

Sept. 2, 1969

E. FOLEY ET AL
PRODUCTION OF ALUMINUM AND ALUMINUM ALLOYS
FROM ALUMINUM CHLORIDE

3,464,900

Filed Dec. 30, 1965

2 Sheets-Sheet 1

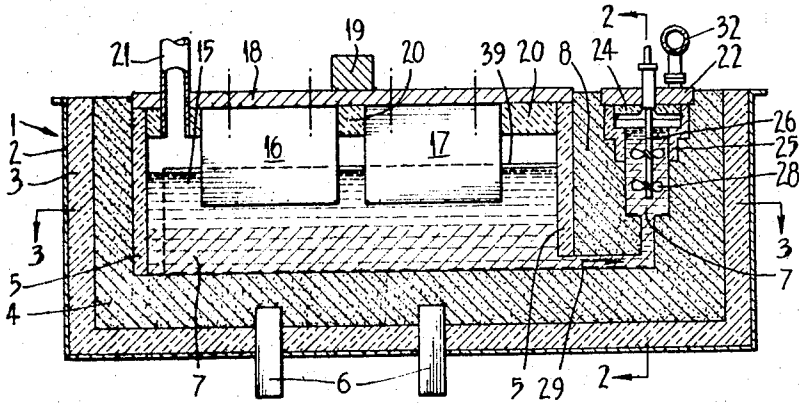


FIG. 1.

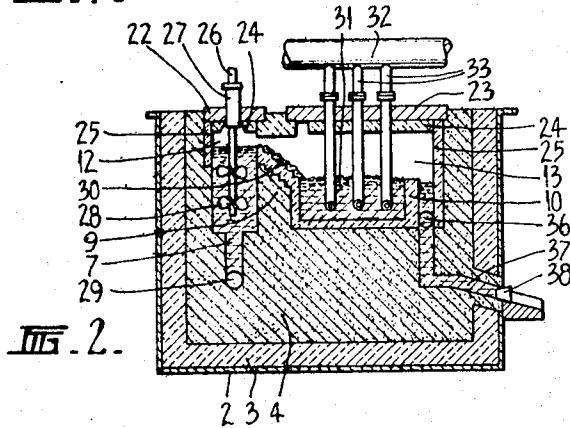


FIG. 2.

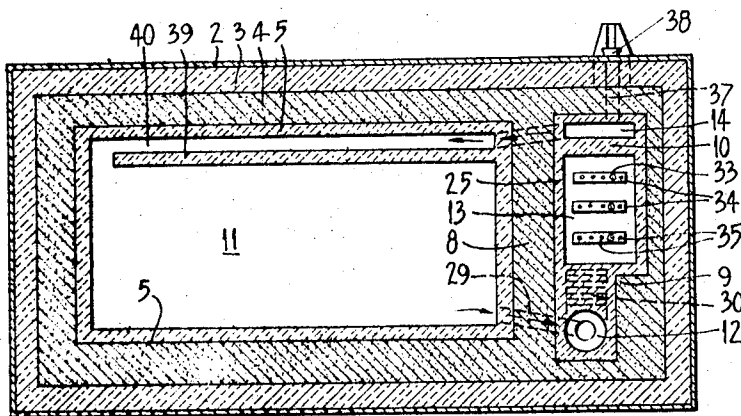


FIG. 3.

