ALUMINA REDUCTION PROCESS


Assignee: Aluminum Company of America, Pittsburgh, Pa.

Filed: June 28, 1973

Appl. No.: 374,802

U.S. Cl. 204/67

Int. Cl. C22d 3/12

Field of Search 204/67

References Cited

UNITED STATES PATENTS
2,464,267 3/1949 Short 204/67
3,006,724 10/1961 Harrell 204/67 X
3,128,151 4/1964 Zanon et al. 204/67 X
3,294,656 12/1966 Schmitt 204/67

ABSTRACT

A process for producing aluminum, including electrolytically decomposing alumina to aluminum metal in an electrolyte bath between a carbon anode and a cathodic interface formed between metal and the electrolyte bath, the bath
a. consisting essentially of \(\text{Al}_2\text{O}_3\), NaF, and AlF₃, and
b. having a weight ratio NaF to AlF₃ up to 1.1:1, while maintaining the bath at an operating temperature effective for preventing bath crusting in interfacial areas between bath and aluminum metal, while enclosing the top of the cell for keeping the surface of the bath molten, and while feeding alumina
a. substantially continuously onto the molten bath surface,
b. the alumina having a water content effective for preventing anode dusting,
c. the carbon anode being exposed to the gaseous water evolved from the alumina, whereby anode dusting is prevented.

15 Claims, 5 Drawing Figures
ALUMINA REDUCTION PROCESS  
BACKGROUND OF THE INVENTION

The present invention relates to the electrolytic reduction of alumina to aluminum metal, and, more particularly, to a modified Hall-Heroult process for producing aluminum.

The conventional Hall-Heroult cell for producing aluminum is beset with a number of problems. For example, it is customary to feed alumina into the molten electrolytic bath through openings in the solid crust which covers the upper surface of the bath. This allows pot gases to escape.

In conventional operations, exposed carbon is lost to air burning. This imposes a limitation on using taller, pre-baked anodes for the purpose of reducing labor costs, because increased air burning offsets the advantage.

Furthermore, pre-baked carbon anodes must be stubbed, i.e., molten cast iron is poured into a recess in the top of the anode to form an electrical connection to receive an anode rod for feeding current to the cell. Stubbing is a costly operation. Used carbon anode butts are re-cycled by crushing them and employing the crushed material as part of the mixture of carbon and binder which is molded and baked to form additional anodes. This re-cycling adds expense and also results in fluoride attack on refractories in the kilns used in the baking operation.

In some cells, self-baking carbon anodes (i.e., so-called Soderberg electrodes) are employed, but air-burning is likewise a problem with such anodes. Moreover, both pre-baked anodes and self-baking anodes are subject to attack by fluoride gas evolved from the electrolytic bath, which results in sloughing of carbon dust from the anodes and causes increased anode cost and other problems described below.

A number of factors operated to limit the cell life of the conventional Hall-Heroult cell. Sodium intercalation and formation of sodium aluminum oxide cause heaving and cracking of the cell lining with resultant interference with the operating characteristics of the cell, and shortened cell life, thus necessitating periodic cell re-lining.

Fume control is likewise a problem for the conventional Hall-Heroult cell. An air sweep which dilutes pot gases up to 100-fold has been inherent in previous attempts to efficiently hood for capture of fumes. The requisite hooding is costly and requires considerable maintenance as individual sections are easily deformed by harsh usage. Fluoride, which is in short supply, must be added continually to maintain proper bath composition. And, with all precautions, fume not intercepted by the hooding escapes through roof vents.

Process control is another problem area in the conventional Hall-Heroult cell. Addition of alumina by using the crust insulation upsets the alumina control. Unnecessary anode effects reduce production. As make-up for fluoride, AlF₃ must be added to maintain the NaF/AlF₃ ratio necessary to obtain high current efficiency. Continual additional anode-cathode distance adjustment is required because of anode changing and alumina feeding, which require breaking of the crust and upsets heat balance.

Concerning the cathodes of conventional Hall-Heroult cells, the carbon lining of the cell, which forms a component of the cathode assembly, has a higher voltage drop than is desired, and as the cell ages and bath penetrates into the carbon lining, collector bar to lining interface voltage drop increases further. Magnetic effects result in deterioration of the carbon lining, reduce aluminum production, and shorten cell life.

Power efficiency also is somewhat low in the conventional Hall-Heroult cell process.

SUMMARY OF THE INVENTION

In view of the above, it is an object of the present invention to provide a new process for electrolytically reducing alumina to aluminum, which process overcomes many of the disadvantages of the conventional Hall-Heroult cell.

This, as well as other objects which will become apparent in the description that follows, are achieved, according to the present invention, by a process for producing aluminum, including electrolytically decomposing alumina to aluminum metal in an electrolyte bath between a carbon anode and a cathodic interface formed between aluminum metal and the electrolyte bath, the bath a. consisting essentially of Al₂O₃, NaF, and AlF₃, and b. having a weight ratio NaF to AlF₃ up to 1:1:1, while maintaining the bath at an operating temperature effective for preventing bath crusting in interfacial areas between bath and aluminum metal, while enclosing the top of the cell for keeping the surface of the bath molten, while feeding alumina a. substantially continuously onto the molten bath surface, b. the alumina having a water content effective for preventing anode dusting, c. the carbon anode being exposed to the gaseous water evolved from the alumina, whereby anode dusting is prevented.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an elevational, cross-sectional, broken-away view of a Soderberg anode type cell for use in the present invention.

FIG. 2 is an elevational, cross-sectional view of a pre-baked anode type cell for use in the present invention.

FIG. 3 is a schematic, cross-sectional illustration of equipment for illustrating a principle of the present invention.

FIG. 4 is a part of the cryolite-AlF₃ phase diagram. The term "ΔConc." used in FIG. 4 is an abbreviation of ΔConcentration and refers to the concentration change at the indicated temperature subscript required to initiate crystallization.

FIG. 5 is a schematic representation, in elevational cross section of bench-scale equipment for illustrating a part of the present invention.

GENERAL ASPECTS OF THE INVENTION

a. The Operation Temperature

Operating a Hall-Heroult cell at bath weight ratios NaF/AlF₃ equal to or below 1.1:1 has held the promise of higher current efficiencies due to lower bath operating temperatures. Higher CO₂/CO ratios would mean less consumption of the carbon in the carbonaceous anodes. Experimentation with baths having weight ratios of 1.1:1 or below has however presented a problem of crust formation over the molten aluminum pad cathode.
during electrolysis. Analysis led to the discovery that the problem must have resulted from maintaining a 20° to 30°C difference between the electrolyte bath operating temperature and its liquidus temperature, i.e., $\Delta T = 20°$ to 30°C. This temperature difference is measured at the hottest location in an industrial smelting cell. The maintaining of this 20° to 30° difference was a practice of long standing in the operation of conventional Hall-Heroult-type aluminum smelting cells.

