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METHOD AND APPARATUS FOR IMPROVING RECOVERY OF
PLUTONIUM-GALLIUM ALLOYS BY ELECTROREFINING

Filed June 15, 1965 2 Sheets-Sheet 1

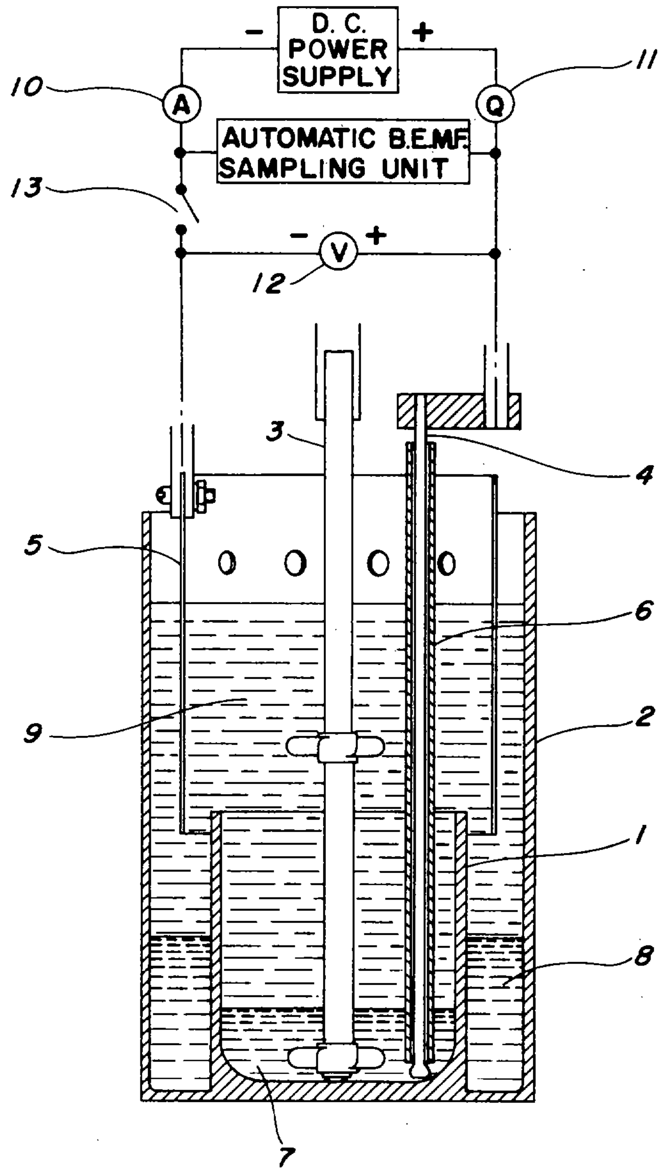

Fig. 1

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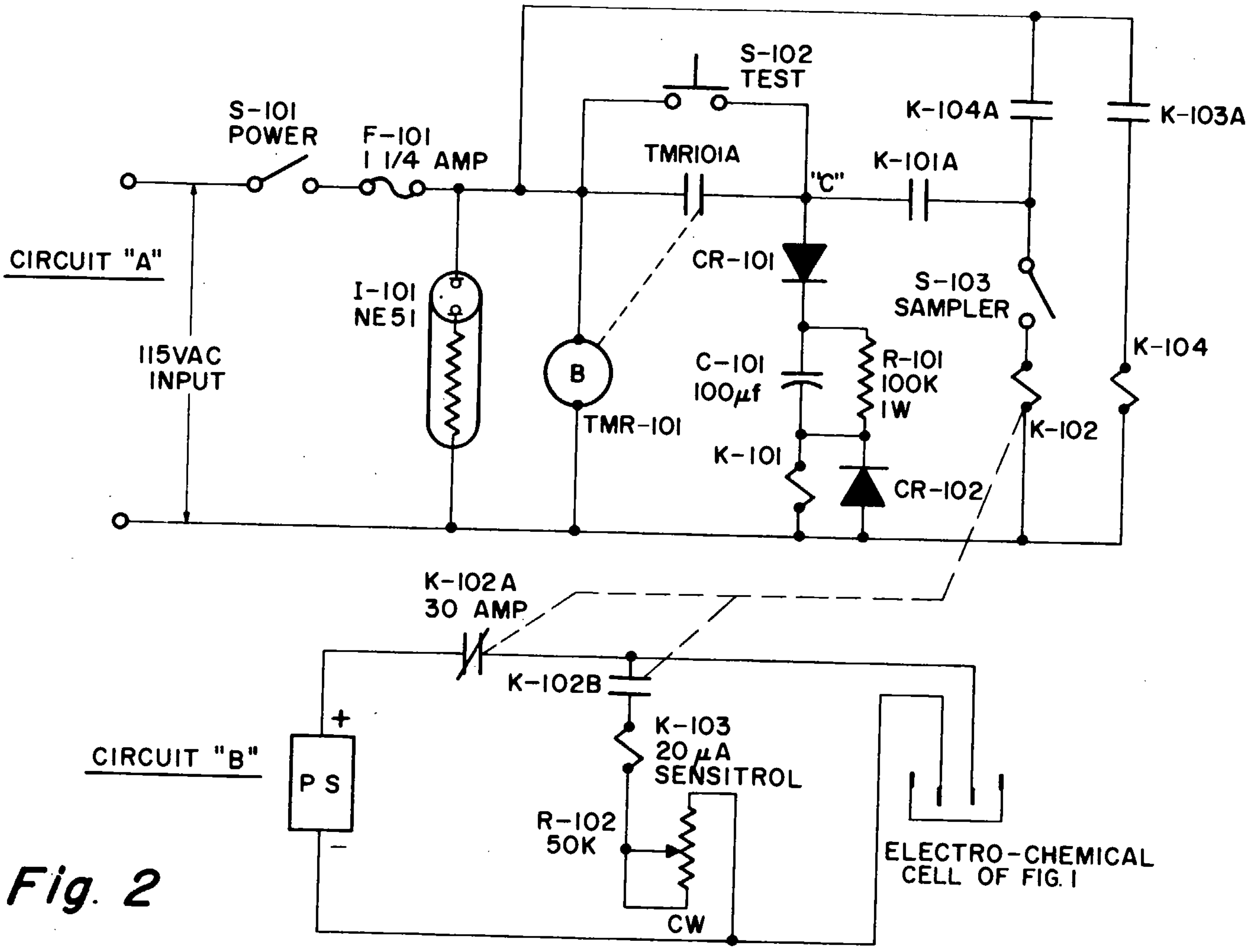

Fig. 2

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METHOD AND APPARATUS FOR IMPROVING RECOVERY OF PLUTONIUM-GALLIUM ALLOYS BY ELECTROREFINING

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ABSTRACT OF THE DISCLOSURE

A device and method for recovering plutonium from plutonium-gallium alloys by an electro-refining process in which the said alloy is the anode of the electrorefining cell and the E.M.F. of the said cell reaction between the cathode and anode supplies the voltage to drive a control circuit, and said method consists of adding to the anode iron, cobalt, or nickel in an amount equal to about 25 weight percent of the gallium present.

This invention relates to an apparatus and method for extending the amount of plutonium which can be recovered in an electrorefining process and more particularly to an apparatus and method in which the source of the plutonium is a plutonium-gallium alloy, said alloy being the anode of the electrorefining cell and said process consisting of adding a small amount of iron, cobalt, or nickel in powdered form to the liquid metal anode before initiating the electrorefining operation.

Normally, alloys of plutonium and gallium contain about one percent by weight of gallium in order to stabilize the delta phase of plutonium. This composition is a uniform liquid metal solution at 750° C. which is the normal operating temperature of the electrorefining operation. The liquid metal