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J. WEBER ET AL

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PROCESS OF PRODUCING ALUMINUM

Filed June 3, 1926

Fig. 1.

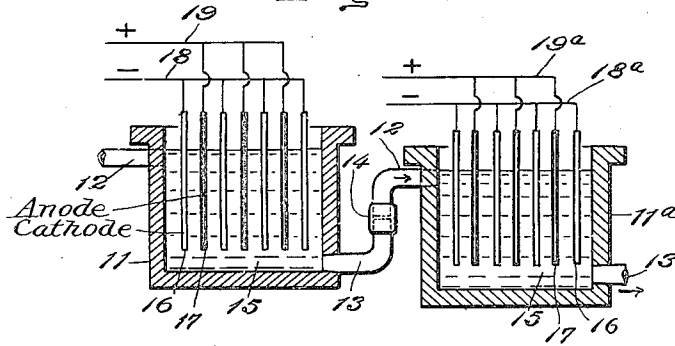


Fig. 2.

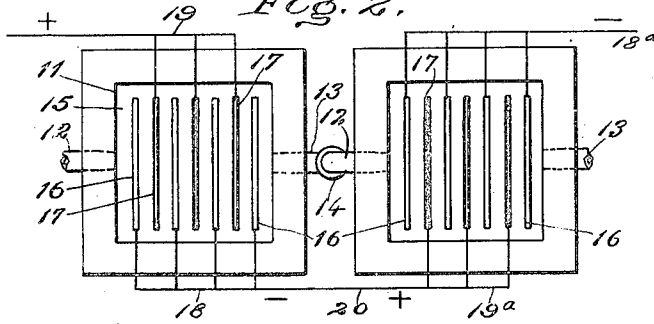


Fig. 3.

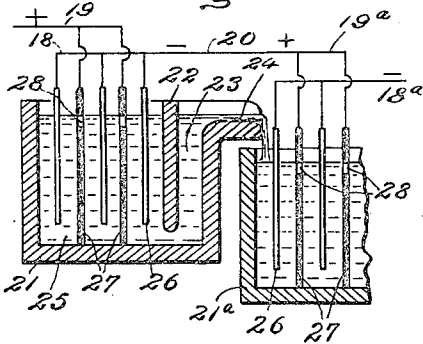
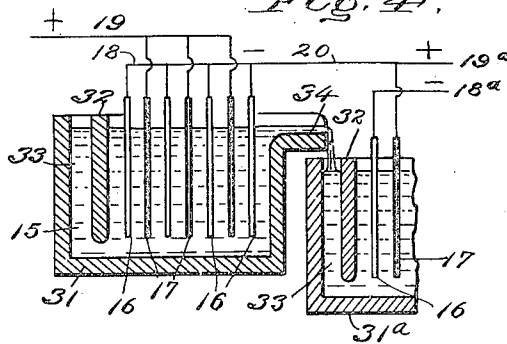


Fig. 4.



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PROCESS OF PRODUCING ALUMINUM.

Application filed June 3, 1926, Serial No. 113,561, and in Germany January 27, 1926.

This invention relates to the production of aluminum of substantially any desired high degree of purity, by the electrolytic refining of impure aluminum or aluminum alloys; and includes the process, the steps thereof, and the apparatus herein disclosed.

It has been proposed in the past to produce pure aluminum by means of an electrolytic refining process corresponding to the process generally used for refining other metals, for instance, copper, but it is believed that none heretofore proposed has been entirely successful for commercial operation. This failure is partly due to difficulties arising from the construction of the apparatuses formerly used and which involve a very high consumption of energy and require an extremely careful supervision of the electrolysis, whereby high expenses for wages, etc. are caused. Besides, an essential impediment of carrying out such processes in practice is the fact that, with regard to the high temperatures in question, and to the relatively high anodic current densities required, the selective action of the different electrolytic solution tensions of the individual metals cannot become effective. Thus, it has been heretofore considered to be inherently impractical to use chlorides as main constituents for preparing the fused electrolyte or bath, because in such molten baths the silicon contained in the anodic aluminum alloys would be dissolved, and then deposited on the cathode along with the aluminum, thereby incorporating an intolerable impurity with the aluminum deposited on the cathode.

The general objects of the present invention are to afford an aluminum refining process and apparatus of improved efficiency and reliability of action, and of convenience and economy of operation. A particular object is to overcome the above recited difficulties presented by prior known refining processes; and other and further objects and advantages of the invention will be pointed out in the hereinafter following description of one or more illustrative embodiments thereof, or will be apparent to those skilled in the subject. To the attainment of such objects and advantages the present invention consists

in the novel aluminum refining process and apparatus and the novel features of reaction, operation, step, arrangement and combination herein described or illustrated.

