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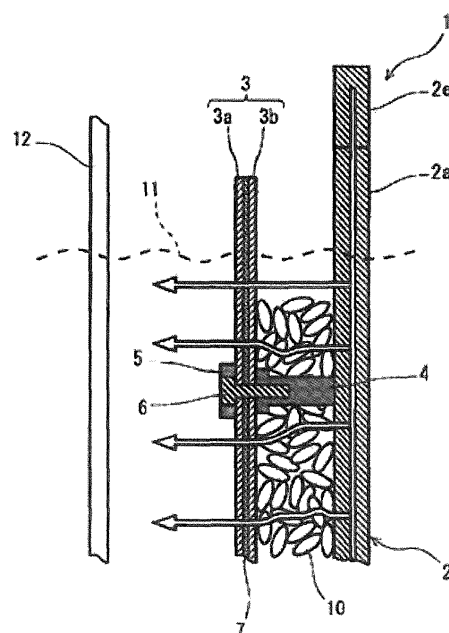
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(54) **BASKET TYPE ANODE**

(57) A basket-type anode stores plating pellets in a plating bath and is used for electrolytic plating of a steel strip. The basket-type anode comprises a reticulated member made of Ti to be placed facing the steel strip. The reticulated member contains one or more platinum group elements. When the reticulated member contains one or more platinum group elements, the corrosion of the reticulated member can be prevented, and the life-time of the reticulated member can be improved.

**FIG. 2**



**Description**

## Technical Field

5 **[0001]** The present invention relates to a basket-type anode used for the electrolytic plating of a steel strip.

## Background Art

10 **[0002]** In electrolytic plating in which plating is continuously performed on the surface of a steel strip, a box-shaped basket-type anode is widely used. In the basket-type anode, the front surface that faces the steel strip in the plating bath is formed of a reticulated member (laths), and plating pellets are stored. During electrolytic plating, by passing a current through the main body of the basket-type anode, the plating pellets in the basket-type anode are electrolyzed and ionized, and the metal ions are guided to the surface of the steel strip; thus, plating is formed. The main body and the reticulated member of the basket-type anode are required to have corrosion resistance, and are therefore made of pure Ti (pure titanium).

15 **[0003]** These days, there are demands of performing plating on a large-sized steel strip and performing plating with a large film thickness. In the operation of electrolytic plating that responds to these demands, it is necessary to supply a large current to the anode main body. However, the supply of a large current to the anode main body may cause the reticulated member to be corroded and damaged. For example, in the case of electrolytic Ni plating in which the plating pellets are Ni particles and the plating bath is a Watts bath, with the progress of the operation, part of the reticulated member is corroded, and a hole is made in the reticulated member.

20 **[0004]** When the damage to the reticulated member is significant, it is highly likely that plating pellets will leak out of the basket-type anode. If plating pellets leak out, the amount of plating pellets stored in the basket-type anode decreases rapidly, and the amount of metal ions in the plating bath varies. Furthermore, plating pellets that have leaked out in the plating bath may get between rollers that convey the steel strip. Such situations cause a reduction in the quality of the plated steel sheet.

25 **[0005]** As a conventional technology to address this problem, the following is given. JP-UM H4-37907B (Patent Literature 1) and JP 2011-89148A (Patent Literature 2) describe technologies, in which the reticulated member is insulated from the anode main body to suppress undesired corrosion of the reticulated member and thereby the damage to the reticulated member is suppressed.

30 **[0006]** Specifically, Patent Literature 1 describes a basket-type anode, in which the structure of attachment of the reticulated member to the anode main body is improved. In the basket-type anode described in this literature, the reticulated member is attached to the anode main body via an insulating material.

35 **[0007]** In Patent Literature 2 describes a basket-type anode, in which the structure of the reticulated member itself is improved. In the basket-type anode described in this literature, an  $\text{Al}_2\text{O}_3$  (alumina) insulating coating is formed on the surface of the reticulated member, and the insulating coating is processed by sealing with a coating of PTFE (polytetrafluoroethylene).

40 **[0008]** However, even when the conventional technologies mentioned above are applied, in practice the damage due to the corrosion of the reticulated member is not suppressed sufficiently. Consequently, the reticulated member needs to be frequently exchanged in order to prevent a reduction in the quality of the plated steel sheet, and a reduction in the productivity of the plated steel sheet is unavoidable. From such actual circumstances, an improvement in the lifetime of the reticulated member is strongly desired.

## Citation List

45

## Patent Literature

**[0009]**

50 Patent Literature 1: JP-UM H4-37907B  
Patent Literature 2: JP 2011-89148A

## Summary of Invention

## 55 Technical Problem

**[0010]** An object of the present invention is to provide a basket-type anode having the following characteristic:

improving the lifetime of a reticulated member.

#### Solution to Problem

**[0011]** A basket-type anode according to an embodiment of the present invention is a basket-type anode for storing plating pellets in a plating bath and to be used for electrolytic plating of a steel strip, the basket-type anode including a reticulated member made of Ti to be placed facing the steel strip, wherein the reticulated member contains one or more platinum group elements.

**[0012]** In the above anode, the amount of the one or more platinum group elements contained is preferably, in mass%, 0.01% to 0.15%.

**[0013]** In the above anode, the reticulated member can further contain one or more of Ni and rare earth elements. In this case, the amount of the Ni contained is preferably, in mass%, 0.2% to 1.0%, and the amount of the one or more rare earth elements contained is preferably, in mass%, 0.0005% to 0.020%. Moreover, in the above anode, as one or more impurity elements, in mass%, Fe: 0.3% or less, O: 0.35% or less, C: 0.18% or less, H: 0.015% or less, N: 0.03% or less, Al: 0.3% or less, Cr: 0.2% or less, Zr: 0.2% or less, Nb: 0.2% or less, Si: 0.02% or less, Sn: 0.2% or less, Mn: 0.01% or less, Co: 0.35% or less, and Cu: 0.1% or less, amounting to 0.6% or less in total, may be contained.

**[0014]** The anode mentioned above can be used for electrolytic plating, in which the plating pellets are Ni particles. Further, the anode mentioned above can be used for electrolytic plating, in which the plating bath is a Watts bath.

#### Advantageous Effects of Invention

**[0015]** The basket-type anode of the present invention has the following prominent effect:

being able to improve the lifetime of a reticulated member.

#### Brief Description of Drawings

##### **[0016]**

[FIG. 1] FIG. 1 is a front view of a basket-type anode.

[FIG. 2] FIG. 2 is a vertical cross-sectional view along the vertical direction of the basket-type anode.

[FIG. 3] FIG. 3 is a schematic diagram of a test apparatus used for a basic test of the investigation of corrosion resistance.

#### Description of Embodiments

**[0017]** The present inventors investigated the cause of a corrosion of a reticulated member made of pure titanium and of damage to the reticulated member in the operation of electrolytic plating, in which a large current is supplied to the main body of a basket-type anode, and remedial measures against it. The investigation was performed using electrolytic Ni plating, which is a typical example of the electrolytic plating, as an example. In the case of electrolytic Ni plating, the plating pellets are Ni particles, and a Watts bath is used as the plating bath.

