

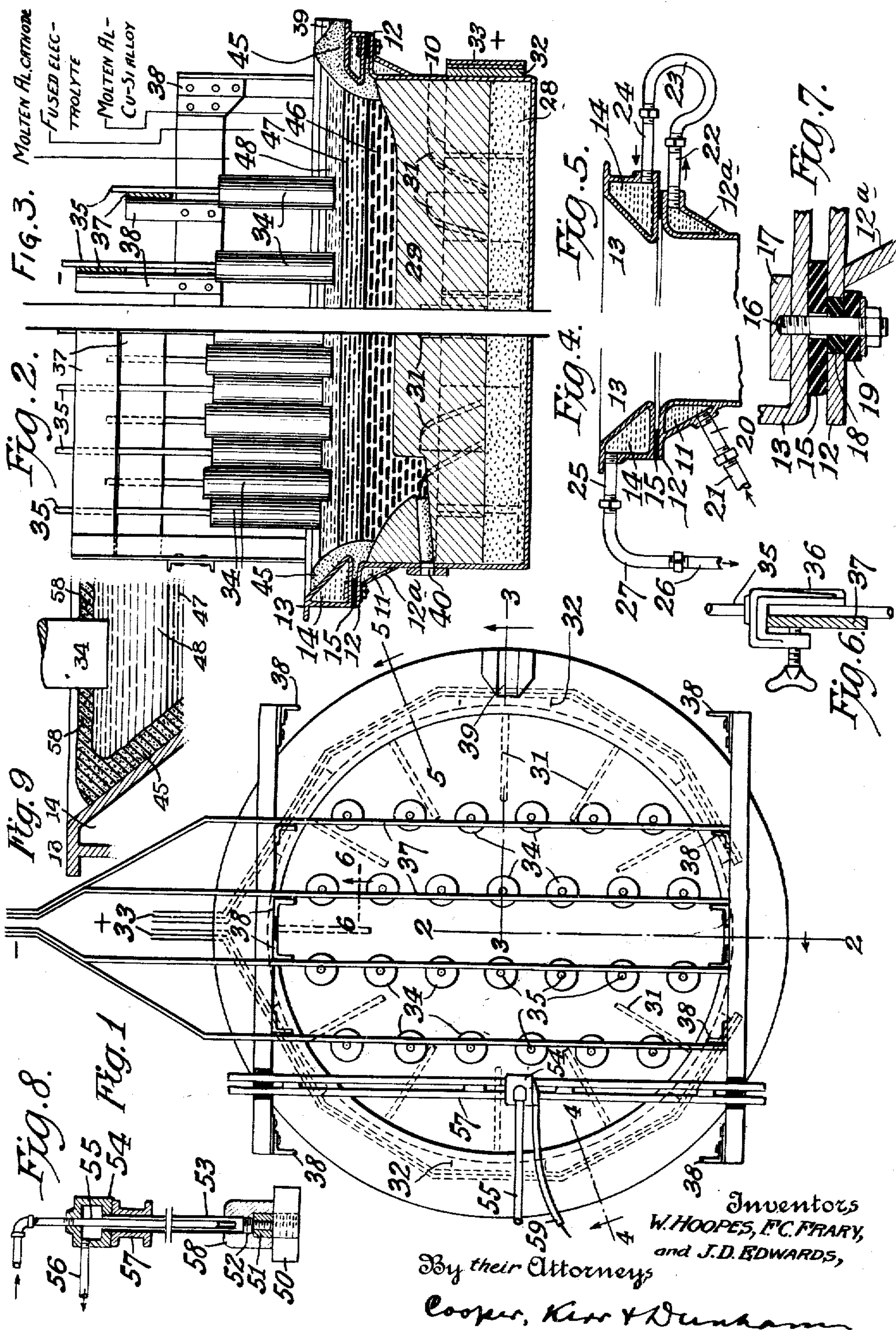
April 21, 1925.

1,534,317

W. HOOPES ET AL

ELECTROLYTIC PRODUCTION OF ALUMINUM

Filed Dec. 21, 1922



Inventors  
W. HOOPES, F.C. FRARY,  
and J.D. EDWARDS,  
By their Attorneys  
Cooper, Kiser & Dunham



UNITED STATES PATENT OFFICE.

WILLIAM HOOPES, OF PITTSBURGH, AND FRANCIS C. FRARY AND JUNIUS D. EDWARDS, OF OAKMONT, PENNSYLVANIA, ASSIGNORS TO ALUMINUM COMPANY OF AMERICA, OF PITTSBURGH, PENNSYLVANIA, A CORPORATION OF PENNSYLVANIA.

ELECTROLYTIC PRODUCTION OF ALUMINUM.

Application filed December 21, 1922. Serial No. 608,284.

To all whom it may concern:

Be it known that we, WILLIAM HOOPES, FRANCIS C. FRARY, and JUNIUS D. EDWARDS, all citizens of the United States of America, the said WILLIAM HOOPES residing at Pittsburgh and the said FRANCIS C. FRARY and JUNIUS D. EDWARDS residing at Oakmont, all in the county of Allegheny and State of Pennsylvania, have invented certain new and useful Improvements in Electrolytic Production of Aluminum, of which the following is a full, clear, and exact description.

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 containing other substances. Several methods for the purpose have been suggested in the past, but it is well known that none heretofore proposed has been capable of commercial operation. In fact it has been widely held among those skilled in the production of aluminum that such processes are inherently impractical. Our invention is the result of extensive investigation and study of the problems involved, combined with practical work on a large scale, and has been found to be thoroughly feasible. With it we have produced commercially, at low cost, metal having a metallic aluminum content as high as 99.98 per cent.

In our method impure aluminum or aluminum alloy is used in a molten state as anode, in contact with a superimposed bath or electrolyte, preferably consisting of or containing one or more fused fluorids, with or without the addition of chlorids; the pure aluminum being deposited on a cathode of molten aluminum, preferably floating on the bath or electrolyte. The invention embraces several advantageous features which, although capable of use separately, are especially effective when employed conjointly. One of the most important of these is the provision of an alloy, for use as anode, which at the operating temperature will be sufficiently mobile to permit the aluminum contained in it to continually replace, at the surface of the anode alloy, aluminum removed therefrom by the electrolysis. Without such provision impurities in the alloy may be dissolved in the electrolyte and deposited at the cathode in such amount as to seriously

affect the purity of the refined metal. Another feature of importance in our invention resides in promoting the secondary reactions by which impurities dissolved from the anode alloy are re-precipitated thereon and those deposited on the cathode are re-dissolved in the bath; as for example by producing an energetic circulation whereby the bath freely washes, or is freely washed by, the contiguous surfaces of the anode and cathode respectively. A further advantageous feature consists in maintaining at least a certain minimum proportion of aluminum in the anode alloy, as by withdrawing more or less of the latter and supplying fresh alloy in its place, for the purpose of preserving the selective aluminum-dissolving action of the bath.

