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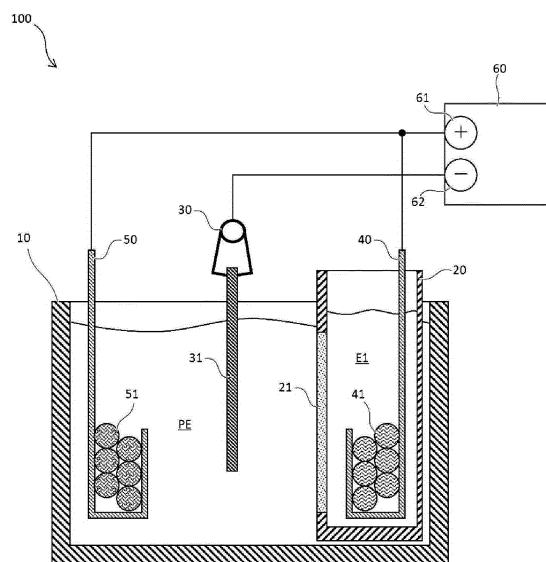
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(54) **METHOD FOR SUPPRESSING INCREASE IN ZINC CONCENTRATION IN PLATING SOLUTION, AND METHOD FOR PRODUCING ZINC-BASED PLATING MEMBER**

(57) Provided is a method for suppressing an increase in the zinc concentration of a plating solution when a zinc alloy plating member using nickel as an alloy element is manufactured using a zinc alloy plating apparatus. The plating apparatus includes: a plating tank capable of accommodating the plating solution which is acidic; a first diaphragm tank which is capable of accommodating a first electrolytic solution and has a first diaphragm composed of a cation exchange membrane; a cathode holding member for cathode-electrolyzing a member to be plated that is in contact with the plating solution inside the plating tank during use; a first anode holding member for anode-electrolyzing a soluble zinc-containing member that is in contact with the first electrolytic solution inside the first diaphragm tank during use; the soluble zinc-containing member held by the first anode holding member; a soluble metal-containing member containing the nickel which is the alloy element; and a second anode holding member for anode-electrolyzing the soluble metal-containing member. The first diaphragm tank is arranged in a manner that the first electrolytic solution is in contact with one surface of the first diaphragm and the plating solution is in contact with the other surface of the first diaphragm during use.



**FIG. 1**

## Description

### BACKGROUND

5 Technical Field

**[0001]** The present invention relates to a method for suppressing an increase in the zinc concentration of a plating solution, and a method for manufacturing a zinc-based plating member.

10 Related Art

**[0002]** Patent literature 1 describes a zinc alloy electroplating method including energization in an alkali-zinc alloy electroplating bath equipped with a cathode and an anode, wherein a cathode region including the cathode and an anode region including the anode are separated from each other by a separator containing an electrolytic solution gel that can be energized.

**[0003]** Patent literature 2 describes a plating bath characterized in that an anode (2) is isolated from an alkaline electrolytic solution (plating bath) by an ion exchange membrane (6) in an alkaline plating bath (1) for zinc-nickel film electrodeposition which has the anode (2) and a cathode (3).

20 Literature of related art

Patent literature

**[0004]**

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Patent literature 1: Japanese Patent No. 58320202

Patent literature 2: Japanese Patent No. 4716568

### SUMMARY

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Problems to be Solved

**[0005]** The present invention provides a method for suppressing an increase in the zinc concentration of a plating solution when an anode is soluble, and a method for manufacturing a zinc-based plating member.

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Means to Solve Problems

**[0006]** The present invention includes the following aspects.

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(1) A zinc-based plating apparatus for manufacturing a zinc-based plating member, including: a plating tank capable of accommodating a plating solution; a first diaphragm tank which is capable of accommodating a first electrolytic solution and has a first diaphragm including a first ion exchange membrane; a cathode holding member for cathode-electrolyzing a member to be plated that is in contact with the plating solution inside the plating tank during use; and a first anode holding member for anode-electrolyzing a soluble zinc-containing member that is in contact with the first electrolytic solution inside the first diaphragm tank during use; wherein the first diaphragm tank is arranged in a manner that the first electrolytic solution is in contact with one surface of the first diaphragm and the plating solution is in contact with the other surface of the first diaphragm during use.

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(2) The zinc-based plating apparatus according to (1), wherein the plating solution is acidic.

(3) The zinc-based plating apparatus according to (1) or (2), wherein the first ion exchange membrane includes a cation exchange membrane.

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(4) The zinc-based plating apparatus according to any one of (1) to (3), wherein the first ion exchange membrane includes an anion exchange membrane.

(5) The zinc-based plating apparatus according to any one of (1) to (4), further including the soluble zinc-containing member held by the first anode holding member.

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(6) The zinc-based plating apparatus according to any one of (1) to (5), further including a second anode holding member for anode-electrolyzing a soluble metal-containing member that is electrically connected to the plating solution during use.

(7) The zinc-based plating apparatus according to (6), further including the soluble metal-containing member held

by the second anode holding member.

(8) The zinc-based plating apparatus according to (6) or (7), wherein the soluble metal-containing member contains a metal nobler than zinc as a soluble metal.