[Standard configuration of the basket-type anode]

**[0018]** FIG. 1 is a front view of a basket-type anode. FIG. 2 is a vertical cross-sectional view along the vertical direction of the basket-type anode. In FIG. 2, the hollow arrow indicates the flow of the current supplied to the main body of the basket-type anode.

**[0019]** A basket-type anode 1 is immersed in a plating bath 11 and stores plating pellets 10 in the plating bath 11, and is used to perform electrolytic plating on a steel strip 12. The basket-type anode 1 is in a box shape, in which the upper surface is opened, and comprises an anode main body 2 and a reticulated member 3 that forms the front surface. The reticulated member 3 is placed facing the steel strip 12 in the plating bath 11. The internal space of the basket-type anode 1 is charged with the plating pellets 10.

**[0020]** The anode main body 2 comprises a rear surface plate 2a, a pair of side surface plates 2b and 2c on the left and right, and a bottom surface plate 2d. A bus bar 2e for supplying a current to the anode main body 2 is provided on the upper side of the rear surface plate 2a. The reticulated member 3 is installed on the front surface side of the anode main body 2 of such a configuration. Specifically, a plurality of support columns 4 protrude forward from the rear surface plate 2a. The reticulated member 3 is attached to the front ends of the support columns 4, and a pressing plate 5 is attached to the reticulated member 3 at the position of each support column 4. The pressing plate 5 is fastened to each

support column 4 by a bolt 6. Thereby, the reticulated member 3 is held on the front surface side of the anode main body 2 in a state of being sandwiched between each support column 4 and each pressing plate 5.

[0021] The reticulated member 3 is configured exactly in such a manner that two wire nets 3a and 3b are stacked. The front surface side of a bag 7 made of cloth is sandwiched between the wire nets 3a and 3b. The bag 7 allows the metal ions of the plating pellets 10 electrolyzed during electrolytic plating to permeate, and at the same time prevents the plating pellets 10 with the size reduced by electrolysis from leaking out through the meshes of the reticulated member 3. The technology described in Patent Literature 2 mentioned above may be applied to the wire nets 3a and 3b herein. That is, in the wire nets 3a and 3b, an insulating coating of  $\text{Al}_2\text{O}_3$  may be formed on the surface, and the insulating coating may be processed by sealing with a coating of PTFE.

[0022] In general, a reticulated member 3 divided in a plurality of stages in the vertical direction is attached to the anode main body 2. In the basket-type anode 1 shown in FIG. 1, a configuration in which the reticulated member 3 is divided in four stages is shown.

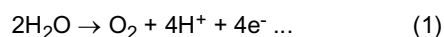
[0023] During electrolytic plating, a current is supplied to the main body 2 of the basket-type anode 1 through the bus bar 2e of the rear surface plate 2a. By the current passage, the plating pellets 10 in the basket-type anode 1 are electrolyzed and ionized, and the metal ions are guided to the surface of the steel strip 12; thus, plating is formed.

[Outline of the cause of damage due to the corrosion of the reticulated member and countermeasures against it]

[0024] In a conventional basket-type anode, the reticulated member has been made of pure Ti, including the case of employing the technology described in Patent Literature 2 mentioned above. The occurrence manner of damage (hole making) to the reticulated member was investigated in the operation of electrolytic Ni plating in which the conventional basket-type anode was used and a large current was supplied to the anode main body. As a result, the following findings have been obtained.

[0025] The damage to the reticulated member is likely to occur in the upper portion of the reticulated member. This is presumed to be due to the fact that, as shown below, the pH of the plating bath is reduced particularly in the upper portion of the reticulated member.

[0026] With the progress of the operation of electrolytic Ni plating, the Ni particles in the basket-type anode are consumed gradually and become smaller, and the total volume decreases. Therefore, particularly in the upper portion of the reticulated member, a state, in which Ni particles are insufficient (not present), occurs and a current flows directly from the anode main body to the plating bath. In the area where a current flows directly from the anode main body to the plating bath,  $\text{O}_2$  gas is generated from the plating bath, with the anode main body as an electrode. The generation of  $\text{O}_2$  gas is based on the reaction of Formula (1) below.



[0027] As shown in Formula (1) above, hydrogen ions are generated in association with the generation of  $\text{O}_2$  gas in the plating bath in the upper portion of the reticulated member. Accordingly, the pH of the plating bath is greatly reduced in the upper portion of the reticulated member.

[0028] Actually, however, in the case where a Watts bath is used in electrolytic Ni plating, the Watts bath contains boric acid for pH buffering. Even in this case, when  $\text{O}_2$  gas is generated in the plating bath in the upper portion of the reticulated member based on Formula (1) above, a great reduction in the pH of the plating bath occurs likewise.

[0029] When the pH reduction of the plating bath is small, the reticulated member made of pure Ti is not corroded, nor is damaged. However, when the pH of the plating bath has reached the region where the de-passivation of Ti is caused, the reticulated member made of pure Ti is corroded, and is damaged as a result of this.

[0030] From these points, it is presumed that the cause of the occurrence of damage due to corrosion in the upper portion of the reticulated member is that the pH of the plating bath has reached the region where the de-passivation of Ti is caused. The upper limit of the pH at which the de-passivation of Ti occurs is approximately 1.

[0031] Based on such findings, the present inventors conducted extensive studies on the countermeasures that can prevent the corrosion of the reticulated member even when the pH of the plating bath is greatly reduced. As a result, it has been revealed that it is effective to improve the chemical components of the reticulated member itself, with Ti as the base, and produce a reticulated member made of Ti containing one or more platinum group elements.

[0032] When one or more platinum group elements are contained in Ti material, either of following states is occurred: the platinum group element(s) is dissolved as a solid solution in Ti or a Ti-platinum group compound(s) is(are) generated. In such a reticulated member made of Ti containing one or more platinum group elements, when the pH reduction of the plating bath is significant, the passive coating of the surface dissolves and Ti dissolves out, and in association with this also the platinum group element(s) dissolves out. However, the platinum group element(s) that has dissolved out together with Ti has a very noble oxidation-reduction potential, and is therefore immediately electrodeposited on the surface of the reticulated member.

**[0033]** The platinum group element(s) electrodeposited on the surface of the reticulated member is a metal having a low hydrogen overvoltage, and reduces the hydrogen overvoltage. Therefore, in the reticulated member, the corrosion potential of Ti is ennobled, and the surface is re-passivated. By the re-passivation, the dissolution of Ti can be stopped.

[Basic test concerning the cause of damage due to the corrosion of the reticulated member and countermeasure against it]

**[0034]** To verify the appropriateness of the countermeasure mentioned above, the following basic test was performed. In the basic test, a simulated situation was employed in which a current flows directly from the main body of the basket-type anode to the plating bath in electrolytic plating using a Watts bath as the plating bath. At this time, a cathode was likened to a steel strip to be plated, an anode was likened to the main body of the basket-type anode, and a test piece was likened to the reticulated member of the basket-type anode, and the corrosion resistance of the test piece was investigated.

