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Bottom lining for electrolytic cells and process for its manufacture

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ABSTRACT

The invention relates to a bottom lining for electrolytic cells, in particular for aluminum electrolytic cells in both primary production and secondary refining, whereby the basic body of the electrolytic cells is formed by steel pots, and whereby at least part of the bottom lining consists of a monolithic stamping containing a finely granular powder product with high alumina content obtained in the recovery of dross and salt slags of the aluminum industry, said powder product having at least the following components based on the weight of the dried substance:

Al_2O_3	40	-	90%
AlN	.1	-	25%
MgO	4	-	20%
SiO_2	.5	-	15%
CaO	.1		15%
Al (metallic)	.1	-	10%
Si (metallic)	.1	-	10%
Fe_2O_3	.1	-	5%
C			5% max.
F			5% max.
Na_2O	.1	-	5%
K_2O	.1	-	2%
TiO_2	.1	-	2%
Others			5% max.
Loss on ignition			10%

The invention, furthermore, relates to a process for producing a bottom lining for electrolytic cells.



AUSTRALIA

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ORIGINAL
COMPLETE SPECIFICATION
STANDARD PATENT

Application Number: 69822/98
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Invention Title: BOTTOM LINING FOR ELECTROLYTIC CELLS AND PROCESS FOR ITS
MANUFACTURE

The following statement is a full description of this invention, including the
best method of performing it known to US :-

BOTTOM LINING FOR ELECTROLYTIC CELLS AND PROCESS FOR ITS MANUFACTURE

The invention relates to a bottom lining for electrolytic cells, particularly but not exclusively for aluminum electrolytic cells for both primary production and
5 secondary refining, whereby the basic body of the electrolytic cells is formed by steel pots, as well as to a process for producing such a bottom lining.

According to the prior art, aluminum metal is produced by reducing metallurgical alumina by means of melt electrolysis at about 950°C as a primary aluminum pig. High-purity aluminum metal is produced from primary aluminum
10 pig by refining electrolysis at about 800°C. Fluoride-containing salt melts are used as electrolyte in either process. In both processes, the electrolytic cell consists of a steel pot with dimensions of about 10 m length and about 5 m width. The bottom surface of such a pot is lined with carbon blocks which, at the same time, act as electrodes. A heat-insulating lining is present under the bottom
15 carbon. As a rule, such lining consists of about 3 layers of dense fire-clay bricks (in the bottom zone) and about 2 layers of highly porous diatomite bricks, vermiculite bricks, or calcium silicate plates (in the colder zone underneath).

Bottom insulations produced by stamping metallurgical alumina powder or refractory masses (compounds) based on chamotte or olivine into the electrolyse
20 pots are known as well, and are employed instead of brick linings. Stamped insulating beds have an advantage over bricks and plates in that the monolithic, ramming mix has no joints facilitating infiltration of the insulating bed by the electrolyte melt. Furthermore, less time and labor are required for producing a ramming mix. Moreover, as opposed to bricks, which are solidly installed in the
25 form of a brickwork with the help of mortar, a stamped insulating bed can be removed again and replaced more easily and faster after the useful life of the electrolytic cells has expired.

Molten and gaseous components of the electrolyte infiltrate the bottom insulation during operation of the cell and, in the course of time, fill there the open
30 pores, leading to mineralogical transformation of the insulating material. This causes increasing deterioration of the thermal insulating property of the bottom



lining and limits the useful life of the electrolytic cell. In primary electrolysis, a used bottom lining in the form of a stamped insulating bed made from metallurgical alumina can be completely reused as an aluminum oxide source in spite of its impregnation with electrolyte melt, whereas a consumed bottom lining
5 based on chamotte brick or refractory compounds can be reconditioned and reused for some other purposes only in part.

As compared to chamotte bricks or a refractory ramming based on chamotte or olivine (bulk density about 2 to 2.5 g/cm³, open porosity about 20%), a stamped lining or bed made from metallurgical aluminum oxide powder
10 (stamping density about 1.0 g/cm³, open porosity about 70%) has a superior thermal insulating property, to begin with, because of its higher porosity after an electrolytic cell has been put into operation. However, the structural change caused by infiltration of melt and thus the deterioration of the thermal insulating property are stronger with an aluminum oxide stamping than with bricks because
15 of the higher starting porosity of the former.

Various processes are available for inhibiting the infiltration of the bottom insulation. For example, chemical barrier layers based on SiO₂-containing melts are used, which are formed by the reaction of electrolyte components with SiO₂-containing components of the bottom lining. In addition, physical infiltration
20 barriers in the form of steel panels are known, which are placed between the bottom carbons and the bottom insulation. The bottom insulation of an aluminum electrolytic cell is described in DE 43 36 024, where the open pores of chamotte bricks are impregnated with tar for reducing the infiltration property.

