[54] **DIRECT REDUCTION PROCESS FOR PRODUCTION OF ALUMINIUM**

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[58] Field of Search.......................... 75/68 R, 68 A

[56]   **References Cited**
           UNITED STATES PATENTS

2,198,673   4/1940   Loevenstein....................... 75/68 R

3,234,008   2/1966   Johnson............................... 75/68 A

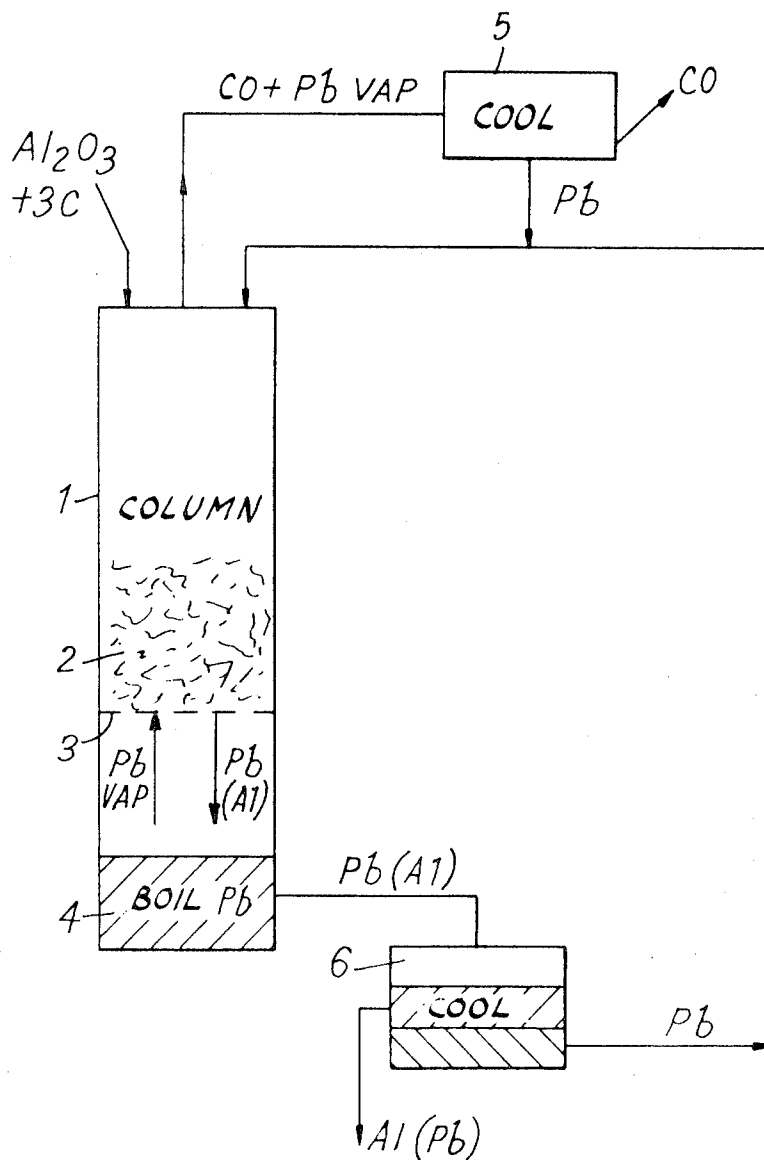*Primary Examiner*—L. Dewayne Rutledge
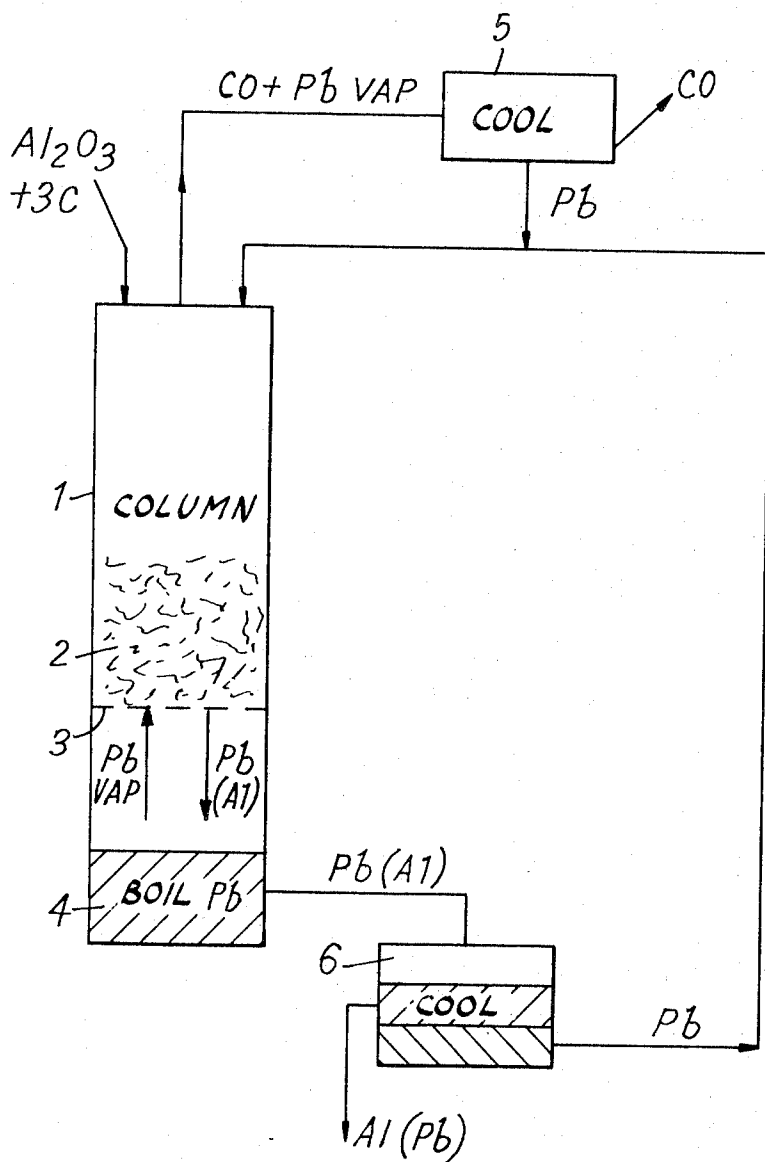*Assistant Examiner*—M. J. Andrews
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[57]   **ABSTRACT**

