

Nov. 24, 1931.

J. WEBER ET AL

1,833,806

ELECTROLYTIC REFINING OF ALUMINUM

Filed Jan. 8, 1929

Fig. 1.

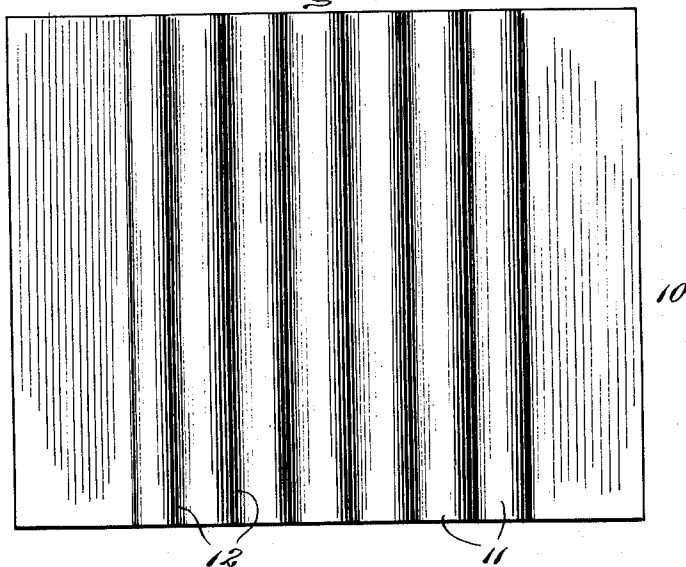


Fig. 2.

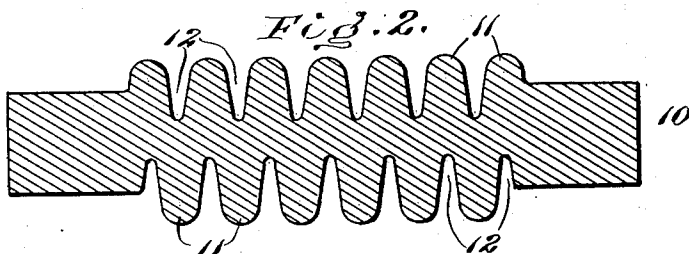
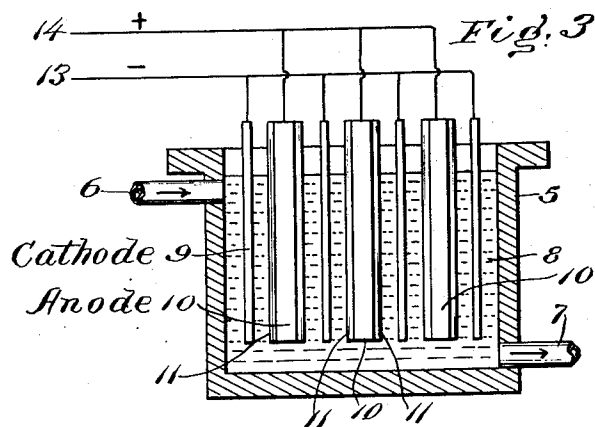


Fig. 3.



Inventors
Julius Weber & Alfred von Zeerleder
by
Morrison, Kennedy & Campbell
Attorneys.

UNITED STATES PATENT OFFICE

JULIUS WEBER AND ALFRED VON ZEERLEDER, OF NEUHAUSEN, SWITZERLAND, ASSIGNORS TO ALUMINIUM INDUSTRIE AKTIENGESELLSCHAFT, OF NEUHAUSEN, SWITZERLAND, A JOINT-STOCK COMPANY OF SWITZERLAND

ELECTROLYTIC REFINING OF ALUMINUM

Application filed January 8, 1929, Serial No. 330,987, and in Germany February 4, 1928.