The electrolyte or bath which we prefer to employ in the present method contains aluminum fluorid, with the addition of one or more fluorids of metals more electropositive than aluminum. Preferably the bath is of about the following composition:

	Per cent.	
Aluminum fluorid	25 to 30	
Barium fluorid	30 to 38	
Sodium fluorid	25 to 30	
Alumina	0.5 to 3	
Calcium and magnesium fluorids, present as unavoidable impurities, about	2	

The addition of fluorids of other of the alkali or alkali-earth metals is permissible, but the presence of halogen anions other than those of fluorin is undesirable, and indeed is highly objectionable if aluminum of a high degree of purity is to be obtained. On the other hand, the presence of oxygen anions is not usually objectionable, and accordingly alumina may be an ingredient of the bath. In some cases alumina is a desirable ingredient, but not, in general, in amount sufficient to saturate the mixture. The use of a bath containing between 20 and 60 per cent of barium fluorid, or strontium fluorid in like amount, or a mixture of the two, is claimed broadly in our copending application Serial No. 608,285. Barium and strontium are alkali earth metals having atomic weights above 80.

Speaking generally, the bath or electrolyte



employed should be capable, under normal conditions, of acting selectively with respect to aluminum, so that the latter can be dissolved from the anode alloy to the substantial exclusion of the other ingredients thereof. This important capability is possessed in high measure by electrolytes of the class described in the foregoing.

A bath such as the above is fluid within the range of suitable working temperatures, and is of lower density than the impure aluminum or aluminum alloy which has been found in general most suitable for the process. Hence the bath will float on the molten alloy. At the same time the bath is of higher density than the refined or pure aluminum, so that the latter will float on the former. Moreover, the bath described is capable of dissolving a substantial amount of alumina. For a more extended discussion of electrolytes for the electrolytic refining of aluminum reference may be had to the copending application of William Hoopes and Francis C. Frary, Serial No. 608,286; and to our copending application, above mentioned, wherein the electrolyte preferred for our present invention is claimed broadly.

In general, any alloy of aluminum may be refined which has a greater density than the bath or electrolyte and which will remain satisfactorily mobile while the refining process is going on. In case the density of the alloy is too low it may be raised by the addition of a heavier metal or metals. Of the metals that may be used for such purpose copper has been found preferable. In practice the working temperature of the preferred bath lies between 850° and 1,100° C., approximately, with a preferred temperature of about 950° C. A bath of the above analysis has at the preferred temperature mentioned a density of between about 2.5 and 2.7 grams per cc. Aluminum at the same temperature has a density of about 2.3 grams per cc. and, if it contains only small quantities of heavy metals or even considerable quantities of silicon or other impurities of low density, will float on instead of sinking in the bath. The presence of about 25 per cent of copper gives an alloy mixture which at a temperature of 950° C. has a density of about 2.8. This is sufficiently above the density of the bath to insure that the alloy will not float but will remain at the bottom. A greater proportion of copper may be used, however, provided the alloy is satisfactorily mobile at the upper limit of temperature for smooth working, say between 1050° and 1100° C.

The freezing point of pure copper is around 1083° C., but the addition of 2 per cent of silicon reduces the freezing point to about 1050° C., and an alloy containing 82 per cent of copper and 18 per cent of silicon

has a freezing point of about 815° C. Further additions of silicon have the effect of raising the freezing point above this eutectic temperature, with the result that an alloy of 31 per cent silicon and 69 per cent copper has a freezing point of about 1050° C. Silicon is also effective in lowering the freezing point of an alloy of copper and aluminum. For example an aluminum-copper alloy corresponding in composition to the formula  $\text{Cu}_3\text{Al}$  (87.6% Cu+12.4% Al) has its freezing point lowered from about 1050° C. to about 930° C. by the addition of 5 per cent of silicon, and to about 795° C. by the addition of 10 per cent of silicon. The presence of silicon in amount between 2 per cent and 32 per cent of the copper-plus-silicon therefore prevents the alloy from freezing at a temperature of 1050° C. or higher, and thus permits the removal of all or substantially all of the aluminum without causing the residual alloy to freeze at the temperature mentioned. The presence of iron and titanium, or either of them, tends to raise the freezing point, which is, of course, objectionable. Other materials than silicon will serve the purpose of preventing the freezing of the alloy as the aluminum is removed, but silicon is preferred, and its cheapness permits it to be thrown away in the form of slag when the residual alloy is afterwards treated for recovery of the copper. On the other hand, tin or other low-melting material miscible with aluminum and copper, would have to be thrown away, or would have to be recovered in the course of reclaiming the copper. In either case the net cost of the process would be increased.

Aluminum has of itself the capability of lowering the freezing point of copper, and advantage may be taken of this fact, when necessary or desirable, by removing the alloy from the cell while it still contains some aluminum. In other words, the amount of aluminum and the amount of silicon should be so adjusted with respect to the other constituents that the anode alloy will at all times remain mobile within a range of working temperatures which will not cause objectionable alteration of the bath as by volatilization of one or another of its ingredients. Thus if it is desired to remove all of the aluminum, the silicon content when the aluminum has been removed should be not less than about 2 per cent of the copper-plus-silicon; but if the silicon content is not of itself sufficient to maintain the desired mobility it may be necessary to remove the alloy (or replace a portion of it with fresh metal, or add silicon) before all the aluminum is extracted. Generally speaking there ought to be enough silicon to keep the alloy mobile at a temperature of 1000° C., or thereabouts, when the aluminum content has been reduced to the desired extent. Silicon to



the amount of 5 per cent of the copper-plus-silicon is ordinarily ample for the purpose if the iron content is not more than about 5 per cent. It is to be understood that it is not in all cases necessary to have the alloy completely molten. Under some circumstances the presence of a limited amount of solid high-freezing material entrained in the anode alloy is not objectionable so long as it does not reduce the mobility of the alloy enough to prevent its free circulation and flow.

For the above reasons, the anode alloy used is preferably one containing copper in amount above 20 per cent, and silicon in amount between 2 and 32 per cent of the copper-plus-silicon, approximately. One of the applications of our invention is for the recovery of aluminum from electrothermally produced aluminum-copper alloys, as for example one of about the following composition:

	Per cent
Aluminum-----	30
Copper-----	55
Silicon-----	10
Iron, less than-----	5
Titanium, less than-----	1

A convenient and practical method for producing an anode-alloy such as the above is described and claimed in our copending application Ser. No. 608,283, filed December 21, 1922.

In the refining operation, unidirectional or continuous current from any suitable source is led into the anode alloy or impure aluminum and passes upward therefrom through the bath or electrolyte to the cathode above, with resulting deposition of aluminum thereat. High enough current density is used to make the resistance losses within the cell sufficient to maintain the working temperature.

Convenient and suitable apparatus for practicing the present invention is illustrated in the accompanying drawing, but it is to be understood that the invention is not limited thereto. The apparatus illustrated is claimed broadly in a copending application of William Hoopes.

Referring to the drawing,

Fig. 1 is a plan view of the cell.

Figs. 2 and 3 are cross sections on lines 2—2 and 3—3, respectively, of Fig. 1.

Figs. 4 and 5 are detail cross sections on lines 4—4 and 5—5, respectively, of Fig. 1, illustrating the water connections to and from and between the water jackets.

Fig. 6 is a detail cross section on line 6—6 of Fig. 1, showing the method of connecting the upper electrodes to the negative bus-bars.

