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(54) **ANODE**

(57) The invention relates to a titanium-based anode in the form of a plate of porous titanium with a thickness of 3 mm and more and a porosity of 5 to 45 %.

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## Description

Technical Field

**[0001]** This invention relates generally to electrochemical production practice and more specifically, to anodes.

Background Art

**[0002]** Some prior-art anodes are known to comprise a titanium base coated with an active coating from manganese dioxide, such anodes being produced by intermixing powdered titanium and powdered manganese, followed by molding and sintering the resultant mixture, applying a manganese nitrate solution to said base, and heat-treatment of the latter (cf. US Patent No4,269,691, IPC C 25 B 11/16, 1981).

**[0003]** The closest to the herein-proposed invention as to its technical essence and the obtainable result is an anode as disclosed in the USSR Inventor's Certificate No 1,713,983, IPC C 25 B 11/16, 1989. The anode in question comprises a titanium base appearing as a rod made of a titanium alloy to which a manganese-dioxide coating is applied, using any heretofore-known technique, viz., direct electrolytic deposition of manganese dioxide or thermal decomposition of a solution containing sulfuric acid and manganese sulfate.

**[0004]** However, said known anodes suffer from a number of disadvantages, namely, poor adhesion of a layer of manganese dioxide to the titanium metal base; an increase in the anode potential to an impermissible high value (over 2.5 V); a considerable difference between the values of the thermal expansion coefficient of titanium and of manganese dioxide resulting in destruction of the manganese dioxide layer and separation of large coating areas which as a whole affects adversely the quality of a finished anode due to titanium passivation.

**[0005]** With a view to increasing the adhesive properties of manganese dioxide towards the titanium base attempts were made to subject the surface of said base to special perforating; however, said procedure only added to complexity of the anode production process.

Disclosure of the Invention

**[0006]** It is a principal object of the present invention to provide a titanium-base anode, wherein the manganese-dioxide layer thereof features higher adhesive properties towards said titanium base, as well as a higher strength of said coating layer, with a simple production process of said anode.

**[0007]** Said object is accomplished due to the fact that in an anode comprising a titanium base coated with a manganese-dioxide coating, according to the invention, the titanium base appears as a plate made of porous titanium and having a thickness of 3 mm and over and a void content of from 5 to 45%.

**[0008]** While being crystallized in the initial period of time in the voids of the titanium base and then on the surface of said base-plate, manganese dioxide forms strong bonds throughout the bulk of the anode, said bonds preventing the exterior layer from spalling and the anode itself from passivation. Effect of a difference between the values of the thermal expansion coefficient of manganese dioxide and of titanium on the strength of coating is much reduced due to the fact that the exterior working layer of manganese dioxide is crystallized predominantly on those manganese-dioxide crystals which have grown into the voids of the titanium base which in this particular case serves as a metal framework of the entire anode, adapted to impart bending and tensile strength to the anode and to serve as a current-carrying element of the working member of the manganese-dioxide anode.

**[0009]** The lower limit of thickness of the porous titanium base depends on the required bending and tensile strength of the anode, as well as electric conductance thereof. Provision of the titanium base more than 5 mm thick does not affect the technological characteristics of the anode but results in an unjustified increase in the production costs of the anode due to a higher consumption of titanium.

**[0010]** The lower limit of the void content of the titanium base (below 5%) is dictated by the production capability of said porous plate and by poor adhesion of manganese dioxide to said base, and rather frequent spalling of the manganese-dioxide layer. It is recommended that the lower limit of the void content preferably be at 25%.

**[0011]** The upper limit of the titanium base void content, i.e., 45% is determined by economic expediency in view of the fact that any increase in the void content of the titanium base will result in a higher consumption of the agents involved in establishing a required manganese-dioxide layer and in a reduced bending strength of the titanium base due to higher brittleness of the plate, whereby said upper limit of the titanium base void content is recommendable to lie within 40%.

**[0012]** In what follows the invention will be disclosed in its specification with reference to a specific embodiment thereof.