#### 1. Preparation of test pieces

##### (1) Comparative Material 1: pure Ti

**[0035]** A sheet material of pure Ti (type 2 of the JIS standards) with a thickness of 1 mm was prepared.

##### (2) Comparative Material 2: the technology described in Patent Literature 2 mentioned above

**[0036]** A sheet material of pure Ti (type 2 of the JIS standards) with a thickness of 1 mm was obtained, and the surface of the sheet material made of pure Ti was subjected to alumina thermal spraying processing. Specifically, employing the Ar plasma thermal spraying method, a plasma jet produced by a plasma thermal spray gun was used to heat and accelerate alumina of the thermal spraying material (gray alumina,  $\text{Al}_2\text{O}_3$ -2.5%  $\text{TiO}_2$ , produced by Sanko Shokai Co., Ltd.), and thereby the alumina was made into a molten state or a state close to it and was sprayed on the surface of the sheet material made of pure Ti; thus, an insulating coating was formed. Since air pores were present in the insulating coating, the insulating coating was further processed by sealing with a PTFE coating.

##### (3) Test materials of the inventive examples: improvements of the chemical components with Ti as the base (titanium alloys)

##### (a) Source materials

**[0037]** As the source materials, an industrial pure Ti sponge (type 1 of the JIS standards), a Pd (palladium) powder with a purity of 99.9% (produced by Kishida Chemical Co., Ltd.), a Ru (ruthenium) powder with a purity of 99.9% (produced by Kishida Chemical Co., Ltd.), Y (yttrium) turnings with a purity of 99.9% (produced by Kishida Chemical Co., Ltd.), massive rare earth elements, and massive electrolytic Co (cobalt) with a purity of 99.8% were obtained. As the massive rare earth elements, Mm (misch metal, mixed rare earth metals), La (lanthanum), and Nd (neodymium) were used, and those with a purity of 99% were used except for Mm. The chemical components of Mm were, in mass%, La: 28.6%, Ce (cerium): 48.8%, Pr (praseodymium): 6.4%, and Nd: 16.2%.

##### (b) Preparation of test pieces

**[0038]** Using an arc melting furnace with an argon atmosphere, rectangular ingots with different chemical components were prepared, with the mixing ratio of the source materials mentioned above variously altered. The size of each rectangular ingot was set to a thickness of 15 mm, a width of 75 mm, and a length of 95 mm. Here, when preparing each rectangular ingot, for each, five 80-g ingots were prepared first, then those ingots were re-melted together to prepare a rectangular ingot with a thickness of 15 mm, after that the rectangular ingot was re-melted for homogenization, and a rectangular ingot of the size mentioned above was prepared.

**[0039]** All the prepared rectangular ingots contained a minute amount of one or more platinum group elements, and in some cases further contained one or more rare earth elements; hence, heat treatment for homogenization was performed in order to lessen the segregation of each element. The conditions of the homogenization heat treatment were as follows.

- Atmosphere: a vacuum ( $< 10^{-3}$  torr (0.133 Pa))
- Heating temperature: 1100°C
- Heating time: 24 hours

**[0040]** The rectangular ingot that has undergone the homogenization heat treatment was rolled under the following conditions and was finally made into a sheet material with a thickness of 1 mm.

- $\beta$ -Phase region hot rolling: with the heating temperature set to 1000°C, rolling was performed to reduce the thickness from 15 mm to 9 mm
- $\alpha$ + $\beta$ -Phase region hot rolling: with the heating temperature set to 875°C, rolling was performed to reduce the thickness from 9 mm to 1 mm

**[0041]** The sheet material obtained by the rolling was subjected to annealing for strain relief. The conditions of the annealing were as follows.

- Atmosphere: a vacuum ( $< 10^{-3}$  torr (0.133 Pa))
- Heating temperature: 680°C
- Heating time: 7 hours

**[0042]** The hot-rolled sheet thus obtained was subjected to machining to prepare a test piece. The size of all the test pieces of test materials of the inventive examples and comparative materials 1 and 2 mentioned above was set to a thickness of 1 mm, a width of 15 mm, and a length of 15 mm. The surface of each test piece of test materials of the inventive examples and comparative material 1 mentioned above was mirror-polished using a #600 buff.

**[0043]** The chemical components of test materials 1 to 17 of the inventive examples and comparative materials 1 and 2 mentioned above were as shown in Table 1 below.

[Table 1]

| Test piece                               | Chemical components (unit: mass%; balance: Ti and impurities) |                    |                    |          |       |       |       |        |
|------------------------------------------|---------------------------------------------------------------|--------------------|--------------------|----------|-------|-------|-------|--------|
|                                          | Platinum group element                                        | Ni etc.            | Rare earth element | Fe       | O     | N     | C     | H      |
| Comparative material 1                   | -                                                             | -                  | -                  | 0.061    | 0.079 | 0.004 | 0.005 | 0.0019 |
| Comparative material 2                   | -                                                             | -                  | -                  | 0.061    | 0.079 | 0.004 | 0.005 | 0.0019 |
| Test materials of the inventive examples | 1                                                             | Pd:0.148           | -                  | -        | 0.070 | 0.109 | 0.008 | 0.010  |
|                                          | 2                                                             | Pd:0.061           | -                  | -        | 0.021 | 0.030 | 0.001 | 0.004  |
|                                          | 3                                                             | Pd:0.042           | -                  | -        | 0.022 | 0.032 | 0.001 | 0.003  |
|                                          | 4                                                             | Ru:0.078           | -                  | -        | 0.033 | 0.050 | 0.001 | 0.003  |
|                                          | 5                                                             | Ru:0.054           | Ni:0.47            | -        | 0.021 | 0.043 | 0.002 | 0.004  |
|                                          | 6                                                             | Ru:0.034           | Ni:0.29            | -        | 0.018 | 0.039 | 0.001 | 0.003  |
|                                          | 7                                                             | Pd:0.024           | -                  | Mm:0.002 | 0.022 | 0.033 | 0.001 | 0.005  |
|                                          | 8                                                             | Ru:0.041           | -                  | Y:0.002  | 0.026 | 0.041 | 0.003 | 0.004  |
|                                          | 9                                                             | Pd:0.021           | Ni:0.24            | Mm:0.002 | 0.024 | 0.038 | 0.004 | 0.005  |
|                                          | 10                                                            | Pd:0.014           | -                  | -        | 0.018 | 0.067 | 0.003 | 0.004  |
|                                          | 11                                                            | Ru:0.013           | Ni:0.38            | -        | 0.023 | 0.088 | 0.003 | 0.004  |
|                                          | 12                                                            | Pd:0.009           | -                  | -        | 0.058 | 0.065 | 0.004 | 0.006  |
|                                          | 13                                                            | Pd:0.02<br>Ru:0.02 | -                  | -        | 0.066 | 0.075 | 0.008 | 0.006  |
|                                          | 14                                                            | Pd:0.02            | -                  | Y:0.023  | 0.031 | 0.041 | 0.009 | 0.004  |
|                                          | 15                                                            | Pd:0.042           | Ni:0.21<br>Cr:0.11 | -        | 0.022 | 0.032 | 0.004 | 0.005  |
|                                          | 16                                                            | Ru:0.04            | Ni:0.25<br>Al:0.08 | -        | 0.031 | 0.051 | 0.001 | 0.003  |
|                                          | 17                                                            | Pd:0.03            | Zr:0.07            | Mm:0.01  | 0.039 | 0.047 | 0.003 | 0.003  |

**[0044]** The test pieces of comparative materials 1 and 2 are pure Ti. Of them, comparative material 2 is a material employing the technology described in Patent Literature 2 mentioned above, in which an insulating coating is formed on the surface and the insulating coating is processed by sealing with a PTFE coating.

**[0045]** All the test pieces of test materials 1 to 17 of the inventive examples are a Ti alloy containing one or more platinum group elements. Of them, test materials 5, 6, 9, 11, 15, and 16 are materials further containing Ni, and test materials 7 to 9, 14, and 17 are materials further containing one or more rare earth elements. Test material 13 is a material containing two kinds of platinum group elements. Test material 12 is a material, in which the amount of the platinum group element contained, is below the preferred lower limit of the present invention. Test material 14 is a

material, in which the amount of the rare earth element contained, exceeds the preferred upper limit of the present invention. Test materials 15, 16, and 17 are examples containing Cr, Al, and Zr, respectively, as an impurity element.

## 2. Content of the basic test (corrosion resistance investigation)

### (1) Test method

**[0046]** FIG. 3 is a schematic diagram of a test apparatus used for the basic test of corrosion resistance investigation. The test apparatus used for the basic test comprises a plating vessel 20 storing a plating solution (a plating bath). The plating vessel 20 is immersed in a constant temperature vessel 21, and the temperature of the plating solution in the plating vessel 20 can be kept constant.

**[0047]** In the plating solution in the plating vessel 20, a cathode 22 likened to the steel strip to be plated was immersed, and an anode 23 likened to the main body of the basket-type anode was immersed. As the cathode 22, a soft steel sheet with a thickness of 1 mm and a width of 20 mm was used. The immersion length of the cathode 22 in the plating bath was set to 20 mm. As the anode 23, a sheet material of pure Ti (type 2 of the JIS standards) with a thickness of 1 mm and a width of 20 mm was used. The pure Ti sheet that is the anode 23 is a sheet cut out of the same material as that used in Comparative Material 1 mentioned above, and the immersion length thereof in the plating bath was set to 20 mm like in the cathode 22.

**[0048]** Further, a test piece 24 likened to the reticulated member of the basket-type anode, that is, the test piece of test materials 1 to 11 of the inventive examples and comparative materials 1 and 2 mentioned above was immersed in the plating solution in the plating vessel 20. Here, each test piece 24 was hung between the anode 23 and the cathode 22 with a platinum wire 25 so as not to be directly electrically connected to either of the anode 23 and the cathode 22.

**[0049]** A Watts bath was used as the plating bath (plating solution). As the Watts bath, one in which the nominal composition is  $\text{NiSO}_4$  (nickel sulfate): 300 to 380 g/L,  $\text{NiCl}_2$  (nickel chloride): 60 to 80 g/L, and boric acid: 35 to 55 g/L was used. The amount of the solution of the Watts bath was set to 60 cc.

**[0050]** In the basic test, for each test piece of test materials 1 to 11 of the inventive examples and comparative materials 1 and 2, a constant current of 3 A was passed through the anode 23 from a direct-current power source device continuously for 24 hours. At this time, the current density was set to  $37.5 \text{ A/dm}^2$ , and the temperature of the Watts bath was set to  $55^\circ\text{C}$ . In order to lessen the influence of the water evaporation of the plating solution during the test, a current was passed in a state where the plating vessel 20 was covered with a Parafilm from above.

### (2) Evaluation method

**[0051]** For each test on each test piece, the pH of the plating solution was evaluated. Specifically, after the current passage of 24 hours, the pH of the plating solution was measured with a pH measuring device (pH Meter D-70 Series/ES-71/OM-71, manufactured by Horiba, Ltd.).

**[0052]** Further, for each test piece, the rate of corrosion was evaluated. Specifically, on the assumption that the entire surface of each test piece corrodes uniformly, the corrosion thickness (mm) per 24 hours was calculated from Formula (2) below on the basis of the corrosion weight loss (weight loss) of each test piece due to the current passage of 24 hours and the specific gravity of the test piece ( $4.51 \text{ g/cm}^3$ ). At this time, as the surface area of each test piece, a value calculated from the thickness, width, and length of the test piece before the test was used.

$$\text{Corrosion thickness per 24 hours} = \text{corrosion weight loss} / (\text{specific gravity} \times \text{surface area}) \dots (2)$$

**[0053]** Then, from the corrosion thickness per 24 hours calculated from Formula (2) above, the rate of corrosion (mm/year) at the time when one year has elapsed was found using Formula (3) below.

$$\text{Rate of corrosion} = \text{corrosion thickness per 24 hours} \times 365 \text{ days} \dots (3)$$

### (3) Results of the basic test

**[0054]** The results are shown in Table 2 below.

[Table 2]

| Test piece                               |    | Chemical components<br>(unit: mass%; balance: Ti and impurities) |                    |                    | pH of plating solution |            | Rate of corrosion<br>(mm/year) |
|------------------------------------------|----|------------------------------------------------------------------|--------------------|--------------------|------------------------|------------|--------------------------------|
|                                          |    | Platinum group element                                           | Ni etc.            | Rare earth element | Before test            | After test |                                |
| Comparative material 1                   |    | -                                                                | -                  | -                  | 4.6                    | 0.6        | 2.0                            |
| Comparative material 2                   |    | -                                                                | -                  | -                  | 4.6                    | 0.5        | 0.38                           |
| Test materials of the inventive examples | 1  | Pd:0.148                                                         | -                  | -                  | 4.6                    | 0.3        | ≈ 0                            |
|                                          | 2  | Pd:0.061                                                         | -                  | -                  | 4.6                    | 0.3        | ≈ 0                            |
|                                          | 3  | Pd:0.042                                                         | -                  | -                  | 4.6                    | 0.3        | ≈ 0                            |
|                                          | 4  | Ru:0.078                                                         | -                  | -                  | 4.6                    | 0.3        | ≈ 0                            |
|                                          | 5  | Ru:0.054                                                         | Ni:0.47            | -                  | 4.6                    | 0.3        | ≈ 0                            |
|                                          | 6  | Ru:0.034                                                         | Ni:0.29            | -                  | 4.6                    | 0.4        | 0.01                           |
|                                          | 7  | Pd:0.024                                                         | -                  | Mm:0.002           | 4.6                    | 0.4        | 0.02                           |
|                                          | 8  | Ru:0.041                                                         | -                  | Y:0.002            | 4.6                    | 0.3        | ≈ 0                            |
|                                          | 9  | Pd:0.021                                                         | Ni:0.24            | Mm:0.002           | 4.6                    | 0.4        | 0.02                           |
|                                          | 10 | Pd:0.014                                                         | -                  | -                  | 4.6                    | 0.4        | 0.06                           |
|                                          | 11 | Ru:0.013                                                         | Ni:0.38            | -                  | 4.6                    | 0.4        | 0.05                           |
|                                          | 12 | Pd:0.009                                                         | -                  | -                  | 4.6                    | 0.3        | 0.1                            |
|                                          | 13 | Pd:0.02<br>Ru:0.02                                               | -                  | -                  | 4.6                    | 0.3        | ≈ 0                            |
|                                          | 14 | Pd:0.02                                                          | -                  | Y:0.023            | 4.6                    | 0.4        | 0.1                            |
|                                          | 15 | Pd:0.042                                                         | Ni:0.21<br>Cr:0.11 | -                  | 4.6                    | 0.3        | ≈ 0                            |
|                                          | 16 | Ru:0.04                                                          | Ni:0.25<br>Al:0.08 | -                  | 4.6                    | 0.3        | ≈ 0                            |
|                                          | 17 | Pd:0.03                                                          | Zr:0.07            | Mm:0.01            | 4.6                    | 0.4        | ≈ 0                            |

Notes: "≈ 0" in the section of the rate of corrosion indicates that the rate of corrosion is less than 0.01 (mm/year).

**[0055]** From the results of the basic test shown in Table 2, the following is shown. In all the tests, the pH of the plating solution was 4.6 before the start of the test; but after the current passage of 24 hours, the pH was well below 1.0, and reached the region where the de-passivation of Ti is caused. From this, it has been found that, when a current flows directly from the anode 23 likened to the main body of the basket-type anode to the plating solution (the plating bath), the passive coating dissolves and corrosion progresses in case where the test piece likened to the reticulated member of the basket-type anode is pure Ti.

**[0056]** In the test piece of comparative material 1, because of being pure Ti not containing a platinum group element, a significant weight loss and a significant wall thickness loss were found, and the rate of corrosion reached 2.0 mm/year.

**[0057]** In the test piece of comparative material 2, since the surface was covered with an insulating coating, the occurrence of corrosion was limited to a portion where the formation of the insulating coating was imperfect, and the rate of corrosion was reduced to approximately 1/5 of that of comparative material 1. However, since the material is still pure Ti not containing a platinum group element, the rate of corrosion reached 0.38 mm/year.

**[0058]** In all the test pieces of test materials 1 to 17 of the inventive examples, since they are a Ti alloy containing one or more platinum group elements, the rate of corrosion was less than 0.1 mm/year, and a significant corrosion resistance was exhibited. In particular, in test materials 1 to 5, 8, 13, 15, and 16 in which the amount of the one or more platinum group elements contained is 0.04 mass% or more, the rate of corrosion was less than 0.01 mm/year, and in spite of the pH of the plating solution being well below 1.0, an almost perfect corrosion resistance was exhibited.

**[0059]** Other than the above, in the test pieces of test materials 6, 7, 9, 14, and 17 in which the amount of the platinum group element contained is not less than 0.02 mass% and less than 0.04 mass%, the rate of corrosion was approximately 0.02 mm/year. Further, in the test pieces of test materials 10 and 11 of the inventive examples in which the amount of the platinum group element contained is less than 0.02 mass%, the rate of corrosion was approximately 0.05 mm/year. In the test piece of test material 12 in which the amount of the platinum group element contained is below 0.01 mass%, the rate of corrosion was 0.1 mm/year. The corrosion resistance of the test pieces of these test materials 6, 7, 9, 10, 11, 12, 14, and 17 was distinctly improved as compared to comparative materials 1 and 2 although not as good as the perfect corrosion resistance of test materials 1 to 5, 8, 13, 15, and 16.

**[0060]** Here, the rate of corrosion of test material 12 was 0.1 mm/year, and slightly exceeded the standard that is assessed as corrosion-resistant (< 0.1 mm/year). Test material 14 is a material in which the amount of the rare earth

element contained slightly exceeds the preferred upper limit. In this case, the rate of corrosion was 0.1 mm/year, and slightly exceeded the standard that is assessed as corrosion-resistant ( $< 0.1$  mm/year). Test materials 15, 16, and 17 are materials containing an impurity, but are unaffected in corrosion resistance and exhibited an excellent corrosion resistance in the test.

**[0061]** Thus, from the results of the basic test, it has been found that, in order to prevent the corrosion of the reticulated member of the basket-type anode and improve the lifetime of the reticulated member, it is effective to produce a reticulated member made of Ti containing one or more platinum group elements.

**[0062]** The basket-type anode of the present invention has been completed based on the above findings. In the following, an embodiment of the basket-type anode of the present invention is described.

[Basket-type anode according to an embodiment of the present invention]

**[0063]** In a basket-type anode according to the embodiment, the reticulated member contains one or more platinum group elements. The reticulated member may further contain one or more of Ni and the rare earth elements. When the reticulated member contains one or more platinum group elements, the corrosion of the reticulated member can be prevented, and the lifetime of the reticulated member can be improved.

**[0064]** Six kinds of elements of Ru (ruthenium), Rh (rhodium), Pd (palladium), Os (osmium), Ir (iridium), and Pt (platinum) fall under the platinum group elements. There are no limitations on the kind of the platinum group element(s) as long as the element(s) is selected from these six kinds of elements. That is, the platinum group element(s) may comprise one or more of the six kinds of elements. However, since the platinum group elements are rare and very expensive, it is preferable to select Ru or Pd among the six kinds of elements from the economic point of view. This is because recycling technology is established for Ru and Pd and in particular Ru can be obtained stably at relatively low cost.

**[0065]** The amount of the one or more platinum group elements contained is not particularly limited. However, containing a large amount of one or more platinum group elements is not preferable from the economic point of view. Hence, the upper limit of the amount of the one or more platinum group elements contained is preferably set to 0.15 mass%. A more preferred upper limit of the amount of the one or more platinum group elements contained is 0.08 mass%.

**[0066]** The lower limit of the amount of the one or more platinum group elements contained is preferably set to 0.01 mass% in order to improve the lifetime of the reticulated member sufficiently. A more preferred lower limit of the amount of the one or more platinum group elements contained is 0.02 mass%, and a still more preferred lower limit is 0.04 mass%.

**[0067]** Here, when Ni or one or more rare earth elements are contained compositely in addition to the one or more platinum group elements, by the synergy by the containing of Ni or the one or more rare earth elements, it becomes possible to reduce the amount of the one or more platinum group elements contained. Thus, the containing of Ni or one or more rare earth elements has an advantage from the economic point of view.

