United States Patent [19]
Masotti

[11] 3,773,639
[45] Nov. 20, 1973

[54] PROCESS FOR THE DEPOSITION OF METALS OR OXIDES ON A METALLIC SUPPORT BY CATHODIC SPUTTERING AND APPLICATIONS THEREOF

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[22] Filed: **Apr. 5, 1971**

[21] Appl. No.: **131,497**

[30] **Foreign Application Priority Data**

Apr. 21, 1970 France 7014327

[52] **U.S. Cl.** **204/192**
[51] **Int. Cl.** **C23c 15/00**
[58] **Field of Search** 204/192

[56] **References Cited**

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[57] **ABSTRACT**

A process for depositing a precious metal or its oxide on a metallic support by first submitting the metallic support to ionic bombardment in a rare gas atmosphere, then without cooling below 300°C. depositing the precious metal by cathodic sputtering conducted first in a rare gas atmosphere and then in an atmosphere of mixed oxygen and rare gas.

8 Claims, No Drawings

PROCESS FOR THE DEPOSITION OF METALS OR OXIDES ON A METALLIC SUPPORT BY CATHODIC SPUTTERING AND APPLICATIONS THEREOF

The present invention relates to the deposition of precious metals or their oxides onto a metallic support by cathodic sputtering so as to improve the properties of the support, such as its resistance to medium corrosion as well as electrochemical activity.

The composite product which is obtained can be used successfully as an electrode in electrolysis cells having a diaphragm or a mercury cathode, in fuel cells, and in desalination equipment.

The electrodes generally used as anodes are often made of graphite. Their use has always involved some drawbacks resulting from their wear which causes an increase of the voltage required for a good working of the electrolysis cell, because of the increase of the distance between the two electrodes and a contamination of the reaction medium.

Research has accordingly been conducted to develop anodes made of a metal which has a good resistance to the medium corrosion and which is coated with a precious metal which is electrochemically active. The anode is then subjected to a treatment promoting the activation. These anodes have stable dimensions and do not have the drawbacks recited above.

It has been proposed to make an anode of zirconium, or a zirconium-titanium alloy which is coated with platinum (Swiss patent No. 236,579 of Mar. 17, 1943).

It has also been proposed to make an anode of tantalum or of niobium coated with platinum (U.S. Pat. No. 2,719,797 of Oct. 4, 1955).

It has further been proposed to make an anode of titanium coated with platinum, the titanium being able to form an oxide barrier layer in electrolysis solutions, so as to protect the surface from corrosion at the places where platinum is porous. (French patent No. 1,200,841 of Apr. 8, 1958).

It has further been proposed to provide an electrode made of a metal capable of forming a barrier layer coated with a precious metal oxide (French patent No. 1,479,762 of May 12, 1966) or with a mixture of precious or not precious metal oxides (French patent No. 1,555,960 of Feb. 9, 1968).

Many processes have been suggested for increasing the adhesion of precious metal deposits ono the support metal and its elctrochemical activity. As examples, there may be mentioned depositions by vacuum evaporation, by thermal decomposition of metallic compounds, electrochemical or mechanical means.

Cathodic sputtering, a technique which has been known for a long time, has been found to give depositions having an excellent adhesion on the different supports which have been used, a good regularity, a good homogeneity, and purity of the deposited layer. The conditions under which this technique is undertaken have an influence particularly on the electrochemical properties of the electrodes so made.

It has now been found that cathodic sputtering, carried out under well defined conditions, has resulted in obtaining electrodes which are perfectly suited for their subsequent use.

An object of the present invention is to provide a process of deposition of a precious metal or its oxide on a metallic support by cathodic sputtering which comprises the steps of first submitting the metallic support

to a bombardment with ions in a residual atmosphere at reduced pressure of pure rare gas then without waiting a drop in the high temperature which results therefrom, depositing thereon a precious metal or its oxide by means of cathodic sputtering which is achieved first in a residual atmosphere at reduced pressure of pure rare gas. then in a mixed atmosphere of rare gas and oxygen.