Fig. 7 is a detail cross section on the same plane as Fig. 2, illustrating the method of securing the upper and lower shell sections

together to give adequate mechanical strength without connecting the two electrically.

Fig. 8 is a detail sectional view illustrating a suitable anode for use in deoxidizing the electrolyte.

Fig. 9 is a detail section on the same plane as Fig. 2, showing the heat-insulating top-crust above the cathode metal.

The lower shell or shell section 10 is preferably made of steel in the form of a cylindrical vessel of considerably greater diameter than height, and at or near its top it is provided with a water jacket 11 which is most conveniently formed by providing at the upper edge of the shell section an outwardly extending flange 12 of suitable width, and a flaring or conical ring 12<sup>a</sup> welded or otherwise hermetically joined to the underside of the flange and to the body of the shell below.

Above the lower shell section 10 is an upper shell section 13 which may also be of steel and formed with hollow walls to provide an upper water jacket 14. The inner surface of the upper shell section is preferably flaring, as indicated. To keep the sections electrically insulated or separated from each other a flat ring or gasket 15, of asbestos or other suitable material, may be used between the two.

In order to give the shell structure sufficient mechanical strength the sections may be secured together by means of machine studs 16 passing upwardly through the flange 12 and threaded into pads 17 welded on the bottom of the upper shell inside the water jacket. To prevent electrical connection the holes in the flange 12, through which the studs pass, may have insulating bushings 18 and insulating washers 19 may be used. If the water jackets are used, as in most cases they will be, the bushings and washers will not be subjected to a high temperature and hence they can be made of practically any insulating material which will not soften at temperatures below 100° C. and which can withstand the crushing stress exerted by the studs. Mica has been found suitable for the purpose.

Suitable water connections for the water jackets are provided, and for the sake of simplicity and convenience these connections may be so constructed and arranged that the water flows through the two jackets in succession, preferably through the lower jacket first. For this purpose the jacket 11 may be provided at the bottom with an inlet nipple 20 connected by a pipe 21 to any convenient source of water, not shown, and at the top (to prevent pocketing of air) with an outlet nipple 22 connected by a pipe 23 to the inlet nipple 24 by which water from the lower jacket is led into the bottom of the upper. The latter is equipped with an out-



let nipple 25 (at the top to prevent air pocketing) which may be connected to a waste pipe 26 by means of a pipe 27. To avoid electrical grounding the pipes 21 and 27 may consist of rubber hose, as may also the pipe 23 to keep the two shell sections electrically separate. The water used when the jackets are connected should be of sufficient purity to prevent the flow of a substantial amount of current from one shell section to the other at the voltage employed in operation.

In the bottom of the lower shell section a layer 28 of heat-insulating material may be provided, as powdered bauxite, alumina, magnesia, or refractory bricks, to decrease or minimize loss of heat through the bottom of the cell, and above this layer is a bottom lining 29 of refractory electrically conducting material, preferably carbon, and preferably having a cavity or depression in its upper portion to receive the alloy or other material to be refined. The bottom lining can be conveniently and satisfactorily made by tamping into the shell a mixture of tar, pitch and granular or powdered coke, at a temperature high enough to make the mass plastic, and placing the shell and contents in an oven in which the temperature is gradually raised, say to about 600° C., for the purpose of baking and solidifying the carbonaceous mass.

Good electrical connection may be provided between the shell and its bottom lining by means of metal collector plates 31, welded to the inner surface of the shell so as to be electrically and mechanically continuous therewith. These plates extend inwardly into the bottom lining, which is molded around them. At the plane of the collector plates the shell may be provided on the outside with metal contact pads 32, preferably welded to the shell so as to be mechanically and electrically continuous therewith, to which pads busses or busbars, of copper, aluminum or other suitable metal may be bolted tightly in place. The busbars may be in the form of long flat plates 33 embracing the lower shell section, with their ends brought out at one side of the cell for convenient connection to one terminal of a suitable source (not shown) of continuous or unidirectional current. During the refining operation these busses are connected to the positive terminal or pole of the source, so that the current enters the cell at the bottom. The carbon bottom or bottom-lining, 29, constitutes what may for convenience be termed the lower electrode of the cell.

The upper electrode may be multiple, composed preferably of a suitable number of short thick rods or cylinders 34 of graphite, arranged vertically and having copper or other metal rods 35 threaded or otherwise suitably secured to the tops of the elec-

trodes. These metal rods serve to support the graphite cylinders and convey current to or from the same, and for this purpose they may be releasably and adjustably secured, as by means of clamps 36, to metal busbars 37 extending horizontally across the cell. For convenience of access to the electrodes, for adjustment, replacement, etc., the busbars may be arranged at two or more different levels, as indicated, and may be supported on and secured to a plurality of legs 38 to form a rigid framework. The latter may rest on the upper shell section, in which case it is preferable to have them insulated from the shell section, as by any convenient and suitable means, not shown.

It is recognized that, strictly speaking, the aluminum layer floating on the bath and the layer of alloy underlying the bath, are the upper and lower electrodes, respectively, but these layers are termed herein the cathode and the anode, and hence it is deemed permissible as well as convenient to refer to the graphite cylinders and the carbon bottom-lining, or their equivalents, as the upper and lower electrodes.

Metal or other molten material may be withdrawn from the upper portion of the cell through a tapping notch 39, which may be closed by means of any suitable refractory material which will not contaminate the cell contents with which it comes in contact. Molten metal or other material may be withdrawn from the lower part of the cell through a port or tapping hole 40, normally closed by means of a plug of dense charcoal or other suitable material.

On the inside of the cell is a side-lining 45 extending upwardly from the carbon bottom 29, over the joint between the shell sections and well up toward or even over the top of the upper shell section. This side-lining should be thermally and electrically insulating, to decrease or minimize the conduction of heat to the water jackets as well as to prevent by-passing of current around any part of the cell contacts undergoing electrolytic treatment in the refining operation. The lining should also be chemically unobjectionable, and refractory enough to remain solid at the temperatures to which it is subjected in the electrolytic refining operation. To meet these conditions a lining composed of or formed from a mixture of metal fluorids and alumina, as more fully explained in the application of William Hoopes, Junius D. Edwards and Basil T. Horsfield, Serial No. 608,289, has been found highly satisfactory in practice.

In the refining process the aluminum alloy or mixture of aluminum and other substances lies in molten form at the bottom of the cell as indicated at 46. Floating on this is a layer 47 of fused bath or electrolyte, and on the latter is a layer 48 of molten alumi-



num, with the upper electrodes extending into it far enough to insure good electrical contact, say an inch or two. The molten layers may be established in the cell in any convenient manner, as for example by pouring the previously fused materials into place, using for the original aluminum layer the purest metal conveniently available. The busbars 33 are connected to the positive terminal of the source of electrolyzing (unidirectional) current, and the busbars 37 are connected to the negative terminal of the same source. Any convenient and suitable means, not shown, may be employed to regulate the voltage and current supplied. Apparently the effect of the passage of the current is to set free fluorin or oxygen anions, or both, in contact with the surface of the anode metal. The effect of the liberation of these anions is to dissolve, from the anode alloy, aluminum and any impurity present in the alloy which is more electropositive than aluminum and to leave behind the impurities which are less electropositive. Any of the latter impurities which may be attacked by the anions tend to be immediately re-precipitated by a secondary reaction between the aluminum, with which they are in contact, and the fluorids or oxids of these less electropositive metals, with the result that only aluminum and impurities which are more electropositive pass into solution in the bath. In the anode alloy described above there are no impurities which are more electropositive than aluminum and practically only aluminum goes into solution so long as the aluminum content remains relatively high and the aforesaid secondary reactions can occur freely.