The present invention is based upon our discovery that all the drawbacks and difficulties mentioned above are overcome by using as electrodes an anode of the material to be refined as well as a metallic cathode, both in a solid state and under temperature conditions avoiding the customary fusing of the electrodes.

Under our invention the electrolyte to be employed must have a melting point lower than the melting point of the anode material to be refined as well as that of the cathode metal and thus render it practicable to operate with such low anodic current densities as will permit of making the best of the advantages resulting from the high electrolytic solution tension of aluminum in comparison with that of the metals usually present as alloying constituents.

The current concentration in the electrolyte can in this case be reduced, so that only a minimum consumption of energy is required for the flow of the current. The distance between the anodes and the corresponding cathodes is fixed by any suitable means in a manner to give the best possible results of electrolytic deposition combined with a minimum consumption of energy.

It has been ascertained by us that, for the electrolyte, a great number of double salts of aluminum chloride with chlorides of alkali metals or alkali earth metals fully meet the purposes stated above. Besides, other halogen salts can be used, the bromides and iodides, of course, being of less technical importance because of their high price; furthermore, sulphides can be used; whereas fluorides by themselves will not be desirable because of their high melting points; however, they may be advantageously used as additions to the salts mentioned above. In a very simple embodiment of our invention electrolysis is performed with aluminum-potassium chloride or aluminum-sodium chloride or both of these chlorides as a molten electrolyte.

When using an electrolyte of the composition $\text{NaCl} \cdot \text{AlCl}_3$, or aluminum sodium chloride, the process can be carried out at a temperature between 150° and 300° C. By adding further aluminum chloride, the temperature of the bath can be reduced even more, whereas in the presence of less aluminum chloride the temperature of the bath can be raised up to 600° C. Generally speaking we find it possible to lower the melting point of the electrolyte by using suitably composed mixtures of salts. By the aid of various salt mixtures of the kind it is possible to carry out our electrolytic process at temperatures from 80° to 600° C. Besides using in the electrolyte various alkali metal salts, certain alkali earth metal salts, such as, for instance, calcium, strontium, lithium or magnesium chlorides may be added to the aluminum halide; this latter group comprising metals whose hydroxides have alkaline properties but less marked than with the potassium group or alkali metals.

We prefer working with anodic current densities between 1 and 10 amperes or even less; however, they may be increased above 10 amperes, in which case the voltage of the bath is raised. Still, in the most frequent cases the current densities are approximately one ampere per square decimeter. At the cathodes refined aluminum is deposited in a fairly compact form. Satisfactory results are obtained with cathodic current densities of about 1 to 10 amperes per square decimeter; however, it is quite possible to produce a coherent cathodic metal deposit when using current densities above 10 amperes per square decimeter. In this case the electrolyte is preferably agitated. Putting up with the requirement of larger expanse of surface, one can even operate with current densities below 1 ampere.

It is thus seen that by the process described, pure aluminum can be produced from various materials, such as aluminum of commercial grades produced by the electrolysis of a bath of aluminum dissolved in cryolite as commonly used at present (Hall process), as well as waste or chips of aluminum and aluminum alloys. A particular advantage is that the process is workable with aluminum alloys directly produced from suitable raw materials by thermic reduction or by electrolysis, and containing the natural proportions of the accompanying substances present in these raw materials. For instance, aluminum alloys are produced from bauxite, clay (kaolin) or the like, by thermal reduction (with carbon or coke) in an electric furnace. In the case of using bauxites, which contain but little iron, or which are practically free thereof, the material after being finely ground may be directly introduced into the electrolytic bath of the Hall process, without being previously purified and converted into alumina,

thus saving considerable cost. In this case, the resulting product is a crude aluminum relatively rich in silicon and poor in iron, and frequently with a small content of titanium. If aluminum manufactured by the customary fluoride electrolysis is used as anode material, it is possible to produce a refined metal having a metallic aluminum content as high as 99.9 per cent or higher.

