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3,392,092 ACTIVATION OF CRYOLITE-ALUMINA COMPOSITIONS

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In my copending application Ser. No. 241,895, filed Dec. 3, 1962, now U.S. Patent No. 3,244,604, issued Apr. 5, 1966, I have shown that it is possible, with certain brief surges of moderately high electrical energy, to so alter the nature of a cell containing cryolite and alumina in condition for the electrowinning of aluminum, that such a cell now operates at substantially lower voltage for the same production rate and permits increased production rates with much lower power penalties, to continue to do so for economically useful periods following cessation of one or a group of such surges, and that the benefits may be maintained notwithstanding any annealing of the effect by additional such surges.

I have previously shown electrodes for firing the surges entering the bath from the top. Thus I have shown firing electrodes singly or in groups, the pot or the portion of the pot which normally serves as an electrode doubling as counter electrode to the inserted electrodes. I have shown electrode pairs inserted through the top of the bath.

In the course of developing my method and apparatus, I have found that it may be advantageous to insert the firing electrodes or firing electrode pairs through the wall of the pot. Tubes or poorly conducting material are cemented into the wall and the firing conductors are passed through the tubes. The impulse source is connected to the conducting electrodes either as required or the connections are fixed and the conductors are inserted. If the tubes are emplaced horizontally, it is necessary to use a packing. I prefer to insert the tubes at an angle as shown in the drawing so as to obviate the difficult application of packing in the hot, corrosive melt.

Other objects and features of the invention, in addition to those described above, will become apparent in the following description and claims, and in the drawings in which:

FIG. 1 is a schematic representation of a vertical section through a cell for the electrolytic reduction of aluminum and shows auxiliary electrodes extending through the walls of the cell into the interior portion of the cell, and

FIG. 2 is a schematic representation of means for providing a source of high energy surges which is connected to the auxiliary electrodes.

The advantage of using auxiliary firing electrodes in this manner is that it is not necessary to chop a hole into the crust for the insertion, inspection or refurbishing of the firing surfaces. Another advantage is that the level above the molten surfaces of deposited metal is more easily controlled. It will be appreciated that the metal and crust surface heights are not static.

With this improvement, it is more convenient to install the auxiliary firing electrodes so that they are out of the way, so that they are emplaced for long periods, and so that they are easily engaged by corresponding terminals of a stationary or mobile surge generator. For this purpose, it is preferred to use conductors which are capable of long contact with the corrosive cryolite-alumina-aluminum containing bath. The capability of refractory hard metals particularly titanium diboride and zirconium diboride to withstand such contact is known. As low voltage electrolyzing anodes, they would be too costly and current efficiency would suffer. I have used them successfully as auxiliary high tension anodes for my activation

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process. The anodic wear is very small being the equivalent of but a few seconds of use as low voltage anodes and, when my process is more effectively applied, the re-use of the high tension is not required more often than hours to days apart.

I have found it desirable in some instances to improve the power factor of the impulses by inserting a deliberate resistance between the source and the firing anodes. When auxiliary firing anodes are used, their initial resistance is lower than it is after current has passed for a few seconds. I find that such resistance can be used as part of the power factor improving resistance and I now apply a low voltage to them several seconds before use for firing and, as a convenience in narrowing the time gap between the surface conditioning and the impulse arrival, I leave it on during the moderate high energy firing. To avoid excessive loss of surge energy, I conduct the low voltage conditioning current through an impedance to a fast rise surge.

It will be seen that by passing the high tension auxiliary electrodes through the pot wall, the connection fittings are in a cooler area. If the normal cathode is used as part of an auxiliary pair, connection to it is also in a comparatively cool location.

I have found that vanadium as a very small impurity in the firing electrodes or wall surfaces can seriously affect the efficiency of my activation impulses. The bath itself, on sufficient ordinary operation, is apt to purge itself with the vanadium impurity entering and being sequestered by the metal pad. It is desirable to see that the refractory hard metal or other firing electrodes contain no more than about ten parts per million of vanadium. This also applies to the wall from which the activating phonons are reflected.

The occasional low voltage source for conditioning firing auxiliary electrodes may also be used to clean them of oxides and frozen cryolite.

FIGURE 1 in the drawing shows a pot 1 containing a metal pad 2, a bath 17 and a low voltage electrolyzing anode 3. The metal pad 2 and the anode 3 are connected to the negative and positive terminals respectively of a low voltage source of direct current 16. Inserted and cemented or gasketed into the pot wall 4 are one or more slanting tubes of low conductivity 18 or similar horizontal tubes 18 and these are made of a resistant ceramic such as cemented silicon carbide or boron nitride. Into these tubes are placed auxiliary electrodes 5 and 8, respectively. The protruding portions 20 extending into the bath 17 are the firing surfaces and they are positioned with respect to gap length to the mating firing surface and they are further positioned to permit the maximum available clearance with respect to the wall 4 and the regular anode 3. When one of the regular electrodes 2, 3 is used as a firing electrode, electrode 5 or 8 alone is positioned, firstly as to gap and secondly as to minimal obstruction to flow of the excitation gradient. The auxiliary firing electrodes 5, 8 and their mating electrodes 5', 8' or 1 or 3 are preferably provided with connection couplings 19, 12 for connecting the surge generator.