This invention relates to the electrolytic refining of aluminum, and includes a novel process for producing highly pure metallic aluminum from less pure metal, and a special electrode used therein. The invention is directed particularly to the extraction of refined aluminum in a solid and dense form from pig or ingot aluminum, aluminum alloys and the like. It constitutes an improvement more particularly in that refining processes wherein the electrodes, used in a solid form, are immersed in a molten electrolyte, for example containing halogen salts, which electrolyte has a melting point lower than that of either electrode and is maintained in a molten condition below the melting point of either electrode. Such a process has been described in and made the subject of the prior application of Weber & Hauser, Serial No. 113,561, filed June 3, 1926, patented April 16, 1929, No. 1,709,759, also in an improved form in the application of Weber & Zeerleder, Serial No. 195,861, filed June 1, 1927. These prior applications may be referred to for details and features not herein fully described.

The general objects of the present invention are to render more efficient the refining process, to increase the purity of the product, and to enlarge the rate of output or production. Other objects and advantages of the invention will be explained in the hereinafter following description of an illustrative embodiment thereof or will be understood to those conversant with the subject. To the attainment of such objects and advantages the present invention consists in the novel electrolytic process of producing pure metallic aluminum, and the novel materials or electrodes used therein, and the novel features of process, operation and means herein described or illustrated.

The nature of the present improvement can best be explained by first pointing out the conditions which pertain to the processes already known and the considerations involved in further perfecting or improving the same. In practicing the described refining process we have determined that the aluminum which is deposited in solid form at the cathode may

be rendered the more pure by maintaining the current density lower at the anode. The reason underlying this is that the selective action of the electric current on the various constituents of the anode is far more effective at low than at high current densities. By the use of low current densities it is possible particularly to restrain the taking up of iron at the anode, although iron, which is invariably present in pig aluminum, has a considerably greater tendency to enter into solution than other constituents, for example silicon, which is an equally unavoidable and undesirable impurity in pig aluminum.

While, as stated, the use of lower current density at the anodes is found to enhance the purity, on the other hand we find that far higher current densities are permissible at the cathodes without impairing the purity of the deposited metal.

Observation of the described process shows that the electrolytic tension of the bath commences to increase at a rapid rate as soon as the aluminum at the anode has been dissolved to a depth of several millimeters, the remaining undissolved constituents, consisting chiefly of iron and silicon, forming a sort of coating or crust. This coating of impurities upon the anode acts as a membrane or skin tending to resist the passage of the electric current and thereby increasing the electrolytic tension of the cell. Moreover this resulting increase in tension tends to bring about still other obstacles to the action taking place at the anode, due partly to local elevations of temperature, and partly to a tendency to increase the electrolytic potential at the surface of the anode. The harm of these disadvantageous actions is that in due time the increasing potential will reach that potential at which the iron impurity starts to dissolve at the external layers of the anode.

We have determined however that the described interfering alteration of electrolytic tension at the surface layers formed by the undissolved impurities of the anode is materially smaller at the low current densities than at high ones. In other words there is a critical potential at which the iron and other undesirable impurities commence to go

into the solution, which critical point is not reached when using the low current densities, or is only reached when the aluminum has been dissolved from the deeper layers of the anode, whereas with the higher current densities appreciable amounts of iron and silicon inevitably pass into solution.

While it therefore appears that the lower current densities are desirable in order to reduce the amount of impurity in the product deposited at the cathode, yet, on the other hand, it is considered to be necessary, in a commercial sense, to operate with current densities as high as possible in order to carry on the process in the most economical way to afford the maximum output. The reason for this latter consideration is that the high current densities produce at the cathodes more metal per unit of surface in a given time, thereby not only increasing rate of output, but effecting an economy in electrolyte material and a saving space and cost. For instance, production economies may be effected by reducing the size of the electrodes and thereby the quantity of electrolyte, which at the same time means a substantial saving of current employed in the electric heating of the electrolyte.

Clearly therefore it would not be economical to employ a relatively small size of cathode in conjunction with a large size of anode in order to permit high current densities at the cathodes and low densities at the anodes, because by this plan it would not be possible to reduce the size of the cell, nor the quantity of electrolyte, nor the amount of current required. Neither are the desirable results obtainable by the use of cathodes and anodes which have the same size or dimensions (length and breadth) and the usual platelike form with plane sides, because with this plan it would not be possible simultaneously to maintain high current densities at the cathodes and low densities at the anodes. In order to insure a thorough exhaustion of the anode material, anodes in the form of a plain plate would have to be made relatively thin, and would therefore have to be replaced with objectionable frequency, or else the total amount of electric current passed through the bath would have to be reduced considerably, consequently rendering far less the rate of metal produced per unit of surface, resulting in a most uneconomical system.