plutonium-gallium alloy serves as the anode of the electrorefining cell, and the plutonium is dissolved selectivley out of the solution thereby concentrating the gallium in the anodic solution. Eventually, this liquid metal anode composition reaches a point where no liquid remains and the anode becomes completely polarized. At 750° C. this point is reached when the atomic ratio (R) of gallium to plutonium reaches the value of about 0.30. The electrorefining operation must be terminated at this point and yet gross amounts of plutonium still remain in the polarized anode. The invention herein disclosed relates to a method for extending the amount of plutonium that can be dissolved anodically before anode polarization becomes serious; that is, the ratio (R) of gallium to plutonium is greater than 0.30. This invention is also concerned with an electronic system or apparatus for the electrorefining of plutonium from its alloys and in particular plutonium-gallium alloys. This system insures the production of high purity plutonium metal in optimum yield by permitting the electrorefining process to continue only as long as high purity metal is being produced safely. Without this control system, previous experience has shown that unsafe quantities of pyrophoric alkali metals could be generated within the cell and the high yields of pure plutonium metal could not be obtained reliably. The system consists basically of two components, an external electronic control system and an electrorefining cell. The signal for the electronic control circuit is derived from a rapid increase in the back electromotive forces that develops in the cell when alkali metal is generated, there is a malfunction of the cell, or when the plutonium value in the alloy has been depleted.

The apparatus of this invention is best understood by reviewing the previous development history. In early work on the electrorefining of plutonium alloys, much difficulty was experienced on knowing when to terminate the electrorefining process. When the electrorefining run was terminated prematurely the process was inefficient. If the operation was carried beyond a certain degree of depletion of the liquid plutonium anode an unsatisfactory product was obtained, even though the concentration of plutonium ions in the molten salt electrolyte remained essentially unchanged. It was therefore necessary that some property of the liquid metal plutonium anode must be monitored and correlated with the impurity of the product obtained by the electrorefining process. The inventors have discovered that the back electromotive forces measured only on an open circuit between the anode and the cathode of the cell was essentially independent of the concentration of plutonium ions present in the molten salt electrolyte. However, when this same back E.M.F. increased from the very low normal operating value of approximately 0.1 volt to the value of 0.25 volt, it was essential to terminate the process in order to insure both maximum yield and purity. In the apparatus of this invention the back E.M.F. monitors the condition of liquid plutonium metal at the anode and does not monitor the concentration of plutonium ions in the molten salt electrolyte, and therefore, does not use the concentration of the molten salt electrolyte as the control signal which is the case in electrorefining cells of the prior art. This method of using the back E.M.F. is unique to our electrorefining system which employs a stirred liquid metal anode and it is also noteworthy that in the process of this invention the impure feed material is a plutonium metal alloy and not plutonium chloride. This difference necessitates differences in the cell design and the use of the back E.F.F. method to control same.

Accordingly, there is provided by the present invention an automatic control system for the electrorefining of plutonium alloys and in particular plutonium-gallium alloys. The system consists basically of two components, an external electronic control system and the addition of a certain amount of a metal added to the anode of the system selected from the class consisting of iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium and platinum. For other objects and advantages of the invention and for other modifications thereof, reference is now to be had to the following detailed description taken in conjunction with the accompanying drawings, in which:

FIGURE 1 shows a vertical cross-sectional view of the electrorefining cell; and FIGURE 2 diagrammatically illustrates a wiring diagram exemplary of the preferred form of the invention.

Turning now to FIGURE 1, it will be seen that the cell consists essentially of an outer ceramic vessel **2** containing a fused salt electrolyte **9** and an inner shorter ceramic vessel **1** separated from outer vessel **2** by an annulus filled with electrolyte **9**. Inner vessel **1** serves as the container for the impure anode **7**. Depending upon exterior structure (not shown) and extending into anode **7** is a metallic rod **4** and a ceramic stirrer **3**. This rod **4** is sheathed by a ceramic tube **6** and serves as the anode lead **4**. The anode lead **4** is connected to the power supply through Q, an ampere-hour meter **11**, and in the same circuit is a voltmeter **12** that is a back E.M.F. indicator. The stirrer can be rotated by means well known in the are with the upper stirrer circulating the electrolyte and thus preventing the isolation of a plutonium depleted layer adjacent to the cathode **5** while the lower stirrer promotes contact between plutonium anode **7** and electrolyte **9**. The plutonium which plates out on the cathode drips to the bottom of vessel **2** and collects in a pool **8**. Cathode **5** is mounted inside of outer vessel **2** partially extending therefrom and largely immersed in the electrolyte. Cathode **5** is connected to a power supply through switch **13** and ammeter **10**. Switch **13** permits interrupting the power supply to the cell during the period the cell potential is being measured.

Electrolyte **9** is a combination of fused salts having a relatively low melting point and must include a plutonium salt. The inventors have found that a chloride or chloride-fluoride electrolyte consisting of 10 weight percent plutonium trichloride or plutonium trifluoride or plutonium tetrafluoride, 50 weight percent potassium chloride, and **40** weight percent sodium chloride is a useful electrolyte solution. This cell is essentially the same as appears in U.S. Patent No. 3,098,028 and this patent is hereby expressly incorporated as part of this application.