FIGURE 2 shows a surge generator and means for conditioning auxiliary electrode surfaces. The capacitor 11 is charged by direct current source 21 at a rate which is slow compared with the rate of discharge of the capacitor 11. The capacitor 11 is preferably of a type which is capable of particularly fast rise time and discharge rate. The capacitor 11 is connected to output terminals 9 and 10 through a switch 12 and, optionally, through resistor 13. The switch 12 is a fast acting high current density type, for example, an ignitron or triggered spark gap, which is actuated by the device 22 such devices being known to the art. The terminals 9 and 10 mate with terminals 19, 19' of electrodes 5 and 5' or 8 and 8' or 5

and 1 or 5 and 3 or similar such firing pairs or a plurality of such pairs. A plurality of surge generators may be used firing together or in sequence firing on the same firing electrode pair or in groups of pairs, and each pair of a group of pairs may be connected to different impulse sources or any combination of these means may be used. A low voltage source 14 preferably D.C. may be connected at junctions 24 and 25 through an impedance 15 and 15'.

FIGURE 1(a) is a cross section taken through lines 1a of FIGURE 1. FIGURE 1(a) shows the lateral to vertical disposition of a pair of auxiliary firing electrodes such as 5 and 5' disposed in electrically insulating tubes 18 and 18'. Such tubes 18 and 18' may be of cemented silicon carbide compositions even though they are slightly conducting.

When it is desired to use a single auxiliary electrode and one of the regular electrodes 2 or 3 to complete a pair, the electrode 5 can be pushed downward and inward to provide the desired gap with pad 2 or electrode 3. The level of auxiliary electrode 8 is fixed but it can be pushed inward to gap with electrode 3 as mating member of a pair. The use of a large surface such as mating surface of 3 or of 2 provides a combination of dense impulse energy at one part of a pair and dispersed impulse energy at the other part of a pair. The use of a pair such as 5 and 5' provides a greater concentration of the energy at both mating surfaces. I have found either situation to give satisfactory results. Indeed, as stated in my copending application, it is possible to use the regular electrode pair without any auxiliary. However, to maintain the required impulse duration at both the peak and the body of the impulse, the capacitor 11 becomes much larger and the resistor 13 is apt to be used so as to take up a greater portion of the capacitor voltage and the capacitor must be large enough to accept the higher voltage to compensate for the greater drop in resistor 13. The auxiliary electrode area should not be less than about 2% of the regular electrode area.

For example, I placed each of two auxiliary electrodes in the form of tube $\frac{3}{4}$ " O.D. and $\frac{1}{4}$ " I.D., one of the tubes being of titanium diboride, the other of zirconium diboride into the shielding tubes with I.D. of 1" and an O.D. of $1\frac{3}{4}$ " and made of silicon carbide bonded with silicon oxy nitride compositions. The two sets were mounted together. The inner tubes protruded $\frac{1}{2}$ " the protrusions being immersed in the bath and their centers were 2" apart. This pair was mounted at one end of a pot whose inside dimensions were 9" by $4\frac{1}{2}$ ". The pot contained 10 lbs. of cryolite and one pound of alumina and 3 oz. of aluminum. The temperature of the melt was between 990° C. and 1010° C. The cryolite had usual additives for reducing the viscosity and it had the known additive of 3% LiF to lower the solidification temperature.

The titanium boride electrode was connected to the positive side of the capacitor bank 11 of the circuit shown in FIG. 2. The resistor 13 had a value of 0.04 ohm. The capacity of the condenser bank 11 was 25.5 μ F and the voltage across it was 6000 volts. Switch 12 was a 7701 ignitron. The inductance of the capacitor bank and of the associated high tension path was about 0.06 μ H. A polarizing D.C. voltage from source 14 was placed across the refractory hard metal electrodes so as to deliver

40 amperes between them. The resistor 15' was 0.3 ohm and inductance 15 was about 2 μ H. The polarizing and cleaning voltage was applied about two minutes before firing and was maintained during the firing cycle.

I fired the high voltage 10 times at intervals of 2 seconds.

The bath temperature measured at the far end of the pot dropped 30° within 10 seconds of the first firing. The temperature was restored in about one minute.

The low voltage on the anode 3 was adjusted initially to provide 100 amperes. The voltage was 4.8 volts between measurement points in 1 and 3. The floor 1 was of graphite. The current rose to 450 amperes and after ten minutes was still rising although slowly now. The voltage from source 16 was lowered to restore the initial current. The new voltage between measurement points at 1 and 3 was 1.9 volts.

In similar tests I used titanium diboride as single auxiliary electrode, the other electrode being the graphite pot bottom 1. The results were similar to those shown in the example of my copending application Ser. No. 241,985, filed Dec. 3, 1962.

In my process, to produce an enduring effect, it appears necessary to establish a density of phonons in a critical range of concentration and the volume of the condensation gradient is related, by less than a linear ratio, to the volume of the bath material. For larger amounts of cryolite, the total area between the firing electrodes is increased. Obstructions, or surfaces having excessive phonon absorption, will cause the need of larger concentrations and may involve quantities of activation energy above the critical range.

The guides to change of size and configuration are further provided in my above referenced copending application.

Having described my invention, I claim:

1. The process of activating molten cryolite-alumina compositions ready for the electrowinning of aluminum so as to increase the power efficiency at a given production rate by means of firing high energy surges into the melt of cryolite-alumina compositions through a system including at least one auxiliary high tension electrode, wherein the improvement comprises prepolarizing the auxiliary electrode by the passage of electrical current therethrough before firing high energy surges into the melt.

2. The process according to claim 1 in which the polarizing current is maintained during the surge period.

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