Aluminum or magnesium is produced electrolytically from the light metal chloride dissolved in molten halide of higher decomposition potential, in a cell which includes at least two opposed electrodes providing at least one inter-electrode space therebetween, while maintaining an effective anode-cathode distance less than % inch.
LIGHT METAL PRODUCTION

BACKGROUND OF THE INVENTION

This invention relates to a process for producing aluminum or magnesium from the light metal chloride dissolved in a molten halide, by electrolyzing the bath in a monopolar or bipolar cell employing unusually close anode-cathode spacing.

Commercial production of aluminum is presently effected by electrolyzing a bath of alumina dissolved in a molten halide composed essentially of sodium fluoride, aluminum fluoride and calcium fluoride. In this process, commonly known as the Hall process, carbon anodes are employed which are gradually consumed by the oxygen produced on the anode surfaces, and this represents a considerable economic loss attendant upon such operations. The bath is maintained at temperatures over 900° C. Power efficiency is limited by the practical necessity of maintaining an effective anode-cathode distance through the bath of at least about ¼ inches (from carbon anode to the underlying layer of molten aluminum which is the effective cathode surface in the Hall process). This spacing is required in order to reduce intermittent shorting and loss of current efficiency caused by undulations of the aluminum layer induced by magnetic fields.

The present invention is directed particularly to the use of aluminum chloride as the source material for aluminum metal, although it also has application to use of magnesium chloride as a source material for magnesium.

Electrolytic reduction of aluminum chloride, for example, does not produce oxygen, and since it may be electrolyzed at appreciably lower temperatures than alumina, two inherent economic limitations of the conventional Hall process are avoided. Although the possibilities of achieving these and other advantages attendant the use of aluminum chloride as a source material in the electrolytic production of aluminum have long been recognized and avidly sought, commercial realization thereof has been precluded by numerous other unsolved problems attendant upon the use of this source material and the concurrent production of chlorine in such a process.

Among the problems to be overcome by a commercially viable process for producing aluminum from aluminum chloride by electrolysis are the achievement of high power efficiency, desirably through both relatively high current efficiency and relatively low voltage. The prior art has recognized the desirability of achieving some of the advantages hereinbefore mentioned, especially through the use of cells employing bipolar electrodes, but without recognition of the unexpectedly high current efficiency obtainable with the use of effective anode-cathode spacings less than ¼ inch.

SUMMARY OF THE INVENTION

This invention may be briefly described as a process for the electrolytic production of light metal from the light metal chloride in a cell which includes at least two opposed electrodes providing at least one inter-electrode space therebetween, particularly one which includes an anode, at least one intermediate bipolar electrode, and a cathode in superimposed, spaced relationship defining a plurality of inter-electrode spaces therebetween. The electrodes may be made of any inert highly conducting material and are conveniently carbonaceous. Broadly, the process comprises electrolyzing bath composed essentially of at least one light metal chloride dissolved in molten halide of higher decomposition potential in at least one inter-electrode space, producing anode product which is primarily chlorine on the anode surface thereof and light metal on the cathode surface thereof. The bath is usually one containing alkali metal halide which may result in the production of some reduced alkali metal also. With the advantages discussed hereinafter, the effective anode-cathode distance in the inter-electrode space is maintained at less than ¼ inch, preferably less than ¼ inch, and this is found to be a unique factor in obtaining such advantages. When the anode-cathode spacing is so maintained, the anode product, including some of the chlorine produced, is dissolved and dispersed in the bath flowing through the narrow, extended inter-electrode space, thus causing the anode product to contact the effective cathode surface. The process involves establishing and maintaining a flow of bath through each inter-electrode space, the flow preferably being such that it will supply fresh bath to each such space, and sweep depleted bath, chlorine and metal therewith, out of each such space. Desirably the bath for producing aluminum contains between about 1% and 10 percent by weight aluminum chloride along with alkali metal chlorides. For producing magnesium the bath preferably contains between about 1% and 20 percent magnesium chloride. Additional light metal chloride may be incrementally or continuously fed into the depleted bath, and the bath as so replenished may be continuously re-cycled through the inter-electrode space or spaces. The temperature of the bath is desirably above the solids, and preferably above the liquidus, of the light metal produced.

