.

So that the invention is more clearly understood the following examples are given:

I

One hundred pounds of KCl were placed in an iron pot of 18" inside diameter and 28" depth. The pot had a round-bottom and a water-cooled jacket surrounding the upper 6" of the pot wall. The top of the pot was provided with a flange so that it could be clamped with adjustable toggle clamps to the flange of an identical inverted pot. Trunnions were provided on the side of the pot so that the pot could be lifted out of a pot furnace by a crane.

The pot was placed into a gas-heated pot furnace to a depth of about 20", and when the KCl melted, a cylindrical graphite anode about 10" in diameter, supported by an electric furnace electrode clamp and arm mounted on a hydraulic lift, was lowered into the molten salt until it was about 4" from the bottom of the pot. Connections were made to a rectifier and a current of about 100 amps. was passed through the cell to protect the pot (cathode) from the corrosive components to be added. A mixture of 100 pounds of KF and 35 pounds of B_2O_3 was added to the bath. The level of the bath was then adjusted to about the same level as the top of the furnace by the addition of a mixture comprising 42.5% KCl, 42.5 KF, and 15% B_2O_3, and the temperature was adjusted to 850° C. Anhydrous HCl gas was bubbled through the bath with a graphite tube until the pH of a 0.3% aqueous solution of the electrolyte was 6.0. The top of the pot was closed, to minimize contact of air with the bath, by means of a refractory cover made in three sections which fit snugly around the anode.

The gas heat was turned off and the electric current increased to 5000 amps., the voltage being about 7 to 8 volts. The temperature was maintained at 850° C. It will be understood that if necessary the gas heat could be used to maintain the temperature at 850° C.

At hourly intervals the bath was skimmed of a black scum which formed on the surface and the pH checked as previously explained. HCl gas was bubbled through the bath when necessary to keep the pH at 6.0. The bath level was maintained by addition of a mixture of 42.5% KCl, 42.5% KF and 15% B_2O_3, and additionally about 4 lbs. of B_2O_3 were added each hour.

After about 11 hours the current was lowered to about 100 amps., the cover removed and the "protective anodes" inserted into the bath. This consisted of two graphite rods about 1" in diameter, one extending downwardly into the electrolyte and one extending the same distance upwardly. The "protective anodes" were held in a holder which rested on an insulator on the flange of the pot. The large anode was removed from the bath by means of its hydraulic lift, while a current of about 100 amps. was maintained through the "protective anodes." Another insulator was placed on top of the protective anode support and a similar iron pot was inverted and placed on top of the pot containing the bath. The flanges of the two pots were clamped together and the air was displaced from the interior of the two pots by blowing in about 25 cubic feet of nitrogen through a pipe provided in the "protective anode" support. The combined pots were lifted out of the furnace by the trunnions of the upper pot with a crane. The pots were inverted and lowered back into the furnace. The upper pot was removed as soon as it cooled to below a red heat. The large anode was again inserted into the bath and the "protective anodes" removed. The bath was brought to its original state by addition of the proper amounts of KCl, KF and B_2O_3, as calculated from analysis. The lid was replaced and a similar 11-hour run was made.

The pot containing the boron deposit was filled with water and allowed to stand for several hours until the deposit was loose and could be readily brushed from the walls and bottom of the pot.

The solids were washed three times with water, boiled several hours in 20% HCl, washed with water and dried at 110° C.

The yield was 12 pounds, analyzing 96% boron.

II

The same equipment as in the foregoing example was used.

The bath comprised 200 pounds of a mixture comprising 1 part CaO, 1 part B_2O_3, and 5 parts $CaCl_2$.

The procedure of Example I was followed except the HCl gas and the "protective anodes" were not used. The temperature was kept from rising above 850° C. by blowing air through the furnace as necessary.

At hourly intervals the bath was skimmed of a black scum, 4.1 lbs. of a mixture comprising 3 moles of B_2O_3 to 1 mole CaO was added, and the original level restored by the addition of the above original bath composition.

