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ELECTROLYTIC CELL

Filed May 15, 1967

Fig. 1.

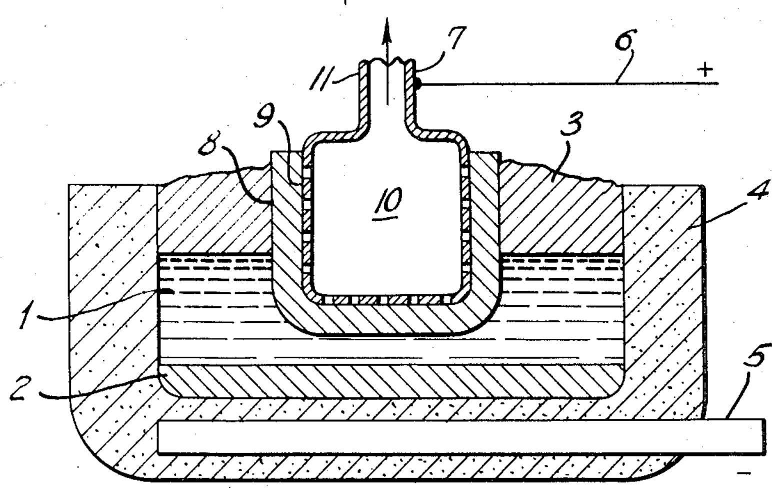
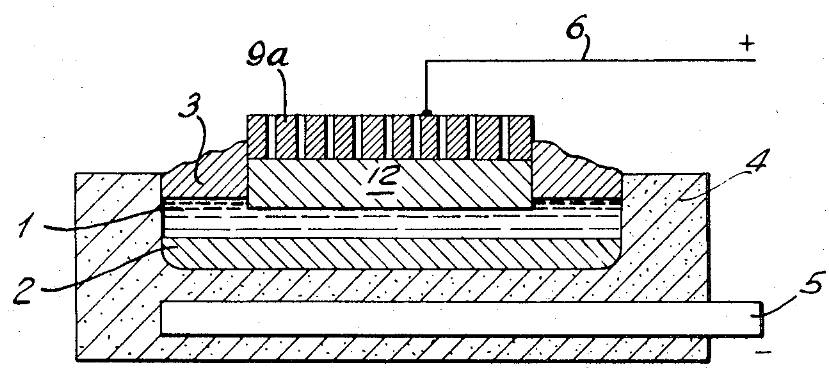



Fig. 2.

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ELECTROLYTIC CELL


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U.S. Cl. 204—243 4 Claims



## ABSTRACT OF THE DISCLOSURE

A cell for the electrolysis of molten oxides, especially of alumina, in which the anode is separated from the melt being electrolysed by a layer of an oxygen-ion-conducting material, for example zirconium oxide stabilised with calcium oxide or other oxides, which is resistant to the melt at the temperature of the electrolysis.


The electrolysis of molten materials, for example of alumina, is carried out today with carbon anodes. In the case of alumina, the oxygen ions formed during the electrolysis react with the carbon of the anode at the process temperatures of 900 to 1000° C. and form carbon dioxide, which is partly reduced to carbon monoxide by the aluminum itself. Owing to the oxidation of the anode by the nascent oxygen, the carbon anode is consumed and, in fact, if only carbon dioxide were to be formed, 334 kg. of carbon per ton of aluminum produced would be consumed. In practice, about 400 to 450 kg. of anode carbon are consumed per ton of aluminum, which corresponds to about 8 to 10% of the cost of crude aluminum. It has only recently been possible to reduce the consumption of anode carbon even to this figure, and with the present method of working using carbon anodes, reduction of the consumption of anode carbon below the theoretically smallest amount, that is 334 kg. of carbon per ton of aluminum, is not possible.

It has now been found that it is possible to carry out the melt electrolysis of oxides without using carbon anodes, but using electrodes which are oxygen-resistant without necessarily being resistant to attack by the melt being electrolysed, so that the oxygen can be obtained as a valuable by-product of the process. About 600 cu. m. of pure gaseous oxygen are formed per ton of aluminum; the value of the oxygen is about 3% of the cost of the crude aluminum. The oxygen which can be recovered in carrying out the process according to the invention into effect can be used for various oxidising processes, such as for example, steel production (by the oxygen blow method), the gasification of fuels (for producing synthetic gas) and the preparation of reducing gases for iron reduction.

According to the invention we use an anode of any suitable conducting material, and we separate this anode from the melt being electrolysed by a layer of material which is oxygen-ions-conducting but non-permeable to and resistant to the melt at the temperature of the electrolysis, so that the oxygen ions diffuse through the layer and are then discharged at the anode with the formation of oxygen gas. The anode itself preferably consists of an electron-conducting material which does not react with oxygen or at least does not form with oxygen any compound impairing the conduction of electrons. Suitable materials include heat-resistant alloys, platinum or other noble metals, electron-conducting oxides, such as for example, wustite, certain materials with semi-conductor properties, and metals with a passivated surface. The thickness of the oxygen-ion-conducting layer may be very small so that the voltage drop across it is also small; this reduces losses of energy during the electrolysis.



We have found that known stabilised forms of zirconium oxide are very suitable as the material which separates the anode from the melt. By stabilised, we mean zirconium oxide in which is incorporated proportions of other oxides such as calcium oxide, magnesium oxide and yttrium oxide, whcih serve firstly to stabilise the cubic (fluorite) lattice of the zirconium oxide, and secondly to confer on it the necessary oxygen-ion conductivity. By suitable choice of oxides and their proportions, a stabilised zirconium oxide can have a resistance as low as 10 ohms·cm. at 1000° C. Other refractory oxides which have fluorite lattices can be used, such as for example, rare earth oxide-uranium oxide compositions, thorium oxide-uranium oxide compositions and cerium oxide suitably stabilised with calcium oxide or magnesium oxide. Substances which reduce the solubility of the oxygen-ion-conductng material may be added to the fused melt.

The invention will be described hereinafter with specific reference to the electrolysis of alumina for the production of aluminum. In such an electrolysis, the oxygen ions which are formed in accordance with the equation

$$2Al_2O_3=4Al^{+++}+6O^{--}$$

diffuse through the oxygen-ion-conductive layer and are discharged at the anode in accordance with the equation

$$6O^{--}=3O_2+12e$$

i.e. the oxygen ions combine to form oxygen gas and electrons are released in the process. These electrons are conducted away by the anode. Other oxides such as for instance, MgO, $Na_2O$, CaO, $Fe_2O_3$, can also be electrolysed by the process according to the invention and similar equations can be formulated. In the electrolysis of alumina for example, cells according to the invention afford the following advantages, inter alia, in comparison with the present state of the art.

(1) There is no consumption, or only a very low rate of consumption, of anode material with the result that the rate of production of anode material can be substantially reduced.

(2) The formation of carbon scum in the bath results in a loss of operating efficiency, and this formation will not occur if the anodes are of material other than carbon.

(3) There is improvement of the quality of the aluminium metal produced, since no impurities, such as iron, silicon or vanadium are introduced from the anode material.

(4) There is less down-time of the cell, since the anodes do not have to be replaced.

(5) There is a reduction of the consumption of fluxing materials, since the cell can be sealed off more satisfactorily and this also gives an improvement in the shop atmosphere.

(6) Pure oxygen can be produced and collected as a byproduct.

(7) There is no re-oxidation of the liquid aluminum by carbon dioxide and thus, there is increased output from the cell and a reduction in the energy required to produce a given weight of aluminium.

Cells according to the invention can readily be adapted for automation of operation with for example, continuous addition of alumina to the fused melt and maintenance of constant interelectrode gap or cell voltage.

Cells according to the invention may be constructed in two ways. In the first of these, the anode is coated with or is in contact with the layer of oxygen-ion-conducting material over at least that part of its surface which is immersed in the melt; the anode must then be in such a physical state that oxygen gas can pass through it.

The anode may be solid, in which case it must be porous, perforated or reticulated.

If the anode is solid, the layer of oxygen-ion-conducting material may be applied directly to it by pressing or casting with subsequent drying and sintering or by plasma spraying. Alternatively a body of the material may be preformed quite separately and put in contact with the anode, if the latter is, for example, a metal network. As a further possibility, a porous layer of platinum black may be applied to a preformed body of the material, and electrically connected to one terminal of the current supply. This last proposal is found to be very satisfactory, as platinum black is particularly suitable for the discharge of oxygen ions and the formation and removal of oxygen gas.

The invention will now be described with reference to FIGS. 1 to 2 of the accompanying drawings, each of which represents a section through an electrolytic cell for the electrolysis of fused alumina-cryolite mixtures. In each of the figures, a carbon tank **4** contains the fused alumina-cryolite melt indicated as **1**, and the liquid, electrolytically produced aluminum, which accumulates on the bottom of the cell and at the same time acts as a cathode in the arrangements according to FIGS. 1 and 2 is shown as **2**. The fused melt is covered by a layer **3** consisting of solidified melt and alumina. A bus bar **5** conducts the current from the tank.

In FIGS. 1 and 2, the anode consists of a gas-permeable, electron-conducting body which is covered with the oxygen-ion conductive material over at least the portion of its surface immersed in the fused melt. In FIG. 1, the oxygen-ion conductive material **8** is in the form of a hollow cup-shaped body, the inner surface of which is lined with a layer **9** of platinum black as anode. The layer **9** is electrically connected to a terminal **7** which is itself connected to a source of direct current by means of a lead **6**. During the electrolysis the oxygen ions of the electrolyte diffuse through the oxygen-ion conductive layer **8**, are discharged at the surface of contact between the oxygen-ion conductive layer **8** and the layer of platinum black **9** and combine in the layer of platinum black to form gaseous oxygen which collects in the hollow space **10** and escapes through a vent **11**. In the construction shown, the terminal **7** forms the upper end of the hollow space **10** and incorporates the gas vent **11**. The electrons that are liberated flow off by way of the anode **9**, the terminal **7** and the lead **6**. The oxygen gas evolved can escape under atmospheric pressure, be drawn off under reduced pressure or be collected under pressure in excess of atmospheric in the space **10**.

In FIG. 2, the oxygen-ion conductive material is in



the form of a plate **12** which is in contact with a porous anode **9***a*. The porous anode is connected to the cource of direct current by means of the lead **6**.

What I claim is:

**1**. A cell for the electrolytic production of metals from metal oxides contained in a molten electrolytic bath, this cell comprising a container for the melt being electrolysed, a cathode for contact with the melt and a gas permeable anode resistant to the formation with oxygen of any compound impairing its conduction of electrons, a layer of oxygen-ion-conducting material in direct electric contact at one side with said anode substantially over at least that part of its area to be immersed in a melt in said container and freely exposed at its other side to said melt, said layer being non-permeable to and resistant to the melt at the temperature of the electrolysis, and a source of direct current connected between said anode and said cathode to maintain said electrolysis, said current during said electrolysis effecting the diffusion of oxygen ions through the layer and their discharge at the anode with the formation of oxygen gas which escapes through the gas-permeable anode which is uncovered on its other side.

**2**. A cell according to claim **1** in which the anode is in contact with the layer of oxygen ion-conducting material over at least that part of the surface which is immersed in the melt and is in such a physical state that oxygen gas can pass through it.

**3**. A cell according to claim **2** in which the anode is solid, and is porous, perforated or reticulated.

**4**. A cell according to claim **3**, in which the anode is formed by a porous layer of platinum black applied to a preformed body of oxygen-ion conducting material.

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