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G. DE VARDA

3,029,194

FURNACE AND PROCESS FOR THE ELECTROLYSIS OF ALUMINUM

Filed Jan. 7, 1955

2 Sheets-Sheet 1

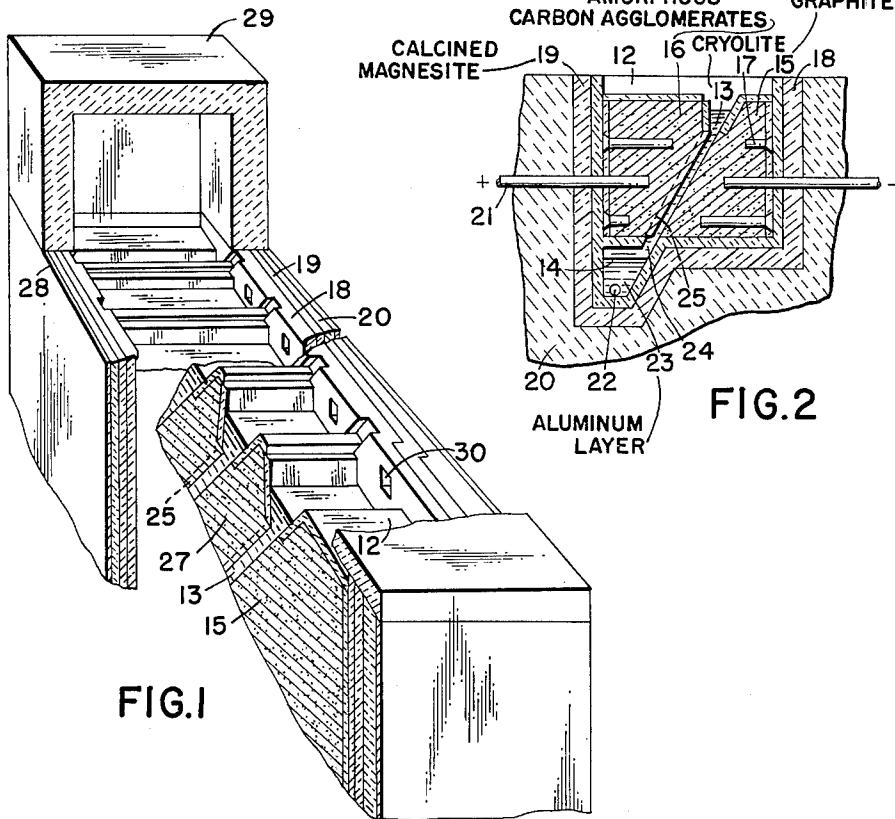


FIG. 1

FIG. 2

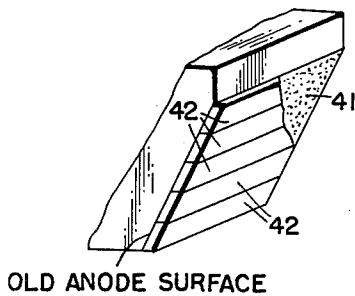


FIG. 6

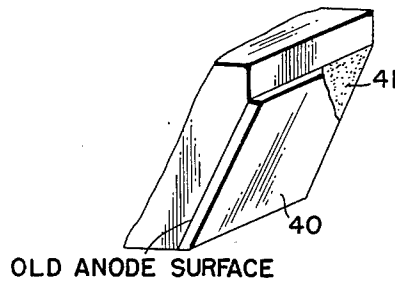


FIG. 5

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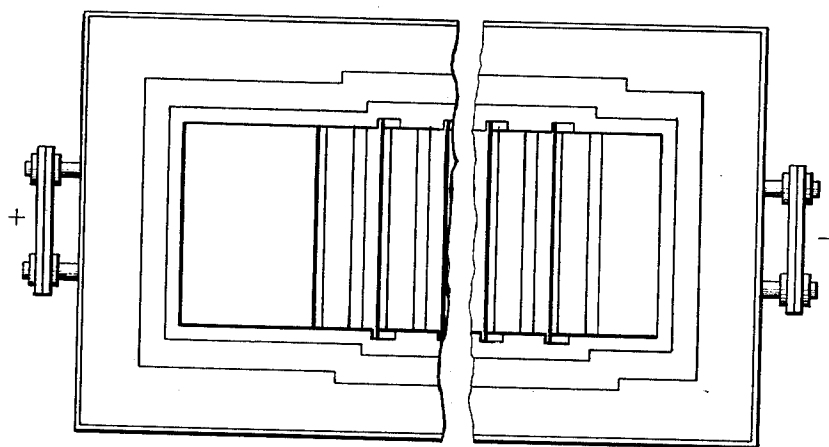
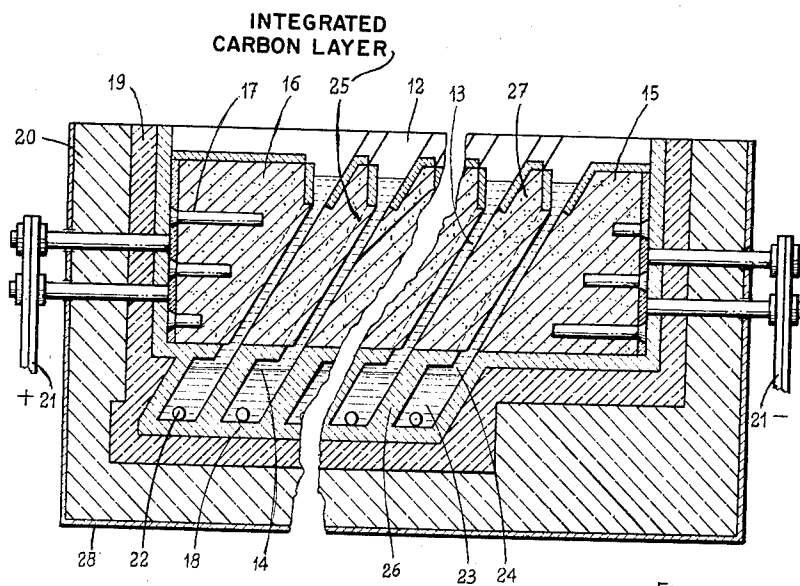
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## FURNACE AND PROCESS FOR THE ELECTROLYSIS OF ALUMINUM

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21 Claims. (Cl. 204-67)

My invention relates to the electrolytic production of aluminum and is described in the following with reference to the drawings in which:

FIG. 1 is a prospective view, partly in section along the line A-A of FIG. 4, showing a multiple furnace employing a series of bipolar inclined electrodes for the electrolysis of aluminum;

FIG. 2 is a vertical cross-sectional view of an elemental furnace, according to the invention, for the electrolysis of aluminum;

FIG. 3 is a vertical cross-section of a multiple furnace according to the invention;

FIG. 4 is a plan view of the multiple furnace shown in FIG. 3;

FIG. 5 is an oblique view of a portion of an anode structure illustrating one way in which the anodic surface may be integrated or renewed;

FIG. 6 is a view similar to that of FIG. 5 showing an alternative way for renewing the anode.

