Aug. 18, 1959 E. W. ANDREWS 2,900,318

ELECTROLYZING DEVICE

Filed Nov. 29, 1955

FIG. 1

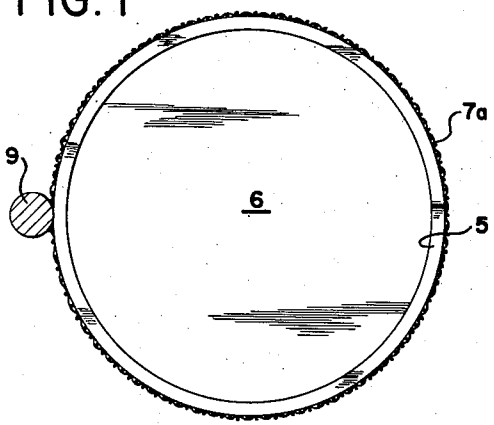



FIG. 2

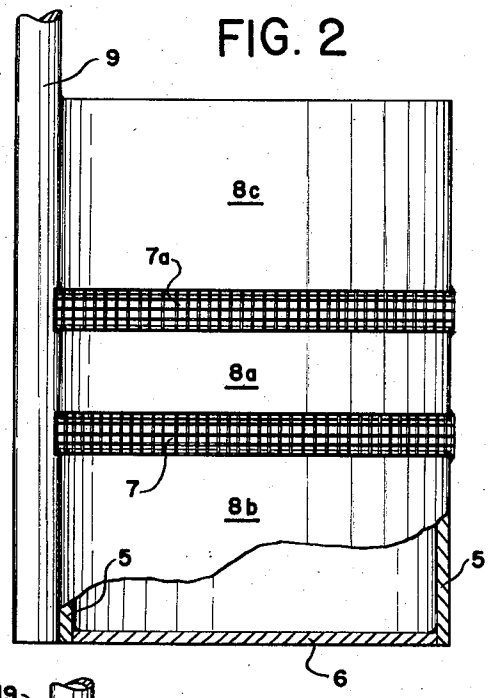



FIG. 4

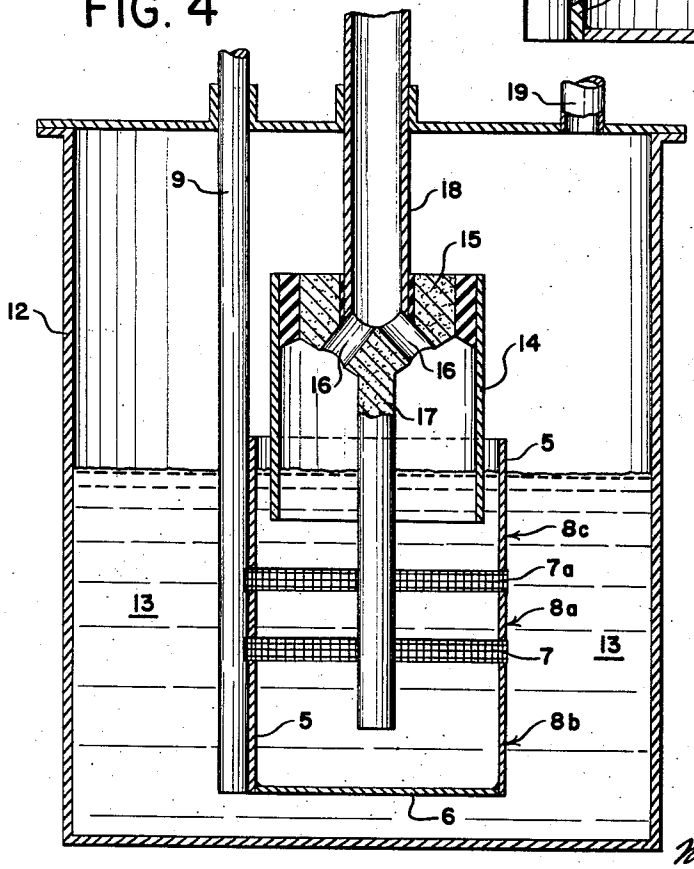
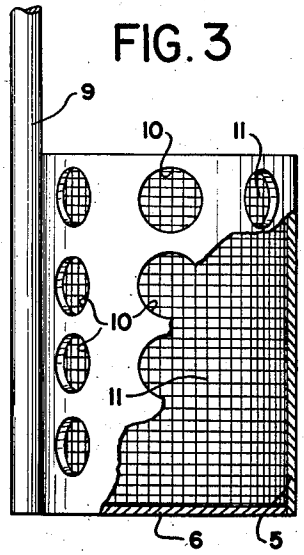



