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(54) **Title:** METHOD FOR EXFOLIATING COATING LAYER OF ELECTRODE FOR ELECTROLYSIS

(57) **Abstract:** The present invention relates to a method to effectively exfoliate a coating layer from the surface of the conductive substrate comprising titanium or titanium alloy substrate material of a used electrode for electrolysis comprising an insoluble metal electrode having the coating layer containing electrode substance comprising noble metals and/or their metal oxides on the surface of the used electrode substrate comprising valve metals, such as titanium and tantalum or valve metal alloys and then to recover the electrode substances and/or electrode substrates for recycling use. A method for exfoliating the coating layer from the surface of the electrode substrate, characterized in that in the exfoliation method for the coating layer from the surface of the electrode substrate, wherein the insoluble metal electrode surface having the coating layer containing electrode substance comprising noble metals and/or metal oxides thereof on the surface of the electrode substrate comprising valve metals including titanium and tantalum or valve metal alloys is treated, in succession, with the alkali treatment process using a caustic alkali aqueous solution, the heating and baking process and the acid treatment process by immersion in hydrochloric acid, sulfuric acid, nitric acid or the mixture thereof, the alkali treatment process is conducted by applying an alkali treatment solution prepared by adding thickener to the caustic alkali aqueous solution.



DESCRIPTION

Title of Invention

METHOD FOR EXFOLIATING COATING LAYER OF ELECTRODE FOR
5 ELECTROLYSIS

Field of the Invention

The present invention relates to a method to effectively exfoliate a coating layer from the surface of the conductive substrate comprising titanium or titanium alloy
10 substrate material of a used electrode for electrolysis comprising an insoluble metal electrode having the coating layer containing electrode substance comprising noble metals and/or their metal oxides on the surface of the electrode substrate comprising valve metals, such as titanium and tantalum or valve metal alloys and then to recover the conductive substrate of noble metals and/or titanium or titanium alloy substrate
15 material for recycling use.

Background Art

This kind of electrode for electrolysis, however, has a problem that in a certain time lapse of use, corrosion is generated in the interface between the electrode
20 substrate comprising valve metals, such as titanium and tantalum or valve metal alloys and the coating layer including the electrode substance comprising noble metals and/or noble metal oxides thereof, which forms a passive layer on the surface of the substrate, leading to a poor reactivation processing. As a result, the substrate has to be shaved off until a new surface appears or an electrode has to be newly
25 manufactured from the electrode material.

Among electrodes for electrolysis, in the case of an electrode for oxygen generation, interface corrosion does not occur between the electrode substrate and the coating layer, when the electrode for electrolysis is applied having a thin film of 0.5

- 3 μm comprising such metals as tantalum and niobium formed by the vacuum sputtering, including ion plating, on the surface of the electrode substrate comprising valve metals, such as titanium and tantalum, or valve metal alloys, and an electrode coating layer containing iridium oxide coated on the surface of the thin film. (As citation, refer to PTL 1.)

However, if this electrode for oxygen generation is applied for the electrolytic reaction to produce copper foil, electrolytically, chemical compounds containing lead and antimony in the electrolyte for the electrolytic copper foil production deposit on the surface of the electrode for electrolysis. At the electrolytic reaction, lead in the electrolyte deposits as lead oxide, which is a good conductor, but antimony deposits as antimony oxide, a poor conductor. Meanwhile, lead oxide, which is conductive, turns to lead sulphate, non-conductor, at the time of shut-down of electrolysis operation. Moreover, lead and antimony, which have deposited on the surface of electrode fall off from the surface of the electrode for electrolysis at the time of start-up and shut-down and during of electrolytic reaction. As a result, the afore-mentioned electrode for oxygen generation has a defect as an electrode for electrolysis that electric current distribution becomes uneven, causing a poor quality in thickness of copper foil and a long-time, develop continuous service as an electrode for electrolysis is not available.

In such case, deposit on the electrode surface including lead and antimony is scraped off from the surface of the electrode for oxygen generation used in electrolytic reaction with Scotch-Brite (Registered trademark), which is an abrasive manufactured by Sumitomo 3M Limited, for reactivation of the electrode for electrolysis. However, it is found that if the electrode for oxygen generation is used for consecutive 3 months, reactivation of the electrode for electrolysis is difficult by the abrasive.

It has been well known that an insoluble metal electrode with a coating of

ruthenium oxide or iridium oxide on the surface of conductive titanium substrate is widely applied in the industrial electrolysis represented by chlor-alkali electrolysis. The life of this electrode is remarkably long, often for more than 10 years as it is. However, it has been experienced that electrode substance only deteriorated because of a system trouble or a non-conductive form was formed between the coating layer and the substrate titanium, leading to malfunction as electrode which is similar in the case of the electrode for oxygen generation, in relatively a short period of time, even without deterioration of electrode substance.

