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[54] MANUFACTURE OF LEAD DIOXIDE/TITANIUM COMPOSITE ELECTRODES

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[51] **Int. Cl.** **B01k 3/06;** C23f 17/00
[58] **Field of Search** .... 204/38 A, 290 F, 57, 42; 136/120 R, 26

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[57] ABSTRACT

A method of producing lead dioxide/titanium composite electrodes by anodic deposition of lead dioxide on a titanium surface, in which an intermediate layer of a carbide or boride of an element of sub-group 4 or 5 and/or silicide of an element of sub-group 4, 5 or 6 of the periodic table of the elements and/or silicon carbide, is applied to the titanium surface before depositing the lead dioxide.

8 Claims, No Drawings

MANUFACTURE OF LEAD DIOXIDE/TITANIUM COMPOSITE ELECTRODES

This invention relates to a process for the production of lead dioxide/titanium composite electrodes which are specifically useful as anodes in electrolysis cells of high current density.

Composite electrodes of a base consisting of titanium to which lead dioxide coatings have been applied are known. Such electrodes are manufactured by conventional methods, through anodic deposition of the oxide from lead-II salt solution onto the titanium substrate. Because titanium blocks the passage of current if it is wired as the anode in an electrolysis system, it is however not possible anodically to deposit an even and well-adhering lead dioxide coating on a titanium surface. It is known to avoid this blockage by adding fluorides to the lead salt bath or by mechanically roughening, and degreasing, the titanium surface.

According to a known proposal, smooth, even, very well-adhering coatings of lead dioxide on titanium surfaces, which even as thin coatings are stable to anodic polarization, are attained by using oxidative treatment in the presence of compounds of metals of sub-groups 1, 6, 7 and 8 of the periodic table and of aluminum, vanadium and bismuth to produce a titanium dioxide coating, modified with the oxides of these metals, on the titanium surface prior to depositing the lead dioxide coatings.

Finally, it is also known to manufacture lead dioxide/titanium composite electrodes by applying seeds of finely divided platinum, palladium, gold, magnetite, graphite and/or lead dioxide to the titanium surface before the anodic deposition of lead dioxide.

The electrodes produced in accordance with the processes which have been disclosed are not equally suitable for all applications. Thus, for example, they suffer from the disadvantage that — if they are employed as anodes in electrolysis cells of high current throughput — the lead dioxide layers flake off, especially after prolonged anodic polarization, and this results in the gradual formation of a blocking layer of titanium dioxide between the titanium and the lead dioxide. If the process carried out uses noble metals, such electrodes can, for example when employed as anodes in electrolysis cells with cathodes of high hydrogen overvoltage, inactivate the cathodes. Furthermore, some of the conventional processes are costly and time-consuming.

It is an object of the present invention to provide a process for the production of lead dioxide/titanium composite electrodes which provides electrodes which do not show the said disadvantages and which can be used as anodes in electrolysis cells of high current throughput without showing the disadvantage that the lead dioxide layers flake off. Other objects will be apparent from the description.

We have found that this object is achieved by a process for the production of lead dioxide/titanium composite electrodes by anodic deposition of lead dioxide on titanium surfaces wherein an intermediate layer of a carbide or boride of an element of sub-group 4 or 5 and/or a silicide of an element of sub-group 4, 5 or 6 of the periodic table of the elements and/or silicon carbide, is applied to the titanium surface before depositing the lead dioxide.

Particularly suitable carbides and borides are those of titanium and tantalum, and titanium carbide, tantalum carbide and tantalum boride should be singled out specifically.

Preferred silicides for use in the intermediate layers are titanium disilicide, zirconium disilicide, tantalum disilicide, chromium disilicide and niobium disilicide, amongst which chromium disilicide, titanium disilicide and zirconium disilicide give particularly dense intermediate layers because of their low melting points, which are from 1,500° to 1,700°C. Silicon carbide is also preferred.

Of course, the intermediate layers can also consist of a mixture of these compounds.

To manufacture the electrodes, the base is first cleaned, preferably mechanically, for example by sandblasting or corundum blasting. Thereafter, the carbides and borides of the elements of sub-groups 4 and 5 of the periodic system (Ti, Zr, Hf, V, Nb and Ta) and the silicides of the elements of sub-groups 4 to 6 of the periodic system (Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W) and/or silicon carbide are applied. For this purpose, the plasma spraying process can be used and is advantageously carried out under a protective atmosphere of argon gas; in this process, the powders of the compounds mentioned, of particle sizes preferably from 15 to 90 μ, are fed to a plasma torch with argon plasma. The thickness of the intermediate layers produced in preferably from about 60 to 200 μ, but where the layers contain more than 20 percent by weight of the silicides mentioned, and/or of silicon carbide, a thickness down to 20 μ suffices.