According to the present invention, there is provided a bottom lining for
25 electrolytic cells whereby the basic body of the electrolytic cells is formed from steel pots, wherein at least part of the bottom lining consists of a monolithic stamping containing a finely granular powder product with high alumina content obtained in the recovery of dross and salt slags of the aluminum industry, said product having at least the following components based on the weight of the dried
30 substance:

Al ₂ O ₃	40	-	90%
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	AlN	.1	-	25%
	MgO	4	-	20%
	SiO ₂	.5	-	15%
	CaO	.1	-	15%
5	Al (metallic)	.1	-	10%
	Si (metallic)	.1	-	10%
	Fe ₂ O ₃	.1	-	5%
	C			5% max.
	F			5% max.
10	Na ₂ O	.1	-	5%
	K ₂ O	.1	-	2%
	TiO ₂	.1	-	2%
	Others			5% max.
	Loss on Ignition			10% max.

- 15 According to the present invention, there is also provided a process of producing a bottom lining of an electrolytic cell, whereby the basic body of the electrolytic cell is formed by a steel pot, wherein the process includes the following steps:

- (a) a finely granular powder product is produced from the recovery of dross and salt slags of the aluminum industry by grinding, leaching, filtration and/or thermal treatment, said powder product having the following chemical composition based on the weight of the dried substance:

	Al ₂ O ₃	40	-	90%
	AlN	.1	-	25%
25	MgO	4	-	20%
	SiO ₂	.5	-	15%
	CaO	.1	-	15%
	Al (metallic)	.1	-	10%
	Si (metallic)	.1	-	10%
30	Fe ₂ O ₃	.1	-	5%
	C			5% max.



	F			5% max.
	Na ₂ O	.1	-	5%
	K ₂ O	.1	-	2%
	TiO ₂	.1	-	2%
5	Others			5% max.
	Loss on ignition			10% max.

(b) the powder product is pelletized, briquetted or extruded to form shaped bodies; and

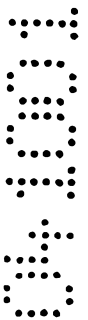
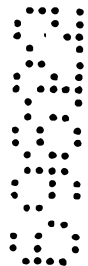
(c) the shaped bodies are thermally treated or calcined to less than 5%
10 loss on ignition moisture, filled in the electrolytic pot, and compacted by stamping or vibrating.

In order that the invention might be more fully understood, embodiments will be described by way of example only.

Embodiments of the invention relates to improving the bottom lining of
15 electrolytic cells both for primary production and secondary refining of aluminum. Such improvement comprises simpler incorporation of the insulating material in the cell pots, higher resistance to infiltration and reaction versus electrolyte melt, as well as easier exploitation of the consumed bottom insulation. Said enhanced bottom lining is a stamped tub filling produced from unfired, precompacted
20 shaped bodies (pellets, briquettes or bricks) based on powder products with high contents of alumina, such powder products being collected as residual materials in the recovery of aluminum wastes and aluminum salt slags.

An advantage of embodiments of the invention is an improvement in the bottom lining of aluminum electrolyte cells with respect to simpler incorporation of
25 the insulating material in the cell tubs, higher resistance to infiltration and reaction versus electrolyte melt, as well as easier exploitation of the consumed bottom lining.

According to a preferred embodiment, the pot lining is a monolithic stamping consisting of unfired and/or calcined shaped bodies, for example in the
30 form of spherical pellets, egg briquettes or bricks in the normal shape based on finely granular powders with high alumina contents, such powders being collected



in the recovery of dross and salt slags in the aluminum industry in the form of residual materials.

"Unfired and/or calcined" means that the shaped bodies are dried and thermally treated to such an extent that they

- 5 (a) are mechanically sufficiently stable, so that they can be transported,
 (b) but not yet solidly sintered, so that they can be easily stamped, and
 (c) that they have an annealing-loss moisture of less than 5%, as too much moisture would be liberated otherwise during the operation of the electrolyse pot, which would pose the risk of cracking.