FIG. 3




INVENTOR

Earl W. Andrews

BY Pennie, Edmonds, Morton, Barrows & Taylor

ATTORNEYS

United States Patent Office 2,900,318 Patented Aug. 18, 1959



2,900,318

# ELECTROLYZING DEVICE

Earl W. Andrews, Slatington, Pa., assignor to The New Jersey Zinc Company, New York, N.Y., a corporation of New Jersey

Application November 29, 1955, Serial No. 549,765

6 Claims. (Cl. 204—246)

This invention relates to the production of metallic titanium and, more particularly, to an electrolyzing device capable of being used as a diaphragm or as a combination deposition cathode and diaphragm in the fused salt bath electrodeposition of metallic titanium.

In the electrodeposition of metallic titanium by electrolysis of a titaniferous material contained in a fused salt bath, it has generally been found difficult to produce a metallic titanium deposit on a cathode in such form that the deposit will adhere to the cathode with sufficient tenacity to permit harvesting the deposited titanium by removing the cathode from the cell. The same problem of tenacity of the deposited titanium applies to the use of a metallic screen on which a titanium deposit is built up for the purpose of developing a titanium-metal diaphragm which can be used to maintain separate anolyte and catholyte compartments in the cell.

I have now found that a certain mechanical structure lends itself to use both as a screen-type diaphragm or as a combination screen-type diaphragm and deposition cathode by virtue of its ability to establish a tenacious bond between itself and the electrodeposited titanium. The electrolyzing device of the present invention, embodying the aforementioned structure, comprises an open-topped vessel composed essentially of impervious sections and at least one pervious section, each pervious section of the vessel being bordered by the impervious sections thereof. By virtue of this structural arrangement, fluid communication between portions of the fused salt bath within and without the vessel is possible only through a pervious section of the vessel when the device is so immersed in the bath as to prevent the bath flowing over the top of the vessel. In the presently preferred embodiment of the invention, the open-topped vessel comprises side walls and a bottom wall, the side walls being composed essentially of impervious sections and at least one pervious section, each pervious section being bordered by the impervious sections.

These and other novel features of the electrolyzing device of my invention will be more clearly understood from the following description taken in conjunction with the drawings in which

Fig. 1 is a plan view of the electrolyzing device;

Fig. 2 is a side elevation of this device;

Fig. 3 is a side elevation of another modification of the electrolyzing device of my invention; and

Fig. 4 is a sectional elevation showing the electrolyzing device mounted in an electrolyzing cell wherein the device is being used as a combined diaphragm and electrodeposition cathode.

As can be seen readily from Figs. 1 and 2, the presently preferred embodiment of my electrolyzing device comprises side walls 5 which are in fluid-tight contact with an impervious bottom wall 6. This fluid-tight contact may be the result either of an integral construction of the lower portion of the side walls and the bottom wall or the two walls may be joined together by welding or the like. The side walls 5 are composed essentially of at



least one pervious section 7 and at least two impervious sections 8*a* and 8*b*. These sections of the side walls are so arranged that the pervious section is bordered by the impervious sections 8*a* and 8*b*. Although the side walls 5 may be composed merely of these three sections, it may also be composed of two or more pervious sections comprising the sections 7 and 7*a* each bordered by impervious sections 8*a*, 8*b* and 8*c*, as shown in Fig. 2. Moreover, it will be readily understood that, instead of the aforementioned cylindrical shape, the vessel can advantageously have the shape of a hemisphere or the like. Regardless of the number of pervious and impervious sections and regardless of its geometric shape, the open-topped vessel is supported in a fused salt bath within an electrolyzing cell by a supporting rod 9 secured to any convenient part of the vessel such as the side wall 5. The supporting rod 9 also provides an electrical connection from an external source to the side wall structure of the device.