To improve the electron conductivity, the silicides or the silicon carbide can also be modified with metals or halides of the iron group, especially with iron itself. The proportion of metals or halides of the iron group is so chosen that the content, based on pure metal, in the silicide does not exceed 5 percent by weight.

Further suitable methods for applying the borides, carbides or silicides and the silicon carbide are the flame spraying process and high vacuum vapor-coating. In these processes, as in the plasma spraying process, it is important that the electrically conducting base should be freed from oxides on the surface which is to be coated.

A particularly suitable process for applying intermediate layers of silicon or silicon carbide to electrically conducting shapes has proved to be vapor phase deposition by a chemical reaction with application of radiant energy or heat energy. Thus, for example, halides of elements of sub-groups 4 to 6 can be reacted with silanes or silicon halides and hydrogen or base metals to give silicides which deposit as dense coatings on the surface of the electrically conducting bases.

In this process it is again possible to produce intermediate layers modified with metals or halides of the iron group, by introducing metals or halides of the iron group into the vapor phase. A particularly advantageous feature of the chemical vapor phase deposition method is that non-porous coatings can be produced on the base.

In addition to this process, it is also possible to deposit or produce the silicides or the silicon carbide by cathodic spraying, electrophoretic deposition from suspensions, or chemical reduction.

The titanium bodies pretreated in this way are then provided with a PbO_2 coating by conventional anodic methods.

For this purpose, they are anodically polarized in aqueous 1 to 25 per cent strength lead(II) nitrate or lead(II) perchlorate solutions which can advantageously contain up to 0.5 percent of copper(II) nitrate and up to 0.2 percent of a wetting agent, for example based on ethoxylated alcohols. The current density is advantageously from 1 to 10 A/dm^2 and the temperature is advantageously from 40° to 80°C. Copper is a suitable cathode material. Good convection is advantageously ensured by stirring or circulation. The pH value of the solution, which decreases during the electrolysis, is preferably maintained within the range $1 < pH \leqslant 5$ by adding basic lead carbonate.

It is an advantage of the process that the intermediate layers thus produced can be re-used as a base for fresh PbO_2 coatings even after the PbO_2 has detached completely, which permits the use of the electrodes in secondary batteries.

EXAMPLE 1

An expanded metal mesh of titanium, of dimensions 100 × 40 mm, was corundum-blasted and coated with fine-grained titanium carbide, particle size from 40 to 90 μ, to a thickness of about 0.15 mm by means of a plasma torch, under a blanket or argon gas. In carrying out the coating, the plasma torch was operated with argon containing less than 0.5 percent of nitrogen. The expanded titanium metal was at a temperature of $\leqslant$ 60°C during coating.

The expanded titanium metal mesh pretreated in this way was dipped to a depth of 5 cm, along its longitudinal axis, into a solution which was prepared by dissolving 300 g of $Pb(NO_3)_2$, 3 g of $Cu(NO_3)_2 \cdot 3\ H_2O$ and 1 g of a wetting agent based on ethoxylated alcohols in water to make a total of 1 liter, and was coated at a temperature of from 60° to 70°C for 3 hours, using a current of 0.8 A ± 0.1 A (= 4 ± 0.5 A/dm^2). A copper sheet was used as the cathode. This treatment resulted in the deposition of 10.96 g of PbO_2.

The lead dioxide/titanium composite electrode thus produced was subjected, in approx. 20 percent strength sulfuric acid at from 30° to 35°C, to a current of 4 A (= 20 A/dm^2) for 24 hours, a current of 10 A (= 50 A/dm^2) for 24 hours and a current of 20 A (= 100 A/dm^2) for 20 hours. The cell potentials remained constant within ±0.2 V for the period of observation at a given current. The anode potential against a silver electrode (Ag/AgCl, saturated KCl) was approx. 2.1 V at a current density of 20 A/dm^2. The weight loss of the anode was about 0.6 mg/ampere hour at a current density of 100 A/dm^2.

EXAMPLE 2

An expanded titanium metal mesh was coated with tantalum carbide of particle size from 40 to 90 μ as described in Example 1.

The mesh was then immersed, as the anode, into a lead-II salt bath under the same conditions as in Example 1, causing the deposition of 10.68 g of PbO_2.

EXAMPLE 3

The mesh was first coated with tantalum boride of particle size from 40 to 90 μ and then with lead dioxide, using the methods described in Example 1. A total of 10.20 g of PbO_2 were deposited.

EXAMPLE 4

An expanded titanium metal mesh of dimensions 100 × 40 mm was corundum-blasted and coated with fine-grained titanium disilicide, particle size from 20 to 40 μ, to a thickness of about 100 μ by means of a plasma torch, under a blanket of argon gas. In carrying out the coating, the plasma torch was operated with argon containing less than 0.5 percent of nitrogen. The expanded titanium metal was at a temperature of $\leqslant$ 60°C during coating.

