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METHOD OF CONTROLLING ALUMINA CONTENT DURING ALUMINUM ELECTROLYSIS

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This invention relates to the art of fused salt electrolysis, and, more particularly, to the control of the metallic compound or solute constituent of a fused electrolyte in an electrolytic cell producing molten metal, with reference to maintaining the concentration of the solute within closely prescribed limits. In its primary adaptation, the invention is directed to improved method and control means for the electrolytic production of aluminum.

As is well known, commercial production of aluminum is by electrolysis of molten cryolite-alumina salts in high anode-cathode cells of either the pre-baked anode or the continuous, self-baking Soderberg anode type. Usually, a multiplicity of like cells are arranged in what is called a potline, in series electrically, and direct current of the order of fifty thousand to one hundred thousand amperes, and more, is used in the cells, depending upon their size, with a voltage drop of generally between 4 and 6 volts across each cell. As normal electrolysis proceeds, aluminum is deposited at the cathodic bottom of the cell where it collects as a molten pool of metal, while the oxygen of the alumina combines with the carbon of the anode to form principally carbon monoxide and carbon dioxide.

One of the principal and continuing problems encountered in the electrolytic aluminum reduction process is the control of the dissolved alumina concentration of the electrolyte or bath. If the concentration is depleted or drops below a certain critical limit, depending primarily on the anode current density, the phenomenon known as anode effect occurs, with its consequent well known disadvantages. The anode effect is known as an anodic spark or arc discharge, and is characteristic of the electrolysis of molten salts and especially of the electrolysis of cryolite-alumina salts. It is stopped and normal electrolysis restored by the expedient of breaking the frozen top crust of bath and adding and stirring alumina into the bath. However, care must be taken not to charge too much alumina or it will not dissolve because it exceeds the solubility capacity of the electrolyte for alumina at the prevailing temperature of the bath and the excess can sink through and collect under the aluminum pool and result in what is known as a "sick" cell with decline in efficiency.

In both cases of anode effect and of a sick cell the cell is working under abnormal conditions and the net result is an undesirable decline in the overall efficiency of the process.

Heretofore, practices involving semi-continuous and continuous alumina feeding have been employed to add alumina to the bath in amounts adapted to avoid development of a sick cell and to stretch out the time interval between successive anode effects. Due to the fact that such feeding techniques do not take into account the percentage of alumina dissolved in the bath, they rely on an underfed practice and allow the cell to undergo as much as one anode effect per day, as a safety precaution against feeding too much alumina into the cell. Moreover, the electrolysis is carried out in baths having a widely varying content of alumina and with like variations in efficiency. Typically, the alumina content variation may be from a maximum of about 7% to 10% down to the critical minimum of about 0.5% to 1.5% at which the anode effect occurs.

The present invention, therefore, aims to provide an improved method of carrying out electrolysis of a molten bath of metallic compounds to produce molten metal which obviates disadvantages and disadvantages of the character hereinabove related.

The invention further provides in fused bath electrolysis of alumina-cryolite compounds a method of operation which controls the alumina content of the bath within closely prescribed limits so as to secure continuous normal electrolytic action and improved efficiencies.

Another object of the invention includes the provision of novel method and means for eliminating the occurrence of anode effect in a molten salt bath electrolytic cell susceptible thereto; for sensing and controlling the concentration of the solute constituent of such molten salt bath so as to keep the solute concentration within closely prescribed percentage limits; and especially for avoiding the decrease in the efficiency of electrolysis, as exemplified by the increase in power consumption and reduction in production from an aluminum reduction cell due to the large increased cell voltage as a result of depletion of dissolved alumina in the electrolyte of the cell to a critical concentration or the inefficiency of the process when the cell has an excess of alumina or is sick.

A further object of the invention is to provide for the electrolytic reduction of aluminum under a pilot anode method of alumina control to secure continuous electrolysis with improved efficiency, and additionally to provide new and improved mode of pilot anode operation to minimize consumption of the pilot anode.

Still another object is to provide for pilot anode sensing periodically of the dissolved alumina concentration in a fused cryolite electrolytic bath at predetermined periods, and for responsively thereto selecting the rate of alumina feed to the bath accordingly as more is needed to be added either at a normal or slow rate or at an accelerated or fast rate to keep the concentration within prescribed limits between successive periods.

These objects, as well as other novel features and advantages of the invention, will become more apparent by reference to the following detailed description and the drawings referred to therein of which:

FIG. 1 is a diagrammatic representation of a multiple prebaked anode type of aluminum reduction electrolytic cell or furnace equipped with a pilot anode and an automatic alumina or ore feeder, and schematically showing electrical power supply to the cell and the pilot anode;

FIG. 2 is a schematic, across-the-line circuit diagram of a control system for controlling the operation of the pilot anode and, in turn, the operation of the cell in accordance with the present invention;

FIG. 3 is a circuit detail of another form of regulated ore feed which may be used;

FIG. 4 is a view similar to FIGS. 1 and 2 combined, but showing a separate or external power supply for the pilot anode and a modified and simplified control system for the pilot anode in the practice of the invention under pilot anode control, and

FIG. 5 is a timing diagram of the program timer employed in the control system of FIG. 4.

According to the invention in its primary adaptation, an aluminum reduction electrolytic cell is operated with tight control about a preselected percentage content of the alumina in solution in the electrolyte under a pilot anode control program consisting essentially of a stand-by phase and a sensing phase. A pilot anode is provided which is immersed or dipped into the electrolyte of the cell to a given immersion depth. During standby, the pilot anode is maintained on continuous anode effect, which condition has been discovered to be essential in order to minimize consumption thereof and thus make the pilot anode control practical and reliable. Also,
alumina is added to the electrolyte or bath at the slow or the fast feed rate depending on the selection made at the input, depending on the selection made at the input, depending on the selection made at the input, depending on the selection made at the input.