Among the advantages of the invention, whether the process is performed with or without accumulation of light metal as a pool or as substantial droplets or the like on the cathode surfaces, is the discovery that the employment of a low effective anode-cathode spacing, i.e. an anode-cathode distance, less than ¼ inch, preferably less than ¼ inch, means that the process operates not only with a consequent reduced cell resistance, but surprisingly without an economically defeating re-chlorination of the light metal. This means that current efficiency is unexpectedly high. It also means less heat generation and improved voltage efficiency, with attendant economic advantages, especially in large multi-electrode cells. Accumulation of metal on the cathode surfaces may be permitted, in which case the effective anode-cathode distance is the distance from anode to light metal layer. The anode product, which is primarily chlorine, will pervade the bath, and much of the chlorine will rise and continually pass out of the inter-electrode spaces. The anode product prevailing the bath, however, continually comes into contact with the effective cathode surface and thereby both flux the aluminum or magnesium and inhibit alkali metal reaction with a carbonaceous cathode surface.

It is notable that the opportunity herein afforded to employ close anode-cathode spacing surprisingly leads to an overall improvement in current efficiency, despite the close proximity of chlorine and light metal confined in narrow inter-electrode spaces of substantial extent. As suggested above, the anode product in the bath has access to the cathode surface and fluxes the aluminum, despite the presence of oxide impurities in
the bath, and promotes molten metal particle coalescence, and surprisingly does so without economically defeating re-chlorination of the metal. Also, surprisingly, it has been observed that, with the employment of close anode-cathode spacing, less than \( \frac{3}{8} \) inch and preferably less than \( \frac{1}{2} \) inch, reaction with carbonaceous cathode material that is otherwise caused by the presence in the bath of reduced alkali metal especially sodium or potassium, is distinctly minimized. Still further advantages flow from the low heat generated and the reduced operating temperatures that may be employed.

While achieving the various advantages referred to above may not alone render the electrolytic reduction of aluminum from aluminum chloride, for example, a commercially viable reality, the advances herein disclosed provide an answer to fundamental problems of long standing which have impeded progress in this field and, as such, represent marked contributions to the desired attainment of the ultimate and long standing objective of providing an economically feasible and commercially viable process, especially for the production of aluminum from aluminum chloride.

**BRIEF DESCRIPTION OF DRAWINGS**

In the accompanying drawings, FIG. 1 is a sectional elevation of a cell for producing light metal in accordance with the invention, the cell having a plurality of electrodes in superimposed relationship in the cell cavity.

FIG. 2 is an enlarged view taken along the line II—II of FIG. 1, showing the underside (anode surface) of a bipolar electrode employed in the cell of FIG. 1.

FIG. 3 is a vertical section of the bipolar electrode shown in FIG. 2, the section being taken on the line III—III of FIG. 2.

FIG. 4 is a left end view of the bipolar electrode shown in FIG. 2, the orientation thereof being shown by the line IV—IV in FIG. 2.

**DETAILED DESCRIPTION OF THE INVENTION**

**Cell Structure**

A preferred cell structure for producing light metal in accordance with the principles of the invention is illustrated in the drawings. Referring particularly to FIG. 1, the cell illustrated includes an outer steel shell 1, which is lined with refractory sidewall and end wall brick 3, made of thermally insulating, electrically non-conductive material which is resistant to molten alkali metal and light metal chloride-containing halide bath and the decomposition products thereof. The cell cavity accommodates a sump 4 in the lower portion for collecting the metal produced. The sump bottom 5 and walls 6 are preferably made of graphite. The cell cavity also accommodates a bath reservoir 7 in its upper zone. The cell is enclosed by a refractory roof 8, and a lid 9. A first port 10, extending through the lid 9 and roof 8, provides for insertion of a vacuum tapping tube down into the sump 4, through an internal passage to be described later, for removing molten metal. A second port 11 provides inlet means for feeding the light metal chloride into the bath. A third port 12 provides outlet means for venting chlorine.