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2 Sheets-Sheet 2

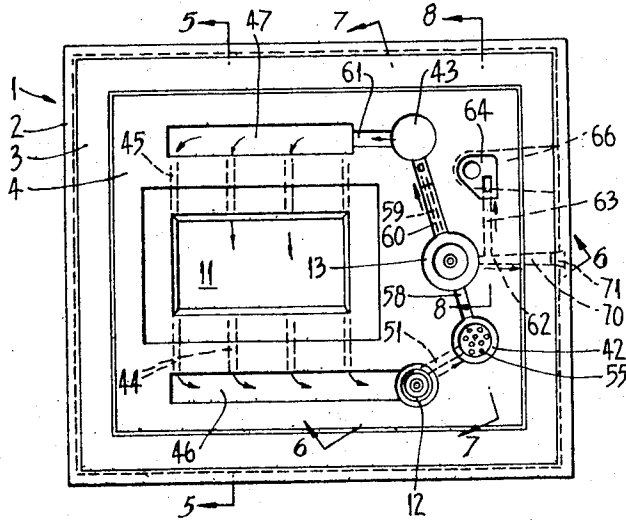


FIG. 4

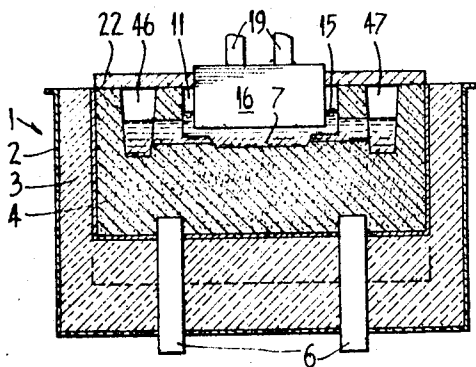


FIG. 5

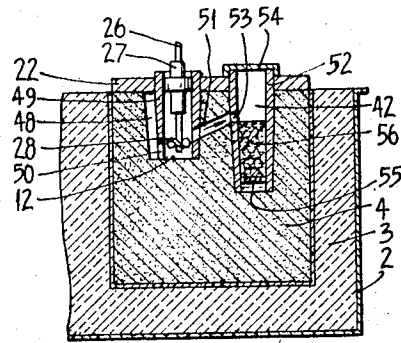


FIG. 6

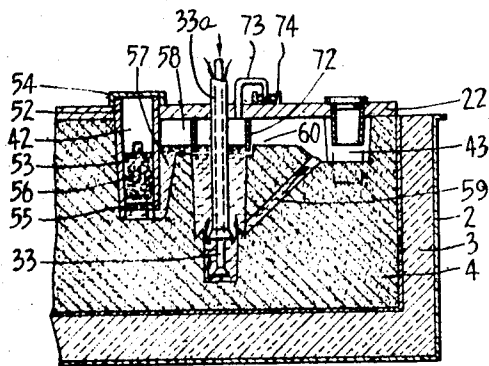


FIG. 7

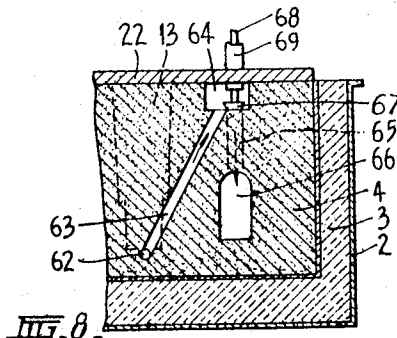


FIG. 8

1

3,464,900

PRODUCTION OF ALUMINUM AND ALUMINUM ALLOYS FROM ALUMINUM CHLORIDE

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53,446/64

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9 Claims

ABSTRACT OF THE DISCLOSURE

In the electrolytic production of aluminum from alchlor, a nascent metallic reductant (e.g., magnesium) is dissolved in a molten metal (aluminum) or alloy thereof serving as the cathode of the electrolytic cell and the resulting solution is contacted with alchlor out of contact with the fused salt electrolyte in which the metallic reductant was formed from its chloride.

This invention relates to the electrolytic production of aluminum and aluminum alloys, and refers especially to a continuous process of and apparatus for the production of molten aluminum by a fusion electrolysis using aluminum chloride (hereinafter termed "alchlor,") as a source of feed material.

Electrolytic processes for the production of aluminum which are in present day use employ aluminum oxide as a source of feed material and electrolyse this as a solution in a double salt of sodium and aluminum fluorides. Disadvantages of this system include (1) the consumption of high purity carbon electrodes by the oxygen component of the feed material at a rate which varies from 0.6 to 1.0 lb. of carbon per lb. of aluminum produced; (2) the low voltage efficiency of the cell of 35 to 45% which results from a summation of high voltage drops across the anode which must be adapted to continuous feeding, across the carbon lining which must be thick to contain the high temperatures within the cell, across the polar gap which must be large to allow clearance between the distorted cathode metal surface and the anode, and finally due to polarisation effects on the anode as a result of intermittent charging and variation of electrolyte compositions; (3) losses of expensive electrolyte by vapourisation occasioned by the open top construction of the cell necessitated by the need to intermittently and evenly feed solid alumina to the electrolyte; (4) severe corrosion and low cell life resulting from the high cell temperature of 950 to 1000° C., and (5) an appreciable labour requirement for introducing feed material.

The art contains records of attempts to produce aluminum from anhydrous alchlor by electrolysis of an electrolyte composed of alchlor dissolved in certain fused metal halides. A number of disadvantages have prevented commercial acceptance of such processes. Alchlor is a volatile solid subliming at about 178° C. Although its vapour pressure may be lowered substantially in molten alkali metal

2

chloride baths, alchlor is readily distilled from such baths when operating at or about the melting point of aluminum (661° C.). As a consequence these processes are operated at low temperatures or under a positive pressure. Eutectic or low melting point fused salt mixtures containing alchlor have very poor electrical conductivity, especially below the melting point of aluminum. At the operating temperatures of such processes molten solutions of alchlor are corrosive towards graphite and carbon which are essentially the only practical anode materials which can withstand the co-produced chlorine. At low temperatures aluminum is deposited as a solid commingled with electrolyte which is inconvenient to separate from the metal crystals, and cell voltages at practical current densities are very high. At high temperatures cell voltages can be reduced and liquid metal obtained but the pressurised equipment is expensive and corrosion is severe.