The various reactivation methods are proposed to cope with it. In case that electrode substrate is adequately thick and in plate form, the electrode surface is sharpened by manufacturing, and a residual substance is removed by manufacturing after a surface affix was removed by blast processing, and the surface was made to decrease naturally by acid or alkali treatment, a surface residual substance is removed. A method of these has been used alone or in combination. In such cases of processing, titanium or titanium alloy is used as the substrate may be recycled, but the coating layer containing noble electrode substance cannot be substantially recovered, since such substance is small in amount, compared with processing or by-product materials by machine processing or blast treatment. In other words, trial of the electrode substance and/or the electrode substrate recovery was carried out and possibility was confirmed, but in most cases, recovery cost becomes almost more expensive and has not been substantially practiced from a point of economy. Another trial has been chemical immersion in alkali molten salt, from which substrate titanium or titanium alloy can be recovered, but the coating layer containing electrode substance dissolves in excessive molten salt, proving technical feasibility of recovery but not economically.

If recovering only the coating layer containing electrode substance is considered, such methods have been proposed: a chemical peeling process after rolling treatment

to facilitate exfoliating mechanically or a process of high temperature heating followed by quenching. By these methods, electrode substance can be recovered, but the titanium which cannot be applied as it is as substrate must be re-dissolved for recycling as raw material.

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In recent years, acquisition of titanium and titanium alloy substrate has been difficult due to a hike in price and supply shortage, from which recovery is desired for recycle use as it is. In addition, platinum group metal which is contained in the coating layer with electrode substance is rare metal which is extremely expensive, and is expected to be recovered together, but the recovery has been impossible by the conventional methods, with some exceptions. For example, if the substrate is thick enough, surface grinding is applicable for recovery, but if the thickness is 1 mm or less, grinding is practically impossible. Even if it is achievable, the substrate becomes thin for satisfactory current supply or may warp, and reuse as substrate is extremely limited. A lot of these recovery technologies are suggested. The following are representative well-known technologies.

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PTL 1 discloses that the coating is separated by dissolving the surface of the electrode substrate with corrosive acid as an exfoliation method of a coating layer containing electrode substance and the coating and the substrate are recovered. However, exfoliation of the coating is not easy in reality because it often happens that there is a stable and strong oxide existing between the electrode substrate and the coating, or chemical bonding occurs between the coating layer containing the electrode substance and the substrate metal.

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PTL 2 shows a method to recover the substrate and the coating in such a manner that highly concentrated alkali aqueous solution is coated on the surface of electrode, followed by heating and dissolving the coating layer containing the electrode substance in an alkali aqueous solution. This method, however, has such problems

that considerable depletion of the titanium substrate occurs at the same time in the alkali aqueous solution and the coating dissolves in alkaline matrix, which makes recovery difficult.

5 PTL 3 and PTL 4, as well, disclose a method for recovering the coating layer containing electrode substance after the coating layer containing electrode substance is exfoliated physically and/or chemically. As a method for exfoliation, PTLs 3 and 4 indicate acid corrosion or grinding of the substrate, but these methods recover the coating through consumption of the substrate, which may lead to an excessive degree
10 of depletion for recycle of the substrate.

PTL 5 discloses a method for exfoliation of the electrode substance through corrosion of the titanium surface by acid treatment after adhesion between the coating layer containing electrode substance and the titanium is physically weakened by
15 applying roll processing to the used electrode. This method is also effective to simultaneously recover the titanium substrate and the coating layer containing electrode substance, but still the titanium cannot be recycled as it is, requiring re-dissolution for recovery.

20 PTL 6 shows a method wherein the electrode is cut into pieces and subjected to barrel polishing in order to separate and recover coating and the substrate titanium. This method is relatively simple and effective, but the substrate cannot be recycled as it is.

25 In addition, PTL 7 proposes such processes as (1) caustic alkali aqueous solution is coated on the electrode surface as pre-treatment, (2) retaining it for 10 - 60 min. at 350 - 450 degrees Celsius for reaction, and (3) immersing it in hydrochloric acid, sulfuric acid, and nitric acid, or the mixture thereof. Even by this method, coating substance cannot be separated from the electrode substrate and the electrode

substrate cannot be used as it is for recycling, from a point of the keeping of the caustic solution. As above-mentioned, the conventional methods do not provide a method to recover the coating layer containing electrode substance and the substrate metal at the same time. Thus, simultaneous recovery of titanium or titanium alloy of the electrode substrate as substrate as it is and of the coating layer containing electrode substance has not been substantially practiced at all.

Citation List

10 Patent Literature

PTL 1: JP59-123730A

PTL 2: JP2002-088494A

PTL 3: JP2002-212650A

PTL 4: JP2002-194581A

15 PTL 5: JP2001-294948A

PTL 6: JP2001-303141A

PTL 7: JP2008-081837A

Summary of the Invention

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Problems to be Solved by the Invention

The present invention aims to provide a method for separating the coating layer containing electrode substance comprising noble metals and/or metal oxides thereof coated on the surface from the surface of the electrode substrate comprising valve metals including titanium and tantalum or valve metal alloys, to recover the electrode substrate comprising valve metals including titanium and tantalum or valve metal alloys in a state enabling recycle use, and to recover the electrode substance efficiently.

Means for Solving the Problem

As the first solution to solve the above-mentioned problems, the present invention provides a method for exfoliating the coating layer from the surface of the electrode substrate, characterized in that in the exfoliation method for the coating layer from the surface of the electrode substrate, wherein the insoluble metal electrode surface having the coating layer containing electrode substance comprising noble metals and/or metal oxides thereof on the surface of the electrode substrate comprising valve metals including titanium and tantalum or valve metal alloys is treated, in succession, with the alkali treatment process using a caustic alkali aqueous solution, the heating and baking process and the acid treatment process, the alkali treatment process is conducted by applying an alkali treatment solution prepared by adding thickener to the caustic alkali aqueous solution.

As the second solution to solve the above-mentioned problems, the present invention provides the method for exfoliating the coating layer from the surface of the electrode substrate, characterized in that thickener comprising natural polysaccharide is applied.

As the third solution to solve the above-mentioned problems, the present invention provides the method for exfoliating the coating layer from the surface of the electrode substrate, characterized in that thickeners comprising bio gum or guar gum derivatives or cellulose derivatives are applied as the natural polysaccharide thickener.

As the fourth solution to solve the above-mentioned problems, the present invention provides the method for exfoliating the coating layer from the surface of the electrode substrate, characterized in that thickener comprising carboxymethyl cellulose (hereafter called "CMC") is applied as thickener.

As the fifth solution to solve the above-mentioned problems, the present invention provides the method for exfoliating the coating layer from the surface of the electrode substrate, characterized in that xanthan gum (hereafter called "XAG") is applied as thickener.

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As the sixth solution to solve the above-mentioned problems, the present invention provides the method for exfoliating the coating layer from the surface of the electrode substrate, characterized in that the addition ratio of the thickener in the alkali treatment solution is 0.2 mass % or more but 1 mass % or less.

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As the seventh solution to solve the above-mentioned problems, the present invention provides the method for exfoliating the coating layer from the surface of the electrode substrate, characterized in that the addition ratio of the thickener in the alkali treatment solution is 0.4 mass % or more but 1 mass % or less.

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Advantageous Effect of the Invention

According to the present invention, the electrode substance can be separated from the electrode substrate effectively and at a high yield. At this time, the electrode substrate is not consumed more than required to protect the electrode substrate itself and the stabilized electrode substance does not elute by the molten salt treatment at a relatively low temperature condition and can be separated and recovered as a piece of electrode substance or powder. In addition, because the substrate metal mainly comprising titanium or electrode substance little flows out into the acid, consumption of acid, which is used only neutralization for residual alkali, can be minimized. The present invention is applicable to various electrodes for electrolyses not being limited to electrodes for oxygen generation.

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Brief Description of Drawings

[Fig. 1] Fig. 1 shows an image indicating degree of exfoliation of one of the

examples by the present invention.

[Fig. 2] Fig. 2 shows an image indicating degree of exfoliation of one of the examples by the present invention.

[Fig. 3] Fig. 3 shows an image indicating degree of exfoliation of one of the examples by the present invention.

[Fig. 4] Fig. 4 shows an image indicating degree of exfoliation of one of the examples by the present invention.

[Fig. 5] Fig. 5 shows an image indicating degree of exfoliation of one of the examples by the present invention.

[Fig. 6] Fig. 6 shows an image indicating degree of exfoliation of the comparative example by the present invention.