After 8 hours' operation the pots were clamped and rotated as in Example I except as noted no "protective anodes" were used.

The deposit was about 2" thick on the walls and bottom of the removed pot. Before it cooled enough to harden the deposit was scraped out with a shovel whose blade fitted the curvature of the pot wall.

It was boiled several hours with 15% HCl, washed free of acid with water, dried in a vacuum dryer and crushed.

The yield was 13.7 pounds of 97% pure CaB_6.

Other modes of applying the principle of the invention may be employed, change being made as regards the details described, provided the features stated in any of the following claims or the equivalent of such be employed.

I, therefore, particularly point out and distinctly claim as my invention:

1. In an apparatus comprising an electrolytic cell the combination including a pair of vertically disposed top and bottom receptacles, each adapted to contain an electrolyte and clamped together in mouth-to-mouth relationship, whereby when the positions of said combined receptacles are reversed the contents of the one receptacle can flow freely into the other receptacle; said receptacles comprising the cathode portion of said cell, an anode adapted to be movably inserted in said receptacles, means for supplying electric current to said anode and cathode, and means arranged to rotate said receptacles in a vertical plane while in clamped relationship whereby said top receptacle assumes the position originally occupied by said bottom receptacles.

2. In an apparatus comprising an electrolytic cell the combination including a pair of vertically disposed top and bottom receptacles, each adapted to contain an electrolyte and clamped together in mouth-to-mouth relationship whereby when the positions of said combined receptacles are reversed the contents of the one receptacle can flow freely into the other receptacle; said receptacles comprising the cathode portion of said cell, means for externally heating the bottom receptacles of said cell, an anode adapted to be movably inserted in said receptacles, means for supplying electric current to said anode and cathode and means arranged to rotate said

receptacles in a vertical plane whereby said top receptacle assumes the position originally occupied by said bottom receptacle.

3. In an apparatus for electrolysis the combination including an electrolytic cell comprising top and bottom receptacles, each adapted to contain an electrolyte and clamped together in mouth-to-mouth relationship whereby when the positions of said combined receptacles are reversed the contents of one receptacle can flow freely into the other receptacle; means for externally heating the bottom receptacle, said receptacles comprising the cathode portion of said electrolytic cell; a first anode adapted to be movably inserted substantially vertically in said receptacles and a second smaller anode adapted to be removably inserted substantially vertically in said receptacles, said second anode adapted to extend downwardly into said bottom receptacle and to extend upwardly into said top receptacle a substantially equal distance; means adapted to support said second anode in said receptacles and means for electrically insulating said second anode supporting means from said receptacles, means for supplying electric current to said anodes and cathode; said receptacles each having a flange fixed adjacent to the mouth thereof in contiguous relationship, a cooling jacket fixed substantially adjacent to the underside of the flange and extending along a portion of the wall of said recetpacle, means for supplying a cooling medium to said cooling jacket; and means arranged to rotate said receptacles in a vertical plane while in said clamped relationship whereby said top receptacle assumes the position originally occupied by said bottom receptacle.

4. In an apparatus for electrolysis the combination including a pot furnace adapted to receive an electrolytic cell and means for heating said pot furnace; said electrolytic cell comprising a pair of vertically disposed top and bottom receptacles, adapted to contain an electrolyte, said receptacles each having a flange fixed adjacent to the top edge thereof, the flange portions of said receptacles clamped in contiguous relationship, and said receptacles comprising the cathode of said electrolytic cell; a first anode adapted to be movably inserted substantially vertically in said receptacles, a second smaller anode adapted to be removably inserted substantially vertically in said receptacles, said second anode adapted to extend downwardly into said bottom receptacle and to extend upwardly a substantially equal distance into said top receptacle, means for supporting said second anode in said receptacles, said supporting means arranged to provide an inlet for blowing an inert gas into said receptacles and means for electrically insulating said second anode supporting means from said receptacles; means for supplying electric current to said anodes and cathode, said second anode supporting means and said electrically insulating means being held in position between said flanges of said clamped receptacles; each of said receptacles provided with a cooling jacket fixed substantially adajacent to the underside of said flange and extending along a portion of the wall of said receptacle, means for supplying a cooling medium to said cooling jackets; and means adapted to rotate said clamped receptacles in a vertical plane whereby said top receptacle assumes the position originally occupied by said bottom receptacle.