Our invention seeks to overcome the disadvantages of processes using electrolytes containing alchlor, while retaining the advantages of alchlor as a feed material. By providing a process wherein little, if any, alchlor can ever be present in the electrolyte.

According to the invention, a process for the electrolytic production of aluminum and aluminum alloys comprises electrolysing a fused salt electrolyte containing at least one of the group consisting of alkali metal halides, alkaline earth metal halides, and rare earth metal halides, using as cathode a molten metal or alloy, which cathode metal or alloy contains in solution a metallic reductant deposited from the electrolyte, and contacting the molten metal or alloy and the contained metallic reductant with alchlor. Preferably, the alchlor is contacted with the molten metal or alloy in such a manner that there can be negligible contact between the alchlor and the electrolyte.

More particularly, the invention includes a process for the electrolytic production of aluminum which comprises electrolysing in an electrolysis compartment or cell a fused salt electrolyte containing at least one of the group consisting of alkali metal halides and alkaline earth metal halides, the cathode being molten aluminum or aluminum alloy containing a metallic reductant deposited from the electrolyte by the electrolysis, transferring the molten aluminum or aluminum alloy and reductant to a reactor compartment or vessel, reacting alchlor with the metallic reductant in the reactor compartment or vessel, transferring the chloride product of the metallic reductant to the electrolysis compartment or cell, recycling molten aluminum containing a lower concentration of the metallic reductant back to the electrolysis compartment or cell, and discharging the molten metal product from the reactor compartment or vessel.

According to one aspect of the invention, an important feature resides in effecting the reaction between the metallic reductant and the alchlor which latter is preferably in the vapour state, in a compartment or vessel which is distinct or separate from the electrolysis compartment, so that little or no alchlor is permitted to enter the electrolysis compartment and consequently the possibility of its loss with and contamination of the chlorine produced in the electrolysis, and the attack by the alchlor on the anode material, are substantially prevented.

A further feature of the invention, according to one form thereof, is that the electrolyte contains the halide of

a metal which is deposited in the molten metallic cathode and which when transferred therewith to the reactor compartment functions as a metallic reductant which reacts with the alchlor to form metallic aluminum and the chloride of the said metallic reductant, the said chloride (selected to contain negligible amounts of alchlor) being then transferred to the electrolyte in the electrolysis compartment.

The metallic cathode should comprise a metal or alloy which is molten within the required temperature range, which is a sufficiently good solvent for the metallic reductant used, which is substantially unreactive to alchlor vapour and which can be separated from or is consistent with the final metal product required. Aluminum or those alloys of aluminum meeting the above requirements are preferred.

A further novel aspect of the invention resides in the employment, as components of the fused salt electrolyte, of an alkali metal halide or alkaline earth metal halide or rare earth metal halide, or mixture of alkali metal and/or alkaline earth metal halides, and/or rare earth metal halides, which enable the abovementioned objects and functions of the process to be achieved.

The composition of the fused electrolyte should desirably be such that the metal or metals deposited at the cathode during electrolysis (i.e. the metallic reductant) have adequate solubility in the molten metallic cathode (e.g. in molten aluminum or aluminum alloy) low solubility in the saline phase and, when dissolved in the molten cathode metal, have sufficient reactivity even at low concentration to reduce alchlor vapour, at high efficiency.

The metal or metals deposited at the cathode are desirably such that the corresponding chloride salt or salts have a density lower than that of the molten metallic cathode and a melting point not greatly in excess of the melting point of the cathode.

We have found (a) that magnesium fulfills these requirements in a particularly satisfactory manner and is therefore the preferred reductant, and (b) that magnesium chloride is a preferred constituent of the electrolyte, for the purposes of this invention.

However, the invention also includes the use of other alkaline earth metals (e.g. calcium), rare earth metals, and lithium as the metallic reductant, and the use of other alkaline earth metal halides or alkali metal halides or rare earth metal halides and in particular mixtures thereof, as components of the fused salt electrolyte. Such an electrolyte would have a density lower than that of the molten cathode and preferably a melting point not greatly higher than that of the molten cathode.

Because of its low decomposition voltage magnesium chloride may be used alone or in admixture with the halides of other alkali metals and/or alkaline earth metals. Rare earth halide reductants may be used with the halides of alkali metals and/or alkaline earth metals in the absence of magnesium halides. As a source of reductant lithium chloride and calcium chloride may be used alone or in admixture with each other.

Other alkali metal or alkaline earth metal halides, specifically the fluorides, may be added, within the limitations set out above and provided that they are mutually miscible, to modify and improve the properties of the electrolyte used in this invention.

As previously stated, the metallic reductant (e.g. magnesium) is transferred to a second or reactor compartment, distinct from the electrolysis compartment, wherein chemical interaction occurs between the metallic reductant and the alchlor vapour. By this arrangement it becomes possible to control the amount of reductant to any level deemed necessary to ensure the desired degree of interaction. Contrary to what might be expected we have found by experiment that alchlor vapour will reduce the magnesium content of an aluminum-magnesium alloy to extremely low values (e.g. 0.005%) at high efficiency.

Magnesium chloride is a co-product of the above reaction. It collects as a separate phase prior to being transferred to the electrolytic cell. Our experiments have also disclosed that the solubility of alchlor in molten magnesium chloride in the relevant temperature range is unexpectedly small. The magnesium chloride transferred to the electrolysis compartment in the normal process of the invention therefore contains little or no alchlor even if the rate of injection of alchlor vapour is excessive. Consequently the amounts of alchlor which may enter the electrolysis compartment are relatively small; hence not only are losses of alchlor via the electrolysis compartment substantially avoided, but additionally contamination of the halogen co-product and attack by the alchlor on the anode are either prevented or are of negligible degree.

Therefore, for the successful operation of the process of the invention it is not necessary for the electrolysing current and rate of input of alchlor vapour to be in continuous and exact synchronisation.

It will be appreciated that it is desirable to use a metallic reductant which upon reaction with alchlor yields a chloride with little or no solvent action for the alchlor at the temperature employed. This effect is best realised with reductants of the alkaline earth metal class or with lithium. Chlorides of alkali metals other than lithium form double salts with alchlor which remain stable to some degree at the temperatures of interest. Hence the electrolyte preferably contains chlorides of metals of the alkaline earth class or lithium, which are the component or components decomposed during electrolysis even when admixed with other salts. The appreciable solubilities of magnesium, calcium, lithium and rare earth metals in aluminum alloys at the operating temperatures are a further advantage of the process. As a result the amounts of these metals which dissolve in the molten salt bath are decreased, as are their chemical activities at the cathode, the overall effect being to permit higher current efficiencies and lower decomposition voltages to be realized than would have been the case if a metal of low solubility in molten aluminum such as sodium, had been deposited.

In the preferred process of the invention a molten salt phase comprising either—

- (a) magnesium chloride alone or admixed with halides of the alkali metals and/or of the alkaline earth metals, or
- (b) calcium chloride and/or lithium chloride alone or admixed with magnesium chloride or with each other

is electrolysed in an electrolysis compartment using a dependent graphite or carbon anode and a molten aluminum or aluminum alloy cathode, the relative densities of the liquid phases being such that the molten cathode remains as a discrete phase at the bottom of the electrolytic cell. Under such conditions substantially pure chlorine is evolved from the anode and corresponding amounts of reductant dissolve in the aluminum cathode.

The aluminum plus reductant metal so formed is transferred to a separate second compartment where it is reacted with alchlor gas under conditions of high, but not necessarily 100%, efficiency. The chloride co-product, containing negligibly small amounts of alchlor, is transferred to the electrolysis compartment to maintain the composition of the molten salt phase at an optimum level. Aluminum or aluminum alloy, denuded in reductant, is collected in suitable collection equipment. Part of this aluminum or aluminum alloy is recycled to the electrolysis compartment to maintain the cathode metal at the desired depth. The remainder representing the effective production of aluminum or aluminum alloy, which may be treated further with sufficient alchlor to remove as much reductant as is desired is tapped off as required.

The temperature at which the electrolysis and reduction processes are carried out is desirably maintained at 10–100° C. above the melting point of the electrolyte,

or the cathode metal, or the chloride salt of the reductant, whichever is the highest.

A further feature of one form of the invention resides in enclosing the reactor compartment in such a manner that back pressure in the vapour or gas space is used to control the rate of alchlor addition. Preferably, the reactor compartment is totally enclosed to the gas phase, so that if an excess of alchlor is fed it accumulates as a gas and builds up pressure within the compartment. If the alchlor supply to this compartment is only at low pressure, then the accumulated pressure in the compartment retards or stops the flow of alchlor into the compartment and this state continues until sufficient of the excess alchlor vapour is consumed by fresh reductant contained in the liquid metal received from the electrolytic cell to reduce the back pressure and allow further flow. This is a very desirable feature as the alchlor feed rate is thereby automatically controlled according to demand.

Whereas the normal method of alloy manufacture would be to add the alloying element directly to the metal stream in these instances, where an alloying element forms a volatile chloride, the alloy may be produced by introducing the chloride of the element in addition to alchlor into the reactor compartment at the appropriate rate.

The process of this invention has a number of advantages over existing processes for the electrolytic production of aluminum. It consumes virtually no carbon, continuously produces aluminum at current efficiencies of at least 85% and enables operation at temperatures above the melting point of aluminum yet significantly below those used in current aluminum extractive technology. By the use of gaseous alchlor a high purity feed can be introduced and a closed cell construction used with several attendant advantages.

