Feb. 27, 1973 HANS-JURGEN KLEIN 3,718,550

PROCESS FOR THE ELECTROLYTIC PRODUCTION OF ALUMINUM

Filed Dec. 2, 1970

FIG. 1

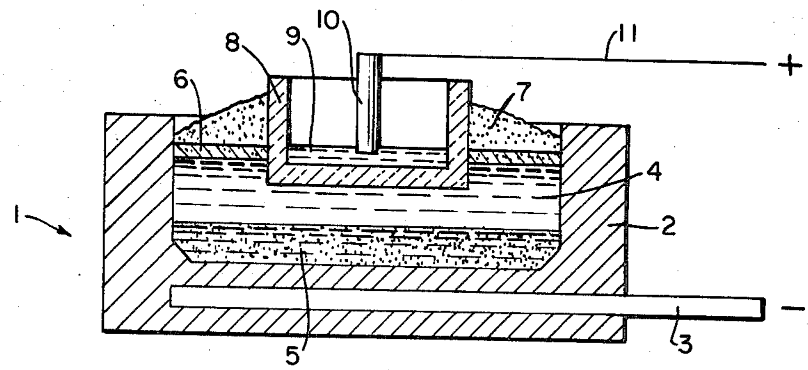


FIG. 2

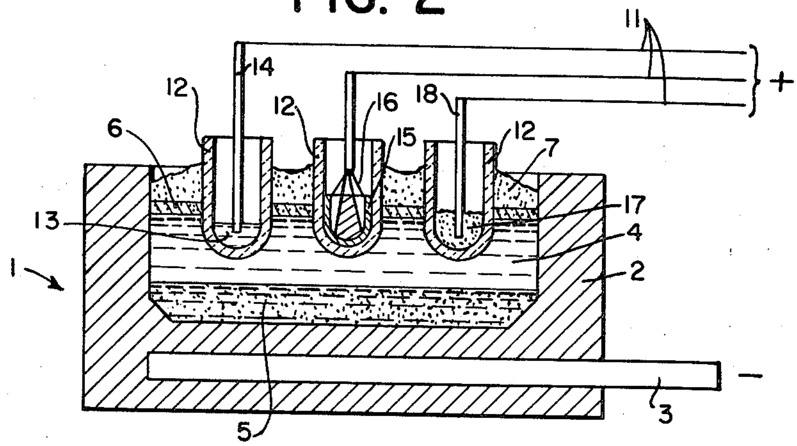
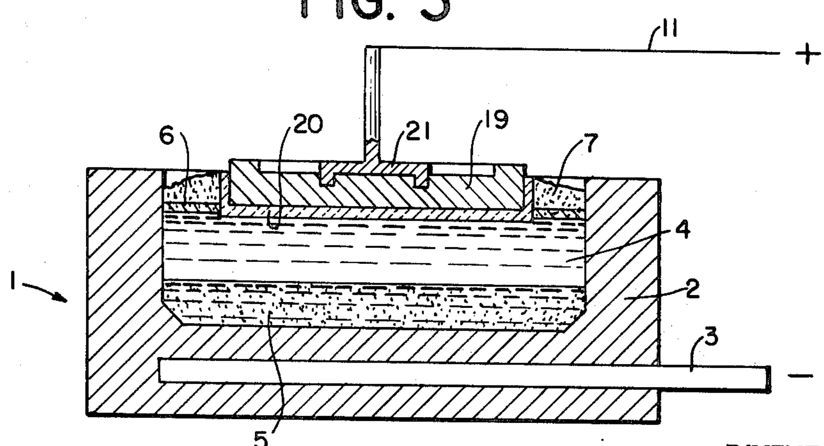


FIG. 3



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PROCESS FOR THE ELECTROLYTIC PRODUCTION OF ALUMINUM

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U.S. Cl. 204—67 5 Claims

ABSTRACT OF THE DISCLOSURE

Process for the electrolytic production of aluminum from a fused alumina-containing bath of alkali aluminum fluoride in which the part of the anode in contact with the bath consists of an oxidic electron-conducting ceramic material chemically resistant to the fluoride bath. Preferably the ceramic material consists predominantly of SnO_2.

This invention relates to processes for the electrolytic production of aluminum in which a fused alumina-containing bath of alkali aluminum fluoride is electrolysed at temperatures between about 940 and 1000° C. with the use of carbon anodes. The oxygen produced at the anode by the decomposition of the alumina reacts completely with the carbon to carbon dioxide and carbon monoxide. Thus the carbon anode is consumed and must be lowered from time to time to the same level in the bath, and it must be exchanged before full consumption. To produce one kg. of aluminum 450 g. anode carbon are consumed in practice.

My object in this invention is to provide anodes which do not react with the oxygen during the fused-bath electrolysis of aluminum and accordingly are not consumed.

In the process according to the invention the part of the anode in contact with the bath consists of an oxidic electron-conducting ceramic material (oxidic semiconductor) chemically resistant to the fused fluoride bath in which the aluminum oxide is dissolved. This oxidic ceramic material preferably consists predominantly of SnO_2.

The anodes can be made by the conventional processes used in the ceramic industry, a powdered mixture being shaped and burned. The mixture should be homogenised and may advantageously be pre-burned, for example at a temperature between 700 and 1500° C. during 24 to 10 hours, before being shaped and finally burned at a temperature between 800 and 1600° C. during 24 to 10 hours. The preburning step may be omitted if the mixture is hot-pressed.

Instead of forming a shaped body and burning it a carrier of the shape desired for the anode may be provided with a coating of the ceramic material, for example by flame-spraying or plasma-spraying with subsequent densification by thermal treatment. Such a carrier may be of wire mesh, a hollow or solid metal body, or a shaped body of electron-conducting carbide, nitride or boride.

Anodes for use in the production of aluminum from fluoride baths preferably contain at least 80% SnO_2. In these anodes it is desirable to include at least one oxide which will improve the sintering together of the particles during the burning or densification, such oxides being Fe_2O_3, ZnO, Cr_2O_3, Sb_2O_3, Bi_2O_3 and V_2O_5. It is desirable also to include at least one oxide which improves the electrical conductivity, such oxides being Ta_2O_5, Nb_2O_5 and WO_3. Antimony oxide has the advantage of improving both these properties.

Electrical conductivity at 1000° C. of between 0.1 and $10\Omega^{-1}cm.^{-1}$ is obtained when the composition consists by weight of:

	Percent
SnO_2	94–83
Fe_2O_3	2–6
ZnO	3–7
Ta_2O_5	1–4

A very suitable composition of the ceramic material for use in a fluoride bath for the production of aluminum, taking into account both the electrical conductivity and the resistance to attack by the bath, is:

	Percent
SnO_2	94
Sb_2O_3	1.5
Fe_2O_3	1.5
Ta_2O_5	1.75
ZnO	1.0
Cr_2O_3	0.25

This composition may be pre-burned for example at a temperature between 1000 and 1100° C. during 15 to 12 hours and finally burned between 1350 and 1450° C. during 20 to 15 hours, the longer durations corresponding to the lower temperatures and reversely. Another suitable composition comprises 98% SnO_2, 1.5% Sb_2O_3, 0.3% Fe_2O_3 and 0.2% ZnO, and may be prepared under similar conditions.

The invention specifically includes anodes consisting of bodies shaped from or of carriers coated with ceramic materials consisting of at least 80% SnO_2 together with one or more of Fe_2O_3, Sb_2O_3, ZnO, Cr_2O_3, Bi_2O_3 and V_2O_5 and one or more of Ta_2O_5, Nb_2O_5 and WO_3.

The anodes must of course not only be in contact with the bath, the discharge of ions taking place at the interface between the bath and the ceramic material and the gas that is evolved escaping through the bath, but must also be in such connection with the source of current supply; that electrons can flow from this interface. These connections can be effected in various ways, some of which are shown in the accompanying diagrammatic drawings, in which:

FIG. 1 is a purely diagrammatic vertical section through one electrolytic cell, is not to scale and shows only those parts required to illustrate the invention;

FIG. 2 is a similar section illustrating three different ways of connecting the anodes to the current supply; and,

FIG. 3 is a similar section showing an anode formed by coating a carrier.

The cells shown in the drawings are all intended for the production of aluminum, and are conventional except for the anodes. Referring first to FIG. 1, the cell **1** comprises a pot **2** of carbonaceous material in which iron bars **3** are embedded as cathode conductors and which contains a bath **4** of alkali aluminum fluoride with alumina dissolved in it. On the application of direct current liquid aluminum **5** separates on the bottom of the pot. By **6** is denoted a slag crust consisting of solidified bath and undissolved alumina, which is covered by a layer **7** of alumina.

One or more anodes **8** dip into the bath **4**. Each such anode consists of a crucible, rectangular in horizontal section, with rounded edges and corners which holds liquid silver **9**. One or more rods **10** of titanium diboride dip into this liquid silver and are connected to cathodic conductors **11**. The crucible **8** is made of a ceramic electron-conducting material, preferably having one of the compositions described in detail above.

FIG. 2 shows anodes **12** of a different shape, being in tubes with closed and rounded lower ends, each again being made of the suitable ceramic material described above. This figure shows three ways by which such anodes may be connected to the current supply. In the left-hand tube **12** there is molten silver **13** into which a rod **14** of titanium carbide projects, this rod being connected to the conductor **11**. In the middle tube **12**, the inner surface thereof being covered with a thin layer of silver or platinum, a hollow cylinder **15** of nickel-alloy wire mesh is inserted and is connected by nickel-alloy wires **16** to the conductor **11**. In the right-hand tube **12** a rod **18** of zirconium diboride is used to connect nickel powder **17** to the conductor **11**.

FIG. 3 shows an anode consisting of an essentially rectangular body **19** of a conducting material, for example ZrB_2, TiB_2 or TiC, carrying a coating **20** of ceramic material as described above, applied by spraying and subsequently densified by heat-treatment. A metal bell **21** is embedded in the body **19** to make connection with the conductor **11**.

What I claim is:

1. A process for the electrolytic production of aluminum from a fused alumina-containing bath of alkali aluminum fluoride in which the part of the anode in contact with the bath consists of an oxidic electron-conducting ceramic material chemically resistant to the fluoride bath.

2. A process according to claim **1** in which the ceramic material consists predominantly of SnO_2.

3. A process according to claim **2** in which the ceramic material contains at least 80% SnO_2 together with one or more of Fe_2O_3, ZnO, Cr_2O_3, Sb_2O_3, Bi_2O_3 and V_2O_5 and one or more of Ta_2O_5, Nb_2O_5 and WO_3.

4. A process according to claim **3** in which the ceramic material has the following composition by weight:

	Percent
SnO_2	94–83
Fe_2O_3	2–6
ZnO	3–7
Ta_2O_5	1–4

5. A process according to claim **3** in which the ceramic material has the following composition by weight:

	Percent
SnO_2	94
Sb_2O_3	1.5
Fe_2O_3	1.5
Ta_2O_5	1.75
ZnO	1.0
Cr_2O_3	0.25

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