Best Mode for carrying out the Invention

The present invention relates to a separation recovery method of the electrode substance and the electrode substrate which exfoliates the coating layer including the electrode substance comprising noble metals and/or noble metal oxides thereof from the surface of the electrode substrate comprising valve metals including titanium and tantalum or valve metal alloys, and then recovers and re-use the electrode substrates and/or the electrode substance; more in detail, the present invention relates to the recovery method for the insoluble electrode consisting of:

(1) Process to clean the surface,

(2) Alkali treatment process to treat at least the electrode coating surface with alkali treatment solution comprising caustic alkali aqueous solution,

(3) Baking process for facilitating reaction while keeping the caustic alkali at around fusion point, and

(4) Acid treatment process by immersing in acid.

By these processes performed to the electrode from which adhering substance or impurities on the surface are removed, corrosion of the substrate metal and the electrode substance is minimized between the substrate metal and the electrode

substance, making the interface to be corroded selectively to separate and recover the substrate, and at the same time, the electrode substance can be separated and recovered stably as solid powder.

5 More in particular, the first step is to clean the surface by a suitably applicable method depending on adhering substance. For instance, in case of the electrodes used in the chlor-alkali electrolysis by the ion exchange membrane process, adhering substance usually is little, and therefore, the surface is washed with water or immersed in a dilute hydrochloric acid solution for acid cleaning. For the electrodes
10 used for copper foil production, the surface is often contaminated with chemical compounds of heavy metals, such as lead sulphate and antimony oxide and acid cleaning is conducted. As required, such compounds can also be removed as alkali salt by 10 - 30 mass % alkali cleaning followed by immersing in an inorganic acid solution. By combining these methods, cleaner surface can be obtained.

15 In succession, the alkali treatment process is performed with the alkali treatment solution of a caustic alkali aqueous solution. In this alkali treatment process, alkali treatment solution is coated, at least, on the surface of the electrode coating. Caustic alkali used for the alkali treatment solution is not specifically specified, but caustic
20 soda is most preferable in view of its high reactivity and easy availability. Mixture of caustic soda and caustic potash is also applicable. The actual reaction in the coating of alkali treatment solution on the surface of the electrode is close to a molten salt reaction, and it is desirable to attach at high concentration. Because the viscosity of alkali treatment solution is low and it flows relatively easily in case that the alkali
25 treatment solution is coated on the surface of the electrode, and thus, it is not easy for the coated alkali treatment solution to be attached to the surface of the electrode stably. For this reason, in the alkali treatment process, it is necessary to keep the alkali treatment solution to stay on the surface of the electrode stably. The coating, for instance, is made with an aqueous solution of caustic soda at 50 - 60 mass% to the

electrode to the area where the electrode substance exists. It is also possible that at least the electrode coating surface is immersed for the same purpose in the alkali treatment solution of a similar degree of concentration so that the surface is made acclimated to alkali. The coating should be covered over the entire surface of the electrode and is made impregnated sufficiently. Usually, the electrode surface is repellent to caustic solution. It is desirable that the electrode surface is brushed till the surface becomes adequately wet or is immersed in the solution for a certain period of time. But if only caustic alkali is applied, it is hard to achieve expected alkali treatment because caustic alkali does not attach sufficiently to the surface of the electrode to be treated.

Therefore, in the present invention, thickener is added to the caustic alkali solution to prepare the alkali treatment solution. As thickener, a thickener containing CMC or XAG is applied.

In the present invention, the alkali treatment process is performed using alkali treatment solution prepared by adding the thickener to the caustic alkali solution. As a result, adhesion of caustic alkali on the coating layer increases and exfoliation effect improves. In the present invention, the dosage of the thickener is controlled to 0.2 mass% or more, which further increases adhesion of caustic alkali on the coating layer, leading to enhanced exfoliation effect. Furthermore, it is found that exfoliation effect is made complete by the dosage of the thickener controlled to 0.4 mass% or more. On the other hand, the dosage of the thickener is preferably 1 mass% or less, because if it exceeds 1 mass%, gelation of caustic alkali immersion liquid proceeds and handling of it becomes difficult. Moreover, the dosage of the thickener is more preferably controlled to 0.5 mass% or less, and then, the gelation of caustic alkali immersion liquid can be suppressed and the handling of it becomes easier.

As the thickener, substance which represents thickening effect in alkali solution is applied. For this kind of thickeners, it is preferable to contain natural polysaccharide thickener. As natural polysaccharide thickener, bio gum or guar gum derivatives or

cellulose derivatives, etc. are applicable. Among these thickeners, the following are especially preferable.