5. The method of electrolyzing which comprises putting an electrolyte in a first receptacle adapted therefor; said receptacle adapted to be the cathode portion of an electrolytic cell, melting said electrolyte, inserting an anode in said receptacle containing said melted electrolyte, supplying an electrical current to said anode and cathode, maintaining said electrolyte in a fused state, when sufficient product has deposited on the walls of said receptacle discontinuing said current and removing the anode from said receptacle, inverting a second receptacle substantially identical with said first receptacle and securing said receptacles in mouth-to-mouth relationship, inverting said combined receptacles whereby the electrolyte from said first receptacle flows into said second receptacle, allowing said first receptacle to cool while inverted over said second receptacle, removing said first receptacle from said second receptacle, inserting the anode into said second receptacle and continuing said method and removing the product from said first receptacle.

6. The method of electrolyzing which comprises putting an electrolyte in a first receptacle adapted therefor; said receptacle adapted to be the cathode portion of an electrolytic cell, placing said first receptacle in a pot furnace adapted to contain such receptacle, inserting an anode in said electrolyte contained in said receptacle, supplying an electrical current to said anode and cathode, heating said pot furnace and melting the electrolyte in said receptacle, lowering the heat in said furnace when the electrolyte becomes substantially completely molten and substantially increasing the electrical current to said anode and cathode to a second electrical current, when sufficient product has deposited on the walls of said receptacle removing the anode from said receptacle, inverting a second receptacle substantially identical with said first receptacle over said first receptacle and securing said receptacles in mouth-to-mouth relationship, removing said combined receptacles from said pot furnace and inverting the combined receptacles whereby the electrolyte from said first receptacle flows into said second receptacle, placing said second receptacle into the pot furnace, allowing said first receptacle to cool while inverted over said second receptacle, removing said first receptacle from said second receptacle, inserting the anode into said second receptacle and continuing said method and removing the product from said first receptacle.

7. The method of electrolyzing a metal oxide to obtain the metal which comprises putting an electrolyte in a first receptacle adapted therefor, said receptacle adapted to be the cathode portion of an electrolytic cell, placing said first receptacle in a pot furnace adapted to receive the same, inserting an anode in said electrolyte contained in said receptacle, supplying a first electrical current to said anode and cathode, heating said pot furnace and melting the electrolyte in said receptacle, removing the heat in said furnace when the electrolyte becomes substantially completely molten and substantially increasing the electrical current to said anode and cathode to a second electrical current, when sufficient product has deposited on the walls of said receptacle, inserting a second smaller anode in said electrolyte and supplying current to said second anode substantially less than said second current and completely removing said first anode from said receptacle, said second anode adapted to extend downwardly into said electrolyte and to extend upwardly a substantially equal distance, inverting a second receptacle substantially identical with said first receptacle over said first receptacle and securing said receptacles in mouth-to-mouth relationship, sweeping said combined receptacles with an inert gas, removing said combined receptacles from said furnace and inverting the combined receptacles whereby the electrolyte from said first receptacle flows into said second receptacle, placing said second receptacle into the pot furnace, allowing said first receptacle to cool while inverted over said second receptacle, removing said first receptacle from said second receptacle, inserting said first anode into said second receptacle, supplying a current to said first anode substantially the same as said second electrical current, completely removing the second anode and continuing the method and removing the product from said first receptacle.

References Cited in the file of this patent

UNITED STATES PATENTS

2,151,599 Jaeger ..... Mar. 21, 1939

FOREIGN PATENTS

645,883 Germany ..... Nov. 17, 1935