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(54) Silicon metal lining

(57) The invention relates to refractory materials being used in aluminum reduction cells such as structural parts, mortars, grouts and shaped lining products.

It was dicovered that - if the aluminum cell refractory material consists of more than 50% of silicon metal remains solid at the operating temperatures of aluminum electrolysis cells up to 1000°C.

A process for the manufacture of solid aluminum cell refractory material in the form of tiles, slabs and bricks is characterized in that a dry aggregate composition of

Dust fraction	0-0.5mm = 30%
Particle fraction	0-1mm = 20%
Particle fraction	1-2mm = 20%
Particle fraction	2-4mm = 30%

is mixed with a binder of a colloidal silica solution or with a high-softening coal-tar pitch, the mix is formed to bricks, slabs and tiles which are further treated to form a dense, highly cryolith resistant material, having extremely low electrical and moderate thermal conductivity.

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Description

[0001] The invention relates to innovative materials being used in aluminium reduction cells such as structural parts, mortars, grouts, and shaped lining products.

[0002] A basic prerequisite of materials which are suitable in the lining of electrolytic reduction cells for aluminium production is a good resistance against the constituents of cryolitic melts. According to the invention it was found that silicon metal meets this requirement, especially under reducing conditions. Thermodynamic experiments showed that there is an extremely low probability for the reaction of silicon with cryolite or its constitutional compounds sodium and aluminium fluoride. Silicon also behaves inert against other ingredients of the electrolytic melt such as calcium, magnesium and lithium fluorides as well as against metallic sodium that occurs in the cathodic region of electroytic reduction cells. It was found that silicon used as a lining material has to be kept away only from large amounts of liquid aluminium.

[0003] If prepared under the conditions described below the new pot lining or embedding material remains solid at the operating temperatures of aluminium electrolysis cells up to 1000°C (melting point above 1400°C) and can be considered to be electrically non-conductive. Other favourable features of the new silicon material are its fairly low thermal conductivity and good oxidation resistance forming a basis for its use as a superior refractory lining material.

[0004] The properties of the new silicon pot lining material which are briefly characterised above open up a number of useful applications in aluminium reduction cells which can be grouped as follows:

1. Structural, shaped parts of the new silicon material which are either directly cast or machined (cutting, drilling) from blocks or lumps of solid silicon.
2. Mortars and castables where powdery or fine, granular silicon material is used as filler material.
3. Block, bricks or tiles where a dry aggregate of silicon material ranging from 0 to about 8 mm in particle size constitutes the basis of the formed and fired products.

[0005] The silicon particle range of "0 to about 8" means that all particles above "0" can be used up to a particle size of about "8". A particle diameter of more than "9" mm has certain disadvantages because it is difficult to handle such particles in a colloidal silica solution.

[0006] Of the above-mentioned products some selected examples of preparation and application will be given below whereby the term "silicon" should be interpreted as the new silicon material defined in the claims.

Example 1:

[0007] Structural parts like shaped parts of pure silicon with drilled holes can be used to control the operating temperatures of aluminium reduction cells. The new silicon structural parts like hollow cylinders can, for instance, be either immersed from the top in the electrolytic bath or embedded in the cathode lining as protecting sheathes for example to protect temperatures sensors. The new silicon-protected measuring devices allow to monitor cell temperatures continuously over medium- (weeks or months) or long-term periods (years). The permanent recording of temperature signals represents a great advantage in the optimisation of cell process control.

Example 2:

[0008] New silicon mortars have been made by using pulverised silicon material as filler and a colloidal silica solution as binder. The following filler composition has shown significant properties: 70 % silicon powder of total mortar mass 0 - 0.5 mm and 30 % silicon powder of total mortar mass 0 - 0.2 mm. About 40 % of a colloidal silica solution are added which results to 100 % total mortar mass after a drying step. The silicon-based mortar is applied to lay fireclay bricks in the bottom or side pier lining of reduction cells. Many tests have shown that the joints filled with silicon-based mortar are at least 100 times more resistant to the infiltration and attack of fluoride melts than the fireclay bricks. If the fireclay bricks are bonded with conventional mortars prepared from ceramic filler materials (silica, chamotte, mullite, alumina, silicon carbide) and ceramic binders (sodium silicate, calcium aluminate cements etc.), it is always observed that the joints are attacked and converted first by the infiltrated fluoride bath constituents, i.e. penetration of cryolite bath moves faster and preferentially along the joints between the refractory bricks. This phenomenon is effectively stopped by using a silicon-based, silica-bonded mortar.

