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REFINING ALUMINUM ELECTROLYTICALLY

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This invention relates to improvements in refining aluminum and more particularly to an electrolyte to be used in a refining process wherein the electrolyte floats, in a molten state, upon a molten alloy with other substances of the aluminum to be refined, the alloy being used as an anode and the purified aluminum removed therefrom being deposited on a layer of molten aluminum which floats on the electrolyte and is used as a cathode.

The electrolyte of the present invention provides for the minimizing of undesirable deposits on the electrodes of an aluminum refining apparatus.

The instant invention further provides a bath for the electrolytic refining of aluminum that remains constant in composition during long periods, whereby replenishing the solution is simplified.

In addition, the bath of the instant invention is such as to minimize the deterioration of the walls of the tank in which the process is being carried on.

The bath of the instant invention provides for very little occluded or dissolved gas in the refined aluminum.

Furthermore, the bath of the instant invention provides for considerably less deposit of crust on the side walls of the tank than is found in the use of previously-known electrolytes.

Furthermore, the use of the bath of the instant invention enables the use of a tank having superior thermal insulating properties, with a resultant lowering of heat loss and better electrical and thermal efficiency.

With the foregoing and other objects in view which will appear as the description proceeds, the invention resides in the methods and compositions and in the details thereof hereinafter described and claimed, it being understood that changes in the precise embodiment of the invention herein disclosed may be made without departing from the spirit of the invention.

Refined aluminum having a content of 99.99% of pure aluminum is obtained by means of electrolysis in a cell comprising three superposed layers of molten material. The lower layer is used as an anode and is generally an alloy of the unrefined, commercial aluminum with a heavy metal such as copper. A layer of molten material floats upon the molten alloy and serves as an electrolyte. A layer of molten refined aluminum floats on the electrolyte and is used as a cathode, graphite electrodes being inserted into this layer for that purpose. Any material used as an electrolyte

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in such a process must possess two qualities: it must have a definite melting point and it must be selective in order to obtain very pure refined aluminum. In the past, the electrolytes used contained fluorides and particularly sodium fluoride. For instance, one type of electrolyte generally used is composed of a mixture of barium chloride with aluminum fluoride and sodium fluoride; the proportion of AlF_3 to NaF being larger than in natural cryolite; a small amount of sodium chloride is added to promote stability. Such a bath has a composition somewhat as follows:

	Percent by weight
AlF_3	20
NaF	15
NaCl	5
$BaCl_2$	60

However, a bath such as described above, and particularly one containing halides of alkali metals such as sodium or potassium, has many disadvantages. For instance, the lower part of the graphite electrodes which are immersed in the cathode of molten refined aluminum are subject to being attacked by sodium and the like. An insulating deposit is thus formed which prevents flow of electrical current through the solution. If this deposit is allowed to remain during the operation of the process, there will be many obvious electrical difficulties, such as dangerous overcharging of the anode.

A further difficulty encountered in such prior art electrolytic baths is that the aluminum fluoride is evaporated more than the other components. The composition of the bath must be regularly corrected by the addition of a mixture of salts rich in aluminum fluoride. As a practical matter, about 15 kgs. of $BaCl_2$, 15 kgs. of AlF_3, and 5 kgs. of NaCl have to be added every three days to a cell using 14,000 amperes. This mixture melts at more than 800° C., is very unstable, and cannot be easily purified by electrolysis in a feeding pot before being introduced into the refining cell proper. However, the aluminum fluoride is so impure as to require refining, and it becomes necessary to employ a complicated and generally undesirable method, the details of which are immaterial to the instant application, but which is to be avoided if possible.

Another difficulty encountered in the electrolytes containing halides of alkali metals is their effect on the tank in which the process is carried on. The side walls of these tanks are generally made of magnesium bricks and are rapidly attacked in the portions where they are

contacted by the upper levels of such baths, because such levels are rich in free sodium. The reason for such rapid attack lies in the fact that the composition of these baths is such that the end temperature of the solidification range is substantially lower than the beginning temperature. The beginning temperature of the solidification range is in the order of 700° C., and the cell operates between 750° C. and 800° C. However, there are parts of the bath that remain liquid down to 630° C. and these liquid parts seep into cracks in the walls of the tank and, when they reach isothermal surfaces corresponding to this temperature, the result is deep errosion of the masonry. This is quite important in its effect upon the thermal insulation properties of the wall and, thus, upon the thermal efficiency of the process.

In addition, the prior art baths described above result in refined aluminum that contains undesirable occluded or dissolved gases.

