PREPARATION OF ALKALI METAL CHLORIDE MELT FOR USE IN ELECTROLYSIS OF ALUMINUM CHLORIDE


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26 Claims

ABSTRACT OF THE DISCLOSURE

Advance preparation of alkali metal chloride melt for use in electrolysis of aluminum chloride.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to electrolytic production of aluminum from aluminum chloride. More particularly, it relates to preparation and purification of a melt of high-purity alkali metal chloride and introduction thereof to an electrolytic cell for the production of aluminum from aluminum chloride. When we refer herein to the melt, we refer to the alkali metal chloride electrolyte before the aluminum chloride to be electrolyzed has been added to the cell. By alkali metal chloride, we mean any metal chloride whose decomposition potential is substantially above that of aluminum chloride, including alkaline earth metal chlorides such as magnesium chloride and calcium chloride.

Description of the prior art

The production of aluminum by the electrolysis of aluminum chloride in an alkali metal chloride melt, although a theoretically feasible and long-sought objective of the art, has never been commercially realized because of numerous unsolved technical problems which have precluded the economic continuous operations requisite to commercial production. Among such problems is a progressive deterioration in the operating efficiency of the electrolytic cell, with a marked change in its electrical operating characteristics and diminution of its output of metallic aluminum. Although not fully understood at the present time, we believe that certain of the problems that have long been extant are attributable to the presence of undesired contaminants and finely divided particulate materials in the molten salt bath. The particulate is attracted to the cathode, apparently by electrical forces, where it forms a semipermeable coating. This coating of oxides or other particulates on the cathode surface operates to inhibit transport of the complex Al ion because of its large size-to-charge ratio. In contrast, the alkali metal ions are driven by the electrical potential gradient and, due both to its abundance and a small size-to-charge ratio, easily penetrate the particulate film and are discharged at the cathode. These reduced species, particularly sodium and potassium, enter the graphite or like lattice, with consequent expansion thereof and surface soughing to further add to the particulates present in the system. In this manner, the mobility of aluminum chloride to the cathode surface by both convection and diffusion is markedly impeded.

Apart from the foregoing, the presence of oxide and hydroxide impurities in the melt also causes detrimental consumption of the carbon anodes. Such impurities are slightly soluble in the melt and are electrolytically decomposed simultaneously with the aluminum chloride. Oxygen released at the anode forms carbon monoxide and carbon dioxide, with attendant consumption of the anodes and undesirable increases in the anode-cathode spacing.

SUMMARY OF THE INVENTION

We have found that the aforementioned problems may be minimized, if not effectively avoided, for extended periods of time by forming a melt of at least one alkali metal chloride, the resultant melt containing at least about 75% by weight alkali metal chloride, and feeding this melt to a cell in which AlCl₃ is to be electrolyzed after addition to the melt or electrolyte therein. According to our invention, the melt is preferably purified before being fed to the cell. Purification may be by any conventional means of separating solids, for example, by settling, centrifuging, decanting, freezing and remelting, or the like. Our presently preferred method of preparing the melt is to form it in a separate heated chamber, as for example, a furnace, in an atmosphere of nitrogen, argon, or other inert gas which serves to purge the chamber and prevent the introduction of moisture into the melt. Such inert gas can also be used to force the melt to flow through a filter disposed in the chamber according to a preferred embodiment of our invention, preparatory to its transfer to the electrolytic cell.

The one or more alkali metal or alkaline earth metal chloride ingredients of the melt may be added to the melting chamber in solid form, either mixed together or separately. If desired, some of the melt that is tapped off with the aluminum removed from the electrolytic cell may be separated from the aluminum and introduced to the pre-melt chamber for re-purification prior to being conducted back to the electrolytic cell for reuse.