This technique of cathodic sputtering falls into the category of metallic depositions by electrical discharge in a gas at low pressure.

The apparatus required comprises a vacuum enclosure, a pumping system, a high voltage electrical supply, and an introduction system for gas. The vacuum enclosure contains the cathode made of precious metal and the anode made of the metallic support on which the deposition is accomplished. Cathodic sputtering consists in extraction of atoms from the cathode under the action of the bombardment by the ions which are accelerated by the fall of cathodic potential.

The electrons which are emitted from the cathode which is under a high negative voltage are accelerated and produce ionization of the residual gaseous molecules which are in the space between the electrodes. As a consequence of the impact the positive ion is accelerated again to the cathode and an electron goes to the anode. The impact of the positive ion on the cathode produces the ejection of atoms which deposit on the anodic substrate.

The advantage of such a technique is to give coatings of high purity because of the possibility of degassing the high vacuum enclosure and varying the composition of the gaseous plasma which takes part in the discharge and has an influence on the structure and the properties of the deposited layers.

The metallic support before its introduction into the vacuum enclosure, is subjected to sanding, so as to give the metal a large developed surface favorable to good electrochemical properties an then to a scouring treatment so as to obtain the clean state required. This support is then introduced into the enclosure and the support and the precious metal to be sprayed are put in electrode positions. During the stage of ionic bombardment, the metallic support is put in cathodic position by applying to it the negative high voltage.

The metallic support acts for a time as a cathode and sputters. During this operation the precious metal is protected from support projections by a mask. The ionic bombardment of the support acts to degas and scour the surface which is to receive the deposition by eliminating oxide layers and traces of hydrocarbons, greases, etc. Thus, a support is obtained having a surface which is as near as possible of the pure metallic state. This ionic bombardment, which takes place at atmospheric temperature, is accomplished with an increase of temperature which reaches 300° to 500°C.

The metallic support is then rapidly disconnected from the high voltage supply and put in the position of an anode ready to receive the deposition resulting from the sputtering of the precious metal which is put in cathode position. The latter is freed of its mask and then connected to the high voltage supply. The cathodic sputtering onto the anode is undertaken immediately, while avoiding a sensible decrease of the anode temperature, being then in the region of 300°C. This maintenance of the temperature is very important for the electrochemical properties of the future electrode.

The first stage of the cathodic sputtering of the precious metal is done in a residual atmosphere of pure rare gas for 30 seconds to 5 minutes. This time is sufficient to give the future electrode good properties of resistance to corrosion because the attached layer so formed is very adherent on the metallic support with formation of a diffused microlayer. The presence of rare gas avoids the formation of a metal oxide layer on the support surface. So there is obtained a support very near the metallic state, having a surface without any contamination, coated with a hard and compact layer of precious metal.

When the deposited layer is sufficient to protect the metallic surface of the support from corrosion, the second stage of the cathodic sputtering is accomplished in a residual atmosphere of rare gas and oxygen, the ratio of partial oxygen pressure in the mixture being between 0.1 and 25 percent. The introduction of oxygen at this stage of the process is very significant because it leads to a deposition of precious metal or its oxide having a particular physical aspect. Thus, there is obtained a composition of divided microcrystalline and porous form, which does not need any further activating treatment in order to present good electrochemical properties. It should be pointed out that in the case of precious metal sputtering with a given rate of oxygen in rare gas the metal was not oxidized. A porous precious metal was obtained, having a lower density than normally, this resulting from oxygen adsorption by the metal without oxide formation. Generally a coating of precious metal or oxide in microcrystalline form is obtained, with a large specific surface, this last property being very important because the electrochemical activity is directly proportional to this surface.

Although the use of argon will be specified in detail hereinunder, it should be understood that the argon can be replaced entirely or partly by any rare gas.

