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ELECTROLYTE FOR ALUMINUM REDUCTION

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This invention relates to the production of aluminum by the electrolytic reduction process involving passage of electric current through a molten electrolyte which consists chiefly of cryolite and in which the alumina is dissolved. In a more particular sense, the invention relates to an improved electrolyte for the reduction process, having certain advantages, especially in economy, and to methods of aluminum reduction employing such electrolyte.

Metallic aluminum is conventionally produced by passing electric current of large value through so-called pots or reduction cells wherein one or more carbon anodes project downwardly into a fused, i.e. molten bath, contained in a rather shallow, refractory-walled vessel which has a carbon bottom with means for electrical connection thereto. In the process as generally practiced, i.e. the Hall process, the molten bath is chiefly cryolite (sodium aluminum fluoride) or a similar mixture of sodium and aluminum fluorides, maintained at an appropriate temperature of the order of 1000° C. by the passage of current. Purified alumina is dissolved in this molten electrolyte, in amounts usually ranging from about 2% up to the limit of its solubility, say 10% or so. The effect of the electric current is to deposit aluminum at the submerged cathode, i.e. the carbon bottom, where it collects in molten form and where it may be tapped or siphoned off from time to time. The carbon anode combines with the oxygen of the alumina to form principally carbon monoxide and carbon dioxide so that the electrodes are progressively consumed and must be replaced from time to time, either by physical substitution or by use of so-called continuous electrodes.

In common practice, a typical electrolyte composition comprises cryolite (or a similar mixture of sodium and aluminum fluorides) 88% to 90% and calcium fluoride 10% to 12%, the latter component being introduced for the purpose of lowering the melting point of the bath. Alumina is added to the bath as needed, and it is also necessary to make up the cryolite content from time to time because of loss of fluorine, such make-up being mostly effected by adding aluminum fluoride.

There have been numerous proposals for modification of the electrolyte in this process, as by way of addition of other compounds asserted to improve efficiency in one way or another. However, experience has seemed to indicate that additions are generally undesirable, either in interfering with the dissolution of alumina or in rendering the operation sensitive and difficult to control, or in creating highly undesirable by-products such as fumes or unwanted accumulations in the bath. It will be understood that reduction cells of this type are commonly expected to operate continuously for long periods of time, sometimes as much as years, without shut-down for renovation of the vessel; hence any changes in the bath must be such that they do not tend to build up to an undesirable concentration which cannot be corrected by regular addition of appropriate compounds.

The present invention embraces the discovery of a

new electrolyte composition for the aluminum reduction process, which affords definite improvement and which does not have adverse effects of a troublesome nature. Specifically it has been discovered that an electrolyte consisting of from 6% up to 9% sodium chloride (i.e. in the range below or less than 9%, but very preferably at least about 6%), from 6% to 9% of calcium fluoride, and the balance cryolite, provides definite advantage in several ways. It will be understood that all references to percentage of electrolyte composition herein are given by weight, and that in operation, the electrolyte also includes, of course, alumina dissolved therein, in the usual purified form suitable for reduction by the electrolytic process, and likewise very minor quantities, ordinarily totaling less than one percent, of other compounds such as magnesium fluoride. Whereas cryolite in strict contemplation is a specific composition of sodium aluminum fluoride, viz. Na_3AlF_6, it may be broadly understood as meaning, in electrolytes of this type, either the specific compound or equivalent or like mixture of sodium and aluminum fluorides.

Extensive tests have shown that in operation of the reduction process using the improved electrolyte, the following results are obtained. In the first place, the electrolyte, as compared with conventional bath compositions described above, appears to afford better wetting action. There is a lower consumption of carbon anodes, which is attributed to less oxidation of the carbon by air, this result being understood as deriving to a large extent from improved wetting or adherence of the electrolyte to the anode. While anode consumption by combination with the oxygen of the alumina is essential to the process, the action of air on the anode is undesirable as causing waste of carbon by oxidation or burning. The improved electrolyte reduces this loss, quite apparently by better wetting and subsequent protection of the anode surface.

In the second place, the composition has a lower melting point than conventional electrolytes, i.e. lower even than electrolytes that contain calcium fluoride which is commonly used (in larger amount) for the purpose of reducing melting point. With a lower melting point, the operation is readily performed at a lower temperature. This result is not only of general convenience, but indicates lower specific energy consumption, and also probably involves a reduction in the re-oxidation of cathodic products, so as to reduce current losses occasioned by such re-oxidation.