Impurities or contaminants which may be present, for example, as a result of being introduced during preparation of the alkali metal chloride melt, and not be in solid form, may be precipitated as solids according to our invention. This enables them to be readily removed from the melt. For example, aluminum may be added to precipitate one or more metal chlorides, as for example, in the case of iron of valence 3, present as FeCl₃ in accord with the equation Al⁺⁺⁺FeCl₃ → AlCl₃ + Fe. Such added aluminum, in a slower reaction, also functions to remove some oxygen values if the same are present, as for example, as heavy metal (X) hydroxide, by the illustrative reaction 2nAl⁺⁺⁺X(OH)₃ → nAl₂O₃ + 3X⁺⁺ + 3nH₂O, where n is the valence of the heavy metal. We have also found that addition of aluminum chloride to the pre-melt, in an amount not exceeding 1 to 2% by weight, further facilitates removal of soluble oxygen, as for example, by reaction to form a soluble aluminum-oxygen-chlorine complex which reacts further to form insoluble Al₂O₃. However, if more than 1 to 2% by weight of aluminum chloride is added to the pre-melt, at least some of the so formed alumina is likely to go back into solution, thereby at least partly defeating the purpose of such addition. The precipitated materials and any other insoluble or undissolved matter, including oxides, and perhaps carbon or the like, and precipitates and sludge formed therefrom, in the pre-melt will normally settle to the bottom of the chamber in the form of a sludge, and thus be effectively separated from melt that is transferred into the electrolytic cells. As mentioned hereinabove, any unsettled
matter and/or particulate suspensions which may be present in the melt due to thermal flow conditions such as convection currents or other factors, as well as precipitated solids, may be removed by passage of the melt through a filter such as disclosed above and described hereinafter.

In effecting the removal of purified melt from the chamber, preferably upwardly, through a conduit or the like, and may be conveniently filtered as it is introduced thereinto. The filter material should be alkali metal chloride-resistant and of sufficient permeability to selectively permit passage of the liquid alkali metal chlorides therethrough and to prevent the passage of much of the undissolved or other solid particulate matter therethrough. Such filter may comprise, for example, material of fibrous character covering or wrapped around a perforated metal, metal alloy (such as the nickel base alloy Inconel), refractory or like plate or end section on a pipe, tube or like conduit which may extend into the aforementioned chamber or to a point below the surface of the melt. The perforated plate or end section serves as a support for the filter material.

If desired, the filter material may be secured thereto by means of one or more clamps or the like. Such an arrangement permits easy flow of filtered melt into such conduit and drives the electrolyte to which proper quantities of AlCl₃ may be added. Although we will describe herein a preferred embodiment of said filter, it should be understood that other filtering arrangements can be employed, such as a pad, or the like, of permeable medium over a perforated annular entrance to a pipe or conduit which extends into the chamber, or as a cover for a wire screen or the like of appropriate shape placed over an opening into a line which leaves the pre-melt chamber and leads to an electrolytic cell, regardless of where the opening may be positioned in the chamber, or in what direction the exiting melt may flow.

According to a preferred embodiment of our invention, a multi-element filter medium is employed which comprises at least one fibrous silica-containing or siliceous material. A fused siliceous material fabric, such as one made of fused quartz, and porous carbon have proved especially effective as filter materials for our purposes. We have found a four-layer composite laminated filter medium comprising respective layers, beginning with the side next to the melt to be filtered, of an outer lamina of a fused siliceous material fabric such as fused quartz fabric, aluminia-silica paper, carbon or graphite felt and an inner lamina of a fused siliceous material fabric such as fused quartz fabric to be of particular utility. However, omitting the carbon or graphite felt layer has proved not deleterious. Fused quartz fabric, in addition to being a reasonably good filter medium for the subject environment, additionally provides a sturdy construction which extends the useful life of the filter. An aluminia-silica paper layer affords high resistance to bath flow and aids in the filtering out of unsettled smaller particulates. Carbon felt, when used, has non-wetting characteristics in the molten salt bath such that embrittlement or cracking thereof is minimized, should the bath level drop below the filter such as to expose it to a gas zone.

Among the advantages of the subject invention is the provision of a melt of high-purity alkali metal chloride for the permitted electrolysis of aluminum chloride in a continuous economic manner. Other advantages will become apparent from the following portions of the specification and from the appended drawings, which illustrate, in accordance with the mandate of the statute, preferred embodiments thereof incorporating the principles of the invention.

**BRIEF DESCRIPTION OF THE DRAWING**

For a better understanding of our invention, reference will now be made to the drawing which forms a part hereof and to the following description thereof.

In the drawing, FIG. 1 is a schematic flow sheet representation of the alkali metal chloride melt purification process of the invention.