Within the cell cavity are a plurality of plate-like electrodes which include an upper terminal anode 14, desirably an appreciable number of bipolar electrodes 15 (four being shown), and a lower terminal cathode 16, all of carbonaceous material, preferably of graphitic. These electrodes are arranged in superimposed relation, with each electrode preferably being horizontally disposed within a vertical stack. Sloping or vertically disposed electrodes can also be employed, however, in either monopolar or bipolar electrode cell arrangement. Here, the cathode 16 is supported at each end on sump walls 6. The remaining electrodes are stacked one above the other in a spaced relationship established by interposed refractory pillars 18. Such pillars 18 are sized to closely space the electrodes, as for example to space them with their opposed surfaces separated by less than \( \frac{3}{8} \) inch. In the illustrated embodiment, five inter-electrode spaces 19 are formed between opposed electrodes, one between cathode 16 and the lowest of the bipolar electrodes 15, three between successive pairs of intermediate bipolar electrodes 15, and one between the highest of the bipolar electrodes 15 and anode 14. Each inter-electrode space is bounded by an upper surface of one electrode (which functions as an anode surface) opposite a lower surface of another electrode (which functions as a cathode surface), and the spacing therebetween, e.g. about \( \frac{1}{2} \) inch, is the anode-cathode distance in the absence of a metal layer of substantial thickness. When a layer of metal is present on the carbonaceous cathode surface, the effective anode-cathode distance is shorter than the distance between the carbonaceous electrodes. The bath level in the cell will vary in operation but normally will lie well above the anode 14, thus filling all otherwise unoccupied space therebelow within the cell.

Anode 14 has a plurality of electrode bars 24 inserted therein which serve as positive current leads, and cathode 16 has a plurality of collector bars 26 inserted therein which serve as negative current leads. The bars 24 and 26 extend through the cell wall and are suitably insulated from the steel shell 1.

As noted earlier, the sump 4 is adapted to contain bath and molten metal, and the latter may accumulate beneath the bath in the sump, during operation. Should it be desired to separately heat the bath and any metal in sump 4, an auxiliary heating circuit may be established therein.

With reference now to FIGS. 2, 3 and 4, as well as FIG. 1, the bath flow passages will now be described. A bath supply passage, flow into which is indicated by the arrow at 36, generally extends from the upper reservoir 7 down along the right hand side (as viewed in FIG. 1) of the superimposed electrodes, and such passage has fluid communication with each inter-electrode space 19, and desirably with the sump 4. This bath supply passage is compositely defined by a series of selectively sized and shaped openings in the sides of the electrodes. The general movement of bath will be downwardly from the right side of anode 14, as seen in FIG. 1, through a relatively wide opening in the edge of the anode 14, thus passing into the space on the right hand side of the uppermost inter-electrode space 19. The bath flows downwardly through the bath supply passage openings on the right hand side of the next electrode to the right hand side of the next inter-electrode space 19, and so on. A portion of such bath may flow on through the openings on the right hand side of the cathode 16 into and through the sump 4. In an exemplary construction, the bath supply passage through the marginal edges of the several electrodes may be formed by drilling round holes 31 and saw-
cutting lateral slots 32. In this case, the round holes 31 are conveniently of the same diameter in all of the bipolar electrodes 15 and in the cathode 16, and such holes may conveniently accommodate insertion of a vacuum tapping tube when desired. In contradistinction therewith, the slots 32 are desirably widest in the highest bipolar electrode 15, of decreasing size in the successively lower electrodes, and narrowest in the lowest bipolar electrode 15. The slot may be omitted in the case of cathode 16, if desired. FIG. 1 schematically shows a typical size gradation of such slots, while FIGS. 2, 3 and 4 illustrate an opening 31 and slot 32 suitable for use in an intermediate bipolar electrode position. Thus, the described bath supply passage desirably has a downward size reduction suited to its function as a vertical supply header for downwardly feeding bath from reservoir 7 into each of the inter-electrode spaces 19.