According to the present invention the difficulties referred to are altogether avoided and the desired advantages are obtained by the employment, in the described process, of anodes each having a substantially larger surface than an anode of the same size or dimensions and the same weight, but with plain or flat sides or surfaces. The present invention is characterized by presenting the solid anode metal in a form so departing from a

simple plate or slab as to afford substantially increased exposed surface. Such surface may be increased in various ways, preferably by means of elevations and depressions formed at the surface, or at both surfaces, of the anode. The exposure is much increased, not merely in comparison with a plain plate, but preferably also in comparison with the opposing cathodes, thereby causing the desired differential in current densities at the two electrodes.

It is not at first sight clear that such anodes, formed with elevations and depressions substantially enlarging the surface of exposure, can be used in the described process, because of the known fact that under ordinary conditions the lines of current flow prefer prominent surface portions or elevations to flat portions or depressions and therefore tend to be far more dense at angles, edges and projections than at flat surfaces, depressions or grooves. From this consideration it might be expected that the disintegration of the special anodes contemplated by this invention would tend to take place only at the outstanding portions or elevations and not at the flat portions or depressions, which, if true, would render practically impossible a systematic or complete exhaustion of the anode material.

We have determined however by test and demonstration that with the present invention this drawback does not occur, and that, notwithstanding the expected tendency, the distribution of the current remains practically uniform over all of the surface of the anode. We attribute this largely to the character of electrolyte employed, which has very good conductivity. Actually therefore, the special anodes of this invention, with their large exposed surface, are decomposed in a substantially homogeneous manner. The invention thus makes possible a far better utilization of the anode material than is obtainable with the use of anodes having the same size or dimensions and weight, but having plain side surfaces and being accordingly thicker in section.

Anodes, according to this invention, may be of various form or design, and may afford a surface from twice to eight times the extent of an anode having the same length and breadth but with flat sides. Although in using a simple plate or slab as an anode the tension of the electric current tends to exceed the admissible limit or critical point described as soon as thirty per cent more or less of the contained aluminum has been dissolved, we find that an anode of the same length, breadth and weight, but whose surface has been made large according to the present invention, may not require to be replaced until ninety per cent more or less of its aluminum has been dissolved. We also find that notwithstanding this almost complete utilization of the

aluminum the original form of the anode subsists, and no impairment of the electrolyte from crumbling of the insoluble residues can be observed.

By way of more detailed illustration of the present invention reference is made to the accompanying drawings. Fig. 1 is a side elevation of an anode having a special form with greatly increased exposed surface, by reason of the presence of ribs and grooves.

Fig. 2 is a horizontal section taken through the anode of Fig. 1.

Fig. 3 shows a simple electrolytic cell corresponding with said prior application 113,561 and containing electrodes and electrolyte operating according to the present invention.

The cell 5 is shown as having an entering pipe 6 to permit the circulation or replacement of electrolyte, and an exit pipe 7. The electrolyte or bath 8 is a molten bath having a melting point lower than and maintained below the melting point of either electrode. As described in the prior applications such bath may contain halogen salts, namely halides of aluminum and halides of another metal or metals having alkaline properties, and the bath having good electric conductivity. A typical bath comprises halogen salts of aluminum together with halogen salts either of one or more alkali metals or one or more alkali earth metals, or all of these salts, as more particularly disclosed in the prior applications. A simple bath consists of $\text{NaCl} \cdot \text{AlCl}_3$. In the bath are shown immersed alternated cathodes 9 in the form of plain slabs or plates and anodes 10 of special form, but of the same size, that is length and breadth, as the cathodes.