10 Said finely granular powders with high alumina content have the following chemical composition based on dried substance:

15	Al_2O_3	40	-	90%
	AlN	.1	-	25%
	MgO	4	-	20%
	SiO_2	.5	-	15%
	CaO	.1	-	15%
20	Al (metallic)	.1	-	10%
	Si (metallic)	.1	-	10%
	Fe_2O_3	.1	-	5%
	C			5% max.
	F			5% max.
25	Na_2O	.1	-	5%
	K_2O	.1	-	2%
	TiO_2	.1	-	2%
	Others			5% max.
	Loss on ignition			10%

According to another preferred embodiment, 90% of the particles of the finely granular powder product have a particle diameter of $<200 \mu\text{m}$. It was surprisingly found in a crucible test that such powders, in the compacted form of fluoride containing electrolyte melt, are substantially less infiltrated and attacked than the bottom insulating materials usually employed heretofore. The higher



resistance to infiltration and reaction versus electrolyte melt of the finely granular powders with high alumina content obtained in the recovery of dross and salt slags in the aluminum industry is presumably based on the ideal combination of the chemical and mineralogical compositions present in said powder particles, the mechanical strength and the size distribution of the particles. The Al_2O_3 is present in the form of the hard mineral substances corundum and MgO-spinel. In addition, minerally soft components are present in the form of CaF_2 and metallic aluminum.

A special advantage is the easy reusability of consumed bottom insulations that were stamped based on the finely granular powders with high alumina content obtained in the recovery of dross and salt slags in the aluminum industry. Such bottom insulations including the infiltrated electrolyte components can be recycled into the general recovery of dross and salt slags of the aluminum industry.

For producing the bottom insulation, the powders with high alumina contents obtained in the recovery of aluminum dross and aluminum salt slags, which, as a rule, are already present in the ideal particle size (maximum diameter 200 μm , mean diameter 5 to 30 μm), are shaped into spherical pellets, egg briquettes, or bricks in the normal form. It is advantageous if a binding agent (or vehicle) such as, for example water, cement, clay, aluminum phosphate or methylcellulose is added to the powder in the shaping process.

The shaped bodies are filled in the electrolytic pot and the filling is compacted by stamping, for example with the help of a surface vibrator as used in road construction. As the bottom lining has to be as dry as possible when the electrolytic cell is put into operation, and no moisture may be released during the operation of the cell, the shaped bodies have to be thermally pretreated before they are filled in the electrolytic pot to such an extent that the loss on ignition moisture is as low as possible. It was found in tests that a temperature of up to 700°C suffices for said purpose. The drying or annealing treatment can be carried out, for example in a chamber furnace.



Examples

The packing density of a stamped filling of shaped bodies based on a finely granular powder with high alumina content obtained in the recovery of dross and salt slags of the aluminum industry was determined by weighing and measuring stamped bodies which were compacted with a "Fischer" ram as known in foundry (casting) technology, and compared with stampings as produced according to the prior art from metallurgical alumina powder and commercially available refractory compound.

The resistance of said stampings to electrolyte melt was determined in a crucible test. For producing the crucible from a chamotte brick (stone) as it is usually employed for insulating the bottom of aluminum electrolytic cells, a piece of 12 cm width and length and 7 cm weight was sawed off in each case and a round hole with a diameter and depth of 5 cm was drilled into each piece. A tablet of 5 cm diameter and 2.5 cm thickness pressed at 600 bar and consisting of the bottom insulating material to be tested was inserted in the bore of the crucible. A tablet of the same size consisting of melt electrolyte as used in the primary electrolysis of aluminum was placed on top. The bore was subsequently covered with a plate of 1 cm thickness, which was sawn from the chamotte stone material as well. Following heating in a laboratory chamber furnace to 950°C and a dwelling time of 24 hours, the crucible was cooled and cut with a saw. This revealed to which extent the test tablet was infiltrated by the electrolyte melt.

Example of an embodiment of the invention

The powder with high alumina content obtained in the recovery of aluminum dross and aluminum salt slags and used in the following examples had the following properties:

Chemical Composition

Al ₂ O ₃	65%
MgO	8.6%
SiO ₂	7%
CaO	3%
F	2.2%



	Fe_2O_3	1.6%
	C	1.2%
	Na_2O	1%
	NH_3	.5%
5	K_2O	.4%
	Loss on ignition	8%

Crystalline Components

	Corundum	Al_2O_3
	Spinel	$\text{MgO} \cdot \text{Al}_2\text{O}_3$
10	Fluorite	CaF_2

Particle Size

<200 μm	90%
d50	15 μm

Example of an embodiment of the invention

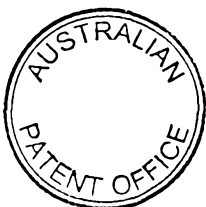
Stamping Material	Packing Density g/cm^3	Crucible Test Infiltration
Shaped bodies (egg briquettes) from powder with high alumina content and 10% binding clay	1.8	low

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Comparative Examples

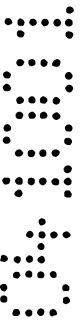
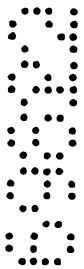
Stamping Material	Packing Density g/cm^3	Crucible Test Infiltration
# 1 Metallurgical Al_2O_3 -powder	1.1	high
# 2 Olivine stamping compound	2.4	low

The examples show by comparison that when a stamped filling of shaped bodies produced from finely granular powder with high alumina content obtained in the recovery of dross and salt slags of the aluminum industry is used instead of metallurgical alumina powder, infiltration of electrolyte melt is similarly low as with a commercially available olivine stamping compound; however, the packing



density is distinctly lower with such a stamped filling, thus resulting in a superior thermal insulation effect and less material consumption.