The maintaining of the 20° to 30° difference in operating cells has been the result of several considerations. For example, this temperature difference has permitted the bath to form a protective frozen or solidified layer over and near the side linings of the cell, and it has been known that for every 1°C increase of the bath operating temperature over the bath liquidus, there is a decrease of about 0.22 percent efficiency. These two factors had indicated that a temperature difference above 30°C would be undesirable. Providing the lower limit on this temperature difference has been the concept that the liquid cavity enclosed by the frozen bath at or near the sidewalls of a cell should not become too small for efficient cell outlets. With this well-established conceptual basis for the 20° to 30° temperature difference, the problem of electrolyte crumbling over the molten aluminum pad cathode during electrolysis at low bath ratios was not attributed by those in the art to the practice of maintaining this temperature difference.

Analysis indicated that, if the 20° to 30° temperature difference is maintained at low bath ratio operations, i.e., low weight ratio NaF to AlF₃, a concentration gradient effect occurs in the catholyte region of the electrolyte directly above the molten aluminum pad cathode to result in the troublesome electrolyte crumbling over the molten aluminum pad cathode. It is believed that the amount results from a depletion of acid (AlF₃-rich) constituents in the catholyte and a concomitant enrichment in basic (NaF) constituents of the catholyte.

A difference to 20° to 30°C between the operating temperature of the electrolyte bath and the liquidus of the electrolyte bath is sufficient for preventing crumbling in the catholyte region of the higher ratio baths used in prior practice, but it is insufficient to prevent crumbling at lower ratios of, for example, 0.8. This is illustrated in FIG. 4. FIG. 4 is a phase diagram for a two component system, i.e., cryolite and aluminum fluoride, and it must be remembered that the situation becomes somewhat different (e.g., lower liquidus temperature) as the components, for instance Al₂O₃, CaF₂, LiF, etc., are added to the bath. Nevertheless, FIG. 4 is sufficient to convey the concept. Point A in FIG. 4 is a point 30°C above the liquidus of an electrolyte bath of 1.3 ratio, such as might be used in a Hall-Heroult cell operating according to previous practice. Enrichment in sodium will move the actual catholyte composition in the direction of arrow Z, but, as is clear from FIG. 4, composition changes in the direction of arrow Z will never result in the entering of a region in the phase diagram where solid phase might precipitate out. The situation is quite different for point B which is 30°C above the liquidus of a bath of 0.8 ratio. There, as soon as sodium enrichment in the catholyte becomes sufficiently great to move the effective composition farther to the left than the Δ Concentration 30°C indicated in the Figure, solid cryolite (Na₃AlF₆) can precipitate out. In this way, it becomes possible for a crust of frozen electrolyte to form over the molten aluminum pad cathode as electrolysis proceeds in a low ratio electrolyte bath operated with the 20° to 30°C difference between bath operating temperature and bath liquidus practiced in the prior art.

Having recognized the source of the problem of crumbling over the molten aluminum pad cathode in low ratio baths, the problem is overcome by increasing the difference between bath operating temperature and bath liquidus temperature. This may be done by raising the operating temperature or by using an additive such as LiF to lower the liquidus temperature. For example, from FIG. 4 it can be seen that crumbling over the pad cathode at a bath ratio of 0.8 is prevented by operating the electrolysis at a bath temperature at point C, which is 100°C above the liquidus of the 0.8 ratio bath. At this higher operating temperature, a considerably greater concentration gradient can be tolerated in the catholyte without suffering the occurrence of crumbling, as is clear from the size of the Δ Concentration 100°C in the Figure as compared with the size of the Δ Concentration 30°C of FIG. 4.

To determine the appropriate operating temperature for any given low ratio electrolyte bath, an estimate of a proper operating temperature is first made based, for example, on the nominal two component composition of the electrolyte and FIG. 4. If crumbling at the cathode-bath interface is occurring under the chosen conditions, it can be noted by the resistance given to the probing or sideways movement of a steel rod down at the interface in the electrolyte bath. Preferably, that operating temperature is chosen at which no significant crumbling is occurring at the interface between the cathode pad and the electrolyte bath, it being remembered that any increase above this minimum adequate temperature means loss in current efficiency. While this procedure has been discussed for constant bath ratio, it will be recognized that a greater difference between bath operating temperature and bath liquidus may be achieved, for instance, by adding more aluminum fluoride. Also, other substances, such as LiF, may be used to lower the liquidus temperature while maintaining bath operating temperature constant.

b. The Alumina

The alumina used in the present invention is generally fed at a rate substantially equal to that at which it is consumed or converted to aluminum, that is at the rate of electrochemical reduction thereof. Within the meaning of the term "substantially continuously" as used herein, we include adding alumina continuously or in small, separate increments at frequent intervals. The alumina feed to any smelting cell must dissolve in the electrolyte at a rate equal to or at least the rate of electrochemical reduction so that the dissolved Al₂O₃ content of the electrolyte is not depleted. If alumina is fed to a cell more rapidly than it can be dissolved, solids then referred to as muck accumulate on the pot bottom, with attendant adverse effect upon operation of the cell. Factors that influence muck formation include the maximum Al₂O₃ solubility in the electrolyte and the solution rate of the particular alumina chosen. The method of feeding and the quantity of alumina introduced to the cell at any one time, along with the difference between cell operating temperature and the liquidus temperature of the NaF-AlF₃ electrolyte, are also
important considerations with regard to muck forma-

The solubility and solution rate of alumina in NaF-
AlF$_3$ electrolytes depends, in part, on the temperature 
and weight ratio of NaF/AlF$_3$ (bath ratio) in the fused 
salt bath. The maximum solubility and solution rate are 
found in pure molten cryolite (bath ratio 1.5:1) at ele-
vated temperatures. As the bath ratio is lowered by ad-

dition of excess AlF$_3$, the temperature at which a com-
pletely liquid NaF-AlF$_3$ fused salt system can be main-
tained, the liquidus temperature, is sharply decreased.

A decrease in Al$_2$O$_3$ solubility and solution rate accom-
panya a decrease in bath ratio. Thus, while the use of 
low ratio fused salt mixtures as electrolytes in smelting 
cells permits lower temperature operations, an alumina 
feed with properties that improve its solution rate in the 
electrolyte is required. The solubility of Al$_2$O$_3$ in a 
given bath at a specified temperature is independent of 
the physical form of the Al$_2$O$_3$ charged to the electro-
lyte, but the solution rate of the alumina in the bath is 
a function of properties of the charged alumina.

