

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 627 505 A1

(12)

EUROPEAN PATENT APPLICATION(21) Application number: **94200655.2**(51) Int. Cl.⁵: **C25C 3/12**(22) Date of filing: **15.03.94**(30) Priority: **17.03.93 NO 930957**(43) Date of publication of application:
07.12.94 Bulletin 94/49(84) Designated Contracting States:
CH DE FR LI NL(71) Applicant: **NORSK HYDRO TECHNOLOGY B.V.**
P.O. Box 2
NL-4540 AA Sluiskil (NL)(72) Inventor: **Foosnaes, Trygve**
Seimsveien 26
N-5875 Ardalstangen (NO)
Inventor: **Bergli, Knut**
Boroningen 28
N-3472 Bodalen (NO)
Inventor: **Naterstad, Tormod**
J.A. Wilhelmsens vei 42
N-1370 Asker (NO)
Inventor: **Bosdal, Audun L.**
Kongshaugveien 4
NI-5875 Ardalstangen (NO)(54) **Composite for oxidation and corrosion protection of anode nipples.**

(57) A composite material for protecting one or more anode hanger nipples against oxidation and corrosion during operation in a Hall-Heroult electrolysis cell, consisting of a base material in the form of a particle aggregate of waste products from anodes consumed in aluminum electrolysis cells, calcium aluminate cement, a catalyst and water. Substances hazardous to health, such as PAH, have been removed. The composite material is characterised in that the particle aggregate can consist of particles between 1 and 2000 μm and make up at least 80 % of the composite material, the cement up to 15 %, the catalyst 0.6 % and the added water approximately 28 % of the solid mass.

The composite material is compressed under pressure to form a collar around the anode hanger nipples and can be prefabricated.

EP 0 627 505 A1

The present invention concerns a composite material for protecting one or more anode hanger nipples (hereinafter called nipples) against oxidation and corrosion during operation in a Hall-Heroult aluminium electrolysis cell, consisting of a particle aggregate of waste products from anodes consumed in aluminium electrolysis, calcium aluminate cement, a catalyst and water. Ready-processed and mounted, the composite material forms a protective collar around the nipple.

There are two main different types of composite materials which are used in this context:

For many years it has been normal practice to use petroleum coke and/or waste from consumed anodes as the base material and pitch as the binder for the first type of material for protecting anode hanger nipples against oxidation and corrosion during operation in an electrolysis cell. The disadvantages of this solution are that the pitch contains elements which are hazardous to health, for example PAH (polyaromatic hydrocarbons) which are released through the high temperature in the electrolysis cell, and that the nipples' resistance to aggressive gases is relatively low because the collar covers the whole of the nipple only for part of the operating time before it is partly dissolved on account of too weak particle binding and dilation forces which arise between the collar and the nipple.

A combination of the components petroleum coke, graphite, semi-graphite and waste electrode material is used as the base material of the second type, as well as a special cement mixture as the binder and water to trigger the hardening process and to obtain a suitable consistency for the composite material.

The disadvantages of this type of composite materials is that the base material not only consists of waste products from carbon and electrolysis processes but also uses raw materials such as petroleum coke, graphite and semi-graphite, each of which is an element which makes the production of the composite material more expensive.

EP application no. 269534 describes a coating of the latter type to achieve a composite material with a view to protecting the nipple against oxidation and corrosion. On the basis of the facts of the application, the assumed new features seem to be that 0.01 to 5 % antioxidant is added to the composite aggregate in the form of a passivated aluminium powder with particle size less than 0.1 mm and that the calcium aluminate cement should not contain more than 2 % contaminated elements.

One disadvantage is that the base material must be a powder, i.e. particles between 1 and 1000 μm , which results in a comprehensive and expensive crushing and screening process as well as in more calcium aluminate cement having to be added to enclose the powder particles so that an even, good bond is achieved in the composite. A further condition is that the base material is selected as stated above for the second type of composite material. Together these disadvantages will make the final composite material considerably more expensive. As a catalyst is not added, the result is that the cement will find it difficult to enclose all the particles in the powder aggregate on account of the surface tension, which leads to the individual parts of the coating having a weaker bond than those enclosed by cement, and that the dilation forces between the nipple and the collar are different, which can lead to cracks in the individual parts of the coating during operation in the electrolysis cell and thereby trigger an attack on the nipples.

The aim of the present invention is to improve protection of the anode hanger nipples against oxidation and corrosion during operation in an electrolysis cell beyond that which is known from the above solutions.

A further aim is to eliminate components which are hazardous to health, use waste products from existing processes to avoid waste storage and to produce a cheap product which effectively protects the nipples.