**[0068]** Similarly to the platinum group element(s), Ni has the effect of reducing the hydrogen overvoltage and ennobling the corrosion potential of Ti. In the case where, in order to obtain this effect, Ni is incorporated for the purpose of reducing the amount of the one or more platinum group elements contained, the lower limit of the amount of Ni contained is preferably set to 0.2 mass%. A more preferred lower limit of the amount of Ni contained is 0.4 mass%. On the other hand, containing a large amount of Ni reduces processability and formability. Hence, the upper limit of the amount of Ni contained in the case where Ni is incorporated is preferably set to 1.0 mass%.

**[0069]** The rare earth element(s), within the range of contained amount in which it is dissolved as a solid solution in Ti, has the effect of, when a Ti material containing one or more platinum group elements is exposed to a corrosive environment, promoting the electrodeposition of the platinum group element(s) on the surface of the Ti material. In the case where one or more rare earth elements are contained in order to obtain this effect, the lower limit of the amount of the one or more rare earth elements contained is preferably set to 0.0005 mass%. A more preferred lower limit of the amount of the one or more rare earth elements contained is 0.001 mass%. On the other hand, if one or more rare earth elements are contained excessively, a simple substance of the rare earth element(s) may be deposited, and the deposited rare earth element(s) may be a factor of corrosion. Although the upper limit of the amount of the one or more rare earth elements contained might be, in terms of the mechanism, the upper limit of the solid solution range of the rare earth element(s), this has a concern that segregation etc. will occur during dissolution. Hence, the upper limit of the amount of the one or more rare earth elements contained in the case where the one or more rare earth elements are incorporated is preferably set to 0.020 mass% from the viewpoint of obtaining a solid solution state reliably.

**[0070]** The rare earth element(s) is a general term of Y and Sc in addition to the 15 elements of the lanthanoids from La of atomic number 57 to Lu of atomic number 71, a total of 17 elements, and may comprise one or more selected from these elements. The amount of the one or more rare earth elements contained refers to the total amount of these elements contained.

**[0071]** As above, the reticulated member (the wire net) of the basket-type anode of the embodiment is a titanium material that contains one or more platinum group elements and in some cases further contains one or more of Ni and the rare earth elements. As one or more impurity elements contained in addition to these elements, Fe, O, C, H, N, etc.

that enter from the source material, the solution electrode, or the environment are given, and further Al, Cr, Zr, Nb, Si, Sn, Mn, Co, Cu, etc. that get mixed in when scrap or the like is used as the source material are given. There is no problem with these impurity elements getting mixed in as long as they are within the range in which the effect by the embodiment is not inhibited. Specifically, there is no problem when the amounts of the impurities are, in mass%, Fe: 0.3% or less, O: 0.35% or less, C: 0.18% or less, H: 0.015% or less, N: 0.03% or less, Al: 0.3% or less, Cr: 0.2% or less, Zr: 0.2% or less, Nb: 0.2% or less, Si: 0.02% or less, Sn: 0.2% or less, Mn: 0.01% or less, Co: 0.35% or less, and Cu: 0.1% or less, and the total amount of these is 0.6% or less.

**[0072]** Other than the above, the present invention is not limited to the embodiment described above, and various alterations are possible without departing from the spirit of the present invention. For example, although the basket-type anode of the embodiment can be suitably used for electrolytic Ni plating in which the plating pellets are Ni particles and a Watts bath is used as the plating bath, there are no limitations on the types of the plating pellets and the plating bath to the extent that they are used for electrolytic plating. As the plating pellets, that is, the type of plating for which the basket-type anode of the embodiment can be used, gold, silver, copper, tin, zinc, etc. are given as well as Ni. As the shape of the plating material particle, a spherical shape, a crown-like shape, etc. are given. As the type of the plating bath for which the basket-type anode of the embodiment can be used, a nickel sulfamate sergeant bath, a nickel sulfamate high-speed bath, a strike bath (a Wood's bath), a black nickel plating bath, etc. are given as well as a Watts bath.

[Examples]

**[0073]** To verify the effect by the present invention, using the basket-type anode shown in FIG. 1 and FIG. 2 mentioned above, an actual operation test was performed with an electrolytic Ni plating line in which a Watts bath was used as the plating bath.

[Test conditions]

**[0074]** In the test, five kinds of reticulated members (exactly, wire nets) were prepared. For the reticulated members of the inventive examples, three kinds of test materials 21, 22, and 23 with different chemical components were used as shown in Table 3 below. For the reticulated members of comparative examples, two kinds of comparative materials 1 and 2 in which the chemical components of the material are the same but the surface form is different were used.

[Table 3]

| Test materials of the inventive examples                                  | Chemical components (unit: mass%) |       |      |      |       |       |      |       |       |      |
|---------------------------------------------------------------------------|-----------------------------------|-------|------|------|-------|-------|------|-------|-------|------|
|                                                                           | Pd                                | Ru    | Ni   | Fe   | C     | H     | O    | N     | Mm    | Ti   |
| 21                                                                        | -                                 | 0.046 | 0.51 | 0.04 | 0.01  | 0.002 | 0.04 | 0.01  | -     | BAL. |
| 22                                                                        | 0.06                              | -     | -    | 0.02 | 0.004 | 0.002 | 0.03 | 0.004 | -     | BAL. |
| 23                                                                        | -                                 | 0.032 | -    | 0.01 | 0.004 | 0.003 | 0.06 | 0.004 | 0.002 | BAL. |
| Notes: For Mm, the total amount of La, Ce, Nd, and Pr contained is shown. |                                   |       |      |      |       |       |      |       |       |      |

**[0075]** As shown in Table 3, all the reticulated members of test materials 21, 22, and 23, which are examples of the present invention, were formed of a Ti alloy containing a platinum group element. Of them, the reticulated member of test material 21 was made to further contain Ni, and the reticulated member of test material 23 was made to further contain Mm (misch metal, mixed rare earth metals), which is rare earth elements. On the other hand, all the reticulated members of comparative materials 21 and 22, which are comparative examples, were formed of pure Ti (type 2 of the JIS standards). Of them, the reticulated member of comparative material 22 was configured to be a member in which the surface of the net was subjected to alumina thermal spraying processing, similarly to comparative material 2 in the basic test mentioned above.

**[0076]** The five kinds of reticulated members thus configured were each installed as the reticulated member of the uppermost stage of the basket-type anode. Then, each basket-type anode was immersed in the same Watts bath, and electrolytic Ni plating was continuously performed on the surface of the steel strip. The operation of the electrolytic Ni plating was continuously performed for three months.

**[0077]** The composition of the Watts bath was nickel sulfate: approximately 340 g/L, nickel chloride: approximately 70 g/L, and boric acid: approximately 45 g/L. The temperature of the Watts bath was approximately 55°C, and the pH of the Watts bath was 3.5 to 4.6. A current was continuously passed through the anode main body by applying an electrolysis voltage of approximately 30 V, at a current density in the steady state of 34.5 A/dm<sup>2</sup>. Each basket-type

anode was charged with crown-like Ni particles, and was replenished periodically. At this time, with the consumption of Ni particles, often a state where only the plating solution was present immediately below the surface of the solution of the Watts bath appeared.