The present invention makes use of the discovery 
that alumina having, as compared with the "metal 
grade alumina" conventionally used for producing alu-
minate metal by the electrolytic reduction of Al$_2$O$_3$ in 
cryolite-based electrolyte, a higher water content and 
a higher surface area and charged directly into contact 
with molten electrolyte exhibits a significantly higher 
solution rate. It is believed that the higher water con-
tent, and in particular a higher chemically combined 
water content, acts to instantaneously disperse the 
charged alumina through the electrolyte by the sudden 
release of steam as the charge comes in contact with 
the hot electrolyte bath. The well-dispersed particles 
themselves dissolve rapidly in the bath.

The thought of introducing the appreciable amounts 
of water in the alumina used in the present invention to 
an alumina electrolytic reduction bath may bring to 
mind the possibility of explosions. Thus British Patent 
Specification No. 274,108 of Societa Italiana di Elett-
rochimica for "Improvements in Processes for the Pro-
duction of Aluminum in Electric Furnaces" states that 
it has not been possible in practice to use the hydrate 
or hydroxide of alumina directly on account of the 
more or less strong explosions produced by the mate-
rial and the resultant projection of igneous liquid.

Methods that have been proposed for avoiding this 
problem are to first agglomerate the hydrate and only 
then feed it into a molten electrolyte bath; see German 
Pat. No. 472,006 of Feb. 21, 1929 issued to Societa 
Italiana di Elettrochimica in Rom for "Verfahren zur 
Herstellung von Aluminium." Also proposed is the 
charging of alumina hydrate onto the crust over a mol-
ten electrolytic bath in a Hall-Heroult cell, with intro-
duction into the bath occurring only after dehydration 
has been achieved; see U.S. Pat. No. 2,464,267 of 
Allen M. Short for "Dehydrating Alumina in the Pro-
2,464,267 is to be contrasted with that of the present 
invention, wherein alumina of relatively high water 
content is added directly to molten electrolyte, rather 
than being allowed to rest for a period on a crust over 
molten electrolyte. It has been discovered that substan-
tially continuous adding of the Al$_2$O$_3$ containing apre-
ciable amounts of combined water does not lead to ex-
plosions. The evolved water appears only to disperse 
the charged Al$_2$O$_3$ rapidly to the bath, thus promoting 
dissolution in the bath.

The thought of purposely adding to a cell an alumina 
with high water content may also indicate danger of a 
major increase in HF evolution. It has been found that 
only 5 percent of the water on the alumina pyrohydro-
lyzes bath to produce HF fume.

The alumina to be used in the present invention may 
be fed to individual cells or to a plurality of cells in a 
potline. The cells may employ either pre-baked anodes 
or anodes baked in situ, such as the Soderberg type.

Generally, calcining alumina hydrate, such as Bayer 
process alumina trihydrate will produce alumina for 
use in the present invention. In general, calcining tem-
peratures in the range of about 300° to 600°C are suit-
able for the purpose. Apparatus and methods for heat-
ing alumina to the desired water content and surface 
area in kilns or so-called "flash" heating (see U.S. Pat. 
No. 2,915,365 of F. Saussol; French Pat. No. 1,108,011) are 
well-known.

Aluminas with surface areas as high as 350 m$^2$/g can 
be obtained by heating α-alumina trihydrate (gibbsite) 
for 1 hour at 400°C in dry air. Such materials are rap-

didly soluble in electrolyte baths according to the pres-

tent invention.

For any alumina which is to be used as feed to the 
alumina smelting cell, it is possible to run an exper-
iment of the type set forth in Example II below, or the 
like, for the purpose of determining the minimum water 
content desirable. The water content is preferably ef-

cfective for dispersing the individual particles of the alu-
mina when the alumina is added to the electrolytic 
bath. If the water content is too low, steam evolution 
will not be effective for dispersing the particles, and a 
clumping of particles together will result, with resultant 
decrease in the effective dissolution rate of the alumina 
in the smelting bath. For any alumina, the most pre-
ferred particle size is 100 to 150 microns. The upper 
limit of water content in the alumina is not determined 
by the need to avoid explosions but rather by the quan-
tity of heat that must be removed from the bath to drive 
off water as steam. This quantity cannot be sufficient 
to cause solidification of bath around solid alumina 
particles, thereby contributing to muck formation. In 
general, when this second criteria is satisfied, no dan-
gerous explosions will occur according to the practice 
of the present invention. In general, if the water con-
tent is effective for dispersing the individual particles, 
it is also effective for preventing anode dusting.

c. The Enclosing of The Bath

In the closing of the top of the cell in the method of 
the present invention, certain guidelines are used. The 
cover must (1) prevent heat loss from the top of the 
bath to a sufficient degree that the bath surface remains 
molten, (2) it must prevent any substantial amount of 
air from diluting fumes arising due to cell operation, 
and (3) by barring air, it is to eliminate air burning of 
the carbonaceous anode material.

It is important that the bath surface remain molten in 
order that alumina being charged contact molten bath. 
This causes the water in the alumina to disperse the 
particles for rapid dissolution in the bath, as well as 
providing water vapor which inhibits attack on exposed 
carbon anode surfaces, as discussed below. It may hap-
pen sometimes that some undissolved substance will be 
floating on the bath surface, but this undissolved sub-
stance must not be present in such quantities as to dis-
rupt the dispersing of the alumina and lead to mucking.

A basic concept behind minimizing the air entering the cell is the undesirability of the resulting dilution of the fumes, such as gases given off by the anode (e.g., hydrocarbons), those resulting from the electrolysis reaction (e.g., CO₂), and those evolved from the bath (e.g., gaseous fluorides). Of course, the cell cannot be completely closed, for openings must be provided for venting from the cell the above-mentioned gases produced therein.

d. Anode Dusting

Depending upon operating conditions, consumption of carbon anodes in Hall-Heroult process cells ranges from one-third to three-quarters of a pound of carbon per pound of aluminum produced. The preferred conditions are those leading toward the stoichiometric minimum consumption, 0.33 lbs. C/lb.Al, predicted by the net cell reaction:

\[ 2\text{Al}_2\text{O}_3 + 3\text{C} \rightarrow 3\text{CO}_2 + 4\text{Al} \]

One of the problems encountered heretofore in closing off the space above the electrolyte bath of a Hall-Heroult cell from the air has been that carbon scum accumulates on the bath surface and carbon dust is even distributed throughout the electrolyte. This carbon scum and dust is caused by a deterioration of the carbon anodes. The phenomenon is referred to as anode dusting.