In a process for the production of aluminium, alumina is reacted with carbon at an elevated temperature in the range of 1,600° – 2,500° C. The heat to support the endothermic reaction is provided by passing a stream of lead and/or bismuth vapour into the mass and allowing the metal vapour to condense to the liquid phase. The liquid metal alloys with the produced aluminium to reduce its activity and to remove it from the reaction zone whilst the flow of metal vapour through the reaction zone reduces the concentration of carbon monoxide.

3 Claims, 1 Drawing Figure

Al_2O_3
+3C

5

CO + Pb VAP

COOL

CO

Pb

1 — COLUMN

2

3

Pb VAP

Pb (Al)

4 — BOIL Pb

Pb (Al)

6

COOL

Pb

Al (Pb)

DIRECT REDUCTION PROCESS FOR PRODUCTION OF ALUMINIUM

The present invention relates to the production of aluminium and in particular relates to an entirely new process for the production of aluminium metal from alumina.

The production of aluminium by the Hall-Heroult process has remained unchanged in principle. Although a number of attempts have been made to find new routes for the commercial production of aluminium at lower cost than can be achieved by the Hall-Heroult process, all have so far proved unsuccessful in development to commercial operation.

In considering the practicality of a new process for the production of aluminium account must be taken of many factors, including:

(a) cost of raw materials
(b) energy requirements
(c) original cost of plant
(d) cost of maintaining plant
(e) control of pollution
(f) cost of operating plant.

Whilst the principal disadvantage of the Hall-Heroult process is the high capital and operating costs, the use of fluoride fluxes results in considerable problems in the prevention of emission of fluorides in impermissible quantities.

All the common metals occur in nature as oxide ores, or as sulphides which are readily converted to oxides. In all direct reduction smelting processes, carbon is employed as reducing agent and is oxidised to CO or CO_2. The less reactive metals (Fe, Cu, Pb, etc.) can be produced directly in a blast furnace or electric furnace; the more reactive metals (Al, Na, Mg) have usually been produced by electrolysis using, in effect, the electric current to increase the energy input of the system. The direct thermal reduction of a metal oxide obviously has tremendous economic advantages over an electrolytic process and for aluminium it is nearly feasible to reduce alumina to aluminium by direct thermal reduction. Alloys containing around 50 percent Al can be made without difficulty in an arc furnace. However, to make pure aluminium with no alloying elements by direct reduction seems impossible owing to the formation of aluminium carbide and excessive quantities of fume. The basic simplicity and economy of the thermal reduction nonetheless leave a big incentive to make an alloy by direct thermal reduction and then to obtain pure aluminium from the alloy.

From such an alloy the more obvious route to obtain pure aluminium is to extract the aluminium from the alloy, since this effects purification of the aluminium at the same time. The alternative is to extract the alloying material from the alloy, leaving the aluminium as residue and it is that alternative that is employed in the process of the present invention.

There is no possibility of removing in an economically viable process the elements — Fe, Si, etc. — which would occur in alloys produced by direct reduction of bauxite or other ores.

In the process of the present invention an alloy of aluminium with lead and/or bismuth is produced by direct thermal reduction of alumina in the presence of vapours of lead and/or bismuth and in the presence of liquid lead and/or bismuth so as to form an alloy of aluminium with lead and/or bismuth in the thermal reduction stage. These metals can be very largely separated from a molten lead-aluminium alloy by cooling. For example, below 1,400° C, Pb-Al alloys will separate into two layers, and the top layer at 660° C, the freezing point of Al, contains only 0.2 atom percent Pb (1.5 wt. percent). Although this is far too much to meet purity specifications of aluminium it is nonetheless a remarkably small quantity of material to remove from aluminium in a final purification stage.

Since lead boils (at 1 atm. pressure) at 1,743° C and bismuth at 1,579° C, while the reduction of alumina by carbon occurs around 2,000° C, it is obvious that Al-Pb and/or Bi alloys cannot be made in an arc furnace open to the atmosphere. However, in a closed system a totally different situation arises. Taking lead as an example, it may be boiled at any desired temperature by adjusting the pressure in the system. The smelting reaction is

$$Al_2O_3 + 3C \rightleftharpoons 2Al + 3CO$$
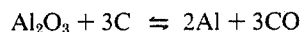
(1)

and this is driven to the right (at a given temperature) by lowering the activity of Al (by alloying it) and/or by lowering the partial pressure of CO. The lead vapour serves this latter function by diluting the carbon monoxide. The endothermic smelting reaction causes lead to condense from the vapour, and the liquid lead so produced alloys with the aluminium, lowering its activity. The lead therefore serves two functions simultaneously; liquid lead serves as an alloying agent to decrease the activity of the aluminium formed and gaseous lead serves to dilute the carbon monoxide in the gas phase and carry it out of the reaction zone. Furthermore, heat is supplied to the reaction zone through the latent heat of condensation of lead from the vapour phase to the liquid phase. Sufficient heat for the reaction to proceed may be supplied by condensation of lead vapour, and no other heating of the charge is necessary. If all heat for the system is supplied by boiling lead to produce lead vapour, the electrical properties of the charge, which are very important in arc furnace operation, become irrelevant.