(9) The zinc-based plating apparatus according to any one of (6) to (8), wherein the second anode holding member is arranged in a manner that the soluble metal-containing member is in contact with the plating solution during use.

(10) The zinc-based plating apparatus according to any one of (6) to (9), further including a second diaphragm tank which is capable of accommodating a second electrolytic solution and has a second diaphragm including a second ion exchange membrane, wherein the second diaphragm tank is arranged in a manner that the second electrolytic solution which is in contact with the soluble metal-containing member inside the second diaphragm tank is in contact with one surface of the second diaphragm and the plating solution is in contact with the other surface of the second diaphragm during use.

(11) The zinc-based plating apparatus according to (10), wherein the second ion exchange membrane includes a cation exchange membrane.

(12) The zinc-based plating apparatus according to (10) or (11), wherein the second ion exchange membrane includes an anion exchange membrane.

(13) A method for manufacturing a zinc-based plating member, in which a first diaphragm tank which has a first diaphragm including a first ion exchange membrane and accommodates a first electrolytic solution is arranged in a manner that the first electrolytic solution is in contact with one surface of the first diaphragm and a plating solution accommodated inside the plating tank is in contact with the other surface of the first diaphragm, a member to be plated that is in contact with the plating solution in the plating tank is cathode-electrolyzed, and a soluble zinc-containing member that is in contact with the first electrolytic solution inside the first diaphragm tank is anode-electrolyzed.

(14) The method for manufacturing a zinc-based plating member according to (13), wherein the plating solution is acidic.

(15) The method for manufacturing a zinc-based plating member according to (13) or (14), wherein the first ion exchange membrane includes a cation exchange membrane.

(16) The method for manufacturing a zinc-based plating member according to any one of (13) to (15), wherein the first ion exchange membrane includes an anion exchange membrane.

(17) The method for manufacturing a zinc-based plating member according to any one of (13) to (16), wherein a soluble metal-containing member that is in contact with the plating solution in the plating tank is anode-electrolyzed.

(18) The method for manufacturing a zinc-based plating member according to any one of (13) to (16), wherein a second diaphragm tank which has a second diaphragm including a second ion exchange membrane and accommodates a second electrolytic solution is arranged in a manner that the second electrolytic solution is in contact with one surface of the second diaphragm and the plating solution is in contact with the other surface of the second diaphragm, and a soluble metal-containing member that is in contact with the second electrolytic solution in the second diaphragm tank is anode-electrolyzed.

(19) The method for manufacturing a zinc-based plating member according to (18), wherein the second ion exchange membrane includes a cation exchange membrane.

(20) The method for manufacturing a zinc-based plating member according to (18) or (19), wherein the second ion exchange membrane includes an anion exchange membrane.

(21) The method for manufacturing a zinc-based plating member according to any one of (17) to (20), wherein the soluble metal-containing member contains a metal nobler than zinc as a soluble metal.

[1] A method for suppressing an increase in the zinc concentration of a plating solution when a zinc alloy plating member using nickel as an alloy element is manufactured using a zinc alloy plating apparatus, wherein the plating apparatus includes: a plating tank capable of accommodating the plating solution which is acidic; a first diaphragm tank which is capable of accommodating the first electrolytic solution and has a first diaphragm composed of a cation exchange membrane; a cathode holding member for cathode-electrolyzing a member to be plated that is in contact with the plating solution inside the plating tank during use; a first anode holding member for anode-electrolyzing a soluble zinc-containing member that is in contact with the first electrolytic solution inside the first diaphragm tank during use; the soluble zinc-containing member held by the first anode holding member; a soluble metal-containing member containing the nickel which is the alloying element; and a second anode holding member for anode-electrolyzing the soluble metal-containing member; and the first diaphragm tank is arranged in a manner that the first electrolytic solution is in contact with one surface of the first diaphragm and the plating solution is in contact with the other surface of the first diaphragm during use.

[2] The method for suppressing an increase in the zinc concentration of a plating solution according to [1], wherein the second anode holding member is arranged in a manner that the soluble metal-containing member is in contact with the plating solution during use.

[3] The method for suppressing an increase in the zinc concentration of a plating solution according to [2], further including a second diaphragm tank which is capable of accommodating a second electrolytic solution and has a second diaphragm composed of a cation exchange membrane, wherein the second diaphragm tank is arranged in a manner that the second electrolytic solution which is in contact with the soluble metal-containing member inside the second diaphragm tank is in contact with one surface of the second diaphragm and the plating solution is in contact with the other surface of the second diaphragm during use.

[4] A method for manufacturing a zinc-based plating member, in which a first diaphragm tank which has a first diaphragm composed of a cation exchange membrane and accommodates a first electrolytic solution is arranged in a manner that the first electrolytic solution is in contact with one surface of the first diaphragm and an acidic plating solution accommodated inside a plating tank is in contact with the other surface of the first diaphragm, a member to be plated that is in contact with the plating solution in the plating tank is cathode-electrolyzed, a soluble zinc-containing member that is in contact with the first electrolytic solution inside the first diaphragm tank is anode-electrolyzed, and a soluble metal-containing member containing nickel which is an alloy element is anode-electrolyzed, and thereby zinc-nickel plating is formed on the member to be plated while an increase in the zinc concentration of the plating solution is suppressed.