Carbon scum causes alumina feeding problems. The carbon scum has made it impossible to replenish alumina consumed during electrolysis. As the dissolved alumina content of the bath decreases, scum formation accelerates. Carbon dust and scum increases the bath viscosity and hinder diffusion of oxygen-bearing ions to the anode, thus limiting anode current densities and affecting the heat balance of the cell. Increases in the viscosity and density of the bath lower the current efficiency and contribute to poor metal coalescence. The carbon in the scum and dust is not available for reaction with oxygen at the anode and so the gross consumption of carbon is increased by dusting. Because of carbon scum, the bath agitation supplied by anode bubble evolution is reduced and the tendency for electrolyte to solidify at the metal pad-bath interface increases. Ultimately, enough carbon dust can be distributed throughout the bath in closed cells to allow for electronic conduction and complete loss of metal production. These conditions must be avoided for successful operation of an enclosed cell according to the present invention.

Prolonging the life of anodes will not only decrease carbon consumption, but in the case of pre-baked anodes will decrease the amount of anode butts to be recycled to the production of additional anodes and thereby decreases problems attendant upon evolution of fluorides during baking of anodes.

It has been discovered that the phenomenon of anode dusting in closed cells can be prevented by providing at the anode within the cell an atmosphere containing water. Thus, it is possible to provide within the closed cell a skirt around the anode and to create within this skirt a partial pressure of water effective for preventing the anode dusting. The present invention utilizes the discovery that, when the above-described, water-containing alumina is charged onto the bath, preferably onto locations of the bath surface where gas is evolving alongside the anode, the water given off as the alumina contacts the bath surface will create in a closed cell the water-containing atmosphere at the anode required for preventing anode dusting. If the alumina is charged to the bath elsewhere than alongside the anode, venting of the cover over the cell should be placed and regulated such that the released gaseous water will in fact contact the anode to prevent anode dusting.

It is believed that anode dusting is caused by atmolite or sodium aluminum tetrafluoride, NaAlF₄, in vapor form. This substance attacks an anode and causes anode dusting.

Thus, in cell operation, a gaseous effluent containing gaseous fluorides is evolved from the electrolytic bath of alumina dissolved in molten cryolite (primarily cryolite or cryolite plus additional fluorides such as excess AlF₃, CaF₂, and LiF), and among such gaseous fluorides is atmolite.

Attack by atmolite on exposed carbon anode surfaces is particularly a problem when using closed cells, e.g., cells which are closed at the top by a plate.

It is believed that the amount of water vapor to be provided in an atmosphere around an anode surface depends to some extent on the amount of atmolite to be neutralized. In general, it is desirable to provide at least enough water vapor to react the atmolite stoichiometrically with the water vapor in accordance with the equation

\[ \text{NaAlF}_4 + \frac{3}{2}\text{H}_2\text{O} \rightarrow \text{NaF} + \frac{1}{2}\text{Al}_2\text{O}_3 + 3\text{HF} \]

e. Advantages

The process of the present invention solves many of the problems associated with conventional Hall-Heroult cell practice. For example, current efficiency is improved and operation at low bath ratio, i.e., low sodium, contributes toward eliminating swelling and heaving in the carbon lining. Also, closing the cell makes possible total fume collection. There is no roof vent loss from the smelting building. Since pot gas is not diluted with air, scrubber treatment or treatment according to U.S. Pat. No. 3,503,184 is simplified and need only handle as little as 1/100 of the gas volume previously handled. Lack of air sweep (e.g., U.S. Pat. No. 3,708,414), low operating temperatures, and low fluoride partial pressure reduce the amount of fluoride and other materials that must be recovered. Conventional cells must recover, e.g., 24 pounds particulate per ton of aluminum produced; operation according to the present invention at 800°C has been found to mean recovery of only 3.2 pounds per ton, while operation at 900°C has yielded only 14.6 pounds particulate per ton.

Because there is no crust over the bath, alumina delivered to the bath can be carefully controlled and an optimum concentration maintained. The higher water content alumina itself permits closer control of dissolved alumina concentration. Stable heat balance results in minimum anode-cathode distance variation. Crust breaking for anode changing and alumina additions is eliminated.

The higher water content alumina has enabled for the first time satisfactory operation of closed Hall-Heroult cells. By minimizing carbon scum formation in such closed cells, there is continued easy access of feed alumina to the molten bath surface.
Slightly increased HF emission is more than offset by the complete capture of pot gases made possible by closing the top of the cell. There is no discernible drop in current efficiency as a result of the use of higher water content alumina in the present invention.

Carbon consumption is less in the present invention, because there is practically no air burning of the anodes and because operation is at higher CO/CO₂ ratio.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Preferably, the bath weight ratio NaF to AlF₃ is less than 1.0. A ratio less than 0.9 can be used. It is preferred to maintain the bath ratio at a value at least greater than 0.5.

The concentration of Al₂O₃ dissolved in the bath should be above that at which an anode effect would occur and is selected to optimize the current efficiency of the cell. It is believed possible, perhaps on a transient basis, to have some alumina in solid, particulate form in the bath. Mucking, i.e., a settling of excessive amounts of solid alumina onto the bottom of the cell, does not occur, due to an increased alumina solubility at the metal/bath interface caused by concentration gradients in the catholyte. Because of the relatively small difference between the alumina concentration at which anode effect begins and the alumina saturation concentration in the low bath ratio operation according to the present invention, it is additionally preferred that alumina be fed to the bath in a form having a high dissolution rate as discussed above. Preferred embodiments of such alumina are discussed below.

While the bath may consist only of Al₂O₃, NaF, and AlF₃, it is possible to provide in the bath at least one halide compound of the alkaline earth metals other than sodium in an amount effective for reducing the liquidus temperature of the bath below which it would have if only Al₂O₃, NaF, and AlF₃ were present. Suitable alkali and alkaline earth metal halides are LiF, CaF₂, and MgF₂. In a preferred embodiment, the bath contains lithium fluoride in an amount between 1 and 15 wt. percent.