In the process of the present invention lead and/or bismuth vapour at a temperature in the range of 1,600° to 2,500° C and correspondingly elevated pressure is continuously passed through an alumina-carbon charge, where some of it condenses to provide heat input and the resultant alloy (containing about 10 atom percent Al under optimum conditions) descends to the bottom of the chamber, whilst the uncondensed lead and/or bismuth vapour passes through the charge and is recovered by cooling the gas. The alloy is preferably conducted back into the metal vapour generator until the Al concentration builds up to around 25 atom percent; this liquid is tapped, cooled, separated into two layers, and the lead and/or bismuth layer is recycled. The temperature at which the smelting process operates is governed by the pressure maintained in the system; this controls the temperature at which the lead (and/or bismuth) boils and at which the metal vapour can condense in the alumina-carbon mass to supply the necessary heat to make an alloy. The boiling of lead (and/or bismuth) coupled with condensation of metal vapour at a position beyond the charge results in a pressure difference across the charge to displace carbon

monoxide from the reaction zone, so that there is no requirement for any mechanical pump or blower for hot gases.

A system for carrying out the process of the invention is shown in diagrammatic form in the accompanying drawing.

Alumina and carbon are charged in successive increments to a vertical vessel 1, in which the charge 2, which must readily permit passage of gas, is supported on a grid 3, which is located above a mass of boiling lead 4, to which heat is supplied in any convenient manner. As already stated, part of the lead vapour condenses in the charge 2 and returns with dissolved aluminium to the mass 4, whilst the remaining lead vapour and carbon monoxide generated in the reduction of alumina is passed to a condenser 5, from which the condensed lead is passed back to the mass 4, conveniently, but not essentially, through the column 1. The condenser 5 may form an upper region of the vessel 1. The permanent gas, principally carbon monoxide, which is at substantially the same pressure as in the vessel 1, may be further cooled before discharge through a pressure-reducing device to a gas holder.

Lead-aluminium alloy from the mass 4 is periodically withdrawn to a cooling vessel 6, in which it is separated into two layers by cooling to about 700° C, i.e. to a temperature somewhat above the melting point of aluminium. The lead layer (containing a small proportion of aluminium) is then recycled to the mass 4, preferably through the column 1. The liquid lead may be sprayed into the condenser 5 so that it is reheated substantially to reaction temperature before coming into contact with the alumina-carbon charge. The aluminium layer (containing a small proportion of lead) is then withdrawn for purification and removal of the small remaining proportion of lead.

Substantially lead-free aluminium may be obtained by fractional crystallisation of the aluminium-rich layer from the vessel 6. This molten metal may be run into an upright vessel which tapers from its mouth to its bottom end. By slow cooling in this vessel a substantially lead-free layer of solid aluminium will form on the surface, which may be removed in any suitable way when the freezing is about 80 – 90 percent complete. Fresh molten metal can then be added and the process repeated until there is sufficient lead separated at the bottom of the vessel to warrant recycling it.

The carbon electrode in the conventional electrolytic process is made of petroleum coke, bound together with pitch. In the present process, petroleum coke will preferably be used as the source of carbon in the furnace charge since it is low in metallic impurities. Any other similar source of relatively pure carbon will also be acceptable. The coke requires to be combined with the alumina into pieces large enough and strong enough to allow gas and molten lead to pass between them and to withstand crushing.

To produce the charge, purified alumina, produced in conventional manner by the Bayer process, is preferably incorporated with a liquid residual oil before it is coked. Coking of the oil produces a very intimate mixture of alumina and coke. The alumina-containing coke product can be broken to the size required. The expense of the pitch, normally provided as a binder for the anodes in the conventional electrolytic process, may thus be avoided.

