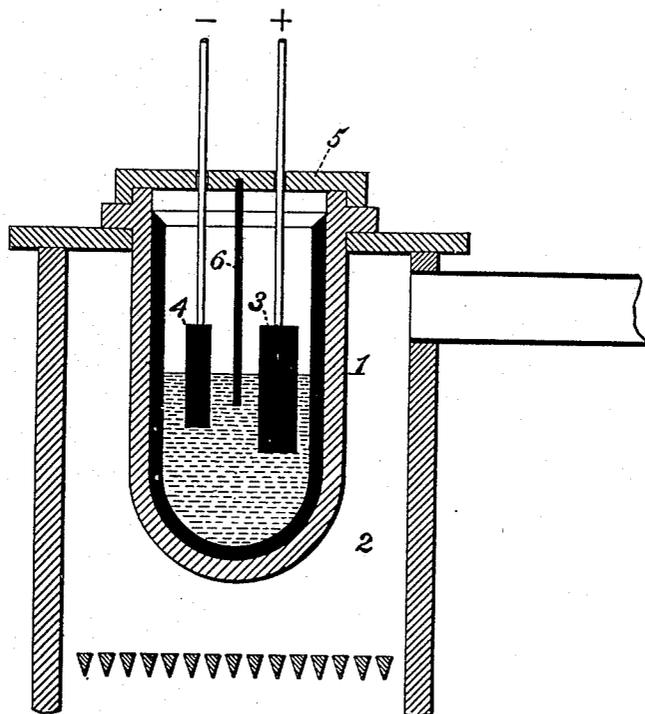


(No Model.)

C. M. HALL.
MANUFACTURE OF ALUMINIUM.

No. 400,665.

Patented Apr. 2, 1889.



WITNESSES:

E. Newell.
F. E. Gaither.

INVENTOR,

Charles M. Hall
by *Darwin B. Wolcott*
Att'y.

UNITED STATES PATENT OFFICE.

CHARLES M. HALL, OF OBERLIN, OHIO

MANUFACTURE OF ALUMINIUM.

SPECIFICATION forming part of Letters Patent No. 400,665, dated April 2, 1889.

Application filed August 17, 1888. Serial No. 232,954. (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, of which improvements the following is a specification.

In applications filed by me July 9, 1886, and February 2, 1887, numbered 207,601 and 226,206, respectively, I have described and claimed certain processes for the reduction of aluminium, wherein I employ fluoride salts of aluminium or double fluorides of aluminium and electro-positive metals—as, for example, sodium or potassium—in a fused state to dissolve alumina, and the alumina is subjected to electrolysis when in a state of solution in the fused salts, thereby reducing aluminium at the negative electrode, the oxygen going to the positive electrode. The bath formed of the double fluoride of aluminium and an alkaline metal, as described in the above application, becomes less efficient after being subjected to electrolytic action for some time. This change does not result from any removal of aluminium fluoride or of fluorine from the bath, as no fluorine is separated; but a black or dark substance is formed in the bath, apparently from the alkaline constituent of the same, which interferes with a free electrolytic action and increases the electrical resistance; hence it has been found necessary when employing the salts named to change the bath after a continuous use of the same.

The object of the invention described herein is to provide a bath wherein the reduction of aluminium from its oxide may be carried on continuously without diminution and without increasing the electro-motive force of the current.

The accompanying drawing, forming a part of this specification, is in sectional elevation a form of apparatus applicable for carrying out my invention.

In carrying out my invention I prefer to employ a double fluoride of aluminium and calcium having a composition represented by the formula CaAl_2F_6 . This composition is formed by one hundred and sixty-nine parts of alumin-

ium fluoride to seventy-eight parts of calcium fluoride or fluor-spar, the aluminium fluoride being artificially prepared by saturating hydrated alumina with hydrofluoric acid. The fluorides of calcium and aluminium unite in forming a double fluoride more fusible than the fluoride of calcium, and, as I believe, more fusible than either constituent alone.

While I prefer to use the double fluoride of calcium and aluminium represented by the formula CaAl_2F_6 in carrying out my process, there are a large number of similar double fluorides of the same metals which may be used and which closely resemble the one named, and answer almost, if not quite, as well as a bath for dissolving the alumina. Thus the double salt of the formula $\text{Ca}_3\text{Al}_2\text{F}_{12}$ has been successfully employed in the electrolytic reduction of aluminium. Whether the bath employed contains proportionately more or less aluminium fluoride within wide limits seems to make little difference.

