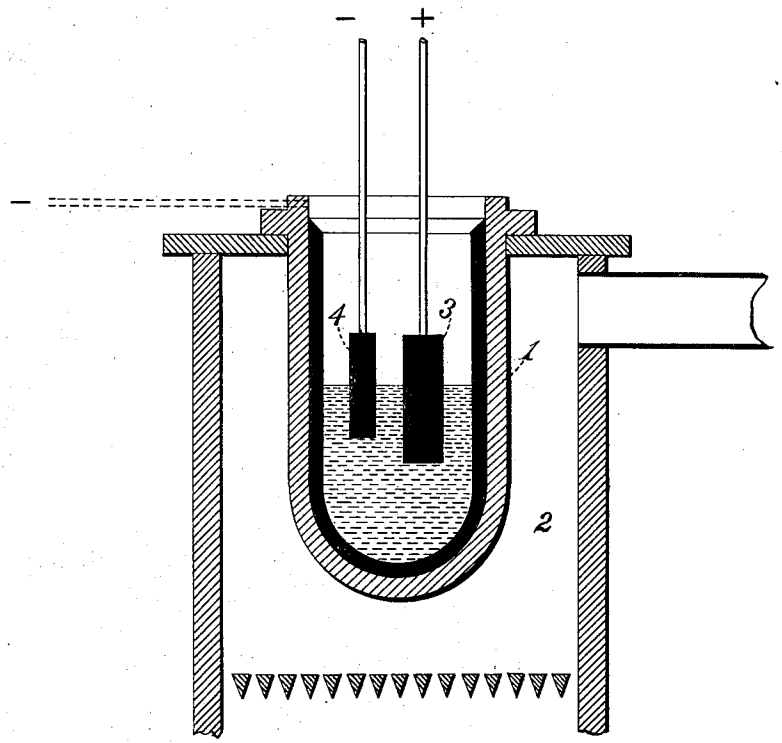
(No Model.)

C. M. HALL.

PROCESS OF ELECTROLYZING CRUDE SALTS OF ALUMINIUM.

No. 400,666. Patented Apr. 2, 1889.



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PROCESS OF ELECTROLYZING CRUDE SALTS OF ALUMINIUM.

SPECIFICATION forming part of Letters Patent No. 400,666, dated April 2, 1889.

Application filed August 17, 1888. Serial No. 282,955. (No specimens.

To all whom it may concern:

Be it known that I, CHARLES M. HALL, a citizen of the United States, residing at Oberlin, in the county of Lorain and State of Ohio, have invented or discovered certain new and useful Improvements in the Manufacture of Aluminium by Electrolysis of its Fused Salts, of which improvements the following is a specification.

In applications filed July 9, 1886, and February 2, 1887, and serially numbered 207,601 and 226,206, respectively, I have described and claimed processes for the reduction of aluminium by dissolving alumina in a bath formed of a fused fluoride salt of aluminium and then separating the aluminium by an electric current. In the process described in application, Serial No. 207,601, I employed a bath formed of the fluorides of sodium and aluminium, (represented by the formula $Na_2Al_2F_8$,) with or without the addition of the fluoride of lithium, and in the process described in application, Serial No. 226,206 I employed a bath formed of the fluorides of potassium and aluminium, (represented by the formula $K_2Al_2F_8$,) with or without the addition of the fluoride of lithium. The salts forming either of the above-mentioned baths are placed in a suitable vessel, preferably one formed of metal and lined with carbon, and then subjected to sufficient heat to fuse them and form a homogenous bath. Electrodes formed of carbon or any suitable metal and connected to opposite poles of a dynamo-electric machine are then placed in the bath, or the containing-vessel may be employed as the negative electrode. The alumina is now added to the bath, and being dissolved aluminium is reduced at the negative electrode, and being fused by the heat of the bath sinks to the bottom of the vessel, the oxygen being liberated at the positive pole.

By the above-described processes I have been able to obtain good results, but have found that during a continuous use of either of the above baths for a considerable time a black compound is formed which clogs the bath, thereby increasing the resistance thereof, and to the extent of such increased resistance decreasing the amount of aluminium produced. The formation of the black compound, which occurs sooner in the bath composed of the fluorides of sodium and aluminium than in that composed of the fluorides of potassium and aluminium, necessitates a comparatively frequent renewal of the bath.

The object of the invention described herein is to provide a bath wherein the objections heretofore mentioned do not obtain, and which can be used continuously without changes or renewal, except to supply loss occurring from evaporation.

In the accompanying drawings forming a part of this specification is shown a construction of apparatus applicable for carrying out my improved process.

In the practice of the present invention I form an electrolyte or bath of the fluorides of calcium, sodium, and aluminium, the fluorides of calcium and sodium being obtained in the form of fluor-spar and cryolite, respectively, and the fluoride of aluminium being obtained by saturating hydrated alumina (Al_2HO_6) with hydrofluoric acid. The compound resulting from the mixture of the above-mentioned fluorides, which is represented approximately by the formula $Na_2Al_2F_8 + CaAl_2F_8$, is placed in a suitable vessel, 1, preferably formed of metal and lined with pure carbon, for the purpose of preventing the admixture of any foreign material with the bath or with the aluminium when reduced. The vessel 1 is placed in a furnace, 2, and subjected to sufficient heat to fuse the materials placed therein. Two electrodes, 3 and 4, of any suitable material, preferably carbon, when pure aluminium is desired, and connected to the positive and negative poles of any suitable generator of electricity, preferably a dynamo-electric machine, are placed in the fused bath; or, if desired, the carbon-lined vessel may be employed as the negative electrode, as represented in dotted lines. Alumina in the form of bauxite, anhydrous oxide of aluminium, or any other suitable form of alumina, preferably the pure anhydrous oxide Al_2O_3 artificially prepared, is then placed in the bath, and, being dissolved thereby, aluminium is reduced by the action of electric current at the negative electrode and being fused by the heat of the bath sinks down to the bottom of the vessel, the bath being of a less specific gravity than the aluminium.

This difference in specific gravity is an important feature of my process, as the superincumbent bath serves to protect the aluminium from oxidation. The oxygen of the alumina is liberated by the action of the electric current at the positive electrode, and, when the latter is formed of carbon, combines therewith and escapes in the form of carbonic oxide (CO) or carbonic acid (CO_2).

As the aluminium is reduced, more alumina is added, so that the bath may be maintained in a saturated condition with the fused alumina. The addition of more alumina than can be dissolved at one time is not detrimental, provided the bath is not chilled, as such excess will sink to the bottom and be taken up by the bath, as required.

The proportions of the materials employed in forming the bath or electrolyte are approximately as follows: Fluoride of calcium, two hundred and thirty-four parts; cryolite, the double fluoride ($Na_6Al_2F_{12}$) four hundred and twenty-one parts, and fluoride of aluminium, eight hundred and forty-five parts, by weight. These proportions can, however, be widely varied without materially changing the efficiency of the bath. During the reduction of the aluminium the positive electrode, when formed of carbon, is slowly consumed and must be renewed from time to time; but the bath or electrolyte remains unchanged for a long time. In time, however, a partial clogging occurs, which, however, does not render the bath wholly ineffective, but does necessitate an increase in the electro-motive force of the reducing-current, the resistance of the bath being increased in proportion to the degree to which the bath becomes clogged, thereby increasing the cost of reduction. In order to entirely prevent any clogging of the bath, I add approximately three or four per cent. (more or less) of calcium chloride to the bath or electrolyte hereinbefore described. As the addition of the calcium chloride prevents, as stated, any clogging or increase of resistance in the bath, it can be used continuously without renewals or any additions, except such as may be needed to replace loss by evaporation, and without increasing the electro-motive force of the reducing-current; and, further, the addition of the calcium chloride enables each atom of carbon of the positive electrode to take up two atoms of oxygen, forming carbonic acid, (CO_2,) thereby reducing the amount of carbon consumed in proportion to the amount of aluminium produced. The calcium chloride being quite volatile is subject to loss faster than the rest of the bath, and must be renewed occasionally on this account.

In reducing aluminium, as above described, I prefer to employ an electric current of about six volts electro-motive force; but the electro-motive force can be varied within large limits.

I claim herein as my invention—

1. As an improvement in the art of manufacturing aluminium, the method herein described, which consists in fusing a combination of the fluoride of aluminium, the fluoride of calcium, and the fluoride of sodium, adding alumina to the bath so formed, and then passing a current of electricity through the fused mass, substantially as set forth.

2. As an improvement in the art of manufacturing aluminium, the method herein described, which consists in fusing a combination of the fluoride of aluminium, the fluoride of calcium, the fluoride of sodium, and the chloride of calcium, adding alumina to the bath so formed, and then passing a current of electricity through the fused mass, substantially as set forth.

In testimony whereof I have hereunto set my hand.

CHARLES M. HALL.

Witnesses:

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DARWIN S. WOLCOTT.