With a bath containing sodium and barium fluorids there is also deposited at the cathode, along with the aluminum, some barium and some sodium, the amounts being dependent to some extent at least upon the current density used, and the quantitative composition of the bath. It has been found, however, that both barium and sodium react, at the working temperature, with aluminum fluorid to produce metallic aluminum and barium or sodium fluorid, as the case may be. Consequently so long as there is a sufficiently high proportion of aluminum fluorid in the bath, and the bath can freely wash the bottom of the cathode metal layer, no barium is found in the latter metal; but at the working temperature sodium, which is nearly insoluble in aluminum, is set free in gaseous form and small proportions of it escape before the secondary reaction can completely redissolve all of it. Hence minute traces of sodium are often found in the cathode metal, and some sodium escapes into the heat-insulating crust maintained above the top metal. This quantity, however, is usually very small when the bath is kept in

the proper condition of fusion and is not allowed to become deficient in aluminum fluorid.

Leading electrolyzing current to the anode and from the cathode in such manner that a magnetic field is produced in the cell, is considered to be an advantageous feature. Thus in the apparatus illustrated the currents in the upper transverse horizontal busbars 37 and vertical electrodes 34, and in the lower encircling horizontal busses 33 and tapering horizontal distributor or collector plates 31, produce in the cell a powerful and non-uniform magnetic field having both vertical and horizontal components. On account of the relatively high specific resistance of the electrolyte, as compared with that of either the anode alloy or the top metal layer, the current density throughout the horizontal cross section of the electrolyte and hence at its upper and lower surfaces, is substantially uniform. Likewise, the current density at the surface of contact between the conducting bottom lining and the anode alloy (which latter has much better conductivity than the former) is substantially uniform, although the conducting plates or ribs in the bottom lining tend somewhat to concentrate the current. But in the anode alloy the current flow may have horizontal as well as vertical components, due in part to the concentrating effect of the aforesaid plates in the bottom lining, and, probably more especially, to the bowl-like receptacle in the bottom lining, whereby some of the current can flow between the anode alloy and the conducting side walls of the receptacle. These horizontal components of current-flow in the alloy are largely radial in direction. The interaction of the current flowing in the anode alloy and the non-uniform magnetic field produced as explained above, causes the anode alloy (which, being molten, is in effect composed of movable conductors) to flow in various directions, and produces a powerful circulation and mixing of the alloy. The stirring thus produced is, we believe, an important factor in replenishing the active surface of the anode alloy with aluminum fast enough to satisfy the anions set free thereat, making possible more extensive removal of aluminum from the alloy or the use of a higher current density, or both, without depositing impurities at the cathode in such amount as to seriously affect its quality. Moreover, the interaction of currents and magnetic field in the bath and in the cathode produces a like stirring effect in these layers which is advantageous in promoting homogeneity of composition and temperature and especially in preventing the bath from being impoverished of aluminum at the surface in contact with the cathode. The stirring effect described also



insures intimate contact of the bath with the anode and cathode throughout their contiguous surfaces, thereby giving adequate opportunity for the secondary reactions by which elements (other than aluminum) deposited at the cathode are re-dissolved in the bath and by which impurities dissolved from the anode are re-precipitated thereon.

As the refining operation proceeds, aluminum dissolved out of the anode alloy is deposited in molten form on the cathode, and when the desired amount of aluminum has been deposited a portion of the top metal is removed and the impoverished anode metal is withdrawn through the tap hole 40, fresh anode metal in the molten state being supplied in any convenient way, such that the refined metal floating on the bath will not be contaminated. This operation may be conveniently performed by means of a carbon funnel, which, after being preheated, is let down until it nearly reaches the bottom of the cell, which has preferably been cut out of the circuit. The refined metal entrapped in the funnel may be dipped out with a hand ladle, after which the fresh anode metal is poured in. The funnel is then lifted out. The fresh anode metal introduced is preferably sufficient in amount to raise the bath and top metal until the surface of the latter is at the same level as before the withdrawal.

The tapping out and replenishing operations may be repeated from time to time as necessary or desirable without seriously interrupting the refining process, which otherwise can go on continuously.

Notwithstanding the greater density of the bath, a portion of it is carried up by capillary action at the area of contact between the liquid aluminum and the solid boundary crust and rises to the surface of the former, where it spreads in a thin layer, the weight of which is insufficient to overcome the surface tension of the liquid aluminum. Consequently it spreads over the entire surface of the latter, and by reason of the escape of heat into the air, solidifies there, forming a crust such as is indicated, for example, at 58, Fig. 9. This process goes on until the resulting crust thickens so much that (the escape of heat being thus retarded) the temperature of its under surface can rise to the melting point of the bath. When this thickness is attained, quantities of unsaturated bath subsequently carried up by capillary action can accumulate in liquid form under the crust and finally grow to a mass of sufficient dimensions to be able to sink through the aluminum. Hence if the bath is kept unsaturated with alumina the top crust forms up to a certain thickness, after which its growth ceases. On the other hand if the freezing point of the bath is

raised by allowing it to become saturated, liquid bath finding its way to the under-surface of the crust partially solidifies there and increases the thickness. This action would, if unchecked, result eventually in bringing up a large portion of the bath from below the aluminum and causing it to attach itself to the top crust. At the same time, the boundary crust at the sides of the cell thickens in the same manner, and the net result would ultimately be more or less complete solidification of the bath unless its temperature is raised correspondingly. For these reasons it is desirable to keep the bath unsaturated in the normal operation of refining.

The bath crust formed on the aluminum layer as above described serves as a convenient and good heat insulating medium to minimize loss of heat from the top of the cell, but it also entraps sodium as already explained, with consequent increase of alumina in the bath. The amount of sodium which thus escapes from the bath can be minimized by using in the latter the highest permissible amount of aluminum fluorid.

Instead of forming the heat-insulating top crust in the manner hereinbefore specifically described, such a crust may be produced by dusting over the upper surface of the aluminum layer, soon after it is put in place, a layer of finely divided alumina, carbon, magnesia, or other suitable powdered material. This layer of finely divided material is rapidly cemented together by the liquid bath coming up from below and wetting it. The heat-insulating property of the top crust may be increased by dusting any suitable powdered material over it after it has been formed, so that it is covered by a layer of such material, which is an excellent insulator by reason of its porous condition. Being supplied to the surface of the top crust after the latter has solidified, the additional heat-insulating material is not cemented together and therefore retains its porosity. In general, the best material for the purpose is bath which has been allowed to solidify, since if any of it accidentally or incidentally finds its way below the top metal it does not contaminate the electrolyte.