The system in the vessel in which the mass of lead is boiled to generate lead vapour and the column of charge 2 operates under the following conditions :

1. the alloy in the boiler has a vapour pressure of Pb equal to the total pressure in the system;

2. the alloy in the boiler should not be so rich in Al that it forms Al_4C_3 with the carbon lining, if carbon is used for that purpose;

3. each local region of the charge in column 2 approaches the conditions of mass balance, heat balance, equilibrium between Pb in the alloy and Pb vapour in the gas, and equilibrium between Al in the alloy, Al_2O_3, C and CO in the gas phase. These four conditions leave no degrees of freedom and the temperature and alloy composition are uniquely determined at all levels of the column in terms of conditions in neighbouring regions;

4. the charge must remain solid when using a vertical column of charge arranged in the illustrated manner. This in practice limits the temperature range of the incoming metal vapour to a temperature in the range of 1,600° to 2,040° C to avoid melting of the alumina. In terms of thermal efficiency it would be desirable to let it melt and with differently engineered apparatus the charge might be molten. However, it is preferred to operate at a temperature above 1,600° C and preferably above 1,700° C, but below 2,040° C. Most preferably the temperature of the incoming metal vapour is at about 2,000° C.

Calculations have been made, employing available thermodynamic data, assuming that (a) the charge and liquid lead entering the converter are at 677° C (950° K), (b) the lead tapped from the boiler and cooled to that temperature to separate the aluminium still contains 1.5 percent Al when it is recirculated.

At 2.75 atm. total pressure, and a liquid-vapour ratio of 0.62 (ratio of liquid lead entering the top of the reaction zone to gaseous lead entering the bottom of the reaction zone), it was found that the bottom of the column of charge was running at 1,917° C and the alloy leaving it contained 9.92 atom percent Al. The top of the charge column was at 1,793° C, and 20.4 percent of the lead evaporated was still in the gas phase. 6.312 mol of lead were evaporated from the boiler in order to have 1 mol of aluminium removed from the column. However, 3.9 percent of this aluminium was not recovered when the product was cooled, and the lead was recirculated to the top of the column. The efficiency was thus 0.961, and the power required was the latent heat of evaporation of lead plus the heat required to raise the returned liquid lead alloy back to the boiler temperature, divided by the efficiency. The required lead boiler temperature was 2,010° C and the alloy in it contained 27.6 atom percent Al. The activity of Al in this alloy is 0.529, whereas the critical value for formation of Al_4C_3 is at least 0.533; Al_4C_3 should therefore not form. The lead to be circulated is 2.733 mol per mol of Al produced, or 21.0 lb. of lead per lb. of aluminium.

The eutectic between Al_2O_3 and Al_4O_4C is at 1,904° C; between this point and the melting point of pure Al_2O_3 (2,042° C) there will lie a line separating the solid and liquid phases. From the available information it appears that with a temperature of 1,917° C at the bottom of the charge, the composition of the alloy at this line contains 9.95 atom percent Al; since the alloy

at this point only contains 9.92 atom percent Al, the charge should remain solid.

The conditions specified are just about optimum. At a ratio of 0.62 a pressure of 2.75 atm. is just acceptable, both from the point of view of the charge remaining solid and from not forming Al_4C_3 in the boiler. If the pressure is raised the charge will melt; if it is lowered, Al_4C_3 may form. At higher ratios and higher pressures, acceptable conditions can be found with lower power requirements, but additional quantities of liquid lead must be handled. For general convenience it is preferred to operate at a pressure in the range of 2.7 – 2.8 atmospheres and a liquid-vapour ratio in the range 0.55 – 0.7. In this range the power input required for generating metal vapour is about 5.5 kilowatt hours/lb. of aluminium product.

As already stated, the alloy tapped from the boiler in the present example of the operation of the invention is at 2,010° C and contains 27.6 atom percent Al; its vapour pressure is 2.75 atm. To separate the aluminium it needs to be cooled to below 700° C. As far as possible the alloy should be cooled by evaporation of lead.

An advantage of the evaporative cooling is that it not only removes heat from the system, but also removes lead. This improves the overall efficiency, since evaporated lead does not recycle aluminium to the top of the converter. The evaporated lead is first cooled to the liquid state and then introduced to the stream of liquid lead returned to the converter.