During the sensing phase, the anode effect on the pilot anode is eliminated preferably by reversing the current flow through it. Then forward current calculated to give a specific control current density on the pilot anode is applied thereto, this current density exceeding that on the working anode or on the rest of the cell. Accordingly, the anode effect will or will not be induced on the pilot anode depending on the percentage of alumina in solution in the electrolyte. If none is induced, the rate of alumina feed is selected to be the slow rate and, at the end of the sensing phase, the current density on the pilot anode is increased to such value as to induce an anode effect thereon for the next standby period. On the other hand, if an anode effect is induced during sensing, the rate of alumina feed is selected to be the fast rate and, at the end of the sensing phase, the current density is again increased to assure maintenance of the anode effect during the next standby stage.

Herein, "slow feed rate" means a rate calculated to deliver less alumina than the cell will consume by electrolysis during a standby stage, whereas "fast feed rate" means a rate calculated to deliver more alumina than the cell can consume during such stage. Whenever it is being fed at the fast rate to increase the alumina concentration in the bath during a standby stage, the fast rate is cut back to the slow rate at the next sensing cycle and is reselected only if an anode effect appears on the pilot anode during sensing. Thereby, the alumina delivered to the bath is kept from exceeding the solubility capacity of the electrolyte by maintaining the alumina concentration within a desired range. If no anode effect appears, the slow feed rate is allowed to continue throughout the next standby stage. Thus, by the method of the invention, the electrolysis is carried out with close control of the upper and lower percentage limits of dissolved alumina in the electrolyte.

Referring now to the drawings, particularly FIG. 1, numeral 1 denotes a conventional aluminum reduction cell or pot which may be connected in series with like cells 1', . . . 1n in a potline and supplied with direct current power from a source (not shown). Numeral 2 denotes the carbon cathode lining of the cell, 3 the molten aluminum pool cathode, 4 the molten electrolyte or bath consisting essentially of dissolved aluminum oxide or aluminum hydroxide, along with impurities customarily employed in a commercial Hall bath, and 5 the carbon anodes which dip into the bath and are periodically adjusted vertically to the proper working distance with respect to the top of the cathode. The top crust normally present is indicated at 6. From a hopper above the cell, alumina may be added to the bath by operation of a feeder 7 of any conventional type. The one shown includes an air-cylinder operated crust-breaking plugger 8, controlled by solenoid operated valve 9, and measuring means 10 having inlet and outlet valve means operatively connected to the plugger for discharging a measured quantity of alumina each time the plugger is actuated.

In this conventional electrolytic furnace, electrolysis proceeds with the current flowing through the electrolyte from the anode to the cathode, thereby decomposing the aluminum oxide into metallic aluminum with evolution of gases at the anode which eventually escape from the cell. The alumina in solution is used up in direct proportion to the production of metal and more must be introduced into the bath without overfeeding it, so as to avoid development of a sick cell. Due to the prevalent variable conditions, it has been found not possible to feed the alumina precisely in accord with the consumption rate so underfeeding is the rule with sufferance of anode effects and all of the attendant disadvantages and adverse effects.

According to the invention, however, electrolysis is carried out with continuous control of the alumina in solution within a narrow range of a preselected percentage level, such as 4½ percent, for example, by pilot anode sensing of the alumina concentration of the bath at regular time intervals and selecting one of two alumina feed rates in accord with the results of each sensing operation. Accordingly, a pilot anode 12, suitably of carbon or graphite, or of suitable conductive material, is adjustably and insulatedly mounted at the pot 1 with its lower end dipped into the bath. Since it is to carry current and the current density is a function of the extent it is immersed or dipped into the bath, it is desired to set it to a given immersion depth, a depth of about 4½ inches having been found to be quite satisfactory. Of course, this may be varied within limits, as also may the size and shape of the pilot anode. Preferably it should be as small as possible, such as between ¼ in. and 2 in., so that the surface area wetted by the bath is limited, thereby reducing its current requirements and operating power cost.

Power for the pilot anode may be taken or shunted from the potline bus several pots upstream from pot 1, as at tap 13, to make available a voltage between 12 and 20 volts across the pilot anode. Accordingly, the forward current supply is arranged as a dual or variable voltage source for the pilot anode by means of a voltage dropping ballast resistor 14 having high voltage tap A and low voltage tap B, both adjustable and preset for impressing preset high and low voltages on the pilot anode for the purposes hereafter described. Selection of the voltage taps is by means of contacts CR2 in circuit lines 1A and 1B of FIG. 1, while contactor CR in line 1A is operable to open and close the circuit between contacts CR2 and the pilot anode. Contactor CR is normally energized when the circuit extending from power tap 13 through voltage adjusting resistor 15 in line 2B, normally closed contacts CR1 in line 2A, its operating coil to tap 16 of the cathode bus of pot 1. The pilot anode is adapted to be shunted directly to tap 16 to place it at cathode potential for reverse current flow through it by means of contactor RC whose contact controls the reverse current circuit, this RC contactor being controlled by normally open contact CR1 in line 2B. It is to be noted that by means of the contacts CR1 in the lines 2A and 2B, only contactor CR or contactor RC can be energized at any one time. In addition, the pilot anode is adapted for connection to tap 16 for a sensitive sensing circuit, normally open contact CR3 and normally closed contact TR7 in line 1A and a sensor relay CR4, which senses and is responsive to the voltage on the pilot anode when the sensing circuit is closed as hereafter described.

At this point, it may be pointed out that it has long been known that interruption of normal electrolysis by the occurrence of the anode effect has to do with a critical anode current density, which is a function of the dissolved alumina concentration in the bath. The relationship between the critical current density and the alumina concentration is essentially linear. As the alumina concentration is lowered, the critical current density is likewise lowered. When it reaches the actual current density, the critical relationship between concentration and density exists and an anode effect occurs. Heretofore, attempts have been made to utilize this knowledge by use of a pilot anode connected in parallel with the main anode of a cell and charged at a higher current density than the main anode so as to go on anode effect at a higher alumina concentration and thus foretell the approach of anode effect conditions in the cell. This has been entirely unsuccessful because such pilot anode worked as a sensing electrode but as a regular anode in the electrolytic furnace and consequently was consumed at such a rapid rate that it quickly became unreliable and inoperative for the purpose intended.