Several methods are available for keeping the alumina content of the bath below the saturation point. For example, the top metal (aluminum) can be ladled or tapped off and a portion of the saturated or nearly saturated bath dipped out, liquid or solid alumina-free or deoxidized bath being added to take the place of that which was removed. The resulting mixture will then be well below the saturation point. Or a portion of the crust can be broken away and removed, whereupon it will reform at the expense of the saturated bath within the cell, the excess alumina crystallizing out in co-



rundum-like form. New alumina-free or de-oxidized bath can be added either in solid or liquid form to take the place of that which went to form the new crust. In the first method the saturated bath removed from the cell can be regenerated and prepared for reentry into the process by crushing it and electrolyzing it.

Another method of preventing saturation of the bath with alumina is to deoxidize the alumina continuously, or from time to time, in the refining cell itself, for example by electrolyzing the bath according to the Hall process of producing aluminum from alumina. This may be accomplished by placing a carbon electrode in contact with the bath and connecting it with the positive terminal of the cell, thus making the carbon electrode an anode. Any current leaving this carbon anode serves to electrolyze alumina in the usual manner, depositing aluminum on the cathode metal, or on the anode alloy, or on both, depending upon the voltage used; the oxygen being liberated at the carbon anode and forming  $\text{CO}_2$  with a portion of the carbon. The preferred way of using a carbon anode for the purpose is illustrated in Figs. 1 and 8 of the drawings. In these figures 50 represents a carbon disk into which is threaded a carbon stud 51, into the upper end of which is threaded a water-cooled iron terminal 52. The latter is screwed into the bottom of a pipe 53 which serves to support the terminal and the disk and also to supply the electrolyzing current and the cooling water. At its top the pipe is fitted into the underside of a closed chamber 54 through which a water supply pipe 55 projects down into the pipe and well to the bottom of the latter. Water thus introduced into contact with the iron terminal 52 rises around the pipe 55 and flows out of the chamber 54 by way of pipe 56. The pipe 53 is fastened on an insulated support 57 in such manner as to hold the carbon disk 50 submerged in the bath below the aluminum layer 48. Around the carbon stud 51, water-cooled terminal 52, and the lower end of pipe 53, is an insulating and refractory crust 58 which may consist of a mixture of bath and corundum previously cast in place. This crust serves to prevent the aluminum top metal from making contact with the carbon disk or with the electrically associated parts, and thereby prevents a short-circuit between the top metal and the deoxidizing anode. The latter can be electrically connected with the positive bus in any convenient manner, preferably through a suitable circuit-breaker, not shown, from which current may be carried by means of a cable 59 connected with the pipe 53. In practical operation it is usually sufficient to deoxidize the bath intermittently, depending upon the rate (as

determined by experience) at which oxygen finds its way into the bath.

The energy-efficiency in electrolytic processes of refining aluminum is dependent largely upon the perfection of the measures taken for preventing escape of heat. Theoretically almost no energy is required for the refining; but practically, in the absence of some other adequate source of heat, sufficient electrical energy must be expended to maintain the anode, the bath, and the cathode, in a fused condition, and consequently the amount of electrical energy which must be supplied is almost exactly the equivalent of the heat permitted to escape. After the heat insulation of the cell has been perfected to the maximum practicable extent, nothing further can be accomplished in limitation of the amount of heat escaping from a heated body of given dimensions, and with the minimum heat-loss the energy input required by the cell will also be a minimum. In the interests of power economy the cell should be operated at the lowest practicable voltage. Accordingly the electrolyte, which furnishes the major portion of the resistance, should be in as thin a layer as is permissible, and it has been found that a layer from  $2\frac{1}{2}$  to 4 inches thick is in general satisfactory. With a bath or electrolyte of any predetermined workable depth, the current density permissible varies between a lower limit which is sufficient to maintain the anode, the bath and the cathode in a molten state, and an upper limit at which volatilization of the bath is excessive or at which too large a proportion of anode impurities go into solution. These limits, with the various bath-compositions which have been found practicable, are approximately  $800^\circ\text{C}$ . and  $1100^\circ\text{C}$ ., respectively, with a preferable working temperature of about  $950^\circ\text{C}$ . The permissible lower limit of current density also varies inversely with the dimensions of the cell, since the heat loss per unit of volume in a large cell is less than that in a small cell on account of the smaller ratio of heat-dissipating area to the volume. In a cell having a cross section through the electrolyte of 9.6 square feet it has been found that the preferable current is, in general, 8500 amperes, but that the process is workable with currents between 7500 and 12000 amperes. The preferable current density in a cell having the electrolyte cross-sectional area mentioned is therefore 885 amperes per square foot, with a permissible minimum of about 780 amperes and a permissible maximum of about 1250 amperes, per square foot. With the preferred current density mentioned, the total voltage between the terminals of the cell may be about 6 volts. Larger cells may be operated with lower current densities and at lower volt-



ages, and by varying the size of the cell, the composition of the bath, the conductivity of the bath, and the effectiveness of the heat insulation, the present electrolytic refining process is workable with current densities between about 500 and about 2500 amperes per square foot of cross section of the bath. In general the lower practicable limit of voltage is about 3.5 volts and the upper limit is of course indefinite.

The layer of aluminum floating on the molten bath or electrolyte should be of sufficient expanse to touch the boundary crust of the cell around the entire perimeter thereof and should be thick enough to insure firm contact with this crust, in order to prevent or minimize volatilization of the bath, which occurs to a greater or less extent at working temperatures and increases as the temperature rises. On account of the surface tension of molten aluminum the top layer should be of substantial depth, and it is therefore desirable to maintain a thickness of at least 2 inches at all times.

So long as the aluminum content of the anode alloy is not much below 10 per cent, by weight, no difficulty is ordinarily experienced in obtaining a cathode metal having a purity adequate for commercial requirements. On the other hand, as the anode alloy becomes impoverished of aluminum the selective action of the bath becomes more and more impaired, impurities in the anode are dissolved in larger amount, and more and more of such impurities are deposited on the cathode. But by removing impoverished alloy and substituting fresh whenever the aluminum content has fallen too low the major portion of the latter metal can be obtained in very pure form. The impoverished alloy can be disposed of in any advantageous manner, but for the purpose of making the copper re-useable the alloy may be sent to a copper refining furnace where the major portion of the remaining iron, titanium, and silicon may be removed by the common method of oxidation and slagging. Or, in case these impurities are low, the alloy may be diluted with impure aluminum, such, for example, as is produced by the Hall process, and then returned to the cell. If molten impure aluminum be conveniently available, the impoverished alloy may be tapped into a crucible containing the desired amount of molten aluminum, thoroughly stirred, and promptly returned to the cell, so that the refining operation proceeds with the use of the same copper.

It is to be understood that the invention is not limited to the specific procedure and apparatus herein illustrated and described but can be practiced in other ways without departure from its spirit.

We claim—

1. In the refining of aluminum, the steps

comprising electrolyzing a molten bath with a molten alloy as anode containing aluminum materially in excess of the amount required to maintain the alloy mobile at a temperature too low to cause objectionable alteration of the bath, and depositing said excess aluminum in the molten state on a molten aluminum cathode in contact with said bath.

2. In the refining of aluminum, the steps comprising electrolyzing a molten bath with a molten aluminum alloy as anode compounded to remain mobile below a temperature causing material alteration of the bath, and depositing in the molten state on a molten aluminum cathode in contact with said bath, aluminum removed electrolytically from the anode.