[5] The method for manufacturing a zinc-based plating member according to [4], wherein the soluble metal-containing member is in contact with the plating solution in the plating tank.

[6] The method for manufacturing a zinc-based plating member according to [4] or [5], wherein a second diaphragm tank which has a second diaphragm composed of a cation exchange membrane and accommodates a second electrolytic solution is arranged in a manner that the second electrolytic solution is in contact with one surface of the second diaphragm and the plating solution is in contact with the other surface of the second diaphragm, and the soluble metal-containing member that is in contact with the second electrolytic solution in the second diaphragm tank is anode-electrolyzed.

## Effect

**[0007]** According to the present invention, a method for suppressing an increase in the zinc concentration of a plating solution when an anode is soluble, and a method for manufacturing a zinc-based plating member are provided.

## BRIEF DESCRIPTION OF THE DRAWINGS

### [0008]

FIG. 1 is an illustrative diagram of a zinc-based plating apparatus according to a first embodiment of the present invention.

FIG. 2 is an illustrative diagram of a zinc-based plating apparatus according to a second embodiment of the present invention.

## DESCRIPTION OF THE EMBODIMENTS

**[0009]** Hereinafter, embodiments of the present invention are described.

**[0010]** FIG. 1 is an illustrative diagram of a zinc-based plating apparatus according to a first embodiment of the present invention. A zinc-based plating apparatus 100 according to the first embodiment is used for manufacturing a zinc-based plating member. Zinc-based plating is a general term for zinc plating and zinc alloy plating. A specific example of the zinc alloy plating may be zinc-nickel plating.

**[0011]** The zinc-based plating apparatus 100 includes a plating tank 10, a first diaphragm tank 20, a cathode holding member 30, and a first anode holding member 40.

**[0012]** The plating tank 10 is capable of accommodating a plating solution PE, and in FIG. 1, the plating solution PE is inside the plating tank 10. A specific example of the material constituting the plating tank 10 may be polypropylene. The plating tank 10 may be equipped with a stirring apparatus for stirring the plating solution PE, or may be equipped with a filter for removing insoluble substances generated in the plating solution PE. The plating tank 10 may be equipped with a circulation pump for stirring the plating solution PE and removing the insoluble substances.

**[0013]** The composition of the plating solution PE is appropriately set according to the type of the zinc-based plating. As a specific example, the plating solution PE is acidic. That is, in the embodiment, the plating solution PE is an acidic zinc-based plating solution. In the specification, the zinc-based plating solution is an electrolytic solution containing ions including zinc elements and is a liquid capable of forming a zinc-containing plating film on a member to be plated that has been cathode-electrolyzed. Moreover, the zinc-based plating solution may contain insoluble components and may be in the form of a dispersion.

**[0014]** The first diaphragm tank 20 is capable of accommodating a first electrolytic solution E1, and in FIG. 1, the first electrolytic solution E1 is inside the first diaphragm tank 20. The first diaphragm tank 20 has a first diaphragm 21 including a first ion exchange membrane. The first ion exchange membrane may include a cation exchange membrane or an anion exchange membrane. As described later, the first ion exchange membrane may preferably include a cation exchange membrane.

**[0015]** In the zinc-based plating apparatus 100 according to the first embodiment, the first diaphragm tank 20 is located inside the plating tank 10, and the first diaphragm tank 20 is arranged in a manner that the first electrolytic solution E1 is in contact with one surface of the first diaphragm 21 (on the inner side of the first diaphragm tank 20) and the plating solution PE is in contact with the other surface of the first diaphragm 21 (on the outer side of the first diaphragm tank 20).

**[0016]** A specific example of the material constituting the first diaphragm tank 20 may be polypropylene. The first diaphragm tank 20 may be equipped with a stirring apparatus for stirring the first electrolytic solution E1 inside the first diaphragm tank 20, or may be equipped with a filter for removing insoluble substances generated in the first electrolytic solution E1. The first diaphragm tank 20 may be equipped with a circulation pump for stirring the first electrolytic solution E1 and removing the insoluble substances.

**[0017]** In the embodiment, the first diaphragm tank 20 is arranged inside the plating tank 10, but a part of the inside of the plating tank 10 may be partitioned and the first diaphragm 21 may be arranged in the partition. In this case, the inner side of the partitioned part becomes the first diaphragm tank 20, the first electrolytic solution E1 may be located inside the first diaphragm tank 20, and the plating solution PE may be located on the outer side of the partitioned part inside the plating tank 10.

**[0018]** The cathode holding member 30 is used for cathode-electrolyzing the member to be plated 31 that is in contact with the plating solution PE inside the plating tank 10 during use. That is, the cathode holding member 30 has a function of holding the member to be plated 31 and a function of passing a cathode electrolytic current through the member to be plated 31. A shape of the cathode holding member 30 is appropriately set according to a shape of the member to be plated 31 to be held. In FIG. 1, the cathode holding member 30 has the shape of a clip that clamps the member to be plated 31 having a plate shape. The cathode holding member 30 is connected to a cathode terminal 62 of a power supply apparatus 60 via wiring in order that the member to be plated 31 can be cathode-electrolyzed.

**[0019]** Moreover, in the specification, cathodic electrolysis means that electrolysis is performed at a negative potential relative to the potential of anodic electrolysis, and in relation to the ground potential, the potential of cathodic electrolysis may be a positive potential or a negative potential. Similarly, anodic electrolysis means that electrolysis is performed at a positive potential relative to the potential of cathodic electrolysis, and in relation to the ground potential, the potential of anodic electrolysis may be a positive potential or a negative potential.

**[0020]** The first anode holding member 40 is used for anode-electrolyzing a soluble zinc-containing member 41 that is in contact with the first electrolytic solution E1 inside the first diaphragm tank during use. That is, the first anode holding member 40 has a function of holding the soluble zinc-containing member 41 and a function of passing an anode electrolytic current through the soluble zinc-containing member 41. A shape of the first anode holding member 40 is appropriately set according to a shape of the soluble zinc-containing member 41 to be held. In FIG. 1, the first anode holding member 40 has the shape of a cage that holds the soluble zinc-containing member 41 composed of a plurality of zinc ingots (lumps). The first anode holding member 40 is connected to an anode terminal 61 of the power supply apparatus 60 via wiring in order that the soluble zinc-containing member 41 can be anode-electrolyzed.

**[0021]** The first electrolytic solution E1 is an electrolytic solution containing ions including zinc elements, and when the soluble zinc-containing member 41 is anode-electrolyzed, the zinc contained in the soluble zinc-containing member 41 can be dissolved as an ion. Moreover, the first electrolytic solution E1 may contain insoluble components and may be in the form of a dispersion.

**[0022]** The zinc-based plating apparatus 100 further includes a second anode holding member 50 for anode-electrolyzing a soluble metal-containing member 51 that is electrically connected to the plating solution PE during use. That is, the second anode holding member 50 has a function of holding the soluble metal-containing member 51 and a function of passing an anode electrolytic current through the soluble metal-containing member 51. A shape of the second anode holding member 50 is appropriately set according to a shape of the soluble metal-containing member 51 to be held. In FIG. 1, the first anode holding member 40 has the shape of a cage that holds the soluble metal-containing member 51 composed of a plurality of nickel ingots (lumps). The second anode holding member 50 is connected to the anode terminal 61 of the power supply apparatus 60 via wiring in order that the soluble metal-containing member 51 can be anode-electrolyzed.

**[0023]** The soluble metal-containing member 51 is held by the second anode holding member 50 and located inside the plating tank 10, and is electrically connected to the plating solution PE in a manner of being in direct contact with the plating solution PE. The soluble metal-containing member 51 can be a source of alloy elements in the zinc alloy plating. As described above, when the soluble metal-containing member 51 is composed of the plurality of nickel ingots (lumps), the zinc alloy plating can be zinc-nickel plating. The soluble metal-containing member 51 may contain a metal nobler than zinc as a soluble metal, such as the nickel described above.

**[0024]** Moreover, in FIG. 1, the first anode holding member 40 and the second anode holding member 50 are connected to the same anode terminal 61, but the present invention is not limited hereto. The anodic electrolysis potential of the first anode holding member 40 and the anodic electrolysis potential of the second anode holding member 50 may be different from each other.

**[0025]** FIG. 2 is an illustrative diagram of a zinc-based plating apparatus according to a second embodiment of the present invention. A zinc-based plating apparatus 101 according to the second embodiment has the same basic configuration as the zinc-based plating apparatus 100 according to the first embodiment. The difference of the zinc-based plating apparatus 101 according to the second embodiment when compared with the zinc-based plating apparatus 100 according to the first embodiment is that the second anode holding member 50 is located inside a second diaphragm tank 70 which accommodates a second electrolytic solution E2.

**[0026]** That is, the zinc-based plating apparatus 101 includes the second diaphragm tank 70 having a second diaphragm 71 including a second ion exchange membrane. The second diaphragm tank 70 is arranged in a manner that the second electrolytic solution E2 is in contact with one surface of the second diaphragm 71 (on the inner side of the second diaphragm tank 70) and the plating solution PE is in contact with the other surface of the second diaphragm 71 (on the outer side of the second diaphragm tank 70). The second electrolytic solution E2 is in contact with the soluble metal-containing member 51 held by the second anode holding member 50 inside the second diaphragm tank 70.

**[0027]** A specific example of the material constituting the second diaphragm tank 70 may be polypropylene. The second diaphragm tank 70 may be equipped with a stirring apparatus for stirring the second electrolytic solution E2 inside the second diaphragm tank 70, or may be equipped with a filter for removing insoluble substances generated in the second electrolytic solution E2. The second diaphragm tank 70 may be equipped with a circulation pump for stirring the second electrolytic solution E2 and removing the insoluble substances.

**[0028]** In the embodiment, the second diaphragm tank 70 is arranged inside the plating tank 10, but a part of the inside of the plating tank 10 may be partitioned and the second diaphragm 71 may be arranged in the partition. In this case, the inner side of the partitioned part becomes the second diaphragm tank 70, the second electrolytic solution E2 may be located inside the second diaphragm tank 70, and the plating solution PE may be located on the outer side of the partitioned part inside the plating tank 10.