In the practice of my invention the fluorides above mentioned are placed in the carbon-lined crucible or vessel 1, arranged in the furnace 2, and subjected to sufficient heat to fuse the material. Electrodes 3 and 4, formed of carbon when pure aluminium is desired, are connected to a suitable electric generator, as a dynamo-electric machine. If an alloy is desired, the negative electrode 4 is formed of the metal with which it is desired to alloy the aluminium. 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 dissolved in the fused bath, and being subjected to the action of the electric current aluminium is reduced at the negative electrode 4, and, if said pole is formed of some heavy metal, forms an alloy with it, which drops off and sinks to the bottom of the bath. Oxygen goes to the positive electrode, and combining therewith when formed of carbon, forms carbonic-acid gas or carbonic oxide, the carbon being gradually consumed. Alumina is added to the bath from time to time as the process is continued.

The solution of alumina in the fused bath of the double fluoride aluminium and calcium

is apparently heavier than the metal aluminium, and hence this metal, if unalloyed, rises after being reduced and floats on the surface of the bath, where it is liable to loss by oxidation, on contact with the air or with the positive electrode, where it is subjected to a strong oxidizing action; hence when reducing pure aluminium the crucible 1 is provided with a cover, 5, provided with openings for insertion of the electric conductors and the escape of gas from the crucible, and with a partition, 6, of carbon extending down into the bath and from side to side of the crucibles and separating the two electrodes. As the aluminium is reduced at the negative electrode alone, it will rise on the same side of the partition with said electrode, and hence will be protected by the cover and partition from any oxidizing influences, the carbonic-acid gas and carbonic oxide being formed on the opposite side of the partition. As the operation continues, the cover is removed from time to time and the aluminium removed from the surface of the bath.

When it is desired to form alloys of aluminium with iron, copper, or other heavy metal, the negative electrode is formed of iron, copper, or other metal with which the alloy is to be formed. The aluminium, as it is reduced at the negative electrode, takes up a portion thereof, and if the electrode is formed of heavy metal the alloy thus formed sinks to the bottom of the crucible. In forming alloys with heavy metals the cover and partition may be dispensed with, as the bath will protect the alloy from any oxidizing influences.

It may be stated that means may be used to lower the specific gravity of the bath by the addition to it of other salts lighter than the double fluoride of calcium and aluminium, so that the pure aluminium will sink in the combination and thus be protected from oxidation. Thus by the addition to the bath above described of about two-thirds its weight of the double fluoride potassium and aluminium, ($K_2Al_2F_8$) which is comparatively a very light salt, is formed a composition lighter than aluminium, which will therefore sink when reduced and be thoroughly protected.

The double fluoride of aluminium and the alkaline-earth metals, calcium, strontium, and

barium resemble each other very closely and may be employed interchangeably in this process—as, for example, the salts represented by the formulas $CaAl_2F_8$, $BaAl_2F_8$, and $SrAl_2F_8$, may be employed in the same way and the salts of strontium and barium, as well as other double fluorides of strontium and aluminium and barium and aluminium, may be used in the manner stated in regard to the double fluoride of calcium and aluminium. The salts of strontium and barium are heavier than the calcium salt, but more fusible, the salt of barium being the most fusible, and appear especially well adapted for the reduction of aluminium from alumina dissolved in them into its alloys with heavy metals, especially copper, the negative electrode in such case being formed of copper.

The double fluorides of aluminium and the alkaline-earth metals, barium, calcium, and strontium resemble each other and differ from the double fluorides of aluminium and the alkaline metals, as potassium and sodium, in that they do not change in efficiency or action on being charged with alumina and subjected to electrolytic action for the reduction of aluminium, as is the case with the double fluorides of aluminium and the alkaline metals.

I claim herein as my invention—

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

2. As an improvement in the art of manufacturing aluminium, the herein-described method, which consists in fusing a combination of the fluoride of aluminium and the fluoride 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:

W. B. CORWIN,
DARWIN S. WOLCOTT.