In a similar manner, a bath return passage, flow from which is indicated by the arrow at 35, provides for the upward transport of the bath material to the reservoir 7 after passage thereof through the inter-electrode spaces 19, the flow preferably being induced as described hereinafter by the gas lift pump effect of the chlorine gas internally produced, by electrolysis in the inter-electrode spaces 19. The bath return passage generally extends upwardly along the left hand side (as viewed in FIG. 1) of each inter-electrode space 19, i.e., opposite the supply passage, and this bath return passage has fluid communication with each inter-electrode space 19 and desirably also communicates with the sump 4. Such return passage is compositely defined by selectively sized and shaped openings in the sides of the electrodes, with a relatively wide opening in the edge of anode 14. In an exemplary construction the bath return, gas lift passage through marginal edges of the several electrodes may be formed by drilling round holes 36 and saw-cutting lateral slots 37. In this case, the round holes 36 are conveniently of the same diameter in all of the bipolar electrodes 15 and such holes may conveniently accommodate the taking of bath samples when desired. In contradistinction therewith, the slots 37 are desirably widest in the highest bipolar electrode 15, of decreasing size in the successively lower electrodes, and narrowest in the lowest bipolar electrode 15. FIG. 1 schematically shows a typical size gradation of such slots, while FIGS. 2, 3 and 4 illustrate an opening 36 and slot 37 suited for use in an intermediate bipolar electrode position. Thus the bath return, gas lift passage desirably has an upward size increase, i.e., it is preferably larger at the uppermost bipolar electrode levels than at the lowermost bipolar electrode levels and is generally increased in size from lower to higher levels to accommodate additional chlorine and bath flowing thereinto from successive inter-electrode spaces. The gas lift passage openings may be generally compositely sized to provide a passage area at each level of about 0.05 to 0.15 square inches per standard cubic foot per hour (SCCFH) of chlorine passing through (standardized at a pressure of one atmosphere and a temperature of 70° F). The selective flow of gas and bath across each inter-electrode space 19 is desirably selectively directed by the configuration of its upper or anode surface, a preferred configuration being illustrated in FIGS. 2, 3 and 4. Each bipolar electrode 15 has a flat cathode surface 40, as does cathode 16, which functions as the lower bounding surface of an inter-electrode space 19; and each bipolar electrode 15 also has a transversely channelled anode surface 41, as does anode 14, which functions as the upper bounding surface of an inter-electrode space 19. The anode surface of each electrode is preferably undercut or relieved around its perimeter 42, in the side edge portions of which bath flow passage openings 31, 32 and 36, 37 are provided. Such relief operates to minimize electrolysis at the perimeter of the electrodes and thereby reduces any tendency toward short circuiting at the sides and edges of the cell.

Each anode surface includes a plurality of spaced rectangular slots or channels 45 which transversely extend to the relieved side edge of each electrode at the bath return-gas lift passage side thereof. Such slots operate to conduct chlorine upwardly away from the balance of the lower anode surface 41 and thereby effect removal of much of the chlorine from a location within the minimum anode-cathode space to a location further from the metal produced on the cathode surface, with a concomitant minimizing of re-chlorination of the metal produced. The channels 45 do not extend to the relieved edge at the bath supply passage side but terminate in fluid communication with a common lateral connecting channel 46. The lateral channel 46 is desirably located inboard of the bath supply passage and is defined in part by a downwardly depending marginal ledge 47 serving as a gas dam to obstruct, if not effectively prevent, back flow of chlorine gas into the bath supply passage 33. Transverse and lateral channels, similar to channels 45, 46 as just described, are incorporated on the underside of each bipolar electrode 15, and are also preferably included in the lower surface of anode 14. By way of example, the anode surface of each electrode desirably has a total projected channel area which is substantial but constitutes less than half the total projected area of the anode surface. The slot area and depth is desirably chosen so as to readily direct the transport of chlorine away from the lowermost anode surface 41.

THE MOLTEN BATH

The electrolyte employed for producing light metal in accordance with the subject invention normally will comprise a molten bath composed essentially of aluminum or magnesium chloride dissolved in one or more halides of higher decomposition potential than aluminum chloride. By electrolysis of such a bath, chlorine is produced on the anode surfaces and light metal on the cathode surfaces of the cell electrodes. The metal is conveniently separated by settling from the lighter bath, and the chlorine rises to be vented from the cell. In such practice of the subject invention, the molten bath may be positively circulated through the cell by the buoyant gas lift effect of the internally produced chlorine gas, and light metal chloride is periodically or continuously introduced into the bath to maintain the desired concentration thereof.