The operating temperature of the bath is preferably maintained at a temperature greater than 40°C above the cryolite liquidus temperature of the bath. The cryolite liquidus temperature is that temperature at which cryolite first begins to crystallize on cooling the bath. Where the bath composition is such that cryolite is the first substance to crystallize on cooling, the intersection of the line of the constant bath composition versus temperature with the uppermost liquidus temperature surface gives the cryolite liquidus temperature. Where Al₂O₃ is the first substance to crystallize, a reasonably good approximation of cryolite liquidus temperature is the "eutectic" temperature determined by finding the liquidus temperature for progressively decreasing Al₂O₃ content, correspondingly increasing NaF + AlF₃, and constant bath ratio NaF/AlF₃ and selecting the minimum liquidus temperature on the basis of the resulting group of liquidus temperature values. The operating temperature must be effective for preventing bath crust in interfacial areas between the bath and the molten aluminum metal pad cathode. It is preferred that the operating temperature lie below 935°C, and baths have been operated successfully at operating temperatures below 900°C, 850°C, and 800°C. In some embodiments, the operating temperature is at least 70°C, sometimes at least 100°C, above the liquidus temperature of the bath.

The electrolytic decomposition of Al₂O₃ in the present invention may be carried out at an anode current density of 1 to 20 amperes per square inch, while current densities of 1 to 15 and 1 to 10 amperes per square inch represent preferred current density ranges.

It is additionally preferred that carbon anodes used in the present invention be protected by a water-bearing atmosphere. An appropriate water-bearing atmosphere is created when the bath is sealed off from the air and when the alumina is preferably fed onto locations of the bath surface where electrolysis gas is evolving alongside the anodes. The alumina is in the form of the herein described high dissolution rate, water containing alumina. The resulting water-bearing atmosphere prevents anode dusting, a condition which can prove intolerable for the present invention.

Up to 100 percent of the feed alumina, and at least 50 percent more preferably at least 90 percent, by weight, is high dissolution rate alumina containing sufficient water to create an atmosphere above the electrolyte bath effective for preventing anode dusting. The alumina is fed substantially continuously, directly to the molten electrolyte of the cell. Water content and dissolution rate are indicated by, among other parameters, the total water and the surface area of the alumina. The term "total water" is defined herein as follows: Expose a sample of alumina to 100 percent humidity for several hours, then equilibrate the sample at 44 percent relative humidity, 25°C, for 18 hours, then accurately weigh the sample, then ignite it to 1,100°C, then weigh again. The loss in sample weight on going from the equilibrated state at 44 percent relative humidity to the ignited state after heating at 1,100°C, divided by the sample weight at 1,100°C, and multiplied by 100 is the percent total water.


The use of alumina of the high water content of the present invention is contrary to the commonly-held view set forth at p. 34 of "The Chemical Background of the Aluminum Industry" by Pearson, published by The Royal Institute of Chemistry in 1955, that alumina used in electrolytic production of aluminum should be moisture-free.

In addition, it is desirable that the alumina used in carrying out the invention handle and convey easily.

The properties according to the present invention that enhance the solution rate of alumina in fused NaF-AlF₃ salt systems also improve its ease of handling and serviceability in operations as in U.S. Pat. No. 3,503,184. Because the alumina used in the present invention has higher water content, less energy, as compared to the energy used in producing conventional metal grade alumina, is required to produce it from Bayer process hydrated alumina.

The alumina added to the bath according to the present invention may be preheated, if desired, so long as it retains the above-mentioned water content and surface area characteristics. Preferably, the alumina has a total water of 8 to 20 percent, more preferably 10 to 18 percent.
The alumina surface area may preferably lie in the range 135 to 180 m$^2$/g. A maximum rate of solution of alumina in a fluoride bath is obtained when heated, attrition resistant, high surface area, 8 to 20 percent total water alumina of 55–154 microns diameter (−100 mesh +170 mesh) particles is charged directly to the unfrozen surface of agitated bath at temperatures above its liquidus temperature continuously or in small separate portions, i.e., a time interval between separate shots equaling or less than 10 minutes. The phrase “small separate portions” is underlined because of its importance with regard to the $\Delta T$ at which the cell is operated. The $\Delta T$ is the difference between the operating temperature and the liquidus temperature of the NaF-AlF$_3$ fused salt mixture. This liquidus temperature can be lowered by addition of other salts to the bath such as CaF$_2$, LiF, MgF$_2$, etc., but for simplicity a pure NaF-AlF$_3$ system is visualized. Conventional smelting cells operate with $\Delta$Ts of 10$^\circ$–30$^\circ$C. In conventional operations a low $\Delta T$ is desirable since the current efficiency of the cell increases as the operating temperature decreases. Because of improved control on conventional potlines the anode cathode distance (ACD) in operating cells has been reduced in some cases to a nominal 1 inch distance. Since the heat input to cells depends on line electrical current and internal resistance, the low ACD has enabled the lowering of $\Delta T$ to, for example, 10$^\circ$C ± 5$^\circ$C. While these low $\Delta$Ts are advantageous from a current and power efficiency viewpoint, they tend to increase mucking problems in the cell even when an alumina with properties that maximize its solution rate is fed to the pots. Automatic ore feeders which introduce e.g., only approximately 2 lb. of Al$_2$O$_3$ into the bath per increment may be used. This is a reasonably low rate of introduction of Al$_2$O$_3$ to the cell. However, if the $\Delta T$ of the bath is low, even this quantity of alumina may be so large that the heat removed from the bath to drive off water, bring the charge to temperature, and dissolve it can easily result in localized solidification of electrolyte. If this occurs then alumina encased in solidified bath will sink to the bottom of the cell to create muck instead of dissolving. The point is, it is important to balance the size of the portion of Al$_2$O$_3$ fed to a pot at any given time against the $\Delta T$ of the cell. Low $\Delta T$ and large slugs of alumina, particularly when high surface area and water containing aluminas are used. A proper particle size distribution is advantageous with regard to ease of dissolution in a smelting cell. Alumina fines, e.g., particle size less than 44 microns (−325 mesh), tend to dust over the surface of the molten bath, agglomerate, and sink to the bottom of the cell, where they contribute to mucking problems. Large particles, having diameters, e.g., greater than 150 microns (+100 mesh), also contribute to mucking problems, particularly when they are fed in large portions to pots operating with small $\Delta$Ts. The large particles acquire a layer of solidified electrolyte on contacting molten bath which causes them to sink to the pot bottom, rather than rapidly dissolve. This is the same mechanism as that discussed earlier to explain muck formation in cells that receive Al$_2$O$_3$ feed in quantities too high to be accommodated by the low $\Delta$Ts. The difference is that particle sizes in excess of +100 mesh lead to muck even when $\Delta$Ts are in the vicinity of 25$^\circ$C. At small $\Delta T$, attention must likewise be paid to the heat of evaporation of the water in the alumina.