FIG. 2 depicts a schematic longitudinal cross section of a filter which may be used according to a preferred embodiment of the invention. In FIG. 1, alkali metal chloride is introduced to furnace 10 heated by electrical, gas or other conventional means (not shown) via line 12. The temperature is raised sufficiently to form a melt 14 of molten salt of the added alkali metal chlorides. Nitrogen or other inert gas, for example, argon or the like, is introduced via line 16 above molten mass 14 in the furnace 10 such that sufficient pressure differential exists to filter the melt through filter 18 and out through conduit 20 to electrolysis cell 22, wherein aluminum chloride added via line 24 may be electrolyzed to aluminum 26 (shown settled to the bottom of cell 22), with chlorine, which escapes via line 28, also being formed, the melt in cell 22 being designated 30. Aluminum may be introduced to the melt in chamber 10 via line 12 or separate opening (not shown) so as to precipitate iron and other heavy metal impurities bound before precipitation in the form of chlorides or other halides soluble in the melt. The aluminum chloride melt mixed with oxygen or hydroxide as explained hereinabove to form insoluble aluminia, which settles to the bottom of the furnace 10 together with the iron and other insoluble solids. Settled particulate and sludge 32 may be removed via outlet 33. 1 to 2% by weight aluminum chloride may also be introduced via line 12 or separate opening (not shown), if desired, to react with any hydroxide which may be present in the melt and precipitate aluminia and form hydrochloric chloride gas (when the reacting hydroxide is water). Any solids which are not settled to the bottom to form the layer of precipitates and sludge 32 are prevented by filter 18 from passing on via line 20 to cell 22 and interfering with efficient electrolysis.

The filter 18 may be constructed so as to be substantially impervious to much of the solid contaminants and precipitates in the melt. Aluminum containing a small amount of alkali metal chloride from the melt may be tapped from cell 22 as desired and introduced to settler 34 via line 36. Alkali metal chloride 38 may be skimmed or poured from the surface of aluminum 39 in settler 34 and then conducted via line 40, and added as desired, to pre-melt chamber or furnace 10. Substantially pure molten aluminum may be withdrawn from settler 34 as indicated at line 41 by tapping or the like.

In FIG. 2, the illusory filter is constructed of four layers wrapped around the perforated end section 42 of a conduit 44, the respective layers being fused quartz fabric 46, carbon felt 48, aluminia-silica paper 50 and again fused quartz fabric 52. According to the preferred embodiment of filter structure useful according to the invention, pipe 44 extends into substantially cylindrical perforated filter support 42 (shown partly in broken section to illustrate wall perforations) almost to the end thereof. This permits the filter to still permit passage of melt therethrough and on into pipe 44 through the open end thereof even when the tip or end of the filter extends only slightly below the surface of the melt being filtered. The four-layer filter material may be secured to the perforated support 42 by clamps (not shown), if desired.

**DESCRIPTION OF THE PREFERRED EMBODIMENT**

The following example is illustrative of our invention.

**Example**

Two thousand pounds (2000 lbs.) of alkali metal chloride salt containing 60% NaCl and 40% LiCl are melted over an 8-hour period in a purification furnace, for
example, as depicted schematically at 10 in FIG. 1. During a second 8-hour period, 0.5% by weight aluminum (10 lb. Al) and 1–2% by weight AlCl₃ (20–40 lb. AlCl₃) are added, and the precipitates formed settle to the bottom. A 10 s.c.f.h. (standard cubic feet per hours) inert gas (nitrogen) purge into a vapor space above the molten salt in the furnace is used to prevent moisture in ambient air from entering the furnace. The resulting melt is transferred to an electrolysis cell during a third 8-hour period by pressurizing the purification furnace with inert gas (nitrogen), causing melt to flow through a filter, for example, depicted at 18 of FIG. 1 and in FIG. 2 and into a transfer pipe leading to the cell. The filter consists of an 0.05 in.-thick layer of fused quartz fabric, a 0.4 in.-thick layer of alumina-silica paper, a 0.4 in.-thick layer of carbon felt, and a second layer of 0.05 in.-thick fused quartz fabric wrapped around a perforated metal support frame. Flow through the filter is 50–60 lb. melt/min./ft.² filter area, with a pressure drop of approximately 1.5 psi for the replicate and transfer line. Settled sludge is removed from the bottom of the furnace as required.

By using a fritted quartz filter (instead of the 4-layer filter recited above), the bath contaminants were decreased from 0.22% oxygen in the melt to 0.005% oxygen, as measured by neutron activation analysis, when the 26 stoichiometric quantity of AlCl₃ was used. The oxygen was reduced to only 0.125% when 2.3% excess AlCl₃ was used.

While the invention has been described in terms of preferred embodiments, the claims appended hereto are intended to encompass all embodiments which fall within the spirit of the invention.

Having thus described our invention and certain embodiments thereof, we claim:

1. In a process for electrolytic production of aluminum by electrolysis of aluminum chloride in a cell, said electrolysis being performed in an alkali metal chloride electrolyte, the steps comprising forming a melt of at least one alkali metal chloride, the resultant melt containing at least 75% by weight alkali metal chloride, and feeding at least part of said resultant melt to said cell.