[Evaluation method]

**[0078]** After the continuous operation of three months, the conditions of corrosion and dissolution loss were investigated for the reticulated member of the uppermost stage of each basket-type anode. In this investigation, for the reticulated member of the uppermost stage after the continuous operation, the presence or absence of dissolution loss was checked by visual inspection over the entire surface.

**[0079]** Further, in this investigation, the thickness of the net of each reticulated member was measured before and after the continuous operation, and the degree of corrosion was evaluated from the thickness loss. The measurement of the thickness of the net of each reticulated member was performed on three points A, B, and C specified in advance. Measurement point A was set to a point in a position 50 mm inside from the left end of the reticulated member of the uppermost stage and 200 mm below from the upper end thereof. Measurement point B was set to a point in a position at the lateral center of the reticulated member of the uppermost stage and 200 mm below from the upper end thereof. Measurement point C was set to a point in a position 50 mm inside from the right end of the reticulated member of the uppermost stage and 200 mm below from the upper end thereof. These measurement points A, B, and C correspond to positions immediately below the surface of the solution of the Watts bath, which have been positions where damage to the reticulated member is likely to occur.

[Results]

**[0080]** The results are shown in Table 4 below.

[Table 4]

| Test material                            |    | Measurement position | Thickness before immersion (mm) | Thickness after 3 months (mm) | Corrosion depth (mm) | Conditions of net                                            |
|------------------------------------------|----|----------------------|---------------------------------|-------------------------------|----------------------|--------------------------------------------------------------|
| Comparative material 21                  |    | A                    | 1.6                             | Dissolution loss              | -                    | Part of the net experienced dissolution loss and hole making |
|                                          |    | B                    | 1.6                             | 0.6                           | 1.0                  |                                                              |
|                                          |    | C                    | 1.6                             | 0.4                           | 1.2                  |                                                              |
| Comparative material 22                  |    | A                    | 1.7                             | 1.6                           | 0.1                  | Corrosion was present locally                                |
|                                          |    | B                    | 1.8                             | 1.2                           | 0.6                  |                                                              |
|                                          |    | C                    | 1.7                             | 1.5                           | 0.2                  |                                                              |
| Test materials of the inventive examples | 21 | A                    | 1.5                             | 1.5                           | 0                    | No corrosion                                                 |
|                                          |    | B                    | 1.5                             | 1.5                           | 0                    |                                                              |
|                                          |    | C                    | 1.5                             | 1.5                           | 0                    |                                                              |
|                                          | 22 | A                    | 1.6                             | 1.6                           | 0                    | No corrosion                                                 |
|                                          |    | B                    | 1.6                             | 1.6                           | 0                    |                                                              |
|                                          |    | C                    | 1.6                             | 1.6                           | 0                    |                                                              |
|                                          | 23 | A                    | 1.5                             | 1.5                           | 0                    | No corrosion                                                 |
|                                          |    | B                    | 1.5                             | 1.5                           | 0                    |                                                              |
|                                          |    | C                    | 1.5                             | 1.5                           | 0                    |                                                              |

**[0081]** In the reticulated member of comparative material 21, part of the net was corroded and experienced dissolution loss, and the thickness of the net, even though it remained, became 1/2 or less. Further, in the reticulated member of comparative material 22, a reduction in the thickness of the net due to corrosion was found in a portion where the formation of the insulating coating was imperfect. In contrast, in the reticulated members of test materials 21 to 23, which are examples of the present invention, a reduction in the thickness of the net due to corrosion was not found at all.

**[0082]** From the above results, it has been verified that the basket-type anode of the embodiment can improve the lifetime of the reticulated member.

Industrial Applicability

**[0083]** The basket-type anode of the present invention can be effectively used for any electrolytic plating.

## Reference Signs List

**[0084]**

|    |        |                             |
|----|--------|-----------------------------|
| 5  | 1      | basket-type anode           |
|    | 2      | anode main body             |
|    | 2a     | rear surface plate          |
|    | 2b, 2c | side surface plate          |
|    | 2d     | bottom surface plate        |
| 10 | 2e     | bus bar                     |
|    | 3      | reticulated member          |
|    | 3a, 3b | wire net                    |
|    | 4      | support column              |
|    | 5      | pressing plate              |
| 15 | 6      | bolt                        |
|    | 7      | bag                         |
|    | 10     | plating material particle   |
|    | 11     | plating bath                |
|    | 12     | steel strip                 |
| 20 | 20     | plating vessel              |
|    | 21     | constant temperature vessel |
|    | 22     | cathode                     |
|    | 23     | anode                       |
|    | 24     | test piece                  |
| 25 | 25     | platinum wire               |

**Claims**

- 30 1. A basket-type anode for storing plating pellets in a plating bath and being used for electrolytic plating of a steel strip, the basket-type anode comprising a reticulated member made of Ti to be placed facing the steel strip, wherein the reticulated member contains one or more platinum group elements.
- 35 2. The basket-type anode according to claim 1, wherein the amount of the one or more platinum group elements contained is, in mass%, 0.01% to 0.15%.
3. The basket-type anode according to claim 1 or 2, wherein the reticulated member further contains one or more of Ni and rare earth elements.
- 40 4. The basket-type anode according to claim 3, wherein the amount of the Ni contained is, in mass%, 0.2% to 1.0%, and the amount of the one or more rare earth elements contained is, in mass%, 0.0005% to 0.020%.
- 45 5. The basket-type anode according to any one of claims 1 to 4, containing, as one or more impurity elements, in mass%, Fe: 0.3% or less, O: 0.35% or less, C: 0.18% or less, H: 0.015% or less, N: 0.03% or less, Al: 0.3% or less, Cr: 0.2% or less, Zr: 0.2% or less, Nb: 0.2% or less, Si: 0.02% or less, Sn: 0.2% or less, Mn: 0.01% or less, Co: 0.35% or less, and Cu: 0.1% or less, amounting to 0.6% or less in total.
- 50 6. The basket-type anode according to any one of claims 1 to 5, wherein the plating pellets are Ni particles.
7. The basket-type anode according to any one of claims 1 to 6, wherein the plating bath is a Watts bath.

