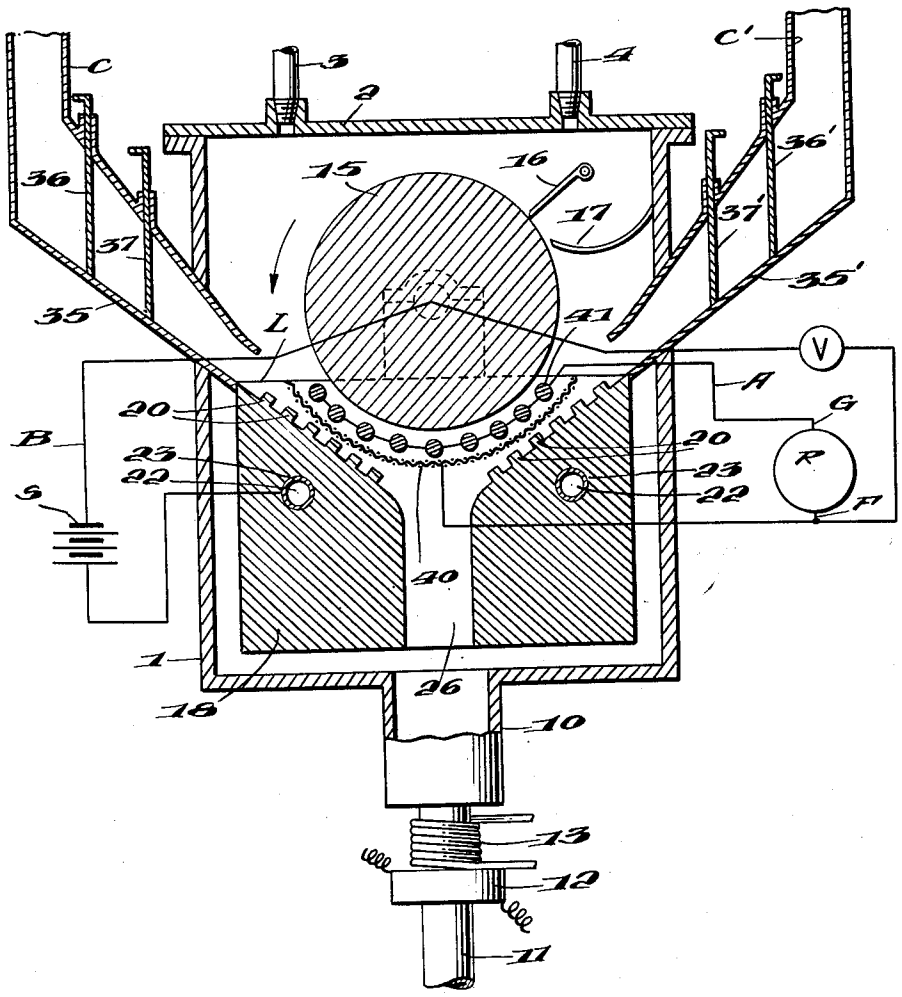
Jan. 5, 1960 R. S. DEAN 2,920,027

ELECTRICAL CIRCUITS FOR METAL REFINING CELLS

Filed July 1, 1955 2 Sheets-Sheet 1

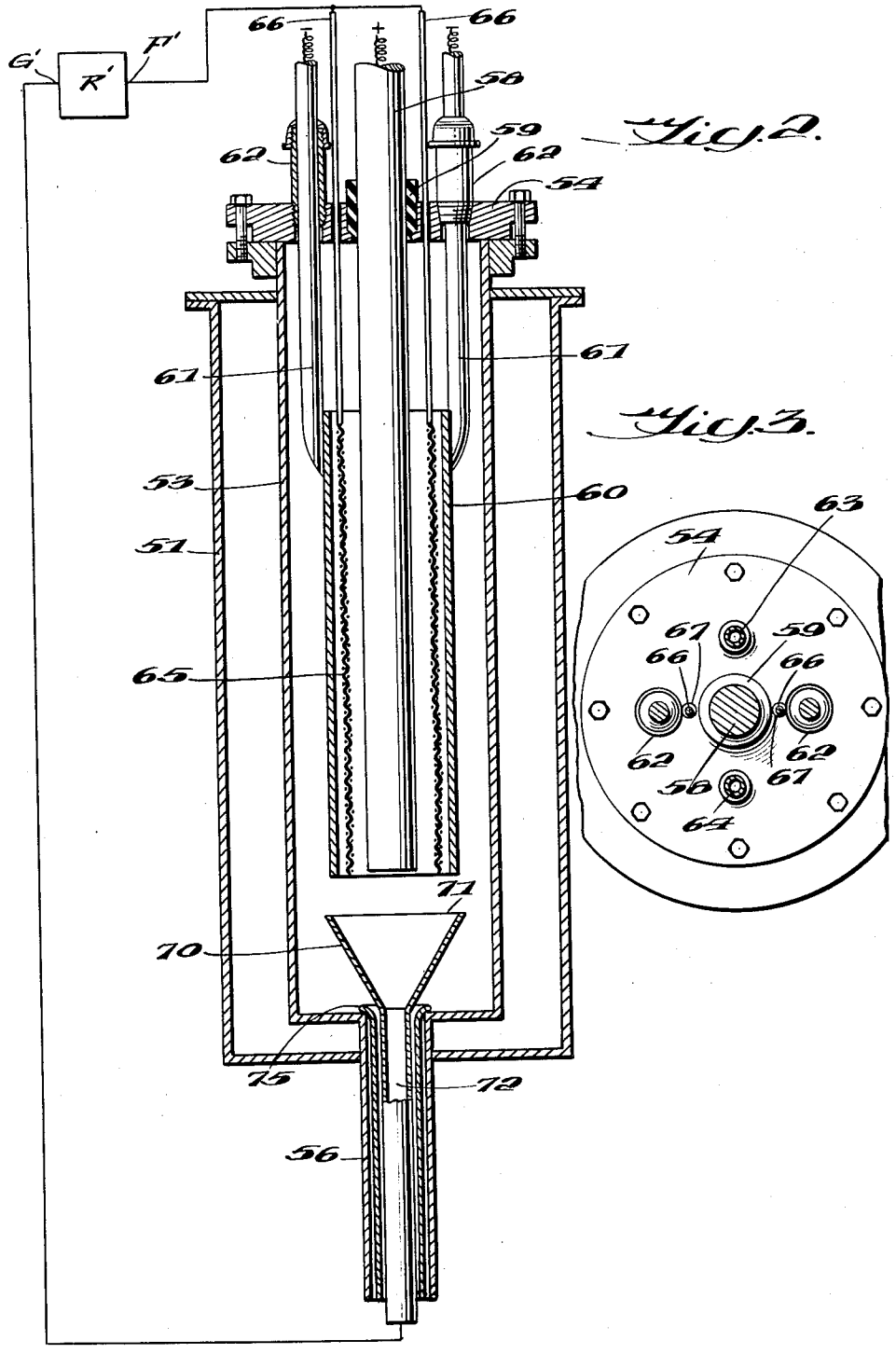
Fig. 1.



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ELECTRICAL CIRCUITS FOR METAL REFINING CELLS

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2,920,027

ELECTRICAL CIRCUITS FOR METAL REFINING CELLS

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2 Claims. (Cl. 204—218)

This invention relates to electrical circuits for metal refining cells. It relates in particular to such circuits for the refining of metals in fused salt electrolytes and still more particularly to the refining of metals of the group consisting of titanium, zirconium and hafnium.

In my copending application Serial No. 470,610, filed Nov. 23, 1954, I have disclosed the use of foraminous potential dividers in electrolytic refining cells using electrolytes composed principally of alkalinous metal chlorides. In such cells the cathode potential is raised by the co-discharge of alkalinous metal ions, and hence to establish a practical current density it is necessary to impress a voltage which causes impurities in the anode to go into solution. To correct this I provided a foraminous metal baffle between anode and cathode which is maintained at the potential against the electrolyte which the anode would have if there were no co-deposition of alkalinous metal at the cathode. Under these circumstances, the more noble impurities which dissolved from the anode would be deposited on the foraminous baffle. Looked at in another way, a concentration of alkalinous metal dissolved in the fused salt would be developed at the foraminous baffle which would precipitate the impurities but not the metal to be refined.

In my copending application Serial No. 513,759, filed June 7, 1955, now Patent No. 2,785,066, I have disclosed the use of an auxiliary inert electrode, preferably of graphite, at which the lower chloride of the titanium-group metal present in the electrolyte may be oxidized to a higher chloride. This permits the maintenance of the most favorable relationship between the lowest and higher valence chlorides in the cathode area. Such a relationship is necessary to minimize co-discharge of alkalinous metal and to provide the desired crystal size of the deposited metal.

The use of these electrodes in an independent manner as set forth in my copending applications is effective but presents a number of problems in control and coordination.

In my present invention, I combine these two auxiliary electrodes in a second circuit which is separate from the one used for electrorefining. In this way I automatically balance the reactions in the cell.

It will be seen, for example, that when chlorination takes place at the insoluble (graphite) anode a corresponding amount of alkali metal must be discharged at the cathode. This results in an increase in cathode potential which, to bring the refining cell into balance, requires an increase in the potential of the foraminous barrier.

In accordance with my present invention, I connect the foraminous barrier as cathode in a separate circuit with the graphite as anode. It then follows that the alkalinous metal formed at the barrier is equivalent to the chlorination at the graphite, so that by suitable geometric arrangement the cathode film can be maintained in a suitable state of oxidation and the concentration of

alkalinous metal at the barrier maintained in the equivalent and required amount.

The current flowing in this independent circuit can be controlled either automatically or manually by the OC voltage maintained between the cathode and the barrier. The two effects of current flowing in this circuit are in the same direction; that is, increased chlorination lowers cathode potential while increased current in the circuit increases alkalinous metal concentration at the barrier. The result is, therefore, that with enough current in this separate circuit the OC voltage between cathode and barrier can be reversed and by the same token be brought to any positive voltage desired. By positive voltage I mean that voltage by which the cathode is negative or cathodic to the barrier.

The whole system lends itself to servo mechanism control, since when current flows in the cell the voltage from barrier to cathode equals the IR drop of the electrolyte, which value is constant, plus the open circuit voltage. The operating voltage may therefore be coupled to the separate circuit to provide current flow in it any time the operating voltage reaches a predetermined maximum.

The geometry of the cell for the application of my present invention is subject to many modifications. Conveniently, I use a cell as described in my copending application Serial No. 513,759, Figure 7. The graphite funnel in this cell serves the purpose of an anode residue sump, and an auxiliary electrode chlorinates near the cathode. The foraminous barrier has the form of a portion of a cylinder and is disposed between the anode and cathode.

The problem of a cell with moving cathode requires special consideration. A moving cathode in relationship to a smaller stationary anode possesses a range of cathode potentials only one of which is the optimum for metal deposition.

Since in my invention we are concerned with OC voltage between the foraminous barrier and the main cathode, the situation may be corrected by a foraminous barrier or potential divider coextensive with the immersed cathode area. The OC voltage between main cathode and barrier is thereby maintained constant, as is the character of the deposit.

The positioning of the insoluble auxiliary anode in a cell having a rotary main cathode also presents certain problems. I prefer to use an insoluble auxiliary anode made up of a number of graphite rods spaced across the path of movement of the main cathode. In this way the lower chloride of the titanium-group metal to be deposited is chlorinated in alternate zones. This is illustrated in Figure 1 of the accompanying drawing, which figure is a diagrammatic representation of an organization embodying principles of the present invention. Figure 2 is a diagrammatic representation of a cell, embodying principles of the invention, having a stationary cathode, and Figure 3 is a top plan view of the apparatus shown in Figure 2.

In Figure 1 of the drawing, **1** is the stainless steel pot of the electrolytic cell and **2** is its cover. Maintenance of an argon atmosphere within the cell is effected by means of inlet **3** and outlet **4**. The pot **1** is provided, centrally of its bottom, with sump means **10**; **11** is a sump conduit for use in emptying the sump (and, if desired, the pot itself), the same being associated with heating means **12** and cooling means **13** for fusing and freezing the contents thereof.

Centrally arranged for rotation within pot **1** is a horizontally disposed, cylindrical and rotatable, steel main cathode member indicated at **15**. For removing plates of electrodeposited titanium from the main cathode

surface and from the cell interior, there is provided an arrangement including a scraper 16, a co-operating trough 17, and a gas lock and cooling receptacle, not shown, for removing electrodeposit from the cell.

Beneath and spaced from the rotatable cathode is a massive graphite main anode 18 of unique form. The upper face of anode 18 is formed as a portion of a cylinder substnatially the whole of the upper surface of which is provided with a series of horizontal, relatively deep corrugations 20, 20, the function of which latter is to support and retain scrap fragments or pellets of titanium on the sloping surface. The main cathode and main anode are so disposed with reference to each other that a minor portion of the peripheral surface of the cathode extends into the cylindrical cavity within the upper face of the anode. Conductive elements 22, 22 are accommodated in borings 23, 23 within anode 18 for leading direct current to the anode. At the base of the cylindrical depression in the face of the anode 18 is a central slot or boring 26 which extends through the anode and communicates with sump means 10.

