(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

PCT

(43) International Publication Date
28 December 2006 (28.12.2006)

(10) International Publication Number
WO 2006/137739 A1

(51) International Patent Classification:
C25C 7/00 (2006.01) *C25C 3/12* (2006.01)
C25C 3/08 (2006.01)

(21) International Application Number:
PCT/NO2006/000221

(22) International Filing Date: 9 June 2006 (09.06.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
20053072 22 June 2005 (22.06.2005) NO

(71) Applicant *(for all designated States except US)*: **NORSK HYDRO ASA** [NO/NO]; N-0240 Olso (NO).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: **STORESUND, Arild** [NO/NO]; Eidsbakkane 111, N-4250 Kopervik (NO).

(74) Agent: **BERG, André**; Patent and Trademark Department, Hydro Aluminium AS, N-0240 Oslo (NO).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

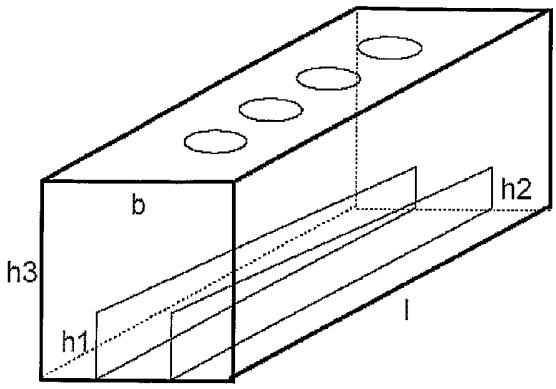
(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) **Title:** A METHOD AND A PREBAKED ANODE FOR ALUMINIUM PRODUCTION

h1 = 350 mm
h2 = 320 mm
slot width = 3 - 8 mm
l = 1510 mm
h3 = 600 mm
b = 700 mm



(57) **Abstract:** Present invention relates to a method of producing aluminium in an Hall-Héroult cell with prebaked anodes, as well as anodes for same. The anodes are provided with slots in its wear (bottom) surface for gas drainage. The slots are 2-8 millimetres wide, preferably 3 millimetres.

WO 2006/137739 A1

A method and a prebaked anode for aluminium production

A method and a product for Aluminium production

The present invention relates to an optimised method for performing an electrolysis process for producing aluminium in accordance with the Hall-Héroult process with prebaked anodes, and anodes therefore.

In a process as described above, there will be evolved gas at the wear-surface (primary the underside or bottom side) of anodes due to the reduction of alumina. In particular carbon dioxide gas will accumulate at this surface, causing variations and instabilities in the electrical contact from the anode to the electrolyte. This physical phenomena have several drawbacks, such as:

- Increased back reaction and loss of current efficiency due to close contact between the produced aluminium layer and $C0_2$ gas bubbles.
- Increased possibility and duration of anode effects
- Heat production in the gas layer results in a reduced interpolar distance and reduced current density on the cell. An increase in current density will increase the production on the cells.

The extra IR-drop (Interpolar Resistance drop) because of the gas bubbles in the electrolyte has been measured to be 0,15 – 0,35 volt in alumina reduction cells (1992, The 11th International Course on Process Metallurgy of Aluminium page 6 -11).

There have been several proposals for minimizing the above mentioned problem, such as introducing anodes with a sloped or tilted bottom, forming slots or tracks in the wear surface of the anodes to drain said gas away from this area.

Slots in prebaked anodes are normally produced in a vibrator compactor when the anode mass is in a green state, or in a dry milling process that is performed on the calcinated anodes. The dry milling process is normally performed by the use of a circular saw. In accordance with commonly available production methods of today, slots can be produced with a width that is approximately 13-15 mm.

There are some minuses by having slots in the anode surface, and it will be mentioned here:

- Reduced anode life time in the cell because anode mass is removed
- Reduced anode working surface area
- Extra carbon material have to be transported back to the carbon mass factory (dry milling)
- Extra energy in the milling operation (dry milling)

All these drawbacks can be reduced by making the slots more narrow. Thus, the slots should not be wider than necessary to effectively drain the anode gases from the working surface.

A study carried out and reported in "R.Shekar, J.W.Evans, Physical modelling studies of electrolyte flow due to gas evolution and some aspects of bubble behaviour in advanced Hall cells, Part III. Predicting the performance of advanced Hall cells, Met. and Mat. Trans., Vol. 27 B, Feb. 1996, pp. 19-27", indicates that tracks with a width less than 1 cm did not drain the gas properly.

Despite the teaching above, the applicant now has performed initial studies in an electrolysis cell applying anodes with very thin slots, which has proven to give sufficient gas drainage.

The anodes involved in the studies where calcinated and processed by implementing a processing technique known from processing/cutting other types of materials.

By making the slots in the calcinated anode thinner than that of the prior art, the above mentioned disadvantages will be less.

Since the thin slots take away only a small fraction of the anode mass, potentially a high number of slots can be used.

The drop in bath voltage when using slots allows amperage increase in the alumina reduction cell, increasing the production of aluminium and decreasing the specific energy consumption. This advantage is improved when using narrow slots, because of the earlier

mentioned fact that only a small fraction of the anode mass is removed even when using several narrow slots.

These and further advantages can be achieved with the invention as defined in the accompanying set of claims.

In the following, the invention shall be described further with reference to examples and figures where:

Fig. 1 discloses one sketch of one anode in accordance with the present invention

Fig. 2 discloses bath voltage drop in alumina reduction cell versus number of slots

Fig. 3 discloses a photo of one anode in accordance with the invention,

Fig. 4 discloses process data extracted from one full-scale study, applying anodes in accordance with the present invention

As disclosed in Figure 1, there is shown an anode having slots processed into it and where the width of said slots are between 3 – 8 millimetres. Further, there are indicated two slots having a cantilevered bottom, where its depth at one end of the anode h2 is 320 millimetres and the depth at the other end h1 is 350 millimetres. The overall dimensions of the anode in this example is length, l=1510 millimetres, height h3=600 millimetres and width b=700 millimetres. Thus, the slots in this embodiment extend through more than 50% of the height of the anode. The cantilevered bottom can be sloped corresponding to >0° and < 10°.

In Figure 2 is indicated how the bath voltage might decrease when an increasing number of slots is introduced in the anode. Actual numbers would vary with the anode width and length, the current density, and slot design. Voltage is indicated at the vertical axis, number of slots at the horizontal axis.

In the full-scale studies carried out, it has been observed that the depth of the slots will increase slightly due to the erosion in the electrolysis process. This effect is caused by the fact that the gas drained into the slots from the bottom of the anode will consume carbon

material in the bottom of the slot due to the Boudoard reaction ($CO_2 + C = 2CO$). A consumption of 2-3 centimetres of carbon material in the bottom of the slots has been observed in an anode that had been utilised in the cell for 17 days, i.e. 60% worn anode. This self-propelled slot extending effect must be taken into account when determining the processing depth of the slots.

By the new method of processing the slots, there will be produced fine-grained dust that can easily be returned back to the mass factory. In fact, the dust produced will replace a certain type of dry dust that is needed in the mass factory anyway. Thus, instead of having a problem with excessive material to be recycled, one now have production of useful material due to the new processing method.

Figure 3 discloses a photo of one anode in accordance with the present invention, showing the wear surface (the bottom side) of the anode. The anode has been removed from the cell after a period of production. The two longitudinal lines disclosed in the photo are the slots.

Fig. 4 discloses cell noise data, extracted from one full-scale study, applying anodes in accordance with the present invention. As shown in the Figure, it is possible to run the electrolysis process in a more stable manner than that of non-processed anodes.

The drop in voltage noise in the cell is at least the same as obtained earlier in cells having traditional slots of width of 12-15 millimetres, indicating that the 3 mm slot width is sufficient to remove the carbon dioxide gas from the working surface of the anode.

A further comparison between anodes with 3 millimetres wide slots and anodes with 15 millimetres wide slots shows that even with the same number of slots the advantage is considerable: For an anode of 100 cm width and provided with two 15 millimetres wide slots, the anode working surface was reduced by 3%. In an anode in accordance with the present invention, two slots of 3 millimetres width reduces the working surface by only 0,6%.