3. In the refining of aluminum, the steps comprising electrolyzing a molten bath with a molten aluminum alloy as anode containing silicon proportioned to cause said alloy to remain mobile below a temperature causing material alteration of the bath, and depositing in a molten state on a molten aluminum cathode the aluminum removed from said alloy.

4. In the refining of aluminum, the steps comprising removing aluminum electrolytically from a molten aluminum alloy as anode containing silicon in amount adapted to maintain the alloy in a mobile state regardless of its diminishing aluminum content, and depositing the removed aluminum on a molten aluminum cathode through a molten bath.

5. In the refining of aluminum, the steps comprising removing aluminum electrolytically from a molten aluminum alloy as anode and depositing the aluminum upon a molten aluminum cathode through a molten bath, and controlling the bath and anode compositions to provide a common low temperature of mobility and maintain a definite relation of their densities.

6. In the refining of aluminum, the steps comprising electrolyzing a molten bath with a molten aluminum alloy as anode compounded to remain mobile below a temperature causing material alteration of the bath, depositing said excess aluminum in the molten state on a molten aluminum cathode in contact with said bath, and correcting the composition of the alloy from time to time to maintain its mobility.

7. In the refining of aluminum, the steps comprising electrolytically removing aluminum from a molten alloy thereof having a composition enabling the alloy to remain mobile at the operating temperature and depositing the aluminum on a molten aluminum cathode through a molten bath capable of acting selectively to dissolve aluminum from the alloy, and by withdrawal and replenishment of the alloy as it becomes im-



poorly maintained maintaining an alloy composition adapted to preserve said selective action of the bath.

8. In the refining of aluminum, the steps comprising electrolytically removing aluminum from a molten alloy thereof and depositing the same on a molten aluminum cathode through a molten bath capable of acting selectively to dissolve aluminum from the alloy, and maintaining the aluminum content of the alloy high enough to preserve said selective action of the bath.

9. In the refining of aluminum, the steps comprising electrolytically removing aluminum from a molten alloy thereof containing copper and silicon in proportions adapted to keep the alloy mobile during the electrolysis and depositing the aluminum on a molten aluminum cathode through a molten bath capable of acting selectively to dissolve aluminum from the alloy, and by withdrawal and replenishment of the alloy as it becomes impoverished maintaining an alloy composition adapted to preserve said selective action.

10. In the refining of aluminum, the steps comprising electrolytically removing aluminum from a molten alloy thereof containing copper and silicon in proportions adapted to keep the alloy mobile during the electrolysis and depositing the aluminum on a molten aluminum cathode through a molten bath capable of acting selectively to dissolve aluminum from the alloy, while maintaining the aluminum content of the alloy high enough to preserve said selective action of the bath and maintaining a current density and circulation of the bath, with respect to the contiguous anode surface, adapted to permit at said surface secondary reactions adequate to prevent permanent solution of anode impurities in the electrolyte.

11. In the refining of aluminum, the steps comprising electrolytically removing aluminum from a molten alloy thereof containing copper and silicon in proportions adapted to keep the alloy mobile during the electrolysis and depositing the aluminum on a molten aluminum cathode through a molten bath capable of acting selectively to dissolve aluminum from the alloy; while maintaining an alloy composition, and a current density and circulation of the bath, with respect to the anode and cathode surfaces, adapted to permit at said surfaces secondary reactions adequate to precipitate, on the anode, impurities removed therefrom, and to prevent permanent deposition on the cathode, of bath components more electropositive than aluminum.

12. In the refining of aluminum, the steps comprising electrolytically removing aluminum from a molten alloy thereof as anode and depositing the aluminum on a molten aluminum cathode through a molten bath

capable of acting selectively to dissolve aluminum from the alloy, while maintaining bath and alloy compositions, and an anode current-density and circulation, adapted to minimize removal of metals more electronegative than aluminum from the alloy, and cause precipitation, on the alloy, of said more electronegative metals.

13. In the refining of aluminum, the steps comprising removing aluminum electrolytically from molten alloy thereof as anode and depositing the aluminum on a molten aluminum cathode through a suitable molten bath, and giving free play to secondary reactions at the active surfaces of the anode and cathode, by maintaining intimate contact between the bath and the anode and cathode, maintaining active circulation of the bath and anode, and controlling the composition of the bath and anode and the current densities at the active surfaces thereof.

14. In the refining of aluminum, the steps comprising removing aluminum electrolytically from a molten alloy thereof as anode and depositing the aluminum on a molten aluminum cathode through a suitable molten bath, said anode alloy having a composition enabling it to remain mobile below a temperature causing material volatilization of the bath; and giving free play to secondary reactions at the active surfaces of the anode and cathode, by maintaining intimate contact between the bath and the anode and cathode, maintaining active circulation of the bath and anode, and controlling the composition of the bath and anode and the current densities at the active surfaces thereof.

15. In the refining of aluminum, the steps comprising removing aluminum electrolytically from a molten alloy thereof as anode and depositing the aluminum on a molten aluminum cathode through a suitable molten bath compounded to be fluid at a temperature below that of material volatilization, said alloy being compounded to remain mobile at a temperature below that of material volatilization of the bath, and giving free play to secondary reactions at the active surfaces of the anode and cathode, by maintaining intimate contact between the bath and the anode and cathode, maintaining active circulation of the bath and anode, and controlling the composition of the bath and anode and the current densities at the active surfaces thereof.

16. In the refining of aluminum, the steps comprising the establishing in a suitable cell a molten bath of fluorides containing aluminum fluorid, compounded to be fluid below the temperature of material volatilization of aluminum fluorid; a molten anode of aluminum alloy to be refined, compounded to remain mobile, within a working range of aluminum content, below the temperature of material volatilization of the bath; and a



molten aluminum cathode; and passing electrolyzing current from the anode through the bath to the cathode in sufficient quantity to maintain said anode, cathode, and bath in mobile condition and transfer aluminum from the anode to the cathode.

17. In the refining of aluminum, the steps comprising establishing in a suitable cell the gravitatively arranged layers, a molten bath of fluorids containing aluminum fluorid, compounded to have a density higher than that of molten aluminum and to be fluid below the temperature of material volatilization of aluminum fluorid; a molten anode of aluminum alloy to be refined, compounded to have a density higher than that of said bath and to remain mobile, within a working range of aluminum content, below the temperature of material volatilization of the bath; and a molten aluminum cathode; and passing electrolyzing current from the anode through the bath to the cathode in sufficient quantity to maintain said elements in mobile condition and transfer aluminum from the anode to the cathode.

18. In the refining of aluminum, the steps comprising removing aluminum electrolytically from a molten aluminum-copper alloy of low iron and titanium content, as anode, containing silicon in such proportion to the copper as to maintain adequate mobility of the alloy during the electrolysis; and depositing the aluminum so removed from a molten cathode.

19. In the refining of aluminum, the steps comprising removing aluminum electrolytically from a molten aluminum-copper alloy of low iron and titanium content, as anode, containing silicon in such proportion to the copper as to maintain adequate mobility of the alloy during the electrolysis, with a suitable electrolyte and a current density between 500 and 1,250 amperes, approximately, per square foot of cross sectional area of the electrolyte; and depositing the aluminum so removed upon a molten aluminum cathode.