Today, aluminum is exclusively produced in electrolytic furnace either with prebaked anodes or with Soderberg carbon anodes. The metal is produced by electrolysis of a bath of molten cryolite containing dissolved alumina. Alumina ( $Al_2O_3$ ) breaks up into metallic aluminum and oxygen which combines with the anodic carbon. The anodes dip partially into the bath of molten cryolite and receive the current from above through metallic conductors, whence the current passes over to iron stubs or nipples which intimately contact the anodic carbon. The current passes from the foot of the anode (i.e. from its horizontal submerged surface), through the bath to the cathode, the latter being formed by the furnace bottom consisting of a carbon sole with a layer of liquid aluminum on top. The current leaves the carbon bottom through iron cathodes which are in intimate contact with the cathodic carbon. The whole is thermically insulated on the outside with layers of refractories and insulating material held in place by a strong external metal shell. The refractory lining should never come into contact with the bath, being separated from the latter as long as the furnace is new at least, by means of carbon sides. During furnace operation anodic carbon will be consumed, but the level of liquid aluminum increases during electrolysis. The level of aluminum goes down immediately upon tapping. In order to maintain the proper voltage drop across the furnace, mechanism is provided for moving the anode up and down. The distance between carbon anode and liquid aluminum (called the "electrode spacing") is kept approximately constant and may vary in commercial aluminum furnaces from 3.5 to 9 cm., in different installations. The electrode spacing is one of the peculiarities of the conventional furnace, and its adjustment, at first sight, seems simple enough. When the alumina content in the bath drops below a certain value, the so-called anodic effect will take place and the furnace voltage will increase suddenly from 5 v. up to between 30 and 60 v. The crust (not shown) formed by freezing on top of the bath has to be broken up by mechanical means so that a new charge of alumina may be fed into the bath to restore normal operating conditions. The new charge of alumina is always put upon the crust in advance, both to pre-heat it and to better insulate the bath. The gases

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evolving from the bath surface (usually  $CO_2 + CO$ ) are removed, in a closed furnace, by means of a big exhaust system (not shown) that will also remove the volatile hydrocarbons caused by cokification of the fresh carbon paste fed from the top to the self-baking Soderberg anodes. If pre-baked anodes are used, the consumed anodic parts are taken out of the bath and replaced periodically by entirely new anodes.

In comparison with the progress attained in many other industries, only minor advances seem to have been made in the electrolysis of aluminum. Suffice it to say that efficiencies, electrical ones especially, are still surprisingly low (energy efficiency is less than 35%). The furnaces are still complicated and expensive, and their operating conditions are apt to change, not only from one furnace to another but, in time, also in the same furnace.

High unit consumption of power is one of the main drawbacks of present day furnaces. Overall power consumptions of less than 18 kwh. on direct current, and about 20 kwh. on alternating current, are hard to obtain even if optimum values of about 16 kwh. per kilogram aluminum can be attained for short lengths of time.

Assuming an electrolytic decomposition voltage requirement of between 1.3 and 1.7 v. and about 3000 ah. (the theoretical coulombs required per kg. of aluminum), theoretical per unit power consumption would be as much as 4 to 5 kwh. in the processes heretofore used. The average commercial ampere efficiency may be assumed to be between 80% and 90%. Thus the main source of waste can easily be traced back to the voltage drop which is necessary to send current through the furnaces heretofore used. As a matter of fact, these furnaces are usually operated at voltages between 4.5 and 6 v.

If commercial unit power consumption is to be kept within the above-mentioned limits, large anodic surfaces have to be used to afford running the furnaces at reduced current density (0.6 to 1.1 a./sq. cm. of horizontal anodic surface). On the other hand, if proper heat transfer conditions are to be maintained, very high amperages—from 30,000 to 50,000 a. or more—must be resorted to. Heretofore, the trend has been toward the adoption of very high currents in order to reduce installation cost and labor charges per unit production coat.

The problem of matching those high currents with the low voltages has been solved, as far as electric machinery is concerned, by connecting for instance one hundred furnaces in series and, at the same time, connecting two or more converters or rectifiers in parallel, the amperage thus fed being, as a rule, roughly constant.

The above-mentioned shortcomings of commercial aluminum furnaces, however, increase the unit costs of the electric machinery. Not only does high power consumption influence the cost of the product, but it also limits the potential output (during dry seasons or during industrial booms, for instance). The aluminum industry must today be confined to sides where plenty of electric power, at extremely low rates, is available. But the aluminum industry will not be able to keep abreast of paying increasing power rates while a gradual industrialization of the surrounding country takes place. For some decades past the industry has made but little progress as far as the basic principles of furnace construction are concerned. Today it is being threatened by having its vital power supply curtailed, as electric power rates tend to increase.

The extreme difficulty of the problems regarding conventional furnaces, both from a technological and from an economical point of view, can be realized if the following is taken into consideration. Even if further reduction of the voltage of the furnaces in commercial opera-

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tions were technically possible and economically convenient, other problems like thermal insulations, size, etc., would still have to be faced. It remains to be pointed out that the operating variables today involved in a commercial electrolytic aluminum furnace and which have a bearing on the process, are too many. It is actually very difficult to keep them constant, or nearly so, for sufficient lengths of time. The same holds true for what has been defined above as the "electrode spacing."

Of the above-mentioned operating variables, the three following interdependent groups are fundamentally important. They have always to be kept in mind by those with whom the responsibility of furnace operation rests.

(a) Temperature and bath-composition (as it may be affected by the conditions of the bottoms or of the anodes, etc.)

(b) Quality and labor attendance (feeding of alumina and carbon paste, adjustment of electrode spacing, abating the anode effect, bath corrections, setting the anodic stubs, etc.)

(c) Electrical variables such as irregular ampere distribution, current efficiency, etc.

It is an object of my invention to greatly minimize or eliminate all above-mentioned disadvantages by a radical change in furnace design as regards shape, arrangement, and capacity of the commercial cells, as well as in furnace operation.

Another object of my invention is to provide a new type of furnace having a very low unit consumption of power as well as of other items affecting the cost of the aluminum produced.

Other objects consist in limiting both direct and indirect installation costs, in achieving greater flexibility of production and enabling the design of plants having far apart limits of productive capacity. It will be no longer necessary to reach a huge productive capacity (e.g. 20,000-80,000 metric tons per year) in order that new plants according to the invention can be run on an economical basis. Still other objects will become apparent from the following description.

In brief, the present invention contemplates the provision of a new elemental furnace having an electrically consumable but stationary anode as well as a multiple furnace derived therefrom. The elemental furnace for electrolytic production of Al from  $Al_2O_3$  is characterized by its electrolytic cell having an inclined interspace between plane parallel faces of two stationary carbon block electrodes arranged side by side, one anodic and the other cathodic, into which there penetrate the metal conductors (nipples) carrying the current. The metal conductors or nipples may terminate respectively at equal distances from their electrode faces; and the lateral walls of the interspace, as well as all the other internal surfaces of the furnace, are lined with a non-conductive protective layer. Below the interspace there is provided a chamber for collecting the liquid aluminum formed by the electrolytic process, which chamber is provided with a tap hole. A chamber is provided above the interspace for the gases developed between the carbon electrodes during the electrolysis. The anodic electrode has an active layer built up from the bath side. By "stationary" electrodes or blocks are meant at least two electrodes or blocks every two points of which have a permanent distance relationship between each other while the spacing relationship between the electrodes or blocks may vary (e.g. because of increases of the electrode spacing on account of the anodic consumption). The term "carbon" is used herein to designate any carbonaceous electrode materials such as conventional prebaked carbon anodes or amorphous carbon agglomerates, as well as graphite, or compositions containing a prevailing proportion of the chemical element C or of said carbonaceous materials,

The multiple furnace is characterized by a plurality of analogous cells with lower metal (collecting) chambers and with upper gas chambers like those of said elemental

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furnace, the interspaces constituting said cells being formed by stationary carbon blocks, without metallic conductors, having cathodic and opposed built-up anodic faces, and aligned between two stationary blocks of nipped carbon arranged at the ends of the multiple furnace and acting as first anode and as last cathode respectively, for the two terminal cells.

These and other inventive characteristics are herein-after set forth more in detail.

#### Structural Features of Elementary Furnace

As schematically shown in FIG. 2, by way of example but not for limitation of my invention, the basic elements of the furnace for the electrolysis of aluminum according to my invention consist of the three following parts: a practically horizontal upper chamber 12 for gases; an inclined gap 13 below, which communicates with the upper chamber 12 and constitutes the electrolytic cell proper and has inclined conducting main walls; and a lower chamber 14 for the molten metal, which is located beneath the electrolytic cell proper and communicates with the cell, being preferably wider and shallower than the latter.

The cell is essentially made up of two electrodic carbons, one of which may be of graphite 15 and the other 16 of amorphous carbon agglomerates such as are manufactured by known methods for electrodic purposes. Both electrodes are planar on all sides. Both conducting faces slope downwards, and are parallel, of substantially the same area and face each other. Preferably the angle of inclination of electrode faces is between 15 and 45 degrees with respect to the vertical. The faces are usually less than 12 cm. apart, the gap between them being preferably from 4 to 8 cm. wide. As illustrated, the upper bath surface is equal to or greater than the area of the horizontal cross-section of the gap. Also the ratio between the measure of the gap's horizontal cross-section and the corresponding cell volume of the electrodic gap is less than  $0.10 \text{ cm.}^{-1}$ , and preferably less than  $0.03 \text{ cm.}^{-1}$ .

The current arrives at or starts from either carbon electrode through metallic stubs or nipples 17 of iron for example. The stubs are in intimate and extensive contact with the carbons. The ends of all stubs of each electrode are equally distant from the sloping surface which acts as anode (carbon 16) or, respectively, as cathode (carbon 15), the distance from said sloping surfaces being less than 50 cm. and preferably less than 20 cm. The number and size of the stubs 17 are such as to allow a most uniform current distribution and flux lines as parallel as possible across both electrodic surfaces.

The cell side-walls are made of one or more sufficiently bath resistant, electrical and thermal insulating materials. The inner layer 18 in contact with the molten cryolitic bath is preferably made of a solid material which has previously been fused or sintered at extremely high temperature (in order also that its porosity be reduced); it must resist the bath components and be a non-conductor of the current or at least a poor one. Linings of aluminum nitride, aluminum oxide, magnesia and other known inert materials the latter preferably fused or sintered, are suitable for those purposes. The walls, bottom and covering of the lower chamber for the metal, are entirely lined with said inert material. The lining is supported by a refractory layer 19 preferably of calcined magnesite. After this comes a heat-insulating layer containing, possibly, alumina in the form of fine dust 20. In the figure the terminal bars 21 are shown going through all these layers, but other suitable arrangements may be adopted.

Lower chamber 14 and cell 13 are of nearly the same length and communicate between them through a passage whose width is somewhat less than that eventually attained by the gap above. Wider passages may, however, be adopted.

The lower chamber 14 is appreciably wider and, as a rule, shallower than the cell between both carbon electrodes. The volumetric content of the lower chamber should preferably be about equal to or somewhat greater than the maximum capacity of the cell above.

In FIG. 2, the cross-section of the lower chamber is trapezoidally-shaped, but rectangular, rhombic shapes etc., or sections similar to those, may as well be adopted.

Since the furnace sidewalls are preferably higher than the carbon electrodes, an upper chamber on top of the electrolytic gap is formed, into which gases that develop during electrolysis will evolve.

The upper chamber 12 may be closed by means of an easily removable cover (not shown in FIGURE 2). This part of the furnace, in fact, has to be readily accessible for inspection, control and operation.

As a matter of fact, the cover, provided there is one, will insulate the upper chamber from the outside and allow for disposal, by known methods, of electrolytic gases in a more practical manner. To this end, the sidewalls of the upper chamber are provided with gas ducts (not shown in FIG. 2). Both upper and lower level surfaces etc. of the carbon electrodes are covered with the usual layer 18 of refractory and inert material such as previously described. Alumina may be spread over the top layer both to reduce heat dispersion and to pre-heat the charge which has to be added to the bath at regular intervals.

The lower chamber of the metal can be reached either from above, through the upper chamber and electrolytic cell, or from below, through one or two sub-horizontal tapping channels 22 whose orifices are placed under the head of molten aluminum 23 and the overlying cryolitic bath 24. Preferably, the volumetric capacity (for aluminum) of the lower chamber 14 is 0.8 to 1.5 times the maximum capacity of the cell gap.

#### Operation of Elementary Furnace

In the gap, which is filled with molten bath 24 and is between the sloping and parallel faces of the two carbons, electrolysis will take place. The bath is made up of cryolite, alumina and other well known bath-components (for instance cryolite aluminum fluoride, calcium fluoride, etc.). Carbon 16 which forms, so to say, the sloping roof of the cell, acts as the anode. The gases which develop from the bath against its sloped but planar face are conveyed by the latter out of the bath and into the upper chamber.

The second carbon 15 acts as the cathode; upon its inclined face aluminum produced will settle downwards in the form of little drops and/or a veil conveyed by gravity into the lower chamber 14 whose walls have little or preferably no conductivity.

The metal layer 23 which collects into the lower chamber 14 can be in electrical contact, or nearly so, with the cathodic surface of the cell by virtue of the stream of molten aluminum flowing from said surface without leading to trouble.

The molten bath may be partly covered by a thin crust of frozen bath (not shown in the figures). The alumina layer on top of the bath and/or of the electrodes for isolation or preheating, is not shown either.

For the sake of exemplification only, a description of one among many convenient ways to operate the present elementary furnace will now be made, no limitation of this invention, however, being meant.

If direct current, kept at constant value of 0.4 amp./sq. cm., or gradually decreasing from 0.5 to 0.3 amp./sq. cm., is sent through a furnace of this kind, whose electrodic faces are, for instance, initially about 4 cm. apart, a voltage drop of 2.8 to 3.6 v. between anodic and cathodic bars will occur, and a power consumption amounting to from 11 to 15 kwh. per kg. of aluminum produced will result.