This cell is arranged to have fragments or pellets of unrefined titanium fed into the anode cavity during operation of the cell. This arrangement includes a pair of similar feeding chambers C and C' which are inclined from the horizontal sufficiently to promote the sliding of solid fragments or pellets over their inclined bottoms 35, 35' and into the cylindrical cavity in the upper face of anode 18. The chambers are provided with a first barrier 36, 36', and a second barrier 37, 37' to provide, therebetween, a gas lock whereby fragments or pellets may be fed to the anode without admitting air to the interior of the cell and without substantial wastage of the cell's atmosphere.

Disposed in the space between rotatable cylindrical main cathode 15 and massive main anode 18 are (*a*) a metallic screen or foraminous barrier or potential divider 40 which is shaped substantially to conform to the shape of cathode 15, and (*b*) between barrier 40 and main cathode 15, a series of spaced graphite electrode rods 41, 41. These rods are disposed parallel to each other and with their axes parallel to the axis of cathode 15; in length, these rods are coextensive with the face of the cathode. Rods 41, 41 are arranged in the form of a portion of a cylinder coaxial with respect to cathode 15. Rods 41, 41 are electrically connected, at their ends, to one pole, G, of a conventional regulatable source R of direct current, whilst the other pole, F, of said source is electrically connected to said barrier 40 to constitute circuit A, i.e., the auxiliary circuit.

Circuit B is constituted by said rotatable main cathode 15, said massive main anode 18, a conventional source S of direct current (e.g., rectified alternating current) and suitable electrical connections therebetween.

The letter L indicates the level at which the electrolyte should be maintained.

A voltmeter, V may, as shown in the drawing, be suitably connected electrically between rotary main cathode 15 and barrier 40 whereby to make possible measurement of the voltage between said members.

It is to be noted that the sump means 10 may be periodically emptied of accumulated anode residue by appropriately thawing its contents, and may be closed by appropriately freezing its contents.

It is to be noted, also, that circuit A is adjustable or regulatable so that the voltage between the rotary cathode and the barrier or potential divider, as measured by voltmeter V is 0.05–0.10 volt when the two circuits A and B are both broken.

The precise level of the open circuit voltage will be determined by the impurities in the metal to be refined.

It will be clear that as the metal is deposited on the main cathode it passes through zones of alternately higher and lower oxidation state of the electrolyte. In my co-pending application I have disclosed that with an electrolyte containing 2–5% barium or strontium chloride the titanium-group metal will be deposited as plates containing barium, or strontium, but that as the state of oxidation increases with respect to the current density the alkalinous metal is removed from the plates by reaction with the higher chloride of the titanium metal being replaced by the metal so reduced. The result is plates of pure metal. The arrangement shown in the drawing is ideally suited for the production of such plates.

It will be clear that the same principle may be applied to a rotary disc or other moving cathode.

In Fig. 2, 51 represents a furnace in which is disposed an elongated cylindrical stainless steel pot 53 provided with a cover member 54 removably secured to pot 53. At its bottom, pot 53 terminates in a depending elongated cylindrical open-bottomed sump means 56 extending beneath furnace 51.

A main anode 58 is disposed partially within, and axially of, pot 53, being supported by insulating sleeve 59 accommodating the anode in cover 54. A main cathode 60, in the form of a hollow cylinder, is axially disposed about main anode 58 and is supported by a pair of electrically conductive supporting rods 61, 61 which extend above cover 53 and are insulated from the latter by means of insulating sleeves 62, 62. The lower end of main anode 58 and the lower edge of main cathode 60 preferably are spaced at substantially the same distance above the bottom of pot 53.

At their upper (outer) ends, main anode 58 is connected to one pole, and supporting rods 61, 61 are connected to the opposite pole, of a conventional source of unidirectional current (e.g., a battery), not shown, by means of conventional electrical connections (not shown) to constitute the main circuit of the cell.

The cell is provided with means for maintaining within it an atmosphere of an inert gas (e.g., argon), such means including gas inlet 63 and gas outlet 64 pipes let into cover 54.

According to the principles of the invention, the cell is equipped with means constituting an auxiliary electrical circuit. For that purpose, a foraminous, electrically conductive auxiliary anode 65, in the form of a hollow cylinder of expanded metal substantially co-terminous with main cathode 60 and axially disposed within and spaced from main cathode 60, is suspended about (but spaced from) main anode 58 by means of supporting members 66, 66 which extend through insulating sleeve members 67, 67, let into cover 54. An auxiliary cathode 70 formed of graphite is provided adjacent the bottom of pot 53 and spaced beneath main anode 58 and main cathode 60. The upper part of auxiliary cathode 70 is hollow and funnel-shaped and having a mouth 71 disposed directly beneath main cathode 60 and having a diameter at least as great as is the diameter of main cathode 60. The lower part of auxiliary cathode 70 is in the form of a tube 72 which is disposed within, and extends beneath the end of, sump means 56, tube 72 being insulated from the latter by means of a quartz insulating tube 75.