It has been discovered, however, that by operating the
pilot anode continuously on anode effect, except for brief sensing periods, the basic problem of its rapid rate of consumption effect is induced on the pilot anode about a thirty-three-fold decrease in its consumption rate is realized. Hence, according to the invention, the electrolysis is carried out under a pilot anode control program sequence which comprises the following steps or conditions, each of predeslected duration:

- **Stage A period**—This stage is of multiple minutes duration, during which a first or high voltage is impressed on the pilot anode and it is on anode effect, whereby its rate of consumption is minimized, it is kept at operating temperature and in a condition ready to be used for sensing. Herein, said “first or high voltage” means a voltage which causes the resultant current flow to provide a current density on the pilot anode, in amps./sq. in. of bath wetted area thereof, sufficient to induce and maintain an anode effect thereon. This voltage is always greater than the low or sensing voltage herebelow described.

The duration of the standby period regulates the frequency of sensing the level of dissolved alumina in the bath. Since frequent sensing is conducive to the attainment of closer and more uniform alumina content of the bath, it is desirable to select the time length of the standby period on the basis of sensing frequency. Hence, the time length may be within a multiple minute range which provides at least 2 to 4 sensing periods per hour. During this stage, power to the pilot anode is through the high voltage tap A and the feedback is operating to supply alumina to the bath either at the slow or the fast rate depending on the rate selection made at the preceding sensing stage.

- **Stage 2**—Reverse current stage.—The current direction through the pilot anode is reversed in order to eliminate the anode effect which has been maintained thereon during the standby stage. The time interval for this stage may suitably be about 8 to 10 seconds for example.

- **Stage 3**—Sensing stage.—At this stage a second or low voltage, predeslected in dependence on the level of alumina control desired and derived through tap B, is impressed on the pilot anode to cause the resultant current through it in the forward direction to provide a given control current density thereon in order to determine the alumina content of the bath by whether or not an anode effect appears on such anode. In other words, the sensing current density on the pilot anode is selected to correspond to a desired dissolved alumina concentration so that when the concentration declines to the predetermined control value, an anode effect is produced. After a brief pause of a few seconds to allow the current to stabilize, the sensor associated with the pilot anode circuit is rendered effective to detect if an anode effect has appeared or not and responsive to select the fast or the slow feed rate for the standby stage which follows. The time interval for the sensing stage is preferably made quite brief, within the range of between about 10 and 20 seconds, in order to minimize the pilot anode consumption which occurs when it is working as a sensing electrode. At termination of the sensing stage, the voltage on the pilot anode is switched from the low to the high voltage tap of the supply in order to assure inducing an anode effect thereon, or to maintain it if one is present, for the succeeding standby stage, and the cycle repeats. Stages 2 and 3 constitute a sensing cycle.

With the above program sequence in mind, it will now be easier to understand the operation of the control system of Fig. 2 in accomplishing the same. In this figure, the numerals along the left side identify individual across-the-line circuits, in each of which is a specified component, named as a control relay, timer, etc., as the case may be, and identified by a reference numeral. Contacts of a component are identified by the reference numeral of that component, and the numerals along the right side of the figure identify the circuit lines of Figs. 1 and 2 in which such contacts are to be found. Thus, for example, control relay CR12 in line 3 has four sets of contacts to be found in lines 3-5-16-17, respectively, a line under a numeral indicating that the referenced contact in that line is normally closed.

In the description which follows, reference will be made to voltage and current values for the standby and sensing stages or cycles which have been found effective when using a pilot anode of 1 1/4 inch diameter at an immersion dept of about 4 inches, ± 1/4 of an inch, and needing depth resetting only once per 8 hour shift, or after tapping, to control the alumina content of the bath at the selected percentage level of about 4½ percent. Also, specific time intervals for the respective stages of the control program and of the feeder operation will be specified as exemplary of the practice of the invention.

Assuming that we are starting into the standby stage, through high voltage tap A, the high voltage of between 14—16 volts is impressed on the pilot anode 12 and its current density is suddenly raised to a value sufficient to induce an anode effect thereon, which then persists until eliminated. The duration of the standby stage is controlled by a conventional synchronous motor-driven reset timer TM3 in line 18, set to provide a 20 minute timing period. It is now timing, as also are conventional synchronous motor-driven repeat cycle timers TM1 and TM2 in lines 20 and 19 which run continuously and serve as slow and fast feed timers, respectively, for the anode (see Fig. 1). They are set for 120 seconds and 60 seconds timing periods, respectively. While both of these timers provide feeder operating signals at their respective timing periods by closure of their contacts in lines 16 and 17, only one timer is allowed to be effective at any one time depending on which set of CR12 contacts in lines 16 and 17 are closed. As shown, contact CR12 in line 16 is closed so timer TM1 is controlling the ore feeder 7 by periodically operating the feeder solenoid S1 in line 16, and also shown in Fig. 1, for ore feeding at the slow feed rate during this standby stage. Also, all of the components in the respective circuit lines 1 through 15 are deenergized.

At time-out of reset timer TM3, which ends the standby stage and starts the reverse current stage, its control contact TM3 in line 1 closes. Thereby, control relay CR3 in line 1 energizes or picks up and locks in through its contact CR3 and series contact TR2 in line 3 so that it will remain energized throughout the remainder of the program sequence.

Control relay CR3 closes its contact CR3 in line 1A to close a point in the sensing circuit and it also closes its contact CR3 in line 13 to energize the adjustable pneumatic time delay relays TR1 and TR7 in lines 11 and 12, control relay CR4 in line 13, control contactor CR2 in line 14, and clutch coil TM3 in line 10 of the reset timer TM3. This timer is reset to its time set point by energization of its clutch coil and it runs toward zero for timing, but it does not start timing until its clutch coil is deenergized. Timing relay TR1 is set for 10 seconds before its contact in line 13 opens and it regulates the duration of the reverse current stage. Timing relay TR7 immediately opens its contact TR7 in line 1A to open the sensing circuit to prevent the sensing relay CR4 from being exposed to transient surges when reverse current is removed and forward sensing current is supplied to the pilot anode, this contact closes after a 5 seconds delay in order to close the sensing circuit, upon de-energization of timing relay TR7. Control contactor CR2 switches the forward current supply circuit from high voltage tap A to low voltage tap B by its contacts in lines 1A and 1B, and remains energized to the end of the sensing cycle.