The pervious section of the electrolyzing device of my invention is advantageously, though not necessarily, composed of wire mesh screen. The size of the screen openings may vary considerably, depending upon the type of mesh and the number of layers of screen used, provided that the resulting structure forms a pervious section having very fine and preferably labyrinth openings. For example, I have found that a double thickness of a Dutch weave screen having 14 mesh per inch in one direction and 120 mesh per inch in the other direction provides a very effective pervious side wall structure. However, a single thickness of this screen can be used satisfactorily. Moreover, other types of screen mesh having different ranges of screen openings as well as other perforate structures may be used in practicing my invention. Thus, a twill mesh fine screen is effective, as are also a calendered wire filter cloth composed of XXD400 nickel wire (a product presently made and sold under the trade name "Multi-Braid"), a combination of two perforated plates welded together so that their perforations are out of registry so that fluid flow is restricted to the space between the plates (a product also presently made and sold under the trade name "Neva Clog"), and porous sintered structures made by conventional powder metallurgy techniques. All of these types of previous structures are understood to be included in the expression "screen-like" used elsewhere herein. The only essential requirement of the pervious section of the side walls of my electrolyzing device is that its openings be sufficiently small to permit the building up thereover of a metallic titanium deposit by electrodeposition in a fused salt bath.

The construction of a side wall composed of a pervious section bordered by two impervious sections can be readily obtained by welding the edges of a strip of screen material to adjoining edges of impervious sheet material. On the other hand, as shown in Fig. 3, I have constructed a wholly suitable device by using a cylindrical side wall 5 composed of sheet material having large openings 10 punched at intervals throughout its surface and by securing to the inner surface of this cylinder a lining of screen material 11 such as that referred to hereinbefore. It will be readily appreciated, accordingly, that a variety of other geometrical variations can be used, the important criterion being that each pervious section of the structure be bordered on all sides by impervious sections so that when the device is immersed in a fused salt bath in such manner that the salt bath does not overflow the upper edge of the side walls, fluid communication between portions of the fused salt bath within and without the side walls is possible only through the pervious sections of the device.

The electrolyzing device of my invention may be composed of any electrically conductive material which is resistant to attack by the composition of the fused salt

bath containing the normal products of the electrolysis. Thus, nickel or nickel base alloys, molybdenum, mild steel and iron may be used for this structure. All of these materials, under the electrolytic conditions prevailing in the use of my device, are relatively corrosion-resistant and do not significantly contaminate the bath.

The use of the electrolyzing device of my invention as a combined diaphragm and deposition cathode is illustrated in Fig. 4. As shown in this figure, a closed cell **12** is provided with a fused salt bath **13** in which the electrolyzing device is nearly but not completely immersed. A silica dome **14** extends downwardly into the interior of the side walls **5** of the electrolyzing device, the lower extremities of the dome being immersed in the fused salt bath. The dome is secured to a graphite anode base **15** which is provided with ports **16** and a depending anode section **17**. The ports **16** permit the escape of chlorine gas from the surface of the bath within the dome **14** into a chlorine effluent tube **18**. Both the chlorine effluent tube **18** and the supporting rod **9** for the electrolyzing device extend through the top of the cell. When the electrolyzing conditions are such that metallic titanium is electrolytically deposited on the outermost surface of the side walls **5**, that is, on the surface of the walls distal with respect to the anode **17**, the titanium deposit forms an adherent layer on the impervious sections **8***a*, **8***b* and **8***c* and forms a bridge over the intermediate pervious sections of the side wall. The bridge portion of the titanium deposit on the outer surface of the pervious sections **7** and **7***a* is sufficiently porous to permit the maintenance of the electrolyzing conditions required to deposit metallic titanium on this distal cathode surface.