By use of the electrolytic bath of the applicant's invention, it is possible to refine aluminum, and, at the same time, do away with the drawbacks inherent in those electrolytes containing aluminum fluoride and compounds, particularly halides, of alkali metals. While baths generally used in the refining of aluminum always contain these objectionable salts and their presence was always thought to be necessary, the applicant discovered the surprising fact that far better results in every way are obtained with particular compositions of electrolyte without sodium and other alkali metals salts present. The baths invented by the applicant enable the cells to operate at the usual temperatures between 700° C. and 800° C. with electrical efficiencies as high as and with the production of refined aluminum as pure as with the use of known baths, without the difficulties inherent in the latter. According to the present invention, electrolytic baths of the following general composition are used:

	Percent by weight
$BaCl_2$	37 to 47
CaF_2	18 to 28
AlF_3	25 to 35
BaF_2, MgF_2, oxides, and other impurities	5

A bath of this composition is more stable than one containing sodium halides and the like. In fact, the appearance of the applicant's bath is entirely different from former baths: it is more transparent, which signifies that it contains less oxide formed by decomposition of the salts which comprise the mixture. For this reason, less crust is formed on the side walls of the tank, particularly at the level of the electrolytic layer. An examination of the compositions possible within the scope of the applicant's invention will show that each of the components, namely $BaCl_2$, CaF_2, and AlF_3, may vary within limits of 10% of the weight of the mixture; the result is that the ratio of aluminum fluoride to calcium fluoride may vary from 0.9 to 2.0.

An example of a bath within the scope of this invention is as follows:

	Percent by weight
$BaCl_2$	42
CaF_2	28
AlF_3	25
BaF_2, MgF_2, oxides, and other impurities	5

A bath of this composition yields an aluminum which is 99.99% pure and has a ratio of aluminum fluoride to calcium fluoride of 0.9.

Another example of a bath within the scope of this invention and which is richer in aluminum fluoride is as follows:

	Percent by weight
$BaCl_2$	42
CaF_2	18
AlF_3	35
BaF_2, MgF_2, oxides, and other impurities	5

A bath of this composition will operate for several weeks, but loses aluminum fluoride until the bath reaches a point of stable composition wherein the aluminum fluoride content is 30%.

When a bath which acts with high selectivity with respect to aluminum is desired, it is preferable to use an aluminum fluoride content which is not appreciably lower than the content of calcium fluoride. If too small an amount of aluminum fluoride is used, deposits of calcium or barium may develop on the cathode. It has been found that very good results are obtained when the percentages of aluminum and calcium fluorides are chosen so that the ratio of AlF_3 to CaF_2 is in the neighborhood of 1.5, say 1.3 to 1.6. Such a bath which operates very satisfactorily is as follows:

	Percent by weight
$BaCl_2$	45
CaF_2	20
AlF_3	30
BaF_2, MgF_2, oxides, and other impurities	5

It can be seen that the ratio of AlF_3 to CaF_2 here is 1.5; this bath is very stable and does not change in composition during the electrolysis.

Baths of the above compositions within the scope of the invention and, in general, chloride and fluoride baths, or merely fluoride baths, which are free of alkali metals, and, in particular, substantially free of sodium have many advantages which in part will be outlined below.

In the use of the baths of the invention there is no considerable deposit on the faces of the graphite electrodes immersed in the liquid aluminum cathode. The number of times that these electrodes must be scraped is diminished by two-thirds. The electrical contact between the aluminum and the graphite is considerably better, and a gain of 0.2 volt may be obtained when the current density in the graphite is, for example, in the order of 3.5 amperes per sq. cm.

In addition, a bath within the philosophy of the instant invention is very stable, and the total consumption of chloride-fluoride compounds is only about 60 per cent of the consumption where the prior-art type of bath is used; that is to say about 7 kg. daily instead of 12 kg., when operating with a 14,000 ampere cell. Moreover, the composition of the bath remains constant over a given length of time, which enables one to feed the cell with material always having the same composition. This material to be added can be melted and refined electrolytically in a feeding-cell before being added to the main refining cell, principally because of the absence of sodium compounds and the like.