- 1) Bio gum: XAG
- 2) Guar gum derivative: Guar gum
- 5 3) Cellulose derivative: CMC
- 4) Others: Carrageenan, pectin

Usually, the electrode surface on which the thickener is coated is left for 10 - 30 min. at room temperature, and then dried at 60 - 200 degrees Celsius. By this
10 operation, most of the water in the caustic alkali evaporates and anhydride of caustic alkali deposits on the surface. Drying time is not specifically specified but 10 - 30 min. is preferable. However, the drying process is not essential. In case that alkali solution is uniformly maintained on the electrode surface, the drying process can be eliminated and the following heating process will serve the same function.

15 Then, the electrode surface is heat-treated at a temperature slightly higher than the melting point of caustic alkali. Namely, in case of caustic soda, the melting point is about 330 degrees Celsius and then the preferable temperature is in the range of 350 - 450 degrees Celsius. At this temperature, reaction is made to occur in 10 - 60 min.,
20 usually in 30 min. The reaction mechanism is not clear, but later on, the electrode substance being reacted with acid, can be separated. Then, it is considered that alkali ion in caustic alkali reacts with the electrode substance, the oxide existing between the electrode substance and the substrate, and the surface of the substrate titanium to become alkali complex salt. Moreover, in view of the fact that elution of electrode
25 substance or titanium substrate is extremely small in volume, reaction with the oxide between the electrode substance and the substrate seems to occur selectively. After such treatment, the electrode is left to cool down. The cooling can be done in the furnace, but in view of efficiency, the cooling is preferable to be made in the atmosphere outside the furnace. It is also possible to advance to the following

treatment of inorganic acid immersion without the cooling; in that case, splash of acid must be cautioned.

Then, the electrode thus treated with alkali is immersed in the inorganic acid solution including that of nitric acid, hydrochloric acid or sulfuric acid. The concentration of the inorganic acid is not specifically specified, but usually, diluted acid around 10 - 20 mass % is preferable. The temperature of inorganic acid also is not specified but to expedite the reaction, the inorganic acid solution is preferably heated to 40 degrees Celsius or more. By the immersion treatment, alkali titanate dissolves in the acid and at the same time, the electrode substance exfoliates and separates from the substrate metal comprising titanium or titanium alloy. At this time, the exfoliation can be accelerated by stirring of the acid solution or brushing to the electrode surface for better liquid contact. One cycle of treatment can usually separate the electrode substance from the substrate metal sufficiently, but as required, repetition of two to three cycles from the alkali treatment to the baking can separate them completely. The electrode substance at this stage is stabilized by heating and does not dissolve in the acid solution and can be recovered as precipitate. By this method, titanium or titanium alloy as substrate metal does not deplete and the electrode substance can be recovered as an oxide solid.

For the acid treatment, any of inorganic acids, namely hydrochloric acid, nitric acid and sulfuric acid or mixed acid is applicable. However, in view of solubility of the exfoliation, nitric acid or hydrochloric acid is preferable. In the case of sulfuric acid, caution is needed when it used repeatedly because electrode substrate dissolves slightly or electrode substance may precipitate in the solution as titanium sulfate. But it does not become the problem in particular. But, if such precipitation occurs, it is apparent that operation should be performed so that such precipitation is eliminated because the separation from the electrode substance becomes troublesome.

The oxide solid which is separated electrode substance can be recovered under usual conditions. For instance, platinum group metal component in the electrode substance is reduced by hydrogen reduction and metalized for recovery. If the component is ruthenium, it is recovered as ruthenium chloride acid in such a manner that after metallization, it is vaporized as RuO_4 by heat-oxidation in hypochlorite solution, and trapped in hydrochloric acid. If the component is iridium, it is transformed into chloroiridates with chlorine gas together with alkali chloride and then alkali is separated and the iridium component is recovered as hexachloroiridic acid hexahydrate or iridium chloride. For others, recovery is available by dissolving in aqua regia. Also, electrolytic recovery is possible. In this case, titanium oxide or tantalum oxide, which is the same electrode substance, is not reduced by hydrogen, and therefore, is neither chlorinated nor dissolved; and then complete separation from platinum group metals is possible. Part of electrode substance can be dissolved in acid. In this case, recovery is almost completely possible in such a way that it is precipitated as ammonium salt of the platinum group metal through neutralization by adding ammonia to used acid, followed by filtration separation. The recovery can be conducted either separately from the oxide precipitate in the early period, or simultaneously with the oxide precipitate after ammonia treatment by precipitate filtration.

Then, the present invention is explained by the example and the comparative example concretely, but the present invention is not the thing which should be limited to these examples.

Example

The electrode substrate was treated with the cleaning process in such a manner that the surface of titanium plate was subjected to dry blast processing with iron grit (#120 size), followed by acid cleaning for 10 min. in an aqueous solution of 20 mass% sulfuric acid at 90 degrees Celsius. The cleaned electrode substrate is installed to an

arc ion plating device to give spattering coating with pure titanium material. Coating conditions are as follows.

Target: Titanium disc (Rear surface was water-cooled.)

Degree of vacuum: 3.0×10^{-1} Torr (Ar gas replacement introduced)

5 Applied Power: 25V-150A

Substrate temperature: 150 degrees Celsius (at Spattering)

Time: 35 min.

Coating thickness: 2 microns

10 The X-ray diffraction after the spattering coating shows a sharp crystalline peak belonging to the substrate bulk and a broad pattern belonging to the spattering coating, indicating that the coating was amorphous.

The coating solution prepared by dissolving iridium tetrachloride and tantalum
15 pentachloride in a 35 mass% hydrochloric acid solution is applied using a brush on the substrate treated with the spattering coating treatment, followed by drying. The substrate is processed by thermal decomposition coating in an electric furnace of air-circulation type for 20 min. at 550 degrees Celsius to form an electrode coating layer in solid solution comprising iridium oxide and tantalum oxide. The amount of
20 coating is specified so that the thickness of the coating per brush is equivalent to approx. 1.0 g/m^2 as iridium metal. The operation of coating-baking was repeated 12 times. The unused electrode for electrolysis that prepared in this way was cut to 30mm x 30mm and made a sample (hereafter called "The Sample".)

25 ◇Preparation of the alkali treatment solution containing thickener

As thickener, XAG and CMC were selected and observed the state that dissolved this in pure water each for 1 mass% and confirmed a preferable range of concentration.

As a result of observations, it is judged that the thickener is preferable to be

used at 1.0 mass% or less. If it exceeds 1.0 mass%, XAG becomes muddy white ,
and when it is left gelated and becomes difficult to stir. On the other hand, the
CMC maintains water-clear and slightly thick state, and a higher concentration
seems possible, but for both, 1.0 mass% or less is judged to be the optimal
5 concentration.

After having the above thickener of predetermined quantity less than 1.0 mass%
in pure water, NaOH-KOH was dissolved to become 50 mass%. Then, the alkali
treatment solution containing thickener was prepared to the following
10 concentration.

- A) 0.2 mass% XAG added alkali treatment solution
- B) 0.5 mass% XAG added alkali treatment solution
- C) 0.1 mass% CMC added alkali treatment solution
- D) 0.2 mass% CMC added alkali treatment solution
- 15 E) 0.4 mass% CMC added alkali treatment solution
- F) 0.5 mass% CMC added alkali treatment solution

The 0.2 mass % XAG addition alkali processing solution of condition A) was
prepared by the following manner. At first XAG of 0.2g was dissolved in water of 49.8g
20 and prepared 0.4 mass% XAG aqueous solution. Then, NaOH of 25g and KOH of 25g
were dissolved in 0.4 mass % XAG aqueous solution and made 100g of 50 mass %
NaOH-KOH alkali processing solutions which 0.2 mass% XAG included in.

The XAG addition alkali processing solution of condition B) and the CMC addition
alkali processing solutions of condition C), D), E), F) were prepared in a similar
25 manner.

◇Exfoliation process

After having soaked the sample into in the alkali processing solution
containing thickener mentioned above, the sample was placed in a crucible with

its coating face positioned downward.

The Sample was baked for 30 min. at 360 degrees Celsius and the coating was exfoliated with the hydrochloric acid treatment.

This exfoliation process was repeated twice to examine the reproducibility.

5

◇Exfoliation results

The state and the adhesion condition of the alkali processing solution which used for an examination are shown in Table 1.

The state of the alkali processing solution is indicated as follows:

10

○: Preparation is easy and stability is good.

△: Not good. (As to the reason for △, see the column of comment.)

Quantity of adhesion of the processing solution which did not include a thickener is set to 1 and the adhesion condition of each processing solution is shown by the ratio.

15

[Table 1] The state and the adhesion condition of the alkali processing solution

Content of the thickener	The state of solution	The adhesion condition of solution	Comments
A) 0.2mass% XAG	○	1.5	
B) 0.5mass% XAG	△	3	It is gelated when it is left.
C) 0.1mass% CMC	○	1	Slightly thick state
D) 0.2mass% CMC	○	2	
E) 0.4mass% CMC	○	2	
F) 0.5mass% CMC	△	3	It may gelate during alkali addition.
G) No thickener	○	1	

In the case of thickener addition being 0.2 mass% or more, the effect of thickener

on the quantity of adhesion of the immersion liquid was proven to be higher than the conventional method not containing thickener. Meanwhile, in the case of 0.1 mass % CMC of C), the quantity of adhesion of the processing solution was 1, the increase of the quantity of adhesion was not seen.