In FIGURE 2 we have a diagram of the electrorefining electronic circuit which is divided into circuit A and circuit B. The combination of cell and electronic circuit can accomplish what neither can do alone in that the cell of FIGURE 1 has a unique feature that its back E.M.F. is negligible when the cell is functioning properly. The back E.M.F. rises rapidly when either the plutonium value in the alloy is depleted or a mechanical failure such as a stirrer stoppage occurs. The electronic system measures the back E.M.F. of the cell once each hour or at any desired preset time interval and if the said E.M.F. is within allowable limits the circuit permits the electrorefining process to continue; otherwise, the electrorefining cell is automatically disconnected from the power supply thus terminating the process. The following is a description of circuit A as used in a preferred embodiment of this invention:

CIRCUIT A

The control power for circuit A is derived from the 115 volt 60 hertz AC line through **S101** "power," and the circuit protection fuse **F101**. The coil of relay **K102** of circuit A with its contacts **K102A** and **K102B** of circuit B is energized once each hour. Relay **K102** is energized once each hour or at any preferred time interval for a period of approximately 2 to 4 seconds. This energizing of the relay is accomplished by a motor driven cam switch composed of time control **TMR101**, its contacts **TMR101A**, and the combination of rectifier **CR101**, capacitor **C101**, resistor **R101**, relay coil **K101** and rectifier **CR102**. **S102** "test" is connected in parallel with the contacts **TMR101A** to provide for manually energizing the sampling system at any time between hourly sampling intervals controlled by the timer **TMR101** and its contacts. To keep the dwell time of such a switch to about 2 to 4 seconds is the purpose of the combination of **CR101**, **C101**, **R101**, **K101**, and **CR102**. When the contacts **TMR101A** are closed during the sampling interval they supply current to rectifier **CR101** and the common point C. Current will flow through relay coil **K101** only long enough to charge capacitor **C101**. This time interval is about 2 seconds. Rectifier **CR102** is in the circuit merely to prevent relay coil **K101** from "chattering" due to the pulsating current following through capacitor **C101** and rectifier **CR101**. The contact of relay coil **K101** (**K101A** closes for 2 seconds during the sampling period, and assuming switch **S103** to be closed) energizes the relay coil **K102** (see description of circuit B below). If the cell potential or voltage circuit B is sufficient to energize relay coil **K103** it remains closed by the magnetic lock-in in that device. This condition holds sensitrol contact **K103A** closed and through the combination of relay coil **K104** and its contact **K104A** energizes **K102** and holds relay contact **K102A** (of circuit B) open. This turns off the power supply PS to the cell and the relay **K103** must be mechanically reset for the next electrorefining operation. Relay coil **K104** is inserted in the circuit to reduce the current requirements on the contacts of **K103A**. The relay **K103** is a sensitive device with contacts for a very low current rating such that said contacts are insufficient to reliably energize the large contactor or relay **K102**. The switch **S103** provides the operator with the option of eliminating a sampling interval without loss of time continuity.

The following is a description of circuit B of FIGURE 2 as used in a preferred embodiment of this invention:

CIRCUIT B

The coil **K102** of circuit A energizes two contacts **K102A** and **K102B** of circuit B. **K102A** is normally closed while **K102B** is open so that power supply **PS** can deliver current to the electrochemical cell. During the sampling period, approximately 2 seconds, the power supply is disconnected from the cell and at that time the cell potential is measured. The relay coil **K103** and resistor **R102** constitute a variable span voltmeter whose range is variable from 0 to 1.0 volt. Since the back E.M.F. of the cell during favorable operating conditions is less than 0.25 volt, the sensitrol and resistor **R102** combination is set at a value of 0.25 volt. A back E.M.F. greater than 0.25 volt will energize **K103** and contacts **K103A** in circuit A during the 2 second sampling period.

Using the device as described above in FIGURE 1 and 2 and in which the anode of the electrorefining cell contains a plutonium-gallium alloy, the inventors have discovered a method for extending the amount of plutonium that can be dissolved anodically before the anode polarization with its resulting increased back E.M.F. causes the electrorefining operation to be terminated. The following are several experiments conducted showing the range of additions to the plutonium-gallium anode in preferred embodiment of this invention so as to maximize the amount of plutonium recovered using the electrorefining system as previously described.

Experiment 1

A one percent by weight gallium-plutonium alloy was electrorefined by the method described above. Before the electrorefining operation was commenced, approximately 0.24 percent by weight of iron was added to the impure anode. The ratio of iron to gallium by weight was approximately 0.24. The electrorefining of the plutonium was terminated automatically at an R value (R being the atomic ratio of gallium to plutonium) of 0.66 which is more than twice the normal ratio of plutonium depletion compared to the theoretical value of 0.33.

Experiment 2

In this experiment the starting gallium concentration was 1.95 percent by weight the balance plutonium and 0.52 iron was added to the anode to give a weight ratio of iron to gallium of approximately 0.25. This run was terminated automatically at an R value of 0.52.

Experiment 3

The starting gallium concentration was 1.81 weight percent, the balance being plutonium. Again 0.24 weight percent of iron was added to the anode (same amount of iron as Experiment **1**), to give a weight ratio of iron to gallium of 0.133 while the weight ratio of iron to plutonium was essentially the same as Experiment **1**. This run was terminated at an R value of 0.33 thus showing that amount of iron added to the anode must be based on the gallium concentration and not on the plutonium concentration.

Experiment 4

Using the same plutonium-gallium composition and conditions as Experiment **1**, 0.007 weight percent iron plus 0.015 weight percent nickel, a total of 0.022 percent iron and nickel is added to the plutonium-gallium anode. The run was automatically terminated at an R value of 0.30.

Experiment 5

Under the same conditions as used in Experiment 3 except 0.028 weight percent iron and 0.011 weight percent nickel, a total of 0.039 percent being introduced into the anode, the electrorefining process was terminated at an R value of 0.39.

Experiment 6

Keeping the same operational procedure as Experiments 1, 3, and 4, 0.041 weight percent iron and 0.025 weight percent nickel, a total of 0.066 percent was added to the anode. An R value of 0.42 was obtained before the process was automatically terminated.

The results of these experiments indicate that the adding of a small amount of iron or iron and nickel to the anode is most beneficial and that the amount of iron added should be based on the gallium concentration and not on the plutonium concentration in the alloy which serves as the anode in the electrorefining process. From the experiments 1–3 above, the effective and desired amount of iron added per unit weight of gallium is about 0.24 to 0.27 gram of iron per gram of gallium present in the anode alloy. Experiments 4–6 show the amount of iron and nickel that must be present is about 0.25 gram per gram of gallium. The following elements either alone or in combination with iron also have beneficial effects in extending the amount of plutonium which is to be recovered using the process and apparatus of this invention:

A. Cobalt, nickel—The total amount of iron plus cobalt and nickel should be about 0.25 gram per gram gallium present in the anode alloy.

B. Ruthenium, rhodium, palladium, osmium, iridium, and platinum are metallurgically similar to the iron-cobalt-nickel additive but require an underetermined but higher weight ratio of the additive as compared with the said iron, cobalt, nickel additive.

What is claimed is:

1. An E.M.F. feed-back control circuit which derives its electrical energy from the back electromotive force of

a plutonium electrorefining cell reaction between the cathode and anode comprising in combination a plutonium electrorefining cell, a power supply, and a relay means that can be energized for a period of about 2 seconds at any preset time interval, said means comprising a motor driven cam switch that disconnects the power supply and places a calibrated sensitrol voltmeter across said cell, said voltmeter being preset so at its full scale reading it will magnetically lock and prevent the said relay means from reconnecting the power supply back across the electrorefining cell cathode-anode circuit.

2. A method for extending the amount of plutonium recovered in the electrorefining of plutonium in a molten salt electrolyte wherein the source of plutonium is a plutonium-gallium alloy forming the anode in the electrolytic cell, comprising the step of initially adding to the anode an amount equal to 24 to 27 weight percent of the gallium present in the said anode of at least one element selected from the class consisting of iron, cobalt, and nickel.

3. The method of claim **2** in which the said element is iron and the said weight percent of iron that is added to the anode is 25 percent.

4. The method of claim **2** in which the said element is a combination of iron and nickel.

5. The method of claim **2** in which the said element is a combination of iron, nickel, and cobalt, and is added to the anode in an amount equal to 25 weight percent of the gallium present.

References Cited

UNITED STATES PATENTS

3,098,028	7/1963	Mullins et al.	204—1.5 X

REUBEN EPSTEIN, *Primary Examiner.*

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204—228, 243