The embodiments have been achieved by way of example only, and modifications are possible within the scope of the invention as defined by the 5 appended claims.



THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A bottom lining for electrolytic cells whereby the basic body of the electrolytic cells is formed from steel pots, wherein at least part of the bottom lining consists of a monolithic stamping containing a finely granular powder product with high alumina content obtained in the recovery of dross and salt slags of the aluminum industry, said product having at least the following components based on the weight of the dried substance:

Al ₂ O ₃	40	-	90%
AlN	.1	-	25%
MgO	4	-	20%
SiO ₂	.5	-	15%
CaO	.1	-	15%
Al (metallic)	.1	-	10%
Si (metallic)	.1	-	10%
Fe ₂ O ₃	.1	-	5%
C			5% max.
F			5% max.
Na ₂ O	.1	-	5%
K ₂ O	.1	-	2%
TiO ₂	.1	-	2%
Others			5% max.
Loss on Ignition			10% max.

2. The bottom lining according to claim 1, wherein the bottom lining consists of unfired and/or calcined shaped bodies by layers.



3. The bottom lining according to any one of the preceding claims, wherein the following mineralogical main phases are present in the bottom lining:

Corundum	$\alpha\text{-Al}_2\text{O}_3$
Spinel	$\text{MgO} \times \text{Al}_2\text{O}_3$,

whereby the spinel component amounts to 15 to 70% by weight based on the powder product in the bottom lining.

4. The bottom lining according to any one of the preceding claims, wherein 90% of the particles of the finely granular powder product have a particle diameter of $<200\text{ }\mu\text{m}$.

5. The bottom lining according to any one of the preceding claims, wherein the finely granular powder product has a mean particle diameter of 5 to $30\text{ }\mu\text{m}$.

6. The bottom lining according to any one of the preceding claims, wherein the bottom lining consists of a layered composite of monolithically stamped shaped bodies and additional refractory insulating materials.

7. The bottom lining according to any one of the preceding claims, wherein the lining is adapted to be used in aluminum electrolytic cells both in primary production and secondary refining.

8. A process of producing a bottom lining of an electrolytic cell, whereby the basic body of the electrolytic cell is formed by a steel pot, wherein the process includes the following steps:

(a) a finely granular powder product is produced from the recovery of dross and salt slags of the aluminum industry by grinding, leaching, filtration and/or thermal treatment, said powder product having the following chemical composition based on the weight of the dried substance:

Al_2O_3	40	-	90%
AlN	.1	-	25%



MgO	4	-	20%
SiO ₂	.5	-	15%
CaO	.1	-	15%
Al (metallic)	.1	-	10%
Si (metallic)	.1	-	10%
Fe ₂ O ₃	.1	-	5%
C			5% max.
F			5% max.
Na ₂ O	.1	-	5%
K ₂ O	.1	-	2%
TiO ₂	.1	-	2%
Others			5% max.
Loss on ignition			10% max.

(b) the powder product is pelletized, briquetted or extruded to form shaped bodies; and

(c) the shaped bodies are thermally treated or calcined to less than 5% loss on ignition moisture, filled in the electrolytic pot and compacted by stamping or vibrating.

9. The process according to claim 8, wherein the thermal treatment is carried out by drying, calcining and/or sintering.

10. the process according to any one of claims 8 or 9, wherein the powder product is crushed to particles with a maximum diameter of 200 μm and a mean diameter of 5 to 30 μm .

11. The process according to any one of claims 8 to 10 wherein the powder product is crushed in a ball mill.

12. The process according to any one of claims 8 to 11, wherein inorganic and/or organic binding agents are used in the production of the shaped bodies.



13. The process according to any one of claims 8 to 12, wherein water, cement, clay, aluminum phosphate and/or methylcellulose are used as binding agents.

14. The process according to any one of claims 8 to 13, wherein 5 to 20% clay is used as binding agent.

15. A process for recovering a consumed (used) bottom lining of an aluminum electrolytic cell according to any one of claims 8 to 14, wherein the consumed or used bottom lining is removed from the electrolytic cell, and that following grinding, leaching, filtering, drying, calcining and/or sintering, a finely granular powder product is obtained again, in which MgO is present mineralogically bonded as spinel.

16. A bottom lining substantially as hereinbefore described.

17. A process of providing a bottom lining substantially as hereinbefore described.

DATED this 1st day of October, 2001

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