Further illustrative of the present invention are the following examples:

**EXAMPLE I**

The purpose of this example is to illustrate basic principles concerning the prevention of anode dusting, using a gaseous water partial pressure. With reference to FIG. 5, there is shown a graphite crucible 51 and an alumina crucible 52 having a hole 53 at its lower end. A molten aluminum metal pad 54 sits in the bottom of the alumina crucible and contacts the graphite crucible 51 to be in electrical contact with cathode lead 55. Resting on pad 54 is electrolyte bath 56 containing 4 wt.% Al$_2$O$_3$ and NaF + AlF$_3$ at a bath weight ratio NaF/AlF$_3$ = 0.8. The electrolyte bath is at 900°C. Carbon (pre-baked, petroleum coke) anode 57 is immersed in the electrolyte bath to provide an electrical current density of 3 amperes per inch$^2$ on the anode. Alumina anode skirt 58 surrounds the anode 57 as shown and is sealed at its top by plug 59 provided with orifices for the passage of anode lead 60 and gas flow pipe 61. Appropriate piping is provided for allowing varied amounts of argon gas to flow from tank 62 through impinger bottle 63 containing water 64 surrounded by an ice water bath 65. Carbon consumption was 0.33 to 0.38 pounds per pound of aluminum produced at a current efficiency of 100 percent in 29 to 41 amperes-hour tests using water vapor shielding for preventing anode dusting. With 4 to 22 torr water partial pressure in the argon, no carbon froth or scum was detected. When the impinger bottle 63 was bypassed so that only argon moved down around anode 57, a carbon scum formed on the bath, and electronic shorting from anode to cathode through the carbon scum occurred.

**EXAMPLE II**

This and Example III are provided to illustrate the increased dissolution rates obtainable with the alumina used for preventing anode dusting according to the present invention. The apparatus used in this example is shown in FIG. 3. Pot furnace 70, which heated by electrical resistance heating, served for bringing a cryolite-base bath in a graphite crucible 71 supported on firebrick 72 to a temperature of 740°C. The nominal bath composition was 64 weight percent cryolite and 36 weight percent aluminum fluoride (AlF$_3$). This corresponds to a bath weight ratio NaF/AlF$_3$ = 0.65. The quantity of bath was 500 grams and 200 milliliters volume in the molten state. The bath contained 14 grams or 2.8 weight percent of Al$_2$O$_3$ as an impurity. At 740°C, this bath is molten (liquids = approximately 724.5°C) and crystal clear. A one-grain quantity of alumina having a total weight of 17 percent and a surface area of 170 m$^2$/g was sprinkled onto the exposed, uncrusted surface of the molten bath. With the bath illuminated with light source 73, the time was recorded for which no remainder of the sprinkled alumina particles could be seen in the look through viewing tube 74. This time was 2 minutes and 58 seconds, which equals a solution rate, in milligrams per milliliter bath-minute equal to 1.65. By way of comparison, a so-called metal grade-alumina of surface area of 40 m$^2$/g gave a solution rate of 0.14 milligrams per milliliter bath-minute under like conditions.

**EXAMPLE III**

Using the apparatus of FIG. 3 and alumina of 17 per-
cent total water, 170 m²/g surface area, gave, at a bath weight ratio NaF/AlF₃ = 1.5 and a bath temperature of 980°C, a solution rate of 16 milligrams of Al₂O₃ per milliliter of bath each minute. The solution rate measured under the same conditions for an alumina of 20 percent total water and 100 m²/g surface area was 8 milligrams alumina per milliliter bath each minute. By way of comparison, metal-grade alumina of 30 m²/g surface area gave under like conditions a solution rate of approximately 0.36 milligrams alumina per milliliter bath each minute.

EXAMPLE IV

This Example illustrates how alumina appropriate for the present invention may be produced.

Bayer-process alumina hydrate was treated in a kiln to produce kiln activated alumina suitable for use in the process of the present invention as follows. Kiln dimensions were 360 feet length and 9¾ feet inner-diameter. Residence time of the material in the kiln was 1 to 1½ hours. The charged hydrate moved countercurrent to the combustion gases introduced into the lower end of the kiln. A maximum temperature of 400° to 500°C was achieved to 10 to 15 feet inside the lower end of the kiln. Natural gas was burned at a rate of 6,500 cubic feet (standard temperature and pressure) per hour to produce the combustion gases. This natural gas flow rate was selected by testing the product for the desired total water. The volume ratio of air to gas was approximately 10:1. An alumina having a 12.5 percent total water was produced. Anywhere from 88 to 95 weight percent of the particles had a size greater than 325 mesh.

EXAMPLES V AND VI

Aluminum was produced in the cell of FIG. 1. The maximum dimensions of the steel shell 20 in the horizontal were 18 feet 6 inches X 10 feet 2 inches. Its maximum height was 3 feet 9 inches. The maximum dimensions of the molten aluminum metal pad 21 in the horizontal were 17 feet 8 inches X 9 feet 4 inches. The electrolyte bath had the same maximum dimensions as the metal pad.

A mica mat 22 was provided between the steel shell 20 and graphite block 23 for the purpose of preventing current flow through shell 20. Mat thicknesses of from 6 to 20 mils have been used.

The pad 21 of molten aluminum was supported on carbonaceous cathode block lining 24 and carbonaceous tamped lining 25. The carbonaceous linings were supported on an alumina fill 26, there being interposed between the tamped lining and the fill some quarry tile 27. A layer of red brick 28 was provided between the graphite block 23 and quarry tile 27.

FIG. 1 is a representative vertical section through the cell and it will be realized that, for instance, similar graphite blocks 23 would appear in other elevational sections through the cell.

The anode 29 was a Soderberg-type carbon anode. The composition charged to form this self-baking anode was 31 percent pitch of softening point equal to 98°-100°C (cube-in-air method) and 69 percent petroleum coke. The coke fraction was 30 percent coarse, 16 percent intermediate and 54 percent fine, the size distributors of the coarse, intermediate, and fine coke being given in Table I.

The cathode current was supplied through steel collector bars, such as bar 30, to the block lining 24. The current supply is indicated by the plus and minus signs on the anode and on collector bar 30 respectively.

The space above the bath 31 was sealed from the surrounding air by a closure 32, including a cast iron manifold 33, Ceraform Refractory board 34, which is a soft (for obtaining a good seal) fibrous electrical and heat insulating board available from the Johns-Manville Co., steel shell 35, steel plate 36, and fire clay brick, e.g., 50% Al₂O₃ and 50% SiO₂, 37. Within shell 35 there was provided a castable 38 serving a primarily insulative function and a castable 39, e.g., calcium-aluminate bonded tabular alumina, selected for its refractory properties. The particular heat transfer situation was chosen to maintain the upper surface 45 of bath 31 substantially in molten condition, i.e., free of any crusting.

Alumina is charged from hopper 40 through a fill valve and feeder assembly 41 of the type disclosed in U.S. Pat. No. 3,681,229 issued Aug. 1, 1971 to R. L. Lowe entitled "Alumina Feeder." Measured quantities of alumina are fed onto the exposed molten bath surface through Inconel-600 pipe 42. The distance between the bottom of pipe 42 and the top of bath 31 is about 1 foot. The feeder 41 is a shot-type feeder, i.e., separate quantities of alumina are fed at timed intervals. In Examples V and VI, two feeders 41 were used, and these fed-in alumina approximately every 5 minutes, the quantities of alumina being adjusted to maintain the desired alumina concentration in the bath. It takes about 1 minute to discharge the alumina increments which were about 1,500 grams. Pipe 42 is directed so as to impinge alumina onto the bath 31 where gas 44 is rising alongside the anode. This assures that the water evolved from the charged alumina protects the anode against production of carbon dust therefrom. This practice also promotes dissolution because of the bath agitation caused by the gas evolution. By charging the alumina in line with a spike row (spikes 45a, b and c lie in a vertical plane parallel to the plane of FIG. 1, which plane also contains pipe 42) in the Soderberg anode (cracks usually occur in the anode in line with spike rows), the dissolution rate is enhanced by the increased gas evolution occurring at the cracks. Feeders 41 were operated using air as the fluidizing medium, it being recognized that this represents a small leakage of air past cover 32 to the bath.

The particular alumina used for Examples V and VI had a total water of 16.95 percent. This alumina was 98 percent plus 325 mesh and its water content alone

<table>
<thead>
<tr>
<th>Tyler Sieve</th>
<th>Coarse</th>
<th>Intermediate</th>
<th>Fine</th>
</tr>
</thead>
<tbody>
<tr>
<td>.371</td>
<td>31.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>50.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>66.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>91.7</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>97.9</td>
<td>48.9</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>98.8</td>
<td>75.5</td>
<td></td>
</tr>
<tr>
<td>48</td>
<td>99.1</td>
<td>93.5</td>
<td>2.4</td>
</tr>
<tr>
<td>100</td>
<td>98.4</td>
<td>98.0</td>
<td>10.4</td>
</tr>
<tr>
<td>200</td>
<td>99.7</td>
<td>99.0</td>
<td>39.7</td>
</tr>
<tr>
<td>pan</td>
<td>100</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

Table I Coke Size Distribution

Cumulative % Greater than Sieve Size
was sufficient to prevent anode dusting, i.e., a decomposition of the anode such that carbon particles build up in and on the bath. The production data for Examples V and VI are presented in Tables II to IV.

### Table II

<table>
<thead>
<tr>
<th>Pot Production Data</th>
<th>Example No.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pot Days Operated</strong></td>
<td>32 96</td>
</tr>
<tr>
<td><strong>Total Lbs. Net Aluminum (Al)</strong></td>
<td>35,172 110,740</td>
</tr>
<tr>
<td><strong>Lbs. Net Al/Pot-Day</strong></td>
<td>1099.2 1153.5</td>
</tr>
<tr>
<td><strong>Average % Al</strong></td>
<td>99.74 99.75</td>
</tr>
<tr>
<td><strong>Electrical Current Efficiency</strong></td>
<td>92.6 90.0</td>
</tr>
<tr>
<td><strong>Kilowatt-Hours/Lb. of Al</strong></td>
<td>7.49 7.76</td>
</tr>
<tr>
<td><strong>Anode Effects/Pot-Day</strong></td>
<td>.91 1.21</td>
</tr>
<tr>
<td><strong>Lbs. Soderberg Paste/Al</strong></td>
<td>56 N.M.</td>
</tr>
<tr>
<td><strong>Lbs. Cryolite Used</strong></td>
<td>1850 3600</td>
</tr>
<tr>
<td><strong>Lbs. Fluoride Used</strong></td>
<td>6105 21,731</td>
</tr>
<tr>
<td><strong>Lbs. Li₂CO₃ Used</strong></td>
<td>682 1400</td>
</tr>
<tr>
<td><strong>Anode to Cathode Distance, inches</strong></td>
<td>1.4 1.5</td>
</tr>
</tbody>
</table>

1. N.M. = not measured

### Table III

<table>
<thead>
<tr>
<th>Pot Electrical Data</th>
<th>Example No.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Volts/Pot</strong></td>
<td>5.13 5.17</td>
</tr>
<tr>
<td><strong>Average Amperes</strong></td>
<td>66,674 72,207</td>
</tr>
<tr>
<td><strong>Kilowatt/Pot</strong></td>
<td>343.1 373.3</td>
</tr>
<tr>
<td><strong>Ohmic Voltage Drop in Bath</strong></td>
<td>1.70 1.68</td>
</tr>
</tbody>
</table>

### Table IV

<table>
<thead>
<tr>
<th>Pot-Bath Data</th>
<th>Example No.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Wt.% CaF₂</strong></td>
<td>3.11 3.17</td>
</tr>
<tr>
<td><strong>Wt.% Al₂O₃</strong></td>
<td>4.09 4.00</td>
</tr>
<tr>
<td><strong>Wt.% AlF₃</strong></td>
<td>48.97 45.08</td>
</tr>
<tr>
<td><strong>Wt.% LiF</strong></td>
<td>5.61 10.165</td>
</tr>
<tr>
<td><strong>Wt.% NaF</strong></td>
<td>38.13 36.94</td>
</tr>
<tr>
<td><strong>Wt.% MgF₂</strong></td>
<td>38 28</td>
</tr>
<tr>
<td><strong>Liquidus Temperature, °C</strong></td>
<td>882 906</td>
</tr>
<tr>
<td><strong>Calculated Wt-% NaF/AlF₃</strong></td>
<td>78 82</td>
</tr>
<tr>
<td><strong>Calculated Wt-% Cryolite</strong></td>
<td>63.4 61.9</td>
</tr>
<tr>
<td><strong>Calculated Excess AlF₃</strong></td>
<td>23.4 20.5</td>
</tr>
<tr>
<td><strong>Bath Operating Temperature, °C</strong></td>
<td>898 922</td>
</tr>
<tr>
<td><strong>&quot;Eutectic&quot; Temperature, °C</strong></td>
<td>799 814</td>
</tr>
<tr>
<td><strong>Conductivity, ohm⁻¹ cm⁻¹</strong></td>
<td>4.87 5.67</td>
</tr>
<tr>
<td><strong>Bath Depth, inches</strong></td>
<td>8.26 7.62</td>
</tr>
<tr>
<td><strong>Metal Depth, inches</strong></td>
<td>6.02 6.25</td>
</tr>
</tbody>
</table>