The upper (outer) ends of supporting members 66, 66 are electrically connected to pole F', and the lower (exposed) end of tube 72 is electrically connected to pole G', of a regulatable rectifier R', to constitute the auxiliary electrical circuit of the cell.

When the cell is in use, sump means 56 will be provided with heating means and cooling means, similar to members 12 and 13 shown in Fig. 1, a showing of which heating and cooling means has been omitted from Fig. 2.

Example 1

In this example I use an apparatus like that described in Figures 2 and 3. I place an electrolyte of 95% NaCl, 3% $BaCl_2$ and 2% $TiCl_2$ in the cell which is constructed of stainless steel. The main cathode and foraminous potential divider are of steel and the main anode is

composed of a titanium alloy containing 2% chromium and 1% iron, balance essentially all titanium. In order to refine this alloy the open circuit potential between divider and main cathode must be less than 0.2 volt.

The following table shows the interrelationship between the various factors in the refining operation:

Amperes	Circuit B				Circuit A—Operating	
	Operating V		Open V			
	An.–Cath.	Div. Cath.	An.–Cath.	Div. Cath.	Amps.	Volts
100	1.0	0.60	.45	.30	0	0
	.95	0.55	.40	.25	2	2.1
	.90	0.50	.37	.20	5	2.8
	.80	0.40	.35	.10	10	3.5
	.70	0.30	.30	0	15	4.0
	.60	0.20	.20	−.10	20	4.5
200	1.60	.95	.50	.35	0	0
	1.57	.90	.45	.30	2	2.1
	1.55	.80	.42	.25	5	2.8
	1.50	.70	.40	.15	10	3.5
	1.45	.60	.35	0	15	4.0

In this example the cell was operated .20 volt OC from divider to main cathode at 100 amperes operating current. The deposit on the divider was 5% of that on the main cathode and analyzed 40% chromium and 20% iron. The main cathode deposit consisted of plates of titanium containing a little barium which could be removed by leaching.

Example 2

In this example I use an apparatus like that described in Figure 1. I place on the supporting graphite block 10 mesh particles of a reaction mixture of TiO_2, Mg and Cu which has been heated to 1200° C. to consolidate into a mass having an electrical resistivity of .001 ohm cm., and then comminuted to pass a 10 mesh screen. I feed this comminuted alloy on to the graphite block so as to maintain a layer several particles thick over the graphite surface. I use an electrolyte consisting of 92% NaCl, 3% $BaCl_2$ and 5% $TiCl_2$. I connect the graphite electrodes across the face of the rotary cylindrical main cathode as auxiliary anodes in a separate circuit in which the foraminous electrode is an auxiliary cathode. Since there are no metals in the anode which are near titanium in the free energy of their lower chlorides, I permit the voltage between foraminous electrode and cathode to rise to .25 volt. At 500 amperes in the main circuit, I find that 4 amperes in the auxiliary circuit will maintain the necessary voltage between foraminous electrode and cathode.

The cathode product is composed of plates and crystals of titanium of high purity.

What is claimed is:

1. In an electro-refining cell for a titanium-group metal, a rotary cathode adapted, during use, to be partially immersed in a fused chloride electrolyte, an anode of the metal to be refined, a foraminous intermediate electrode co-extensive with the immersed portion of the cathode, a multiplicity of elongated graphite members spaced from and extending across the cathode surface normal to the direction of its movement and between the main cathode and the auxiliary cathode, means for passing direct current separately from the anode to be refined to the rotary cathode and from the graphite members as auxiliary anodes to the foraminous electrode as auxiliary cathode, and means for adjusting the current in the second circuit with respect to that in the first circuit so as to provide during the operation of the cell an instantaneous open circuit voltage between the foraminous electrode and the rotary cathode of 0.01–0.2 volt.

2. In an electrorefining cell for a titanium group metal including a main anode, a main cathode and a source of direct current in electrical connection therebetween to constitute a main electrical circuit, the provision of means constituting a second separate circuit, said means comprising a foraminous inert metal electrode, an auxiliary graphite electrode and a source of direct current in electrical connection therebetween, and means in said second circuit for regulating the current therein so that the instantaneous open circuit voltage between said foraminous inert metal electrode and said main cathode may be maintained at a predetermined voltage, the main electro-refining circuit and the separate circuit between the graphite electrode and the foraminous electrode being so interconnected that when the operating voltage rises the current in the separate circuit will increase until the operating voltage again falls.

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