Example 3:

[0009] To manufacture slabs, bricks or tiles on the basis of silicon, silicon particle fractions must be prepared at first. Since Silicon is very brittle it should be crushed carefully and comminuted. According to the invention a preferred composition of the dry aggregate is the following:

Dust fraction	0 - 0.5 mm = 30 %
Particle fraction	0 - 1 mm = 20 %
Particle fraction	1 - 2 mm = 20 %
Particle fraction	2 - 4 mm = 30 %

[0010] The silicon particles exhibit an extremely low porosity. Thus, a dense product of low permeability can be made. Compared with a standard lining material the porosity and permeability of the new silicon material is below 1 % measured under identically conditions according to DIN 1306.

[0011] Various binders can be used to manufacture a shaped product from the preceding dry aggregate. Two examples will be described below.

Example 4:

[0012] The silicon dry aggregate is mixed with a 30 % colloidal silica solution. 0.5 % of wheat or rye flour may be added to facilitate forming. The green mix is compacted and formed by means of a hydraulic press to bricks or tiles. The bricks and tiles are dried or tempered, and thereafter are ready for use. Their cryolite resistance turned out to be excellent, even after long-term periods and strong turbulence conditions of the electrolytic bath.

Example 5:

[0013] Another bond structure of the electrolytic cell is produced by the following method: A new silicon dry aggregate is mixed with a high-softening coal-tar pitch at 180-200°C. One part of the silicon/pitch paste is formed to bricks, slabs and blocks by pressing another part, by vibration moulding under vacuum. The green shaped products are baked and calcined in an anode-carbon baking furnace under a nitrogen atmosphere up to 1200°C. During heat-treatment in an anode baking furnace the carbon residue of the coked pitch reacts with silicon to form β-silicon carbide as a bond matrix. This procedure was conducted in a nitrogen atmosphere until silicon nitride was formed in the presence of carbon monoxide which lead to partial preferably more than 30 % formation of silicon oxicarbide and oxinitride. It was found that some nitridation and oxygenation creates a microporosity and renders a less permeable product. The silicon-based product obtained by the preceding process is a dense, highly cryolite-resistant material of extremely low electrical and moderate thermal conductivity. It offers new possibilities in minimising the heat losses from electrolytic cells in conjunction with carbon & graphite as hot face materials.

[0014] Economic efficiency and life time of the reduction cells are noticeably improved by the silicon-based refractory materials outlined above. For comparison with a product made under the conditions of the prior art the following example 6 has been drawn up:

Example 6:

[0015]

I. Comparison test of density (100 % = not permeable)

Temperature = 1000°C - pressure: 10 bar

	Invention	Standard product
1)	rod of pure silicon	fire clay brick
	100%	55%
2)	product of example 4	mortar
	98%	45%

II. Comparison test of cryolite resistant
(attack in mm after 10 h)
Temperature: 1000°C

	Invention	Standard product
1)	rod of pure silicon	fire clay brick
	0 mm	18 mm
2)	product of example 4	mortar
	1 mm	25 mm

III. Thermal conductivity
(standard fire clay brick = 100 %)

	Invention	Standard product
1)	rod of pure silicon	fire clay brick
	18 %	100 %
2)	product of example 4	mortar
	21 %	96 %

[0016] The comparison test shows that the new innovative materials can be favourably used in aluminium reduction cells such as structural parts, mortars, grouts, and shaped lining products. They are principally made on the basis of silicon metal > 50 % and are corrosion-resistant against cryolitic melts and sodium. They have a low permeability and, compared to carbon & graphite, a very high electrical resistance and low thermal conductivity.

Claims

1. Aluminium cell refractory material comprising structural parts, mortars, grouts and shaped lining products
   characterized in
   that the refractory material consists in more than 50 % of silicon metal.

2. Aluminium cell refractory material according to claim 1,
   characterized in
   that the silicon metal consists of a dry aggregate

having a composition as follows

Dust fraction	0 - 0.5 mm = 30 %
Particle fraction	0 - 1 mm = 20 %
Particle fraction	1 - 2 mm = 20 %
Particle fraction	2 - 4 mm = 30 %.

3. Aluminium cell refractory material according to claim 2,
characterized in
that the silicon metal consists of 65 - 75 % dry aggregate and 25 - 35 % colloidal silica solution.

4. Aluminium cell refractory material according to claim 2,
characterized in
that the refractory material consists in a mixture of 65 - 75 % dry aggregate and 25 - 35 % high-softening coal-tar pitch.

5. Aluminium cell refractory material according to claim 4,
wherein the carbon residue of the coked pitch is reacted with silicon to β-silicon carbide as a bond matrix.

6. Aluminium cell refractory material according to claim 4 or 5,
characterized in
that the carbon residue of the pitch is reacted with silicon in the presence of nitrogen to silicon oxicarbide and/or oxinitride.

7. Aluminium cell refractory material according to claim 1,
characterized in
that the refractory material is a mixture of a binder and silicon metal which is a pulverised silicon filler having the following composition:

- 60 - 75 % silicon powder of 0 - 05, mm
- 25 - 35 % silicon powder of 0 - 0,2 mm and that
- 30 - 50 % of a colloidal silica solution is used as a mortar-binder.

8. Process for the manufacture of an aluminium cell refractory material in the form of tiles, slabs and bricks,
characterized in
that a dry aggregate composition of

Dust fraction	0 - 0.5 mm = 30 %
Particle fraction	0 - 1 mm = 20 %
Particle fraction	1 - 2 mm = 20 %
Particle fraction	2 - 4 mm = 30 %

is mixed with a binder of a colloidal silica solution to a green mixture,
the green mix is compacted and formed to bricks, slabs and tiles and
the compacted bricks, slabs and tiles are dried and tempered to receive a dense, highly cryolith resistant material, having extremely low electrical and moderate thermal conductivity.

9. Process for the manufacture of an aluminium cell refractory material,
characterized in
that a dry aggregate composition of

Dust fraction	0 - 0.5 mm = 30 %
Particle fraction	0 - 1 mm = 20 %
Particle fraction	1 - 2 mm = 20 %
Particle fraction	2 - 4 mm = 30 %.

is mixed with a high-softening coal-tar pitch at 180 - 200°C,
the silicon/pitch paste is formed to bricks, slabs and blocks by pressing and/or vibration moulding under vacuum and
the green shaped products are baked and calcined under a nitrogen atmosphere with a temperature between 1000 and 1200°C.

10. Process for the manufacture of an aluminium cell refractory material according to claim 9,
wherein the baking and calcining step is conducted for a time sufficient to react the carbon residue of the coked pitch with silicon to form better-silicon carbide as a bond matrix.

11. Process for the manufacture of an aluminium cell refractory material according to claim 9 or 10,
characterized in
that the baking step is conducted in the presence of carbon-mono-oxide to form silicon-oxicarbide and/or silicon-oxinitride.

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EUROPEAN SEARCH REPORT

Application Number
EP 02 00 5745

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X A	US 4 043 823 A (WASHBURN MALCOLM E ET AL) 23 August 1977 (1977-08-23) * column 1, line 27 - column 1, line 31 * * column 2, line 21 - column 2, line 25; examples 1-4 * ---	1 3,7-9	C25C3/08 C04B35/65
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A	US 5 494 267 A (ANDERSON MICHAEL W ET AL) 27 February 1996 (1996-02-27) * column 1, line 61 - column 2, line 24; examples 1,2 * ---	2,3,7,8	
A	GB 1 453 409 A (HOOGOVENS IJMUIDEN BV) 20 October 1976 (1976-10-20) * claim 1 * ---	4,9,10	
A	DE 22 32 719 A (VAW VER ALUMINIUM WERKE AG) 24 January 1974 (1974-01-24) * the whole document * -----	4,9,10	**TECHNICAL FIELDS SEARCHED (Int.Cl.7)** C25C C04B C22C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	5 September 2002	Hammerstein, G

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 02 00 5745

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