With special reference to Table IV, the excess AlF₃ indicates the quantity of AlF₃ above the present under the heading cryolite, formula 3NaF·AlF₃. In each of Examples V and VI, Al₂O₃ would be the first substance to crystallize on going below the given liquidus temperature. The "eutectic" temperature provides an estimate of the cryolite liquidus temperature in this case. The "eutectic" temperature is determined by finding the liquidus temperature for progressively decreasing Al₂O₃ content, correspondingly increasing NaF + AlF₃, and constant bath ratio NaF/AlF₃, and selecting the minimum liquidus temperature on the basis of the resulting group of liquidus temperature values. The Al₂O₃ in solution is that at the particular bath operating temperature. Conductivity data is likewise for the given operating temperature.

Gases evolved from the Soderberg anode (e.g., hydrocarbons), fluorides from the bath, and anode reaction gas (e.g., CO₂) were vented from cover 32 through an opening (not shown), and passed through a burner to burn the hydrocarbons. Because it is difficult to provide an absolute sealing of the bath from the air using cover 32, i.e., leaks can be present in cover 32, a pressure of 0.03 to 0.1 inches of H₂O, measured negatively from atmospheric pressure, is maintained between cover 32 and the burner in order to prevent fume leakage from the cover 32. The burned gases were then fed to a scrubber system.

**EXAMPLE VII**

Aluminum was produced in the cell of FIG. 2 shown in longitudinal, elevational cross section. The cell had external dimensions equaling approximately 48 inches height, 89 inches length and 56 inches width. Two carbon, pre-bake anodes 10a and 10b were suspended into electrolyte bath 11 resting on a pad of molten aluminum 12. The molten bath and aluminum were contained laterally by refractory, nonconductive material 13. Refractory material 13 includes a side lining in contact with the molten bath and the molten aluminum and other outwardly situated insulating material with internal structural members of, for example, steel. Refractory alumina brick and silicon carbide brick were the particular side lining materials chosen in this example. Lining the bottom of the cell were graphite blocks 14a through 14d, which were connected into the electrical system by steel bars 15a to 15d. Alumina was fed to bath 11 through a suitable port (not shown) in graphite roof 16; the particular alumina used for feed had a surface area of 245 miles² per gram and a total water of 13 percent. Graphite roof 16 functioned to seal the bath from the air. The electrolyte bath 11 had a composition of 5% LiF and 4 to 5% Al₂O₃, with the balance being cryolite and AlF₃ in proportions giving a weight ratio NaF/AlF₃ equals 0.8. Al₂O₃ would be the first substance to precipitate when cooling bath 11. The liquidus for Al₂O₃ precipitation in the bath at 5% Al₂O₃ is 911.5°C. At 4% Al₂O₃, the liquidus is 863.0°C. Bath operating temperature in FIG. 2 was 910° ± 10°C. No rusting was noted at the interface between the molten aluminum cathode and the bath. The cryolite liquidus, as estimated by the "eutectic" temperature (determined as explained above) at bath ratio = 0.8 was 815°C.

It will be understood that the above description of the present invention is susceptible to various modifications, changes, and adaptations and the same are intended to be comprehended within the meaning and range of equivalents of the appended claims. It will likewise be recognized that the action of water in the present invention will be subject to energy-related laws such as rates of reaction and chemical equilibrium constants and that anode dusting need only be prevented to an extent such that there be no dusting-related impairment of cell operation.

All percentages given herein are in percent by weight unless indicated otherwise.
What is claimed is:

1. A process for producing aluminum, comprising electrolytically decomposing alumina to aluminum metal in an electrolyte bath between a carbon anode and a cathodic interface formed between aluminum metal and the electrolyte bath, the bath consisting essentially of $\text{Al}_2\text{O}_3$, NaF, and $\text{AlF}_3$, and

   b. having a weight ratio NaF to $\text{AlF}_3$ up to 1.1:1, while maintaining said bath at an operating temperature effective for preventing bath crusting in interfacial areas between bath and aluminum metal, while enclosing the top of the cell for keeping the surface of the bath molten, and while feeding alumina

   a. substantially continuously onto the molten bath surface,
   b. the alumina having a water content effective for preventing anode dusting,
   c. the carbon anode being exposed to the gaseous water evolved from the alumina, whereby anode dusting is prevented.

2. A process as claimed in claim 1 wherein the alumina is fed onto locations of the bath surface where gas is rising alongside the anode.

3. A process as claimed in claim 1 wherein the operating temperature of the bath is greater than 40°C above the cryolite liquidus temperature of the bath.

4. A process as claimed in claim 1, wherein said ratio is less than 1.0.

5. A process as claimed in claim 1, wherein said ratio is less than 0.9.

6. A process as claimed in claim 1, said operating temperature being below 935°C.

7. A process as claimed in claim 1, said operating temperature being below 900°C.

8. A process as claimed in claim 1, wherein said operating temperature is at least 70°C above the cryolite liquidus temperature.

9. A process as claimed in claim 1, wherein said operating temperature is at least 100°C above the cryolite liquidus temperature.

10. A process as claimed in claim 1 wherein said alumina is added in increments at intervals of up to 10 minutes.

11. A process as claimed in claim 1 wherein said alumina has a total water from 8 to 20 weight percent.

12. A process as claimed in claim 1 wherein said alumina has a total water of from 10 to 18 weight percent.

13. A process as claimed in claim 1 wherein said alumina amounts to at least 50 percent by weight of the total amount of $\text{Al}_2\text{O}_3$ fed to the cell.

14. A process as claimed in claim 1 wherein said alumina amounts to at least 90% of the $\text{Al}_2\text{O}_3$ fed to the cell.

15. A process as claimed in claim 1 wherein said alumina having a water content effective for dispersing its individual particles upon addition thereof to said bath, but insufficient to cause mucking.

* * * * *
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION


It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 17 After "0.22%" add --in current--.
Column 13, line 62 Change "poing" to --point--.
Column 14, line 42 Change "pine" to --pipe--.

Signed and sealed this 18th day of March 1975.

(SEAL)

Attest:

RUTH C. MASON Attesting Officer

C. MARSHALL DANN Commissioner of Patents and Trademarks