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FIG. 1

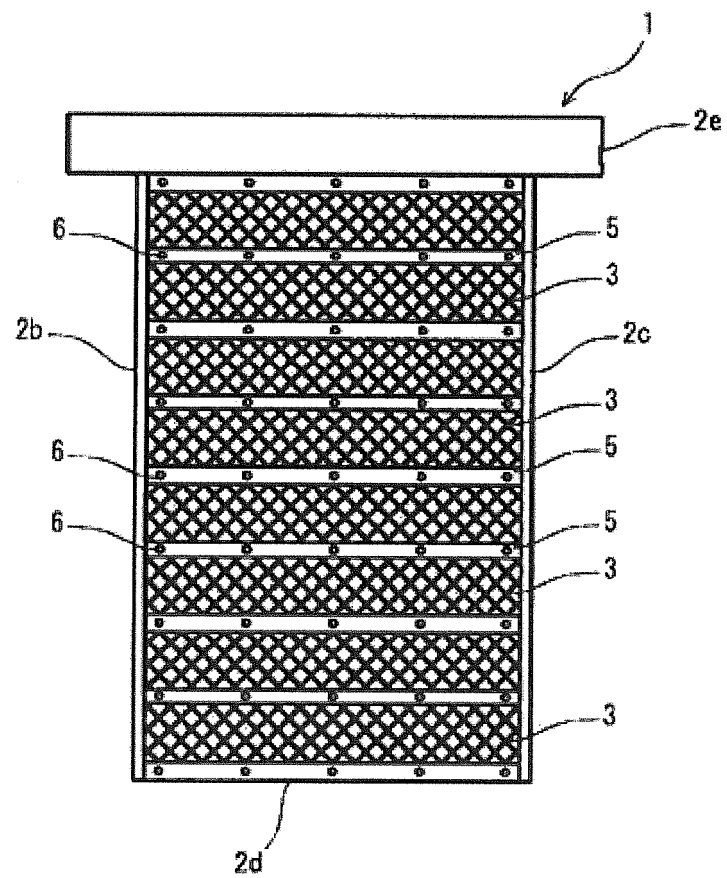


FIG. 2

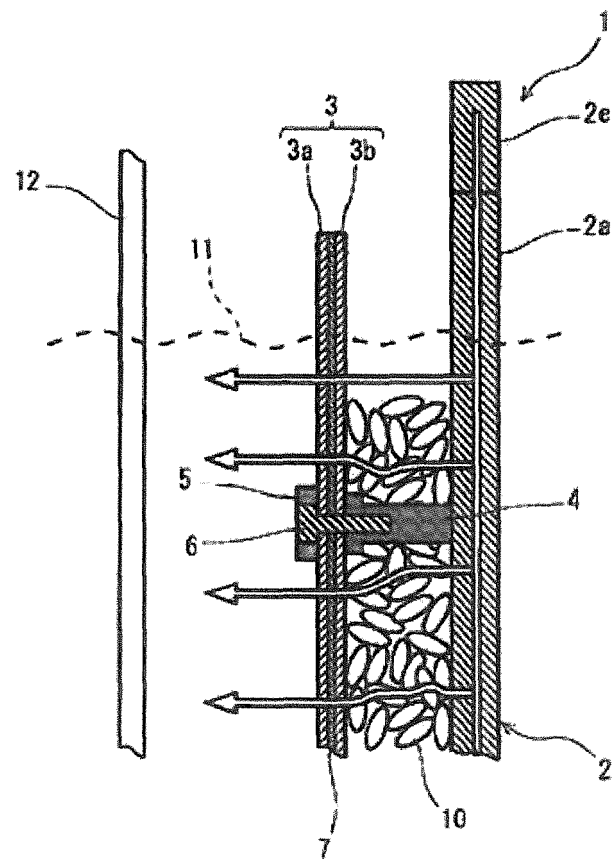
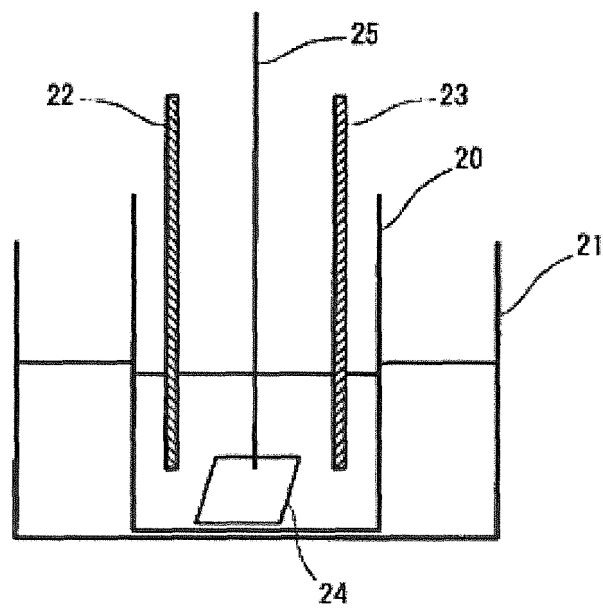


FIG. 3



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2015/067588

## A. CLASSIFICATION OF SUBJECT MATTER

C25D17/12(2006.01)i, C23F13/00(2006.01)i, C25D5/26(2006.01)i, C25D17/10(2006.01)i

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)

C25D17/12, C23F13/00, C25D5/26, C25D17/10

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

Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2015  
Kokai Jitsuyo Shinan Koho 1971-2015 Toroku Jitsuyo Shinan Koho 1994-2015

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

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## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category*     | Citation of document, with indication, where appropriate, of the relevant passages                                                  | Relevant to claim No.    |
|---------------|-------------------------------------------------------------------------------------------------------------------------------------|--------------------------|
| X<br><u>A</u> | JP 1-247592 A (Nisshin Steel Co., Ltd.),<br>03 October 1989 (03.10.1989),<br>claims; examples<br>(Family: none)                     | 1<br><u>2-7</u>          |
| Y<br><u>A</u> | JP 2011-89148 A (Nippon Steel Corp.),<br>06 May 2011 (06.05.2011),<br>claims; paragraph [0008]<br>(Family: none)                    | 1, 2, 5-7<br><u>3, 4</u> |
| Y<br><u>A</u> | Karl-H. TOSTMANN, Korrosion von Titan im<br>galvanotechnischen Einsatz, Galvanotechnik,<br>1980.12.15, Vol.71 No.12, Page.1310-1313 | 1, 2, 5-7<br><u>3, 4</u> |

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

\* Special categories of cited documents:

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document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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Date of the actual completion of the international search  
04 September 2015 (04.09.15)

Date of mailing of the international search report  
15 September 2015 (15.09.15)

Name and mailing address of the ISA/  
Japan Patent Office  
3-4-3, Kasumigaseki, Chiyoda-ku,  
Tokyo 100-8915, Japan

Authorized officer

Telephone No.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2015/067588

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                     | Relevant to claim No. |
|-----------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| A         | Microfilm of the specification and drawings annexed to the request of Japanese Utility Model Application No. 120268/1980 (Laid-open No. 44183/1982)<br>(Dainippon Printing Co., Ltd.),<br>11 March 1982 (11.03.1982),<br>entire text<br>(Family: none) | 1-7                   |
| A         | JP 2010-265519 A (Nippon Steel Engineering Co., Ltd.),<br>25 November 2010 (25.11.2010),<br>entire text<br>(Family: none)                                                                                                                              | 1-7                   |

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

**REFERENCES CITED IN THE DESCRIPTION**

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