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(54) Titre : PROCEDE DE PRODUCTION D'UN BLOC CATHODIQUE POUR CELLULE D'ELECTROLYSE D'ALUMINIUM  
ET BLOC CATHODIQUE CORRESPONDANT  
(54) Title: PROCESS FOR PRODUCING A CATHODE BLOCK FOR AN ALUMINIUM ELECTROLYSIS CELL AND A  
CATHODE BLOCK

(57) **Abrégé/Abstract:**

The invention relates to a process for producing a cathode block, comprising the following steps: providing starting materials, including coke and a hard material powder, such as  $TiB_2$ , and also if appropriate a carbon-containing material, mixing the starting materials, forming a cathode block, carbonizing and graphitizing, and also cooling. According to the invention, the graphitizing step is carried out at temperatures of between 2300 and 3000°C, in particular between 2400 and 2900°C.

ABSTRACT

The invention relates to a process for producing a cathode block, comprising the following steps: providing starting materials, including coke and a hard material powder, such as  $TiB_2$ , and also if appropriate a carbon-containing material, mixing the starting materials, forming a cathode block, carbonizing and graphitizing, and also cooling. According to the invention, the graphitizing step is carried out at temperatures of between 2300 and 3000°C, in particular between 2400 and 2900°C.

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PROCESS FOR PRODUCING A CATHODE BLOCK FOR AN ALUMINIUM  
ELECTROLYSIS CELL AND A CATHODE BLOCK

The present invention relates to a process for producing a cathode block for an aluminium electrolysis cell and a cathode block.

A known process for producing metallic aluminium is the Hall-Heroult process. In this electrolytic process, the base of the electrolysis cell is typically formed by a cathode surface comprising individual cathode blocks. The cathodes are contacted from beneath via steel bars, which are introduced into corresponding elongated recesses in the underside of the cathode blocks.

The production of cathode blocks conventionally takes place by mixing coke with carbon-containing particles, such as anthracite, carbon or graphite, compacting and carbonising. If need be, this is followed by a graphitising step at higher temperatures, at which the carbon-containing particles and the coke are converted at least partially into graphite.

As a result of the graphitising, the thermal conductivity of the cathode material is greatly increased and the specific electrical resistance is greatly reduced.

Graphitized carbon and graphite are however poorly wetted or are not wetted at all by liquid aluminium. The power requirement and therefore also the energy requirement of an electrolysis cell is thus increased.

In order to solve this problem,  $TiB_2$  is introduced into an upper layer of a cathode block in the prior art. This is described for example in DE 112006004078. Such an upper layer, which represents a  $TiB_2$ -graphite composite, is in direct contact with the aluminium melt and is therefore crucial for the current coupling from

the cathode into the aluminium melt.  $TiB_2$  and similar hard-ceramic materials produce an improvement in the wettability of the cathode in the graphitized state and therefore a better energy efficiency of the electrolysis process. Ceramic hard materials can moreover increase the bulk density and the hardness of cathodes, which leads to a better resistance to wear especially with respect to aluminium and cryolite melts. Hard materials are also referred to as RHM (refractory hard material).

However, during a graphitising process,  $TiB_2$  powder and similar hard material powders partially lose their effect of increasing the wettability and wear resistance.

The problem of the present invention, therefore, is to provide a simple process for the production of a  $TiB_2$ -graphite composite cathode which is readily wettable with respect to aluminium melts and has good wear properties, as well as a corresponding cathode block.

The problem is solved by the process according to claim 1.

A process according to the invention for the production of a cathode block comprises the steps of providing starting materials, including coke and a hard material powder, such as for example  $TiB_2$ , and if appropriate a further carbon-containing material, mixing the starting materials, forming a cathode block, carbonising and graphitising, and also cooling, and is characterised in that the step for graphitising is carried out at temperatures between 2300 and 3000°C, in particular between 2400 and 2900°C.