It is assumed that the invention will work with even more narrow slots, for instance 2 millimetres, but it has not been practically possible to verify that as of yet.

Claims

1. A method of producing aluminium in an Hall-Héroult cell with prebaked anodes, where the anodes have one or more slots in its wear (bottom) surfaces for gas drainage,
   characterised in that
   the gas drainage is performed by one or more slots being 2-8 millimetres wide.

2. A method in accordance with claim 1,
   characterised in that
   the gas drainage is performed by two or more slots in each anode.

3. A method in accordance with claim 1,
   characterised in that
   the slots have a cantilevered bottom > 0° and < 10°.

4. A prebaked anode for a Hall-Héroult cell for production of aluminium, the anode having one or more slots arranged in its bottom part (wear surface) for gas drainage,
   characterised in that
   said one or more slots are of 2-8 millimetres width.

5. A prebaked anode in accordance with claim 4,
   characterised in that
   said one or more slots are of 3 millimetres width.

6. A prebaked anode in accordance with claim 4,
   characterised in that
   the anode has two or more slots.

7. A prebaked anode in accordance with claim 4,
   characterised in that
   the said one or more slots penetrates the anode to an extent that represents more than 50% of the anode height.

8. A prebaked anode in accordance with claim 4,
characterised in that
the said one or more slots is cantilevered at an angle between 0° and 10°.