In accordance with the present invention, this has been achieved by means of a composite material as mentioned in the introduction and which is further characterised in that the particle size of the waste products from consumed anodes can be between 1 and 2000 μm and make up at least 80 per cent dry weight of the composite material. Furthermore, the composite material consists of up to 15 per cent dry weight calcium aluminate cement and up to 28 per cent dry weight water and 0.6 per cent dry weight catalyst, as defined in claim 1. Moreover, the present invention includes removal of substances hazardous to health, such as PAH, as defined in claim 7.

Other particularly advantageous features of the present invention are defined in claims 2-6.

The present invention will now be described in further detail by means of an example and with reference to the enclosed drawing which shows a perspective sketch of an anode hanger 1 with three nipples which are lowered into three holes in a carbon anode 4, and where each nipple 2 has a collar 3 of compressed composite material added to protect the nipple against oxidation and corrosion. The nipples are fastened, in a manner not described in further detail, to the carbon with cast iron filled in an annulus between the carbon and nipple. During operation the positive current is conducted down through the anode hanger and the nipples, the carbon anode, the oxide/cryolite bath and the liquid aluminium bath to the carbon cathode under high resistance which gives off strong heat and results in a cell temperature of approximately 960 degrees Celsius. The high temperature causes the reaction between the oxide and the cryolite, plus other components so that liquid aluminium is produced. During the reaction phase, which takes place continu-

ously, highly aggressive gases are given off which attack, in particular, the anode hanger nipples and release iron into the bath and aluminium which greatly reduces the quality of the aluminium. The collar, made either as a prefabricate or stamped when mounted, protects the nipples very well during the whole operating period. This results in higher aluminium purity and higher prices.

5 As mentioned in the introduction, the composite material consists of a particle aggregate of waste products from anodes consumed in an electrolysis cell, binding material in the form of calcium aluminate cement, a catalyst and water. The composite material is compressed and hardened at 60-90 degrees Celsius to a compressive strength of 1 MPa. The collar 3 is preferably prefabricated and mounted in the rodding department, i.e. the department where the carbon anode and the anode hanger are mounted
10 together.

There are a number of different types of calcium aluminate cement on the market for use as a binder in composite material for the protection of anode nipples against oxidation and corrosion. Undesired elements in the calcium aluminate cement, such as Fe_2O_3 , SiO_2 , Na_2O , Cr_2O_3 and K_2O can vary considerably between various manufacturers but the total should not exceed 7 per cent dry weight in the present
15 invention.

EXAMPLE

60 carbon anode/anode hanger installations were produced for this experiment, of which 40 had cardboard around the anode hanger nipples. No significant difference (at the 5 % significance level) could be discovered between the installations with and without cardboard. The following formula was used for the composite material:

25	Waste products from consumed anodes	$\geq 80 \%$
	Calcium aluminate cement	$\leq 15 \%$
	Catalyst	$= 0.6 \%$
	Water	approx. 28 %

30 20 kg mixtures were produced. The solid matter was mixed well before the water was added. The required quantity of water to be added was measured out (28 %) and the catalyst was dissolved in water before the solid matter was added. The water and the solid matter were mixed well by means of a mortar beater. A mould formed an annulus around the nipple into which the composite material was poured and compressed manually with a hammer and ramming shoe. Subsequently, the collar was hardened at 60-90
35 degrees Celsius. The anode installations were mounted in 6 electrolysis cells. The collars and the anodes were observed thoroughly by measuring the gases, temperature and density during operation in the electrolysis cell. The quantity of composite material which was left on the nipples after use in the electrolysis cell covered the whole nipple and the ring coverage was considerably thicker than when traditional composite material is used. The iron content of the aluminium metal showed no tendency to
40 change over a 60-day period.

Claims

- 45 1. A composite material for protecting one or more anode hanger nipples against oxidation and corrosion during operation in a Hall-Heroult electrolysis cell, consisting of a base material in the form of a particle aggregate of waste products from anodes consumed in aluminium electrolysis and calcium aluminate cement, a catalyst and water,
characterised in that the particle size of the waste products are between 1 and 2000 μm and represents 80 or more per cent dry weight of the composite material which in addition consists of up to
50 15 per cent dry weight calcium aluminate cement, up to 28 per cent water of the dry weight of the waste products and cement and up to 0.6 per cent dry weight catalyst.
2. A composite material in accordance with claim 1,
characterised in that the cement consists of up to 70 per cent weight of alumina.
- 55 3. A composite material in accordance with claim 1,
characterised in that the particle aggregate consists of at least 1 per cent dry weight ash.