Since the charge is composed of Bayer alumina and petroleum coke there are only two major impurities which enter the system. The alumina contains ~0.5 percent Na_2O and the coke contains 1–4 percent sulphur. Both of these are volatilized from the top of the column, the sodium as Na atoms and the sulphur as COS and PbS molecules. At the temperature to which the gas must be cooled to remove lead from the vapour, the Na will react with the sulphur compounds to form Na_2S, and any remaining sulphur will be left as PbS, which is undesirable.

Preferably, therefore, Na and S are present in equivalent amounts so that formation of Na_2S is complete and neither is left over, thus avoiding any discharge of sulphur into the atmosphere. To get the sodium and sulphur into balance is not difficult by addition of soda or other alkali metal oxide or carbonate to the charge.

The foregoing discussion and examples have been based on the use of lead. It can be advantageous to add bismuth to the lead, despite its lower boiling point and the consequently higher pressure in the system. If this is done the liquid condensing in the charge 2 contains Bi, and this is advantageous since its effect is to increase the solubility of Al in Pb (i.e., additions of Bi lower the activity coefficient of Al). The corresponding disadvantage of increasing the solubility of Al in the alloy at the temperature at which separation is carried out is mitigated because the bismuth is evaporated preferentially during the evaporative cooling of the alloy withdrawn to the cooling vessel 6.

The following features of the new process are apparent:

1. the power requirements are comparable with or lower than the conventional electrolytic process;

2. the process needs nearly twice as much petroleum coke as the conventional process but, if the proposed method of making the charge is adopted, this is partly offset by not using pitch as a binder;

3. no fluorides are used. This saves both money and pollution control equipment;

4. the relative proportions of soda and sulphur in the ingredients may readily be controlled so that the sulphur from the coke is left in the concentrated form of sodium sulphide which would be a great advantage in overcoming pollution resulting from release of sulphur to the atmosphere.

I claim:

1. A process for the production of aluminium which comprises reacting a charge of alumina and carbon in a reaction zone at a temperature in the range of 1,600° to 2,500° C in the presence of liquid lead and/or bismuth and in an atmosphere consisting essentially of lead and/or bismuth vapour, supplying heat to the reaction zone to maintain the charge within the temperature range by introducing a stream of lead and/or bismuth vapour into the reaction zone and into contact with the charge and allowing lead and/or bismuth to condense from the vapour phase to the liquid phase in the reaction zone to form an alloy with aluminium produced by the reaction of the alumina and carbon of the charge, leading the resultant alloy out of the reaction zone, and recovering aluminium from such lead and/or bismuth-aluminium alloy.

2. A process according to claim 1 which comprises maintaining in a reaction zone a charge in the form of solid pieces of an intimate mixture of carbon and alumina, maintaining a body of boiling metal composed of lead and/or bismuth in a vapour generating zone, passing the evolved metal vapour into the solid charge to maintain the temperature of the charge in the range of 1,600° to 2,040° C, maintaining liquid lead and/or bismuth in contact with the charge to alloy with aluminium formed in the reaction zone, withdrawing such alloy from the reaction zone to the vapour generating zone, withdrawing aluminium-enriched lead and/or bismuth from the vapour generating zone to a cooling zone, cooling to a temperature somewhat above the melting point of aluminium such withdrawn metal to produce an aluminium-rich layer and a lead and/or bismuth-rich layer, returning the lead and/or bismuth-rich metal in the liquid state to the reaction zone to pass therethrough in a direction countercurrent to the stream of metal vapour, cooling the gas issuing from the reaction zone to condense the lead and/or bismuth to the liquid state, exhausting permanent gas from the system and returning the condensed lead and/or bismuth to the reaction zone to pass therethrough countercurrent to the stream of metal vapour from the generator, the cooled aluminium-rich layer of metal being withdrawn from the cooling zone and further treated for removal of lead therefrom.

3. A process according to claim 2 wherein the pressure maintained in the reaction zone is 2.7 – 2.8 atmospheres and the ratio of liquid lead — lead vapour entering the reaction zone is 0.55 – 0.7.

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