Important advantages derive from the introduction of the gaseous alchlor in a separate compartment to be electrolysis, in that a wide selection of cell electrolytes is possible and a composition can be used which gives high conductivity and low specific gravity. Resulting from this, high current densities are possible, close electrode spacing can be used and voltage drop across the electrolyte can be minimised. Fixed anodes of optimum design can be used with a low voltage drop across them similarly cathode connector design can be improved to reduce voltage drop at this point. Cell designs are possible which are amenable to automation so that routine labour and supervision requirements are reduced to a minimum.

Because aluminum compounds are not directly electrolysed but instead a metal reductant is deposited as a solution in a flowing stream of aluminum or aluminum alloy, problems such as cathode over potential and fog formation are substantially reduced and high voltage and current efficiencies are possible. By recycling the aluminum at a sufficient rate to ensure that the solution of reductant in the molten cathode is relatively dilute, the higher voltages required for decomposition of the reductant salt in the electrolyte rather than of alchlor are largely offset by the reduced activity of the reductant dissolved in the molten cathode.

Examples of the operation of the process of this invention are as follows:

Example 1

A fused salt electrolyte comprising 20% w/w. magnesium chloride 40% w/w. lithium chloride and 40% w/w. sodium chloride was electrolysed at 670°-700° C. in an alumina-lined cell fitted with a vertical carbon rod as anode and having a pool of commercial-grade aluminum as cathode. The interpolar gap was 0.71 inch, the current density 1080 amps per square foot and the overall voltage 3.2 to 3.4 volts.

After electrolysis for one hour the magnesium chloride content was replenished to 25% by adding additional molten magnesium chloride. Electrolysis was then con-

tinued for a further period of one hour after which the aluminum metal product was removed and on analysis was found to contain 3.97% w/w. metallic magnesium.

The said aluminum-magnesium alloy was transferred to a 2½ inch internal diameter alumina crucible enclosed in an evacuable steel vessel. After evacuation and filling the vessel with argon the metal alloy was melted by heating to 800° C.

Pure aluminum chloride vapour at a rate equivalent to 500 mls. chlorine per minute measured at S.T.P. was bubbled through the molten metal alloy by means of a ¼-inch bore tantalum tube which dipped to a level 7½ inches below the surface of the metal. During the operation the temperature was controlled within the range 800° to 900° C. The flow of aluminum chloride vapour at the stated rate continued until aluminum chloride was detected in the exhaust gases. The tantalum tube was then retracted and the metal product allowed to solidify.

Analysis showed the metal product to be aluminum containing less than 0.002% w/w. of magnesium.

Example 2

A fused salt electrolyte comprising 40% magnesium chloride, 30% w/w. chloride and 30% w/w. sodium chloride was electrolysed at 725-750° C. using a current density of 1000 amps per square foot and an interpolar gap of 0.75 inch, in an alumina-lined cell with a vertical carbon rod as anode and a pool of commercial-grade aluminum as cathode. The aluminum alloy produced after 25 minutes contained 13.5% w/w. of magnesium, the overall current efficiency being 90%.

The aluminum alloy was transferred to a 2½-inch bore alumina crucible and melted under argon with the addition of sufficient aluminum to produce an aluminum alloy containing 6.12% w/w. of magnesium. Aluminum chloride vapour was then bubbled, at a rate corresponding to 4500 mls. per minute of chlorine measured at S.T.P., through the molten metal by means of a ¼ inch bore tantalum tube dipping 7½ inches below the metal surface. The flow of aluminum chloride was continued at the stated rate until aluminum chloride was detected in the exit gases, the temperature of the metal being controlled within the temperature range 800° C. to 950° C.

Analysis of the metal produced showed it to be aluminum containing less than 0.002% w/w. of magnesium.

The forms of apparatus for carrying out the invention, which are shown diagrammatically in the accompanying drawings, will now be described. These drawings and the description thereof are illustrative only, and are in no way to be regarded as limitative of the invention. In the drawings the same reference numerals are used to refer to like or corresponding parts. In the drawings:

FIGURE 1 is a view in sectional elevation of apparatus for the electrolytic production of aluminum.

FIGURE 2 is a sectional view taken on the line 2-2 of FIGURE 1, and

FIGURE 3 is a sectional plan view taken on the line 3-3 of FIGURE 1.

FIGURE 4 is a view in plan of an alternative and preferred form of apparatus for carrying out the invention,

FIGURE 5 is a view in sectional elevation taken on the line 5-5 of FIGURE 4,

FIGURE 6 is a view in sectional elevation taken on the line 6-6 of FIGURE 4,

FIGURE 7 is a view in sectional elevation taken on the line 7-7 of FIGURE 4, and

FIGURE 8 is a view in sectional elevation taken on the line 8-8 of FIGURE 4.