4. A composite material in accordance with claim 1,
characterised in that the composite material is either processed to form a prefabricated collar or is compressed around the anode nipple so that a collar is formed.
- 5 5. A composite material in accordance with claim 1,
characterised in that the collar is hardened at 60-90 degrees Celsius for 60 minutes to a compressive strength of 1 MPa.
- 10 6. A composite material in accordance with claim 1,
characterised in that an inoxidisable, tight intermediate layer, for example of paper material, can be inserted between the collar and the nipple to prevent the collar bursting in the event of a difference of dilation between the anode nipple and the collar.
- 15 7. A composite material in accordance with claim 1,
characterised in that the waste products used in the particle aggregate have had substances hazardous to health, such as PAH components, removed by processing.

20

25

30

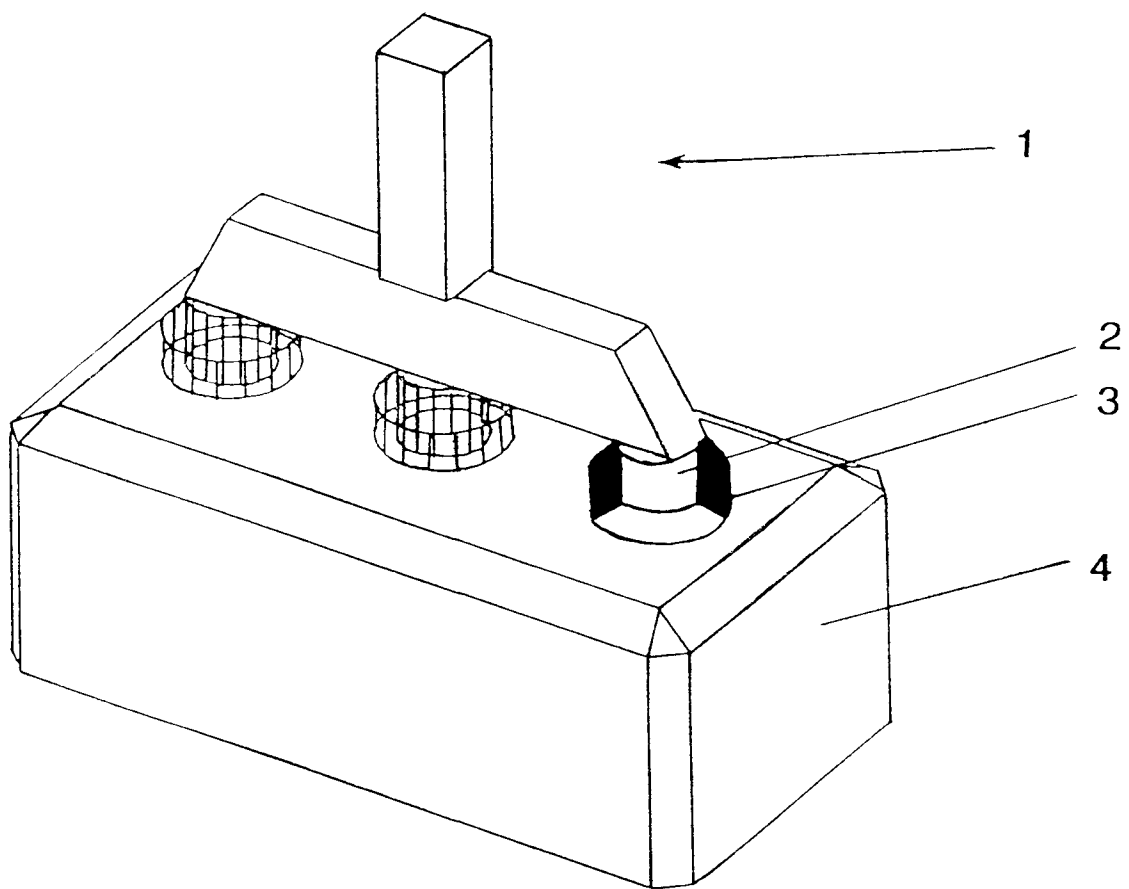
35

40

45

50

55





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 20 0655

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.5)
D,A	EP-A-0 269 534 (S.E.R.S. SOCIETE DES ELECTRODES & REFRACTAIRES SAVOIE) 1 June 1988 * page 7; claims 1-9 * ---	1	C25C3/12
A	EP-A-0 322 326 (S.E.R.S. SOCIETE DES ELECTRODES & REFRACTAIRES SAVOIE) 28 June 1989 * page 5; claims 1,2 * * page 6; claim 4 * -----	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			C25C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 14 July 1994	Examiner Groseiller, P
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	