As metallic support constituting the anode a metal capable of forming a barrier layer in electrolysis solutions, can be used, for example, tantalum, zirconium, niobium, titanium and their alloys. There can also be used a corrodable support which is a good conductor of electricity, such as copper, steel, aluminum previously coated with a protecting layer of these metals sufficient to form a barrier layer of film.

The precious metals constituting the cathode and which are to be deposited on the anode are metals of the platinum group, that is, platinum, iridium, palladium, ruthenium, osmium, rhodium, or their alloys or oxides, employed alone or mixed.

The ionic bombardment on the metallic support, when it is connected as a cathode must be done for a sufficient period so as to allow a good degassing and scouring of the surface. Generally 10 to 30 minutes are enough to obtain the required result.

The duration of cathodic sputtering of the precious metal in pure argon phase must be sufficient to obtain a microlayer of diffusion allowing a good protection of the metallic support. A period of from 30 seconds to 5 minutes generally gives the required result. The period of this phase could be increased, but this would have no particular practical advantage, because the precious metal layer would be increased; thus resulting in an economical disadvantage without contributing a particular technical advantage.

The second phase of cathodic sputtering in mixed argon-oxygen atmosphere is conducted until the deposition of a precious metal or its oxide in a divided and porous state of 0.1 to 1 micron thick is obtained. This thickness of the layer results in an electrode which has a suitable activity life. It is generally reached with a sputtering time of 2 to 30 minutes in mixed atmosphere of argon-oxygen. When this deposition is finished the anode so obtained is allowed to cool down in the vacuum enclosure.

The percentage of oxygen is important. A minimum of oxygen is required to produce an electrode with a good activity. However, it is not necessary to use too high a percentage of oxygen which does not improve the electrochemical activity of the electrode, but on the contrary has the tendency of decreasing the yield of sputtering of the precious metal or its oxide and to increase abnormally the period of sputtering.

The cathodic sputtering which is only done in pure argon atmosphere can be used for depositing a metal which forms a barrier layer on a good electrical conductor support such as copper, iron, or aluminum. In such a case, the conductor metal shows a good passivation towards corrosion agents and can be used as a metallic support on which a deposition of precious metal or its oxide is done by cathodic sputtering according to the present invention.

The cathode sputtering of the precious metal which is done directly in the mixed atmosphere of argon-oxygen, leads to an electrode having no protective diffusion microlayer which comes from the deposition in pure argon atmosphere. The entire deposit has a microcrystalline and porous form. The electrode of this kind presents a correct polarization curve in an electrolysis bath but its activity life is reduced, its electrochemical activity decreases rapidly, due to the peeling tendency of the metal deposit. An electrode of the same kind is obtained if after the phase of ionic bombardment of the metallic support, the temperature is permitted to drop down to about 50°C. before the cathodic sputtering of the precious metal.

The following examples are representative of the invention without limitating it.

EXAMPLE 1

A titanium plate which is 30 millimeters by 50 millimeters and 3 millimeters thick was cleaned by sanding, brushed under running water, then scoured in trichloroethylene vapors. It was then rinsed, with methanol and then introduced into a vacuum enclosure. The pressure in the enclosure was of 10^{-6} torr.

The phase of ionic bombardment of this titanium plate was accomplished by connecting it to a current source with a voltage of 3,000 volts. After having introduced pure argon at a partial pressure of 40×10^{-3} torr, the ionic bombardment intended to clean the titanium was conducted for 30 minutes, under a sputtering power of 1.8 watt/cm^2. The temperature of the titanium plate was stabilized at 350°C. at the end of the operation. During the preliminary phase the platinum cathode has been protected by a mask movable by sliding.

The titanium plate was then disconnected from the high voltage which was applied to the platinum cathode. The process took place rapidly so as to avoid the temperature dropping which was at that time between 300° to 350°C.

The first phase of platinum deposition on the titanium plate was done in pure argon atmosphere for 2

minutes at a temperature about 300°C. The deposited platinum had a high density and had no porosity.