In accordance with our process, aluminum, because of its high electrolytic solution tension, will first be dissolved out of the anodes in the course of electrolysis, while other metals such as iron and silicon are left undissolved, and can be collected and commercially utilized as anode residues either in the shape of loose particles or of coherent skeletons. Next to aluminum, iron has the greatest tendency to enter into the solution. This can be obviated by taking care that, at any stage, the anode alloy contains as much silicon as is requisite for maintaining the whole of the iron present combined with the silicon (in the form of ferro-silicon, FeSi) which will not enter the solution. Any free silicon in excess may be converted into large crystals by suitable thermal treatment of the anode alloy when being manufactured, for instance, by causing the anode alloy to cool at a very slow rate when solidifying from the molten state.

After having grown to a suitable weight the cathodes are removed from the bath. The pure metal can be brought into commercial form in remelting furnaces as commonly used in aluminum works, or in any other way.

In commencing our electrolytic process preferably aluminum sheets, or matrix sheets of other metals, as cathodes, are suspended in the bath, these sheets being thin plates suitably shaped to the dimensions of the cell and bath. Since a great number of these cathode sheets, connected for example in parallel, are suspended at one time in the bath, it is feasible to replace the individual cathodes without interrupting the electrolytic process. Because of this and of the continuous progress of the electrolyte from cell to cell the entire process is truly a continuous and uninterrupted one in a practical sense.

In the accompanying drawings Fig. 1 is a longitudinal vertical section of a series of units constituting an apparatus embodying features of the invention and by which the described method may be carried out, the elements shown largely in diagram.

Fig. 2 is a diagrammatic plan view of the apparatus shown in Fig. 1, but with a modification in the electric wiring diagram.

Fig. 3 is a diagrammatic sectional view of a modified form of apparatus, and Fig. 4 is a similar view showing a further modification.

Referring to Fig. 1 the successive electrolytic units, tanks or cells 11, 11^a, etc., can be composed of any suitable material, whether

conducting or non-conducting, which resists injury from the molten electrolyte. The second cell 11^a is shown set at a slightly lower level than the first cell, and this arrangement may be carried through to the end of the series so that the electrolyte can flow by gravity from the first unit to the final one, from where it is led by any suitable means to the first one again, or to the first cell of another series. An inlet pipe 12 is shown leading into the upper part of each cell, and an outlet pipe 13 leads from the lower part of each cell at the end opposite to the inlet. Each outlet 13 may be extended upwardly and connected with the succeeding inlet 12, so as to maintain the desired progress of flow. When the cells are constructed of conducting material, it is preferable to connect the inlets and outlets 12 and 13 by an insulating joint or coupling 14, as shown, and so prevent electric conduction from cell to cell.

Immersed in the molten electrolyte 15 are shown a series of cathodes 16 and alternated with them a series of anodes 17. Each cathode may consist of a matrix plate or sheet acting as a carrier upon which the aluminum is to be electrolytically deposited. For this purpose plates of pure aluminum may be employed, but other metals may sometimes be used. When the aluminum deposit on each cathode has grown up to a substantial thickness, the cathode may be removed from the electrolytic bath, whereafter the aluminum deposit may be stripped off by mechanical means, or subjected to any further treatment, along with the carrier or matrix sheet when composed of pure aluminum. A fresh matrix sheet may be inserted in place of each one removed. Each anode 17 is shown as a plate or sheet of the impure aluminum which is to be refined, such as ordinary commercial aluminum or an alloy produced directly from raw material with natural impurities, as described. The anodes and cathodes are suspended or immersed in the electrolyte and any support or mounting may be used which permits them to be set or adjusted to maintain the proper spacing between them.

Preferably the anode plates and the cathode plates in each cell are connected in parallel. The several cathodes 16 are shown connected together by a conductor 18, and the several anodes by a conductor 19. When a series of cells is employed, the successive cells are connected in series with the source of current or line wires. Thus as shown in Fig. 2 the conductor 18 connecting the cathodes of one cell may be connected across by a conductor 20 with the conductor 19^a connecting the anodes of the succeeding cell, thus giving a series connection. In either case the entire series of cells will be operated to cause the electrolytic deposition of aluminum as a continuous process while the

electrolyte progresses from cell to cell, being caused to flow from the last cell of a series to the first one again, or to the first cell of another series, or otherwise.

The connecting pipes 12 and 13 in Figs. 1 and 2 carry the progressing liquid from the lower part of one cell to the upper part of the next cell, so that in each cell the material enters at one level and leaves at another, thus improving the circulation and thoroughness of the operation. This may be varied as indicated in Figs. 3 and 4.