The above figures apply to known baths for the elec-

trolysis of aluminum, operating at known temperatures, for instance between 930° C. and 1000° C., provided from 3 to 6 charges of alumina per day are made, the furnace being heated from the outside by means of an independent heat source (not shown in the drawing).

When the distance between electrodes is 4 cm., the metal chamber will just have been emptied of molten aluminum, or nearly so. Therefore, with the possible exception of a thin layer of aluminum on its bottom, both chamber and cell above are full of a new molten bath having, preferably, an alumina content of from 6% to 13%. As electrolysis goes on, metallic aluminum will be produced. Anodic carbon will also be consumed, as is known. The molten metal which collects on the bottom of the lower chamber will displace an equal volume of bath. As soon as the alumina content in the bath, drops below a certain percentage (e.g. 3% to 5% or less) a new alumina charge, that has previously been heated in the upper chamber or on the bathcrust, will be fed into it.

On the other hand, the good heat-insulation provided by a layer of alumina 8 to 10 centimeters thick will prevent both heat dissipation and a tendency of the bath to form thick crusts. Alumina feeding thus becomes an appreciably simpler operation.

The increased cell capacity due to the gradual anode consumption will be roughly compensated for by reason of the increased amount, and consequently higher level, of metallic aluminum which collects on the bottom of the lower chamber.

After a 4 to 5 day normal run, the distance between electrodes is no longer 4 cm. but about 8 cm. The bath level in the cell will be but slightly changed while the lower chamber will be about  $\frac{3}{4}$  full of metal.

The metal will be tapped as usual or through the spilling channel, whose orifice is kept sealed during operation by means of a refractory plug; or it may be lifted successively from above, until preferably only a thin layer of liquid aluminum is left upon the bottom of the lower chamber. The molten aluminum can also be removed by a suction pipe lowered down through the cell to the bottom of the lower chamber. The metal thus obtained will be subjected to known further treatments.

After tapping, the bath level, in the case of the example, will go down to about one half the cell depth. It is however advisable to expose the whole anodic surface by emptying the cell—but not the lower chamber—of the molten bath. The molten bath which, in a cell about 80 cm. wide and having a cell depth of 60 cm., amounts to some 20 to 22 liters, is preferably poured into a suitable well-insulated container, to be put back into the cell as soon as the anode has been integrated as explained below. To prevent freezing of this removed portion of the bath during the short interval of anodic integration, well-known devices such as heating ovens, etc., are resorted to.

The integration of the partially combusted anode is one of the operations strictly peculiar to the new cell. A regular plate 40 of electrodic carbon (see FIG. 5) less than 12 cm. thick, and in this case, about 4 cm. thick, and as wide as the anodic face to be covered, is applied against the consumed anode surface. Such a plate, rectangular for instance, and measuring 80 by 70 cm., is slipped into the gap between the electrodes forming the cell and made to adhere to the anode in such a way that the current will not meet, during cell operation, an excessive resistance in passing through the separating layer between old and new anode. For this purpose Soderberg paste 41, or graphitic dust and suitable cokifiable carbonaceous binding agent, is to be spread beforehand over the surface of the plate to be contacted.

Instead of integrating the anode by means of one single plate, it may be advisable to prepare, in advance, a number of rectangular strips, 42 (see FIG. 6), all equally thick, to be juxtaposed onto the anodic face. They may be as long as one dimension of the anodic face,

their width being a submultiple of the other dimension. By the expressions "one dimension" and "other dimension" it is intended to indicate that the strips need not be disposed in the direction shown in FIG. 6. If, for instance, the anodic face is 80 by 70 cm., one may employ five strips about 16 cm. by 70 cm. which will of course cover the face entirely. The single pieces are then pasted against the anodic surface alongside one another until the old anode has been entirely covered by the new one. Although the anode portions shown in FIGS. 5 and 6 are shown separately, it is to be understood that the above-described integrating procedure is carried out without removal of the electrodes from the furnace.

As soon as the anode has been renewed, a quantity of molten bath equal to that previously removed is poured gradually back into the cell, while the voltage is adjusted so that a normal heat-balance can be restored and baking of the thin layer of binding material forming the mechanical and electrical connection between the new and old anode, can be quickly completed. This having been done, the operating cycle of the cell is resumed.

A most evident feature of my invention is that in this type of cell every mechanical device for adjusting the electrode spacing has been abolished. On the contrary, electrode spacing in operating commercial furnaces is critical. Therefore it is kept constant within rather narrow limits ( $\pm \frac{1}{2}$  cm.). In other words, my electrodes are stationary; they are partially combusted or consumed during operation (while electrode spacing increases), and periodically and conveniently integrated "in situ."

Anodic faces, in the new cell, are virtually equal to cathodic faces while, in conventional cells, they are about 50% to 60% of the cathodic area. Thus, the electric resistance in the contact layer between anode and bath can be reduced and, at the same time, the necessary conditions are created in order that conventional anodic current densities may be considerably lowered. Apart from current density (amperage per unit cross-sectional area) and current (amperage), ohmic voltage drops in the anode can be reduced to very low figures on account of the metallic stubs being stationary. Consequently their layout may be easily planned for most convenient dimensions.

Cathodic voltage drop will also be considerably reduced since, in the new furnace, the cathodic electrode is no longer acting as bottom of the furnace.

The head of molten metal in known commercial furnaces is partially isolated from the cathodic carbon bottom by thick bath-crusts (rich in alumina and but slightly soluble), and by carbides (originating from irregular furnace operation, local superheatings), etc.

In order to be operated at lower anodic current densities than that now employed in commercial aluminum electrolysis, the above-described furnace may be conveniently heated by means of an auxiliary heat source, since heat developed by the passage of the current through the electrodes and bath will not, as a rule, be sufficient. In other words, the total external surface of the furnace may actually turn out to be too great for the small amount of kwh. or of calories/hr. to be dissipated. If heat dissipation is to be balanced with or reduced to the amount of available calories, one may operate with high current densities, or adequate insulation (either very bulky or particularly efficient) may be provided, or an additional heat source, other than the electrolytic current, may be resorted to. External heating may be used especially for small furnaces of the new type herein disclosed, e.g. for laboratory pots.

Moreover, as electrolysis is carried on, anodes are consumed and the gap between the parallel, sloped, conductive faces of the electrodes will become wider. The electric resistance of the bath will increase and, conse-

quently, more heat will ensue, provided current density remains constant. On the other hand, it is convenient to keep bath temperature within preestablished limits, determined by experience. For this purpose one may gradually reduce either the current or external heat, or resort to other methods.

The mode of operating the cell follows the conventional practice described in numerous publications, among which are the following:

(a) Chemical Engineers' Handbook, John H. Perry, editor, third ed., New York, etc.; McGraw-Hill Book Company Inc., 1950, page 1811, left column (text and Table 26);

(b) Encyclopedia of Chemical Technology edited by Kirk and Othmer, volume 1. The Interscience Encyclopedia, Inc., New York, 1947, page 602/603;

(c) Ullmanns Encyclopädie der technischen Chemie, 3rd edition, volume 3, Urban and Schwarzenberg, Munich, 1953, pages 343 and 349;

(d) "L'Alluminio" by Koelliker and Magnani, Ulrico Hoepli, Milan, 1930, page 186;

(e) "The Electrolytic Production of Aluminum" by Francis C. Frary, in "Journal of the Electrochemical Society," vol. 94, No. 1, July 1948, pages 32 and 34;

(f) Symposium sull'elettrolisi dell'alluminio-Programma e Memorie, Milan, October 12-13-14, 1953, page 27.

The temperatures employed are in the conventional range. For example, reference (a) describes a range of 900-1000° C., reference (b) an operating range just under 1000° C., reference (c) states that the temperature of the electrolyte should be between 930 to 950° C., reference (e) states that the electrolytic production of aluminum from a fused cryolite bath is carried out at a temperature between 950° and 1000° C.

The energy consumption, 11 to 15 kwh. per kg. of aluminum produced, is described above, and also the current and voltage drop. This is to be favorably compared with that of reference (a) which describes an energy consumption of 10 kw. hr./lb. Al, which is equivalent to 22 kw. hr./kg. Al, and also with that of reference (b) which states that the gross power requirement is about 10 kw. hr. per lb. of aluminum.

The concentration of  $Al_2O_3$  in the bath is also conventional. We have stated, above, that a new alumina charge is fed in when the alumina content of the bath drops below a certain percentage, such as 3 to 5 percent. This is common practice, and is described in references (a), (b), (c) and (e).

The bath composition is also conventional. As stated above, it comprises molten cryolite containing dissolved alumina. It is common practice to add small amounts of other substances to increase current efficiency. Various bath compositions are disclosed in references (a), (b), (c), (d), (e), and (f).

#### Multiple Furnace With Inclined Conducting Walls

My new multiple furnace shown in FIGS. 1, 3, 4 and 7 which constitutes one variant of the present invention also solves, in a surprisingly practical and efficient way, the above-mentioned problems.

FIGS. 3 and 4 show a longitudinal section in a vertical plane and a plan view, respectively, of my multiple furnace such as it may preferably, but not solely, be built for industrial purposes. The multiple furnace may be schematically represented as a set of elementary furnaces, or elements of FIG. 2, from which refractory and insulating head walls together with their metallic conductors (bars, nipples or stubs) have been removed. Only the two ends of the multiple furnace, of course, maintain said insulating and refractory head walls with the metallic fittings conducting the current.

In FIG. 3 are shown the upper gas-chambers 12, the electrolytic gaps 13 and the lower metal-chambers 14. Near one end of the elongated multiple furnace the cathodic carbon 15 and, at the opposite end, the anodic

carbon 16 are shown, both carbons being connected with their respective terminal bars 21 by means of iron stubs 17. The cover is fragmentarily indicated at 29 in FIG. 1. The gas outlets are shown at 30.

The bath-resistant and insulating layer 18 will, here also, line the inside walls of the lower chambers as well as the sides of the cells.

Carbon blocks 27 spaced between the nipple-fitted end electrodes are nippleless themselves and will act as anodes on their sloping surfaces facing the cathodic electrode 15 and as cathodes on their other sloping, and parallel surface, facing the anode 16.

Graphite, as is known, is more expensive than carbon agglomerates for electrodes, is a better electrical conductor, will offer a greater resistance to oxidizing gases, etc. On the other hand, it requires higher decomposition voltage when in contact with the electrolytic bath and, consequently, a higher unit power consumption per kg. of produced aluminum. For these reasons, the intermediate electrodes 27, instead of being carbon only, may be entirely of graphite or partly of graphite, viz. graphite-covered as far as the cathodic portion is concerned.

The dotted line 25 represents the contact surface between the old anode and the newly applied one. The anode surfaces are renewed "in situ" when necessary as described above in connection with FIGS. 5 and 6.

Both the refractory layer 20, preferably of calcinated magnesite, and the insulating layer 19, preferably containing alumina, are enclosed in an iron casing 28.

The channels 22 at the bottom of lower chambers are normally plugged shut with refractory material of known composition. Through these channels the aluminum 23 which collects in a layer underneath the liquid bath 24, may be tapped.

The lower chambers are separated from one another by means of bathproof little partitions 26 which are entirely made up of, or simply lined with, the above-mentioned bath and metal-resistant material 18.

Nothing need be added to what has been said above as to the shape and dimensions of the lower chambers as well as the electrolytic gaps or cells.

In FIG. 3 neither a cover, nor exhaust ducts for electrolytic gases and for vapours which develop when the anodic binding material is baked, nor alumina layers being preheated, are shown. In FIG. 7 the upper chamber of an open multiple furnace is shown. Optional, partition walls dividing said chamber into a number of individual compartments, one for each cell, are not shown in the drawings, said partitions resting on the electrodic carbons and joining obviously both sidewalls of the multiple furnace.

#### *Operation of the Multiple Unit Furnace*

In order to keep nearly constant the total heat which is being generated in the furnace, so that balanced conditions with respect to the heat externally dissipated by the multiple furnace may be established, maintaining the temperature of the individual baths within the limits required in practice, the sum of the gap widths might, for instance, be kept approximately constant.

In other words, running for instance a 14 element multiple furnace, one may operate in such a way that the gap-width of each cell differs from that of the one or the two adjacent cells. In most cases it is however advisable, when the current intensity is kept constant, that the sum of all the individual gap-widths be kept rather closely to a predetermined constant average value, not affected by time.

In particular, in the cells of a multi-cell furnace as hereinbefore described, the process may advantageously be carried out, according to this invention, with such a succession of respective electrolysis periods that the stages of electrolysis in adjacent cells are substantially different from each other.

The way each element, as well as the multiple furnace as a whole, operates, is similar to the operation of the elementary furnace previously described. In comparison with the latter, however, notable advantages are attained:

- 5 The daily metal output is many times as much as that of the elementary cell, in fact it may go up, for instance, from between 13 to 14 to between 180 to 200 kg. of aluminum in 24 hours if a 14-element multiple furnace having electrodes of the size stated above is employed. Moreover, a further reduction of power consumption will be obtained. The unit consumption of from 11 to 15 kwh./kg. of aluminum goes down to 9 to 13 kwh./kg. of aluminum, owing to the fact that the ohmic voltage drops in the nipples and in their contact with the two-end carbons are subdivided over a greater number of elementary furnaces, and probably owing also to other reasons.

For instance, when the operation is carried out with substantially equal anodic and cathodic current densities less than 0.8 amp./sq. cm., and preferably less than 0.5 amp./sq. cm., the resulting voltage drops in the cells having the nipples electrodes are less than 4.5 volts and 3.8 volts, respectively; and the voltage drops in the intermediate cells are less than 4.0 volts and 3.3 volts, respectively. Under these conditions, the power consumption drops to below 16 kwh., preferably below 13 kwh. per kg. of metal output. In spite of such improved power economy, additional heat is no longer required for securing a regulated run because, in the multiple furnace, the amount of power available for heat-dissipation per square meter of outside surface has considerably increased. It is possible to operate at a nearly constant amperage without upsetting the heat-balance of the single cells. Since the cells are separated from each other by means of carbon and/or graphite plates of only few decimeters thickness and consequently fairly good heat-conductors, they will act as temperature self-regulators whenever the temperature in individual cells tends to increase or decrease getting off predetermined temperature limits.