20. In the refining of aluminum, the steps comprising removing aluminum electrolytically from a molten anode alloy containing, approximately, 30 per cent of aluminum, 55 per cent of copper, 10 per cent of silicon, less than 5 per cent of iron, and less than 1 per cent of titanium, and depositing the aluminum so removed on a molten aluminum cathode.

21. In the refining of aluminum, the steps comprising removing aluminum electrolytically from a molten anode alloy containing, approximately, 30 per cent of aluminum, 55 per cent of copper, 10 per cent of silicon, less than 5 per cent of iron, and less than 1 per cent of titanium, with a suitable electrolyte and a current density between 500 and 1250 amperes, approximately, per square foot of cross sectional area of the elec-

trolyte; and depositing the aluminum so removed upon a molten aluminum cathode.

22. In the refining of aluminum, the steps comprising removing aluminum electrolytically from a molten aluminum alloy containing copper in amount not less than about 20 per cent, and silicon in amounts between 2 and 32 per cent, approximately, of the copper-plus-silicon content, and depositing the aluminum so removed on a molten aluminum cathode.

23. In the refining of aluminum, the steps comprising removing aluminum electrolytically from a molten anode alloy of low iron and titanium content containing aluminum about 30 per cent, copper about 55 per cent, and silicon about 10 per cent, and depositing the aluminum so removed on a molten aluminum cathode.

24. In the refining of aluminum, the steps comprising removing aluminum electrolytically from a molten anode alloy of low iron and titanium content containing aluminum, copper and silicon in proportions giving the alloy suitable mobility below about 950° C., and depositing the aluminum so removed on a molten aluminum cathode.

25. In the refining of aluminum, the steps comprising removing aluminum electrolytically from a molten alloy containing aluminum, copper, and silicon, in proportions giving the alloy suitable mobility below about 950° C. and a density of not less than about 2.7 grams per cubic centimeter at the temperature named, and depositing the aluminum so removed on a molten aluminum cathode.

26. In the refining of aluminum, the steps comprising removing aluminum electrolytically from a molten aluminum-alloy containing copper and silicon in proportions giving the alloy suitable mobility below about 1000° C. when the aluminum content is reduced to the desired extent, and depositing the aluminum so removed on a molten aluminum cathode.

27. In the refining of aluminum, the steps comprising removing aluminum electrolytically from a molten aluminum-alloy containing silicon, copper, iron, and titanium, in proportions giving suitable mobility below about 1000° C. when the aluminum content is reduced to the desired extent, and depositing the aluminum so removed on a molten aluminum cathode.

28. In the refining of aluminum, the improvement comprising removing aluminum electrolytically from a molten aluminum-alloy containing copper, silicon, iron, and titanium, in proportions giving the alloy, when the aluminum content is reduced to the desired extent, suitable mobility below about 1000° C. and a density not less than about 2.7 grams per cubic centimeter at the temperature mentioned, and depositing the



aluminum so removed on a molten aluminum cathode.

29. In the electrolytic refining of aluminum, the steps comprising establishing a lower layer of molten aluminum-alloy as anode containing copper and a lighter ingredient in proportions giving the alloy suitable mobility below 1100° C. and a density not less than about 2.6 grams per cubic centimeter at the temperature mentioned, an upper layer of molten aluminum as cathode, and an intermediate layer of molten electrolyte composed of a mixture containing fluorids of aluminum and sodium and fluorid of one or more alkali earth metals; and passing current between the anode alloy and the aluminum cathode and through the electrolyte; whereby aluminum is removed from the anode and deposited on the cathode at a temperature below that mentioned.

30. In the electrolytic refining of aluminum, the steps comprising establishing a lower layer of molten aluminum-alloy as anode containing copper and a lighter ingredient in proportions giving the alloy a freezing point below 1100° C. and a density not less than about 2.6 grams per cubic centimeter at the temperature mentioned, an upper layer of molten aluminum as cathode, and an intermediate layer of molten electrolyte composed of a mixture containing fluorids of aluminum and sodium and fluorid of one or more alkali earth metals; and passing current between the anode alloy and the aluminum cathode and through the electrolyte, with a current density between 500 and 1250 amperes, approximately, per square foot of cross sectional area of the electrolyte; whereby aluminum is removed from the anode and deposited on the cathode at a temperature below that mentioned.

31. In the electrolytic refining of aluminum, the improvement comprising establishing in downwardly successive layers a body of molten aluminum as cathode, a body of molten electrolyte composed of a mixture containing aluminum, sodium, and barium fluorids, and a lower body of molten aluminum-alloy as anode containing copper and silicon in proportions giving a density higher than that of the electrolyte mixture and suitable mobility at a temperature not higher than about 1000° C.; and passing current through said layers in succession to remove aluminum from the lower layer and deposit it on the upper layer.

32. In the electrolytic refining of aluminum, the steps comprising establishing in downwardly successive layers a body of molten aluminum as cathode, a body of molten electrolyte composed of a mixture containing aluminum, sodium, and barium fluorids, and a body of molten alloy as anode containing aluminum about 30 per cent, copper about 55 per cent, and silicon about 10

per cent; and passing current through said layers in succession to remove aluminum from the lower layer and deposit it on the upper layer.

33. In the electrolytic refining of aluminum, the steps comprising establishing in downwardly successive layers a body of molten aluminum as cathode, a body of molten electrolyte composed of a mixture containing aluminum, sodium, and barium fluorids, and a body of molten alloy as anode containing aluminum about 30 per cent, copper about 55 per cent, and silicon about 10 per cent; and passing current through said layers in succession with a current density between 500 and 1250 amperes, approximately, per square foot of cross sectional area of the electrolyte, to remove aluminum from the lower layer and deposit it on the upper layer.

34. In the electrolytic refining of aluminum, the steps comprising passing current through upwardly successive molten layers composed respectively of a body of aluminum alloy, as anode, containing copper and a lighter metal in proportions giving a density at least as high as about 2.7 grams per cubic centimeter at a temperature of about 950° C.; a body of electrolyte-mixture containing aluminum, sodium, and barium fluorids; and a body of molten aluminum as cathode; and by the passage of the current maintaining the materials in the molten state and in the layer formation described while simultaneously removing aluminum from the lower layer and depositing it on the upper layer; and maintaining the alumina content of the electrolyte-mixture below the point of saturation.

35. In the electrolytic refining of aluminum, the steps comprising passing current through upwardly successive molten layers composed respectively of a body of aluminum alloy, as anode, containing copper and a lighter metal in proportions giving a density at least as high as about 2.7 grams per cubic centimeter at a temperature of about 950° C.; a body of electrolyte-mixture containing aluminum, sodium, and barium fluorids; and a body of molten aluminum as cathode; with a current density between 500 and 1250 amperes, approximately, per square foot of cross sectional area of the electrolyte; and by the passage of the current maintaining the materials in the molten state and in the layer formation described while simultaneously removing aluminum from the lower layer and depositing it on the upper layer; and maintaining the alumina content of the electrolyte-mixture below the point of saturation.