In Fig. 3 the first cell 21 discharges by gravity into the second cell 21^a. Each cell near the overflow point may be provided with a partition wall 22 extending downwardly nearly to the bottom, so that the electrolyte is drawn from the lower part of the cell, and passes up through the outlet passage 23, thence by a spout 24 discharging into the upper part of the succeeding cell. By this arrangement the electrolyte progressing through each cell is forced to descend from the topmost level to the bottom level, as well as traveling from one end of the cell to the other, thus producing an intensive agitation and thorough mixing so as to prevent impoverishment of individual portions of the electrolyte.

Other arrangements may be employed to improve the circulation and mixing of the electrolyte. Thus in Fig. 3 the electrolyte 25 is compelled to pass underneath each cathode 26, the cathode being the full width of the cell, but not reaching to the bottom; whereas it is compelled to ascend along the surface of each anode 27, between it and a cathode, and progress through a passage or slot or row of apertures 28 near the upper level of the liquid, for example formed directly in the anode, which also is the full width of the cell; so that the flow will be up and down through the length of each cell, and finally from the spout into the succeeding cell.

The electric connections in Fig. 3, and in Fig. 4 as well, as shown of the series kind, corresponding with Fig. 2.

In the arrangement shown in Fig. 4, the cells 31 and 31^a may be arranged at descending levels as before, but in this case the partition wall 32 is shown arranged near the first end of each cell, forming an inlet passage 33 receiving the electrolyte from the overflow or spout 34 of the preceding cell. The electrodes are of the full width of the cell and may be arranged as in Figs. 1 and 2, or as in Fig. 3, the former being illustrated in electrodes 16 and 17.

For the purpose of maintaining the electrolyte in a molten condition and at a temperature most favorable for the reactions, each cell may be heated in any suitable manner, for example by making use of the heat produced by the electrical resistance of the electrolyte itself to the direct electrolytic

current; or the heat may be furnished by a secondary alternating current, or by a suitable source of external heat.

We claim:

5 1. The electrolytic refining process of producing metallic aluminum of a high degree of purity from less pure metallic material which consists in passing an electric current from a solid anode of the less pure metal to
10 a solid cathode through a molten electrolyte having a melting point lower than that of either electrode, and capable during electrolysis of dissolving the aluminum of the anode, while maintaining a temperature hotter than the melting point of the electrolyte
15 but insufficient to melt the electrodes.

2. The electrolytic refining process of producing metallic aluminum of a high degree of purity from less pure metallic aluminum
20 which consists in passing an electrolytic current from an anode composed of the less pure metal in a solid state to a cathode composed of metal in a solid state through a continuous, non-aqueous molten electrolytic bath having
25 a melting point lower than that of either electrode and maintained above its melting point but below the melting points of the electrodes, said bath comprising metal salts and capable during the electrolysis of dissolving
30 the aluminum of the anode and depositing aluminum upon the cathode.

3. The aluminum refining process as in claim 1 and wherein is employed a solid anode comprising an aluminum alloy containing
35 silicon and iron in the proportion of at least one atom of silicon to one atom of iron.

4. The aluminum refining process as in claim 1 and wherein the electrolyte contains halogen salts of aluminum and of a metal
40 the hydroxide of which has alkaline properties.

5. The continuous electrolytic refining process of producing metallic aluminum of

a high degree of purity from less pure metallic aluminum which consists in maintaining a system of anodes composed of the less
45 pure metal in a solid state and a system of cathodes composed of metal in a solid state continuously immersed in a molten electrolytic bath composed of metal salts and capable
50 during the electrolysis of dissolving out the aluminum of the anode and depositing aluminum upon the cathode, while maintaining such bath hotter than the melting point of its ingredients, and passing an electric
55 current from the anodes to the cathodes and progressively circulating the electrolyte through the system.

6. The process as in claim 1 and wherein the electrolysis is carried on with low current
60 densities, approximately one ampere per square decimeter, thereby taking maximum advantage of the high solution tension of aluminum in dissolving it selectively from
65 the anode.

7. The art of producing highly refined aluminum from raw material containing silicon in excess of iron along with aluminum, consisting in, first, reducing such
70 raw material by heat and causing the resultant molten alloy to cool at a very slow rate, thereby to crystallize the excess of silicon, and second employing such cooled reduced alloy as a solid anode, and passing an electrolyzing current from such anode to a solid
75 cathode through a molten electrolyte having a melting point lower than that of either electrode and capable during electrolysis of dissolving the aluminum of the anode, while
80 maintaining a temperature between the melting point of the electrolyte and the melting points of the electrodes.

In testimony whereof, we affix our signatures.

JULIUS WEBER.
HANS HAUSER.