Both the multiple furnace and its related process attain the double advantage of bringing ohmic drops in the anodes as well as in the cathodes down to extremely low figures, with consequent very low kwh. consumption per kg. of aluminum produced, and enabling operation with anodic current densities nearly halved as compared with the commercial densities used in the aluminum industry. This is due to the particular arrangements of my multiple furnace, as well as the small area of the open bath surface. These advantages, moreover, are achieved without resorting to excessive furnace dimensions. Thus it will be possible to keep well within the bounds set both by efficient heat-insulation and by an economic construction cost. Overall dimensions as well as cost of the multiple furnace, as referred to daily aluminum output, will thus become a fraction of the corresponding values of the elementary furnace.

#### *Main Differentiating Features of the Present Invention as Compared With Conventional Known Furnaces*

- 60 (1) The usual mechanical device for adjusting the distance between carbon anode and liquid cathodic metal is dispensed with in the present invention.

*Advantages.*—Constructional as well as operational simplification of the furnace and reduction of costs. Elimination of numerous wrong, hence harmful, adjustments on the part of attendant personnel or due to inaccurate measurement of the metallic level, resulting from the indefinite and not well defined layer of metallic fogs over it, resulting from bottom irregularities, resulting from the metallic surface being more or less convex, resulting from periodical metal waves, etc.

- (2) Minimum area of uncovered bath: Such areas, if referred to output/24 hrs., are several times larger in conventional known furnaces.

75 *Advantages.*—The possibility of reducing heat-dissipa-

tion to a minimum with an open bath as well as with an alumina-covered bath. The possibility of better insulating the bath with a thicker layer at equal charges. Less work to be done by the operators attending the furnace.

(3) Smaller dissipating solid surfaces: The new multiple furnace possesses such structural and constructional features as to cut heat-losses down with respect to conventional furnaces, no overly-thick outer heat insulation layers being needed to achieve this end. My cell will dissipate, through upper anodic surfaces, about half as much heat, for instance, as conventional ones (not even considering dissipation from the nipples, etc.).

*Advantages.*—The possibility of operating at lower total and unit amperages, reduced kwh./kg. Al consumption, greater regularity in operation, etc.

(4) The alumina charged, in the new furnace, will usually be higher than 10 grams per square centimeter of open bath surface and may be even higher than 20 gr./sq. cm. In commercial furnaces, the layer of alumina is usually less than 10 gr./sq. cm. thick. As already described, this increased thickness will favorably effect heat insulation, without, on the other hand, the increased alumina charge per bath surface unit causing difficulties. As a matter of fact the baths in conventional known cells are not deeper than 30 to 40 cm. for constructional, operating and cost reasons. My furnace can easily attain bath-depths of 50 cm. or more, without consideration of the bath-layer in the lower chamber, which varies, for instance, between 10 to 30 cm. in depth.

The downward velocity of alumina must also be taken into consideration. It is low enough, as a rule (a few centimeters per minute), so that the charge may dissolve in the bath before reaching the metal layers and settle onto the cell-bottom of the known types of furnaces.

*Advantages.*—Incrustation of the carbon cathode, with consequent troubles that affect commercial pots, is no longer possible in the new furnace, even though bigger alumina charges are being fed. Even if a limited amount of alumina should settle on the cathode, it would be easily dissolved by the bath, and, not being submerged in the bottom layer of molten aluminum, no harm would be done.

(5) Another feature of the new cell consists in the fact that the electrolytic gases, developing from a smaller bath-surface (per kg. of Al output), are easier to dispose of, and their flow outwards is intensive enough to prevent leakage into the cell, during electrolysis, of the air.

(6) In commercial furnaces the current, in its substantially vertical direction of flow, will meet several perpendicular layers of different resistivity (anodic carbon, bath, molten aluminum, cathodic carbon). In some layers and particularly in contact surfaces between different layers, resistivity will vary from point to point, thus causing non-uniform current distribution. Local superheated areas, as well as physical and chemical alterations, will result which will intensify the above-mentioned phenomenon and eventually cause a lower current efficiency, higher voltage drop, and, consequently, higher unit consumptions, especially kwh. required per kg. of Al produced.

All the foregoing undesirable effects do not occur in the new cell; a lower anodic current density, that now equals the cathodic density, is achieved; the possibility of keeping both temperature and solving-bath composition well within the limits set by experience is possible; and an easy control over cathodic surface and other items, inherent to the particular construction and way of operating of my cell, result in the necessary conditions for a virtually uniform current distribution and flow through layers of resistivity varying from one to another but well-defined and almost constant in each.

This is one of the most important advantages afforded by the present invention.

(7) Power consumption, in the multiple furnace, is surprisingly low; from 9 to 13 kwh. per kg. of Al output.

No industrial furnace has, up to now, attained such low current consumption values. Such a result has been obtained by solving the following three main problems on which the unit consumption can be said to depend:

(a) Abating the voltage drop by means of bigger anodes, more uniform current density, reduction of the over-voltage at the anode, as well as of the anodic and cathodic voltage-drops.

(b) Maintaining ampere efficiency by means of appropriate alumina feeding, sufficient cell proportioning with a view to limiting losses through side-walls, insulating the metal produced in each cell from that of the adjoining cells, a more uniform electrical flux, etc. Cells with multiple bipolar electrodes which can be shifted in the same cell and which date back to the past century can be run at low voltage-drops but they cannot be operated with satisfactory current efficiencies, owing both to a considerable amount of current being by-passed along the sides of the mobile electrodes and to the circumstance that the continuous layer of molten metal collecting on the bottom acts for the greater part of the current, as an easy bridge between the anode and the cathode located at the ends of the cell with only two bath-crossings. Cells of that kind have, moreover, numerous other functional shortcomings.

(c) A stationary, practical and simple arrangement that allows a very good heat-insulation of the furnace.

(8) The primary cost of the new multiple furnace with inclined conducting walls is lower than the cost of conventional horizontal furnaces of the same output capacity.

(9) Readjustment of the volt/ampere ratio which, in the big commercial 50,000 amp. units is as low as 1/10,000 while, for instance in my multiple furnace having 14 cells and being operated at 2000 amp. the ratio is about 2/100. This results in the above-mentioned advantages as regards the conversion plant, the current-carrying bus-bars, the reduction of the minimum plant capacity limit, etc.

(10) The sloping anodic face will more easily convey electrolytic gases upwardly. This is another important advantage over level-layers furnaces. Moreover, the commercial furnaces have to be operated at even higher anodic current densities with consequent considerable anodic overvoltages.

(11) The sloping cathodic face will help to convey molten aluminum downwards; a thin liquid metal film at most, will build up over it, but in no case will a layer having a thickness measured in centimeter cover the cathode.

Although some embodiments of the invention have been shown and described, it will be apparent to those skilled in the art that various modifications may be made therein without departing from the spirit of the invention or the scope of the appended claims:

I claim:

1. A series multicell furnace for fused salt electrolysis of compounds reacting by electrolysis with consumable anodes, comprising more than two stationary carbon electrodes, including two terminal carbon electrodes and at least one intermediate bi-polar carbon electrode defining a plurality of individual electrolysis cells in series, each cell having electrodic surfaces inclined to the vertical and to the horizontal and facing each other, substantially coextensive and substantially parallel to each other to form a slanting laterally confined electrolysis gap, the inclined anode surfaces facing downwardly, and an individual collecting chamber below each gap and communicating therewith, the chambers being separated by electrically insulating partition wall means, and current supply means connected with the two terminal electrodes.

2. A series multicell furnace for fused salt electrolysis of aluminum compounds reacting with consumable anodes, comprising a stationary carbon end anode and a carbon

end cathode and having respective substantially congruent and substantially parallel electrodic surfaces inclined to the vertical and defining an intermediate space, at least one stationary intermediate bipolar carbon electrode member disposed in said space, each of said intermediate electrode members having a pair of faces substantially parallel to said surfaces, said anode and said cathode defining together with said intermediate electrodes a plurality of inclined laterally confined gaps adapted to receive electrolyte, the inclined anode surface facing downwardly, a substantially inert, current insulating and heat resistant container housing said anode and said cathode and said intermediate electrode members, said housing providing a plurality of lower insulated chambers, an individual one thereof being below each of said plurality of gaps and communicating with respective ones thereof for receiving molten aluminum, substantially inert heat-resistant and current insulating partition means in the lower part of said housing supporting the lower end of each of the bipolar electrodes and separating the lower portions of the cells from one another to define individual electrolytic cells and to provide said plurality of insulated chambers, and means for applying a source of current only to said anode and said cathode, the end anode, cathode, intermediate carbon electrode, and gaps being in electrical series.

3. In a process for the production of aluminum by fused salt electrolysis of a compound reacting by electrolysis with a consumable anode, in a furnace cell having stationary carbon electrodes forming an inclined laterally confined electrodic gap containing electrolyte, the gap being defined between a downwardly facing inclined anode surface of the anode and an upwardly facing inclined cathode surface of the cathode, the improvement which comprises supplying electric current in substantially uniform distribution over the surfaces of the anode and of the cathode defining said gap, with substantially the same anodic and cathodic current densities on said surfaces, and feeding said compound into said furnace cell, permitting the resulting aluminum as it is forming to drain from and collect beneath said electrodic gap in a heat-retentive chamber while the evolving gases rise out of the gap, continuing this operation until the gap spacing of the stationary electrodes increases from initial values to predetermined maximum values, thereafter tapping the collected aluminum and restoring, in situ from the bath-side, the anodic electrode on its active surface to such dimensions as to reestablish said initial values, and repeating the electrolysis.

4. In a process for the production of aluminum by fused salt electrolysis of a compound reacting by electrolysis with a consumable anode, in a furnace cell having stationary carbon electrodes forming an inclined laterally confined electrodic gap containing electrolyte, the gap being defined between a downwardly facing inclined anode surface of the anode and an upwardly facing inclined cathode surface of the cathode, the improvement which comprises feeding said compound into said furnace cell, permitting the resulting aluminum as it is forming to drain from and collect beneath said electrodic gap in a heat retentive container while the evolving gases rise out of the gap, containing this operation until the gap spacing of the stationary electrodes increases from initial values to predetermined maximum values, thereafter tapping the collected aluminum and draining the electrolyte from the gap, renewing said anodic carbon by securing new anodic surface portions thereagainst, to restore, in situ from the bath-side, the anodic electrode on its active surface to such dimensions as to reestablish said initial gap spacings, refilling said gap with electrolyte and continually repeating the above defined steps.

5. In a process for the production of aluminum by fused salt electrolysis of aluminum oxide reacting by electrolysis with a consumable anode, which comprises feeding said aluminum oxide during electrolysis into a

furnace cell comprising a gap inclined to the vertical, the gap being defined by a downwardly facing stationary anodic carbon electrode and an upwardly facing cathodic carbon electrode and containing fused cryolite as electrolyte, the improvement comprising collecting below the gap the molten aluminum flowing as it is forming from the cathodic electrode, gradually diminishing the current intensity passing through said fixed electrodes as the gap spacing between said electrodes increases due to the electrolytic oxidation of said anodic carbon, periodically draining the collected aluminum and draining the electrolyte from the gap, renewing said anodic carbon, in situ from the bath-side, by securing a new anodic surface portion thereagainst after said electrolyte is drained, refilling said gap with cryolite electrolyte and continually repeating the above-defined steps.

6. The process of claim 4 in which the compound is alumina and the electrolyte is cryolite.

7. A series multi-cell furnace for fused salt electrolysis, of aluminum compounds reacting with consumable anodes, comprising a stationary carbon end anode and a carbon end-cathode having respective substantially parallel electrodic surfaces inclined with respect to the vertical and defining an intermediate space, said end-anode surface facing downwardly and said end-cathode surface upwardly at least one stationary intermediate carbon electrode member disposed in said space, each of said intermediate electrode members having a pair of opposed, substantially parallel faces aligned parallel with respect to said surfaces, said end anode and said end cathode defining together with said intermediate electrodes a plurality of inclined laterally confined gaps adapted to receive electrolyte, the end anode, cathode, intermediate carbon electrode, and gaps being in electrical series, a plurality of individual, electrically insulated chambers, one below each of said gaps and each communicating with a respective one thereof for receiving molten aluminum separately from each gap, and means for applying a source of current to said end anode and said end cathode.

8. The process for the production of aluminum by fused salt electrolysis of a compound reacting by electrolysis with a consumable anode, particularly of  $Al_2O_3$ , which comprises feeding said compound during electrolysis into a furnace cell comprising a vertically inclined gap defined by an upper stationary anodic carbon electrode and a lower cathodic carbon electrode and containing a fused salt electrolyte, particularly cryolite, collecting below the gap the molten aluminum flowing as it is forming from the cathodic electrode, gradually diminishing the current intensity passing through said fixed electrodes as the gap spacing between said electrodes increases due to the electrolytic oxidation of said anodic carbon, periodically draining the collected aluminum and draining the electrolyte from the gap, renewing said anodic carbon, in situ from the bath-side, by securing new anodic surface portion thereagainst while said electrolyte is drained, refilling said gap with cryolitic electrolyte and continually repeating the above-defined steps.

9. In the process according to claim 4, said restoring of the stationary anodic electrode comprising the steps of fixing a carbon plate against the anodic surface by means of a paste becoming electrically conductive under the action of heat, returning the fused bath to the cell, and again setting said cell into operation whereupon the ohmic heat developed by current will complete the coking of said paste to a solid layer which unifies said integrated anode.