Finally, the electrolyte has a higher electrical conductivity, with the direct result that the process can be performed with a higher electrical efficiency, as to power or current or both. Although the electrolyte may have a somewhat reduced solubilty for alumina, it does not appear that the reduction is sufficient to impair the convenience of the operation or the working capacity of the cells or pots, nor is it sufficient to require extra attention or supervision by attending personnel. The anode gases, i.e. the gases released from the cell (and usually drawn off through appropriate covering or other arrangements), may be a little more irritating, but no serious detriment has been found in practical test.

As indicated above, there have been various prior proposals for incorporation of salts or compounds in the Hall process electrolyte, but in general, as explained, these attempted improvements have been accompanied by serious disadvantages which have made the process impractical for commercial use. For example, it has been proposed to include rather large percentages of sodium chloride, i.e. upwards of 9% and preferably from 12% to 22%, with the object of power and carbon savings, but such electrolyte has been found extremely sensitive to small disturbances in pot operation and fluctuations in anode quality, thus requiring careful

attention to and adjustment of the bath composition at inconveniently frequent times. Large quantities of irritating gases are evolved, which cause trouble in all cases and which in the situation of discontinuous electrodes or of access to the top of the pot during certain steps in the use of continuous electrodes, make the conditions quite undesirable for operating personnel. In contrast, the present, improved electrolyte has been found to have no unusual sensitivity and to present no serious difficulty from the standpoint of released gas. The reduction process involving the improved electrolyte (including sodium chloride from 6% to less than 9%) has specifically been found, in long tests, to be satisfactory for use in regular commercial aluminum production. In a broader sense, electrolytes containing sodium chloride and containing calcium fluoride 6% to 9% also appear to offer some realization of the advantages of the invention with even a little lower percentage of sodium chloride, i.e. above 4%.

As stated, the principal constituent of the electrolyte is the conventional cryolite, such term being here employed to include equivalent sodium fluoride-aluminum fluoride mixtures. Alternatively, references herein to sodium and aluminum fluoride material will be understood to mean cryolite and similar compositions as just stated and as conventionally employed in aluminum reduction cells. The proportion of sodium fluoride to aluminum fluoride, i.e. by weight (or by molecular weight in the specific complex compound) is conventionally called the bath ratio. For the prototype cryolite formula, $3NaF.AlF_3$, this ratio is therefore 1.50 to 1, conveniently expressed as 1.50. It is found that some variation in this ratio is permissible or indeed often desirable, particularly with respect to inclusion of larger relative quantities of aluminum fluoride, and hence may range from 1.10 to 1.60, with operation usually controlled to approximate the ratio of 1.50 or, preferably in some cases, a somewhat lower ratio. Thus the range 1.20 to 1.40 seems to be especially desirable from both operating and economic viewpoints, in the practice of the present invention.

By way of specific example, of experimental runs, six 45 ka. (45,000 ampere) prebake anode pots were operated continuously for six months with an electrolyte of the improved composition. Specifically, the electrolyte was made up to include sodium chloride and calcium fluoride along with the major, conventional cryolite component. The sodium chloride content was kept between 6% and 9%, i.e. inside such range, and most usually at about 7% (a special, preferred feature of invention being a sodium chloride content of 6% to about 8%). Likewise the calcium fluoride was kept within the range of 6% to 9%, generally at about 7%. Losses in bath constituents, occurring to no greater extent than with the conventional electrolyte, were made up by appropriate addition of compounds, the chief loss being fluorine and its replacement being chiefly effected by additions of aluminum fluoride. The bath ratio was maintained at about 1.30 to 1.40 during the operation.

Alumina was supplied to the bath in essentially the same manner and amount as for conventional procedure, i.e. so as to maintain an alumina content of at least about 2%, it being found that the periodic additions could be sufficient to raise the content to as high as 10%. Special observation was maintained throughout the period but no undue sensitivity was noted, nor was it concluded that extra supervision would be necessary for successful operation. As compared with corresponding pots with conventional electrolyte, it was found that these cells showed 6% lower carbon consumption and a 20° C. lower operating temperature. The indication was that the current efficiency was higher by 1.2%. Thus a positive and significant improvement was achieved in economy of carbon and electric current, with no detriment to results in the reduction and recovery of metallic aluminum from the alumina. The test indicated, too, that in addition to the important function of the sodium chloride addition, the presence of calcium fluoride to at least 6% and very preferably more than 6%, was necessary for good operation.

In comparison it may be noted that whereas similar anode pots including sodium chloride in the amount of 15% to 17% showed substantial reduction of carbon consumption, with lower operating temperature and improved current efficiency (all relative to conventional electrolytes) the pots were extremely sensitive in respects that have been noted hereinabove, requiring extraordinarily careful and frequent supervision which would more than counterbalance the apparent economies. Difficulty with off-gases was also found.

A further series of tests, involving continuous operation of a group of 45 ka. prebake anode pots with the improved electrolyte has confirmed the results of the specific example noted above. In this further test, the cells received only the ordinary supervision of the pot room line. It was found that operation was entirely satisfactory, and showed improved performance relative to the remainder of the line in which the conventional electrolyte was employed, such improvement being observed in respect to lower carbon consumption, higher production and lower operating temperature.

By way of special observation, the cells were forced to the point of anode effect at regular intervals i.e. somewhat more often than the usual occurrences. It may be explained that the anode effect is a situation occurring when the alumina content drops too low, i.e. usually below 2%, whereupon the voltage across the cell rises to an abnormally very high value, indicated by the conventional signal, and the operation of the cell deteriorates, especially in exhibiting a sudden increase in energy and anode consumption. With respect to the special cells utilizing the improved electrolyte, no unusual circumstances accompanied the anode effect conditions and correction by addition of alumina was readily accomplished as in the case of conventional pots.

It is therefore to be seen that the improved electrolyte and process herein described afford definite advantages in the aluminium reduction operation, particullarly in economy of carbon and current utilization and indeed in greater or better production.

It will be understood that the percentages of electrolyte ingredients stated herein refer in all cases to the electrolyte without the alumina, i.e. the total of all components except alumina being considered as 100%.

Although the invention is primarily directed to the described combination of calcium fluoride with cryolite and sodium chloride, and although calcium fluoride is not only preferred for its function but in its combined effect with the other ingredients may be deemed to afford a specific feature of invention, it has appeared that magnesium fluoride is capable of somewhat similar effects. Hence in a broader sense, an electrolyte exhibiting some improved characteristics in one or more of the respects explained, may be defined as consisting, with alumina, of cryolite and sodium chloride in the proportions named, and material in amount from 6% to 9%, selected from the group consisting of calcium fluoride and magnesium fluoride. For example, the stated alkaline-earth fluoride component may consist in part of magnesium fluoride and in part (preferably the major part) of calcium fluoride.

It is to be understood that the invention is not limited to the specific operations herein described but may be carried out in other ways without departure from its spirit.

We claim:

1. An electrolyte for an aluminum reduction cell, consisting essentially of sodium chloride in amount from above 4% to less than 9%, calcium fluoride in amount from 6% to 9%, and the balance sodium and aluminum

fluoride material, with alumina dissolved therein as a source of aluminum upon passage of current through said electrolyte in molten form.

2. An electrolyte for an aluminum reduction cell, consisting essentially of sodium chloride in amount from 6% to less than 9%, calcium fluoride in amount from 6% to 9% and the balance sodium and aluminum fluoride material wherein the ratio of sodium fluoride to aluminum fluoride by weight lies between 1.10 to 1 and 1.60 to 1, with alumina dissolved therein as a source of aluminum upon passage of current through said electrolyte in molten form.

3. The electrolyte of claim 2, wherein the ratio of sodium fluoride to aluminum fluoride is between 1.20 to 1 and 1.40 to 1.

4. The method of producing metallic aluminum from alumina which comprises dissolving alumina in a molten electrolyte consisting essentially of sodium chloride in amount from above 4% to less than 9%, calcium fluoride in amount from 6% to 9%, and the balance sodium and aluminum fluoride material, and passing electric current through said electrolyte.

5. The method of producing metallic aluminum from alumina which comprises dissolving alumina in a molten electrolyte consisting essentially of sodium chloride in amount from 6% to less than 9%, calcium fluoride in amount from 6% to 9% and the balance sodium and aluminum fluoride material wherein the ratio of sodium fluoride to aluminum fluoride by weight lies between 1.10 to 1 and 1.60 to 1, and passing electric current through said electrolyte.

6. The method of producing metallic aluminum from alumina which comprises dissolving alumina in a molten electrolyte consisting essentially of sodium chloride in amount from above 4% to less than 9%, material in amount from 6% to 9%, selected from the group consisting of calcium fluoride and magnesium fluoride, and the balance sodium and aluminum fluoride material, and passing electric current through said electrolyte.

7. An electrolyte for an aluminum reduction cell, consisting essentially of sodium chloride in amount from above 4% to less than 9%, material in amount from 6% to 9%, selected from the group consisting of calcium fluoride and magnesium fluoride, and the balance sodium and aluminum fluoride material, with alumina dissolved therein as a source of aluminum upon passage of current through said electrolyte in molten form.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,915,443 December 1, 1959

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

In the grant, lines 2 and 12, and in the heading to the printed specification, line 4, name of assignee, for "Aluminum Laboratories Limited", each occurrence, read -- Aluminium Laboratories Limited --.

Signed and sealed this 19th day of September 1961.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

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Commissioner of Patents

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