The bath composition, in addition to the dissolved aluminum or magnesium chloride, will usually be made up of alkali metal chloride, although, other alkali metal halide and alkaline earth halide, may also be employed. A presently preferred aluminum chloride containing composition comprises an alkali metal chloride base composition made up of about 50-75 percent by weight sodium chloride and 25-50 percent lithium chloride. Aluminum chloride is dissolved in such halide
composition to provide a bath from which aluminum may be produced by electrolysis, and an aluminum chloride content of about 1/4 to 10 percent by weight of the bath will generally be desirable. As an example, a bath analysis as follows (in percent by weight) is satisfactory: 53 percent NaCl, 40 percent LiCl, 0.5 percent MgCl₂, 0.5 percent KCl, 1 percent CaCl₂, and 5 percent AlCl₃. In such bath, the chlorides other than NaCl, LiCl, and AlCl₃ may be regarded as incidental components or impurities. The bath is employed in molten condition, usually at a temperature above that of molten aluminum and in the range between 660° and 730° C, typically at about 700° C. A presently preferred magnesium chloride containing composition comprises about 80 to 98.5 percent by weight lithium chloride and about 1/4 to 20 percent magnesium chloride.

PROCESS

The process for producing light metal is exemplified in the following detailed description of preferred modes of operation of the process for producing aluminum in a bipolar electrode cell, it being understood that references to exemplary cell structure shown in the drawings should be taken as illustrative only. As described hereinabove, bath supplied from reservoir 7 through bath supply passage 30 is electrolyzed in each inter-electrode space 19 in a cell which includes, in superimposed, spaced relationship, an upper anode 14, at least one intermediate bipolar electrode 15 and a lower cathode 16, to produce chlorine on each anode surface thereof 41, and aluminum on each cathode surface thereof 40. The electrode current density may conveniently range from about 5 to 15 amperes per square inch, the practical operating current density suited to any particular cell structure being readily determined by observation of the operating conditions. The chlorine so produced is buoyant and its movement may be employed to effect bath circulation, and aluminum may be swept by the moving bath from the cathode surfaces and settle from the outflowing bath in a manner to be described hereinbelow. An induced flow of molten bath into, through and out of each inter-electrode space 19 may be established which sweeps aluminum produced on each cathode surface 40 through inter-electrode space 19 in a direction concurrent with the flow of the bath. This sweeping action may be employed to effectively prevent aluminum from coalescing in unduly large droplets or from building up into a substantial pool or layer thickness on the cathode surfaces, and the bath flow through each inter-electrode space may be maintained at a rate such that there is no substantial accumulation of aluminum therein. In any given installation, the practical velocity suited to any particular cell structure and anode-cathode spacing will be determined by observation of the operating conditions.

The molten bath exiting from each inter-electrode space 19 is effectively and positively pumped upwardly in the return passage 35, preferably by employment of the gas lift effect thereon of chlorine produced and conducted from each inter-electrode space in the same general direction as the bath and buoyantly rising in the return passage 35. This, in turn, induces the selectively directed, concomitant flow of bath through the inter-electrode spaces. Preferably the bath which is upwardly moving in the return passage 35 is delivered to the reservoir 7 above the anode 14, where the chlorine may be conveniently vented from the bath (at port 12) and the aluminum chloride content of the bath may be replenished (through port 11).

While the bath is being upwardly displaced in the gas lift passage 35 as described above, aluminum swept thereinto from each inter-electrode space 19 may be permitted to settle in a counter current direction therein and, surprisingly, a substantial amount of the aluminum may so settle and may do so without undue re-chlorination of aluminum so produced, although some aluminum may be carried upwardly with the bath to be recirculated with the bath. Conveniently, the settling aluminum accumulates in a sump 4 below the cathode 16, from which it may be tapped as desired. One practical method of removing molten aluminum is to use a vacuum tapping tube inserted into sump 4 through port 10 and the bath supply passage 30.

As will now be apparent, the inclusion of a plurality of spaced transverse passages and associated lateral passage on the underside of anode surfaces not only accommodates the outward flow of chlorine produced without accumulation of a substantial amount of such chlorine on the lowermost anode surfaces 41, but also selectively and unidirectionally directs and channels the flow of chlorine in a substantially unobstructed manner, minimizing or preventing back flow toward the supply passage 30. The desired selectively directed chlorine flow toward the gas lift passage 35 may be established even against a flat anode surface, of course, by various means, such as temporary initial restriction of back flow in the supply passage.

The present invention as applied to aluminum, it will be observed from the foregoing description, provides a process for producing aluminum from aluminum chloride with substantially no consumption of anode carbon by evolved oxygen, with lower heat input and lower temperatures than encountered in the Hall process, and with high power efficiency made possible by the opportunity to employ cell design and operating conditions in which there is a low anode-cathode distance, with low cell resistance and yet minimal re-chlorination of the aluminum produced. Thus, it will now be seen that the subject invention provides a significant contribution to obtaining the long sought economic advantages in producing aluminum from aluminum chloride.

As earlier indicated, the invention may be employed for producing magnesium. In such case the bath may be composed of magnesium chloride dissolved in molten halide of higher decomposition potential. A suitable low density composition is one made up of at least about 80 percent by weight, preferably about 85 percent, lithium chloride and at least about 1 4/₄ percent, preferably about 15 percent, magnesium chloride. From such a bath, magnesium metal is produced in the manner generally described with reference to producing aluminum. If a small amount of aluminum chloride is also present, the metal produced may also contain some aluminum.

What is claimed is:

1. A process for producing light metal in a cell which includes at least two opposed electrodes providing at least one inter-electrode space therebetween, at least one of which has a carbonaceous cathode surface, which process comprises maintaining a flow of bath composed essentially of at least one light metal chloride from the group consisting of aluminum chloride and magnesium chlo-
ride dissolved in molten halide of higher decomposition potential through each inter-electrode space, while
electrolyzing such bath, thus producing light metal and anode product, and
maintaining an effective anode-cathode distance in at least one such inter-electrode space that is less than
¾ inch, thus causing anode product therein to contact the effective cathode surface.

2. The process of claim 1 wherein the effective anode-cathode distance in at least one such inter-electrode space is maintained at less than ¾ inch.

3. The process of claim 1 wherein the molten bath is maintained at a temperature above the solidus of the light metal produced.

4. A process for producing aluminum in a cell which includes at least two opposed electrodes providing at least one inter-electrode space therebetween, at least one of which has a carbonaceous cathode surface, which process comprises
maintaining a flow of bath composed essentially of aluminum chloride dissolved in alkali metal-containing molten halide of higher decomposition potential through each inter-electrode space, while electrolyzing such bath, thus producing aluminum and anode product, and
maintaining an effective anode-cathode distance in at least one such inter-electrode space that is less than ¾ inch, thus causing anode product therein to contact the effective cathode surface and thereby both flux the aluminum and inhibit alkali metal reaction with the carbonaceous cathode surface.

5. The process of claim 4 wherein the aluminum chloride content of the bath supplied to each inter-electrode space is maintained between about 1½ and 10 percent by weight.

6. A process for producing magnesium in a cell which includes at least two opposed electrodes providing at least one inter-electrode space therebetween, at least one of which has a carbonaceous cathode surface, which process comprises
maintaining a flow of bath composed essentially of magnesium chloride dissolved in alkali metal-containing molten halide of higher decomposition potential through each inter-electrode space, while electrolyzing such bath, thus producing magnesium and anode product,

7. The process of claim 6 wherein the magnesium chloride content of the bath supplied to each inter-electrode space is maintained between about 1½ and 20 percent by weight.

8. A process for producing aluminum in a cell which includes an anode, at least one intermediate bipolar electrode and a cathode in superimposed, spaced relationship defining inter-electrode spaces therebetween, at least one of which has a carbonaceous cathode surface, which process comprises
maintaining a flow of bath composed essentially of aluminum chloride dissolved in molten halide of higher decomposition potential through each inter-electrode space, while electrolyzing such bath, thus producing aluminum and anode product, and
maintaining an effective anode-cathode distance in at least one such inter-electrode space that is less than ¾ inch, thus causing anode product therein to contact the effective cathode surface.

9. The process of claim 8 wherein the aluminum chloride content of the bath supplied to each inter-electrode space is maintained between about 1½ and 10 percent by weight.

10. A process for producing magnesium in a cell which includes at least two opposed electrodes providing at least one inter-electrode space therebetween, at least one of which has a carbonaceous cathode surface, which process comprises
maintaining a flow of bath composed essentially of magnesium chloride dissolved in alkali metal-containing molten halide of higher decomposition potential through each inter-electrode space, while electrolyzing such bath, thus producing magnesium and anode product, and
maintaining an effective anode-cathode distance in at least one such inter-electrode space that is less than ¾ inch, thus causing anode product therein to contact the effective cathode surface and thereby flux the magnesium.