Degree of exfoliation was evaluated about A, B, D, E and F, which increased quantity of adhesion, and about G (The comparative example) which is the conventional alkali processing solution without containing thickener. The results are shown in Table 2.

The degree of exfoliation is evaluated as follows.

×: Coating almost remained without being exfoliated

○: Coating slightly remained

⊙: Coating exfoliated completely

[Table 2] Evaluation of degree of exfoliation

Content of the thickener	Degree of exfoliation	Pictorial image
A) 0.2mass% XAG	○	See Fig. 1.
B) 0.5mass% XAG	⊙	See Fig. 2.
D) 0.2mass% CMC	○	See Fig. 3.
E) 0.4mass% CMC	⊙	See Fig. 4.
F) 0.5mass% CMC	⊙	See Fig. 5.
G) No thickener	×	See Fig. 6.

Because improvement of the exfoliation degree was seen in the image mentioned above in all sample (A, B, D, E, F) which quantity of adhesion of the alkali liquid increased in comparison with before, an effect of the thickener addition was confirmed. In contrast, the coating was not exfoliated and almost remained in conventional alkali processing solution G) which does not containing thickener.

Among them, the coating was completely exfoliated in B, E, and F, and

reproducibility was also confirmed. It was judged that a condition of E was the best when the state of alkali processing solution was considered.

From above-mentioned results, the present invention has found that controlling
5 the dosage of thickener to 0.2 mass% or more can improve exfoliation effect and, further, that controlling the addition of thickener to 0.4 mass% or more can achieve complete exfoliation effect.

Industrial applicability

10 The present invention is widely applied in the industrial areas, it can recover and recycle noble metals and/or noble metal oxides belonging to noble, rare metals which constitute the surface coating layer, and electrode substrate of titanium, as well, without deformation from the insoluble metal electrode using electrode substrates mainly of titanium.

CLAIMS

[Claim 1]

A method for exfoliating the coating layer from the surface of the electrode substrate, characterized in that in the exfoliation method for the coating layer from the surface of the electrode substrate, wherein the insoluble metal electrode surface having the coating layer containing electrode substance comprising noble metal and/or metal oxide thereof on the surface of the electrode substrate comprising valve metals including titanium and tantalum or valve metal alloys is treated, in succession, with the alkali treatment process using a caustic alkali aqueous solution, the heating and baking process and the acid treatment process, the alkali treatment process is conducted by applying an alkali treatment solution prepared by adding thickener to the caustic alkali aqueous solution.

15 [Claim 2]

The method for exfoliating the coating layer from the surface of the electrode substrate as in Claim 1, characterized in that the thickener comprising natural polysaccharide thickener is applied.

20 [Claim 3]

The method for exfoliating the coating layer from the surface of the electrode substrate as in Claim 2, characterized in that the thickener comprising bio gum or guar gum derivatives or cellulose derivatives are applied as the natural polysaccharide thickener.

25

[Claim 4]

The method for exfoliating the coating layer from the surface of the electrode substrate as in any one of Claims 1-3, characterized in that the thickener comprising carboxymethyl cellulose is applied as thickener.

[Claim 5]

The method for exfoliating the coating layer from the surface of the electrode substrate as in any one of Claims 1-3, characterized in that the thickener comprising
5 xanthan gum is applied as thickener.

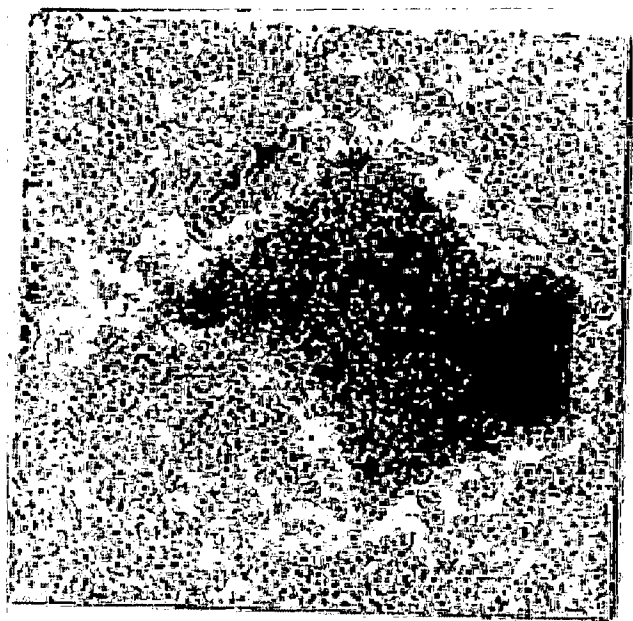
[Claim 6]

The method for exfoliating the coating layer from the surface of the electrode substrate as in any one of Claims 1-5, characterized in that the addition ratio of the
10 thickener in the alkali treatment solution is 0.2 mass% or more but 1 mass% or less.

[Claim 7]

The method for exfoliating the coating layer from the surface of the electrode substrate as in any one of Claims 1-5, characterized in that the addition ratio of the
15 thickener in the alkali treatment solution is 0.4 mass % or more but 1 mass % or less.

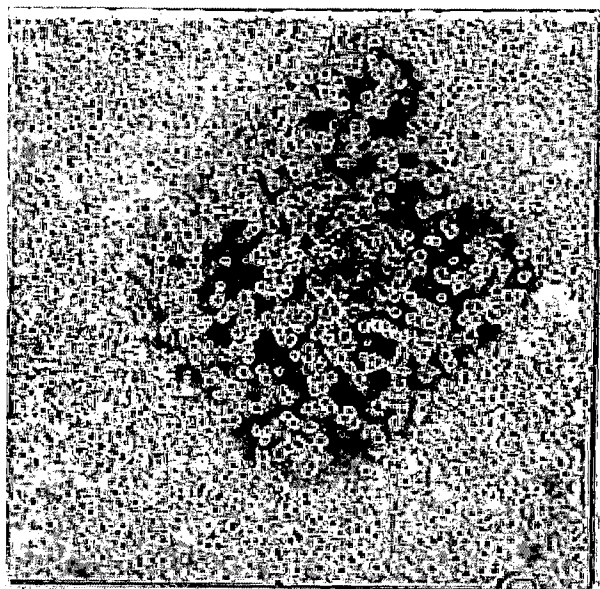
[Fig. 1]



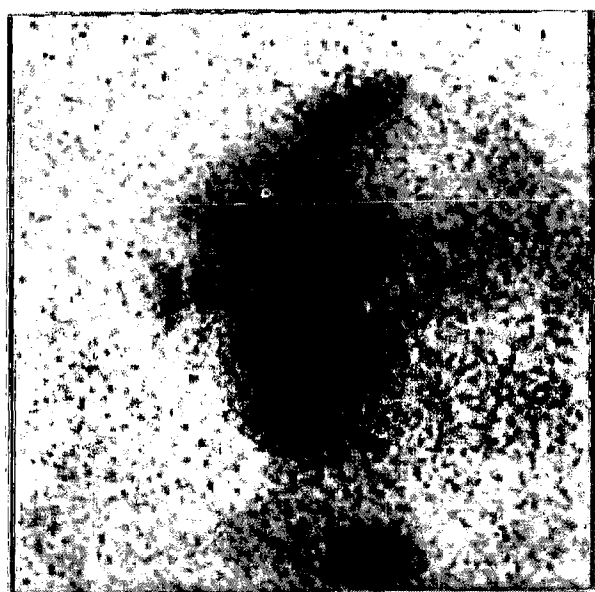
[Fig. 2]



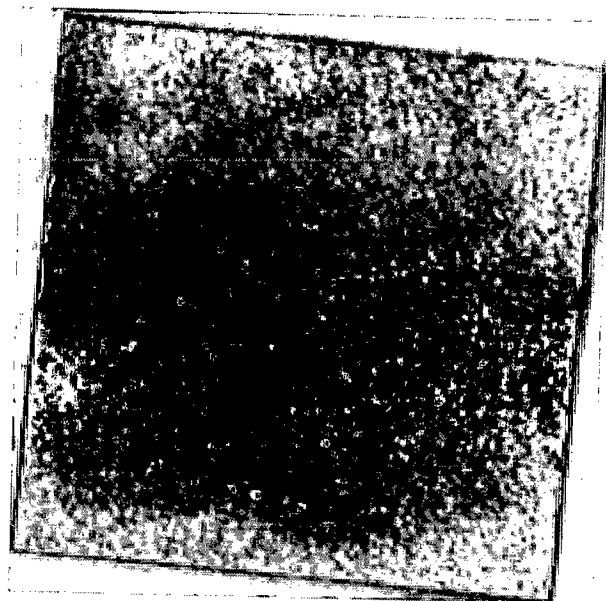
[Fig. 3]



[Fig. 4]



[Fig. 5]



[Fig. 6]