Referring to the FIGURES 1 to 3 of the accompanying drawings, the apparatus indicated generally at 1 is provided with an outer shell 2 which is thermally insulated by the lining 3. An inner graphite and/or carbon lining 4 contains the contents of the apparatus and carries current from the connectors 6 to the cathodic liquid metal layer 7.

The sides of the electrolysis compartment or cell 11 are electrically insulated by a refractory lining 5. The apparatus 1 is divided internally by graphite and/or carbon walls 8 and 9, and by a graphite, carbon and/or refractory wall 10 into four compartments, namely, the electrolysis compartment 11, the pump compartment 12, the reactor compartment or vessel 13 and the return compartment 14.

The electrolysis compartment 11 contains a molten salt electrolyte 15 which is of lower specific gravity than the cathodic metal layer 7 therebeneath. Anodes 16, 17 preferably of graphite or carbon depend into the electrolyte 15 and are secured to the cover 18, the anode connection being indicated at 19. The undersurface of the cover 18 is not protected by the anodes 16, 17 is lined with refractory blocks 20. A chlorine gas outlet 21 is fitted through the cover 18 and block 20 and communicates with the space above the electrolyte 15. Direct current is supplied to the connectors 6 and 19.

Covers 22 and 23 are fitted to the pump compartment 12 and the reactor compartment 13 respectively. Refractory block linings 24 are used to protect the undersurfaces of the covers 22, 23. The covers 18, 22 and 23 are sealed and gas tight.

Refractory block lining 25 protects the walls of the reactor compartment 13 and the top of the pump compartment 12.

A vertical shaft 26 driven by a motor (not shown) projects through a gland 27 in the cover 22 and is fitted with refractory clad impellers 28 which are inclined so as to impart movement to the liquid metal 7 which enters the pump compartment 12 from the electrolysis compartment 11 through passageway 29.

The liquid metal 7 overflows from the pump compartment 12 over a cascade 30 formed of steps, and enters the pool 31 of metal in the reactor compartment 13.

Alchlor vapour is supplied through the main supply pipe 32 and refractory sparger pipes 33 which project downwardly through the cover 23 into the reactor compartment 13 and is bubbled through the metal pool 31. Branch pipes 34 are connected to the lower ends of the sparger pipes 33 and are provided with holes 35 through which the alchlor vapor enters the pool 31.

The wall 10 forms a weir over which molten aluminum and co-products flow into the return compartment 14 and thence are recycled by return passageway 36 into the saline phase contained in the electrolysis compartment 11. A downwardly sloping passageway 37 is provided for periodic tapping of product aluminum, the outlet from the passageway 37 being normally closed by a removable plug 38. Aluminum metal or alloy accumulates in the passageway 37 and its upper level is normally immediately below the return passageway 36. The chloride co-product tends to rise to the surface of the metal or alloy and hence to be recycled with molten metal through the passageway 36. When the product aluminum in the passageway 37 is tapped, tapping is discontinued before any chloride co-product is discharged from the outlet. When the plug 38 is replaced the said chloride co-product is displaced upwardly in the passageway 37 by progressive accumulation of product metal therein, and is then recycled with further metal through the passageway 36.

A wall or baffle 39 is provided in the electrolysis compartment 11 and extends from the end of the said compartment which is nearest to the reactor compartment 13 to a point spaced a short distance from the opposite end of the compartment 11. The wall or baffle 39 forms a trough 40 between it and the adjacent wall of the compartment 11. The passageway 36 communicates with one end of the trough 40 at a level above the upper surface of the cathode metal 7 so as to communicate with the molten salt electrolyte 15. The other end of said trough 40 communicates with the compartment 11.

As illustrative of the process, the cell is filled with sufficient molten aluminum or aluminum alloy 7 to cover

the bottom of the electrolysis compartment 11 and give good electrical contact with the lining 4. Sufficient molten electrolyte 15 is then poured into the cell to cover the bottom of the anodes 16, 17. The molten electrolyte may comprise a selection of alkaline earth metal halides and alkali metal halides, as hereinbefore described, and preferably contains magnesium chloride. The source of direct current is connected to the cell and electrolysis of the electrolyte 15 in the electrolysis compartment 11 takes place with deposition of metallic reductant (e.g. magnesium) in the cathodic layer 7, the metallic reductant entering into solution in the molten aluminum. After a suitable period the recycle pump 26, 28 is started and when molten metal is recirculating through the reactor compartment 13 alchlor vapour is fed from the main 32 through the sparger pipes 33 and branch pipes 34 into the metal in the pool 31.