The expanded titanium metal mesh pretreated in this way was dipped to a depth of 5 cm, along its longitudinal axis, into a solution which was prepared by dissolving 300 g of $Pb(NO_3)_2$, 3 g of $Cu(NO_3)_2 \cdot 3\ H_2O$ and 1 g of a wetting agent based on ethoxylated alcohols in water to make a total of 1 liter, and was coated at a temperature of from 60° to 70°C for 3 hours, using a current of 0.8 A ± 0.1 A (= 4 ± 0.5 A/dm^2). A copper sheet was used as the cathode. This treatment resulted in the deposition of 8.36 g of PbO_2; the geometrical surface area was 0.2 dm^2.

The lead dioxide/titanium composite electrode thus produced was subjected to a current of 20 A (= 100 A/dm^2) in approx. 20 percent strength sulfuric acid at from 30° to 35°C for 100 hours. The weight loss of the anode at this current density was approx. 0.7 mg/ampere hour.

In the case of a lead dioxide/titanium composite electrode produced analogously to the above but having an intermediate layer of zirconium disilicide instead of titanium disilicide, the weight loss under these conditions was approx. 0.8 mg/ampere hour, and if the intermediate layer consisted of niobium disilicide the weight loss was again approx. 0.8 mg/ampere hour.

EXAMPLE 5

An expanded titanium metal mesh was coated with tantalum disilicide of particle size from 20 to 40 μ by the method described in Example 4.

The mesh was then immersed, as the anode, into a lead-II salt bath under the same conditions as in Example 4, causing the deposition of 9.84 g of PbO_2.

The weight loss of the lead dioxide/titanium composite electrode thus produced was approx. 0.9 mg/ampere hour under the conditions specified in Example 1.

EXAMPLE 6

Using the method described in Example 4, the mesh was first coated with chromium disilicide of particle size from 20 to 40 μ and then with lead dioxide. 11.85 g of PbO_2 deposited and the weight loss under the conditions specified in Example 1 was approx. 0.6 mg/ampere hour.

EXAMPLE 7

Using the method described in Example 4, the mesh was first coated with silicon carbide of particle size from 20 to 40 μ and then with lead dioxide. 9.41 g of PbO_2 deposited and the weight loss under the conditions specified in Example 1 was approx. 0.5 mg/ampere hour.

EXAMPLE 8

A titanium mesh as described in Example 4 was exposed to a vapor mixture of 1 mol of tetrasilane and 2 moles of tantalum pentachloride at +800°C, additional heat being supplied to the vapor mixture. To achieve a uniform coating, the reaction gases were fed into the reactor at different positions simultaneously. After a tantalum disilicide coating of 80 μ had deposited, the titanium mesh was coated with PbO_2 as described in Example 1, 10.08 g of PbO_2 being deposited. Under the conditions specified in Example 1, the weight loss was approx. 0.5 mg/ampere hour.

We claim:

1. A process for the manufacture of a lead dioxide/-titanium composite electrode by anodic deposition of lead dioxide on a titanium surface, wherein an intermediate layer of a carbide or boride of an element of subgroup 4 or 5 and/or a silicide of an element of subgroup 4, 5 or 6 of the periodic table of the elements and/or silicon carbide, is applied to the titanium surface before depositing the lead dioxide.

2. A process as claimed in claim **1,** wherein the carbide, boride, silicide and/or silicon carbide is applied by a plasma spraying process, a flame spraying process or vapor deposition.

3. A process as claimed in claim **1,** wherein a carbide or boride is applied in the form of a powder having a particle size of from 15 to 90 μ.

4. A process as claimed in claim **1,** wherein a silicide and/or silicon carbide is applied by chemical vapor phase deposition.

5. A process as claimed in claim **1** wherein the intermediate layer applied is from 60 to 200 μ thick if it contains less than 20 percent by weight of silicide and/or silicon carbide.

6. A process as claimed in claim **1** wherein a carbide or boride of titanium or tantalum or titanium disilicide, zirconium disilicide, tantalum disilicide, chromium disilicide or niobium disilicide is applied.

7. A process as claimed in claim **1,** wherein a silicide is applied which is modified with a metal or halide of a metal of the iron group and the content of the modifying material, based on the pure metal, does not exceed a total of 5 percent by weight.

8. A process as claimed in claim **1** wherein the intermediate layer applied is from 20 to 200 μ thick if it contains more than 20 percent by weight of silicide and/or silicon carbide.

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UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,880,728
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INVENTOR(S) : Wolfgang Habermann et al.

It is certified that error appears in the above–identified patent and that said Letters Patent are hereby corrected as shown below:

In the Heading, insert -- [30] Foreign Application Priority Data- September 5, 1973 Germany 2344645 and July 29, 1974 Germany 2436394--

Signed and Sealed this

fourth **Day of** *May 1976*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

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