An oxygen stream was then introduced so as to form an argon-oxygen composition in the ratio of 80/20. The platinum deposition was then carried on until the platinum layer thickness of about 2,500 Angstroms was obtained. This thickness was measured with a profilometer on glass plate samples. The two phases of the platinum deposition were accomplished under a voltage of 3,000 volts and a power of 2 watts/cm^2. The electrode was taken out of the enclosure after having been cooled for thirty minutes.

The second phase of the platinum deposition in mixed argon-oxygen atmosphere resulted in the platinum in its active form characterized by a lower density compared with that of solid platinum and by a large electrical resistivity, by a very developed specific surface, marked with respect to catalytic activity. The active platinum has a cubic structure with centered faces without oxide after analysis by X ray diffraction, by reflection and transmittance, by electronic diffraction, and by infrared spectrometry.

An examination of the active deposition surface has been accomplished with an electron microscope having a "Stereoscan" scanning which revealed a porous microcrystalline structure. This confirms the density, electrical resistivity and specific surface values that were found.

The platinized titanium electrode which has been made with this plate was introduced into an electrolysis cell containing a 300 grams per liter solution of sodium chloride. The electrochemical characteristics were determined at 90°C., from the polarization curve and from the specific consumption of platinum during a prolonged working under a current density of about 2 amperes/cm^2.

The following were measured:

A minimal discharge voltage of chlorine compared with the saturated calomel electrode E_o = 1.054 volt/SCE (saturated calomel electrode)

A polarization resistance of 0 120 ohm.cm^2

A platinum consumption less than 100 milligrams per metric ton of chlorine produced.

COMPARATIVE EXAMPLES 2, 3 AND 4

These examples were carried out similarly to example 1, but under different conditions from those of the process according to the invention.

The preliminary phase of ionic bombardment of the titanium plate was done under the same conditions as example 1.

After the ionic bombardment the temperature was 300°C.

The conditions of platinum depositing were varied.

EXAMPLE 2

The platinum deposition was done immediately, without cooling, but directly in a mixed argon-oxygen atmosphere having a ratio of 80/20. In such a way, no protective non-porous diffusion microlayer, of high density platinum formed, but a microlayer of active highly porous platinum was directly obtained. This deposition was done under a voltage of 3,000 volts and power of 2 watts/cm^2 for 4 minutes and led to a coating thickness of 2,200 Angstroms.

The electrochemical characteristics of the platinized titanium electrode measured under the conditions of example 1 were as follows:

minimal discharge voltage of chlorine : E_o = 1.056 volts/SCE

polarization resistance : 0.105 ohm per cm^2

platinum consumption 180 milligrams/ton of chlorine produced. EXAMPLE 3

The platinum deposition was accomplished after cooling for 30 minutes down to 30°C., firstly for 2 minutes in pure argon then for 2 minutes in a mixed argon-oxygen atmosphere (80/20) under the same voltage and the same power as examples 1 and 2. The deposited platinum was 2,000 Angstroms thick.

The platinized titanium electrode so made the following electrochemical characteristics measured under the same conditions as examples 1 and 2:

minimal discharge voltage of chlorine E_o = 1.065 volt/SCE

polarization resistance 0.135 ohm per cm^2

platinum consumption 600 milligrams/ton of chlorine produced.

EXAMPLE 4

The deposition of platinum was accomplished after cooling for 30 minutes, at a temperature of 30°C., directly in a mixed argon-oxygen atmosphere (80/20) under the same voltage and the same power as in examples 1, 2 and 3. The deposited active platinum was 2,200 Angstroms thick after a 4 minutes' sputtering.

The platinized titanium electrode obtained had the following electrochemical characteristics, measured under the same conditions as examples 1, 2 and 3:

minimal discharge voltage of chlorine : E_o = 1.060 volt/SCE

polarization resistance 0.105 ohm per cm^2

platinum consumption 1,100 milligrams/ton of chlorine produced.

This comparison shows the advantage of a platinized titanium electrode made by the process according to the invention, which is resistant to a prolonged working in an electrolysis cell, the amount of platinum consumed being very low.

EXAMPLE 5

The platinum deposition on a tantalum plate which was 30 millimeters by 50 millimeters and 3 millimeters thick was done under the same conditions as in example 1, the titanium being replaced by tantalum which is subjected in the first phase to an ionic bombardment under the same conditions. The total thickness of the platinum deposited, platinum microlayer and porous platinum, was of 2,000 Angstroms. The use of this platinized tantalum plate as an electrode under the conditions of example 1, led to the following characteristics:

minimal discharge voltage of chlorine : 1.062 volt/SCE

polarization resistance 0.051 ohm per cm^2

platinum consumption lower than 150 mg/ton of chlorine produced.

EXAMPLE 6

A titanium plate of the same type as in example 1, was subjected to an ionic bombardment under the same conditions, the temperature being 300°C. A ruthenium cathode was used in order to achieve the cathodic sputtering on the titanium plate. The deposition was ac-

complished in a first phase in an argon atmosphere for 45 seconds under a partial pressure of 50×10^{-3} torr and a sputtering power of 2.1 watts/cm^2 and then in a mixed argon-oxygen atmosphere in the ratio 99.8/0.2, for 5 minutes at the same partial pressure, with a sputtering power of 1.9 watts/cm^2. The deposited layer was 2,700 Angstroms thick.

The use of the plate as an electrode under the conditions of example 1 gave the following electrochemical characteristics:

minimal discharge voltage of chlorine E_o = 1.066 volt/SCE

polarization resistance 0.07 ohm per cm^2

ruthenium consumption : 58 mg/ton of chlorine produced.

It will be obvious to those skilled in the art that various changes may be made without departing from the scope of the invention and the invention is not to be considered limited to what is described in the specification.

What is claimed is:

1. A process for coating a metallic substrate by cathodic sputtering of a precious metal which comprises the steps of first submitting the metallic substrate to an ionic bombardment in a residual atmosphere of a pure rare gas, then, while at an elevated temperature and without exposure to another atmosphere, cathodic sputtering on said metallic substrate the precious metal first in a residual atmosphere of said pure rare gas and then in a residual atmosphere of oxygen admixed with said rare gas.

2. A process according to claim **1** in which said cathodic sputtering is conducted at a temperature from 300° to 500°C.

3. A process according to claim **1** in which the ionic bombardment of the metallic substrate is effected for 10 to 30 minutes.

4. A process according to claim **1,** in which said cathodic sputtering in the residual atmosphere of said rare gas is effected for 30 seconds to 5 minutes.

5. A process according to claim **1,** in which the cathodic sputtering in a residual mixed atmosphere of said rare gas and oxygen is effected for 2 to 30 minutes, the partial pressure of oxygen being from 0.1 to 25 percent.

6. A process according to claim **1,** in which the metallic substrate is a metal selected from the group consisting of tantalum, zirconium, niobium, titanium and their alloys.

7. A process according to claim **1** wherein the precious metal to be sputtered is selected from the group consisting of platinum, iridium, palladium, ruthenium, osmium, rhodium, and their alloys, alone and mixed.

8. A process according to claim **1** in which said ionic bombardment is effected for 10 to 30 minutes, said cathodic sputtering is conducted at a temperature from 300° to 500°C. for 30 sec. to 5 minutes in the residual atmosphere of said rare gas and then for 2 to 30 minutes in the residual mixed atmospheres of said rare gas and oxygen, the partial pressure of oxygen being from 0.1 to 25 percent.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,773,639 Dated November 20, 1973

Inventor(s) Robert M. Masotti

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

Column 1, line 47, the word "ono" should be "onto".

Column 2, line 39, the word "an" should be "and".

Column 4, line 26, the word "cathode" should be "cathodic".

Column 6, line 8, "EXAMPLE 3" should be on a separate line.

Signed and sealed this 9th day of April 1974.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents