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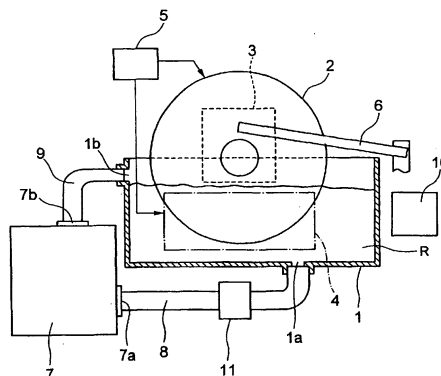
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(54) **APPARATUS FOR RECOVERING METAL**

(57) An apparatus for recovering a metal, which comprises a metal-recovering board (2) having an electrodeposition surface (2a, 2t) for the attachment of a metal component (R) precipitated from a solution and an insulating material (2b) formed around a pattern of the electrodeposition surface (2a, 2t). The metal-recovering board (2) is immersed in a metal-containing solution in

an electrolytic treatment vessel (1), and thereby the metal in the solution is selectively precipitated on the electrodeposition surface (2a, 2t) and is converted to a bulk. The resultant metal bulk is scraped together for recovery with a blade (6) in a form as it is. The above apparatus for recovering a metal can be suitably used for recovering a metal in a solution in a state allowing easy reuse with good efficiency.

FIG. 1



Description

Technical Field

5 **[0001]** The present invention relates to a metal recovery apparatus and more particularly, to a metal recovery apparatus for recovering metal contained in an acidic solution or the like.

Background Art

10 **[0002]** Usually, in producing a copper product or copper alloy product, an oxide is produced on the surface of the copper product or copper alloy product during the process. This oxide is removed by a treatment using a sulfuric acid solution and after the treatment, copper ions remain in the sulfuric acid solution.

15 **[0003]** The copper ion concentration of the sulfuric acid solution increases with increase in number of times of treatment and the oxide removal performance of the sulfuric acid solution is deteriorated. For this reason, the sulfuric acid solution needs to be exchanged regularly, however, this exchange increases the cost.

20 **[0004]** In view of this, developments have been made on the method and apparatus for recycling a sulfuric acid solution. The method for recovering a copper component from the sulfuric acid solution includes crystallization, copper plate electrodeposition, barrel electrodeposition and the like.

25 **[0005]** Crystallization is a method of cooling a sulfuric acid solution containing copper ions to precipitate copper sulfate therefrom. However, cooling of the solution requires much power, which increases the cost.

30 **[0006]** Copper plate electrodeposition is a method of immersing a copper plate as a negative plate in a sulfuric acid solution containing copper ions to deposit copper on the copper plate surface. However, the cost of preparing the negative plate is high. Besides, as the negative plate to which the copper is adhered by copper precipitation is heavy, the negative plate is difficult to take out of the solution.

35 **[0007]** Barrel electrodeposition is a method of putting a copper chip as an electrode into a basket immersed in a sulfuric acid solution to deposit copper on the copper chip surface. However, it is necessary to prepare a mechanism for taking the copper chip out of the basket, which increases the cost of the apparatus.

40 **[0008]** In addition to the above, the documents 1 to 4 listed below also disclose methods of recovering of a copper component. The document 1 discloses a technique of using as a cathode a rotating metal recovery board having a surface of Zr (zirconium) or Zr alloy, immersing a part of the metal recovery board into a treatment solution, carrying a negative current through the rotating metal recovery board to deposit powder copper on the surface by electrolysis and scraping the powder copper by the plate.

45 **[0009]** The document 2 disclose a technique of putting a rotating titanium metal recovery board as a cathode in acid pickling waste water containing copper, carrying a predetermined cathode current therethrough to deposit copper particles on the cathode by electrolysis and scraping the copper particles continuously for recovery.

50 **[0010]** The document 3 discloses a technique of putting an electrode coated with a plastic film containing carbon fine particles in a metal ion containing solution thereby to deposit metal fine particles on the surface of the film for recovery.

55 **[0011]** The document 4 discloses a technique of using as a cathode a copper-plated copper plate which has a surface coated with a plastic film containing carbon fine particles and is subjected to heat treatment, and recovering metal fine particles from a solution containing metal ions by electrolysis.

Patent document 1: Japanese patent application publication No. 53-86627

Patent document 2: Japanese patent application publication No. 53-55410

Patent document 1: Japanese patent application publication No. 62-297485

45 Patent document 1: Japanese patent application publication No. 63-259094

Disclosure of the Invention

Problems to be solved by the Invention

50 **[0012]** When the rotating metal recovery board having a surface of Zr or Zr alloy or the titanium metal recovery board is used to deposit copper on its surface by electrolysis, the copper is adhered to the metal recovery board tightly, and therefore, scraping of the copper becomes difficult.

55 **[0013]** In addition, when the electrodeposition plate is coated with a plastic film containing carbon fine particles, copper is deposited on the film surface in the form of powder, and therefore, the material deposited can be easily removed. However, the recovery amount is less than 1 kg, for example, 210 g per 24 hours and the recovery performance is poor. Further, when the recovered powder copper is dissolved and cast, the yield rate is poor and recycling is difficult because of the powder state.

[0014] The present invention has an object to provide a metal recovery apparatus capable of recovering metal in a solution effectively and in such a manner that the metal is easy to recycle.

Means for solving the problems

[0015] The present invention provides a metal recovery apparatus comprising a metal recovery board having an electrodeposition surface or conductive plate on which a metal component precipitated out of a solution is deposited and an insulator formed around the electrodeposition surface or on a part of a surface of the conductive plate.

Effect of the Invention

[0016] According to the present invention, as a metal recovery apparatus has a metal recovery board having an insulator formed around a pattern of electrodeposition surface or a part of the conductive plate so as to deposit a metal component on an area not coated with the insulator, the metal component deposited on the metal recovery board can take the shape of a cluster large enough to facilitate recovery and recycling.

Brief description of the drawings

[0017]

Fig. 1 is a view illustrating a structure of a metal recovery apparatus according to an embodiment of the present invention;

Fig. 2 is a cross sectional view of a structure of a metal recovery board as a first example used in a metal recovery apparatus according to the embodiment of the present invention;

Figs. 3A and 3B are cross sectional views each of a structure of a metal recovery board as a modification of the first example used in a metal recovery apparatus according to the embodiment of the present invention;

Fig. 4 is a cross sectional view of a structure of a metal recovery board as a second example used in a metal recovery apparatus according to the embodiment of the present invention;

Figs. 5A and 5B are cross sectional views each of a structure of a metal recovery board as a modification of the second example used in a metal recovery apparatus according to the embodiment of the present invention;

Fig. 6 is a plan view illustrating a first example of slits of a metal recovery board used in a metal recovery apparatus according to the embodiment of the present invention;

Fig. 7 is a plan view illustrating a second example of slits of a metal recovery board used in a metal recovery apparatus according to the embodiment of the present invention;

Fig. 8 is a plan view illustrating a third example of slits of a metal recovery board used in a metal recovery apparatus according to the embodiment of the present invention;

Fig. 9 is a plan view illustrating a fourth example of slits of a metal recovery board used in a metal recovery apparatus according to the embodiment of the present invention;

Fig. 10 is a view illustrating a structure of a scraper blade as a first modified example used in a metal recovery apparatus according to the embodiment of the present invention;

Fig. 11 is a view illustrating a structure of a scraper blade as a second modified example and an electrolysis vessel as a modified example used in a metal recovery apparatus according to the embodiment of the present invention;

Fig. 12 is a view illustrating a structure of a scraper blade as a third modified example used in a metal recovery apparatus according to the embodiment of the present invention; and

Fig. 13 is a view illustrating a structure of a scraper blade as a fourth modified example used in a metal recovery apparatus according to the embodiment of the present invention.

Explanation of reference numerals

[0018]

1	electrolysis vessel
2	metal recovery board
2a	conductive plate
2b	insulating film
2s	slit
2t	protuberant portion
3	rotator

4	anode
5	direct-current power source
6, 60, 64, 65	scraper blade
R	acid pickling waste water

Best mode for carrying out the Invention

[0019] With reference to the drawings, embodiments of the present invention will be described in detail below.

[0020] Fig. 1 illustrates a structure of a metal recovery apparatus according to an embodiment of the present invention.

[0021] In Fig. 1, in an electrolysis vessel 1 into which acid pickling waste water R is inject, a circular-shaped metal recovery board 2 is provided with at least a part thereof immersed in the acid pickling waste water R and the metal recovery board 2 is supported rotatably by a rotator 3.

[0022] The metal recovery board 2 is used as a cathode (negative electrode) in the acid pickling waste water R and has a structure as illustrated in cross sectional views of Figs. 2, 3A and 3B.

[0023] The metal recovery board 2 illustrated in Fig. 2 has a circular-shaped conductive plate 2a of corrosion-resistant metal and an insulating film 2b of, for example, 0.1 mm to 10 mm in thickness formed on each surface of conductive plate 2a. Besides, the insulating film 2b on at least one surface of the metal recovery board 2 has slits 2s of a small width, for example, 10 mm or less in width formed thereon. These slits 2s are recesses relative to the surface of the conductive plate 2a.

[0024] The width of each slit 2s may be smaller at the conductive plate 2a side (bottom side) than at the opposite side (surface side) as shown in Fig. 3A or larger at the conductive plate 2a side than at the opposite side as shown in Fig. 3B. When the width of each slit is narrower at the conductive plate 2a side as shown in Fig. 3A, it becomes preferably easy to separate metal deposited on the metal recovery board 2.

[0025] A metal recovery board 2 illustrated in Fig. 4 has a conductive plate 2a of corrosion-resistant metal having narrow protuberant portions 2t of, for example, 0.1 mm to 10 mm in height and 10 mm or less in width formed on at least one surface thereof and an insulating film 2b formed on each surface of the conductive plate 2a except the protuberant portions 2t. Besides, portions of the insulating films 2b where the protuberant portions 2t of the conductive plate 2a are exposed constitute slits 2s. The protuberant portions 2t of the conductive plate 2a are formed by grinding, etching or the like. Here, in the metal recovery board 2 illustrated in Fig. 4, the upper surface of the insulating film 2b and the upper surfaces of the protuberant portions 2t are almost flat.

[0026] The width of each protuberant portion 2t may be smaller at the conductive plate 2a side than at the opposite side (surface side) as shown in Fig. 5A or larger at the conductive plate 2a side than at the opposite side as shown in Fig. 5B. When the width of each protuberant portion is narrower at the conductive plate 2a side as shown in Fig. 5A, it becomes preferably easy to separate metal deposited on the metal recovery board 2.

[0027] In Figs. 2 to 5, used as a corrosion-resistant metal of the conductive plate 2a is, for example, stainless, and used as a material of the insulating films 2b is a resin such as fluorocarbon resin or polypropylene, which serves to prevent deposition of metal on the conductive plate 2a.

[0028] Forming of the insulating films 2b on the conductive plate 2a is carried out by putting the conductive plate 2a and the insulating films 2b together and heating them or bonding the conductive plate 2a and the insulating films 2b by an adhesive agent. In the former case of heating, the heating temperature is determined appropriately in view of a softening temperature of the insulating films 2b or the like. Besides, the adhesive agent is selected in view of an adhesive strength of the solidified conductive plate 2a and insulating films 2b.

[0029] The slits 2s formed in the circular-shaped metal recovery board 2 take the shape of plane rings formed concentrically with a predetermined pitch. The slits 2s are formed by grinding a part of the insulating films 2b to have a desired shape by machine work after fixing and bonding the insulating films 2b on the conductive plate 2a.

[0030] The width of each slit 2s is set to be large enough to facilitate peeling and removing of metal clusters growing on the conductive plate 2a. Besides, when the pitch between adjacent two of the slits 2s is small, the insulating films 2b are easily peeled off while a scraper blade 6, which is described later, slides on the surface of the metal recovery board 2. Hence, the pitch is preferably 1 mm or more.

[0031] In addition, in order to increase an amount of metal precipitated from the conductive plate 2a, it is preferable that the total area of slits 2s is larger.

[0032] In the electrolysis vessel in which the metal recovery board 2 is arranged, an anode 4 of corrosion-resistant material, for example, stainless SUS304, is provided in such a manner that it is immersed in acid pickling waste water R. The anode 4 is arranged with a given spacing from the surface on which the slits 2s exist of the metal recovery board 2, and the anode 4 and the conductive plate 2a of the metal recovery board 2 are connected to the direct-current power source 5.

[0033] Further, above the electrolysis vessel 1, there is provided an angle scraper blade 6 for scraping metal clusters growing inside the slits 2s of the metal recovery board 2, this scraper blade 6 being arranged detachably on the metal

recovery board 2. This scraper blade 6 is arranged inclined gradually downwardly from the center side of the metal recovery board 2 to the periphery side.

[0034] Furthermore, the scraper blade 6 is made of a material such as metal having enough strength to scrape metal clusters growing on the metal recovery board 2. The scraper blade 6 may be made of steel, however a corrosion-resistant material such as stainless is preferably used. Under the lower part of the scraper blade 6, there is provided a metal recovery box 10.

[0035] Connected to an outlet 1a at the bottom of the electrolysis vessel 1 is a first pipe 8 linked to an inlet 7a of the circulating vessel 7. Connected to an outlet 7b on the circulating vessel 7 is a second pipe 9 linked to an inlet 1b of the electrolysis vessel 1.

[0036] A circulating pump 11 is attached to the midpoint of the first pipe 8 so that acid pickling waste water R inside the electrolysis vessel 1 can circulate through the first pipe 8, the circulating vessel 7 and the second pipe 9.

[0037] The next description is made about recovering of metal in the acid pickling waste water R by using the above-described metal recovery apparatus. In this case, in the metal recovery board 2, used as the conductive plate 2a illustrated in Figs. 2 to 5 is a circular-shaped stainless plate and used as the insulating films 2b is a fluorocarbon resin film. Besides, the insulating films 2b used in this case have ring slits 2s of different diameters, 5 mm in pitch and 1 mm in slit width illustrated in Fig. 6 formed thereon.

[0038] First, the acid pickling waste water R in an amount sufficient to immerse a part of the metal recovery board 2 therein is put into the electrolysis vessel 1. The acid pickling waste water R here is, for example, a sulfuric acid solution used to remove an oxide on the surface of a copper product or copper alloy product, which solution contains copper.

[0039] This is followed by passing current through the conductive plate 2a of the metal recovery board 2 and the anode 4 via the acid pickling waste water R with use of the direct-current power source 5. This current passage causes electrolysis, and copper in the acid pickling waste water R is deposited on the surface of the conductive plate 2a exposed inside the slits on the metal recovery board 2.

[0040] When the current density passing through the conductive plate 2a and the anode 4 is small, the recovery performance is reduced. However, when the current density is large, the recovery amount reaches a saturation point early and there is useless current-passing time with increase in cost, and hence, it is required to check in advance an optimal current density. The conditions for current-carrying in this embodiment are a current of 5 to 70 dA/mm² and a voltage of 1 to 20 V.

[0041] When copper is deposited more, copper clusters B grow along and on the slits 2s in the surface of the metal recovery board 2, which is shown in Figs. 2 to 5. As the copper is deposited continuously the copper clusters B jut from the surface of the insulating film 2b.

[0042] When copper is deposited by electrolysis, the metal recovery board 2 is rotated by the rotator 3 at a predetermined speed.

[0043] After the deposition becomes saturated, the scraper blade 6 is pressed against the surface of the metal recovery board 2 in which the slits 2s are formed and the metal recovery board 2 is rotated by the rotator 3. Then, the copper clusters B jutting from the slits 2s are scraped by the scraper blade 6 and removed from the metal recovery board 2. The copper clusters scraped off by the upper part of the scraper blade 6 are, for example, dropped into the recovery box 10 placed under the scraper blade 6.

[0044] Here, as the width of each slit 2s formed on the insulating film 2b of the metal recovery board 2 is 10 mm or less and small, the bottom of the copper cluster B is thin and is easy to be peeled or broken. Hence, removal of the copper clusters B from the metal recovery board 2 by the scraper blade 6 becomes easy and efficient recycling of the copper clusters B recovered is made possible.

[0045] Here, slits 2s of an insulating film 2b covering the conductive plate 2a may be provided on only one surface or on both surfaces of the conductive plate 2a. Preferably, the slits 2s are provided on the both surfaces as a recovery amount is increased. In addition, the metal recovery boards 2 provided may be one or increased in number to be two or more. Preferably, two or more metal recovery boards 2 are provided as a recovery amount is increased. When two or more metal recovery boards are provided, they may be arranged in parallel or coaxially.

[0046] Further, a metal recovery portion of the present invention is not limited to the conductive plate 2a. Any structure other than a plate may be used if it has an electrodeposition surface. For example, an apparatus for recovering metal by depositing the metal on slits 2s provided on a curved surface of a drum is also included in the present invention. Furthermore, an apparatus for recovering metal by depositing the metal on a metal mesh attached to a resin insulating plate is included in the present invention and in this case, the metal mesh pattern is used as an electrodeposition surface and surrounded by the insulating material. In short, any metal recovery apparatus can be used that has an electrodeposition surface on which a metal component is precipitated from a solution and deposited and an insulating film formed on a part of the surface of the electrodeposition surface.

[0047] Furthermore, a metal recovery apparatus of the present invention is not limited to those illustrated in the drawings used for description. In other words, it is necessary only to remove deposited metal by bringing the scraper blade 6 into contact with the metal recovery board 2 and shifting their positional relationship relatively. In addition, the

shape of the metal recovery board 2 is not limited to a circular board or may be a square board. Further, the metal recovery board 2 may not be rotated or may be fixed.

[0048] A metal recovery apparatus of the present invention has a structure for recovering metal and is capable of recovering, among metals, gold or gold alloy, silver or silver alloy, nickel or nickel alloy, zinc or zinc alloy, tin or tin alloy, and copper or copper alloy. What is most suitably recovered is copper or copper alloy.

[0049] Next description is made about copper recovery performance of different structures including three structures each using a metal recovery board 2 and four conventional structures each using a circular plate instead of the metal recovery board 2, based on the experimental results.

[0050] First, prepared as an example 1 was a first metal recovery board 2 having a structure illustrated in Fig. 2 and ring-like slits 2s illustrated in Fig. 6. Prepared as an example 2 was a second metal recovery board 2 having a structure illustrated in Fig. 4 and ring-like slits 2s illustrated in Fig. 6. Each of the metal recovery boards 2 of the examples 1 and 2 had a conductive plate 2a of circular-shaped stainless plate having a diameter of 800 mm and a thickness of 10 mm and insulating films 2b of fluorocarbon resin (Tetra-Fluoro-Ethylene) each having a thickness of 1 mm fixed and bonded to the surface of the conductive plate 2a. Formed on an insulating film 2b were ring-like slits 2s which were concentric circles having a pitch of 5 mm and a width of 1 mm.

[0051] In addition, prepared as an example 3 was a third metal recovery board 2 having a cross section illustrated in Fig. 2 and plural narrow and straight slits 2s extending radially from the center as illustrated in Fig. 7. The metal recovery board 2 of the example 3 had a conductive plate 2a of circular-shaped stainless plate having a diameter of 800 mm and a thickness of 10 mm and insulating films 2b of polyamide each having a thickness of 1 mm fixed and bonded to the surface of the conductive plate 2a. Formed on an insulating film 2b were slits 2s having a pitch of 5 mm and a width of 1 mm.

[0052] As a comparative example 1 having a conventional structure, a stainless circular plate was prepared which was not coated with an insulating material. Prepared as a comparative example 2 was a stainless circular plate having surfaces coated with Zr, and prepared as a comparative example 3 was a titanium circular plate. Further, prepared as a comparative example 4 was a stainless circular plate coated with plastic containing carbon fine particles. The diameter of each circular plate of the comparative examples 1 to 4 was 800 mm.

[0053] Then, the metal recovery boards 2 of the examples 1 to 3 were fixed in turn to the rotator 3 of the metal recovery apparatus illustrate in Fig. 1, and the circular plates of the comparative examples 1 to 4 were also fixed in turn to the rotator 3 instead of the metal recovery board 2 illustrated in Fig. 1. Then, the copper recovery from the acid pickling waste water R was checked in each of the examples and comparative examples, which results are shown in Table 1.

[0054] In the metal recovery apparatus used in the experiment, the anode 4 was made of stainless SUS304. The distance between the anode 4 and the metal recovery board 2 of each example and the distance between the anode 4 and the circular plate of each comparative example were both set at 20 mm. Besides, the scraper blade 6 was made of a rectangular parallelepiped stainless having a width of 50 mm, a thickness of 20 mm and a length of 600 mm.

[0055] Checking before the experiment and before recovery of copper showed ingredients of the acid pickling waste water were 71 g/L (gram/Liter) of copper, 16.5 g/L of sulfuric acid and 2.7 g/L of hydrogen peroxide. The amount of the acid pickling waste water injected in the electrolysis vessel 1 is 200 L. Further, the current-carrying conditions of the direct-current power source 5 were an average voltage of 3.2 V, a current of 542 A and time duration of 32 hours.

[0056]

[Table 1]

	Material of circular plate	Insulator and coating shape	Scraping state (Note)	State of recovered copper	Recovery amount Kg
Example 1	Stainless	fluorocarbon resin Concentric circle shaped slits	○	Copper cluster	10.3
Example 2	Stainless (protuberant portions are formed concentrically)	fluorocarbon resin (Only protuberant portions)	○	Copper cluster	11.9
Example 3	Stainless	Polyamide Radially extending slits	○	Copper cluster	9.7
Comparative example 1	Stainless	None	×	Copper cluster	11.6

(continued)

		Material of circular plate	Insulator and coating shape	Scraping state (Note)	State of recovered copper	Recovery amount Kg
5	Comparative example 2	Stainless Coated with Zr	None	Δ	Copper cluster	10.8
	Comparative example 3	Titanium	None	Δ	Copper cluster	11.1
10	Comparative example 4	Stainless	Plastic containing carbon fine particles	○	Powder	0.3
(Note) Scraping state is good (○), poor (Δ) and failed (×).						

[0057] As is clear from Table 1, when the metal recovery boards 2 of the examples 1 to 3 were used as cathodes, the scraping state by the scraper blade 6 was good and a large amount of copper was recovered.

[0058] On the other hand, in the comparative example 1, copper clusters were adhered to the circular plate tightly and scraping was failed. In the comparative examples 2 and 3, a material deposited on the circular plate could be peeled off and removed, however, could not be scraped off. Further, in the comparative example 4, an appropriate current could not be carried. A material deposited on the circular plate was easily scraped however, its recovery amount was small.

[0059] In the above-described embodiments, the experimental results of recovery of copper have been described. However, an object to be recovered is not limited to copper and may be any other metals. In such a case, it is necessary to select an appropriate material as the insulating film 2b of the metal recovery board 2. For example, when silver is recovered from a cyanide alkaline solution containing silver, fluorocarbon resin or polypropylene is preferably used as a material of the insulating film 2b.

[0060] Here, the slits of the metal recovery board 2 are not limited to the ring-shaped slits or straight slits extending in a radial pattern as shown in Figs. 6 and 7, respectively, and may be combination of concentric-circle-shaped slits and the radially extending slits as shown in Fig. 8, rectangular-shaped slits or island-shaped slits as shown in Fig. 9, or spiral-shaped slits (not shown).

[0061] In the metal recovery board 2 illustrated in Fig. 8, the intervals of concentric-circle-shaped slits and the radially extending slits are adjusted so that the plural island-shaped insulating films 2b separated by slits 2s can be spaced uniformly. In addition, in the metal recovery board 2 illustrated in Fig. 9, when the slits 2s are plural rectangular slits, the size of each slit is about 1 mm x 1 mm. When the slits 2s are dotted slits, each slit is shaped like a ring having a diameter of 1 mm.

[0062] The slits 2s illustrated in Figs. 6 to 9 may have a structure where the conductive plate 2a exists under the hollow portions of the insulating film 2b as illustrated in Figs. 2 and 3 or a structure where the insulating film 2b exists around the protuberant portions 2t of the conductive plate 2a as illustrated in Figs. 4 and 5.

[0063] The metal recovery board 2 as illustrated in Figs. 4 and 5 adopts a method of forming protuberant portions 2t on the conductive plate 2a before filling around the protuberant portions 2t with an insulating material, however, forming of the protuberant portions 2t may be performed by, for example, grinding the conductive plate 2a or etching the conductive plate 2a. For example, the metal recovery board 2 illustrated in Fig. 9 adopts a method of grinding the conductive plate 2a in two intersecting directions to form the rectangular protuberant portions 2t before coating the grinded portions with an insulating material.

[0064] Copper clusters growing on the slits 2s of the four metal recovery boards illustrated in Figs. 6 to 9 were removed. As a result, removal of the copper clusters was easier in the metal recovery board 2 having radially extending slits 2s as illustrated in Fig. 7 than that in the metal recovery board 2 having concentric-circles-shaped slits 2s illustrated in Fig. 6. In case of the metal recovery board 2 having both of the radially extending slits 2s and the concentric-circles-shaped slits 2s as illustrated in Fig. 8, the electrodeposition area was wider than the electrodeposition areas of the metal recovery boards of Figs. 6 and 7 and scrapping off of the copper clusters was easier than that of the metal recovery board 2 illustrated in Fig. 6. Further, in the case of the metal recovery board 2 having rectangular or dotted slits 2s as illustrated in Fig. 9, it was difficult to enlarge the electrodeposition area as compared with the metal recovery board 2 illustrated in Fig. 6, however removal of the copper clusters was relatively easy in the metal recovery board 2 of Fig. 9.

[0065] The scraper blade 6 applied to the above-described metal recovery apparatus is not limited to an angle blade and can adopt a scraper blade as illustrated in Figs. 10 to 12, for example.

[0066] A scraper blade 60 illustrated in fig. 10 has a rectangular blade main body 61 inclined downwardly from the center of the circular metal recovery board 2 to the outside, a vibration device 62 attached to the blade main body 61

and serrate protrusions 63 attached on the upper surface of the blade main body 61 and abutting diagonally across the direction of the slits 2s. The upper surface of the blade main body 61 has an area for sliding metal clusters scraped from the metal recovery board 2 by the protrusions 63.

[0067] The metal clusters on the metal recovery board 2 scraped by the protrusions 63 slide on the blade main body 61 by their self-weights and vibrations of the vibration device 62 and fall into the recovery box 10 behind the scraper blade 60.

[0068] When the protrusions 63 of the scraper blade 60 are serrate, the protrusions 63 are capable of scraping metal clusters at a desired angle of the serrate protrusions. Hence, the scraper blade 60 can remove metal clusters easier than the straight blade 6 illustrated in Fig. 1. When the slits 2s are shaped like rings, the angle is oblique to their tangential direction.

[0069] The scraper blade 60 can have comb-teeth protrusions 63a at positions where the scraper blade 60 moves on the ring-shaped slits 2s of the metal recovery board 2, as illustrated in Fig. 11. In this case, the protrusions 63a scrape metal clusters while moving on the slits 2s by rotation of the metal recovery board 2.

[0070] A scraper blade 64 illustrated in Fig. 12 is a blade traveling in a direction perpendicular to the longitudinal direction of the slits 2s of the metal recovery board 2. Besides, the bottom of the electrolysis vessel 1 under the scraper blade 64 has a inclined surface 1d for sliding scraped and dropped metal clusters C into the circulating vessel 7. A lower portion 1s of the inclined surface 1d is provided with an outlet 1e. Attached to the outlet 1e is a pipe 13 for leading the metal clusters C to a filter 12 of the circulating vessel 7. The metal clusters C passing through the outlet 1e are recovered by the filter 12 of the circulating vessel 7 and the acid pickling waste water is made to pass through the filter 12 to get inside the circulating vessel 7.

[0071] When such a structure is adopted that the metal clusters C are not recovered by the filter 12, a stopper is provided just in front of the lower portion 1s of the electrolysis vessel 1 so that the metal clusters C can be prevented from falling into the circulating vessel 7.

[0072] A scraper blade 65 illustrated in Fig. 13 is fixed rotatably around a supporting point which is an end of the horizontally-long, rectangular blade main body further from the center of the metal recovery board 2. Attached to the supporting point is a rotator 66 striking the blade main body upwardly. Further, a recovery box 10 is provided outside of the supporting point of the scraper blade 65.

[0073] Being struck upward from its horizontal position by the rotator 66, the scraper blade 65 scrapes the metal clusters C and strike the scraped metal clusters C up to put them into the recovery box 10.

[0074] Then, the scraper blade 65 is rotated in the same direction of striking up, scrapes metal clusters on the metal recovery board 2 and strikes up the metal clusters.

Claims

1. A metal recovery apparatus comprising: a metal recovery board having an electrodeposition surface to which a metal component precipitated from a solution is attached and an insulator formed around the electrodeposition surface.
2. The metal recovery apparatus of claim 1, wherein the electrodeposition surface is a surface of a conductive plate and the insulator is formed on a part of the surface of the conductive plate.
3. The metal recovery apparatus of claim 1 or 2, wherein the electrodeposition surface is a cathode for precipitating the metal component from the solution by electrolysis.
4. The metal recovery apparatus of any one of claims 1 to 3, wherein the electrodeposition surface is attached rotatably.
5. The metal recovery apparatus of any one of claims 1 to 4, wherein the insulator has a slit formed for exposing the electrodeposition surface.
6. The metal recovery apparatus of claim 5, wherein the electrodeposition surface is circular and the slit is shaped like a plurality of concentric circles.
7. The metal recovery apparatus of claim 5, wherein the slit is shaped like rectangles extending radially on the electrodeposition surface.
8. The metal recovery apparatus of any one of claims 1 to 7, wherein at least one part of the electrodeposition surface has a protuberant portion and the insulator is formed around the protuberant portion.

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9. The metal recovery apparatus of any one of claims 1 to 8, wherein the insulator is made of a resin.
10. The metal recovery apparatus of any one of claims 1 to 9, further comprising a scraper blade for scraping a cluster of the metal component deposited on the electrodeposition surface.
11. The metal recovery apparatus of any one of claims 1 to 10, wherein the metal component is copper or copper alloy and the solution is an acid pickling solution.

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FIG. 1

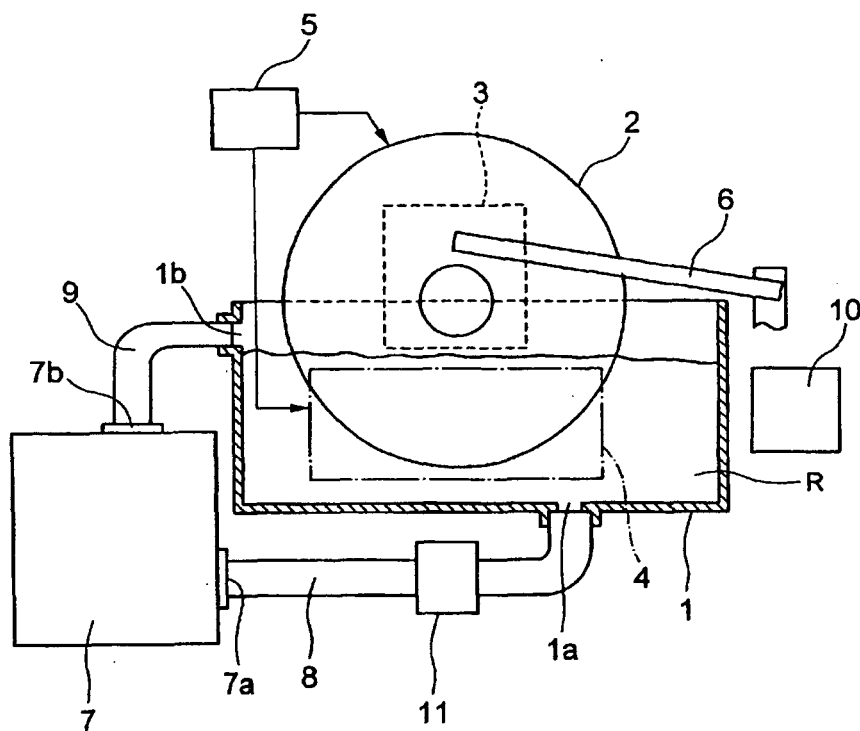


FIG. 2

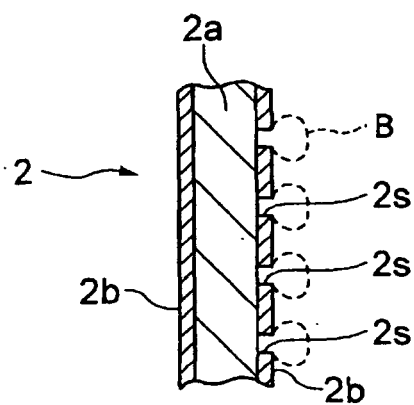


FIG. 3A

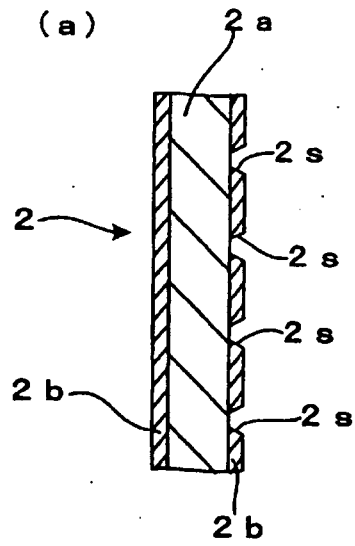


FIG. 3B

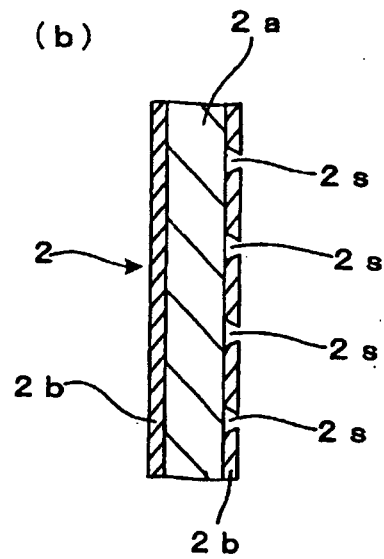


FIG. 4

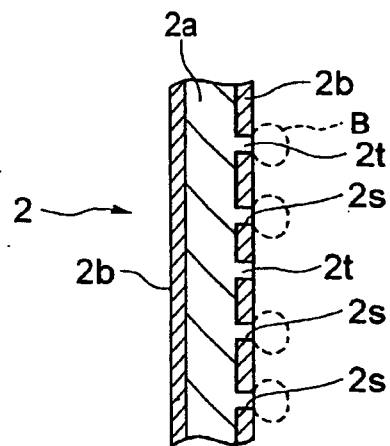


FIG. 5A

FIG. 5B

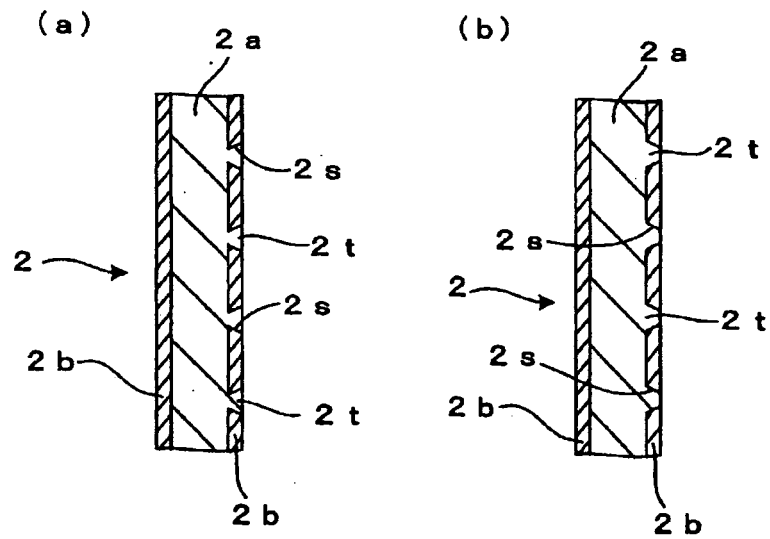


FIG. 6

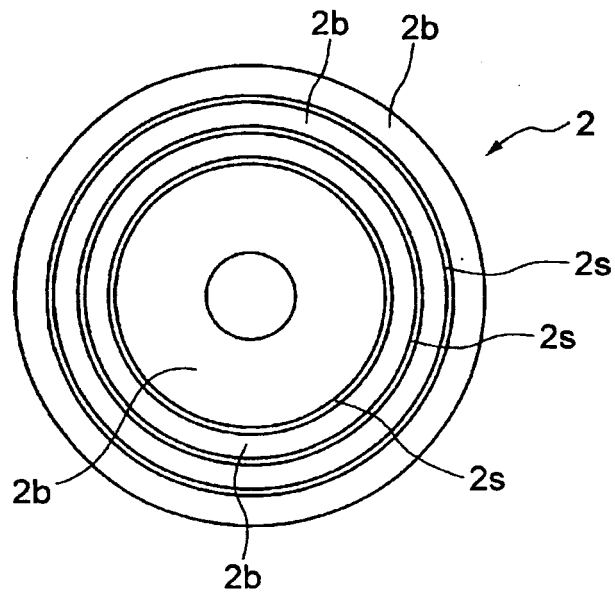


FIG. 7

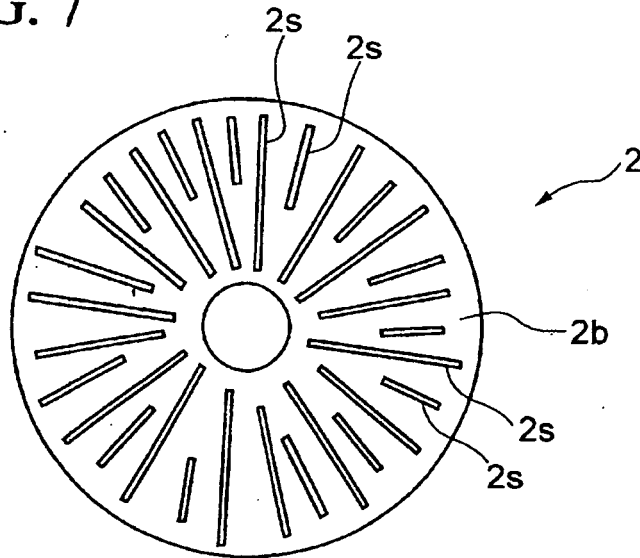


FIG. 8

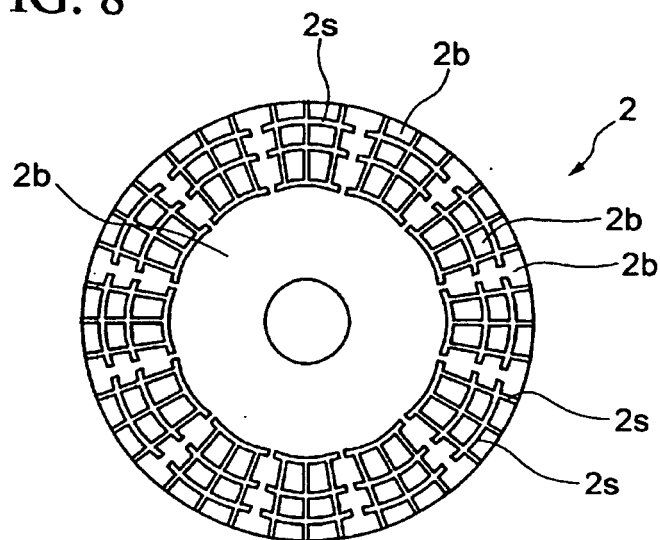


FIG. 9

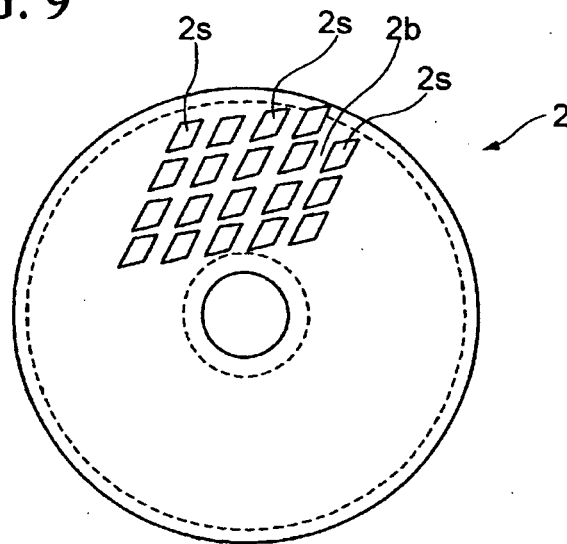


FIG. 10

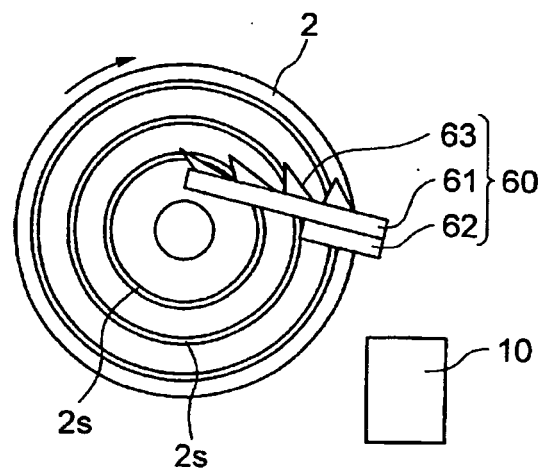


FIG. 11

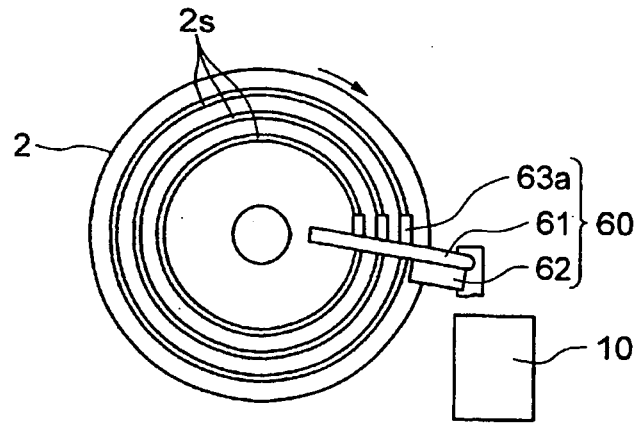


FIG. 12'

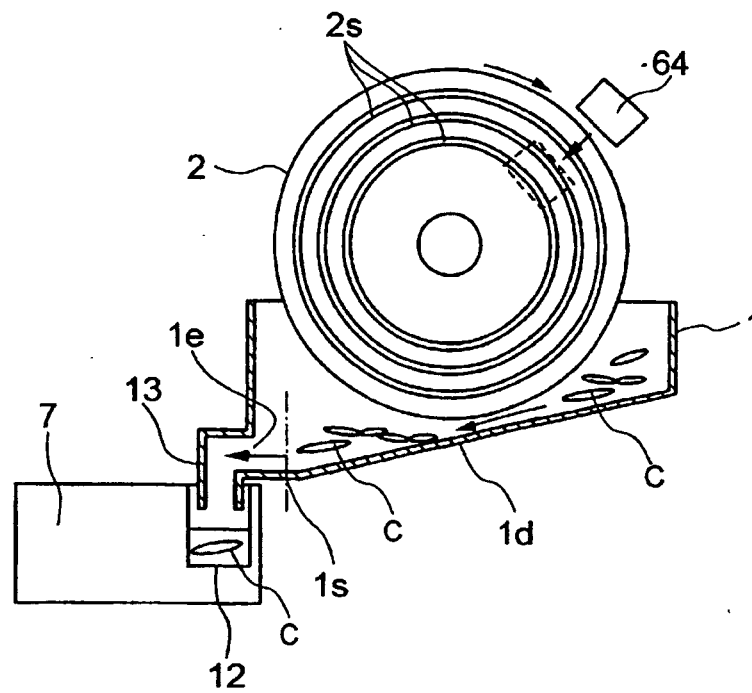
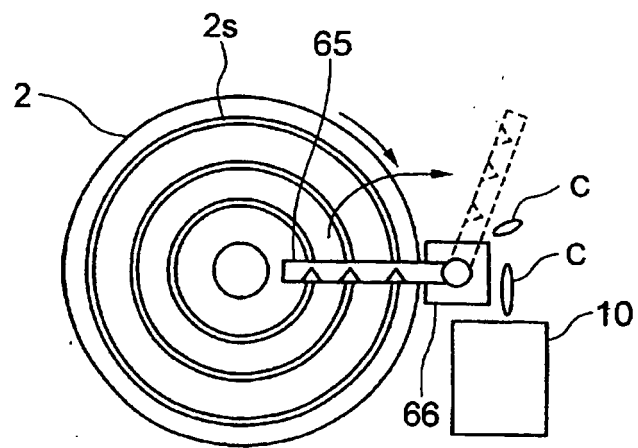


FIG. 13



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2005/014849

A. CLASSIFICATION OF SUBJECT MATTER

C25C7/08 (2006.01), **C25C7/02** (2006.01)

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)

C25C7/08 (2006.01), **C25C7/02** (2006.01)

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	1996-2005
Kokai Jitsuyo Shinan Koho	1971-2005	Toroku Jitsuyo Shinan Koho	1994-2005

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2000-169992 A (Mitsubishi Materials Corp.), 20 June, 2000 (20.06.00), Par. Nos. [0002], [0017]; Fig. 2 (Family: none)	1-11



Further documents are listed in the continuation of Box C.



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Date of the actual completion of the international search
31 October, 2005 (31.10.05)Date of mailing of the international search report
08 November, 2005 (08.11.05)Name and mailing address of the ISA/
Japanese Patent Office

Authorized officer

Facsimile No.

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Form PCT/ISA/210 (second sheet) (April 2005)

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Patent documents cited in the description

- JP 53086627 A [0011]
- JP 53055410 A [0011]
- JP 62297485 A [0011]
- JP 63259094 A [0011]