36. In the electrolytic refining of aluminum, the steps comprising establishing a lower layer of molten aluminum alloy, as anode, containing copper and silicon in pro-



portions giving a relatively high density and adequate mobility when the aluminum content is relatively low, an upper layer of molten aluminum as cathode, and an intermediate layer of molten electrolyte composed of a mixture containing aluminum, sodium and barium fluorids in proportions giving a density between that of the anode alloy and that of the cathode aluminum when all are molten; establishing on the aluminum layer a heat-insulating top-crust composed, at least in part, of electrolyte coming up from below and freezing above the aluminum; passing current through the successive layers to remove aluminum from the anode and deposit it on the cathode; and treating the electrolyte to prevent saturation thereof with alumina and consequent thickening of the top-crust.

37. In the electrolytic refining of aluminum, the steps comprising establishing a lower layer of molten aluminum alloy, as anode, containing copper and silicon in proportions giving a relatively high density and adequate mobility when the aluminum content is relatively low, an upper layer of molten aluminum as cathode, and an intermediate layer of molten electrolyte composed of a mixture containing aluminum, sodium and barium fluorids in proportions giving a density between that of the anode alloy and that of the cathode aluminum when all are molten; establishing on the aluminum layer a heat-insulating top-crust composed, at least in part, of electrolyte coming up from below and freezing above the aluminum; passing current with a density between 500 and 1250 amperes, approximately, per square foot of cross sectional area of the electrolyte, through the successive layers to remove aluminum from the anode and deposit it on the cathode; and treating the electrolyte to prevent saturation thereof with alumina and consequent thickening of the top-crust.

38. In the electrolytic refining of aluminum, the steps comprising establishing a lower layer of molten alloy, as anode, containing aluminum, copper and silicon, on upper layer of molten aluminum as cathode, and an intermediate layer of molten electrolyte containing aluminum, sodium and barium fluorids; passing current through the layers in succession to remove aluminum from the lower and deposit it on the upper layer; and treating the electrolyte at intervals to substantially maintain the same unsaturated with alumina and thereby prevent excessive rise of the freezing point of the electrolyte.

39. In the electrolytic refining of aluminum, the steps comprising establishing a lower layer of molten aluminum alloy as anode containing copper and silicon in proportions giving a freezing point no higher

than about 1050° C., an upper layer of molten aluminum as cathode, and an intermediate layer of molten electrolyte containing aluminum, sodium and barium fluorids; passing current through the said layers in succession to remove aluminum from the lower and deposit it on the upper layer; and deoxidizing the electrolyte as necessary to prevent rise of its freezing point above substantially the temperature mentioned.

40. In the electrolytic refining of aluminum, the steps comprising establishing a lower layer of molten alloy, as anode, containing aluminum about 30 per cent, copper about 55 per cent, silicon about 10 per cent, and containing less than about 5 per cent of iron and less than about 1 per cent of titanium; an upper layer of molten aluminum as cathode; and an intermediate layer of fluorid-electrolyte of intermediate density; passing current through said layers in succession to remove aluminum from the anode and deposit it on the cathode; and from time to time deoxidizing the electrolyte to reduce alumina therein and thereby prevent excessive rise of the freezing point of the electrolyte.

41. In the electrolytic refining of aluminum, the steps comprising establishing a lower layer of molten alloy, as anode, containing aluminum about 30 per cent, copper about 55 per cent, silicon about 10 per cent, and containing less than about 5 per cent of iron and less than about 1 per cent of titanium; an upper layer of molten aluminum as cathode; and an intermediate layer of fluorid-electrolyte of intermediate density; passing current through said layers in succession to remove aluminum from the anode and deposit it on the cathode; from time to time deoxidizing the electrolyte to reduce alumina therein and thereby prevent excessive rise of the freezing point of the electrolyte; and maintaining the aluminum cathode layer sufficient in expanse to prevent excessive volatilization of the electrolyte.

42. An anode alloy of aluminum, containing sufficient silicon to maintain adequate mobility of the alloy as its aluminum content is decreased in refining.

43. An anode-alloy containing aluminum, copper and silicon in proportions adapted to make the alloy adequately mobile below about 1050° C.

44. An aluminum-copper anode-alloy containing silicon in amount at least sufficient to keep the alloy adequately mobile at about 1050° C. when substantially all the aluminum has been extracted.

45. An aluminum anode-alloy containing copper and silicon in amounts adapted to give the alloy a density not less than about 2.7 grams per cubic centimeter at a temperature of approximately 1000° C.

46. An aluminum anode-alloy containing



copper not less than about 20 per cent, and silicon between 2 and 32 per cent, approximately, of the copper-plus-silicon.

47. An anode-alloy containing aluminum, copper and silicon in proportions adapted to make the alloy adequately mobile below about 1050° C., and having low iron and titanium content.

48. An aluminum anode-alloy containing copper and silicon in amounts adapted to give the alloy a density not less than about 2.7 grams per cubic centimeter at a temperature of approximately 1000° C., and having

not more than about 5 per cent of iron and titanium.

49. An aluminum anode-alloy containing copper not less than about 20 per cent, and silicon between 2 and 32 per cent, approximately, of the copper-plus-silicon, and having not more than about 5 per cent of iron and titanium.

In testimony whereof we hereto affix our signatures.

WILLIAM HOOPES.  
FRANCIS C. FRARY.  
JUNIUS D. EDWARDS.



copper not less than about 20 per cent, and silicon between 2 and 32 per cent, approximately, of the copper-plus-silicon.

47. An anode-alloy containing aluminum, copper and silicon in proportions adapted to make the alloy adequately mobile below about 1050° C., and having low iron and titanium content.

48. An aluminum anode-alloy containing copper and silicon in amounts adapted to give the alloy a density not less than about 2.7 grams per cubic centimeter at a temperature of approximately 1000° C., and having

not more than about 5 per cent of iron and titanium.

49. An aluminum anode-alloy containing copper not less than about 20 per cent, and silicon between 2 and 32 per cent, approximately, of the copper-plus-silicon, and having not more than about 5 per cent of iron and titanium.

In testimony whereof we hereto affix our signatures.

WILLIAM HOOPES.  
FRANCIS C. FRARY.  
JUNIUS D. EDWARDS.

#### Certificate of Correction.

It is hereby certified that in Letters Patent No. 1,534,317, granted April 21, 1925, upon the application of William Hoopes, of Pittsburgh, and Francis C. Frary and Junius D. Edwards, of Oakmont, Pennsylvania, for an improvement in "Electrolytic Production of Aluminum," an error appears in the printed specification requiring correction as follows: Page 10, line 33, claim 18, for the word "from" read *upon*; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 18th day of August, A. D. 1925.

[SEAL.]

KARL FENNING,  
*Acting Commissioner of Patents.*



### **Certificate of Correction.**

It is hereby certified that in Letters Patent No. 1,534,317, granted April 21, 1925, upon the application of William Hoopes, of Pittsburgh, and Francis C. Frary and Junius D. Edwards, of Oakmont, Pennsylvania, for an improvement in "Electrolytic Production of Aluminum," an error appears in the printed specification requiring correction as follows: Page 10, line 33, claim 18, for the word "from" read *upon*; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 18th day of August, A. D. 1925.

[SEAL.]

KARL FENNING,  
*Acting Commissioner of Patents.*