The use of the applicant's bath cuts down the deterioration of walls of the tank, this being due, as has been explained, to the absence of sodium and the like. Baths following the teaching of the instant invention have substantially narrower solidification ranges than known baths containing alkali metal salts; for example, the above-described bath containing 45% $BaCl_2$, 20% CaF_2, 30% AlF_3, and 5% of BaF_2, MgF_2, and oxides is characterized by a solidification range from 710° C. to 680° C. as compared with

a range of from 700° C. to 630° C. exhibited by the usual prior-art type of bath. At the same time, the applicant's baths have higher surface tension than in known electrolytes; for instance, the mixture whose composition is recited immediately above has a surface tension of 148 dynes/cm. at 780° C. as compared with 118 dynes/cm. for the described prior-art bath containing halides of alkali metals. The two properties recited above as residing in baths of the composition taught by the present invention, that is, narrower range of solidification and higher surface tension, have an important effect on the action of the baths on the lining, bricks and masonry, of the tank. The penetration of the bath into the cracks in the masonry is not as great as in the case of the previously-known baths; tanks having strong thermal insulation properties may be constructed without the magnesia linings being subjected to rapid deterioration; such tanks, thus, can be built to produce an electrolytic cell which requires less electric current density, less voltage at the terminals and less power consumption because of the lower heat loss through the walls of the tank.

Furthermore, refined aluminum obtained in a bath free of sodium and the like does not contain as much occluded or dissolved gases as aluminum obtained by the previously-known means. Moreover, the cells using baths according to the instant invention, may be fed melted-down chloride-fluoride or straight fluoride compounds. This means that the danger inherent in powdered materials of absorbing water from the air is avoided; the presence of water in powders which are to be introduced directly into a molten-metal bath are obvious. Another advantage resulting from the above-recited properties of the baths of the applicant is the minimizing of crusts of frozen bath that generally form upon the top layer in refining operations, and which must be frequently removed, taking a considerable portion of bath material along with it.

It is evident that in the baths of the instant invention, the composition is critical only with respect to the barium chloride, the calcium fluoride, and the aluminum fluoride; in using commercial materials of this kind, various impurities are certain to be present. We have recited above that barium fluoride, mangnesium fluoride, and various oxides of metals will be present; it is true, of course, that commercial barium chloride will contain some strontium salt and that almost every salt will contain small amounts of the almost universal sodium and potassium compounds. Consequently, it is contemplated that the baths of the applicant must necessarily contain small amounts of these compounds. However, it is obvious that a bath of the type taught by the applicant having as much as 1% of sodium chloride or sodium fluoride as accidental impurities is within the scope of the applicant's invention and is completely different from previously-known baths containing very much higher amounts of these undesirable compounds; that is, at least 5% and usually greater than 15%.

It will be evident to a worker in the art that, although certain salts may be selected within the scope of this invention that will operate properly chemically and electrically, care must be taken to select only compounds of such kind and amount as will produce an electrolytic bath whose specific gravity is such that it will float on the anodic layer and not float on the cathodic layer. The bath mixtures given as examples have this necessary quality and it is contemplated that anyone skilled in the art will be able to select compounds within the scope of the invention in the proper proportions to maintain such a desired quality.

It is to be understood that the invention is not limited to details herein specifically set forth but can be carried out in other ways without departure from its spirit as defined by the appended claims.

I claim:

1. A method of refining aluminum electrolytically by floating molten refined aluminum for use as a cathode on an electrolytic bath which in turn floats on a molten alloy of unrefined aluminum and a heavy metal for use as an anode, said bath comprising approximately 30 per cent by weight of aluminum fluoride, approximately 20 per cent by weight of calcium fluoride, 45 per cent by weight of barium chloride, the remainder being made up of barium fluoride, magnesium fluoride, oxides, and other impurities, there being no more than 1 per cent of sodium and potassium compounds, said fluoride and chlorides being selected in such proportion that the bath will float on the anodic layer but not float on the cathodic layer of a refining apparatus of the type described.

2. A method for the refining of aluminum electrolytically by floating molten refined aluminum for use as a cathode on an electrolytic bath which in turn floats on a molten alloy of unrefined aluminum and a heavy metal for use as an anode, said bath comprising from 37 to 47 per cent by weight of barium chloride, from 18 to 28 per cent by weight of calcium fluoride, the total amount of the three salts making up approximately 95 per cent by weight of the bath, from 25 to 35 per cent by weight of aluminum fluoride, and containing no more than 1 per cent of alkali metal compounds, said fluorides and chlorides being selected in such proportion that the bath will float on the anodic layer but not float on the cathodic layer of a refining apparatus of the type described.

3. A method of refining aluminum electrolytically by floating molten refined aluminum for use as a cathode on an electrolytic bath which in turn floats on a molten alloy of unrefined aluminum and a heavy metal for use as an anode, said bath comprising from 37 to 47 per cent by weight of barium chloride, from 18 to 28 per cent by weight of calcium fluoride and from 25 to 35 per cent by weight of aluminum fluoride, the total amount of the three salts making up approximately 95 per cent by weight of the bath, there being no more than 1 per cent of sodium potassium compounds, said fluorides and chlorides being selected in such proportion that the bath will float on the anodic layer but not float on the cathodic layer of a refining apparatus of the type described.

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