The special anode 10 is shown as formed to present enlarged exposed surface by means of a system of elevations or ribs 11 and depressions or grooves 12. This undulated form materially increases the surface. Preferably the ribs and grooves are formed at both sides of the anode and in such manner that the ribs at one side are opposite to the grooves at the other side, so that the anode is given a substantially uniform thickness from surface to surface at every point, and presents no parts which, being thicker than others, would still contain aluminum, while the thinner parts of the anode would already be completely exhausted. An analogous increase of exposed surface may be effected in various other ways, for example by having the ribs and grooves run in intersecting directions so as to form prominences of the shape of pyramids. The anode may be produced not only by casting but by rolling or by extrusion into appropriate shapes.

The electrical connections may be made in various ways, but for example, as shown, the several anode plates 10 and the cathode plates 9 are connected in parallel. Thus a conduc-

tor 13 connects the cathodes and a conductor 14 connects the anodes, and the proper current may be supplied to these conductors both for the purpose of heating the electrolyte to maintain it in molten condition, and for electrodeposition. Or the heating may be effected by a secondary current or by external means. Other ways of electrical connections may be applied, for example the connection in series, especially according to the well known Hayden or series system, which has been known and used for many years, for example in copper refining, and which is described in various publications, such as *Engineering and Mining Journal*, New York, Vol. LIV (1892) page 126.

An illustrative instance, within the principles described, the anodes and cathodes may be of such relative character or arranged that a cell voltage of 0.3 volt between anodes and cathodes the current density at the anodes may be 0.5 amperes or less per square decimeter, and at the cathodes 1.0 amperes or more, with an appropriate distance of separation and electrolyte of high conductivity as described.

There has thus been described a process for producing highly pure metallic aluminum from less pure metal and a special electrode or anode for use therein embodying the principles and attaining the objects of the present invention. Since various matters of process, ingredient and apparatus may be variously modified without departing from the principles of the invention, it is not intended to limit the invention to such matters except so far as set forth in the appended claims.

What is claimed is:

1. A process of electrolytic extraction of pure aluminum by the refining of pig aluminum, aluminum alloys or the like, and wherein both the aluminum containing anodes made of the material to be refined and the cathodes are used in a solid form together with an electrolytic bath having a melting point lower than that of either electrode, and consisting of halogen salts of aluminum and of alkaline and/or alkaline earth metals, characterized by the use of an anode having a substantially larger surface than an anode of the same size and the same weight but with plane surfaces.

2. The electrolytic process of producing highly pure metallic aluminum from less pure metal wherein the electrodes in solid form are immersed in a molten electrolyte containing halogen salts and having a melting point lower than and maintained below the melting point of either electrode and characterized by presenting the solid anode metal in a form substantially departing from a plain slab or plate so as to afford substantially enlarged surface of exposure, as compared with that of the cathode.

3. The electrolytic process of producing highly pure metallic aluminum from less pure

metal wherein is used a molten electrolyte having a melting point lower than that of the anode, and characterized by the use of a solid anode in a form departing substantially from a plain slab or plate so as to present extensive surface of exposure.

4. The electrolytic process of producing highly pure metallic aluminum from less pure metal wherein the electrodes in solid form are immersed in a molten electrolyte possessing good conductivity and having a melting point lower than and maintained below the melting points of the electrodes, and characterized by presenting the impure metal as solid anodes having substantial elevations and depressions presenting extended surface exposure.

5. The combination with a molten electrolytic bath and means for supplying current, a series of cathode plates and alternated therewith a series of solid anodes formed with substantial surface elevations and depressions, so as to present a larger surface than that of the cathode, whereby to cause a larger current density at the cathode than at the anode.

6. The electrolytic process of producing highly pure metallic aluminum from less pure metal wherein the electrodes in solid form are immersed in a molten electrolyte containing halogen salts and having a melting point lower than and maintained below the melting point of either electrode and wherein the anodes and cathodes are of such different character or arrangement that the current density at the anodes is substantially less than at the cathodes.

In testimony whereof, this specification has been duly signed by:

JULIUS WEBER.

ALFRED VON ZEERLEDER.