**[0029]** The second electrolytic solution E2 is an electrolytic solution, and when the soluble metal-containing member 51 is anode-electrolyzed, the metal contained in the soluble metal-containing member 51 can be dissolved as an ion. Moreover, the second electrolytic solution E2 may contain insoluble components and may be in the form of a dispersion.

**[0030]** The second ion exchange membrane may include a cation exchange membrane or an anion exchange membrane. The second ion exchange membrane may have the same configuration as the first ion exchange membrane, or may have a different configuration.

**[0031]** The above embodiments have been described for facilitating the understanding of the present invention, but not for limiting the present invention. Therefore, each element disclosed in the above embodiments is intended to include all design changes and equivalents belonging to the technical scope of the present invention. For example, the first diaphragm tank 20 may have a plurality of first diaphragms 21 having different configurations, and the second diaphragm tank 70 may have a plurality of second diaphragms 71 having different configurations.

### Example

**[0032]** Hereinafter, the effects of the present invention are described based on examples, but the present invention is not limited hereto.

(Example 1)

**[0033]** An acidic zinc-nickel plating solution having the composition shown in Table 1 was prepared.

[Table 1]

Acidic zinc-nickel plating solution Metas ANK-10 manufactured by Yuken Kogyo Co., Ltd.		
Zinc chloride	73 g/L	(Zn: 35 g/L) (Ni: 20 g/L)
Nickel chloride	81 g/L	
Potassium chloride	206 g/L	
Metas ANK-10K	125 ml/L	
Metas ANK-10D	12 ml/L	

(continued)

Acidic zinc-nickel plating solution Metas ANK-10 manufactured by Yuken Kogyo Co., Ltd.		
Metas ANK-10M	30 ml/L	
Metas ANK-10G	2 ml/L	
Bath temperature	40°C	
pH	5.4	

**[0034]** By using the zinc-based plating apparatus 100 shown in FIG. 1, the above acidic zinc-nickel plating solution was put into the plating tank 10 as the plating solution PE, and any one of the following electrolytic solutions was put into the first diaphragm tank 20 as the first electrolytic solution E1 (internal solution).

(Electrolytic solution A) zinc chloride concentration 50 g/L

(Electrolytic solution B) zinc chloride concentration 500 g/L

(Electrolytic solution C) zinc chloride concentration 0 g/L

**[0035]** As the first diaphragm 21 of the first diaphragm tank 20, any one of the ion exchange membranes shown in Table 2 was used.

[Table 2]

Type of ion exchange membrane		
Product name	Maker	Type
Selemion CMVN	AGC Engineering Co., Ltd.	Cation
Neosepta CMB	Astom Co., Ltd.	Cation
Neosepta AHA	Astom Co., Ltd.	Anion

**[0036]** Plating was performed under the conditions shown in Table 3. Moreover, the unit of energization time in Table 3 is hour.

[Table 3]

No.	Ion exchange membrane	Membrane type	Energization time (hr)	Internal solution			Plating solution		
				Zn before energization (g/L)	Zn after energization (g/L)		Zn before energization (g/L)	Zn after energization (g/L)	
①	None	---	25	---	---		35.0	40.2	↑
②	Neosepta AHA	Anion	25	0	43.1	↑	35.0	20.5	↓
③	Neosepta CMB	Cation	25	25.0	39.5	↑	35.0	30.1	↓
④	Neosepta CMB	Cation	25	250.0	257.0	↑	35.0	32.5	↓
⑤	Selemin CMVN	Cation	25	25.0	28.5	↑	35.0	34.0	↓
⑥	Selemin CMVN	Cation	25	250.0	251.3	↑	35.0	34.5	↓



**[0037]** As shown in Table 3, when the first diaphragm tank 20 was not arranged (Experiment No. 1), the zinc concentration in the plating solution PE was increased by energization (40.2 g/L).

**[0038]** On the other hand, when the first diaphragm tank 20 having an anion membrane (anion exchange membrane) as the first diaphragm 21 was arranged and the zinc concentration of the first electrolytic solution E1 (internal solution) was 0 g/L (electrolytic solution C) (Experiment No. 2), an increase in the zinc concentration of the plating solution PE due to energization was suppressed (20.5 g/L).

**[0039]** When the first diaphragm tank 20 having a cation membrane (cation exchange membrane) as the first diaphragm 21 was arranged and the zinc concentration of the first electrolytic solution E1 (internal solution) was 25 g/L (electrolytic solution A) (Experiment No. 3), an increase in the zinc concentration of the plating solution PE due to energization was suppressed (30.1 g/L).

**[0040]** When the first diaphragm tank 20 having a cation membrane (cation exchange membrane) as the first diaphragm 21 was arranged and the zinc concentration of the first electrolytic solution E1 (internal solution) was 500 g/L (electrolytic solution A) (Experiment No. 4), an increase in the zinc concentration of the plating solution PE due to energization was suppressed (32.5 g/L).

**[0041]** When only the type of the cation exchange membrane was different from that in Experiment No.3 and Experiment No.4 (Experiment No.5 and Experiment No. 6), similarly to Experiment No.3 and Experiment No. 4, an increase in the zinc concentration of the plating solution PE due to energization was suppressed (Experiment No. 5: 34.0 g/L, Experiment No. 6: 34.5 g/L).

**[0042]** Under the condition of Experiment No. 4, the effect of the second diaphragm tank 70 was confirmed. When the nickel concentration after energization was measured under the condition of Experiment No. 4, the nickel concentration after energization was increased from 20.0 g/L before energization to 21.3 g/L. Table 4 shows the results obtained by using the second diaphragm tank 70 containing the second electrolytic solution E2 having an internal nickel concentration of 20 g/L. The nickel concentration when the second diaphragm 71 is an anion membrane (anion exchange membrane) (Experiment No.7) was 16.7 g/L, and the nickel concentration when the second diaphragm 71 is a cation membrane (cation exchange membrane) (Experiment No.8) was 18.5 g/L. In each case, an increase in the nickel concentration could be suppressed compared with the case where the second diaphragm tank 70 was not used.

[Table 4]

No.	Ion exchange membrane	Membrane type	Energization time (hr)	Internal solution		Plating solution		
				Ni before energization (g/L)	Ni after energization (g/L)	Ni before energization (g/L)	Ni after energization (g/L)	
④'	None	---	25	---	---	20.0	21.3	↑
⑦	Neosepta AHA	Anion	25	20	29.9	20.0	16.7	↓
⑧	Neosepta CMB	Cation	25	20	24.4	20.0	18.5	↓

## Reference Signs List

**[0043]**

5	100, 101	zinc-based plating apparatus
	10	plating tank
	20	first diaphragm tank
	21	first diaphragm
	30	cathode holding member
10	31	member to be plated
	40	first anode holding member
	41	soluble zinc-containing member
	50	second anode holding member
	51	soluble metal-containing member
15	60	power supply apparatus
	61	anode terminal
	62	cathode terminal
	70	second diaphragm tank
	71	second diaphragm
20	E1	first electrolytic solution
	E2	second electrolytic solution
	PE	plating solution

**Claims**

1. A method for suppressing an increase in the zinc concentration of a plating solution when a zinc alloy plating member using nickel as an alloy element is manufactured using a zinc alloy plating apparatus, wherein the plating apparatus comprises:

a plating tank capable of accommodating the plating solution which is acidic;  
a first diaphragm tank which is capable of accommodating the first electrolytic solution and has a first diaphragm composed of a cation exchange membrane;  
a cathode holding member for cathode-electrolyzing a member to be plated that is in contact with the plating solution inside the plating tank during use;  
a first anode holding member for anode-electrolyzing a soluble zinc-containing member that is in contact with the first electrolytic solution inside the first diaphragm tank during use;  
the soluble zinc-containing member held by the first anode holding member;  
a soluble metal-containing member containing the nickel which is the alloying element; and  
a second anode holding member for anode-electrolyzing the soluble metal-containing member,  
wherein the first diaphragm tank is arranged in a manner that the first electrolytic solution is in contact with one surface of the first diaphragm and the plating solution is in contact with the other surface of the first diaphragm during use.

2. The method for suppressing an increase in the zinc concentration of a plating solution according to claim 1, wherein the second anode holding member is arranged in a manner that the soluble metal-containing member is in contact with the plating solution during use.

3. The method for suppressing an increase in the zinc concentration of a plating solution according to claim 1 or 2, further comprising a second diaphragm tank which is capable of accommodating a second electrolytic solution and has a second diaphragm composed of a cation exchange membrane, wherein the second diaphragm tank is arranged in a manner that the second electrolytic solution which is in contact with the soluble metal-containing member inside the second diaphragm tank is in contact with one surface of the second diaphragm and the plating solution is in contact with the other surface of the second diaphragm during use.

4. A method for manufacturing a zinc-based plating member, in which a first diaphragm tank which has a first diaphragm composed of a cation exchange membrane and accommodates a first electrolytic solution is arranged in a manner that the first electrolytic solution is in contact with one surface of

the first diaphragm and an acidic plating solution accommodated inside a plating tank is in contact with the other surface of the first diaphragm,  
a member to be plated that is in contact with the plating solution in the plating tank is cathode-electrolyzed,  
a soluble zinc-containing member that is in contact with the first electrolytic solution inside the first diaphragm tank  
5 is anode-electrolyzed, and a soluble metal-containing member containing nickel which is an alloy element is anode-electrolyzed,  
and thereby zinc-nickel plating is formed on the member to be plated while an increase in the zinc concentration of the plating solution is suppressed.

- 10 **5.** The method for manufacturing a zinc-based plating member according to claim 4, wherein the soluble metal-containing member is in contact with the plating solution in the plating tank.
- 6.** The method for manufacturing a zinc-based plating member according to claim 4 or 5, wherein a second diaphragm tank which has a second diaphragm composed of a cation exchange membrane and accommodates a second  
15 electrolytic solution is arranged in a manner that the second electrolytic solution is in contact with one surface of the second diaphragm and the plating solution is in contact with the other surface of the second diaphragm, and the soluble metal-containing member is in contact with the second electrolytic solution in the second diaphragm tank is anode-electrolyzed.

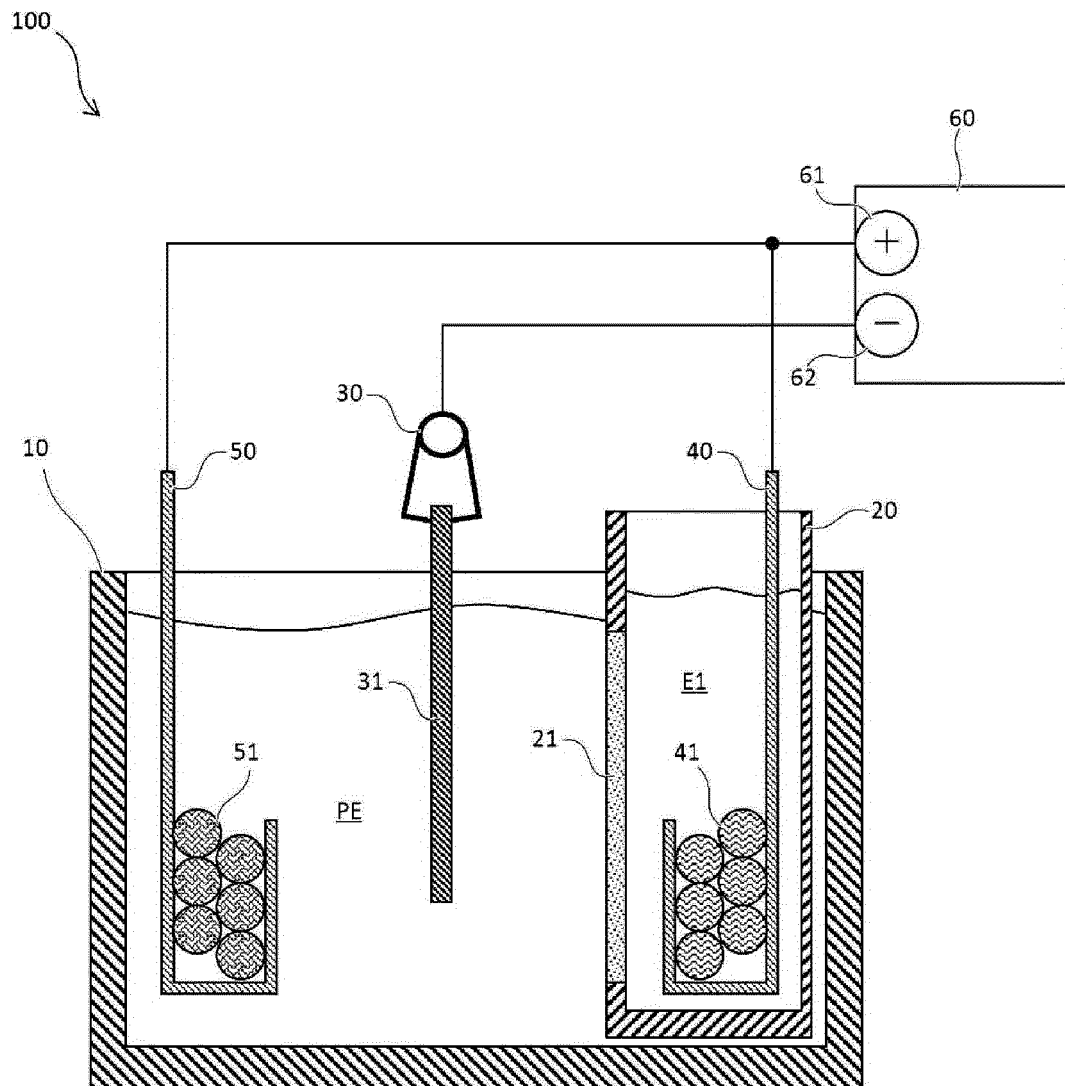


FIG. 1

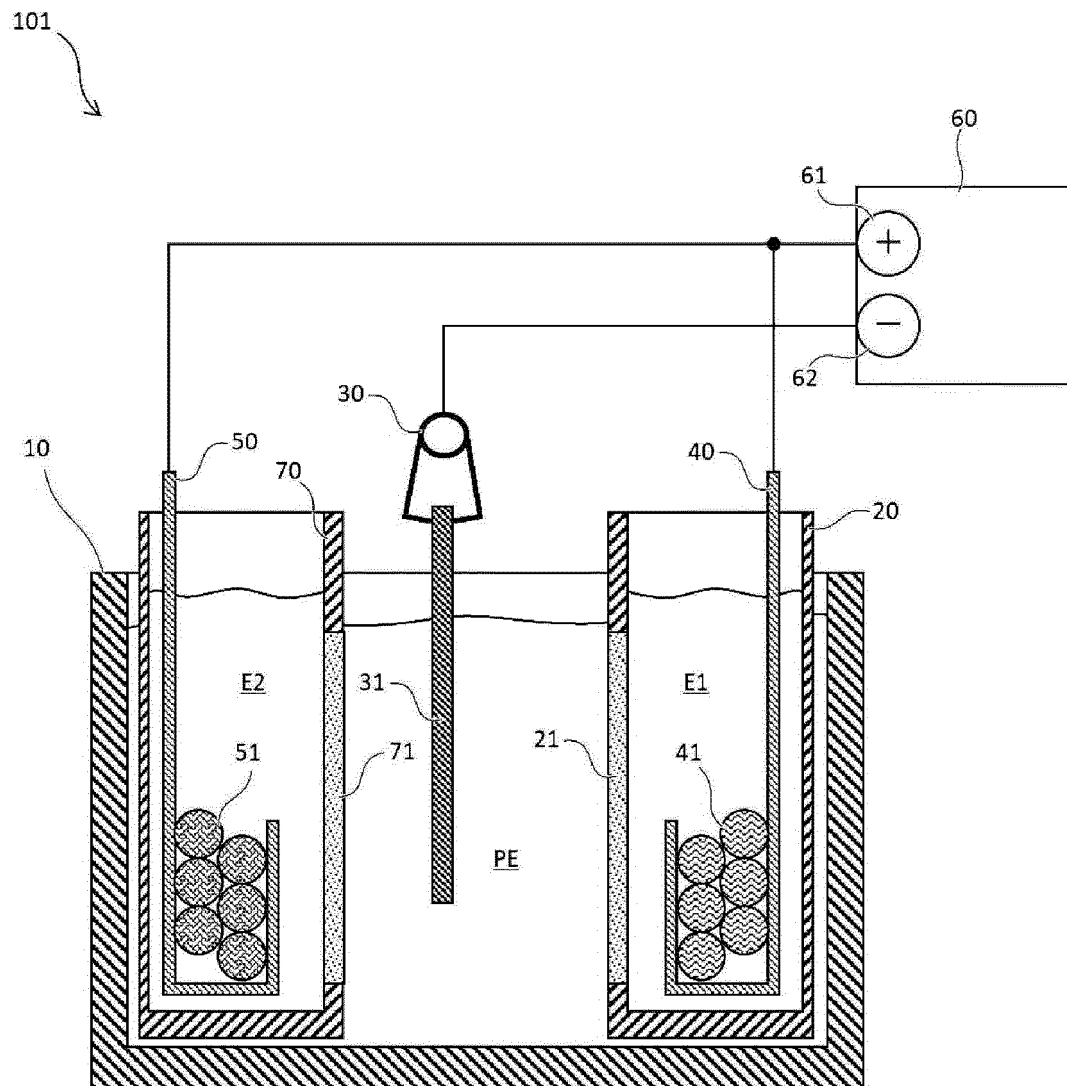


FIG. 2

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2020/031629

## A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl. C25D17/00 (2006.01) i, C25D3/56 (2006.01) i, C25D17/10 (2006.01) i,  
C25D17/12 (2006.01) i  
FI: C25D17/00 H, C25D17/10 101B, C25D17/12 A, C25D3/56 Z, C25D3/56 D  
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)  
Int. Cl. C25D17/00, C25D3/56, C25D17/10, C25D17/12

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

Published examined utility model applications of Japan 1922-1996  
Published unexamined utility model applications of Japan 1971-2020  
Registered utility model specifications of Japan 1996-2020  
Published registered utility model applications of Japan 1994-2020

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.
A	US 2010/0116677 A1 (ENTHONE INC.) 13 May 2010, paragraphs [0023]-[0053], fig. 1, 2	1-6
A	WO 2014/147180 A1 (ATOTEGH DEUTSCHLAND GMBH) 25 September 2014, page 13, line 20 to page 14, line 18, fig. 1	1-6
A	US 2007/0023280 A1 (ECKLES, E. William et al.) 01 February 2007, entire text, all drawings	1-6
A	JP 2007-2274 A (NIPPON HYOMEN KAGAKU KK) 11 January 2007, entire text, all drawings	1-6
A	JP 2006-322069 A (YUKEN KOGYO CO., LTD.) 30 November 2006, entire text, all drawings	1-6



Further documents are listed in the continuation of Box C.



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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"I" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search  
06.10.2020

Date of mailing of the international search report  
20.10.2020

Name and mailing address of the ISA/  
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3-4-3, Kasumigaseki, Chiyoda-ku,  
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Telephone No.

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/JP2020/031629

Patent Documents referred to in the Report	Publication Date	Patent Family	Publication Date
US 2010/0116677 A1	13.05.2010	EP 2184384 A1 DE 102008056776 A PL 2184384 T	
WO 2014/147180 A1	25.09.2014	US 2016/0024683 A KR 10-2015-0132574 A CN 105189831 A	
US 2007/0023280 A1	01.02.2007	WO 2004/108995 A1 BR 318331 A AU 2003239929 A	
JP 2007-2274 A	11.01.2007	(Family: none)	
JP 2006-322069 A	30.11.2006	(Family: none)	

Form PCT/ISA/210 (patent family annex) (January 2015)



**REFERENCES CITED IN THE DESCRIPTION**

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**Patent documents cited in the description**

- JP 58320202 B [0004]
- JP 4716568 B [0004]