The electrolytic conditions which are required to insure the electrodeposition of titanium on the distal surface of the electrolyzing device when it functions as the cell cathode consist essentially of the maintenance of a titanium ion concentration in that portion of the bath between the anode and the proximate cathode surface sufficiently low to preclude deposition of titanium on the proximate cathode surface. This result is achieved primarily by the maintenance of a relatively high current density between the anode and cathode, as well as by feeding titaniferous make-up material only to the portion of the fused salt bath adjacent the distal surface of the side walls **5**. Under these conditions, when once attained, the electrolyzing current flows through each pervious section of the side walls in a path that extends between the distal surface of the side walls **5** and the anode **17** positioned within the confines of the side walls. It will be readily understood, of course, that these same electrolyzing conditions can be obtained when the anode is positioned exteriorly of the side walls **5** of my electrolyzing device, in which event the distal surface of the deposition cathode (the side walls **5**), with respect to the exterior anode, comprises the inner surface of the side walls **5**. Regardless of whether the "distal" surface of the electrolyzing device is the inner or outer surface of its side walls, the formation of a titanium metal deposit on the pervious section of the side walls reduces the size of the openings in this section to the extent that it functions as a cell diaphragm capable of maintaining separate but communicating anolyte and catholyte portions of the cell bath.

The following specific example of the operation of an electrolytic cell using the electrolyzing device described hereinbefore as a combined diaphragm and deposition cathode will further serve to show how this device is used. The electrolyzing device comprised a cylindrical side wall structure 10½ inches high and 5 inches in diameter and having two pervious sections each ½ inch wide and spaced 1½ inches apart. The pervious sections consisted of double thicknesses of 14 x 120 mesh (per inch) Dutch weave screen welded to the exterior adjoining surface of the impervious sections, as shown in Figs. 1 and 2. In this screen, the "14 mesh" wires had a diameter of 0.015 inch and the "120 mesh" wires had a diameter of 0.010 inch. The supporting rod had a diameter of ½ inch and was 30 inches long in order to provide a cathode connection above the top of the cell. The top of the side wall structure was open, but the bottom was closed with an impervious sheet welded to the lower extremities of the side wall structure. All of these components of the device were made of nickel and nickel-base alloy, and the device was immersed in a fused salt bath in an electrolytic cell in an arrangement such as that shown in Fig. 4.

The cell bath was composed of a eutectic mixture of 5 mol percent of sodium chloride, 40 mol percent of potassium chloride and 55 mol percent of lithium chloride, the mixture having a reported melting point of 372° C. but actually melting at a temperature of about 345° C. This bath was brought up to a temperature of 650° C. before the start of the cell operation.

A 50 ampere direct current at approximately four volts was applied to the cell electrodes while a theoretical 1-to-1 feed ratio of $TiCl_4$ to cell current (i.e., one gram mol of $TiCl_4$ to 4 Faradays) was fed to the cell through an inlet **19** (Fig. 4) for about six hours in order to build up a deposit of titanium sponge on the screen. This screen pre-coating treatment was followed by a 2-to-1 feed ratio in which titanium deposition virtually ceased and practically all of the current was used to convert the $TiCl_4$ feed to a lower valent titanium chloride and chlorine. This procedure gradually increased the titanium concentration in the melt to approximately 2.0% by weight of the bath in about 21 hours of operation. At the end of this build-up cycle, the applied voltage required to maintain this condition was approximately 3.6 volts at 50 amperes with an open circuit back E.M.F. of 2.5 volts. The calculated cell resistance was 0.022 ohm.

Following this cycle for building up the desired titanium concentration in the molten bath, the temperature of the melt was lowered to 550° C. and the $TiCl_4$ feed was cut down again to the 1-to-1 feed-to-current ratio theoretically required to maintain a constant titanium concentration in the cell while depositing titanium sponge on the outside of the unitary cathode-diaphragm unit. Thus, a 50 ampere and 50 cc. per hour $TiCl_4$ feed rate was maintained steadily for approximately 62 hours until the desired total of five liters of $TiCl_4$ had been fed to the cell. Readings taken at the end of this steady-state operation showed an impressed voltage of 4.2 volts at 50 amperes with an open circuit back E.M.F. of 2.9 volts. The cell resistance at this time was calculated to be 0.026 ohm.

In order then to strip the cell bath of its titanium content, the current was maintained at 50 amperes without feeding $TiCl_4$. This stripping was continued for 17 hours until a back E.M.F. of 3.4 volts was obtained, which corresponded to a final cell resistance of 0.027 ohm. The melt was then cooled to 450° C. before opening the cell to harvest the product. Argon gas was immediately blown over the hot deposit to cool it quickly and to prevent its oxidation. Thereafter, the entire cathode, with its deposit, was immersed in ice water preparatory to leaching out the entrained salt and further processing of the titanium deposit.

The final deposit on the cathode structure was up to 2 inches thick with most of the coarse crystalline product in the outer ⅜ inch of the deposit. The inner sections closer to the diaphragm were high in solidified salt with some crystalline titanium of finer particle size. The deposit adhered firmly to the impervious sections of the structure and appeared not to adhere to the pervious sections. There was an observable deposit of metallic titanium within the interior of the wire mesh screen of the pervious sections, however, thus indicating that the titanium metal had contributed to the effectiveness of the

fine openings in defining a diaphragm structure. There was practically no sludge on the bottom of the cell and very little on the bottom of the interior of the cathode structure. The over-all titanium recovery based on the $TiCl_4$ feed was over 80%, of which about 70% had a hardness grade of 40 Rockwell A.

Although the electrolyzing device of my invention was used in the foregoing example both as a cell diaphragm and as a deposition cathode, it will be readily understood that after the initial stage of depositing metallic titanium on the distal surface of the pervious section of the device it can be used exclusively as a diaphragm positioned between the anode and a more remote cathode surface. It must also be understood that although the use of my electrolyzing device has been illustrated in connection with the electrolytic conversion of titanium tetrachloride to titanium metal, the device may be used in any other electrolytic process for the production of metallic titanium from other titaniferous materials such as the alkali metal fluotitanates, titanium monoxide, and the like. In all of these electrolytic operations, the device of the present invention, having a metallic titanium deposit on the distal surface of each pervious section of its side walls, provides a highly effective diaphragm for the maintenance of anolyte and catholyte portions of the fused salt cell bath; whether it also functions thereafter as a deposition cathode is determined by whether another cathode surface is provided in the cell bath beyond the titanium-bearing surface of the device. Regardless of whether the device is used merely as a diaphragm or as a combined diaphragm and deposition cathode, I have found that the metallic titanium deposit adheres firmly to the surface of the impervious sections of the side walls adjoining each pervious section, thus insuring a firm footing for a bridge-like deposit which forms on the surface of the intermediate pervious section. As a result, there is no significant sloughing of the titanium deposit on my electrolyzing device even when the deposit is several inches thick, and in this way the electrolyzing device of my invention differs significantly from all-impervious and all-pervious deposition cathode surfaces used heretofore. But in spite of the tenacity of this titanium deposit, it is sufficiently porous over the pervious sections of the device, regardless of the thickness of the deposit, to permit the degree of communication required between anolyte and catholyte compartments of a fused salt bath cell.

I claim:

1. An electrolytic cell for producing metallic titanium by electrolysis of a titanium chloride contained in a fused halide salt bath, the cell comprising enclosing walls adapted to hold a body of the fused bath, there being suspended in the fused salt bath an electrolyzing device capable of being used as a diaphragm and as a combined diaphragm and deposition cathode and comprising an open-topped vessel composed essentially of impervious sections and at least one pervious screen-like section all of electrically conductive material, each pervious section of the vessel being bordered by impervious sections thereof so that fluid communication between portions of the fused salt bath separated solely by the walls of the vessel is possible only through a pervious section thereof, an electronegative connection to said device, and an anode supported in the fused salt bath.

2. An electrolytic cell for producing metallic titanium by electrolysis of a titanium chloride contained in a fused halide salt bath, the cell comprising enclosing walls adapted to hold a body of the fused bath, there being suspended in the fused salt bath an electrolyzing device capable of being used as a diaphragm and as a combined diaphragm and deposition cathode and comprising side walls and an imprevious bottom wall, the side walls of said structure being composed essentially of impervious sections and at least one pervious wire screen section all of electrically conductive material, each pervious section of the side walls being bordered by impervious sections thereof so that fluid communication between portions of the fused salt bath separated solely by the side walls is possible only through a pervious section of the side walls, an electronegative connection to said device, and an anode supported in the fused salt bath.

3. An electrolytic cell for producing metallic titanium by electrolysis of a titanium chloride contained in a fused halide salt bath, the cell comprising enclosing walls adapted to hold a body of the fused bath, there being suspended in the fused salt bath an electrolyzing device capable of being used as a diaphragm and as a combined diaphragm and deposition cathode and comprising an open-topped vessel composed essentially of impervious sections and at least one pervious double-thickness screen section all of electrically conductive material, each pervious section of the vessel being bordered by impervious sections thereof so that fluid communication between portions of the fused salt bath separated solely by the walls of the vessel is possible only through a pervious section thereof, an electronegative connection to said device, and an anode supported in the fused salt bath.

4. An electrolytic cell for producing metallic titanium by electrolysis of a titanium chloride contained in a fused halide salt bath, the cell comprising enclosing walls adapted to hold a body of the fused bath, there being suspended in the fused salt bath an electrolyzing device capable of being used as a diaphragm and as a combined diaphragm and deposition cathode and comprising an open-topped vessel composed essentially of impervious sections and at least one pervious screen-like section all of electrically conductive material, each pervious section of the vessel comprising a Dutch weave wire screen having 14 mesh per inch in one direction and 120 mesh per inch in the other direction and being bordered by impervious sections thereof so that fluid communication between portions of the fused salt bath separated solely by the walls of the vessel is possible only through a pervious section thereof, an electronegative connection to said device, and an anode supported in the fused salt bath.

5. An electrolytic cell for producing metallic titanium by electrolysis of a titanium chloride contained in a fused halide salt bath, the cell comprising enclosing walls adapted to hold a body of the fused bath, there being suspended in the fused salt bath an electrolyzing device capable of being used as a diaphragm and as a combined diaphragm and deposition cathode and comprising side walls in fluid-tight contact with an impervious bottom wall and adapted to be immersed in the fused salt bath, the side walls being composed essentially of impervious material provided with spaced openings and with an adjacent liner of wire screen so as to provide a wall structure of pervious and impervious sections all of electrically conductive material, each pervious section of the vessel being bordered by impervious sections thereof so that fluid communication between portions of the fused salt bath separated solely by the walls of the vessel is possible only through a pervious section thereof, an electronegative connection to said device, and an anode supported in the fused salt bath.

6. An electrolytic cell for producing metallic titanium by electrolysis of a titanium chloride contained in a fused halide salt bath, the cell comprising enclosing walls adapted to hold a body of the fused bath, there being suspended in the fused salt an electrolyzing device capable of being used as a diaphragm and as a combined diaphragm and deposition cathode and comprising an open-topped vessel composed essentially of impervious sections and at least one pervious screen-like section, all of electrically conductive material, each pervious section of the vessel being bordered by impervious sections thereof so that fluid communication between portions of the fused salt bath separated solely by the walls of the vessel is possible only through a pervious section thereof, an electronegative connection to said device, an anode supported

in the fused salt bath within the interior of said device, barrier means for maintaining separation of the portions of the cell atmosphere above the bath on opposite sides of the side walls of said electrolyzing device, discharge means for discharging from the portion of the cell atmosphere above and in contact with the anode the chlorine gas evolved at the surface of the anode in contact with the bath, and delivery means for supplying titanium tetrachloride to the other portion of the cell atmosphere.




**References Cited in the file of this patent**

UNITED STATES PATENTS

| | | |
|---|---|---|
| 2,104,812 | Phillips | Jan. 11, 1938 |
| 2,228,264 | Freedley | Jan. 14, 1941 |
| 2,331,071 | Halvorsen | Oct. 5, 1943 |
| 2,363,386 | Bock | Nov. 21, 1944 |
| 2,848,397 | Reimert et al. | Aug. 19, 1958 |