Temperatures below 2900°C have proved to be particularly advantageous, since conventional TiB<sub>2</sub> does not melt below 2900°C. It is true that melting presumably does not lead to any chemical change in the TiB<sub>2</sub>, since TiB<sub>2</sub> is detected in a cathode block by x-ray-diffraction analysis also after melting and subsequent cooling. However, as a result of melting, finely distributed TiB<sub>2</sub> particles agglomerate to form larger particles. There is also a certain risk of liquid TiB<sub>2</sub> moving in an uncontrolled manner through open porosity.

In the temperature range according to the invention, the graphitising process has progressed so far that a high thermal and electrical conductivity of the carbon-containing material is produced.

The graphitising step is preferably carried out at an average heating rate between 90 K/h and 200 K/h. Alternatively, or in addition, the graphitising temperature is held for a period between 0 and 1 h. With these heating rates and this holding period, particularly good results are achieved in terms of graphitising and preserving the hard material.

A period of the temperature treatment up to the time when the cooling is started can preferably amount to 10 to 28 hours.

It may be advantageous for the composite with hard material and graphite or graphitised carbon to form the whole cathode block. This has the advantage that a single green material composition is required and accordingly only a single mixing step.

Alternatively, it may be advantageous for the cathode block to comprise at least two layers, wherein the



composite layer forms the second layer of the cathode block. This second layer is in direct contact with the melt of the electrolysis cell.

The cathode block preferably comprises at least one further layer (referred to below as the first layer), which comprises less hard material powder than the upper layer or comprises no hard material powder. This can reduce the quantity of expensive hard material powder used. When the cathode is used in an aluminium electrolysis cell, the first layer is not in direct contact with the aluminium melt and does not therefore have to have good wettability and wear resistance.

The second layer can advantageously have a height which amounts to 10 to 50%, in particular 15 to 45%, of the total height of the cathode block. A small height of the second layer, such as 20% for example, may be advantageous, since a small quantity of cost-intensive hard material is required.

Alternatively, a greater height of the second layer, such as 40% for example, may be advantageous, since a layer possessing a hard material possesses a high wear resistance. The greater the height of this highly wear-resistant material in relation to the overall height of the cathode block, the greater the wear resistance of the overall cathode block.

The coke preferably comprises two types of coke which have a different volume-change behaviour during the carbonising and/or graphitising and/or cooling.

Surprisingly, it has been shown that the useful life of the cathode blocks produced with such a process is much longer than in the case of the cathode blocks produced with conventional processes.

The carbon fraction of the cathode block is preferably compacted to a bulk density of over  $1.68 \text{ g/cm}^3$ , in particular of over  $1.71 \text{ g/cm}^3$ , in particular up to  $1.75 \text{ g/cm}^3$ .

A higher bulk density presumably contributes advantageously to a longer useful life. This may on the one hand be based on the fact that more mass is present per unit volume of a cathode block, which, with a given mass abrasion per unit of time, leads to a higher residual mass after a given abrasion period. On the other hand, it can be assumed that a higher bulk density with a corresponding lower porosity prevents an infiltration of electrolyte, which acts as a corrosive medium.

With this variant, the advantages of the graphitising temperature according to the invention in a range between  $2300$  and  $3000^\circ\text{C}$  are combined with the increase in the bulk density of the cathode block. Advantageously, a consequence of the incomplete graphitising is thus at least partially compensated for.

Since the second layer always has a high bulk density of for example over  $1.80 \text{ g/cm}^3$  after graphitising on account of the addition of hard material, it is advantageous if the first layer after graphitising also has a high bulk density of, according to the invention, over  $1.68 \text{ g/cm}^3$ . The small differences in the thermal expansion behaviour and bulk densities during the heat treatment steps reduce production times and reject rates of the cathode blocks. Furthermore, the resistance to thermal stresses and to resultant damage in use is therefore advantageously also increased.

The two types of coke advantageously include a first type of coke and a second type of coke, wherein the first type of coke exhibits a greater shrinkage and/or expansion than the second type of coke during the carbonising and/or graphitising and/or cooling. In this connection, the greater shrinkage and/or expansion is an advantageous development of a different volume-change behaviour, which presumably is particularly well suited for leading to a greater compaction than when types of coke are mixed that possess an identical shrinkage and/or expansion. Thereby, the greater shrinkage and/or expansion relates to an arbitrary temperature range. Thus, for example, only a greater shrinkage of the first coke may be present during carbonising. On the other hand, for example, a greater expansion may be present, additionally or instead, in a transition zone between carbonising and graphitising. Instead or in addition, a different volume-change behaviour may be present during cooling.

The shrinkage and/or expansion of the first type of coke during the carbonising and/or graphitising and/or cooling related to the volume is preferably at least 10% higher than that of the second type of coke, in particular at least 25% higher, in particular at least 50% higher. Thus, for example, in the case of a 10% higher shrinkage of the first type of coke, the shrinkage from room temperature to 2000°C in the case of the second type of coke is 1.0% by volume, but in the case of the first type of coke 1.1% by volume.

The shrinkage and/or the expansion of the first type of coke during the carbonising and/or graphitising and/or cooling related to the volume is advantageously at least 100% higher than that of the second type of coke, in particular at least 200% higher, in particular at least 300% higher. Thus, for example, in the case of a



300% higher expansion of the first type of coke, the expansion from room temperature to 1000°C in the case of the second type of coke is 1.0% by volume, whereas in the case of the first type of coke it is 4.0% by volume.

The case where the first type of coke experiences a shrinkage, but the second type of coke experiences an expansion in the same temperature range, is also covered by the process according to the invention. A 300% higher shrinkage and/or expansion thus also includes, for example, the case where the second type of coke shrinks by 1.0% by volume, whereas the first type of coke expands by 2.0% by volume.

Alternatively, instead of the first type of coke, the second type of coke can exhibit a greater shrinkage and/or expansion in at least one arbitrary temperature range of the process according to the invention, as described above for the first type of coke.

At least one of the two types of coke is preferably a petroleum coke or coal-tar-pitch coke.

The quantity fraction in percentage by weight of the second type of coke in the total quantity of coke preferably amounts to between 50% and 90%. In these quantity ranges, the different volume-change behaviour of the first and second type of coke has a particularly good effect on a compaction during the carbonising and/or graphitising and/or cooling. Conceivable advantageous quantity ranges of the second type of coke can be 50 to 60%, but also 60 to 80%, as well as 80 to 90%.

At least one further carbon-containing material and/or pitch and/or additives are advantageously added to the

coke. This can be advantageous both with regard to the processability of the coke as well as the subsequent properties of the produced cathode block.

The further carbon-containing material preferably contains graphite-containing material; in particular, the further carbon-containing material comprises graphite-containing material, such as for example graphite. The graphite can be synthetic and/or natural graphite. The effect of such a further carbon-containing material is that the necessary shrinkage of the cathode material, which is dominated by the coke, is reduced.

The carbon-containing material related to the total quantity of coke and carbon-containing material is advantageously present at 1 to 40% by weight, in particular at 5 to 30% by weight.

In addition to the quantity of coke and, as appropriate, carbon-containing material, said quantity representing a total of 100% by weight, pitch in quantities of 5 to 40% by weight, in particular 15 to 30% by weight (related to 100% by the weight of the total green mixture), can preferably be added. Pitch acts as a binder and serves to produce a dimensionally stable body during the carbonising.

Advantageous additives can be oil, such as auxiliary pressure oil, or stearic acid. These facilitate mixing of the coke and, if appropriate, the further components.

The coke in at least one of the two layers, i.e. in the first and/or the second layer, preferably comprises two types of coke, which have a different volume-change behaviour during the carbonising and/or graphitising

and/or cooling. This can presumably lead to a compaction of the emerging graphite of over  $1.70 \text{ g/cm}^3$ , in particular over  $1.71 \text{ g/cm}^3$ . Depending on what is desired and/or required, both layers or one of the two layers can therefore be produced, according to the invention, with two different types of coke. The possibility thus arises of adjusting bulk densities and bulk density ratios, as required or desired. According to the invention, solely the first layer can for example be produced with two types of coke, whilst the second layer is produced with only one type of coke, but additionally contains  $\text{TiB}_2$  as a hard material. The expansion behaviours of the two layers are thus made similar, which can advantageously increase the useful life of the layers.

If need be, it may be advantageous for the multi-layer block to comprise more than two layers. In this case, it is possible according to the invention to produce, from the more than two layers, an arbitrary number of layers, in each case with two types of coke having a different volume-change behaviour.

Further advantageous embodiments and developments of the invention are explained below with the aid of a preferred example of embodiment.

For the production of a cathode block according to the invention, a first and a second coke are ground separately from one another, separated into grain size fractions and mixed together with pitch together with, for example, 15 to 25% by weight, such as for example 20% by weight, of  $\text{TiB}_2$ . The weight proportion of the first coke in the total quantity of coke can amount for example to 10 to 20% by weight or 40 to 45% by weight. The mixture is filled into a mould, which largely corresponds to the subsequent shape of the cathode

blocks, and compacted by vibration or block-pressed. The emerging green body is heated up to a final temperature in a range from 2300 to 3000°C, such as 2600 or 2800°C for example, a graphitising step taking place, and is subsequently cooled. The emerging cathode block has a bulk density of 1.68 g/cm<sup>3</sup> and a very high wear resistance to liquid aluminium and cryolite. The thermal and electrical conductivity are high on account of the retained average degree of graphitising. A loss of TiB<sub>2</sub> was not able to be established by x-ray diffraction analysis. The wettability of the cathode block by liquid aluminium is very good.

Alternatively, a single type of coke is used. The wetting behaviour of the resultant cathode block is for the most part just as good as in the first example of embodiment. The thermal and electrical conductivity lie in similar ranges to those in the first example of embodiment.

In a further variant of the example of embodiment, graphite powder or carbon particles are added to the coke mixture.

All the features mentioned in the description, the examples and claims can contribute to the invention in any combination. The invention is not however limited to the stated examples, but can also be performed in modifications that are not specifically described here.

CLAIMS

1. A process for the production of a cathode block, comprising the steps of providing starting materials, including coke and a hard material powder, such as  $TiB_2$  for example, and if appropriate a carbon-containing material, mixing the starting materials, forming a cathode block, carbonising and graphitising, and also cooling, characterised in that the step for graphitising is carried out at temperatures between 2300 and 3000°C, in particular between 2400 and 2900°C.
2. The process according to claim 1, characterised in that the graphitising step is carried out at a heating rate between 90 and 200 K/h and/or at the graphitising temperature between 2300 to 2900°C.
3. The process according to claim 1 or 2, characterised in that the coke comprises two types of coke, which have a different volume-change behaviour during the carbonising and/or graphitising and/or cooling.
4. The process according to claim 3, characterised in that the cathode block is obtained with a bulk density of over 1.68 g/cm<sup>3</sup>, in particular of over 1.71 g/cm<sup>3</sup>.
5. The process according to one more of claims 1 to 4, characterised in that the whole cathode block is produced as a composite with graphite and hard material.
6. The process according to one or more of claims 1 to 5, characterised in that the cathode block is produced as a multi-layer block, wherein a first



layer contains coke as starting material and a second layer contains coke and a hard material, in particular  $TiB_2$ , as starting material.

7. The process according to claim 6, characterised in that the first and/or second layer of the cathode block contains at least one further carbon-containing material as starting material.
8. The process according to claim 6 or 7, characterised in that the second layer is produced with a thickness which amounts to 10 to 50%, in particular 15 to 45%, of the total thickness of the cathode block.
9. The process according to one or more of claims 1 to 8, characterised in that the proportion of graphite and/or graphited carbon related to the total carbon content in at least one layer of the cathode block amounts to at least 60%.
10. The process according to claim 9, characterised in that the proportion of graphite and/or graphited carbon amounts to at least 80%.