The pressure of alchlor in the main 32 is maintained at a constant small positive value. This forces the vapour into the reactor chamber 13 and to then bubble in slight excess through the metal pool 31 until such time as the pressure built up in the gas space of the reactor chamber 13 is sufficient to halt the vapour flow. When this pressure is relieved by further reaction of the alchlor vapour in the gas space with fresh incoming metal descending over the cascade 30, more alchlor will feed from the main 32. The alchlor is reduced by the metallic reductant, forming aluminum and the chloride of the reducing metal (e.g. magnesium chloride). The greater proportion of the alchlor vapor reacts with the reducing metal as it bubbles through the molten alloy in the pool 31. A small proportion of the alchlor escapes this pool and is consumed by surface reaction with the reducing metal at the cascade 30.

The alchlor vapour is thus fed automatically from the main 32 only as fast as it can be consumed by the reductant electrolysed into the metal recycling through the electrolysis section.

Under some circumstances the surface of the metal in the pool 31 may become coated by a thin layer of molten salt product from the alchlor/reductant reaction which tends to prevent further rapid reaction between the metal surface and excess alchlor which escapes the pool 31, and the cascade 30 therefore serves the function of providing sufficient uncoated metal surface for the excess alchlor to be consumed.

Molten aluminum or aluminum alloy, together with the molten salt product of the reduction reaction, overflows the weir 10, and both components are then returned to the electrolysis compartment 11 via passageway 36 and trough 40, and the molten salt product is again electrolyzed in the compartment 11 to form the reductant.

As cell operation continues the quantity of molten aluminum in the system increases. The make is periodically tapped off through outlet 37 at a rate and frequency required to maintain the polar gap and cell operation at close to the optimum values.

Referring to FIGURES 4 to 8 of the accompanying drawings, the apparatus 1 shown therein comprises an outer shell 2, an insulating lining 3, a conductive inner graphite or carbon lining 4, an electrolysis compartment or cell 11, a pump compartment 12, a filter compartment 42, a reactor compartment 13 and a sampling compartment 43. An anode or anodes 16 depend into the electrolysis compartment 11 through the cover 22. Current is supplied to the anodes 16 through cover 22. Current is supplied to the anodes 16 through connectors 19 and is supplied to the cathodic lining 4 through connectors 6.

The electrolysis compartment 11 contains a fused salt electrolyte 15 of lower specific gravity than the molten metal cathode 7 therebeneath, which latter preferably comprises aluminum or aluminum alloy. The anodes 16 depend into the electrolyte 15 but not into the cathode layer 7.

The electrolysis compartment 11 communicates by means of channels 44, 45 with launders 46, 47. The

launder 46 communicates with a chamber 48 which is separated from the pump compartment 12 by a sleeve 49. A passage 50 at the lower end of the sleeve 49 provides communication between the chamber 48 and the pump compartment 12.

The pump compartment 12 is provided with an impeller 28 which imparts upward movement to liquid metal in the pump compartment 12. The impeller 28 is mounted on a shaft 26 which projects through a gland 27 in the cover 22 and is driven by a motor (not shown).

An upwardly inclined passage 51 communicates between the pump compartment 12 and the filter compartment 42. A removable tapered sleeve 52 is fitted in the filter compartment 42 and the passage 51 communicates with an aperture 53 in the sleeve 52. A cover 54 fits over the upper end of the sleeve 52. A perforated horizontal wall 55 is provided at the lower end of the sleeve 52 and the compartment 42 above the wall 55 is filled with filter material 56 such as tabular alumina. The space below the wall 55 communicates with a chamber 57 at the side of the filter compartment 42 and the upper end of this chamber 57 communicates by means of channel 58 with the upper part of the reactor compartment 13.

Two inner and outer concentric alchlor supply tubes 33, 33a depend into the reactor compartment 13 through the cover 22, the open lower ends of the tubes 33, 33a being flared outwardly. The inner supply tube 33 terminates near the lower end of the reactor compartment 13 and the outer supply tube 33a terminates at a higher level in the said compartment 13. The tubes 33, 33a are connected to a source of gaseous alchlor at suitable pressure. The lower end of an upwardly inclined passage 59 communicates with the reactor compartment 13 at a point just above the lower end of the outer tube 33a, and the upper end of the passage 59 communicates with the sampling compartment 43. A channel 60 connects the upper end of the reactor compartment 13 with the sampling compartment 43. A channel 61 connects the sampling compartment 43 to the launder 47.

A product metal outlet passage 62 is provided at the bottom of the reactor compartment and communicates by upwardly inclined passage 63 with intermediate compartment 64 and thence by vertical passage 65 with metal receiver 66. The passage 65 is controlled by 67 attached to spindle 68 passing through gland 69 in the cover 22. The valve 67 controls the flow of metal into receiver 66.

An emergency discharge passage 70 closed by plug 71 connects also with outlet passage 62.