h1 = 350 mm
h2 = 320 mm
slot width = 3 - 8 mm
l = 1510 mm
h3 = 600 mm
b = 700 mm

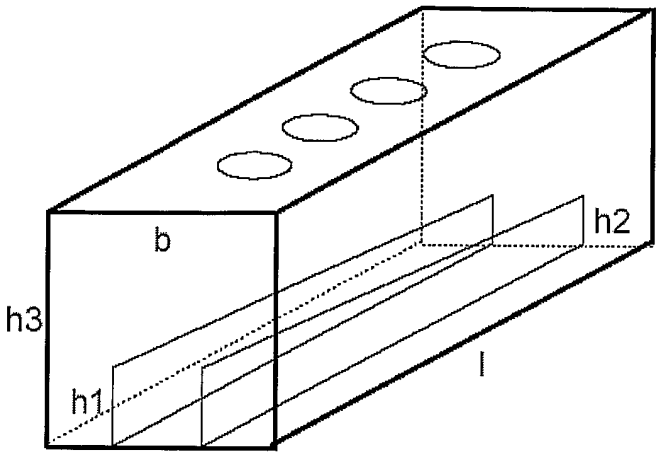


Fig. 1

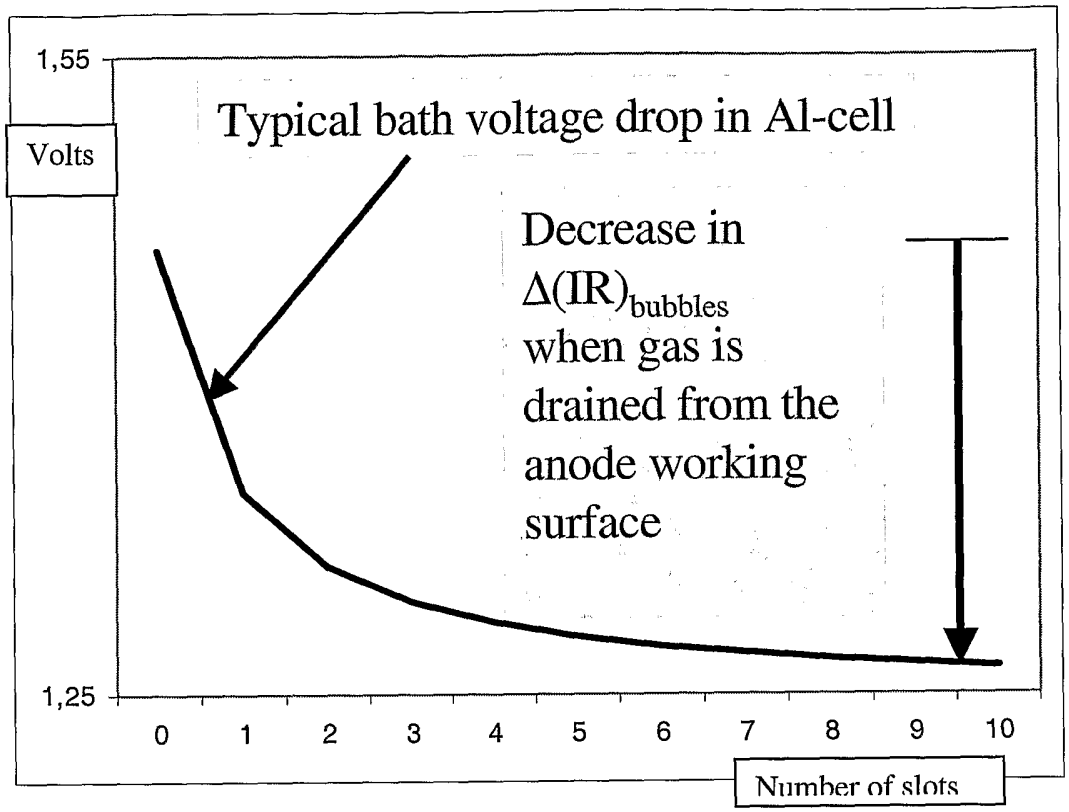

1,55
Volts
Typical bath voltage drop in Al-cell
Decrease in
$\Delta(IR)_{bubbles}$
when gas is
drained from the
anode working
surface
1,25
0
1
2
3
4
5
6
7
8
9
10
Number of slots

Fig. 2

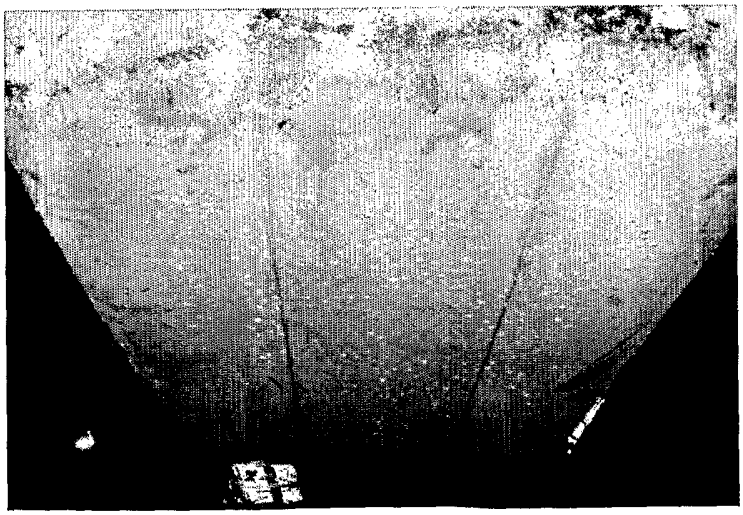


Fig. 3

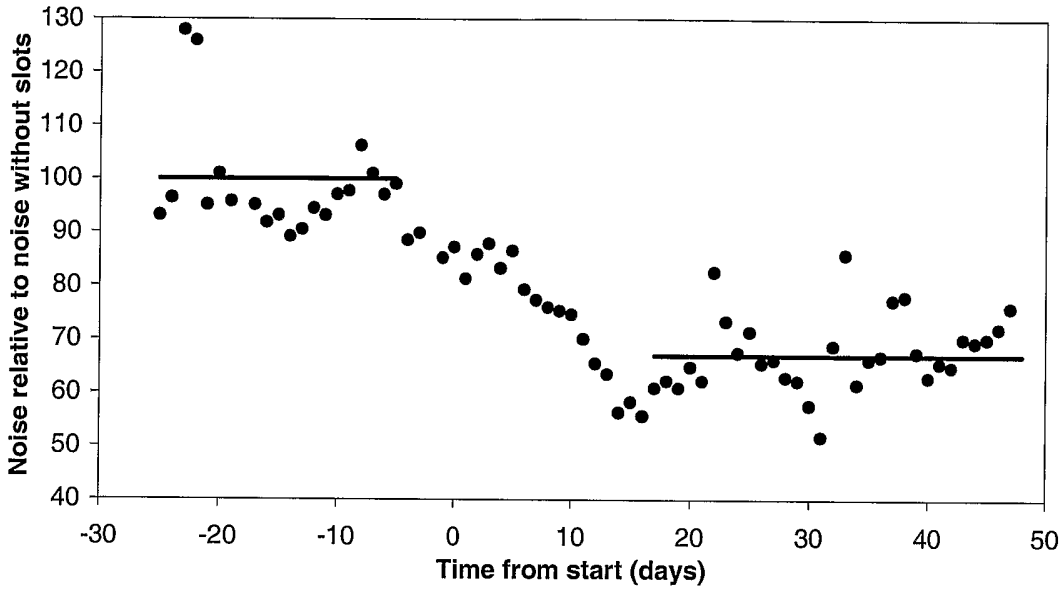

Noise relative to noise without slots
130
120
110
100
90
80
70
60
50
40
-30
-20
-10
0
10
20
30
40
50
Time from start (days)

Fig. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO2006/000221

A. CLASSIFICATION OF SUBJECT MATTER

IPC: see extra sheet
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: C25C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-INTERNAL, WPI DATA, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3438876 A (H C MARSHALL, JR), 15 April 1969 (15.04.1969), column 1, line 21 - line 24; column 2, line 24 - line 55, figures 1,2	1-8
A	US 2958641 A (J L REYNOLDS), 1 November 1960 (01.11.1960), column 4, line 52 - line 61; column 5, line 54 - line 72, figure 3	1-8
A	EP 0264263 A1 (THE BRITTISH PETROLEUM COMPANY PLC), 20 April 1988 (20.04.1988), figures 1,2, claims 1, 7,11	1-8

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 Sept 2006	27-09-2006
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Ulrika Nilsson/EK Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO2006/000221

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4605481 A (LANGON), 12 August 1986 (12.08.1986), figures 5A,5B,5C, abstract -- --------	1-8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO2006/000221

International patent classification (IPC)
C25C 7/00 (2006.01)
C25C 3/08 (2006.01)
C25C 3/12 (2006.01)

Download your patent documents at www.prv.se
The cited patent documents can be downloaded at www.prv.se by following the links:

- In English/Searches and advisory services/Cited documents (service in English) or
- e-tjänster/anförda dokument(service in Swedish).

Use the application number as username.
The password is **RENPQJPWRH**.

Paper copies can be ordered at a cost of 50 SEK per copy from PRV InterPat (telephone number 08-782 28 85).

Cited literature, if any, will be enclosed in paper form.

US	3438876	A	15/04/1969	NONE		
US	2958641	A	01/11/1960	GB	855223 A	30/11/1960
EP	0264263	A1	20/04/1988	AU	592903 B	25/01/1990
				AU	8100687 A	06/05/1988
				BR	8707501 A	21/02/1989
				DE	3771638 D	00/00/0000
				GB	8624561 D	00/00/0000
				US	4869790 A	26/09/1989
				WO	8802793 A	21/04/1988
US	4605481	A	12/08/1986	AT	30746 T	15/11/1987
				AU	568748 B	07/01/1988
				AU	4360885 A	19/12/1985
				BR	8502797 A	18/02/1986
				CN	85104565 A	10/12/1986
				DE	3560953 D	00/00/0000
				EP	0169152 A,B	22/01/1986
				SE	0169152 T3	
				ES	544091 A	16/01/1986
				ES	8604318 A	01/06/1986
				FR	2566002 A,B	20/12/1985
				GR	851407 A	12/07/1985
				HU	38404 A	28/05/1986
				HU	192227 B	28/05/1987
				IS	1290 B	07/07/1987
				IS	3019 A	30/08/1985
				JP	61044192 A	03/03/1986
				NO	852366 A	16/12/1985
				OA	8034 A	31/01/1987
				PL	253887 A	08/04/1986
				RO	92424 A	30/09/1987
				SU	1342427 A	30/09/1987
				YU	96685 A	30/04/1988
				ZA	8504425 A	29/01/1986