Control relay CR1 operates its contacts in lines 2A and 2B thereby de-energizing contactor CR to open the forward current circuit and energizing contactor RC to close the reverse current circuit which shorts the pilot anode to the cathode tap 16 for the duration of the reverse cur-
rent stage. Opening the forward current circuit by contactor CR1 prevents shorting the forward current power supply during the reverse current stage. Relay CR1 stays energized during the 10 second timing period of timing relay TR1 and its contact in line 15 opens to prevent operation of timing relays TR3 and TR2 at this time. At its contact CR1 in line 5, it opens a point in the locking circuit of line 20 and contacts CR2 in line 8. Relay serves as the detect one of the feed rate selector. When energized, it selects the fast feed rate by closing its contact in line 17 and renders the slow feed rate ineffective by opening its contact in line 16. This lets the fast feed timer TM2 control the ore feeder solenoid in line 16. Conversely when de-energized, it selects slow feed and its contact in line 16 to let the slow feed timer TM1 control the ore feeder solenoid and locks out fast feed by its contact in line 17. In order to remain on fast feed during a standby period, selector relay CR12 locks in through its normally open contact in series with normally closed contact CR1 in line 5. Hence, whenever relay CR1 is energized and opens its contact in line 15, as above mentioned, selector relay CR12 will be de-energized or reset, thereby preparing it to be responsive to the following sensing stage and to return ore feed to the slow rate.

During the reverse current stage, current from the pot line source flows from the working anodes 5 into the pilot anode 12 and through the reverse current circuit to cathode tap 16. This reverse current flow through the pilot anode effectively eliminates the anode effect thereon and conditions it for sensing. It will be noted that the method used to obtain reverse current flow through the pilot anode is to make it cathodic with respect to the bath 4 during the reverse current stage.

While this method is preferred, it is contemplated that the pilot anode may be raised clear of the bath briefly and then reimmersed in order to eliminate the anode effect thereon. Alternatively, the anode effect may be eliminated by simply going to zero current, particularly when a pilot anode of a small size, within the lower half of the size range, is being used.

When timing relay TR1 times out, it ends the reverse current stage and starts the sensing stage by opening its contact in line 3 to de-energize relays TR7 and CR1. The contacts of relay CR1 return to normal position. Thereby, its contact in line 5 closes to allow selector relay CR12 to lock-in if it is actuated to select fast feed during sensing; its contact in line 2B opens to de-energize contactor CR2, thus opening the reverse current circuit; its contact in line 2A closes to energize contactor CR, thus re-establishing the forward current circuit to impress the low sensing voltage from tap B on the pilot anode, and its contact in line 15 closes to start adjustable pneumatic timing relays TR2 and TR3 (connected in parallel in line 15) timing out. TR2 controls the duration of the sensing stage and is set for 10 seconds. TR3 determines when the sensor's contact CR4 in line 3 is effective on the feed rate selector CR12 and is set for 7 seconds.

During the sensing stage, the pilot anode is working under the impressed low voltage of about 5 volts and a current of about 200 amperes, giving a control current density which will result in an anode effect thereon if the alumina concentration in the bath has reached the critical density-concentration level, as heretofore described. When it exhibits an anode effect there is a sharp rise in voltage and a rapid change in current through the pilot anode. The sensor CR4 (FIG. 1) responds to the increased voltage to sense the anode effect if it occurs. After elapse of the 5 seconds afforded by timing relay TR7, which time allows the anode voltage and current to stabilize, its contact in line 1A closes to expose the sensor CR4 to voltage. Sensor CR4 energizes if the anode voltage has increased due to the presence of an anode effect and closes its contact CR4 in line 3, otherwise it remains de-energized (no anode effect) and its contact stays open. Timing relay TR3, after its 7 seconds delay, which gives time for the sensor to stabilize, closes its contact TR3 in line 3, whereupon feed rate selector CR12 is directly under control of the sensor's contact CR4. If open, CR12 remains de-energized to select the slow feed rate; if closed, CR12 energizes to select the fast feed rate and locks-in through its contact and contact CR1 in line 5. Timing relays TR2 and TR3 are energized, the anode concentration of the bath is measured as to whether it is above or below the preselected percentage level or control point and respond thereto sensing is selected for the fast or slow feed rate for the next standby period. At the time of sensing, the actual concentration level may be sufficiently above the critical level with respect to the control current density as not to result in fast feed selection, so that it may go somewhat below the selected control level during the next standby stage; but, in such case, the fast feed will be selected at the sensing stage which follows. This condition is minimized by using shorter standby periods and more frequent sensing.

The sensing cycle ends at time-of-out of timing relay TR2 and opening of its contact TR2 in line 3. This opens the locking circuit of relay CR3 and it de-energizes. Responsively thereto, the sensing circuit is opened to de-energize sensor CR4 so its contact in line 3 if it had been closed, timing relays TR1, TR2 and TR3 are reset, contactor CR2 is de-energized and its contacts in lines 1A and 1B switches the forward current circuit from tap B to tap A. This impresses the high voltage on the pilot anode to induce an anode effect thereon if none is present, or to maintain it if one had developed during sensing. Also, the clutch coil of the reset timer TM3 is de-energized and the timer starts to run from its time set point toward zero for timing the standby stage of the program sequence which now repeats.

From the foregoing, it will be apparent that electrolysis proceeds without depletion of the alumina in solution in the electrolyte to the critical anode effect producing level because of the periodic sensing of the concentration level and change in ore feed rate in accord with the outcome of such sensing, thereby maintaining adequate alumina in the bath for continuous normal electrolysis. As shown in FIG. 3, the ore may be fed to the rectification cell by use of a motor driven screw type of feeder 20, an example of which is shown and described in U.S. Patent 2,713,024, and the feed rate controlled by adjustment of motor speed by means of a suitable motor speed controller 21, the specific nature of which is well-known to those skilled in such art, and the selector relay CR12 used to activate controller 20 selectively for the desired fast and slow feed rates.

In the system of FIG. 4, a pilot anode controlled reduction cell which duplicates that of FIG. 1 is shown, but a separate variable voltage rectified power supply is employed for the standby and sensing stages of the program sequence in lieu of using shunted potline power. It is designed to provide for instant change in voltage and sudden rise of current on the pilot anode when anode effect is to be induced thereon at the end of a sensing stage. As shown, three phase AC power at 440 volts, 60 cycles, for example, is supplied through a fused disconnect switch (not shown) to a variable three phase autotransformer TX1. This transformer boosts the voltage applied to step-down transformer TX2 during the standby stage and it allows varying of the magnitude of the sensing current in the electrical circuit through the pilot anode. Transformer TX2 reduces the voltage to the appropriate level for operating the pilot anode. Its respective primary phase windings has two sets of input taps to provide the desired high and low voltage outputs from its secondary windings. One set of taps L0 is connected to the low voltage output of transformer TX4 energizes if the anode voltage has increased due to the presence of an anode effect and closes its contact CR4 in line 3, otherwise it remains de-energized (no anode effect) and its connected to the high voltage output ends of transformer
TX1 through contacts HV1, 2 and 3, respectively (line 3) to give the high voltage for the standby stage. The secondary windings of transformer TX2 are connected to a three phase full wave bridge circuit of which the rectify the three phase AC voltage to DC voltage, the positive side of the DC output circuit being connected to the pilot anode and the negative side to the cathode tap 16 of the cell 1. Fuses in series with the diodes serve to protect the diodes against short circuit currents. In line 8, is the normally open contact of a reverse current relay CR5 which, when closed, makes the pilot anode cathodic during the reverse current stage of the control program. Since closing contact CR5 short the external power supply, the supply must be disconnected during the reverse current stage and this is effected by opening the HV and LV contacts, above described.

Included in the low voltage sensing circuit between contact LV3 and tap Lo of one phase of transformer TX2 is an adjustable rheostat R1 of low ohmic value, across which is connected, through contact PT–3, a full wave rectifier bridge 25, and a voltage responsive sensor relay CR4 is connected to the output side of rectifier 25. Shunted across relay CR4 is capacitor 26 which filters the rectified current to eliminate possibility of relay chatter at pick-up. Resistance R1 provides a voltage drop in direct proportion to the current flow through the rectifier and rectified voltage, is applied to sensor CR4 to determine whether or not an anode effect appears on the pilot anode during sensing, contact PT–3 regulating when such voltage is impressed on the sensor during the sensing stage. Use of DC sensing relay provides sensitive and positive relay action under the low voltage sensing conditions.

Referring now to the control circuitry at the right hand side of FIG. 4, the identification of the across-the-line circuits and the control components follows the same pattern as defined in connection with FIG. 2. CR12 in line 20 identifies the ore feed rate selector and TM1 and TM2 in lines 23 and 22 the timers which effect operation of the ore feeder at the fast or slow rate depending upon which set of contacts CR12 in lines 13 and 14 is closed. Selector relay CR12 is normally energized for the slow feed rate and de-energized for the fast feed rate. In line 3 supplies high voltage power to the taps Hi of transformer TX2, while LV in line 18 identifies the reactor whose contacts in line 2 supplies low voltage power to the taps Lo of transformer TX2. CR5 in line 17 identifies the contactor or relay whose contact in line 8 shorts the pilot anode of PT–2A but TM3 in cathode of cathode rectifier TX3 in line 16 identifies a step-down transformer which supplies through bridge rectifier 27 the voltage to operate contactor CR5 which preferably has a DC operating coil, so TX3 can be considered the same as CR5's coil.

PT in line 24 identifies a conventional synchronous motor driven, repeat cycle program timer, or cam timer, having three sets of cam-operated contacts, PT–1 on cam 1, PT–2A and PT–2B on cam 2 and PT–3 on cam 3, which programmed in sequence and duration of operation in accordance with the program shown in the timing diagram of FIG. 5. It co-ordinates the action of all of the other components of the control system. It may be selected to provide a desired total cycle time, the cycle time being of 30 seconds duration, as shown in FIG. 5. In Proc 21, the time diagram bridge rectifier, the diodes of which have been energized by closure of contact PT–1 (line 12). Hence, it completes one cycle responsively to cam timer PT completing 36 cycles or revolutions, thus providing a standby period of 18 minutes duration. At step 2, contact SR–1A, SR–1B and SR–1C operate, this being the "home" position to which the stepping relay will run whenever pushbutton switch PB–1 in line 11 is depressed. At step 3, contacts SR–1A, SR–1B and SR–1C operate, these contacts being in the positions they have during the standby stage.

In operation, throughout the standby stage, contact SR–1A (line 15) is closed and contactor HV is energized, so that transformer TX2 is being fed by its high voltage taps Hi. Therefore, the pilot anode 12 has high voltage (about 14 to 16 volts) impressed on it and it is on continuous anode effect which reduces the current flow through it. The HV and LV contacts seen in lines 15, 16 and 18 are interlocks which prevent more than one of the contactors HV, LV and CR5 being energized at any one time. Feed rate selector CR12 in line 20 can be either energized or not depending on the selection made at the previous sensing stage. Assuming it to have been energized to select the slow feed rate, then it is now de-energized through closed contact SR–1B in line 20 to maintain its contact CR12 in line 13 open and its contact CR12 in line 14 closed so that the slow feed rate timer TM1 is controlling the ore feeder 7 and the fast feed rate timer TM2 is disabled. Contact SR–1C in line 16 is open.

The program or cam timer PT, of course, is running and during each cycle its cam 2 and cam 3 contacts are operated without any effect since the circuits in which they are located are dead. At time "6," however, its cam 1 contact PT–1 in line 12 closes to energize the stepping relay SR, and at time "42" seconds after energizing the relay it advances one step. This continues for each of the cam timer PT until the stepping relay reaches step 3, thus ending the standby stage and starting the sensing cycle.

At step 3 (corresponding to time "54" on the PT timing diagram), contact SR–1A in line 15 opens to de-energize HV which removes the high voltage power from transformer TX2 and also to disable the ore feeder so as to prevent agitation of the bath during sensing, thereby guarding against possible variation of the pilot anode area exposed to the bath which in turn would affect the sensing current density. Contact SR–1B in line 20 opens with no effect since it is paralleled by PT–2B in line 18 which is closed at this time. Contact SR–1C in line 16 closes to connect the left side of transformer TX3 and contactor LV to one side of the power supply line. Since the contacts in line 3 are open at this time, the transformer is not energized. However, contactor LV in line 18 energizes through closed contact PT–2B when the HV interlock clears, thus switching in the low voltage supply prior to reverse current flow through the pilot anode. This is a matter of switching convenience in the program sequence and may be omitted, if desired.

At time "134," contact PT–2B in line 18 opens to de-energize contactor LV thereby disabling the external power supply, and to reset selector relay CR12 if it had been energized. Contact PT–2A in line 16 closes to energize transformer TX3 and contactor CR5 in line 17 picks-up to close its contact in line 8, thus connecting the pilot anode to the pot cathode for the reverse current flow through it to eliminate the anode effect thereon. At time "144," contact PT–2A in line 16 opens to terminate the reverse current flow; shortly thereafter contact PT–2B closes to energize contactor LV and thus start the sensing stage. These contacts are set for a period of 6 seconds before PT–2B closes and thus provide an interval of about 6% of a second before supplying the forward current to the pilot anode. With no forward current supplied to the pilot anode for this brief interval after termination of the reverse current flow, enough of a gas film builds up at the anode to limit the initial forward current surge. Pick-up of contactor LV closes its contacts in line 2 thus...
feeding transformer TX2 from the low voltage taps of transformer TX1 and impressing the preselected low voltage on the pilot anode for the sensing current flow through it during the sensing stage. The value of this current is preselected to give a current density on the pilot anode in accordance with the preselected alumina percentage control level desired in the bath. As heretofore described, an anode in such a condition will or will not be induced on the pilot anode depending on the density-concentration relationship existing at the time of sensing.

At time "16¾," contact PT-3 in line 2 closes and stays closed for 5 seconds (time 21¾) to expose sensor CR4 to the voltage across R1. The 5 seconds interval between applying forward current and impressing the sensor allows time for the current to stabilize from its peak value. During sensing, if an anode effect appears on the pilot anode, it is a high resistance circuit which causes the supply current to decrease and consequently the voltage drop across R1 to be less than the pick-up voltage of sensor CR4. Thereby selector CR12 remains de-energized and selects the fast feed rate for the following standby period. If no anode effect appears, there is no drop in the supply current and sufficient voltage appears across R1 to energize CR4 and its contact in line 20 closes to pick-up selector CR12, thereby selecting the slow feed rate. CR12 locks-in through its contact in line 21 to enable ore feeding at the slow rate for the ensuing standby period.

At time "30° ("0")," the sensing cycle ends and the program timer PT starts a new cycle, its contact PT-1 in line 12 closing for ¾ of a second and causing the stepping relay to advance to step 4 and begin a new standby period. Thereby, SR-1C in line 16 opens to drop out relay LV which removes the low voltage power from transformer TX2. SR-1A in line 15 closes to enable ore feeding at the rate selected by CR12 and to pick-up HV after the interlock LV in line 15 clears. Pickup of HV, at 11 contacts, in line 3, applies the boosted voltage from TX1 to the high voltage taps Hi of TX2 and thus impresses the high standby voltage on the pilot anode. The initial current surge through the pilot anode is adequate to induce an anode effect thereon with alumina concentrations up to about 7.25 percent thus insuring its inducement at the start of the standby period if none had developed during sensing. Of course, if one had occurred, the same sequence occurs and the high standby voltage maintains the anode effect. Contact SR-1B in line 20 closes at this time to keep CR12 locked-in during the standby period if it had been energized during sensing. Then throughout the standby period, the system remains in the condition described, the stepping relay advancing one step for each cycle of the timer PT until it reaches step 3, whereupon sensing of the alumina concentration is repeated.

The pushbutton switch PB1 enables an operator to go through the sensing cycle at will. When depressed, the stepping relay advances to home position 2 and opens its contact SR-2 in line 11. Then timer PT takes over in order to step relay SR to step 3 in the normal fashion. By this action, the sensing cycle may not be initiated, except at the beginning.

Under conditions of potroom operation, it has been ascertained in practice of the invention that electrolysis is carried out with the alumina concentration in the bath maintained within close limits of a preselected percentage level. Electrolysis tests at various selected percentage levels covering a range of from about 3% to 6% have indicated control of the alumina concentration within limits of ½% to 1% of the percentage level selected. Proper adjustment of the pilot anode in regards to its immersion depth is important to achieving tight control of the alumina concentration. With the circuit parameters set up for a given immersion depth, usually about 4 inches, plus or minus ¼ of an inch, incorrect anode adjustment can change the control level. Unless excessively mal-adjusted, the level change is normally less than 1% difference in alumina concentrations. Hence, by selecting a control level close to 4½ percent, the operator is relieved from the burden of effecting extremely accurate setting of the pilot anode at those times it needs to be reset, and electrolysis is effectuated with a reasonable swing in the concentration of dissolved alumina in the electrolyte. Under these conditions, pot anode effect is eliminated and the electrolysis is made continuous, thereby increasing efficiency in the production of metal, along with lessened consumption of additives for the electrolyte and, of course, less attention and labor to operate the furnace or cell.

Having thus described the invention and many of its advantages, it will be apparent to those skilled in the art that the invention is applicable for the suppression or elimination of anode effect in a molten salt bath electrolytic cell known to be susceptible thereto, and that various changes and modifications may be resorted to without departing from the spirit and scope of the invention as set forth in the appended claims.

What is claimed is:
1. In the art of producing molten metal by electrolysis of a metallic compound dissolved as a solute in a molten electrolyte wherein anode effect is encountered upon depletion of said compound to a critical percentage level, the said following steps and thereby eliminating said compound at a percentage level greater than said critical percentage level, comprising the steps of:
   (a) Feeding ore constituting said compound into said electrolyte during a preselected time period at a rate selected from a fast and a slow feed rate respectively calculated to feed more and less ore than can be consumed by electrolysis during said period;
   (b) Continuously maintaining a pilot anode which dips into said electrolyte to a given immersion depth on anode effect during said period;
   (c) Eliminating the anode effect on said anode at the end of said period;
   (d) Utilizing said anode with a given current density thereon to sense the percentage level of said compound at a value exceeding said critical percentage level by whether or not an anode effect occurs thereon during sensing;
   (e) Selecting said fast feed rate responsive to the occurrence of an anode effect on said anode at sensing for feeding the ore throughout a new one of said time periods which immediately follows sensing, and
   (f) Maintaining the anode effect on said anode during said fast period;
2. In the art of fused bath electrolysis according to claim 1, wherein the slow feed rate is selected responsive to said anode remaining free from the appearance of an anode effect thereon at sensing for feeding the ore throughout said following period, and
   (a) Establishing and maintaining an anode effect on said anode for and during said following period;
   (b) In the art of fused bath electrolysis according to claim 1, wherein said metallic compound comprises aluminum oxide;
   (c) In the art of producing metallic aluminum by electrolytic reduction of alumina dissolved in a molten cryolite bath, the method of maintaining adequate alumina dissolved in the bath for effecting normal electrolysis continuously which comprises the steps of:
   (a) Feeding alumina into the bath during a standby period at a pre-selected rate at a rate selected from a fast and a slow feed rate respectively calculated to feed more and less alumina than can be consumed by electrolysis during said period;
   (b) Continuously maintaining a pilot anode which dips into said bath to a given immersion depth on anode effect during said period;
   (c) Effecting reverse current flow through said anode to eliminate the anode effect thereon at the end of said period;
   (d) Terminating said reverse current, flow and effect-
ing forward current flow for a sensing interval through said anode of such value as to create a specific current density at which an anode effect will be induced thereon in case the concentration of dissolved alumina in the bath has been depleted to the critical percentage level with respect to said current density at the time of sensing;

(e) Selecting one of said feed rates, the fast rate upon induction of an anode effect thereby and the slow rate upon no induction of an anode effect during sensing, whereby alumina is fed at the rate selected throughout the next standby period which immediately follows said sensing interval, and

(f) Maintaining the anode effect on said anode for said next standby period in case one had appeared thereon during sensing and in case one had not appeared establishing and maintaining an anode effect on said anode for said next standby period.

5. The method according to claim 4, wherein said sensing of the dissolved alumina concentration is effected about 2 to 4 times per hour.

6. In the art of producing aluminum by reduction of alumina in a fused bath electrolytic cell having an anode, a cathode and an electrolyte of molten cryolite having alumina dissolved therein by passing direct current through said electrolyte, there is a step of:

(a) Periodically sensing at discrete times the concentration of alumina dissolved in said electrolyte by the tendency for an anode effect to appear on a pilot anode, which dips into said electrolyte to a given immersion depth and carries a current density greater than that on said cell anode, as a result of the alumina concentration being reduced to a critical level with respect to the current density on said pilot anode by electrolysis in a standby interval between successive sensing times;

(b) Feeding alumina into said electrolyte to raise its percentage level as a consequence of an anode effect appearing on said pilot anode during a sensing time;

(c) Maintaining said pilot anode on anode effect during said standby interval between successive sensing times to minimize the consumption rate thereof, and

(d) Eliminating the anode effect on said pilot anode prior to sensing.

7. The process as set forth in claim 6, wherein said pilot anode is connected to said cell cathode and thereby made cathodic for a brief time between said standby interval and the next sensing time, thereby causing reverse current flow through said pilot anode to eliminate the anode effect thereon and condition it for sensing.

8. The process as set forth in claim 7, which includes feeding alumina into said electrolyte at a rate less than that which is consumed by electrolysis between successive sensing times, and increasing the feed rate in response to an anode effect appearing on said pilot anode during sensing for the duration of the ensuing standby interval.

9. In the production of metallic aluminum by the electrolytic reduction of alumina in a bath of fused electrolyte, the method of maintaining adequate alumina dissolved in the bath for effecting continuous normal electrolysis which comprises:

(a) Continuously operating a pilot anode which dips into said bath to a given immersion depth on anode effect with periodic interruptions in said anode effect condition for operation of said pilot anode as a sensor;

(b) Eliminating the anode effect on said pilot anode at the start of each sensing period, and then

(c) Establishing on said pilot anode a current density preselected in dependence upon a desired alumina control level, whereby depletion of the alumina content of the bath of said control level results in induction of an anode effect on said pilot anode; and

(d) Sensing the occurrence of said induced anode effect and feeding alumina into said bath in dependence upon its occurrence to increase the alumina content of said bath, while maintaining said pilot anode on anode effect until the next sensing period.

10. The method according to claim 9, characterized by making said pilot anode cathodic with respect to said bath to eliminate said anode effect thereon.

11. In a control system for a molten metal producing reduction cell having an anode, a cathode and a fused electrolyte bath into which are constituting a metallic compound to be reduced by electrolysis is fed and dissolved, the improvement comprising:

(a) A pilot anode insulatedly supported at said cell with one end immersed into said bath to a given immersion depth;

(b) A dual voltage source of direct current electrically connected to said pilot anode through selectively operable control switches for impressing a first voltage and a second lower voltage thereon during a standby stage and a sensing stage, respectively, of different time durations,

(1) said first voltage causing the resultant current to provide the current density on said pilot anode sufficient to establish and maintain an anode effect thereon during said standby stage, and

(2) said second voltage causing the resultant current to give a selected control current density on said pilot anode which will result in an anode effect thereon during said sensing stage when the ore concentration in said bath has decreased to the critical percentage level with respect to said control current density;

(c) A normally open circuit including a control switch connecting said pilot anode to said cell cathode for reverse current flow through said pilot anode to eliminate the anode effect thereon at a time interposed between said standby stage and said sensing stage;

(d) Timing means for effecting operation of said control switches in a program sequence consisting of said standby stage, said reverse current flow and said sensing stage in the order named;

(e) Feeder means selectively operable to feed ore into said bath at an underfeed rate and at an overfeed rate during said standby stage;

(f) A selector device for selecting the rate of ore feeding by said feeder means, and

(g) Sensor means responsive to the occurrence of an anode effect on said pilot anode during said sensing stage to cause said selector device to select said overfeed rate for the duration of the next standby stage.

12. In a control system for a fused bath electrolytic cell subject to anode effect when the dissolved solute constituent undergoing electrolysis in said bath drops to a critical percentage level, the improvement comprising:

(a) A pilot anode insulatedly supported at said cell with one end dipped into said bath to a given immersion depth;

(b) A dual voltage source of direct current electrically connected to said pilot anode through selectively operable control switches for impressing a first voltage and a second lower voltage thereon during a standby stage and a sensing stage, respectively, of different time durations,

(1) said first voltage causing the resultant current to provide a current density on said pilot anode sufficient to establish and maintain an anode effect thereon during said standby stage, and

(2) said second voltage causing the resultant current to provide a selected control current density on said pilot anode for the occurrence of an anode effect thereon during said sensing stage at a percentage level of said solute constituent in
sensed bath greater than said critical percentage level;
(c) Means including a control switch for making said pilot anode cathodic with respect to said bath for reverse current flow through said pilot anode to eliminate the anode effect thereon at a time interposed between said standby stage and said sensing stage;
(d) Timing means for effecting operation of said control switches in a program sequence consisting of said standby stage, said reverse current flow and said sensing stage in the order named;
(e) A sensor, relay operable responsive to the occurrence of an anode effect on said pilot anode during said sensing stage; and
(f) Means controlled by operation of said sensor relay to aid in maintaining normal electrolytic operation of said cell.

13. In a control system for an aluminum reduction cell having an anode, a cathode and a fused electrolyte bath of cryolite and dissolved alumina, and feeder means normally operable to feed alumina into the bath at an underfeed rate, the improvement for maintaining adequate alumina in the bath for continuous normal electrolytic operation comprising:
(a) A pilot anode insulatedly supported at said cell with one end dipped into said bath to a given immersion depth;
(b) Variable voltage transformer means energizable from an AC source and including rectifying means connected to said pilot anode and to said cell cathode to provide direct current energy to power said pilot anode;
(c) A first control switch controlling said transformer means for energizing said pilot anode at a current density sufficient to establish and maintain it on anode effect during a standby stage of a selected time duration;
(d) A second control switch controlling said transformer means for energizing said pilot anode for a sensing stage of from about 10 to 30 seconds duration at a control current density selected in accordance with a preselected alumina percentage level to be maintained in said bath, whereby depletion of the alumina content of said bath to said percentage level is indicated by an anode effect appearing on said pilot anode during said sensing stage;
(e) A normally open circuit including a third control switch for making said pilot anode cathodic with respect to said bath for reverse current flow through said pilot anode to eliminate the anode effect thereon at a time interposed between said standby stage and said sensing stage;
(f) Timing means for effecting operation of said control switches in a program sequence consisting of said standby stage, said reverse current flow and said sensing stage in the order named, and for actuating said first and second control switches to open position prior to said reverse current flow through said pilot anode;
(g) Sensor means connected to said pilot anode and sensing the presence and the absence of an anode effect thereon during said sensing stage, and
(h) Means controlled by said sensing means upon sensing an anode effect on said pilot anode during one of said sensing stages for actuating said feeder means to feed alumina into said bath at an increased rate only for the duration of the standby stage next to follow said one sensing stage.

14. A control system according to claim 13, which includes means controlled by said timing means for disabling said feeder means for the interval between successive standby stages.

15. A control system according to claim 13, wherein said transformer means comprises a variable three phase autotransformer having low voltage output sliders, and energizable from a three phase AC power supply circuit, and a three phase step-down transformer having primary phase windings each provided with high and low voltage input taps and secondary output windings, and said rectifying means comprises a three phase full wave bridge rectifier connected to said secondary output windings to provide direct current energy to power said pilot anode;
(a) Said autotransformer boosting the voltage derived from said supply circuit and applying the same through contacts of said first control switch to said high voltage input taps of said primary phase windings to provide high voltage energization of said pilot anode for said standby stage, and
(b) Said autotransformer having said sliders thereon connected through contacts of said second control switch to said low voltage input taps of said primary phase windings to provide low voltage energization of said pilot anode for said sensing stage.

16. A control system as in claim 15, wherein the sensor means comprises a DC relay, and said relay is connected through a full wave rectifier bridge and a normally open switch across a resistance of low ohmic value, and said resistance is connected in the low voltage supply circuit to said low voltage input tap of one phase of said primary phase windings to provide a voltage drop in direct proportion to the current flow through said resistance, said voltage drop being less than the pick-up voltage of said relay when an anode effect is present on said pilot anode during said sensing stage, and means controlled by said timing means for actuating said normally open switch to closed position and thereby render said relay effective for sensing during said sensing stage.

References Cited

UNITED STATES PATENTS
3,294,656 12/1966 Schmitt 204—67
3,317,413 5/1967 Chamban 204—243 XR

FOREIGN PATENTS
1,193,683 5/1965 Germany.

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