Best Method of Carrying Out the Invention

**[0013]** Used for producing an anode a plate having a thickness of 4.1 mm and measuring 1100 x 800 mm made of porous titanium having the void content of 25%. The plate having the aforesaid dimensions was positioned horizontally and was coated with a manganese-nitrate solution having a density of 1.65 kg/cu.m, using a brush. Next the applied layer, i.e., a manganese-nitrate coating, was heated in a furnace provided with an exhaust system, at a temperature T = 200 to 250°C. As a result of heating, manganese nitrate is decomposed into manganese dioxide and nitrogen dioxide, the latter being removed, while manganese dioxide is deposited on the porous titanium base to crystallize in the voids of the titanium plate in the initial period of time. The step of applying a manganese-dioxide layer on the plate was repeated ten times in succession, with the result that manganese dioxide crystallized over the entire surface of the porous titanium plate to form a strong bond within the whole bulk of the anode. Hence with the original weight of the titanium plate equal to 8.2 kg, a finished anode was obtained, weighing 12.3 kg and comprising a porous titanium base, i.e., the plate coated with a manganese-dioxide coating.

**[0014]** Given below is a table representing the main anode characteristics, that is, duration of continuous operation and spalling area vs the void content of the titanium plate, the initial two lines presenting the characteristics of the heretofore-known anodes, i.e., those having a titanium base.

Table

| Material of anode base | Void content, % | Continuous operation time, h | Bath voltage, V | Spalling area, % |
|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 |
| 1.Titanium sheets, | 0 | 14 | 5,7 | 20,2 |
| perforation-free | 0 | 25 | 7,8 | 73,0 |
| 2.Titanium sheets, | 0 | 216 | 5,8 | 15,5 |
| perforated | 0 | 350 | 6,7 | 24,5 |
| 3. Porous plate | 5 | 200 | 5,1 | 8,9 |
| 4. Porous plate | 15 | 250 | 4,9 | 4,5 |
| 5. Porous plate | 20 | 350 | 4,7 | 3,1 |
| 6. Porous plate | 25 | 350 | 3,4 | 0 |
| 7. Porous plate | 25 | 700 | 3,4 | 0 |
| 8. Porous plate | 30 | 1000 | 3,4 | 0 |
| 9. Porous plate | 40 | 1000 | 3,4 | 0 |
| 10. Porous plate | 45 | 970 | 3,6 | 1,6 |

Industrial Applicability

**[0015]** The present invention can find application for electrolysis of zinc- and other solutions or in producing electrolytic zinc.

**Claims**

1. An anode for electrolysis of zinc and other solutions, comprising a titanium base in the form of a plate made from porous titanium and having a thickness of at least 3mm, coated with a manganese-dioxide coating, **CHARACTERISED in that** said plate has the same void content uniform throughout the bulk of the anode, strong bonds being established between manganese dioxide and the titanium base, said bonds preventing the exterior layer from spalling and the anode from passivating, the void content being from 5 to 29%.

2. An anode, comprising a titanium base, coated with a manganese-dioxide coating, **CHARACTERISED in that** said base in the form of a plate of porous titanium with a thickness of at least 3 mm and a porosity of from 5 to 45%.

## INTERNATIONAL SEARCH REPORT

International application No.
PCT/RU 00/00208

A. CLASSIFICATION OF SUBJECT MATTER :
IPC7: C25B 11/10

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)
IPC7 C23F 13/00, 13/16, C25B 11/10, 11/16, 11/03, C25C 1/16, 7/02, C25D 17/10, C02F 1/46, 1/461

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document. with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | US 4269691 A (THE DOW CHEMICAL COMPANY) 26 May 1981 (26.05.81), column 2, lines19-33, column 7, lines 52-60, column 8, lines 9-21, 33-46 | 1 |
| Y | SU 1661247 A1 (INSTITUT NEORGANICHESKOI KHIMII I ELECTROKHIMII AN GSSR) 07 July 1991 (07.07.91) column 1 | 1 |
| Y | RU 94018552 A1 (NAUCHNO-PROIZVODSTVENNOE SOVMESTNOE PREDPRYATIE "ESMA-TEKHNOLOGYA LTD.') 10 January 1996 (10.01.96) the abstract | 1 |
| A | SU 1546516 A1 (BELORUSSKY TEKHNOLOGICHESKY. INSTITUT im. S.M. KIROVA) 28 February 1990 (28.02.90) | 1 |

☐ Further documents are listed in the continuation of Box C. ☐ 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

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"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
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