In operation, the electrolysis compartment 11 is charged with molten aluminum or aluminum alloy 7, and with a supernatant layer of molten salt electrolyte of the type previously described, preferably containing magnesium chloride. Direct current is supplied to the cell to effect electrolysis of the electrolyte. Metallic reductant (e.g. magnesium) is deposited and enters into solution in the molten aluminum cathode. The molten cathodic metal and dissolved reductant leaves the cell 11 by channels 44 and launders 46 and enters the lower end of the pump compartment 12 where it is elevated by the impeller 28 through passage 51 and aperture 53 into the reactor compartment 13 which normally is filled with the molten metal. In descending the reactor compartment 13 the molten metal moves countercurrently to upflowing alchlor vapour which is supplied to the reactor compartment 13 through the tubes 33, 33a. The reaction between the alchlor and the reductant, the latter being present in excess at this stage, leads to the total consumption of alchlor and the production of aluminum and the chloride of the reductant, the chloride co-product being displaced upwardly to the surface of the molten metal in compartment 13. Part of the molten metal, denuded in reductant and which may contain a proportion of chloride co-product flows through passage 59 into the sampling compartment 43 while chloride co-product overflows from the reactor compartment 13 through channel 60 into the sampling compartment 43.

The said molten metal, together with the chloride co-product, is recycled to the electrolysis compartment 11 via channel 61, launder 47 and channels 45.

The remainder of the molten metal in the reactor compartment 13 moves to the lower part of the compartment 13 where it is subjected to further reaction with alchlor vapour entering through inner tube 33, the said alchlor vapour being in sufficient excess to ensure the substantially complete removal of the reductant from the molten metal.

The excess alchlor passes upwardly in the reactor compartment 13 where it reacts with further amounts of reductant contained in the molten metal.

Product aluminum or aluminum alloy leaves the bottom of the reactor 13 by passages 62, 63 and enters the intermediate compartment 64. The product metal is tapped periodically from the intermediate compartment 64 into the receiver 66 by means of the valve 67, at a rate normally determined by the rate of production of reductant in the electrolysis compartment 11.

While the alchlor would normally be totally consumed trace quantities of inert gases might occasionally be present in it. These escape above the molten salt layer and are contained by the refractory trap 72 dependent from and sealed to the cover 22. The open base of this trap dips just below the liquid salt surface. The inert gases then expel to atmosphere through the bleed tube 73 which terminates just below the surface of a suitable seal liquid (e.g. molten lead) contained in the pot 74.

What is claimed is:

1. A process for the electrolytic production of aluminum or an aluminum alloy which comprises electrolyzing a fused salt electrolyte containing at least one salt selected from the group consisting of alkali metal halides, alkaline earth metal halides, and rare earth metal halides and containing the chloride of a metallic reductant which reductant is more electropositive than aluminum and is soluble in aluminum, using a cathode of a molten alloy of the said metallic reductant and aluminum, whereby the metallic reductant is preferentially deposited from the electrolyte and enters into solution in the molten alloy cathode; and contacting the molten alloy with alchlor thereby reducing the alchlor to aluminum and reforming the chloride of the metallic reductant.

2. A process according to claim 1 wherein contact between the alchlor and the electrolyte is substantially prevented.

3. A process for the electrolytic production of aluminum which comprises, electrolyzing a fused salt electrolyte containing at least one salt selected from the group consisting of alkali metal halides, alkaline earth metal halides and rare earth metal halides, and containing the chloride of a metallic reductant which reductant is more electropositive than aluminum and is soluble in aluminum, in an electrolysis space using a cathode of a molten alloy of the said metallic reductant and aluminum, whereby the metallic reductant is preferentially deposited from the electrolyte and enters into solution in the molten alloy cathode, transferring the cathode molten alloy to a reactor space, contacting the molten alloy in said reactor space with alchlor thereby reducing the alchlor to aluminum and reforming the chloride of the metallic reductant.

4. A process as claimed in claim 3 wherein the metallic reductant is magnesium.

5. A process as claimed in claim 3 wherein the metallic reductant is a rare earth metal.

6. A process according to claim 4 wherein the chloride product of the metallic reductant is transferred to the electrolysis space and molten aluminum containing a diminished concentration of metallic reductant is recycled to the electrolysis space, product aluminum being discharged from the reactor space.

7. A process according to claim 6 wherein the reducing metal is made to flow over a cascade to react with the alchlor in vapour form.

11

8. A process according to claim 3 wherein alchlor vapour is introduced at two levels into the reactor space.

9. A process for the production of an alloy of aluminum with an element which forms a volatile chloride, which process comprises a process for the electrolytic production of aluminum, according to claim 3 including the step of introducing the chloride of the said element in addition to the alchlor at the appropriate rate.

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12

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15