10. In the process according to claim 4, said restoring of the stationary anodic electrode comprising the steps of fixing a plurality of planar strips of carbon side-by-side against the anodic surface by means of a paste becoming electrically conductive under the action of heat returning the fused bath to the cell, and finally setting

said cell into operation whereupon the ohmic heat developed by current will complete the cokification of said paste to a solid layer which unifies said integrated anode.

11. The process according to claim 3, wherein electrolysis is carried out in a furnace comprising a plurality of cells formed by at least one stationary intermediate bipolar having a graphite cathode portion carbon electrode and by a stationary nipped end carbon anode and a stationary nipped end graphite cathode defining the respective gaps, with such a succession of respective electrolysis periods that the stages of electrolysis in adjacent cells are substantially different from each other.

12. The process of claim 11, wherein the sum of the gap widths of the cells of the furnace is kept nearly constant in time, said furnace being operated with substantially constant current intensity.

13. The process of claim 3, for the production of aluminum by electrolysis of  $Al_2O_3$  in a fused cryolitic bath, wherein the  $Al_2O_3$  to be fed to the furnace cell is preheated by the furnace heat in layers higher than 10 cm. charged above the bath surface.

14. The furnace of claim 7, wherein said carbon at least of the end-cathode and cathodic faces of the intermediate electrode members in graphite.

15. A series multicell furnace as defined in claim 2, wherein said housing and partition means are made, at least in a lining layer thereof, of solid magnesium oxide pre-treated at least to sintering temperature.

16. The process for the production of a metal by fused salt electrolysis of a compound reacting by electrolysis with a consumable anode, in a furnace cell having stationary electrodes forming an inclined laterally confined electrodic gap containing electrolyte, which comprises supplying electric current in substantially uniform distribution, respectively, over the surfaces of the anode and of the cathode defining said gap, feeding said compound into said furnace cell, removing from the gap the resulting metal by specific gravity difference, and restoring the anodic electrode in situ, from the bath side.

17. A multicell furnace for metal production from its oxide by a fused salt bath electrolysis in which anodic carbon is consumed, comprising a housing containing electrode structures comprising a stationary anode terminal element and a stationary cathode terminal element spaced apart in said housing, and at least one bipolar electrode structure stationed in said furnace between and spaced from said anode and cathode terminal elements, said bipolar electrode structure having opposite anode and stationary cathode polar faces, the electrode structures providing pairs of opposite bath-facing cathodic and anodic surfaces, each pair taken together with an intervening electrolysis gap forming a cell, there being at least two of said gaps providing at least two of said cells, the gaps extending generally upwardly-downwardly, means for passing electric current serially through the electrode structures and intervening electrolysis gaps, and consequently serially through said cells, means comprising part of said electrode structures and forming a renewal structure of carbonaceous material consumable in the electrolysis positioned adjacent individual anode faces of said electrode structures, the renewal structure providing a generally downwardly-facing, bath-facing anodic face extending at an angle to the vertical, the furnace having a lower wall and providing lower electrically insulating partitioning means extending from the bipolar electrode structure to the lower wall to provide separate chambers for reception of metal formed in the electrolysis individually form each cell, each chamber having a tap for individual draining of the metal.

18. A multicell furnace for production of aluminum by fused salt bath electrolysis of alumina, comprising a housing containing electrode structures comprising a stationary anode terminal element and a stationary cathode terminal element spaced apart in said housing, and at least one bipolar electrode structure stationed in said fur-

nace between and spaced from said anode and cathode terminal elements, said bipolar electrode structure having opposite anode and stationary cathode polar faces, the electrode structures providing pairs of opposite bath-facing cathodic and anodic surfaces, each pair taken together with an intervening electrolysis gap forming an individual, laterally confined cell, there being at least two of said gaps providing at least two of said cells, the gaps extending generally upwardly-downwardly, means for passing electric current serially through the electrode structures and intervening electrolysis gaps, and consequently serially through said cells, means comprising part of said electrode structures and forming a renewal structure of carbonaceous material consumable in the electrolysis positioned adjacent individual anode faces of said electrode structures, the renewal structure providing a generally downwardly-facing, bath-facing anodic face extending at an angle to the vertical, the renewal structure having a thickness less than the maximum gap width whereby it may be replaced while the said stationary electrodes remain in place, the furnace having a lower wall and providing lower electrically insulating partitioning means supporting the bipolar electrode and extending therefrom to the lower wall to provide separate chambers for reception of metal formed in the electrolysis individually from each cell, each chamber having a tap for individual draining of the aluminum.

19. In a process of producing aluminum by electrolysis of alumina in a fused salt bath furnace, in which an electric current is passed serially through a solid anodic surface, an intervening electrolysis gap of fused bath, through an intervening intermediate, bipolar solid electrode providing opposite anode and stationary cathode polar surfaces, a second electrolysis gap of said bath, and eventually through a stationary cathodic surface, the anodic polar surfaces being consumable in the electrolysis, the improvement comprising collecting and tapping the resulting aluminum below each electrolysis gap, said collecting and tapping from each electrolysis gap being separate from the collecting and tapping below adjacent electrolysis gaps, and restoring the anodic surface adjoining each gap individually by placing a renewal means of carbonaceous material consumable in the electrolysis adjacent the respective anode surface, the latter remaining stationary during the renewal, the gap during the renewal being at least sufficiently wide to admit the renewal means.

20. In a process of producing aluminum by electrolysis of alumina in a fused salt bath in which an electric current is passed serially through a solid anodic surface, an intervening electrolysis gap of fused bath, through an intervening intermediate, bipolar solid electrode providing opposite anode and stationary cathode polar surfaces, a second electrolysis gap of said bath, and eventually through a stationary cathodic surface, the anodic surfaces being consumable in the electrolysis, in which process the electrode spacing varies periodically between predetermined limits, the improvement comprising collecting and tapping the resulting aluminum separately below each electrolysis gap, said collecting and tapping from each electrolysis gap being separate from the collecting and tapping below adjacent electrolysis gaps, periodically restoring the anodic surface adjoining each gap individually by placing a renewal means forming a structure of carbonaceous material consumable in the electrolysis adjacent the respective anode surface, the latter remaining fixed in position during the renewal, the renewal means having a thickness less than the maximum gap width to facilitate the renewal.

21. In a process for the production of aluminum by fused salt electrolysis of a compound reacting by electrolysis with a consumable anode, in a furnace cell having stationary carbon electrodes forming an inclined laterally confined electrodic gap containing electrolyte, the gap being defined between a downwardly facing inclined

anode surface of the anode and an upwardly facing inclined cathode surface of the cathode, the improvement which comprises feeding said compound into said furnace cell, permitting the resulting aluminum as it is forming to drain from and collect beneath said electrodic gap in a heat-retentive chamber while the evolving gases rise out of the gap, continuing this operation until the gap spacing of the stationary electrodes increases from initial values to predetermined maximum values, thereafter tapping the collected aluminum and restoring, in situ from the bath-side, the anodic electrode on its active surface to such dimensions as to reestablish said initial values, and repeating the electrolysis, the compound being alumina, the electrolyte being cryolite.

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