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**ELECTROLYTIC PRODUCTION OF ALUMINUM**  
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8 Claims

## ABSTRACT OF THE DISCLOSURE

An improved electrolytic process for the production of aluminum from a molten salt electrolyte involving the use of hydrogen as an anodic reactant on non-carbon electrodes. The anode may be either porous or non-porous metallic or other conductive material. The reaction occurring on the cathode surface involves the reduction of aluminum cations to form substantially impurity-free aluminum. At the anode, hydrogen is oxidized to water vapor which is driven off and collected from above the cryolite melt.

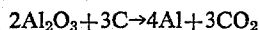
## FIELD OF THE INVENTION

The field of this invention is the electrolytic production of aluminum by the electrolytic reduction of alumina from a cryolite melt using a non-carbon, non-consumable anode structure. In particular, the invention relates to the use of hydrogen as the anodic reactant in the electrochemical production of aluminum. Highly pure aluminum is produced and by-product water vapor is released.

## BACKGROUND OF THE INVENTION

By way of background, the production of aluminum in the mid-1800's was principally by chemical methods. An example was the reduction of aluminum sulfide by hydrogen gas. Strictly chemical processes were supplanted by the Hall electrochemical process in the 1880's. The electrochemical process is fundamentally different than the prior chemical processes in many respects. Principal among these is the fact that two solid electrodes are required having an applied DC field therebetween, and the reactions occur on the electrode surface. In the electrochemical process, the positive aluminum ions obtain the electrons to form the neutral elemental aluminum from the cathode, and not from any chemical reactant. In contrast, in the prior chemical processes the reaction occurred between the chemical reactants throughout the mixture.

Practically all aluminum produced today is obtained by the Hall process, in which a solution of purified alumina in cryolite melt is cathodically reduced to aluminum. The cryolite melt is up to 85%  $\text{Na}_3\text{AlF}_6$ , and also contains  $\text{CaF}_2$ ,  $\text{LiF}$ ,  $\text{AlF}_3$ ,  $\text{NaCl}$  and other additives. The process is carried out at 950–980° C. with anodes of graphite or high-grade coke. The anodes are consumed because of the oxidation of the carbon, the overall process reaction being:



The cryolite-alumina melt floats on the molten aluminum, which serves as the cathode at the bottom of the cell. Product gases evolving from the melt are carbon dioxide and some carbon monoxide. As the carbon-containing anode is used up, it must continuously be readjusted in the melt in order to maintain the critical distance between the cathode and the anode so as to maintain the proper field therebetween.

Since pure carbon is relatively expensive in the quantities required for this Hall process, high-grade but still impure, coke and graphite are used as the anode source materials. However, both of these materials contain substantial mineral impurities which find their way into the end product aluminum and the electrolyte. Impurities in

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the coke and graphite include oxides, silicates and carbonates of titanium and iron, trace amounts of vanadium and nickel, and a significant amount of sulfur. In addition, as some of the evolved  $\text{CO}_2$  dissolves in the bath, it reacts with the aluminum in the melt to produce carbon monoxide and reoxidize the aluminum to aluminum cations.

## THE INVENTION

### Objects

Therefore, it is an object of my invention to electrochemically produce an aluminum more pure than that obtained by the Hall process.

It is another object of my invention to provide an improved electrochemical process for the production of aluminum from alumina in which the anodes are not consumed, and thus provides a process which lends itself to better automation than the existing processes.

It is another object of my invention to provide a process which is less expensive than current aluminum production processes and simple to operate, while producing a high-purity aluminum.

It is another object of my invention to provide hydrogen as an anodic reactant in an electrochemical production of aluminum.

Still other objects and advantages of my invention will be apparent to one skilled in the art from the detailed disclosure which follows:

### Summary

In summary, my invention involves the use of hydrogen as the anodic reactant in the electrochemical reduction of alumina from a molten salt electrolyte, such as a cryolite-type melt, and in which the anode is a non-consumable, non-carbonaceous-material-containing electrode of either porous or solid electrically conductive material.

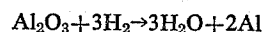
### Detailed description

In more detail, my process involves the use of a molten salt electrolyte maintained at a temperature of between 940 and 1050° C., and preferably at about 950–975° C., such as an alumina in cryolite melt.

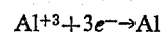
The melt is retained in an electrolytic cell which might be lined along the sides with a corrosion resistant material, such as a refractory or metal material. However, generally, carbon would be employed as the lining, since the gases evolved on the anode do not bathe the lining.

Into the melt, and spaced a suitable distance from the cathode (the molten aluminum pool on the bottom of the cell), is placed, in one embodiment, a porous, electrically-conducting anode. The specific configuration of the anode should provide ample surface area on which the electrochemical reaction is to take place. DC current is supplied at a high current density, for example from about .75 to 5 amperes per sq. cm., and preferably from about 0.9 to 2 amp/sq. cm.

The overall reaction in the "Hydrogen Process" is



involving aluminum cation reduction on the cathode,



and hydrogen oxidation on the anode.

Hydrogen gas, from a suitable source, is piped into the porous anode via a central bore provided therein. In a preferred embodiment, the anode is generally cylindrical, and the bore does not pass completely through to the bottom of the anode. Rather, the hydrogen gas permeates the porous anode structure and is liberated at the surface of the anode at a predetermined rate, depending among others on the porosity of the anode structure and hydrogen partial pressure and flow rate. Other con-

figurations of the electrode may be used, for example square or elliptical in cross section.

The rate of hydrogen supply is thus controllable in response to the desired reaction rate and the electrical parameters of the cell by simple changes in the pressure and/or flow rate of the hydrogen for each anode of preselected porosity.

As the reaction proceeds, the alumina content of the melt is maintained between about 2 to 8% concentration in the melt. The reaction temperature is maintained as in the conventional process, in part by the liberation of energy due to the hydrogen oxidation, and mainly by the supplying from an external DC source.

As the aluminum is formed at the bottom of the cell, the distance between the anode and the molten aluminum surface, which represents the critical distance for maintenance of the appropriate DC field, is maintained by continuously tapping off a portion of the molten aluminum. Thus, none of the serious problems of readjustment of the anode-to-cathode distance is involved since the anode is not consumed in the reaction.

The gases evolved from the reaction may contain the conventional vapors, substantially fluoride containing, above a cryolite melt, except that they will not contain substantial amounts of CO or CO<sub>2</sub>. Rather, the reaction product gases contain water and some excess hydrogen. These reaction product gases are lead off. Hydrogen can then be recovered and recycled to the anode input line.

With respect to the anode structure, the anode must be electrically conductive, and is generally a porous, or non-porous metallic, metal oxide, or refractory material. Among the specific anode materials that may be used are nickel, cobalt, nickel-cobalt alloys, titanium nitride, titanium carbide, tungsten, tungsten alloys, palladium, and conducting refractories. Another type is a palladium diffusion type of anode, formed from finely ground palladium particles mixed with a binder and formed into the anode structure of appropriate form, and then sintered to provide the desired porosity.

In an alternative embodiment, the process of this invention may also be used with a non-porous, electrically-conducting gas anode. In one embodiment, a solid metallic anode, resistant to the corrosive action of the melt, is provided having a hollow center for receiving the hydrogen gas from the supply source leading to fine apertures at the tip, and/or along the vertical sides below the liquid level of the melt.

One of the advantages of my process is that the amount of energy required to be supplied to the system is smaller for the hydrogen process of my invention than in the conventional Hall process. The overall reaction in the Hall process involves the reduction of alumina by reaction with carbon to form carbon dioxide plus aluminum with the  $\Delta H$  being 262.3 kcal./mole of alumina. In contrast, the overall reaction in the electrolytic hydrogen process of this invention involves the reduction of alumina by hydrogen to produce water plus aluminum, with the  $\Delta H$  being equal to 225.3 kcal./mole alumina. Thus, the difference in the energy required is on the order of 37 kcal./mole of alumina.

For the overall reaction in the Hall process, the free energy change,  $\Delta G$ , is on the order of 167.5 kcal./mole alumina, and the theoretical cell voltage is about 1.22 volts. However, the practical cell voltage in the Hall process is close to 1.8 volts due to an overpotential of about 0.6 volt. In contrast, the overall reaction of the hydrogen process of this invention involves a free energy change of 179 kcal./mole alumina with the cell voltage comparable to that for the Hall process of 1.297 volts. However, the real voltage in the hydrogen process should not be as high as in the Hall process and depends in part upon the pressure of hydrogen as well as the overpotential of the particular hydrogen electrodes as noted above.

With the respect to the water vapor produced as a

reaction product, interaction with components of the melt is insignificant. Where proper alumina concentration is maintained, for example above 1 to 2%, the fluorine ion, or other fluorine-containing ions, do not produce the "anode effect" in which they react preferentially to oxygen-containing ions. The electrolyte mist which is also formed in the Hall process is controllable by standard techniques. Some water does dissolve in the electrolyte resulting in oxidation of the elemental aluminum produced in the process, and its subsequent dissolution into the electrolyte.

Porous electrodes are preferred since they more easily support the high current densities required, on the order of 0.75 to 5.0 amperes per sq. cm. and because they provide reliable gas diffusion means. On the other hand, the non-porous type electrodes support about 0.2-1.2 amperes per sq. cm. Among porous electrodes preferred, are a dual-porosity type having the pore size decreasing toward the periphery.

In the Hall process the anodic gases consist mainly of CO<sub>2</sub> with some CO present. The amount of CO corresponds roughly to the current inefficiency of the process and is due to the oxidation of dissolved aluminum by CO<sub>2</sub>. The use of carbon as an anode material results in a number of difficulties. Since the anode is constantly consumed, all the mineral impurities contained in the carbon go into the electrolyte, resulting in lower grade aluminum, disturbances to the electrolytic process, and contamination of the electrolyte. One of the most undesirable impurities in the carbon anode materials is sulphur, which puts special requirements on the purity of coke or graphite use. A particular advantage of the process of this invention is a substantial reduction in the need and cost in further purifying the aluminum produced. Storage, preparation, handling, mixing with binders, feeding to the cell, etc. are laborious and inconvenient procedures required for the production of aluminum according to the Hall process. An additional complication arising in connection with the carbon anode use in the Hall process is that of maintaining reliable contact between the electrolyte and the carbon which is constantly consumed. In addition, there is a voltage drop in the carbon itself of from 0.25 to 0.3 volt. Maintenance of the carbon anode is a predetermined distance from the cathode is also complicated by its consumption. These problems make reliable process control complex and automation of the overall process next to impossible.

Most of the above-noted difficulties are eliminated in the hydrogen process. In addition, substantial savings are realized in that the rather expensive carbon is removed from the anode.

Obviously, hydrogen from any source might be employed in the process of this invention. High purity hydrogen may be used, however, such hydrogen is relatively expensive and thus a more economically feasible source will be the hydrogen obtained by reforming of natural gas. Natural gas, consisting mainly of methane, is mixed with steam and catalytically reformed. The reformed mixture, containing some CO and CO<sub>2</sub>, may be used as such or purified to remove the CO and CO<sub>2</sub>. The minor amounts of CO and CO<sub>2</sub> will not substantially interfere with the present process. Thus, the complications arising from coke impurities are not present in the process of the present invention. Since the anode is maintained in a fixed position, and, with the elimination of the consumable carbon anode, the coke transport, storage, grindings, sieving, and manufacture of the anode etc. is not necessary, the present invention gives rise to better process control and automation.

It is evident from the foregoing that modifications can be made in my process without departing from the spirit thereof, and thus I intend the scope of my invention to be limited to the following claims.

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I claim:

1. A process for the production of aluminum by the electrochemical reduction of alumina from a molten, salt electrolyte in contact with a non-carbonaceous, non-consumable anode, and a cathode, the improvement which comprises the steps of:

(a) supplying gaseous hydrogen substantially free of carbon forming substances to said anode disposed in said melt, and

(b) electrochemically reducing the alumina of said melt by oxidizing said hydrogen with said alumina at the surface of said anode in said melt under an applied current to produce water vapor, and reducing aluminum cations at said cathode to produce molten aluminum, and

(c) withdrawing said aluminum and said water vapor from said melt.

2. A process as in claim 1 wherein the hydrogen is supplied to said anode at a pressure above atmospheric.

3. A process as in claim 1 wherein said anode is an electrically conductive porous anode material selected from the group consisting of porous metallic, metal oxide, and refractory materials.

4. A process as in claim 3 wherein said porous material is selected from the group consisting essentially of nickel, cobalt, nickel-cobalt alloys, titanium nitride, titanium carbide, tungsten, tungsten alloys, palladium, and conducting refractories.

5. A process as in claim 1 wherein the applied electrical

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current is on the order of from 0.75 to 5.0 amperes per sq. cm. of anode surface.

6. A process as in claim 4 wherein the anode material is selected from the group consisting of nickel, nickel-cobalt alloys, and palladium.

7. A process as in claim 1 wherein the anode structure is a non-porous solid structure having passageways for the inlet of hydrogen gas and apertures communicating therefrom to the surface of said anode below the level of said melt.

8. A process as in claim 7 wherein said anode material is selected from the group consisting essentially of nickel, cobalt, nickel-cobalt alloys, titanium nitride, titanium carbide, tungsten, tungsten alloys, palladium, and conducting refractories.

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