2. The process of claim 1 wherein impurities are removed from the melt prior to feeding same to said cell.

3. The process of claim 2 wherein said impurities are removed by separation of solids from said resultant melt.

4. The process of claim 3 wherein the separation of solids is accomplished by settling of the solids and employing resulting supernatant fluid as the melt with impurities removed therefrom to said cell.

5. The process of claim 4 wherein the supernatant fluid is filtered prior to feeding same to said cell.

6. The process of claim 5 wherein aluminum is removed from said cell and alkali metal chloride melt is separated therefrom and added to said melt prior to feeding same to said cell.

7. The process of claim 6 wherein a precipitating agent is added to precipitate solids from said resultant melt, and the resulting precipitated solids, with other substantially insoluble solids in said melt, are settled, thereby permitting impurities to be removed from the melt prior to feeding same, with insoluble solids removed therefrom, to said cell.

8. The process of claim 7 wherein the precipitating agent comprises up to 1 to 2% by weight of said melt aluminum chloride.

9. The process of claim 8 wherein the precipitating agent comprises aluminum or an alloy containing aluminum.

10. The process of claim 9 wherein precipitating agent comprises up to 1 to 2% by weight of said melt aluminum chloride and in addition aluminum.

11. The process of claim 10 wherein said forming of said melt is effected in a chamber under an inert atmosphere.

12. The process of claim 11 wherein said resultant melt is passed through a filter prior to feeding same to said cell.

13. The process of claim 12 wherein the filter comprises fibrous material on a perforated support therefor.

14. The process of claim 13 wherein the fibrous material comprises porous carbon.

15. In a process for electrolytic production of aluminum by electrolysis of aluminum chloride in a cell, said electrolysis being performed in an alkali metal chloride electrolyte, the steps comprising forming a melt of at least one alkali metal chloride, the resultant melt containing at least 75% by weight alkali metal chloride, passing said resultant melt through a filter of fibrous material on a perforated support therefor, and thereafter feeding at least part of said resultant melt to said cell.

16. The process of claim 15 wherein the fibrous material comprises respective layers of fused siliceous material fabric, alumina-silica paper and fused siliceous material fabric.

17. The process of claim 15 wherein the fibrous material comprises respective layers of fused silica paper and fused siliceous material fabric.

18. The process of claim 17 wherein the respective first and last fused siliceous material fabric layers comprise fused quartz fabric.

19. Apparatus for the preparation of high-purity alkali metal chloride for use in electrolysis of aluminum chloride to aluminum comprising, in cooperative association, furnace means for forming a melt of alkali metal chloride,

 means for maintaining an atmosphere of inert gas in said furnace means,

 means for feeding molten alkali metal chloride from said furnace means to an electrolysis cell,

 and means for selectively separating solids from said molten alkali metal chloride prior to feeding same to said electrolysis cell.

20. The apparatus of claim 19 wherein the means for selectively separating solids comprise a filter.

21. The apparatus of claim 20 wherein the filter material comprises siliceous material.

22. The apparatus of claim 21 wherein the fibrous filter material comprises porous carbon.

23. Apparatus for the preparation of high-purity alkali metal chloride for use in electrolysis of aluminum chloride to aluminum comprising, in cooperative association, furnace means for forming a melt of alkali metal chloride,

 means for maintaining an atmosphere of inert gas in said furnace means,

 means for feeding molten alkali metal chloride from said furnace means to an electrolysis cell,

 and means for selectively separating solids from said molten alkali metal chloride prior to feeding same to said electrolysis cell, said means for selectively separating solids comprising respective layers of fused siliceous material fabric, alumina-silica paper and fused siliceous material fabric.
26. The apparatus of claim 25 wherein the fibrous filter material has additionally a layer of porous carbon between at least one of the layers of fused siliceous material fabric and the aluminum-silica paper.

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HOWARD S. WILLIAMS, Primary Examiner
D. R. VALENTINE, Assistant Examiner
U.S. Cl. X.R.

204—245, 246, 276
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION


Inventor(s) Warren E. Haupin and Bernard J. Racunas

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

Col. 6, Claim 17, line 2
After "fused" cancel "sili-" and substitute --siliceous material fabric, porous carbon, alumina-silica--.

Col. 6, Claim 20, line 40
Change "10" to --19--.

Signed and sealed this 26th day of February 1974.

(SEAL)
Attest:

EDWARD M. PLETCHER, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents